



Infinite dilution activity coefficient and thermo-physical properties measurements of deep eutectic solvent mixtures

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DECLARATION

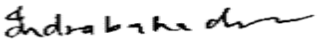
I hereby affirm that the document titled “Infinite dilution activity coefficient and thermo-physical properties measurements of deep eutectic solvent mixtures,” which has been submitted to the Department of Chemistry at North-West University, Mafikeng Campus, in pursuit of a Doctor of Philosophy degree in Chemistry, represents an accurate account of my independent research efforts conducted under the mentorship and supervision of Prof. Indra Bahadur. I attest that none of the content within this work has been previously presented by any other scholar or academic individual. Furthermore, I have appropriately acknowledged and cited all sources of information utilized in this study within the reference section.

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DEDICATION

This thesis is dedicated to Mvuyo Maxwell Mgxadeni, my brother, who encouraged me to continue with postgraduate studies, and his unwavering support played a crucial role in my successful attainment of this significant milestone.

I also pay tribute to my beloved late grandmother and grandfather, Mathoyane Iris Mncetywa and Sityebi Mncetywa respectively, who cherished the importance of education throughout their lives until their final moments on this Earth.

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“Umlilo awuvuthiswa lukhuni olunye, ubamba ngazo zozibini uMaCote, Mdindi, Sukude, Khondwana, Mthwa kaSihula, Gxarheliphezulu, Mfaz' obele lide onyisela phesheya komfula, Santsaba, Sibuthankundleni njengamathole, Xhaphazela njengeenkobe, ooMabhalela ngenxa yokunqaba kwamaphepha. Umtshana nomzukulwana wakwaGingqi, kooZinzela, ooMagoba, umzukulwana wakwaNyathi kooBudede ooNogixa umbengo, isizukuzuku sakwaNcenjani kooNdala. Aphinde abe sisizukulwana sakwaMbotho, ooThoyane ooMadiba ooMyalo.”

ABSTRACT

Deep eutectic solvents (DESs) have emerged as promising alternatives to traditional organic solvents due to their environmentally friendly and sustainable nature. This study focused on the characterization of DES mixtures through the determination of infinite dilution activity coefficients and the measurement of their essential thermo-physical properties. DESs are formed by the complexation of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), resulting in unique solvent properties. In this research, a series of DES mixtures with varying HBA-HBD combinations were prepared and analyzed. The novelty of studying the infinity dilution activity coefficient and thermophysical properties of DES mixtures lies in the fact that DESs are a relatively new class of ionic liquids that exhibit unique properties and behaviors compared to traditional solvents. Understanding the behavior of DES mixtures at low concentrations is important for different applications such as separation processes and extraction.

The thermal stability of the prepared DESs was ascertained via thermogravimetric analysis. Fourier-transform infrared spectroscopy (FTIR) was used to identify any possible shifts when the two compounds were assorted, and differential scanning calorimetry (SDT Q600 V20.9 Build 2D) was utilized to evaluate the formation of DESs using melting point. Furthermore, the density and sound velocity of the pure DESs under investigation were determined using an Anton Paar DSA 5000 M instrument. Additionally, surface tension measurements were conducted using a tensiometer (Attention Sigma 703D, Biolin Scientific, China). All data were collected at standard conditions of 298.15 K and 101.3 kPa.

The infinite dilution activity coefficient, a crucial parameter for understanding solute-solvent interactions, was determined for several solutes across different DES mixtures using gas-liquid chromatography techniques. This encompassed the determination of γ_{13}^{∞} for 34 solutes in DESs, specifically $[\text{ZnCl}_2][\text{acetic acid}]$ at ratios of 1:2 or 1:4, and $[\text{ZnCl}_2][\text{phosphoric acid}]$ at ratios of 1:2 or 1:2.5, spanning a temperature range of (313.15 to 353.15) K. These measurements shed light on the solvation behavior within the DESs, providing valuable insights into their potential applications in separation and extraction processes. Excess thermodynamic parameters, including partial molar excess enthalpies $\Delta H_1^{E,\infty}$, entropies $(T_{ref} \Delta S_1^{E,\infty})$ and Gibbs free energies $(\Delta G_1^{E,\infty})$ were derived from the γ_{13}^{∞} data.

The usefulness of the researched DESs as extracting solvents for possible applications was evaluated by calculating and comparing their selectivity and capacity values with those reported in the literature for other DESs, ionic liquids, and sulfolane. In terms of separation performance, the results revealed that $[\text{ZnCl}_2][\text{acetic acid}]$ (1:2) exhibited superior selectivity and capacity for benzene/ethanol,

cyclohexane/ethanol, and octane/acetonitrile systems, highlighting its potential in industrial separation processes. Conversely, $[\text{ZnCl}_2][\text{phosphoric acid}]$ (1:2) emerged as a promising solvent for replacing conventional solvents due to its outstanding separation parameters (capacities and selectivities) for components with closely matched boiling points. Despite the promise of deep eutectic solvents based on phosphoric acid, certain challenges, such as corrosion caused by phosphoric acid in certain industrial applications, limit its suitability for addressing industrial separation challenges.

Moreover, this study expanded upon the investigation of the thermophysical characteristics of binary combinations consisting of $[\text{ZnCl}_2][\text{acetic acid}]$ or $[\text{ZnCl}_2][\text{phosphoric acid}]$ (1:2) in a 1:4 ratio) and various alcohols (methanol, ethanol, and propanol), at different temperatures (293.15 to 313.15) K. To confirm the occurrence of intermolecular interactions within these mixtures, various thermodynamically relevant parameters, such as density and speed of sound, were employed to compute parameters including excess molar volumes (V_m^E), isentropic compressibility (K_S), intermolecular free length (L_f), and deviation in isentropic compressibility (ΔK_S). The study further emphasized that ion-solvent and solute-solvent interactions prevailed over self-interactions, such as solvent-solvent and ion-ion or solute-solute interactions. Additionally, temperature exhibited a significant influence on all investigated thermodynamic parameters, as their values, (including V_m^E , K_S , ΔK_S , and L_f) were found to either decrease or increase with rising temperature. The Redlich-Kister polynomial expression was effectively employed to correlate excess molar volumes and deviation in isentropic compressibility. In addition, the perturbed chain statistical associating fluid theory equation of state (PC-SAFT EoS) was employed to model the densities of binary mixtures consisting of DES and 1-alkanol. Furthermore, utilized Schaaff's collision factor theory (SCFT) and Nomoto's relation (NR) to model the speed of sounds for these binary mixtures. This comprehensive study significantly contributes to the body of knowledge on DESs by elucidating their thermophysical properties, solvation behavior, and potential applications in separation processes. The findings not only enhance our understanding of DES mixtures but also offer valuable insights for designing more efficient and sustainable solvents for industrial and environmental applications. Future research could delve deeper into exploring the interactions and behaviors of DESs under varying conditions and in diverse applications to further harness their potential benefits.

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LIST OF PUBLICATIONS FROM THIS PROJECT

1. **Ncomeka Mgxadeni**, Oarabile Mmelesi, Bakusele Kabane, and Indra Bahadur* “Influence of hydrogen bond donors on zinc chloride in the separation of binary mixtures: Activity coefficients at infinite dilution”. **Journal of Molecular Liquids**, 351 (2022), 118596 (<https://doi.org/10.1016/j.molliq.2022.118596>).
2. **Ncomeka Mgxadeni**, Bakusele Kabane, Indra Bahadur*, Márcio L. L. Paredes, Rafael de P. Soares, Sailendra Kumar Singh, Faruq Mohammad, Ahmed Abdullah “Thermodynamic Properties, Activity Coefficients at Infinite Dilution, and Cosmo-SAC Modelling of Deep Eutectic Solvents at Different Temperatures’. **ChemistrySelect** 30 (2023) e202204192, (<https://doi.org/10.1002/slct.202204192>).
3. **Ncomeka Mgxadeni**, Bakusele Kabane, Indra Bahadur*, Rajender S. Varma, S. K. Singh “Deep Eutectic Solvents as Sustainable Solvents for Industrial Separation Problems: A Recent Update”. **Journal of Ionic Liquids** (2023), 100065 (<https://doi.org/10.1016/j.jil.2023.100065>).
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Analyst Poster Award

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LIST OF ABBREVIATION

AA	Acetic acid
Ala	Alanine
AP	3-Amino-1-propanol
BZTBCl	Benzyltributylammonium chloride
[BMIM][BF ₄]	1-Butyl-3-methylimidazolium tetrafluoroborate
[BDMIM][Cl]	1-Butyl-2,3-dimethylimidazolium chloride
[BMIMCl][gly]	[1-Butyl-3-methylimidazolium chloride + glycerol]
BEA	2-(Butylamino)ethanol
CO ₂	Carbon dioxide
CCS	Carbon capture and storage
COOH	Carboxylic acid
CdCl ₂	Cadmium chloride
Cl ₂	Chlorine
ChCl	Choline chloride
COSMO-RS	Conductor-like screening model for real solvents
CuCl ₂	Copper (II) chloride
DFT	Density functional theory
DFT	Density functional theory
DESs	Deep eutectic solvents
DEMs	Deep eutectic mixtures
DSC	Differential scanning calorimetry
[DDA][ClO ₄]	Didecyldimethylammonium perchlorate
[DDA][BF ₄]	Didecyldimethylammonium tetrafluoroborate
EG	Ethylene glycol
ERAS	Extended real association model
FTIR	Fourier-transform infrared
GC	Gas chromatography
GLC	Gas-liquid chromatography
Gly	Glycine
GA	Glutaric acid
HBA	Hydrogen bond acceptor

HBD	Hydrogen bond donor
O-H	Hydroxyl
Hdiol	1,6-Hexanediol
[HMIM][Cl]	1-Hexyl-3-methylimidazolium chloride
[HMMIM][BF ₄]	1-Hexyl-2,3-dimethylimidazolium tetrafluoroborate
His	Histidine
[C ₂ OHmim][C ₄ F ₉ SO ₃]	1-(2-Hydroxyethyl)-3-methylimidazolium nonafluoro-1-butanesulfonate
IDAC	Infinite dilution activity coefficient
IGC	Inverse gas chromatography
ILs	Ionic liquids
Fe	Iron
LA	Lactic acid
LiCl	Lithium chloride
LLE	Liquid-liquid extraction
MA	Malonic acid
CH ₃	Methyl
CH ₂	Methylene
MEKP	Methyl ethyl ketone peroxide
MAE	2-(Methylamino)ethanol
NADES	Natural deep eutectic solvents
Ni	Ninhydrin
NR	Nomoto's relation
NRTL	Non-random two-liquid model
NMR	Nuclear magnetic resonance
OA	Oxalic acid
[OMMIM][BF ₄]	1-Octyl-2,3-dimethylimidazolium tetrafluoroborate
PC-SAFT EoS	Perturbed chain statistical associating fluid theory equation
PEG	Polyethylene glycol
PA	Phosphoric acid
KCl	Potassium chloride
PFP	Prigogine–Flory–Patterson
SCFT	Schaaff's collision factor theory
SH-GC	Static headspace gas chromatography
AgCl	Silver chloride

TBABr	Tetrabutylammomium bromide
TBAC	Tetrabutylammonium chloride
THF	Tetrahydrofuran
[C ₄ H ₁₂ NCI][EG]	[Tetramethylammonium chloride + ethylene glycol]
[4C ₁ NCI][Gly]	[Tetramethylammonium chloride + glycerol]
[4C ₁ NCI][Hdiol]	[Tetramethylammonium chloride + 1,6 hexanediol]
TBAHS	Tetrabutylammonium hydrogen sulfate
[4C ₃ N.Br][Hdiol]	[Tetrapropylammonium bromide +1,6-hexanediol]
TCD	Thermal conductivity detector
TGA	Thermogravimetric analyser
SnCl ₂	Tin (II) chloride
SnCl ₄	Tin (IV) chloride
[P ₆₆₆₁₄] [DCA]	Trihexyltetradecylphosphonium dicyanamide
UNIQUAC	Universal quasi-chemical activity coefficient
UNIFAC	Universal quasi-chemical functional group activity coefficient
U	Urea
H ₂ O	Water
ZnCl ₂	Zinc chloride

LIST OF SYMBOLS

ρ	=	density
V_m^E	=	excess molar volume
T	=	temperature
x_1	=	mole fraction of the 1 st component
x_2	=	mole fraction of the 2 nd component
σ	=	standard deviation
M_1	=	molar mass of the 1 st component
M_2	=	molar mass of the 2 nd component
A_i	=	polynomial coefficient
N	=	polynomial degree
n	=	number of experimental points
N_A	=	Avogadro's number
k	=	number of coefficients used in the Redlich-Kister correlation
u	=	speed of sound
K_S	=	isentropic compressibility
ΔK_S	=	excess isentropic compressibility
L_f	=	Intermolecular free length
k_j	=	temperature dependent Jacobson's constant
γ_{13}^∞	=	activity coefficients at infinite dilution, where solute is be denoted as component 1 and solvent as component 3
P_o	=	column outlet pressure
f_2^3	=	pressure correction term
n_3	=	number of moles of solvent in the column packing

T_{col}	=	column temperature
P_1^*	=	saturated vapour pressure of the solute at temperature T
B_{11}	=	second virial coefficient of the pure solute
V_1^*	=	molar volume of the solute
V_1^∞	=	partial molar volume of the solute at infinite dilution in the solvent
B_{12}	=	mixed second virial coefficient of the solute and the carrier gas
t_R	=	retention time of the given solute
t_G	=	retention time of the non-retainable component
q_{ov}	=	carrier gas flow at the column temperature and column outlet pressure
q_o	=	flow rate measured with the bubble flow meter at the column outlet
T_f	=	flow meter temperature measured with a thermometer
P_W^*	=	saturated vapour of water at temperature T_f
P_i	=	column inlet pressure
$\Delta H_1^{E,\infty}$	=	partial molar excess enthalpy at infinite dilution
$\Delta S_1^{E,\infty}$	=	partial molar entropy at infinite dilution
$\Delta G_1^{E,\infty}$	=	partial molar Gibbs at infinite dilution
a	=	slope
S_{12}^∞	=	selectivity at infinite dilution
k	=	capacity
V_R	=	retention volume of the solute
V_3	=	solvent volume
K	=	equilibrium partition coefficient
R	=	universal gas constant
V_G	=	gas hold up volume
T_C	=	critical temperature

V_c = critical volume

$\hat{f}_i$ = fugacity of components

f_i = fugacity for pure substances

INTRODUCTION

1.1. Background of the study

This chapter enumerates the background of the study, the importance of studying the thermophysical properties of deep eutectic solvent mixtures, the importance of understanding the infinite dilution activity coefficient of deep eutectic solvents, the chemical composition and structures of deep eutectic solvents, the problem statement, the aims and the objectives as well as, the scope of the study. DESs refer to a class of ionic liquids (ILs) characterized by their composition, which consists of an eutectic mixture comprising a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) [1-3]. DESs have garnered significant attention as a potentially advantageous group of solvents. This is primarily attributed to their distinctive characteristics, including but not limited to their low toxicity, reduced volatility, elevated thermal stability, and capacity for biodegradation [4, 5]. DESs have demonstrated considerable promise in diverse domains, including chemical synthesis, electrochemistry, and separation processes [6, 7]. The comprehension of the thermodynamic and thermo-physical characteristics attributes of DESs mixtures, specifically at a state of infinite dilution, is of utmost importance in order to optimize their application in various industrial processes.

It is crucial to conduct a thorough analysis of DESs' thermodynamic characteristics to gain a deeper understanding of the behavior they display. This entails studying various properties such as excess molar volumes, isentropic compressibility, excess isentropic compressibility, intermolecular free length, activity coefficients at infinite dilution, and other pertinent characteristics. Excess molar volumes pertain to the discrepancy seen between the molar volume of a mixture and molar volume that would be expected based on the ideal molar volumes of its individual parts [8-10]. When evaluating the DES, the assessment of excess molar volumes offers valuable information into the extent of molecular interactions and structural alterations taking place within the solvent mixture. Positive excess volumes imply an increase in volume due to beneficial interactions, whereas negative values indicate a decrease in volume caused by strong intermolecular forces or structural rearrangements [11, 12]. The concept of isentropic compressibility pertains to quantifying the alteration in the volume of a substance in response to variations in pressure while maintaining a constant entropy [13]. The compressibility of a substance is a defining characteristic that offers insights into the intermolecular forces and molecular arrangement within the system. Through an examination of the isentropic compressibility of DES, valuable insights can be obtained regarding the level of structural arrangement and molecular interplay present within the solvent. The concept of

excess isentropic compressibility refers to the quantification of the deviation between the isentropic compressibility of a mixture and the isentropic compressibility of its ideal components [14, 15].

Understanding the impact of molecular interactions and structural modifications on the compressibility of a system is beneficial. Positive excess isentropic compressibility values are indicated of an increase in compression, whereas negative values suggest a decrease in compression due to specific molecular interactions [16, 17]. The notion of intermolecular free length refers to the average distance between molecules that are adjacent inside a liquid [18]. The observed phenomenon serves as a measure of the level of molecular association or repulsion present within the given system. Through an examination of the intermolecular free length of DESs, it becomes possible to analyze the magnitude and characteristics of intermolecular forces, as well as to evaluate the molecular configuration and efficiency of solvent packing. The thermodynamic parameter known as the infinite dilution activity coefficient (IDAC) characterizes the behavior of a solute within a solvent when the solute is present in extremely low concentrations. The aforementioned statement serves to quantify the degree of interaction intensity between the solute molecules and solvent. Determination of the IDAC is crucial in the study of DES mixtures as it provides valuable insights into the interactions between solute and solvent. Additionally, it allows for the assessment of the solvent's effectiveness in various applications, including separation processes and chemical reactions.

Numerous experimental methodologies have been devised to quantify the activity coefficient of solutes in DES mixtures at infinite dilution. The gas-liquid chromatography (GLC) technique is a frequently employed method in which the solute is introduced into a carrier gas and subsequently traverses a stationary phase composed of a DES [19]. The comparison of the solute's retention time with that of a reference compound enables the determination of the activity coefficient whereas static headspace gas chromatography (SH-GC) technique that quantifies the solute concentration by measuring the equilibrium vapor concentration above the solvent. The thermo-physical properties of DES mixtures are crucial for their practical applications, alongside with the infinite dilution activity coefficients [20]. The aforementioned properties encompass density, surface tension, viscosity, refractive index, and thermal conductivity. A precise understanding of these characteristics is essential in the development of separation techniques, enhancement of reaction parameters, and simulation of the performance of DES mixtures in diverse applications.

There are various experimental techniques that can be employed to measure the thermo-physical properties of DES mixtures. For example, the determination of density can be accomplished through the utilization of density meters or oscillating tube densimeters. Similarly, the measurement of viscosity can be conducted using viscometers such as rotational viscometers or capillary viscometers.

The determination of refractive index can be accomplished through the utilization of refractometers, while the measurement of surface tension can be conducted employing techniques such as the pendant drop method or the Wilhelmy plate method [21]. There are several techniques available for the measurement of thermal conductivity, such as the transient hot-wire method and the heat flow meter method [22].

Comprehending the IDAC and the thermo-physical properties of DES mixtures is of paramount importance for their utilization across various disciplines. The aforementioned measurements offer significant insights for the purpose of designing and enhancing processes that involve DES, including but not limited to solvent extraction, mixture separation, catalysis, and electrochemical applications. The data obtained from this work may be used in thermodynamic modeling, process simulation, and the development of innovative DESs with tailored characteristics for specific applications. The investigation of IDAC and the thermo-physical properties of DES mixtures holds great significance in relation to their practical utilization. Precise quantification of these characteristics offers significant elucidation on the intermolecular interactions between solutes and solvents, as well as the dynamics exhibited by DESs mixtures during diverse processes. Through a comprehensive understanding of these properties, researchers are able to strategically optimize the design and performance of systems based on DES, thereby resulting in improved efficiency and the promotion of sustainable technological advancements. Continued investigation and examination of these characteristics will enhance the advancement and application of DES in various domains.

1.2. Importance of studying thermophysical properties of deep eutectic mixtures

Investigation of the thermophysical properties of deep eutectic mixtures (DEMs) holds a significant importance owing to their diverse array of applications and potential advantages. These mixtures possess distinctive characteristics that render them appealing for a wide range of industrial and scientific applications. The investigation of the thermophysical properties of DEMs is motivated by several compelling justifications, including:

- ❖ understand phase behavior: The examination of the thermophysical properties of DEMs facilitates the comprehension of their phase behavior, encompassing characteristics such as melting points, solidification mechanisms, and phase diagrams [23, 24]. A comprehensive understanding of phase behavior is essential for the effective optimization of process conditions, particularly in the context of extraction, separation, and purification processes, where phase transitions hold significant importance.
- ❖ design new solvents: DEMs exhibit adjustable properties, and investigating their thermophysical properties, contributes to the development of novel solvents with customized

attributes [25]. Researchers can modify the physical and chemical characteristics of DEMs for specific purposes by carefully choosing suitable combinations of HBD and HBA. These modifications include adjustments to viscosity, density, polarity, and thermal stability. This facilitates the advancement of sustainable and enduring substitutes for traditional solvents.

- ❖ enhance solubility and dissolution rates: The solubility and dissolution rates of different substances can be improved by employing DEMs [25]. By understanding the thermophysical properties of DEMs, researchers can find the right combinations of components that improve the solubility and dissolution rates of certain compounds. This is useful in many fields, such as pharmaceuticals, chemical synthesis, and materials science.
- ❖ modulate thermal properties: DEMs display distinctive thermal characteristics, characterized by their relatively low melting points and elevated heat capacities [26, 27]. The characteristics possess inherent benefits in the context of thermal energy storage implementations, particularly in solar energy systems, where the efficient absorption and release of heat play a crucial role. Through the examination of thermophysical properties, researchers could identify and select DEMs that possess ideal thermal characteristics suitable for meeting specific energy storage needs.
- ❖ predict and optimize processes: The comprehension of the thermophysical characteristics of DEMs empowers researchers to construct models and simulations for the purpose of forecasting and enhancing diverse processes that involve these mixtures [27]. These tasks encompass phenomena such as heat transfer, mass transfer, and reaction kinetics. The utilization of precise forecasts derived from thermophysical data plays a crucial role in enhancing the efficacy of process design and operation, ultimately resulting in heightened productivity and cost-efficiency.
- ❖ expand industrial applications: The understanding of the thermophysical characteristics of DEMs presents opportunities for their implementation in diverse industrial contexts [28, 29]. The applications encompass a wide spectrum of areas, including separation technologies such as extraction and chromatography, utilization in electrolytes for energy storage systems, utilization as solvents in biomass processing, and adoption as environmentally friendly alternatives in chemical synthesis. The comprehension of the thermophysical characteristics of DEMs enables their seamless incorporation into pre-existing industrial operations or the creation of novel technological advancements.

1.3. Importance of understanding the IDAC of DESs

The comprehension of the IDACs of DESs holds significant importance for various reasons. The following are several crucial points that underscore their significance:

- ❖ Solvent efficiency: The examination of IDACs offers valuable insights into the solvation characteristics exhibited by DESs [30]. The coefficients serve to quantify the interactions between solutes and solvents, thereby influencing the solvent's effectiveness in dissolving different solutes. Through comprehending these coefficients, scholars can assess the efficacy of a DES in dissolving various substances and enhance their choice of solvents for particular purposes [31].
- ❖ Process optimization: DESs exhibit remarkable versatility and possess a diverse array of applications, including but not limited to extraction, separation, catalysis, and electrochemistry [6, 7]. Understanding the activity coefficients at infinite dilution is crucial for the design and optimization of these processes. Researchers can choose the most appropriate DES by considering the solubility of the solute and the desired conditions for separation or reaction.
- ❖ Thermodynamic modeling: IDACs are of utmost importance in the development of precise thermodynamic models for deep eutectic solvents [20, 32]. The utilization of these models is crucial in the prediction and comprehension of the phase behavior, solubility, and various thermodynamic properties exhibited by DES systems. The utilization of dependable models allows researchers to effectively simulate and forecast the behavior of DES within complex systems, thereby facilitating the design and optimization of said processes.
- ❖ Solvent design and customization: The comprehension of activity coefficients plays a crucial role in the development and tailoring of deep eutectic solvents to fulfill specific criteria. Researchers can change the composition and parts of DES to improve its solubility, selectivity, and other solvent properties by looking at the activity coefficients at infinite dilution. This knowledge holds significant value in the context of customizing DES for specific applications, such as those related to green chemistry or sustainable processes [6].
- ❖ Comparative studies: By conducting a comparison of the activity coefficients at infinite dilution of various deep eutectic solvents, researchers can assess their efficacy and make an informed choice regarding the most appropriate solvent for a specific task [6]. Through a comprehensive understanding of the interactions between solvents and solutes, researchers are able to make well-informed choices regarding the selection of solvents and evaluate the potential benefits or drawbacks associated with various formulations of DESs.

1.4. Chemical composition and structures of DESs

The composition and structure of DESs exhibit variability based upon the specific constituents employed in their formulation [6, 30]. DESs are commonly comprised of a hydrogen bond donor, which may consist of compounds such as urea, glycerol, or oxalic acid (refer to Figure 1.1). Additionally, a hydrogen bond acceptor is typically present, which can be in the form of a metal salt (e.g., choline chloride, ethyl ammonium chloride, etc) (refer to Figure 1.2). The combination of these constituents can yield a multitude of DESs exhibiting diverse properties and characteristics. The typical structural features of DESs are often defined by a hydrogen bonding network established among the hydrogen bond donor and acceptor. This hydrogen bond network can result in a complex three-dimensional structure that can vary depending on the specific components used. The hydrogen bonds present in DESs and their consequent structural arrangement play an important role in determining the distinctive characteristics of DESs, such as their relatively low melting points, exceptional thermal stability, and notable solubility across a broad spectrum of compounds.

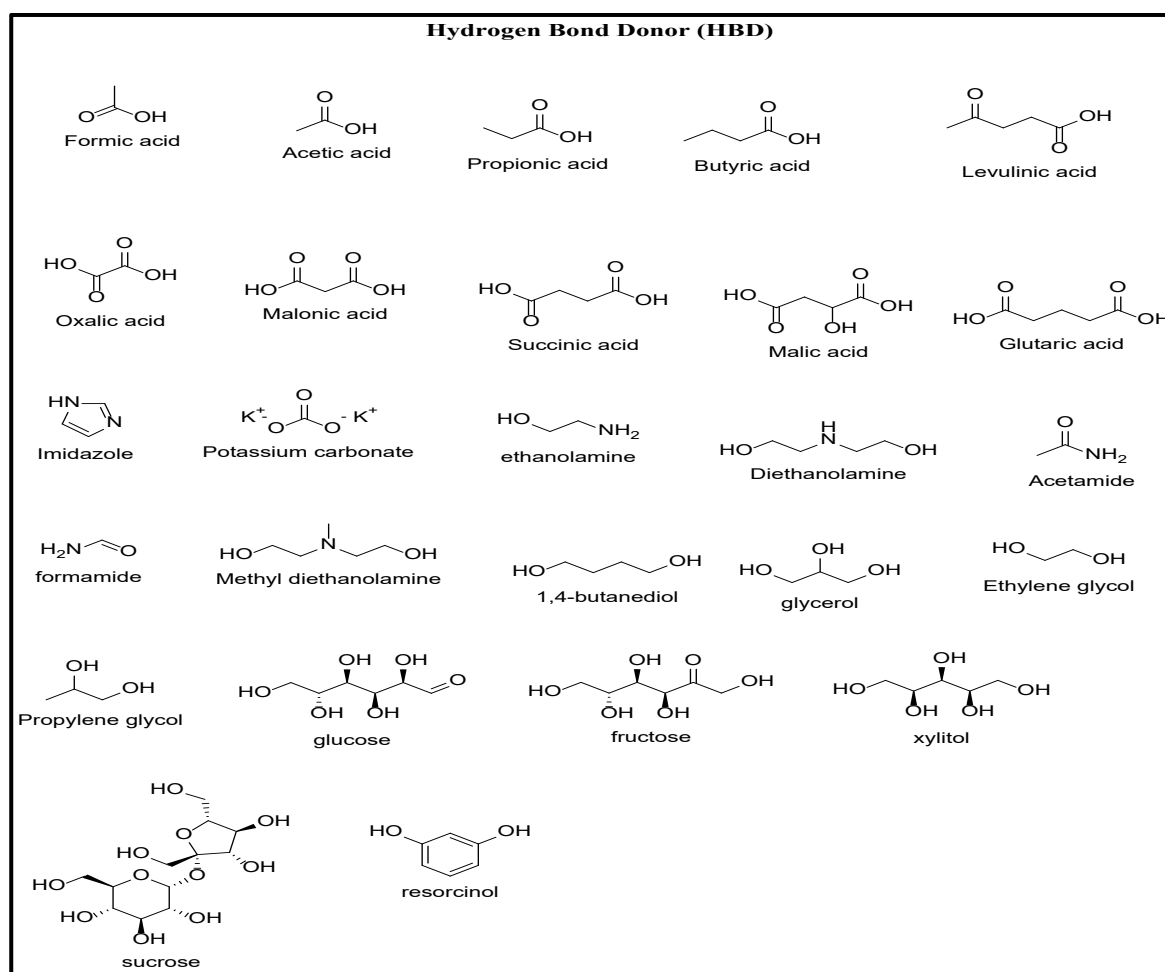


Figure 1. 1: Examples of HBDs used to prepare DESs.

Hydrogen Bond Acceptor (HBA)

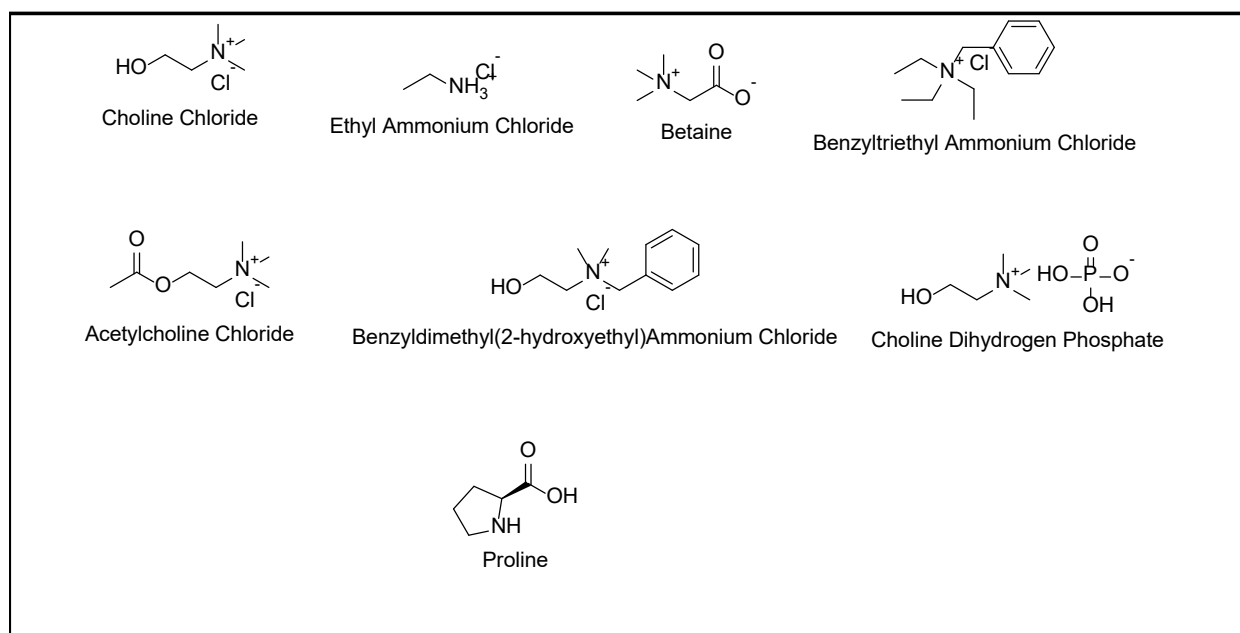


Figure 1. 2: Examples of HBAs used to prepare DESs.

1.5. Problem statement

The exploration of alternative solvents, which exhibit enhanced properties for industrial applications and are more environmentally sustainable, constitutes a pivotal component of green technology. Volatile organic compounds (VOCs) are recognized for their inherent toxicity and significant volatility, both of which are implicated in an increase in air pollution and other environmental concerns [6]. ILs have been the subject of extensive research as a category of environmental friendly solvents, primarily because of their distinctive physical and chemical characteristics. ILs are commonly comprised of organic cations and either inorganic or organic anions. These ILs are characterized by their low volatility, high thermal stability, and effective solvation properties. Nevertheless, as previously indicated, ILs do possess certain limitations, including toxicity, low biodegradability, and high costs, which have hindered their extensive utilization. In order to overcome these constraints, DESs have emerged as a viable and promising alternative [29]. DESs are commonly synthesized through the combination of a HBA, such as a quaternary ammonium salt, with a HBD, which can be a metal salt or a small organic molecule. The resultant solvent demonstrates an eutectic composition and a reduced melting point compared to the constituent elements, resulting in the formation of a liquid solvent.

DESs have garnered significant interest in the scientific community owing to their environmental friendly attributes, which encompass reduced volatility, biodegradability, diminished toxicity, and comparatively affordable costs in relation to ILs. Additionally, these substances exhibit a broad range of liquid states and can be readily synthesized using cost-effective precursor materials [30]. The

aforementioned characteristics render DESs highly appealing for a wide range of industrial applications, encompassing extraction, separation processes, and catalysis. Viscosity, an important characteristic, is crucial, particularly when considering practical aspects like pumping requirements and transportation. It is very important to get measurements of the infinite dilution activity coefficients and the thermophysical properties of DES mixtures in order to better understand the use of DESs. The measurements listed above provide useful information that can be used to improve and design separation processes, figure out how solutes dissolve, and learn how DESs behave in different situations. This knowledge can be utilized in both industrial and academic research settings to optimize process efficiency, decrease energy expenditures, and mitigate environmental consequences. It might be a good idea to look into DESs as solvents that are safe for the environment as an alternative to volatile organic solvents in industrial separation processes. Without the limitations of ILs, DESs have the potential to make big contributions to sustainable and eco-friendly practices in many research areas. This is because they have desirable properties.

Table 1. 1: Relevant literature and research gaps in problem formulation related to deep eutectic solvents

Research Gap/Aspect	Previous Research (Literature)	Present Study Contribution
Alternative Solvents	Previous studies have extensively explored ILs as environmentally friendly solvents due to their unique physical and chemical properties [6].	The present study focuses on exploring DESs as a viable alternative to ILs, considering their reduced toxicity, biodegradability, and cost-effectiveness.
Environmental Impact	Past research acknowledges the limitations of ILs, including toxicity, low biodegradability, and high costs [6].	This study highlights DESs' potential to mitigate environmental concerns by offering reduced toxicity, improved biodegradability, and lower costs compared to ILs.
Synthesis and Properties of DESs	Literature indicates growing interest in DESs due to their environmentally	The study contributes by characterizing DES mixtures' infinite dilution activity coefficients and

	friendly attributes, broad liquid states, and cost-effective synthesis [29, 30].	thermophysical properties, essential for understanding their behavior in various applications.
Industrial Applications	DESs are recognized for their potential in extraction, separation processes, and catalysis, with emphasis on viscosity as a crucial practical consideration [30].	The research aims to provide valuable insights into DESs' industrial applicability through thorough characterization and understanding of their properties and behaviors.
Eco-friendly Solvents	Previous literature suggests exploring DESs as safe, environmentally friendly solvents, particularly in replacing volatile organic solvents in industrial processes [30].	This study contributes by highlighting DESs' potential to drive sustainable and eco-friendly practices in various research and industrial sectors, leveraging their desirable properties.

1.6. Aim of the study

The aim of this study was to separate close boiling mixtures using deep eutectic solvent based on thermodynamic data.

1.7. Objectives of the study

The objectives of this study were to:

- ❖ prepare and characterize the DESs,
- ❖ measure the infinite dilution activity coefficients for selected solutes in DESs using GLC technique,
- ❖ investigate the effect of temperature on infinite dilution activity coefficients,
- ❖ screen the effectiveness of DESs for the separation of close boiling points mixtures by using the selectivity and capacity values,
- ❖ measure the thermo-physical properties: density and sound velocity of DESs and their binary mixtures at several temperatures,
- ❖ determine the intermolecular interactions occurring between the DESs and organic solutes,

- ❖ employ the perturbed chain statistical associating fluid theory equation to model the densities of the binary mixtures consisting of DES and alkanols,
- ❖ utilized Schaaff's collision factor theory (SCFT) and Nomoto's relation (NR) to model the speed of sounds for these binary mixtures,
- ❖ correlate the thermodynamic data using Redlich-Kister equations and equations of state.

1.8. The scope of the current investigation

The thesis primarily comprises two distinct sections:

(a) IDAC measurements of DESs

The present study aimed to examine the interactions between DESs and a range of solutes that possess diverse functional groups. The activity coefficients at infinite dilution for a set of 34 solutes were determined through the utilization of GLC. The solutes comprised a range of organic compounds, namely alkanes, alkenes, alcohols, ketones, thiophene, heterocyclics, cycloalkanes, acetonitrile, tetrahydrofuran, cycloalkenes, aromatic hydrocarbons, and water. The measurements were performed at various temperatures, specifically at (313.15, 323.15, 333.15, 343.15, and 353.15) K.

The selection of these four DES compositions aims to explore a range of factors, including the influence of hydrogen bond donors (acetic acid vs. phosphoric acid), varying molar ratios, and their impact on the resulting DES properties. DESs were chosen based on their ability to form stable eutectic mixtures at specified molar ratios, which are crucial for their application in the purification process. This variation in composition was part of a systematic study to investigate how changes in the molar ratio impact the DES's properties, enhancing our understanding of their behavior and potential applications. It is noteworthy to mention that this study represents the initial exploration of activity coefficients at infinite dilution for the four distinct DESs that were analyzed. The DESs used in the study were:

- ❖ $[\text{ZnCl}_2][\text{acetic acid}]$ with a molar ratio of 1:2 (DES composition),
- ❖ $[\text{ZnCl}_2][\text{acetic acid}]$ with a molar ratio of 1:4 (DES composition),
- ❖ $[\text{ZnCl}_2][\text{phosphoric acid}]$ with a molar ratio of 1:2 (DES composition),
- ❖ $[\text{ZnCl}_2][\text{phosphoric acid}]$ with a molar ratio of 1:2.5 (DES composition).

Excess thermodynamic parameters were to acquire a deeper understanding of the diverse interactions that transpire between DESs and solutes. The parameters encompassed in this study comprise partial molar excess enthalpies, partial molar excess Gibbs free energy, and partial excess molar entropies at infinite dilution. The aforementioned values were derived by utilizing the activity coefficients at infinite dilute. In addition, the researchers conducted calculations to determine the selectivity and

solvents capacity values for the separation of different solute pairs, including benzene/ethanol, cyclohexane/ethanol, *n*-octane/acetonitrile, ethylbenzene/butan-1-ol, and *n*-heptane/butan-1-ol, at a temperature of 323.15 K. The values acquired in this investigation were contrasted with the prevailing literature values pertaining to DESs, ILs, and sulfolane. The objective of this comparative analysis was to evaluate the appropriateness of DESs as potential entrainers for separation processes.

(b) Thermodynamic properties of binary DESs mixtures

In this context, an examination is conducted of various thermodynamic properties, namely density (ρ), speed of sound (u), excess molar volume, isentropic compressibility, deviation in isentropic compressibility, and intermolecular free length. The focus of the investigation is on binary mixtures consisting of {[ZnCl₂][acetic acid] 1:4 or [ZnCl₂][phosphoric acid] 1:2.5 + methanol or ethanol or propanol} at different temperatures (293.15, 303.15, 308.15, and 313.15) K and at a constant pressure of 0.1 MPa. The experimental measurements were conducted using the DSA 5000M. The calculated properties, namely excess molar volumes and deviation in isentropic compressibility, were subjected to correlation analysis using the Redlich-Kister polynomial equation. To ascertain the dependability of the experimental results, it is necessary to conduct validation. In addition to the computed surplus properties, potential molecular interactions among constituent molecules were examined.

Moreover, the perturbed chain statistical associating fluid theory equation of state (PC-SAFT EoS) were used to describe the densities of binary mixtures comprising DES and 1-alkanol. Additionally, Schaaff's collision factor theory (SCFT) and Nomoto's relation (NR) were used to predict the speed of sound for these binary mixtures.

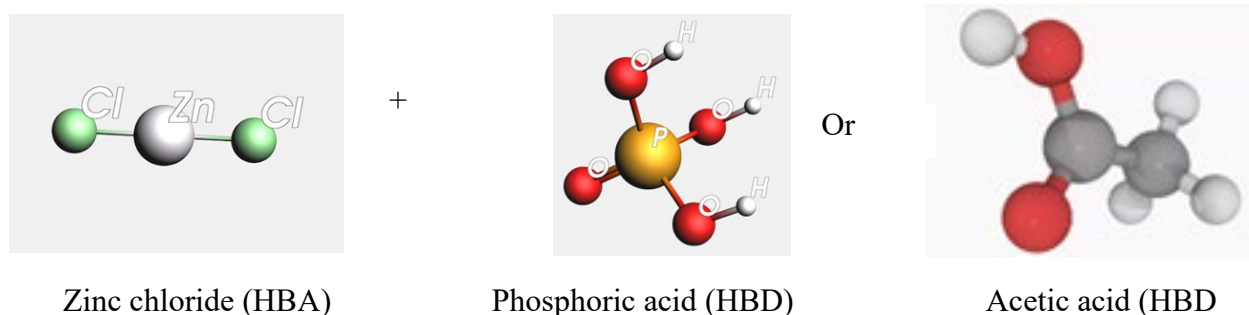


Figure 1. 3: Compounds used to prepare DESs

LITERATURE REVIEW

2.1. General description of DESs

DESs are a category of ILs that include two or more solid or liquid components that display a eutectic point. This eutectic point corresponds to the temperature at which the combination attains its minimum melting point [2]. The resultant solution exhibits characteristics of a non-traditional solvent, being a clear, highly viscous liquid with reduced vapor pressure, thereby exhibiting lower volatility and improved environmental sustainability.

Organic acids, amides, amino acids, sugars, and other hydrogen bond-forming substances are just a few examples of the components that can combine to form DES [33]. The resulting mixture's physical properties, such as polarity, density, and viscosity, can vary significantly based on the specific components employed.

DESs exhibit diverse potential applications in the fields of chemistry and industry. These applications include serving as reaction solvents, electrolytes in batteries, and solvents for natural product extraction and purification [5, 34]. They are being investigated as prospective substitutes for conventional solvents, which exhibit toxicity, volatility, and environmental and health hazards. In general, DESs exhibit great potential as a novel solvent category that could potentially transform various domains of chemistry and industrial applications (Figure 2.1).

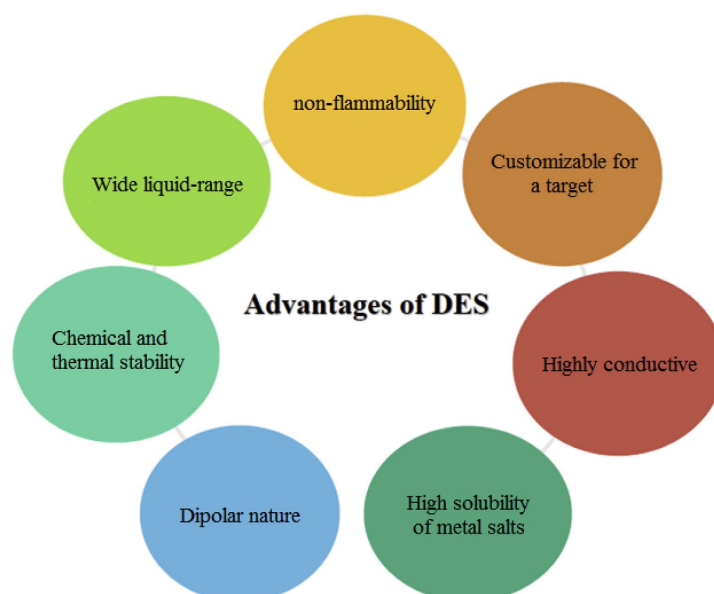


Figure 2. 1: Advantages of DESs [28].

2.2. History of DESs

The notion of DESs has existed for more than a century; however, only in recent decades has their potential as a sustainable and environmentally friendly substitute for conventional solvents been comprehensively acknowledged. In 1884, Friedrich Wilhelm Ostwald, a German chemist, introduced the term "eutectic" to denote a mixture of two or more constituents that exhibits a melting point lower than that of any of the individual constituents [35]. The nomenclature "deep eutectic" was subsequently employed to characterize eutectic mixtures exhibiting markedly depressed melting points.

During the 1960s and 1970s, scientists initiated an inquiry into the characteristics of ionic liquids, which are salts exhibiting a liquid state at or in proximity to ambient temperature [36]. Ionic compounds exhibit intriguing characteristics such as elevated conductivity, reduced volatility, and versatile solvency towards diverse substances. Nevertheless, they were also discovered to be costly.

The Abbott research group conducted an investigation in 2001 on eutectic combinations with the aim of identifying solvents that could address the issues of high moisture sensitivity and cost associated with various conventional IL [2]. In 2001, Abbott conducted a study on the physical properties of various Lewis-acidic ionic liquids by synthesizing them through the combination of different quaternary ammonium salts and metal salts. The ILs that were examined demonstrated that the combination of choline chloride (ChCl) and zinc chloride in a molar ratio of 1:2 exhibited the most minimal freezing point, measuring between 23 and 25°C [2].

Abbott and colleagues coined the term "deep eutectic solvent" in 2003 to describe eutectic mixtures made up of choline chloride and various hydrogen bond donors, such as urea, glycerol, or ethylene glycol. Since then, a wide range of deep eutectic solvents have been developed using different combinations of salts and hydrogen bond donors [37]. In 2003, Abbott et al. introduced the term "deep eutectic solvent" to refer to eutectic mixtures that consist of choline chloride and diverse hydrogen bond donors, including urea, glycerol, or ethylene glycol. Subsequently, an extensive array of compounds has been formulated by employing various permutations of salts and hydrogen bond donors. The ChCl-urea DES with a molar ratio of 1:2 exhibited the minimum freezing point (12°C). The freezing point of the substance in question is significantly lower than that of ChCl (302°C) and urea (133°C) [37]. The strong interaction between urea and chloride ions results in a remarkable decrease in the freezing point. The DESs were proposed by Abbott et al. in 2004 as a viable substitute for ILs one year later [38]. Subsequently, this category of solvents garnered significant interest across various scientific domains, and substantial advancements have been made [39]. The progression of the DES investigation has resulted in the formation of novel subcategories of these solutions. Verpoorte et al. (2011) introduced a novel subset of DES known as natural deep eutectic solvents

(NADES). These solvents are composed of primary metabolites, including amino acids, sugars, sugar alcohols, polyalcohols, organic acids, and choline derivatives [40].

In 2015, water immiscible DESs were generated by the Bernardo and Marrucho groups [41]. In 2019, Coutinho et al. put forth an elaborated depiction of DESs in response to the burgeoning research on this category of solvents [42]. "DES is a mixture of multiple pure chemicals that exhibit a eutectic point temperature lower than that of an ideal liquid mixture," they stated [42]. To emphasize this fact, the nomenclature of this solvent class has been modified to include the term "deep" (i.e., deep eutectic solvents) [42]. Currently, deep eutectic solvents are under investigation for a diverse array of applications, such as serving as solvents for chemical reactions, functioning as electrolytes in batteries, and acting as extraction agents in the separation of compounds. These substances are currently under investigation as a possible substitute for hazardous or economically detrimental solvents in diverse industrial applications.

2.3. Preparation of DESs

Various methods have been employed to prepare DESs with high purity and low cost. The process of heating involves the amalgamation and application of heat to the compounds while maintaining a continuous stirring motion until a uniform liquid mixture is achieved [43, 44]. Typically, the heating temperature falls within the range of (50 to 100) °C. Notwithstanding the preparation method, an elevation in temperature has the potential to cause the degradation of the deep eutectic solvent through an esterification reaction, as evidenced by Rodriguez et al. (2019) research on solvents that rely on choline chloride and carboxylic acids [45].

The grinding technique involves blending the substances at ambient temperature and pulverizing them in a mortar using a pestle until a clear solution is achieved, as reported by Gutierrez et al. (2009) [46]. Then disclosed an alternative technique that involves the freeze-drying of the aqueous solutions containing the constituents of deep eutectic solvents. Dai et al. (2013) reported a method of evaporation, wherein the constituents of deep eutectic solvents were dissolved in water and subsequently evaporated at 50 °C [47]. The resultant solution is subsequently transferred to a desiccator containing silica gel, as described by Dai et al. (2013). In pursuit of time and energy efficiency, Gomez et al. (2018) proposed a more environmentally friendly method utilizing microwave assistance for the rapid synthesis of natural deep eutectic solvents [48]. Finally, an ultrasound-assisted approach for the preparation of innate deep eutectic solvents was recently reported by Santana et al. in 2019 [49].

2.4 Classification of DESs

The DESs were classified into five distinct groups (types I–V) utilizing the fundamental formula Cat^+X^-zY , as depicted in Figure 2.2. The fundamental expression utilized to characterize deep eutectic

solvents is $\text{Cat}^+\text{X}^-\text{zY}$. The Cat^+ component can be any ammonium, phosphonium, or sulfonium cation, while X denotes a Lewis base, typically a halide anion. The formation of complex anionic entities occurs through the interaction of X^- with either a Lewis or Brønsted acid Y, where z denotes the quantity of Y molecules involved in the interaction with the anion [50].

Type I can be synthesized by combining quaternary ammonium salts with metal chlorides. Type I DESs are synthesized through the combination of imidazolium salts and a range of metal halides, including zinc chloride (ZnCl_2), iron (Fe), quaternary ammonium salt with a non-hydrated metal chloride, chlorine (Cl_2), silver chloride (AgCl), copper (II) chloride (CuCl_2), cadmium chloride (CdCl_2), lithium chloride (LiCl), stannous chloride (SnCl_2), and tin (IV) chloride (SnCl_4) [38, 51].

There exists a limited selection of non-hydrated metal halides with a low melting point that are employed in the creation of Type I DESs. Consequently, the number of combinations involving HBD is reduced for this particular category of DES. Type I DESs refer to deep eutectic solvents, which are formed by the combination of a quaternary ammonium salt and a non-hydrated metal chloride [9, 10]. These particular types of DESs are formulated through the amalgamation of imidazolium salts with a diverse array of metal halides, encompassing ZnCl_2 , FeCl_2 , AgCl , CuCl_2 , CdCl_2 , LiCl , SnCl_2 , and SnCl_4 . Type I deep eutectic solvents are synthesized by employing a restricted assortment of metal halides that lack hydration and possess relatively low melting points. Consequently, the range of HBD combinations accessible for this specific category of DES is reduced.

Type II eutectics have the same composition as Type I eutectics, but they contain the hydrated form of the metal halide. Type III eutectics consist of hydrogen bond acceptors, such as quaternary ammonium salts (e.g., choline chloride), and hydrogen bond donors, such as urea and ethylene glycol. The aforementioned are non-metallic deep eutectic solvents [52, 53]. The utilization of Type III eutectics has been efficaciously demonstrated in various metal processing applications, including electrodeposition, electropolishing, and metal extraction. Type IV eutectics exhibit similarities to type III eutectics, though with a distinct variation in the hydrogen bond acceptor component. Specifically, type IV eutectics employ a metal halide, such as urea, as the hydrogen bond donor, in contrast to the quaternary ammonium salt utilized in type III eutectics. The phenomenon of electrodeposition is of particular interest in the context of type IV eutectics due to their ability to form cationic metal complexes. This ensures a high concentration of metal ions within the double layer in proximity to the electrode interface [54]. The current investigation aims to evaluate the separation of close boiling points using Type IV DESs based on thermodynamic data.

Abranches et al. (2021) have recently reported on a Type V drug-eluting stent composed of non-ionic materials. Type V DESs are composed solely of non-ionic chemical constituents and are frequently characterized as hydrophobic, falling under the category of hydrophobic deep eutectic solvents (HDES) [55]. Discriminating between HBAs and HBDs in Type V DESs poses a challenge [55]. Type V DESs are frequently characterized by their hydrophobic nature and higher volatility. This particular attribute enhances the potential for developing efficacious techniques for recycling DES. This particular category of DESs represents a recently developed group of mixtures comprising non-ionic molecular HBA and HBD. Despite displaying a decrease in melting points similar to DESs, there is an absence of any ionic contribution. The class of DESs exhibited a notable abundance of hydrogen bonding. There exists a potential for the emergence of a novel combination class that may not conform precisely to this particular category. Nonetheless, they demonstrate a significant decrease in their melting points, similar to a combination of Brønsted or Lowry acid-base reactions.

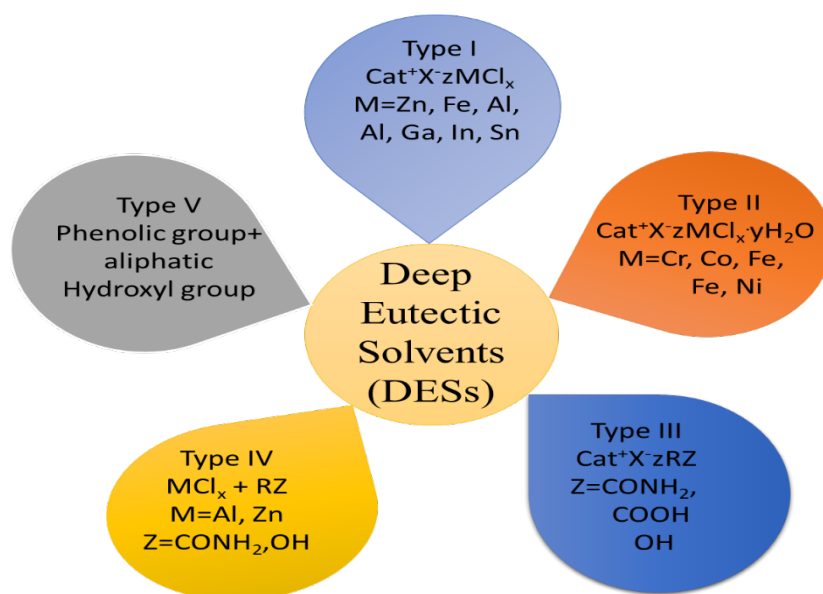


Figure 2. 2: Five categories of DESs [6].

2.5. Properties of DESs

The physicochemical characteristics of DESs are an essential reason for the growing attention of scientists to these solvents. In addition to exhibiting chemical and thermal stability, low vapor pressure, nonflammability, and low volatility, DESs possess the potential to be chemically tailored for targeted applications owing to the extensive range of available DESs, which includes their polarity, surface tension, viscosity, phase behavior, ionic conductivity, and density.

2.5.1 Phase behaviour

DESs are characterized as complex mixtures of two or more pure compounds rather than being considered pure compounds themselves [7]. The representation of this system is depicted through a phase diagram that exhibits the correlation between the melting temperature and the composition of the mixture in the solid-liquid state. This is an important point called the eutectic point. It shows the composition and the lowest temperature at which the melting curves of compounds A and B meet in a binary combination, as shown in Figure 2.3. Martins et al. (2019) have suggested that the term "deep eutectic solvent" should be reserved for mixtures that possess a melting point lower than the ideal eutectic temperature [24]. This is because the nomenclature "deep" would not be applicable to mixtures that do not meet this criterion, and it would be difficult to distinguish them from other types of mixtures. Furthermore, the authors asserted that the requisite characteristic of a DES is its ability to maintain a liquid state during operational conditions, which may necessitate a composition that deviates from the eutectic composition. Thus, the possession of a phase diagram is imperative, and the comprehension of the melting characteristics or freezing temperatures of the pure substances is crucial in ascertaining the optimal solubility curve. It is a common observation that the melting points and T_f values of DESs are comparatively lower than those of the constituent components utilized in their formation. The observed phenomenon can be attributed to the establishment of strong hydrogen bonds between the hydrogen bond donor and acceptor, leading to a disruption of the conventional crystal lattice configuration and impeding the freezing mechanism. However, scant information has been documented regarding the thermodynamic characteristics of the deep eutectic solvents thus far. According to Zhang et al. (2012), the freezing points of most DESs typically fall within the range of (-69 to 149) °C. However, it is noteworthy that all of these solvents exhibit a freezing point that is below 150 °C [56]. The precise freezing point may be subject to alteration based on variables such as the composition and proportion of constituents.

The presence of a hydrogen bond donor, the type of organic salt and its anion, and the molar ratio of the organic salt and the hydrogen bond donor can all have an impact on a mixture's freezing point. These influences have been demonstrated in studies conducted by Abbott, et al. (2004a, b), and Abbott et al. (2003) [37, 38, 43, 57]. According to Abbott et al. (2006) the freezing point value can be affected by the preparation method, but the eutectic composition should remain constant regardless of the technique employed [58]. Abbott and colleagues (2004a, b) discovered that a decrease in the molecular weight of the hydrogen bond donor resulted in a more significant reduction in the freezing point [38, 43].

In contrast to the technique used by Abbott et al. (2006) which involves finding the temperature depression by computing the differences between the linear combination of the melting points of the pure components and the actual eutectic point (referred to as ΔT_1). Martins et al. (2019) introduced an alternative and more appropriate conceptualization of temperature depression, whereby it is defined as the disparity between the ideal and observed eutectic point, denoted as ΔT_2 [24]. The inaccuracy arises from the improper classification of any chemical combination as a deep eutectic solvent, as seen in Figure 2.4 [24]. Nevertheless, it has been documented that several other combinations only demonstrated a glass transition phenomenon devoid of any discernible melting point.

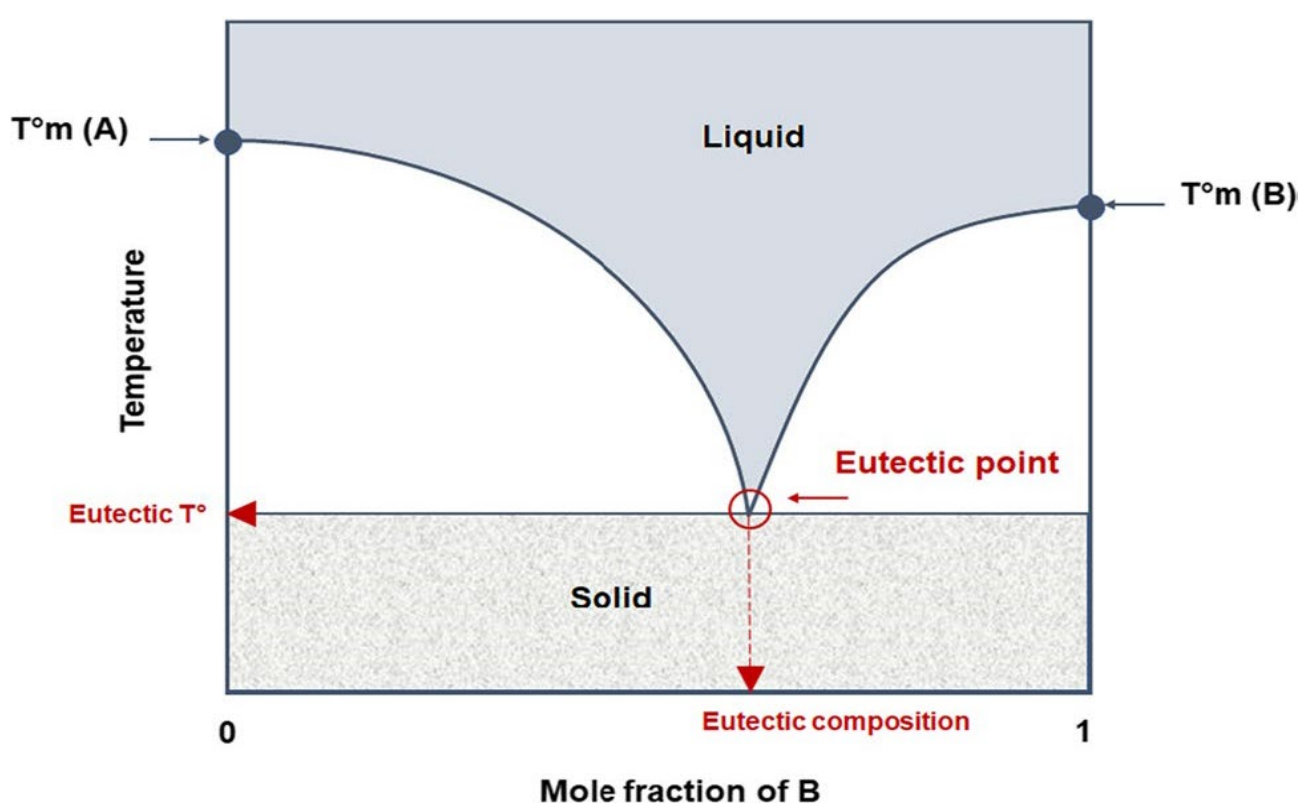


Figure 2. 3: Certain binary mixtures exhibit a typical solid-liquid phase diagram. In this diagram, $T_m(A)$ and $T_m(B)$ denote the respective melting temperatures of substances A and B. The eutectic point signifies both the composition and the lowest melting temperature at which the melting curves of both substances converge [24].

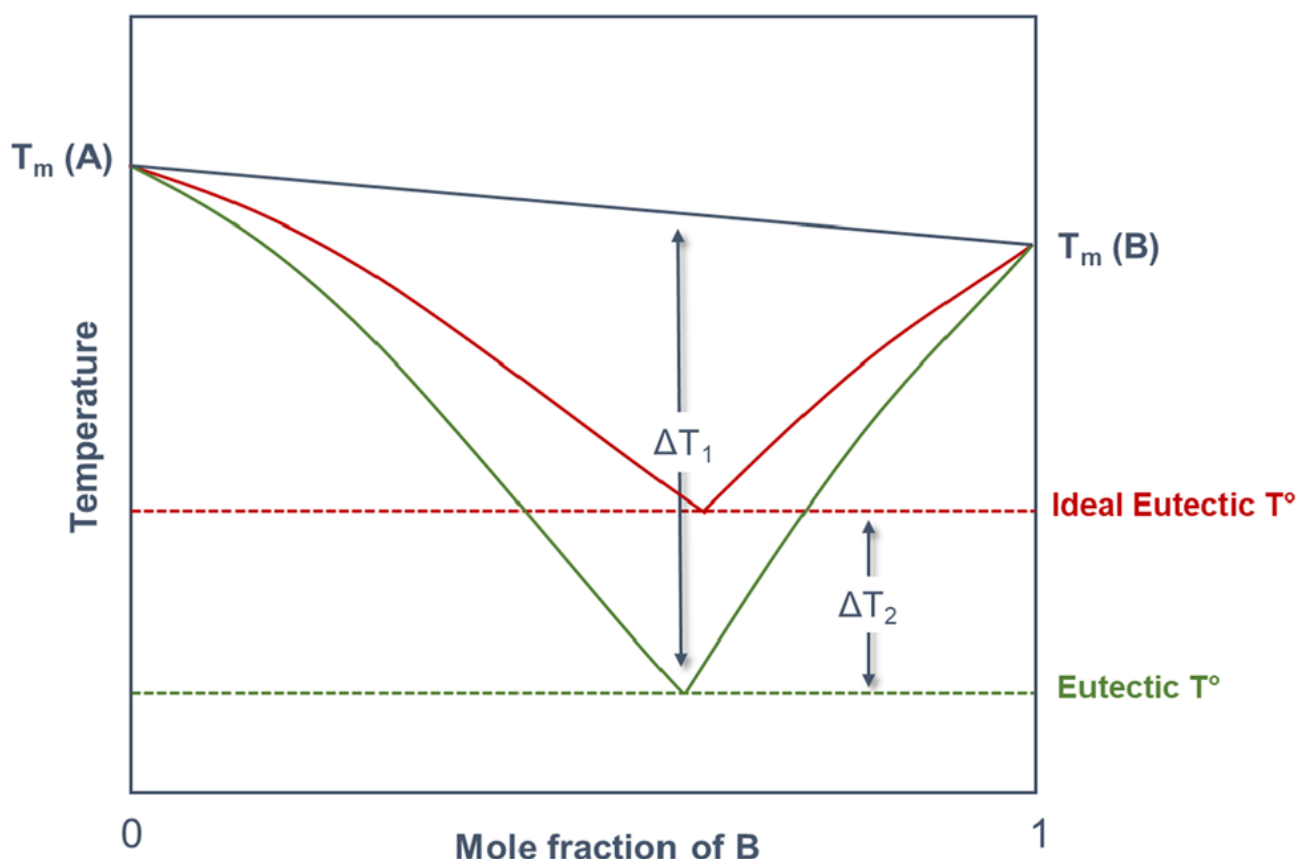


Figure 2. 4: A phase diagram illustrates the freezing behavior of two types of mixtures: one that follows the ideal eutectic pattern (represented by the red line), and another known as a deep eutectic mixture (represented by the green line). In this context, ΔT indicates the degree of freezing point depression under consideration [24].

2.5.2. Density

Density is considered to be an intensive property of DESs. The density of DESs is contingent upon the precise composition and concentration of their constituent elements [25]. The density of a system can exhibit considerable variation dependent upon the specific pairing of the hydrogen bond donor and acceptor, in conjunction with the prevailing temperature and pressure parameters. Furthermore, a multitude of DESs can be acquired, thereby enhancing the versatility of this novel solvent category. At a temperature of 298.15 K, it can be observed that the density of DESs falls within the range of 1.0 to 1.63 g/cm³, surpassing the density of water (refer to Table 2.1). The densities of DESs containing metallic salts, such as ZnCl₂, vary between 1.3 to 1.63 g/cm³ [59]. This variability is dependent upon the molecular packing and density of the DESs, as well as the existence of voids or vacancies within them. In the instance of combining ZnCl₂ with urea, the average hole diameter was observed to diminish, leading to a small increase in the density of DESs in comparison to pure urea. The DESs are extremely reduced by temperature. DESs generally exhibit a decrease in density as temperature increases, but the exact behavior can depend on the specific composition of the solvent and the occurrence of phase transitions.

Another parameter to take into account is the chain length, which may affect the density of DESs [60]. It is crucial to acknowledge that a deep eutectic solvent's density cannot solely depend on the length of its chain. The density of a DES is affected by many parameters, including the type and potency of hydrogen bonding interactions, the existence of supplementary functional groups, and the comprehensive composition of the DES. The increase in chain length of the constituents in deep eutectic solvents is typically associated with an elevation in density. However, it is imperative to note that this is merely one of the several factors that can impact density, and the precise outcome can be dependent on the other constituents and molecular interactions at play.

Table 2. 1: The densities of the chosen DESs at a temperature of 25 °C.

HBD	HBA	Molar Ratio	ρ (g/cm ³)	References
Hexanediol	ZnCl ₂	1:3	1.38	[61]
Ethylene glycol	ZnCl ₂	1:4	1.45	[61]
Acetamide	ZnCl ₂	1:4	1.36	[61]
Urea	ZnCl ₂	1:3.5	1.63	[61]
Levulinic acid	ChCl	1:2	1.138	[60]
Glutaric acid	ChCl	1:1	1.188	[60]
Malonic acid	ChCl	1:1	1.231	[60]
Glycolic acid	ChCl	1:1	1.195	[60]
Oxalic acid	ChCl	1:1	1.259	[60]
Phenol	ChCl	1:3	1.092	[62]
<i>o</i> -Cresol	ChCl	1:3	1.07	[62]
1-(Trifluoromethyl)urea	ChCl	1:15	1.324	[58]
1-(Trifluoromethyl)urea	Ethylammonium chloride	1:15	1.273	[58]
Urea	Ethylammonium chloride	1:15	1.140	[58]
Urea	Choline acetate	1:2	1.206	[58]
Urea	ChCl	1:2	1.25	[58]
Acetamide	Ethylammonium chloride	1:15	1.041	[58]
Glycerol	ChCl	1:2	1.20	[63]
Glycerol	ChCl	1:1	1.16	[59]
Glycerol	Methyltriphenylphosphonium bromide	1:4	1.30	[63]
Glycerol	Methyltriphenylphosphonium bromide	1:3	1.30	[63]
Glycerol	Methyltriphenylphosphonium bromide	1:2	1.31	[63]
Glycerol	<i>N,N</i> -Diethylethanolammonium chloride	1:4	1.22	[63]

Glycerol	<i>N,N</i> -Diethylethanolammonium chloride	1:3	1.21	[63]
Glycerol	<i>N,N</i> -Diethylethanolammonium chloride	1:2	1.17	[63]
Ethylene glycol	<i>N,N</i> -Diethylethanolammonium chloride	1:4	1.10	[63]
Ethylene glycol	<i>N,N</i> -Diethylethanolammonium chloride	1:3	1.10	[63]
Ethylene glycol	<i>N,N</i> -Diethylethanolammonium chloride	1:2	1.10	[63]
Ethylene glycol	Methyltriphenylphosphonium bromide	1:6	1.22	[63]
Ethylene glycol	Methyltriphenylphosphonium bromide	1:4	1.23	[63]
Ethylene glycol	Methyltriphenylphosphonium bromide	1:4	1.25	[63]

2.4.3. Viscosity

The investigation of the viscosity of DESs is a key determinant that warrants scholarly attention [64]. The viscosity of DESs is subjected to various factors, such as the nature and concentrations of the constituents, as well as the strength of the hydrogen bonding interactions [65]. In general, it can be observed that DESs possess higher viscosities in comparison to conventional organic solvents, owing to their ionic character and strong intermolecular associations. Table 2.2 reports that the viscosity of DESs is frequently observed to be high (>100 cP) [66]. Nevertheless, certain DESs can be created by combining choline chloride (ChCl) with ethylene glycol, 1,4-butanediol, o-cresol, or phenol. These DESs exhibit a viscosity that is less than 100 cP at a temperature range of (20 to 30) °C. The viscosities of eutectic mixtures are primarily influenced by the chemical composition of the DESs, including the identity of the salts and hydrogen bond donors, as well as the molar ratio of salt to HBD. The viscosity of ChCl-based DESs is significantly influenced by the characteristics of the hydrogen bond donor. The ChCl/ethylene glycol (1:4) DES displays the least viscosity at 19 cP when measured at 20 °C, while the viscosity of ChCl/ZnCl₂ is notably high at 8500 cP when measured at 25 °C. Moreover, the

utilization of derived sugars such as xylitol and sorbitol, or carboxylic acids such as malonic acid, as hydrogen bond donors resulted in DESs that demonstrated elevated viscosities. For instance, the ChCl/sorbitol DES exhibited a viscosity of 12.730 cP at 20 °C, while the ChCl/malonic acid DES exhibited a viscosity of 1.124 cP at 25 °C. The phenomenon can be attributed to the intermolecular hydrogen bond network.

The viscosity of DESs composed of choline chloride (ChCl) and glycerol shows a declining pattern as the molar ratio of ChCl to glycerol increases. The viscosities of ChCl-glycerol solutions with molar ratios of 1:4, 1:3, and 1:2, were determined to be 503, 450, and 376 cP, respectively, while the temperature was maintained at 20°C. The intermolecular hydrogen bond network of glycerol is of considerable significance, and the decrease in viscosity seen when the ChCl/glycerol molar ratio is increased is thought to be caused by the partial breakdown of this network [21]. A similar trend was seen in the context of ChCl/1,4-butanediol combinations. It is worth mentioning that the viscosity of the ChCl/ethylene glycol combination did not exhibit any noticeable change when comparing a molar ratio of salt to hydrogen bond donor (HBD) of 1:3 to that of 1:4 (19 cP at 20 °C).

The high viscosity of DESs is often attributed to the significant hydrogen bond interactions between their components. These interactions lead to a decrease in the mobility of freely moving species within the solvent system. DESs have a higher viscosity for several reasons, including electrostatic or van der Waals interactions, the fact that most DESs have a small void volume compared to their large ion size, and the fact that they have free volume. The research conducted by Abbott et al. (2006, 2007) [58, 61] demonstrates that the hole theory posits a correlation between the presence of holes in a fluid and its viscosity, as these holes facilitate ionic motion. Consequently, volumetric factors play a dominant role in controlling viscosity, despite the existence of robust intermolecular interactions in such systems. Hence, while ion-hydrogen bond donor interactions hold significance in determining the viscosity of deep eutectic solvents, the influence of steric effects must also be considered. According to the theory of holes, it is possible to obtain DESs with low viscosities by utilizing small cations or fluorinated HBDs [58]. Regarding alternative solvents, it is observed that the viscosity of the solvent is inversely proportional to the temperature, wherein an increase in temperature results in a decrease in viscosity. The experimental results indicate that the temperature increase from 25 to 40 °C caused a reduction in the viscosity of a ChCl/urea mixture from 750 to 169 cP. The literature reveals notable variations in the viscosity of DESs, which can be attributed to factors such as variances in (i) experimental techniques, (ii) DES production methods, and (iii) the presence of impurities, such as water. The viscosity data of deep eutectic solvents was found to vary by 6.5% depending on the method of preparation employed, either through traditional heating and stirring or grinding, as reported in reference [60, 67].

The water content is a significant parameter that can impact the viscosity of DESs due to their high hygroscopicity. Consequently, it is imperative to furnish the water content for the purpose of comparing the data documented in the literature, a practice that is not widely observed. In a study conducted by Yadav and Pandey (2019), it was observed that the viscosity of ChCl/urea (1:2 molar ratio) decreased from 527.3 cP for the pure DESs to 200.6 cP for the DESs including a 0.1 mole fraction of water [68]. DESs with high viscosity, such as choline chloride (ChCl) and oxalic acid in a 1:1 molar ratio, exhibit the ability to absorb a significant amount of water from the atmosphere, up to 19.40 wt%. This phenomenon results in a reduction of the solvent's viscosity from 53.63 to 44.49 cP. The findings underscore the feasibility of reducing the viscosity of extremely viscous DESs through the deliberate introduction of regulated quantities of water. However, it is imperative to exercise caution while undertaking this task, as it has the potential to impact the characteristics of DESs.

Table 2. 2: Viscosity parameter for several DESs at a range of temperatures.

HBD	HBA	Salt:HBD molar ratio	η (mPa · s)	References
ZnCl ₂	ChCl	1:2	85000 (25 °C)	[69]
Glycerol	ChCl	1:4	503 (20 °C)	[59]
Glycerol	ChCl	1:3	450 (20 °C)	[59]
Glycerol	ChCl	1:2	246.79 (30 °C)	[70]
Glycerol	ChCl	1:2	259 (25 °C)	[71]
Glycerol	ChCl	1:2	367 (20 °C)	[59]
Glycerol	Benzyltrimethylammonium chloride	1:5	553.7 (55 °C)	[72]
Glycerol	N,N-Diethylethanolammonium chloride	1:2	351 (30 °C)	[73]
Glycerol	Tetrabutylammonium chloride	1:4	476.1 (30 °C)	[74]
Glycerol	Tetrabutylammonium bromide	1:3	467.2 (30 °C)	[75]
Ethylene glycol	ChCl	1:4	19 (20 °C)	[59]
Ethylene glycol	ChCl	1:3	19 (20 °C)	[59]
Ethylene glycol	ChCl	1:2	35 (30 °C)	[71]
Ethylene glycol	ChCl	1:2	37 (25 °C)	[71]
Ethylene glycol	ChCl	1:2	36 (20 °C)	[59]
Ethylene glycol	N,N-Diethylethanolammonium chloride	1:2	40.68 (30 °C)	[73]
Ethylene glycol	Methyltriphenylphosphonium bromide	1:4	109.8 (25 °C)	[76]
Ethylene glycol	Tetrapropylammonium bromide	1:3	58.2 (30 °C)	[77]
Ethylene glycol	Tetrabutylammonium chloride	1:3	56.9 (30 °C)	[74]
Ethylene glycol	Tetrabutylammonium bromide	1:3	77 (30 °C)	[75]

Triethylene glycol	Tetraproylammonium bromide	1:3	71.9 (30 °C)	[77]
Imidazole	ChCl	3:7	15 (70 °C)	[78]
Imidazole	Tetrabutylammonium bromide	3:7	810 (20 °C)	[78]
Imidazole	Tetrabutylammonium bromide	3:7	314.5 (30 °C)	[78]
1,4-Butanediol	ChCl	1:3	140 (20 °C)	[59]
1,4-Butanediol	ChCl	1:4	88 (20 °C)	[59]
Xylitol	ChCl	1:1	5230 (30 °C)	[79]
D-Sorbitol	ChCl	1:1	12730 (30 °C)	[79]
Phenol	ChCl	1:3	35.17 (30 °C)	[62]
o-Creol	ChCl	1:3	77.65 (25 °C)	[62]
Malonic acid	ChCl	1:2	1124 (25 °C)	[71]
Levulinic acid	ChCl	1:2	164.5 (30 °C)	[60, 67]
Gylcolic acid	ChCl	1:1	394.8 (30 °C)	[60, 67]
Urea	ZnCl ₂	1:3.5	11340 (25 °C)	[59]

2.5.4. Ionic conductivity

Ionic conductivity of DESs typically manifest inferior conductivities in comparison to conventional organic electrolytes or aqueous electrolytes [80]. This is primarily attributed to the relatively high viscosity of DESs, which impedes ionic mobility. It is noteworthy that the ionic conductivity of a deep eutectic solvent is subjected to variation based on its composition, temperature, and the ions present in the system. The DESs' ionic conductivities exhibit a correlation with their viscosity and are comparatively low. Hence, the majority of DESs exhibit an ionic conductivity below 1 mS/cm at ambient conditions [56]. The ionic conductivities of DESs that only consist of ethylene glycol, or imidazole, and ChCl are increased (7.61 mS/cm at 20 °C and 12 mS/cm at 60 °C, respectively) because of their decreased viscosities. The correlation between molar conductivity and fluidity (the reciprocal of viscosity) can be ascertained by graphing them on a logarithmic scale (Walden plot). The plotted curve is compared with the theoretical line acquired for an aqueous solution of 0.01 M potassium chloride (KCl). The theoretical line exhibits a slope of 1 and passes through the origin of coordinates. According to the data, DESs with low viscosity, such as those containing ethylene glycol, exhibit reduced ionic conductivities. On the other hand, highly viscous DESs are situated in closer proximity to the ideal line.

The temperature-dependent increase in ionic conductivities is demonstrated in Table 2.3. The temperature-dependent behavior of conductivity is frequently elucidated using Arrhenius-type kinetics [2, 37, 44, 74, 76, 81]. The modulation of the organic salt/HBD molar ratio [2, 37, 44] can lead to an alteration of ionic conductivity. Abbott et al. (2007) investigated the projection of DES ionic conductivity and established that the ion mobility and, consequently, the conductivity of a

substance are influenced by the existence of suitable holes, as well as the characteristics and strength of ion-hydrogen bond donor interactions [59]. Furthermore, the conductivity fluctuation in relation to salt concentration is contingent upon the salt's type and the HBD. This results in systems exhibiting either a negative correlation between conductivity and salt concentration or a trend of conductivity-salt concentration reaching a maximum.

Table 2. 3: Conductivity parameter for several DESs at a range of temperatures.

HBD	HBA	Salt/HBD molar ratio	mS/cm	References
ZnCl ₂	ChCl	1:2	0.06 (42 °C)	[43]
Urea	Ethylammonium chloride	1:1.5	0.348 (40 °C)	[58]
Urea	Choline acetate	1:2	0.017 (40 °C)	[58]
Urea	ChCl	1:2	0.199 (40 °C)	[58]
Urea	ChCl	1:2	0.75 (25 °C)	[2, 37, 44]
Glycerol	Benzyltriphenylphosphonium chloride	1:4	0.163 (40 °C)	[72]
Glycerol	Methyltriphenylphosphonium bromide	1:1.75	0.165 (25 °C)	[72]
Glycerol	ChCl	1:2	1.18 (25 °C)	[2, 37, 44]
Glycerol	ChCl	1:2	1.05 (20 °C)	[59]
Ethylene glycol	Benzyltriphenylphosphonium chloride	1:3	0.485 (40 °C)	[72]
Ethylene glycol	Methyltriphenylphosphonium bromide	1:4	0.788 (25 °C)	[72]
Ethylene glycol	ChCl	1:2	7.61 (20 °C)	[81]
Acetamide	Ethylammonium chloride	1:1.5	0.688 (40 °C)	[58]
2,2,2-Trifluoroacetamide	Methyltriphenylphosphonium bromide	1:8	0.848 (25 °C)	[72]
2,2,2-Trifluoroacetamide	Ethylammonium chloride	1:1.5	0.39 (40 °C)	[58]
2,2,2-Trifluoroacetamide	ChCl	1:2	0.286 (40 °C)	[58]
Phenol	ChCl	1:3	3.14 (25 °C)	[62]
o-Cresol	ChCl	1:3	1.21 (25 °C)	[62]
Malonic acid	ChCl	1:1	0.55 (25 °C)	1
1,4-Butanediol	ChCl	1:3	1.64 (20 °C)	[59]
Imidazolium	Tetrabutylammonium bromide	3:7	0.24 (60 °C)	[81]
Imidazolium	Tetrabutylammonium bromide	3:7	0.24 (20 °C)	[81]
Imidazolium	ChCl	3:7	12 (60 °C)	[81]
Urea	ZnCl ₂	3:7	0.18 (42 °C)	[43]

2.5.5. Polarity

The property of polarity is crucial as it indicates the solvation capacity of solvents. The solvatochromic parameters are utilized to estimate this characteristic by analyzing the hypsochromic (blue) shift or bathochromic (red) shift of UV-vis bands for negatively solvatochromic dyes (such as Reichardt's betaine dye) or positively solvatochromic dyes (such as Nile red), respectively. The shift is dependent on the polarity of the solvent [82]. The solvent polarity of a ChCl and glycerol mixture was characterized by Abbott et al. (2011) at various salt/HBD molar ratios (1:3, 1:2, 1:1.5, and 1:1) [81], utilizing Reichardt's dye scale (ET(30) parameter) [82] and the Kamlet-Taft scale (π^* , α , and β parameters) [83]. The DESs composed of ChCl and glycerol exhibit polarity similar to primary and secondary alkylammonium ionic liquids, with all fluids being polar in nature [84]. Pandey et al. (2014) conducted an extensive experimental investigation on ChCl-derived DESs employing various solvatochromic probes [85]. Betaine dye 33 was employed for the determination of the ET (30) value. The high polarities of ChCl/ethylene glycol, ChCl/glycerol (1:2), and ChCl/urea (1:2) have been experimentally verified, demonstrating their superior polar nature compared to short-chain alcohols and the majority of widely used ionic liquids. The glycerol deep eutectic solvents provide the largest electron transfer (ET) values, reaching a magnitude of 30. Similarly, the ethylene glycol and urea deep eutectic solvents also display significant electron transfer values. The observed phenomenon was ascribed to the abundance of hydroxyl groups present in HBDs.

Table 2. 4: Polarity parameter of the various DESs.

HBD	HBA	HBD:HBA Molar ratio	ET (30) Kcal·mol ⁻¹	ET (33) Kcal·mol ⁻¹	References
Glycerol	ChCl	1:1	58.49	-	[56]
Glycerol	ChCl	1:1.5	58.21	-	[56]
Glycerol	ChCl	1:2	58.28	-	[56]
Glycerol	ChCl	1:3	57.96	-	[56]
Glycerol	ChCl	1:2	58	66.4	[85]
Urea	ChCl	1:2	57	65.4	[85]
Ethylene glycol	ChCl	1:2	57.3	65.7	[85]

2.5.6. Surface tension

The investigation of the surface tension of DESs is an important aspect in understanding the impact of molecular structure on the intensity of contacts between the hydrogen bond acceptor and hydrogen bond donor in DES mixtures. The intermolecular interactions between hydrogen bond acceptors and hydrogen bond donors plays a crucial role in the formation of DES mixtures and has a major impact on their surface tension. The surface tension of DES may be influenced by several parameters, such as temperature, molar ratio, the characteristics of hydrogen bond acceptors and hydrogen bond

donors, and the length of the alkyl chain in the cation. The surface tension of DES exhibits a notable degree of elevation and is significantly influenced by the magnitude of intermolecular interactions between the hydrogen bond donors and the associated salt. According to the data shown in Table 2.5, ChCl/ethylene glycol and tetraalkylammonium-based DESs exhibit a significantly elevated surface tension. Additionally, it should be noted that the ChCl/malonic acid system as well as the ChCl/fructose or glucose system exhibit a significant surface tension, with values of 65.7, 74.01, and 71.7 mN/m, respectively [71, 88].

This may be attributed to the presence of extensive hydrogen bonding within these systems. The surface tension is also influenced by the type of cation. The presence of a cation that includes a hydroxyl group results in a DES with a significantly elevated surface tension, as shown by the ChCl/glycerol system with a surface tension of 56 mN/m. The surface tension of tetraalkylammonium-based deep eutectic solvents exhibits a positive correlation with the length of the alkyl chains. As an example, the surface tension of tetrapropylammonium bromide/glycerol DES is measured to be 46 mN/m, whereas the surface tension of tetrabutylammonium chloride/glycerol DES is found to be 52.7 mN/m. The molar proportion of salt and temperature variations both have an impact on surface tension. In all the examined DESs, it has been shown that the surface tension exhibits an upward trend as the temperature decreases [74, 81, 86]. The salt molar fraction may have an impact on the weakening of hydrogen bonds with hydrogen bond donors [81], which is what is possibly causing this behavior.

The surface tension statistics of ChCl-based and ZnCl₂-based DESs were published by Abbott et al. [2, 37, 44]. Previous studies have shown that the surface tensions of the values in question surpass those of typical molecular solvents and are comparable to those of imidazolium-based ionic liquids and high-temperature molten salts, such as 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM]BF₄, which has a surface tension of 38.4 mN/m at 63 °C, and KBr, which has a surface tension of 77.3 mN/m at 900 °C. Furthermore, they have shown the presence of a link between viscosity and surface tension.

Table 2. 5: Surface tension parameter for several DESs at a range of temperatures.

HBD	HBA	Salt:HBD molar ratio	γ (mN/m)	References
1,6-Hexanediol	ZnCl ₂	1: 3	19 (25 °C)	[2, 37, 44]
Ethylene glycol	ZnCl ₂	1: 4	56.9 (25 °C)	[2, 37, 44]
Acetamide	ZnCl ₂	1: 4	53 (25 °C)	[2, 37, 44]
Urea	ZnCl ₂	1: 3.5	72 (25 °C)	[2, 37, 44]
Urea	ChCl	1:2	52 (25 °C)	[71]

Glycerol	Methyltriphenylphosphonium bromide	1: 3	58.94 (25 °C)	[86]
Glycerol	<i>N,N</i> -Diethylethanolammonium chloride	1: 4	59.35 (25 °C)	[86]
Glycerol	Tetrabutylammonium chloride	1: 3	52.7 (30 °C)	[77]
Glycerol	Tetrapropylammonium bromide	1: 3	46 (30 °C)	[71]
Glycerol	ChCl	1: 3	50.8 (20 °C)	[71]
Glycerol	ChCl	1: 2	56 (25 °C)	[71]
Ethylene glycol	<i>N,N</i> -Diethylethanolammonium chloride	1: 3	47.51 (25 °C)	[86]
Ethylene glycol	Methyltriphenylphosphonium bromide	1: 4	51.29 (25 °C)	[86]
Ethylene glycol	Tetrabutylammonium chloride	1: 3	46.2 (30 °C)	[77]
Ethylene glycol	Tetrapropylammonium bromide	1: 3	40.1 (30 °C)	[74]
Ethylene glycol	ChCl	1: 3	45.4 (20 °C)	[59]
Ethylene glycol	ChCl	1: 2	48 (25 °C)	[71]
Triethylene glycol	Tetrapropylammonium bromide	1: 3	39.3 (30 °C)	[74]
Triethylene glycol	Tetrabutylammonium chloride	3: 1	46.2 (30 °C)	[77]
Triethylene glycol	Methyltriphenylphosphonium bromide	1: 5	49.85 (25 °C)	[86]
D-Glucose	ChCl	2: 1	71.7 (25 °C)	[87]
D-Fructose	ChCl	2: 1	74.01 (25 °C)	[88]
Phenylacetic acid	ChCl	1: 1	41.86 (25 °C)	[2, 37, 44]
Malonic acid	ChCl	1: 1	65.7 (25 °C)	[71]
1,4-Butanediol	ChCl	1: 3	47.17 (25 °C)	[86]

2.6 Applications of DESs

Currently, the applications and research pertaining to DESs are still in their developing stages, despite their remarkable characteristic of being liquid under normal environmental conditions and exhibiting intriguing advantages. These solvents possess distinctive characteristics that render them attractive for a multitude of industrial applications. Presented herein are several illustrations of the industrial implementations pertaining to DESs (refer to Figure 2.5):

- Green solvents: DESs have garnered considerable interest as viable substitutes for conventional solvents, particularly organic solvents, due to their environmentally friendly

nature [89]. These substances demonstrate high thermal stability, low vapor pressure, and an exceptional ability to dissolve a diverse array of compounds. The utilization of DESs has been observed in various industrial processes, including extraction, catalysis, and separation, thereby leading to a notable reduction in the environmental footprint associated with conventional solvents.

- Metal extraction: DESs have demonstrated potential in the extraction of metals from both ores and waste materials [90]. Selective dissolution of metal ions enables the implementation of highly efficient extraction and separation procedures. DES-based extraction methods exhibit potential for enhanced sustainability and energy efficiency in comparison to conventional techniques, including smelting or leaching processes involving the utilization of hazardous chemicals [91].
- Electrochemistry: The utilization of DES has been observed in a multitude of electrochemical processes. Electrolytes find utility in various applications such as batteries, fuel cells, and electroplating processes [26, 92]. Deep eutectic solvents possess distinct physicochemical characteristics, including elevated ionic conductivity and a broad electrochemical window, making them appealing substitutes for conventional electrolytes.
- Catalysis: DESs possess the ability to function as solvents or co-catalysts within catalytic reactions [93]. Catalysts can be stabilized, resulting in enhanced reaction rates and improved selectivity. The utilization of DES-based catalysis has been extensively investigated in diverse domains, encompassing biomass conversion, fine chemical synthesis, and polymerization reactions.
- Carbon capture and storage (CCS): The suitability of DES as a solvent for carbon capture and storage (CCS) processes has been subject to extensive investigation. The selective capture of carbon dioxide (CO₂) from flue gases released by industrial processes or power plants is one potential strategy. A study using DES-based systems has shown promising results, showing higher capacity and lower energy needs compared to traditional amine-based solvents [94, 95].
- Drug delivery: The utilization of deep eutectic solvents has demonstrated promising prospects in the field of drug delivery systems. One potential benefit is the ability of these substances to enhance the solubility and stability of drugs with low water solubility, thereby enhancing their bioavailability [96]. Formulations based on DES have demonstrated the potential to improve drug delivery across multiple administration routes, such as oral, transdermal, and ocular routes [97].

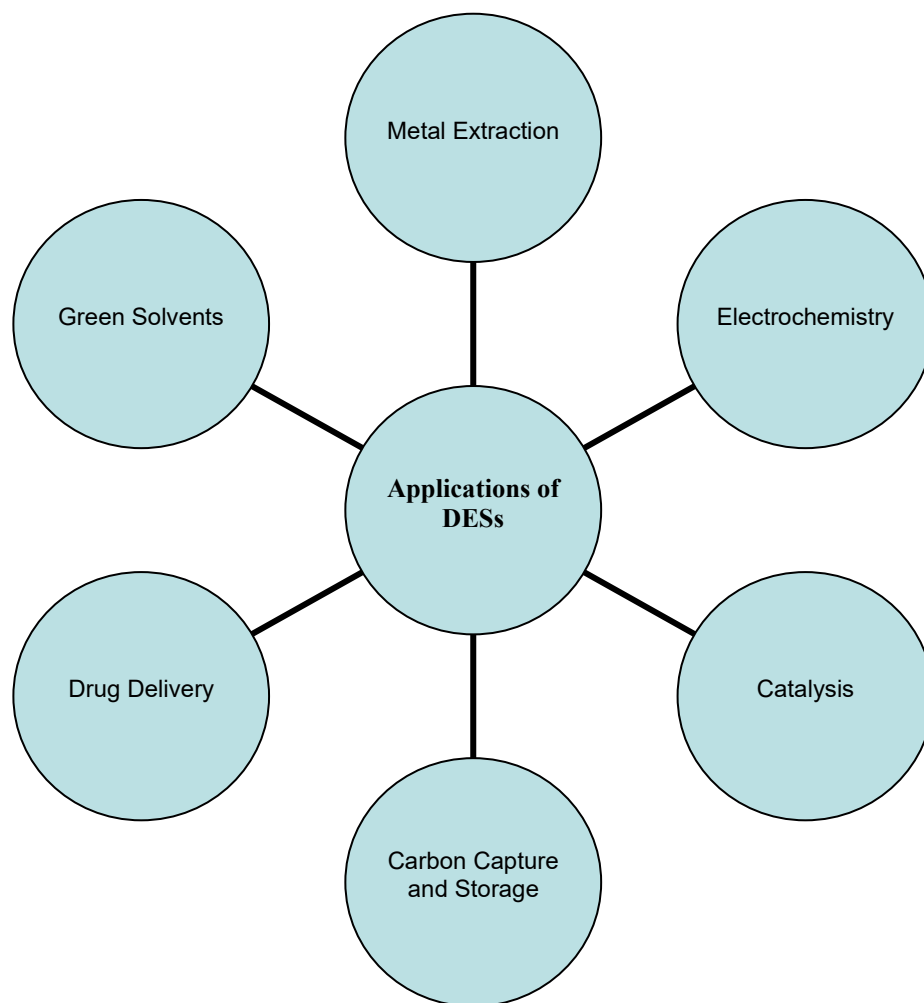


Figure 2. 5: Applications of DESs.

2.7. DESs and industrial separation problem

The implementation of DESs holds promise for improving the efficacy and ecological viability of existing separation techniques. However, the main challenge in the progress of industrial processes employing these innovative and captivating solvents pertains to the separation of DESs [98]. Separation methods comprise a range of techniques utilized to effectively separate and purify components within a mixture. The application of these methodologies is of great significance in various industries, such as pharmaceuticals, food processing, environmental analysis, and chemical manufacturing. Different separation techniques are employed based on the unique properties of the substances being separated, such as their solubility, boiling points, molecular size, or chemical affinity. The separation of solutes from a solvent is dependent on the particular solute and the chosen

method of separation. There are several separation methods that are frequently employed in various fields, such as:

2.7.1. Extractive or azeotropic distillation

The process of distillation is a frequently utilized technique in the realm of chemistry to achieve the separation of different constituents present in a mixture, taking advantage of differences in their individual boiling points. Extractive distillation and azeotropic distillation are specifically used when separation by convectional distillation is not feasible [99].

Extractive distillation is a well-established procedural technique employed in various industries, particularly in chemical engineering and separation processes. This technique involves the introduction of a solvent or entrainer into a mixture, which aids in the efficient separation of its constituent elements [100]. The entrainer facilitates the generation of a separate liquid phase that consists of one or more components from the mixture. As a result, the entrainer alters the relative volatility of these components. The modification in volatility enhances the phenomenon of separation via distillation. The choice of the entrainer is typically determined by its ability to selectively dissolve one or more components from the mixture while also having a low boiling point. The occurrence of an azeotrope formation involving the desired component(s) leads to an increase in their relative volatility, thereby aiding in their separation from the mixture.

Azeotropic distillation is a technique utilized in situations where a mixture suggests the occurrence of an azeotrope, which is a mixture distinguished by a uniform boiling point [101]. An azeotrope is a liquid mixture that demonstrates a consistent boiling point, maintaining its compositional reliability throughout each stage of the process. The conventional distillation method fails to achieve full component separation when employed on an azeotropic mixture. To effectively manage this limitation, azeotropic distillation is employed. The procedure involves the incorporation of an additional component, commonly known as an entrainer or azeotrope breaker, into the azeotropic blend. The entrainer modifies the relative volatility of the components, thus aiding in their separation during the distillation process. The introduction of an entrainer into an azeotropic mixture leads to the creation of a unique azeotrope, wherein one or more components of the original azeotropic mixture undergo alterations, consequently inducing modifications in both the overall composition and boiling points. Figure 2.6 depicts the extractive distillation used to separate aliphatic and aromatic compounds.

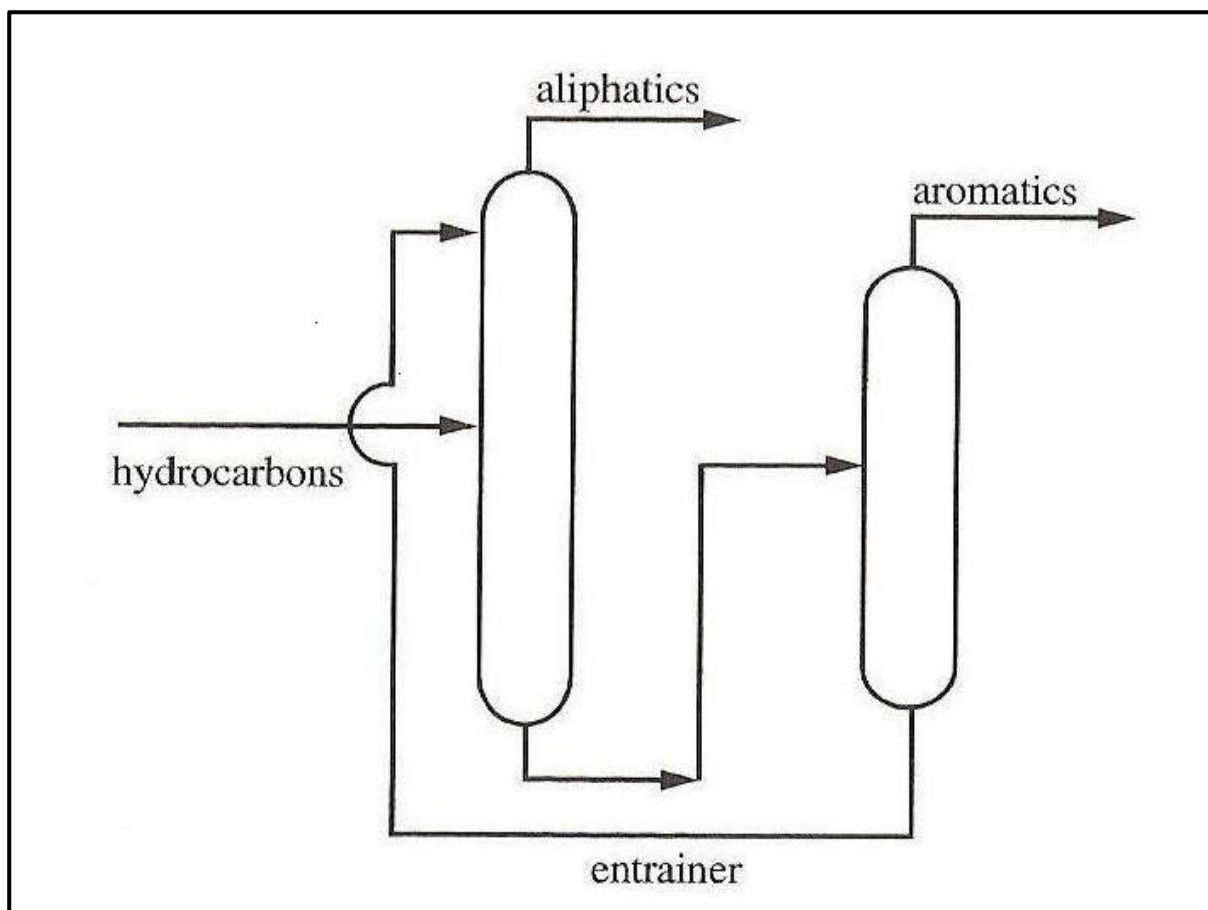


Figure 2. 6: Schematic diagram of an extractive distillation process [104].

2.7.2. Liquid-liquid extraction

Separation and purification of components in a liquid mixture may be accomplished by using liquid-liquid extraction (LLE), also known as solvent extraction or partitioning [102, 103]. It is commonly employed across a wide range of disciplines, encompassing chemistry, pharmaceuticals, environmental science, and the food industry. The procedure involves the movement of one or more solutes from a liquid phase, commonly known as the "feed" or "aqueous phase," to a separate liquid phase that is incapable of mixing, referred to as the "extract" or "organic phase," which typically comprises an organic solvent (refer Figure 2.7). The choice of solvents is dependent on several factors, such as the solubilities of the components and the desired method of separation. The utilization of this separation technique is frequently observed within industrial manufacturing environments, where it is implemented for a multitude of separation procedures, such as [104]:

(a) Separation of systems with similar boiling points: When encountered with a liquid mixture comprising two or more components exhibiting similar boiling points, the process of achieving separation solely through distillation becomes challenging. Liquid-liquid extraction offers a viable method that facilitates the preferential transfer of a particular constituent from either the aqueous phase to the organic phase or vice versa. This phenomenon exploits the distinct solubilities exhibited

by the two phases. This method is commonly utilized to extract aromatic compounds from aliphatic hydrocarbons.

(b) Separation of azeotropic mixtures: Azeotropic mixtures are liquid mixtures that exhibit uniform boiling points and compositions. The process of separating them using traditional distillation techniques may present certain challenges. The implementation of LLE can be utilized as a technique to alter the azeotrope by selectively extracting one of the constituents into the organic phase. The technique is commonly utilized for the purpose of isolating acetic acid or formic acid from aqueous solutions.

(c) Separation of temperature-sensitive compounds: Several compounds display a greater reactivity to increased temperatures and can potentially undergo decomposition or react when subjected to standard distillation conditions. The implementation of LLE provides a more moderate methodology for separation, as it permits the extraction procedure to be carried out at diminished temperatures. The desired compound can be efficiently extracted from the feed solution through the process of transferring it into the organic phase, thus reducing the risk of excessive thermal exposure.

(d) Separation of mixtures with high boiling points: The utilization of LLE proves to be particularly advantageous in the process of separating mixtures containing components with notably high boiling points. Instead of utilizing high-temperature distillation, which entails the potential for decomposition or other associated complexities, the mixture undergoes LLE. The compounds possessing a significantly elevated boiling point exhibit a propensity for selective transference to the organic phase, thereby facilitating their separation from the initial solution.

(e) Extraction of organic solutions: The LLE technique demonstrates its potential as a suitable approach for the effective extraction of organic solutes from a provided solution. The utilization of this technique is commonly observed in the pharmaceutical and chemical industries, particularly in cases where there is a necessity to extract or refine specific compounds from complex mixtures. The careful selection of an appropriate organic solvent allows for the effective extraction of the solute from the aqueous phase, thus enabling the following steps of separation and concentration.

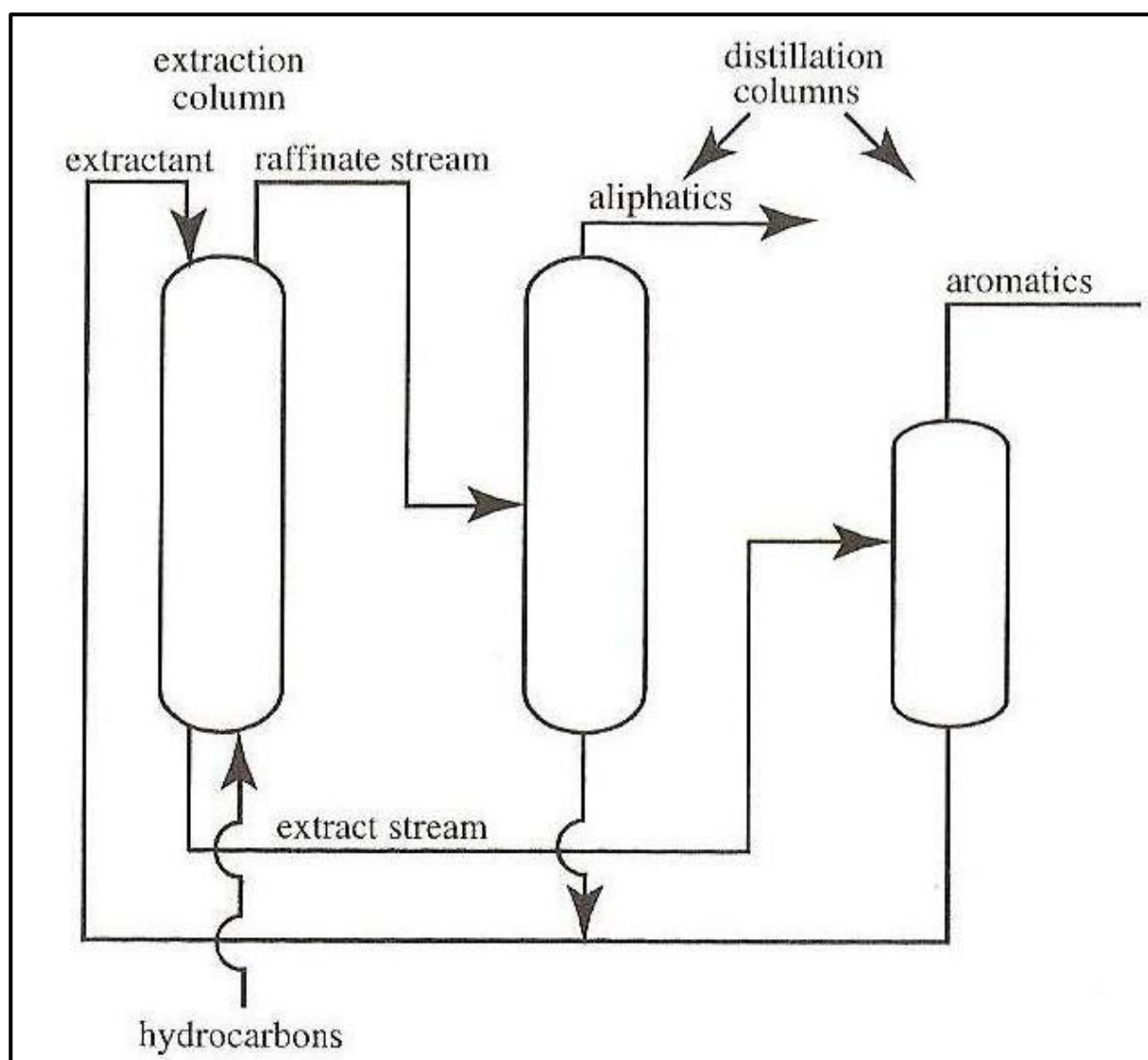


Figure 2. 7: Schematic diagram of typical liquid-liquid extraction process [104].

2.7.3. Membrane separation

Membrane separation is a procedural technique that utilizes a selectively permeable membrane to efficiently separate two constituent elements within a provided feed mixture [105]. The feed mixture undergoes membrane filtration, a process in which certain species are allowed to pass through the membrane while others are held back. The experimental protocol results in the formation of two separate phases, specifically referred to as the retentate and the permeate. The nomenclature "retentate phase" refers to the constituent of the feed mixture that is retained within the membrane. The membrane demonstrates selective permeability, thereby regulating the transportation of species and leading to the accumulation of said components in the retentate phase. The phase known as the retentate is characterized by a decrease in the concentration of the species that can permeate through the membrane.

On the contrary, the permeate phase consists of the species that successfully traverse the membrane. The membrane demonstrates a characteristic of selective permeability, which allows for the passage of specific species. As a result, there is an increased concentration of these components in the permeate phase when compared to the initial feed mixture. The membrane utilized in the procedure has been intentionally designed to demonstrate selectivity towards specific species, thereby enabling the separation of desired constituents. Different categories of membranes, such as polymeric membranes and ceramic membranes, can be employed based on the specific attributes of the feed mixture and the desired separation procedure [106].

2.7.4. Absorption and stripping technique

Absorption and stripping are two interconnected methodologies utilized within the realm of chemical engineering to facilitate the efficient transfer of components between a gaseous phase and a liquid phase. Absorption is a scientific phenomenon characterized by the transfer of one or more constituents from the gaseous phase to the liquid phase [107]. The occurrence of this phenomenon is observed when the elements or compounds existing in the gaseous state encounter a liquid medium in which they exhibit solubility. The facilitation of the dissolution and absorption of gas phase components in the liquid is attributed to their inherent solubility. The purification, separation, and recovery of valuable components from gases are commonly accomplished by employing absorption processes.

On the contrary, the phenomenon of stripping can be perceived as the opposite of absorption. The phenomenon involves the transformation of one or more constituents from a state of matter characterized by a fluid phase to a state of matter characterized by a gaseous phase [108]. During the stripping procedure, the liquid phase, which retains the targeted constituent, is subjected to a gaseous environment, resulting in the selective dissolution of the stated constituent into the gas phase. The gaseous phase is anticipated to demonstrate more affinity for the component when contrasted with the liquid phase. Stripping processes are commonly utilized to remove impurities from liquids or concentrate constituents. The efficacy of both absorption and stripping processes relies on the interplay concerning the gas and liquid phases, which enables the efficient transfer of components [109]. To enhance the efficiency of these processes, it is imperative to maximize the interfacial area between the gaseous and liquid phases. The attainment of this goal is typically achieved by employing equipment that enables significant interfacial interaction between the two phases. Instances of such apparatus encompass packed columns, bubble columns, and trays.

2.8. Review on infinite dilution activity coefficients using DESs

Investigation into the IDAC employing DESs represents a developing and expanding world within the field of solvent dynamics. Infinite dilution activity coefficient serves as a quantification of the non-ideal behavior exhibited by a solvent within a solution when subjected to infinite dilution. The

provided statement quantifies the deviations from ideal behavior, wherein ideal behavior is predicated in the absence of interactions between solute and solvent molecules. The utilization of DESs has been the subject of thorough investigation in diverse fields, encompassing their potential as solvents in extraction and separation methodologies. Scientists can enhance their understanding of solvation behavior and effectively optimize DESs for applications. In the realm of deep eutectic solvents, scientific investigations pertaining to the infinite dilution activity coefficient primarily revolve around comprehending the complex behavior exhibited by solutes within these distinctive solvent systems. Significant scientific insights about solute-solvent interactions and the degree of solute combination or association inside deep eutectic solvents may be obtained from an examination of the infinite dilution activity coefficient. Many different types of experimental methods, such as gas-liquid chromatography, gas solubility studies, and spectroscopic approaches, are used by researchers to discover more about the activity coefficient at infinite dilution in deep eutectic solvents. These techniques facilitate the quantification of solute concentrations in the vapor or liquid phase, thereby enabling the computation of the activity coefficient.

Research has been conducted to investigate the thermo-physical properties and the IDAC of DESs, as outlined in the following summary.

The study by Molefi et al. in 2023, was mostly about figuring out what a DES is made of when 1-butyl-2,3-dimethylimidazolium chloride ([BDMIM] [Cl]) and ethylene glycol (EG) are mixed in a 1:3 ratio. The activity coefficients of organic solutes in the DES in a state of infinite dilution were determined using the GLC technique. The decision to use DES was impacted by several variables, which subsequently had implications for the overall efficacy of the extraction procedure. Researchers found that the DES worked well at separating azeotropes made up of alkane-alcohols and getting rid of sulfur compounds from hydrocarbons. This means that the DES could be used in processes that need to separate mixtures of these different types [110].

In 2023, Yang and colleagues (2023) documented the presence of 27 solutes inside the tetraethylammonium chloride and ethylene glycol DES system and determined the activity coefficient values at infinite dilution for these solutes. The findings obtained from the experiment demonstrate the possibility of using DES as effective extractants for the separation of cyclohexane/ethanol and heptane/thiophene systems, as shown by their selectivity and capacity. This discovery suggests that the DES has the capacity to demonstrate effectiveness in the separation of these combinations. The experimental findings indicated that alcohol exhibited the highest level of solubility among the DESs that were investigated. This implies that the DES has a pronounced propensity for establishing interactions with alcohols when compared to other chemical compounds [111].

The investigation conducted by Mgxadeni et al. (2022) examined a study investigating the impact of hydrogen bond donors on zinc chloride in the context of separating binary mixtures and its influence on activity coefficients at infinite dilution. This is primarily due to their favorable separation parameters, specifically selectivity and capacity, which make them suitable for various systems involving close-boiling mixtures [7]. Furthermore, in a subsequent study by Mgxadeni et al. (2023), they explored the thermodynamic characteristics, activity coefficients at infinite dilution of DESs across varying temperatures [30]. The study findings indicate that the combination of $[\text{ZnCl}_2 + \text{acetic or phosphoric acid}]$ 1:2 ratio has significant selectivity and capacity. This suggests that this solvent mixture has the potential to be a viable substitute for conventional solvents used in the separation of particular azeotropic combinations [30].

Li et al. (2022) and Wang et al. (2022) used IGC methods to evaluate the thermodynamic properties and activity coefficients at infinite dilution of organic solutes in DESs, namely choline chloride + 1,5-pentanediol and choline chloride + oxalic acid [112, 113]. The results of the study revealed that alcohols had advantageous solvent characteristics for the DES. In the year 2022, Manyoni et al. conducted an experiment utilizing GLC to evaluate the potential of (1-ethyl-1-methylpyrrolidinium bromide + glycerol) (DES) as a viable separation agent for a diverse range of organic solutes at different temperatures. The observed results pertaining to selectivity and capacity indicate that the examined DES exhibits unsuitability for the separation of acetone/ethanol, while it shows potential for the separation of cyclohexane/benzene [114].

Additionally, a study was carried out in 2023 by Manyoni and Redhi, investigating a compound known as ethaline [115]. Ethaline is a combination of choline chloride, which acts as a hydrogen bond acceptor, and ethylene glycol, which serves as a hydrogen bond donor. The molar ratio of choline chloride to ethylene glycol in ethaline is 1:2. The objective of their investigation was to examine the thermodynamic characteristics of this particular combination and assess its prospective utility in separation methodologies. In order to elucidate the thermodynamic characteristics of ethaline, the researchers employed a GLC that was fitted with a thermal conductivity detector (TCD). The challenges encompassed the separation of hexane/benzene, cyclohexane/hexane, ethanol/toluene, and acetone/methanol mixtures. The findings of their investigation showed that ethaline did not manifest thermodynamic properties that were considered suitable for potential separation applications. In alternative terms, the observed outcomes were considered ineffective in achieving optimal separation of the designated mixtures owing to the deficiency of the measured thermodynamic data. Consequently, it can be concluded that ethaline did not exhibit promising characteristics for the separation issues under investigation. In their study, Kabane and Redhi (2020) investigated on the thermo-physical properties and activity coefficient of a specific DES composed of 1-butyl-3-

methylimidazolium chloride and glycerol. Their findings revealed that this DES exhibited a notable level of selectivity for the cyclohexane/ethanol mixture when compared to other DES and industrial solvents mentioned in existing literature. Consequently, the DES investigated in this study holds promise for potential utilization in extraction processes [116].

The investigation carried out by Nkosi et al. (2018a, 2018b, 2019) examined the influence of hydrogen bond donors on the infinite dilution activity coefficients. Tetramethylammonium chloride was selected as the hydrogen bond acceptor, and a range of hydrogen bond donors were used. The results of the study indicated that non-polar solutes had a higher infinite dilution activity coefficient in comparison to polar solutes. The observed phenomena may be explained by the existence of strong dipole-dipole interactions between the components of DESs and polar solutes. In addition, it is important to highlight that the solubility of polar solutes in DESs has a relatively elevated level. The aforementioned characteristic makes DESs a feasible alternative solvent for the separation of nitrogen and sulfur compounds from transportation fuels, including thiophene or pyridine, among others [117-119]. Furthermore, research was undertaken by Nkosi et al. in 2018, in which they investigated the infinite dilution activity coefficients of the [tetrapropylammonium bromide + 1,6-hexanediol] system in a DES. The results of their study suggested that the DES being examined showed considerable promise as a viable separation agent [120].

2.9. Review of binary mixtures using DESs

Researchers have done studies to examine the thermodynamic properties of DESs by analyzing their excess/deviation properties [121-123]. The primary objective of this research is to enhance comprehension of DESs and examine its prospective use in diverse procedures. The excess molar volume is a metric used to quantify the deviation of a mixture's volume from ideal behavior. This observation offers valuable information regarding the molecular interactions and structural modifications taking place within the solution. In an analogous way, excess isentropic compressibility quantifies the extent to which the compressibility of a mixture deviates from that of an ideal solution.

Various experimental investigations have examined the excess/deviation properties of DESs. These studies encompass the utilization of various compositions of DESs, which comprise combinations of HBAs and HBDs. Various experimental techniques, including density, speed of sound measurements, and other methods for determining thermodynamic properties, have been employed to ascertain the excess/deviation properties of DESs. The analysis of the effects of variables on the properties of DES mixtures typically involves conducting measurements across a range of temperatures and compositions.

2.9.1 Interactions between DESs and co-solvents

The interactions between DESs and co-solvents are essentially contingent upon the inherent characteristics of the constituent elements used in the formation of the DESs as well as the properties of the co-solvent. Co-solvents often refer to organic compounds that exhibit miscibility or partial miscibility with DESs. These co-solvents are added to the solvent mixture to alter its characteristics.

The following are important considerations pertaining to the interactions between DESs and co-solvents:

- Solubility and miscibility: The presence of co-solvents has the potential to have an impact on the solubility and miscibility characteristics of deep eutectic solvents when they are combined with other molecules. Certain co-solvents possess the capacity to improve the solubility of certain solutes inside DESs, hence leading to improved extraction or separation techniques [124].
- Viscosity: The viscosity of DESs may be influenced by the presence of co-solvents. The use of a co-solvent with a lower viscosity has the potential to reduce the total viscosity of the resultant mixture. This reduction in viscosity may provide certain advantages in certain applications, such as enhancing reaction kinetics and facilitating mass transfer [125, 126].
- Polar and non-polar interactions: Interactions such as hydrogen bonding, dipole-dipole interactions, or Van der Waals forces may occur depending on the specific co-solvent and DESs components involved. The previously mentioned interactions have the potential to have a substantial impact on the collective characteristics of the solvent mixture [127, 128].
- Stability: The thermal and chemical stability of deep eutectic solvents may be influenced by the presence of co-solvents. Several co-solvents possess the capability of enhancing the stability of DESs, rendering them suitable for applications that involve high temperatures or specific chemical processes [129, 130].
- Tuning properties: The use of various co-solvents offers the opportunity to precisely adjust the physical and chemical characteristics of deep eutectic solvents, hence enhancing their suitability for certain applications [131, 132].
- Applications: The interplay between deep eutectic solvents and co-solvents has been observed to have significant implications across a wide range of disciplines, including but not limited to green chemistry, extraction methodologies, catalytic reactions, electrochemical processes, and even the pharmaceutical and biomedical sectors [133, 134].

Hemayat et al. (2019) conducted a series of experiments aimed at determining the density and speed of sound in aqueous solutions. The researchers utilized choline chloride (ChCl) as the HBA, while

malonic acid (MA), oxalic acid (OA), and ethylene glycol (EG) were employed as the HBDs. To enhance comprehension of molecular interactions, various excess molar properties were computed, including limiting apparent molar expansibility, apparent molar volume, excess isobaric thermal expansion, and deviations in isentropic compressibility. Equations such as the Redlich-Kister and the Prigogine-Flory-Patterson (PFP) theory was ultimately employed to establish a correlation between the values of excess molar volumes [121].

Bartosz et al. (2022) evaluated the physicochemical and thermodynamic characteristics of aqueous solutions containing a new DES composed of tetrabutylammonium chloride (TBAC) and 3-amino-1-propanol (AP), tetrabutylammonium bromide (TBAB) and 2-(butylamino)ethanol (BEA), or 2-(methylamino)ethanol (MAE) or 3-amino-1-propanol. The study examined densities, speeds of sound, refractive indices, and viscosities for both pure and aqueous mixtures of DES. The results showed that the Jouyban-Acree model effectively fitted experimental data to the concentration variable. The study also demonstrated that the mathematical equation accurately predicted the properties of aqueous DES. The mixtures were analyzed for key physicochemical properties, including excess molar volumes, excess isentropic compressibility, deviations in refractive indices, and deviations in viscosity. The Redlich-Kister equation was used to calculate and correlate these properties, while the Prigogine-Flory-Patterson theory assessed non-ideal behavior. The findings were interpreted in relation to the interactions among the components of the mixture [122].

Muzammil and colleagues (2019) studied densities and speeds of sound for aqueous DES solutions at various compositions and temperatures from 293.15 K to 323.15 K under atmospheric pressure conditions. They prepared DESs using an equimolar ratio of choline chloride as the HBA and malonic acid and glutaric acid (GA) as the HBDs. The study examined the relationship between DES compositions and water (H_2O), the influence of HBD, and the impact of temperature on excess molar volumes and excess molar isentropic compressibility. The study found that intermolecular interactions were more significant than intramolecular interactions. The study also examined ion-water and hydrogen bond donor-water interactions in relation to DES composition and temperature. The study used the PFP theory and the extended real association model (ERAS) to assess non-ideal characteristics. The findings have potential implications for industrial processes and the development of thermodynamic models for DES [123].

In 2021, Omish et al. conducted a study on the density and speed of sound in binary mixtures of DESs. The researchers investigated the compositions of choline chloride: acetic acid (AA) and choline chloride: L-(+)-lactic acid (LA) in a (1:2) mixture in the presence of water. The thermodynamic parameters were derived and analyzed in terms of intermolecular interactions influenced by the components of the DESs. The negative excess molar volumes observed in the binary

mixtures were attributed to stronger hydrogen bond interactions and efficient molecular packing, outweighing repulsive interactions. The PFP theory was used to examine excess molar volume values, providing a comprehensive explanation for the volumetric behavior of binary mixtures. Density functional theory (DFT) calculations were employed to provide empirical evidence for the observed discrepancies in excess molar volumes and gain insights into fundamental interactions among the constituents of the mixture. The study assessed isentropic compressibility and excess isentropic compressibility through speed of sound measurements. The findings are significant for both academic and industrial sectors, as DESs are increasingly used in diverse applications. The findings contribute to enhancing the understanding of the characteristics and dynamics of binary mixtures of DESs, which can facilitate the advancement and refinement of processes and technologies relying on DESs [135].

Sharma et al. (2022) conducted a study on the excess molar properties of aqueous binary mixtures of PEGylated DESs at temperatures ranging from 293.15 K to 323.15 K and atmospheric pressure. The DESs were synthesized using tetrabutylammonium bromide (TBABr)/ benzyltributylammonium chloride (BZTBCl) HBA and polyethylene glycols (PEGs) with average molar masses of 200, 400, and 600 HBD. The researchers obtained empirical data on density and speed of sound for both individual DESs and DES mixtures in an aqueous environment. The use of the Redlich-Kister equation facilitated the estimation of the standard deviation pertaining to the disparity between experimental and estimated excess attributes. The presence of negative values for excess molar volumes and excess isentropic compressibility suggests stronger interactions between water and the components of the studied DESs. The behavior of the systems was examined using theoretical models such as the ERAS and the Prigogine-Flory-Patterson theory (PFPT). The study found that temperature, HBA structure, and HBD molecular mass influenced the excess molar properties of the binary mixtures of DESs. The researchers used theoretical models to gain a deeper understanding of the interactions occurring within the mixtures [136].

In 2020, Shekaari et. al. conducted research on environmentally friendly solvents made from amino acids and lactic acids. They prepared solvents and measured density and speed of sound data for neat lactic acid (LA)/alanine (Ala), lactic acid/glycine (Gly), and lactic acid/histidine (His) mixtures at different temperatures. The data was used to calculate and analyze thermodynamic properties, including excess molar volumes, apparent molar volumes, excess isobaric thermal expansion, excess molar isentropic compressibility, and limiting apparent molar expansibility. The study found that all DESs exhibited structure-breaker properties in water across all temperatures, as determined by Hepler's constant. The researchers used Redlich-Kister type equations to establish correlations among the properties. The results offer valuable insights into the characteristics and possible uses of these solvents across multiple disciplines [137].

In 2017, Shekaari et al. conducted a study on the thermophysical characteristics of aqueous solutions containing DES such as choline chloride and urea. They conducted experimental measurements across a range of concentrations of choline: urea (U) DES, ranging temperatures from 293.15 K to 323.15 K. The researchers used precise methods to measure densities, speeds of sound, refractive indices, and viscosities of the studied systems. The results were then used to compute thermodynamic and transport properties, including excess molar volumes, partial molar volumes, excess isobaric thermal expansions, excess molar isentropic compressibility, viscosity deviations, and deviations of molar refraction. The study aimed to analyze observed variations in properties, focusing on elucidating the underlying interactions between the solute, DES, and the solvent, specifically water. The researchers used the Eyring theory of viscous flow to compute excess activation properties, including partial excess molar entropies, Gibbs free energy, and partial molar excess enthalpies, to understand the alterations in energy, enthalpy, and entropy during the viscous flow of the solutions. This knowledge is valuable for various applications and industries that use DES, such as chemical engineering, materials science, and environmental studies [138].

The study conducted by Omar and Sadeghi in 2020 focused on the synthesis and characterization of novel ninhydrin-based DESs. In 2020, Omar and Rahmat Sadeghi conducted a study on the synthesis and characterization of novel ninhydrin-based DESs. These DESs were prepared using choline chloride (ChCl) and tetrabutylammonium hydrogen sulfate (TBAHS) as HBAs and ninhydrin (Nin) as HBD. The researchers analyzed properties such as density, sound velocity, viscosity, electrical conductivity, refractive index, and surface tension at different temperatures. Analytical techniques like ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared spectroscopy (FTIR) analysis validated the integrity, molecular composition, and interactions between HBAs and HBDs. The study employed basic linear models, such as the Jacobson equation and the Arrhenius equation, to investigate the impact of temperature on the thermophysical properties of the solvents. The synthesized DESs were used as solvents and indicator reagents for the quantitative and qualitative analysis of alanine. The DESs exhibited a notable level of efficacy in substituting the conventional organic solvents that are often used in the procedures of amino acid identification. This study contributed significantly to the advancement of novel deep eutectic solvents based on ninhydrin and explored their potential as effective solvents and indicator reagents for amino acid detection [139].

The research conducted by Abri et al. (2019) focused on investigating the spectral and thermophysical properties of novel deep eutectic solvents (DESs) based on l-menthol and their mixtures with ethanol. The researchers prepared three DESs by combining l-menthol with hydrogen bond donors such as salicylic acid and ethylene glycol. The DESs' hydrophobic nature allows them to form biphasic media

with water at room temperature, making them useful for separation and extraction processes. The physical properties of the DESs were investigated using density, speed of sound, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), FTIR, and NMR analysis. The study found that excess molar volumes, isentropic compressibility deviations, and speed of sound deviation decreased with increasing temperature, suggesting changes in molecular interactions with temperature variations [140].

A review summary of excess/derived properties of binary mixtures of DESs and co-solvents conducted by various authors [121-123, 135-140] shows that all investigated systems have negative values of excess molar volume and deviation in isentropic compressibility which indicate that DESs interact strongly with co-solvents such as water and ethanol (Table 2.6).

Table 2. 6: A review summary of excess/derived properties of binary mixtures of DESs and co-solvents.

DESs	Co-solvent	V_m^E	$\Delta \kappa_s$	Reference
[ChCl][EG], [ChCl][OA], [ChCl][MA]	Water	Negative	Negative	[121]
[TBAB][AP], [TBAC][AP], [TBAB][MAE], [TBAB][BAE]	Water	Negative	Negative	[122]
[ChCl][MA], [ChCl][GL]	Water	Negative	Negative	[123]
[ChCl][AC] (1:2), [ChCl][LA] (1:2)	Water	Negative		[135]
[TBABr][PEG] (1:2), [BZTBACl][PEG] (1:2)	Water	Negative	Negative	[136]
[LA][Ala], [LA][Gly],[LA][His]	Water	Negative	Negative	[137]
[ChCl][U], [l-methanol][SA], methanol][CSA], methanol][EG]	Water Ethanol	Negative Negative	Negative Negative	[138] [140]

THEORETICAL FRAMEWORK**3.1. Introduction of thermodynamics**

Thermodynamics is a subfield of physical science that focuses on the examination of energy and its conversions within various systems. It serves as a fundamental framework for comprehending the behavior of substances and the principles dictating the transfer of energy [141]. The field of thermodynamics is founded upon a collection of elemental principles and laws that elucidate the characteristics and conduct of energy. These fundamental principles are applicable across a broad spectrum of systems, spanning from elementary entities such as ideal gases to intricate arrangements like engines and power plants.

The 19th century witnessed significant advancements in the field of thermodynamics, particularly with the formulation and establishment of the first and second laws of thermodynamics [142, 143]. These laws serve as the fundamental principles upon which the subject is built. The first law, commonly referred to as the principle of energy conservation, posits that within an enclosed system, energy is imperishable and cannot be generated or annihilated; rather, it can solely undergo transference or conversion. The second law of thermodynamics introduces the fundamental concept of entropy, which quantifies the level of disorder or randomness within a given system. This law offers valuable insights into the direction of energy flow and the efficiency of conversion processes. Thermodynamics encompasses a range of processes, including heat transfer, work, and the relationships between pressure, temperature, and volume. These phenomena are commonly described using mathematical equations and diagrams, such as the Carnot cycle.

The interpretation of experimental results in the field of thermodynamics relies on various theoretical branches, such as hydrodynamics, mechanics, and electrostatics [144]. Hydrodynamics encompasses the study of liquid flow and the application of fluid mechanics principles, whereas mechanics offers valuable insights into the mechanical properties and behaviors of various systems. The field of electrostatics focuses on the examination of charged particles and their interactions, with a particular emphasis on systems that involve ions and other charged species. The contributions made by Jacobus Henricus van't Hoff in 1887, established the fundamental principles for comprehending the thermodynamics of liquid mixtures [145]. The theory of electrolytic dissociation proposed by Svante Arrhenius in 1903 introduced the fundamental concept of ions and charged particles, elucidating their role in the manifestation of electrical conductivity and various other properties exhibited by solutions [146, 147]. The pioneering of the application of thermodynamics to liquid mixtures can be attributed

to Jacobus Henricus van 't Hoff. (1912) [148]. The late 19th century witnessed the notable contributions of Van 't Hoff to the field of thermodynamics, particularly in the year 1887. During this period, Van 't Hoff introduced the concept of chemical equilibrium and subsequently applied it to elucidate the behavior of solutions [149]. Josiah Willard Gibbs. (1906) made significant advancements in the field of thermodynamics, particularly in relation to the study of solutions, by building on van 't Hoff's research [150].

Gibbs's contributions have set up the basic rules we need to understand how liquid mixtures behave. These rules include chemical potential, phase equilibrium, and the Gibbs-Duhem equation. These principles offer a theoretical structure for the prediction and comprehension of mixture behavior without the requirement for extensive experimental measurements [151, 152]. Theoretical solutions rely on two fundamental factors: entropy, which quantifies the level of disorder or randomness within a given system, and molecular interactions occurring between adjacent molecules. The interactions between components in a mixture have a significant impact on the behavior and properties of the mixture. These interactions influence several aspects, such as phase behavior, solubility, and chemical reactivity. Through the application of thermodynamic principles, researchers and practitioners can acquire significant knowledge regarding the characteristics and interrelationships of liquid mixtures, thereby reducing the need for extensive experimental measurements. The application of thermodynamic principles and theories has become an essential component in the industrial utilization of chemistry [153]. This technology facilitates the optimization and design of industrial processes that involve the control of liquid mixtures, thereby enabling the achievement of efficient and sustainable production practices across diverse industries.

Moreover, thermodynamics assumes a crucial role in the fields of engineering, chemistry, and various other scientific disciplines [153]. This methodology finds application in the design and analysis of various systems, including engines, power plants, refrigeration systems, and chemical reactions. The comprehension of thermodynamic principles empowers engineers and scientists to enhance energy utilization, enhance efficiency, and make well-informed judgments in diverse domains.

3.2 Importance of thermodynamics

Thermodynamics plays a crucial role in diverse disciplines and manifests numerous practical implementations. Thermodynamics holds utmost importance due to several compelling factors:

1. Understanding energy conversion: Thermodynamics offers a theoretical framework for comprehending the processes by which energy undergoes conversion between different forms, such as the transformation of heat into work or vice versa. The acquisition of this knowledge is crucial for the development of effective energy systems and the enhancement of energy utilization across diverse industries [154].

2. Engineering applications: The principles of thermodynamics serve as the fundamental framework for numerous branches of engineering, encompassing mechanical, chemical, and aerospace engineering, among others. Thermodynamics aids engineers in the examination and creation of systems, encompassing engines, power plants, refrigeration systems, and turbines. The comprehension of thermodynamic principles enables engineers to maximize the performance, efficiency, and safety of these systems [155].
3. Environmental considerations: In the assessment, one can employ thermodynamic models to investigate the complex operation of combustion processes, carefully examining the efficacy and emissions of engines and power plants. Through their comprehension of thermodynamics, scientists and engineers can embark upon the mitigation of environmental impacts that are significantly influenced by the principles of thermodynamics. In the realm of thermodynamics, the pursuit of formulating sustainable energy solutions and mitigating the ecological impact of diverse processes [156].
4. Material science and phase transitions: The study of materials and their phase transitions greatly relies on the fundamental principles of thermodynamics [157]. Thermodynamics provides elucidation on the processes of phase transition, encompassing phenomena such as condensation, evaporation, freezing, and melting. The comprehension of the thermodynamic properties exhibited by materials across various states and environments facilitates the advancement of novel materials and the enhancement of manufacturing methodologies.
5. Biological systems: The laws of thermodynamics also have an impact on the study of biological systems. Living organisms can be described as detailed thermodynamic systems that rely extensively on the exchange and transformation of energy [158, 159]. Thermodynamic principles serve as a framework for elucidating the intricate mechanisms underlying vital processes, including metabolism, the storage of energy, and the exchange of heat within biological systems.
6. Fundamental laws and principles: The foundation of thermodynamics lies in a collection of essential laws and principles, encompassing the conservation of energy and entropy [160, 161]. The fundamental principles of thermodynamics offer profound insights into the dynamics of energy and its inherent constraints. Their consequences extend well beyond the field of thermodynamics, exerting a profound influence on various domains of physics and scientific inquiry.

3.3. Activity coefficients at infinite dilution

In a binary system, the notion of infinite dilution refers to the hypothetical scenario where the concentration of the solute approaches zero or becomes exceedingly small while the solvent's

concentration remains unchanging [162-164]. The activity coefficient (γ_i) of a substance (i) can be expressed as follows:

$$\gamma_i = \frac{f_i}{x_i f_i^*} \quad (3.1)$$

In the thermodynamic framework, f represents the fugacity of components i in a solution, as can be observed in equation (3.1) mentioned earlier. The fugacity for pure substances is denoted by f_i^* , while the mole fraction of the liquid phase is indicated by x_i . According to Raoult's law or Henry's law [165, 166], the activity coefficient is a measure of how non-ideal a solution's behavior is. Non-ideality means that the behavior doesn't follow what would happen in an ideal solution. The activity coefficient at infinite dilution is the most precise approach to assessing the interplay between the solute and solvent. It demonstrates the degree of deviation from an ideal interaction.

In dilute solutions, where the solute concentration is exceedingly low, the intermolecular forces between solute species control the behavior of the solution. At the infinite dilution activity coefficient, the solute concentration tends towards absolute zero, and the intermolecular forces between solute particles become insignificant in comparison to the interactions between the solute and the solvent. Hence, the infinite dilution activity coefficient imparts valuable insights into the solute-solvent interplay and the solute's behavior in a state of significant separation from other solute particles [167, 168]. According to Kojima et al. (1997), the validity of measurements necessitates the establishment of a concentration range for the solute x_i [169]. This range is typically defined based on the specific system under study. In certain systems, a concentration as low as 1% may be deemed sufficient to reasonably approximate the concept of infinite dilution. Nevertheless, in systems containing compounds with strong associations or interactions, the range of accurate measurements may be limited to as low as 10^{-7} .

3.4. Practical and theoretical applications of IDACs

Activity coefficients at infinite dilution (γ^∞) play a crucial role in various aspects of chemical engineering, both in practical applications and theoretical analyses. Here are some of the key applications:

- **Phase equilibria:** Activity coefficients at infinite dilution are employed for the purpose of forecasting and examining phase equilibria, particularly in the context of determining liquid-liquid and vapor-liquid equilibria from thermodynamic model parameters [170-172]. Engineers can make estimations regarding the distribution of components between various

phases and subsequently design separation processes by considering the behavior of solutes in solutions that are highly dilute.

- Solvent selection: The utilization of activity coefficients at infinite dilution aids in the identification of the optimal solvent for a specific separation procedure [173, 174]. Through the process of comparing the activity coefficients at infinite dilution for various solvents, engineers can discern the solvent that demonstrates the greatest selectivity and efficiency in the extraction or separation of specific solutes from mixtures.
- Process design: Activity coefficients at infinite dilution play a crucial role in the design of diverse separation processes within the field of chemical engineering, including distillation, extraction, and absorption [175-179]. Engineers can enhance the optimization of process parameters, accurate prediction of solute behavior at low concentrations, and efficient operation by integrating precise values of activity coefficients at infinite dilution into process models and simulations.
- Solvent purification: Activity coefficients at infinite dilution are employed in the purification processes of solvents [180]. Through the examination of impurity behavior within solutions of significant dilution, engineers can assess the efficacy of various purification techniques, including distillation, adsorption, and liquid-liquid extraction, in eliminating impurities from solvents [31].
- Solvent design: The utilization of activity coefficients at infinite dilution is significant in the process of designing and assessing novel solvents [116, 181]. These tools assist engineers in evaluating the solvent's capacity to dissolve solutes, estimating the solute's partitioning between different phases, and forecasting the solvent's efficacy in diverse separation procedures.
- Thermodynamic modeling: The consideration of activity coefficients at infinite dilution plays a crucial role in the thermodynamic analysis of liquid mixtures [182-186]. It is important to use these coefficients to improve and develop equations of state and activity models. This makes it easier to predict phase equilibrium and other thermodynamic properties across a wide range of conditions.
- Environmental analysis: Activity coefficients at infinite dilution play a crucial role in environmental analysis, specifically in the estimation of the behavior of pollutants or contaminants in various environmental media [187-189]. Activity coefficients at infinite dilution values can be utilized by engineers to ascertain the transport and destiny of chemicals

in the atmosphere, water, or soil, thereby assisting in the evaluation of risks and the development of remediation approaches.

- Pharmaceutical and biotechnology: Activity coefficients at infinite dilution play a crucial role in various applications within the pharmaceutical and biotechnology sectors [190, 191]. These applications include drug formulation, the extraction of active compounds from natural sources, and the purification of bioproducts. Having a precise understanding of activity coefficients at infinite dilution is crucial for optimizing processes, improving product purity, and maintaining consistent performance.

3.5. Techniques of obtaining activity coefficients at infinite dilution

The determination of limiting activity coefficients poses challenges, necessitating the development of various predictive techniques for estimating these values. The selection of methodology is dependent upon the system being examined, the accessible data, and the desired degree of precision. The assessment of the reliability of any predictive technique depends upon the availability of experimental data and the validation of said technique against established systems. Here are a few commonly used methods:

1. UNIFAC (universal quasi-chemical functional group activity coefficient): The UNIFAC method is a group contribution approach that employs the notion of functional groups for the purpose of estimating activity coefficients [192-194]. The calculation of activity coefficients involves the consideration of interactions among various functional groups within a mixture. The UNIFAC method is extensively employed in the analysis of non-electrolyte systems or the liquid phase and has demonstrated considerable efficacy in the estimation of activity coefficients for various solvents and solutes.
2. COSMO-RS (conductor-like screening model for real solvents): COSMO-RS is a quantum chemistry-inspired technique that effectively merges the COSMO (Conductor-like Screening Model) methodology with the statistical thermodynamic principles of the Real-Space Implementation (RS) approach. Quantum chemical calculations are employed to derive molecular properties and interactions, which are subsequently utilized for the computation of activity coefficients. COSMO-RS exhibits remarkable efficacy when dealing with electrolyte systems and has found extensive application across a diverse range of solvents [195, 196].
3. NRTL (non-random two-liquid model) is a theoretical framework rooted in empirical observations. It employs interaction parameters to make estimations regarding the activity coefficients [197-199]. It suggests the presence of order in the mixing procedure and considers the influence of molecular interactions, encompassing both close-proximity and distant-range

effects. NRTL, a renowned thermodynamic model, has gained significant traction in the scientific community due to its extensive application in diverse binary and multicomponent systems, encompassing both aqueous and non-aqueous solutions [200].

4. Wilson model: The Wilson model, a notable empirical model, considers the non-ideality of mixtures by incorporating the energy of mixing and variations in molecular sizes. To estimate activity coefficients, it employs binary interaction parameters. The Wilson model has demonstrated remarkable efficacy in its application to a diverse array of systems, particularly in describing the dynamic intermolecular interactions governing vapor-liquid equilibria [201, 202].
5. UNIQUAC (universal quasi-chemical activity coefficient): The UNIQUAC method is a derivative of the UNIFAC approach, which is founded on the principles of quasi-chemical theory. The analysis considers both the combinatorial and residual factors that contribute to the activity coefficients. A lot of different systems, including electrolyte solutions, have used the UNIQUAC model. It is famous for being very good at predicting phase equilibrium [203].

3.6. Determination of excess thermodynamic parameters

The thermodynamic parameters, including partial molar enthalpies, Gibbs free energy, and entropy term, were determined at infinite dilution using experimental activity coefficient data. The aforementioned parameters were employed to elucidate the various categories of molecular interactions that take place between the solvent and the solutes. The Van't Hoff relation was employed in the calculation of entropy and enthalpy values under conditions of infinite dilution.

$$\ln(\gamma_{13}^{\infty}) = \frac{\Delta H_1^{E,\infty}}{RT} - \frac{\Delta S_1^{E,\infty}}{R} \quad (3.2)$$

In the given equation, T represents the absolute temperature, while R denotes the universal gas constant. Partial excess enthalpy of a solute at infinite dilution ($H_i^{E,\infty}$) can be achieved by performing linear regression on the natural logarithm of the IDACs in relation to the inverse of temperature.

$$\ln(\gamma_{13}^{\infty}) = a + \frac{b}{T} \quad (3.3)$$

In the aforementioned equation (3.3), the variable "a" is used to denote the slope, while the variable "b" is employed to represent the intercept.

$$\Delta H_1^{E,\infty} = aR \quad \text{and} \quad \Delta S_1^{E,\infty} = -bR \quad (3.4)$$

The values of Gibbs free energies were obtained using equation (3.5) presented below.

$$\Delta G_1^{E,\infty} = RT \ln(\gamma_{13}^\infty) = \Delta H_1^{E,\infty} - T \Delta S_1^{E,\infty} \quad (3.5)$$

3.7. Techniques for determining activity coefficients at infinite dilution

Tumba (2009) presents three assumptions pertaining to the utilization of GLC for measurements conducted in the context of investigating ionic liquids [204].

- **Ideal gas mixture assumption:** This assumption states that the gas phase comprises an ideal mixture consisting of a solute (1) dissolved within a carrier gas (2). In the context of gas liquid chromatography, it is common practice to introduce the solute into the carrier gas in the form of a vapor or gaseous sample. The main idea is that the solute molecules mix completely and behave like a perfect gas, which enables accurate determination of retention times and other related parameters.
- **Real liquid system assumption:** This assumption relates to the stationary phase in GLC. The assumption is made that the solute (1) and the solvent (3) present in the stationary phase constitute a genuine liquid system. The stationary phase refers to a solvent substance that is applied as a coating on the inner surface of the chromatography column. This assumption acknowledges the interactions and behavior of the solute and solvent in the liquid phase and their impact on the separation process.
- **Thermodynamic equilibrium assumption:** This assumption predicts that the liquid and gas phases within the GLC system exist in a state of thermodynamic equilibrium. This happens because there is enough time for the solute molecules to reach a state of equilibrium, where they are evenly spread out between the gaseous and liquid phases, creating a durable equilibrium. This assumption facilitates the acquisition of dependable measurements of retention times and precise determinations of solute concentrations, relying on the partitioning phenomenon between the two distinct phases.

The technique of infinite dilution, derived from chromatography, has gained widespread utilization in various applications. This approach was formulated by Everett in 1965 [205] and further elaborated by Cruickshank, Windsor in 1966 [206]. This method is used to determine the activity coefficients at infinite dilution for a volatile solute dissolved in an involatile solvent using data acquired from gas-liquid chromatography studies. The application of this method was limited to the assumption of an ideal gas, as demonstrated by Cruickshank, Windsor in 1966 [206]. However, it was later discovered that this approach could be reasonably extended to non-ideal carrier gases by incorporating virial coefficients. These coefficients were utilized to estimate the molar vapor volumes in the presence of an imperfect gas mixture.

The activity coefficient at infinite dilution is determined through the utilization of equation (3.6).

$$\ln \gamma_{13}^{\infty} = \ln \frac{n_3 RT}{V_N P_1^*} - \frac{(B_{11} - V_1^*) P_1^*}{RT} + \frac{P_o J_2^3 (2B_{12} - V_1^{\infty})}{RT} \quad (3.6)$$

Where, n_3 signifies the number of moles of solvent in the column packing, T represents the column temperature, V_N represents the net retention volume of the solute, P_o symbolizes the column outlet pressure, J_2^3 denotes the pressure correction term, and P_1^* refers to the saturated vapour pressure of the solute at the column temperature. The equilibrium vapor pressure of the solute at the given temperature is denoted as V_1^{∞} the partial molar volume at infinite dilution of the solute in the solvent, V_1^* the molar volume of the solute, B_{12} the mixed second virial coefficient of the solute and the carrier gas, and B_{11} the second virial coefficient of the pure solute.

The equilibrium vapor pressure in equation (3.6) was determined using the modified Antoine equation [207-209].

The equation is presented by Letcher, Harris in 2001 [209].

$$V_N = (J_2^3)^{-1} U_o (t_R - t_G) \quad (3.7)$$

where t_G denotes the retention time for the unretained gas, while t_R represents the retention time of the solutes. U_o signifies the outlet pressure and carrier gas flow rate at the column temperature.

To measure the flow rate of the carrier gas accurately, a graduated column was employed, wherein a solution containing soap was utilized. Nevertheless, it was imperative to consider the vapor pressure exerted by the aqueous component within the soap solution while rectifying the volumetric flow rate of the carrier gas [211]. This correction was given by Heintz, Kulikov in 2002 [210] and Letcher, Harris in 2001 [209].

$$U_o = U \left(1 - \frac{P_w}{P_o} \right) \frac{T}{T_f} \quad (3.8)$$

The P_w represents the saturated vapour pressure of water at a given temperature T , and U_o denotes the flow rate of the carrier gas measured using a bubble soap flow meter at the column outlet.

The pressure correction term, denoted as J_2^3 , was initially introduced by Everett in 1965 [205] and subsequently computed using the following equation:

$$J_2^3 = \frac{2}{3} \left[\frac{(P_i/P_o)^3 - 1}{(P_i/P_o)^2 - 1} \right] \quad (3.9)$$

The variable P_o denotes the outlet pressure of the gas chromatography column and P_i represents the inlet pressure drops.

Assessing the actual second virial coefficients based on experimental data poses a significant challenge due to their sensitivity to temperature variations. Tsonopoulos et al. (1989) first introduced the second virial coefficient in 1989. Poling et al. (2001) recommended using a dependable correlation [211, 212]. The equation is as follows:

$$\frac{BP_c}{RT_c} = \frac{B}{V^*} = f^0 + \omega f^{(1)} + a f^{(2)} + b f^{(3)} \quad (3.10)$$

$$\text{where } f^{(0)} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \quad (3.11)$$

$$f^{(1)} = 0.0637 - \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8} \quad (3.12)$$

$$f^{(2)} = -\frac{1}{T_r^6} \quad (3.13)$$

$$f^{(3)} = -\frac{1}{T_r^8} \quad (3.14)$$

$$T_r = -\frac{T}{T_c} \quad (3.15)$$

In 2001, Poling and his colleagues used these connections to figure out the second virial coefficients of both pure substances and mixtures, which can have both polar and non-polar parts [212]. They conducted these estimates at a specific temperature, using information derived from the critical properties of the substances. Tsonopoulos and his team created formulas in 1989 that are especially suitable for substances like alcohols, water, and ketones, which are known to form hydrogen bonds

[211]. As for non-polar substances such as alkanes, alkenes, alkynes, and aromatic compounds, a simplified equation derived from the work of Smith and others in 2001 is used below [164].

$$\frac{BP_c}{RT_c} = f^0(T_r) + \omega f^{(1)} \quad (3.16)$$

Furthermore, when equation (3.16) is rearranged, it leads to the subsequent correlation:

$$B_{ii} = B^0 + \omega_i B^1 = \left[0.083 - \frac{0.422}{T_r^{1.6}} \right] + \omega_i \left[0.139 - \frac{0.172}{T_r^{4.2}} \right] \quad (3.17)$$

Poling et al. (2001) proposed that the simplified equation developed by Smith and colleagues in 2001 accurately represents the second virial coefficients only under specific conditions, specifically when the reduced temperature $(T_r) > 0.6$ and the acentric factor $(\omega) < 0.4$ [164, 212].

To evaluate the second virial coefficients of polar components, the equation originally introduced by Tsonopoulos et al. in 1989 was employed [211]. This identical equation was employed to calculate the mixed second virial coefficient, incorporating the values of T_c , P_c , ω , a_t and b_t , as follows:

$$(T_c)_{12} = \sqrt{(T_c)_1 (T_c)_2 (1 - k_{12})} \quad (3.18)$$

$$(P_c)_{12} = 4(T_c)_{12} \left[\frac{\left(\frac{P_c V_c}{T_c} \right)_1 + \left(\frac{P_c V_c}{T_c} \right)_2}{\left[\left(\frac{1}{V_c^2} \right)_1 + \left(\frac{1}{V_c^2} \right)_2 \right]^2} \right] \quad (3.19)$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \quad (3.20)$$

The parameter k_{12} corresponds to the observed binary interactions, and it can be determined using the methods outlined by Tarakad and Danner in 1977 [213].

Furthermore, in the case of polar compounds, the values of a_t and b_t can be expressed as follows:

$$(a_t)_{12} = \frac{(a_t)_{12} + (a_t)_2}{2} \quad (3.21)$$

and

$$(b_t)_{12} = \frac{(b_t)_1 + (b_t)_2}{2} \quad (3.22)$$

The computation of the second virial coefficient of the pure solute B_{11} was conducted using the methodology proposed by McGlashan and Potter in 1962 [214].

$$B/V^c = 0.43 - 0.886(T^c/T) - 0.694(T^c/T)^2 - 0.0375(n-1)(T^c/T)^{4.5} \quad (3.23)$$

In this context, the variable n denotes the number of carbon atoms in the solute. The symbol T^c denotes the critical temperature while V^c representing the critical volume. Equation 3.23 was found to be applicable to non-polar alkynes, alkenes, alkanes, and aromatic compounds. The mixed virial coefficients denoted as B_{12} were computed using mixing rules as described in equations 3.24 to 3.27.

The mixed virial coefficients, denoted as B_{12} , were computed utilizing the mixing rules postulated by Hudson and McCoubrey in 1960 [215], as represented by the subsequent equations 3.24 to 3.27.

$$T_{12}^c = (T_{11}^c T_{22}^c)^{\frac{1}{2}} \frac{2(I_1 I_2)^{\frac{1}{2}}}{I_1 + I_2} \frac{2^6 V_{11}^c V_{22}^c}{\left[(V_{11}^c)^{\frac{1}{3}} + (V_{22}^c)^{\frac{1}{3}}\right]^6} \quad (3.24)$$

$$I_{c,12} \cdot V_{c,12}^2 = (I_{c,11} + I_{c,22}) \left(V_{c,11}^{\frac{1}{3}} + V_{c,22}^{\frac{1}{3}} \right)^6 \quad (3.25)$$

$$V_{12}^c = \frac{1}{8} \left[(V_{22}^c)^{\frac{1}{3}} + (V_{22}^c)^{\frac{1}{3}} \right]^3 \quad (3.26)$$

$$n = \frac{1}{2}(n_1 + n_2) \quad (3.27)$$

Let us consider equations 3.24 – 3.27, wherein we shall elucidate the utilization of subscripts '1', '2', and '12'. These subscripts are employed to symbolize distinct entities within the context of the equations, specifically pertaining to the solute, the carrier gas, and the mixture of the two components. Let n be a variable denoting the count of carbon atoms, where $n = 1$ corresponds to a compound devoid of carbon. The literature has identified critical points T_c , V_c [212, 216], while the ionization energies I_c have been reported in [207].

The determination of molar volumes is influenced by temperature, and in this study, the modified Rackett equation was employed to estimate the molar volumes as described in reference [212].

$$v = V_c (0.29056 - 0.08775\omega) \left(1 - \frac{T}{T_c}\right)^{\frac{2}{7}} \quad (3.28)$$

The acentric factors, represented by the symbol ω , were acquired from existing scholarly sources [217].

3.8. The theories regarding the existence of azeotropes

It is important to find the activity coefficients at infinite dilution to understand the properties of binary mixtures and make predictions about the presence and conditions of azeotropes. When a binary mixture shows azeotropic behavior, it means that the vapor phase and liquid phase have the same composition. This creates a mixture with a stable boiling point. If the activity coefficient is less than 1.0, it signifies a significant intermolecular attraction between molecules, resulting in a higher energy requirement for their separation. If the observed vapor pressure of the mixture is lower than what Raoult's law predicts, this leads to the phenomenon known as the negative deviation from Raoult's law. On the contrary, in cases where the activity coefficient exceeds 1.0, it indicates that molecules experience a significant repulsive force and demonstrate a positive departure from Raoult's law. In this scenario, a reduced amount of energy is required for the separation of the constituent molecules [218]. Through the analysis of activity coefficients at infinite dilution, it becomes possible to make inferences regarding the potential occurrence of azeotrope formation, approximate the composition and conditions associated with azeotropic behavior, and gain insight into the non-ideal interactions between the constituents within a binary mixture [32, 204].

$$(\ln \gamma_j^\infty) > \ln \left(\frac{P_i^{sat}}{P_j^{sat}} \right) > -(\ln \gamma_i^\infty) \quad (3.29)$$

and

$$(\ln \gamma_j^\infty) < \ln \left(\frac{P_i^{sat}}{P_j^{sat}} \right) < -(\ln \gamma_i^\infty) \quad (3.30)$$

where, (P_i^{sat}) is the saturation vapour pressure for both components (i) and (j)

3.9. Screening of solvents for extraction and extractive distillation process

When choosing a solvent for separation processes like azeotropic extractive distillation or liquid-liquid extraction, the activity coefficients at infinite dilution can provide valuable information [104]. The selectivity of a solvent is its ability to preferentially extract one component from a mixture, determined by comparing the activity coefficients at infinite dilutions of different components. A

solvent with relatively high selectivity values has a significantly higher activity coefficients for the desired component, indicating a stronger affinity for the extraction. The capacity of a solvent is its ability to dissolve a large quantity of the desired component, determined by the absolute value of the activity coefficients at infinite dilution. It is essential to choose a solvent with both high selectivity and capacity for efficient separation of the desired component, as well as for dissolving a significant quantity of the component. The examination of IDAC data facilitates the computation of selectivity and capacity for various solvents, enabling a comparison of their efficacy. This analysis is of utmost importance in the determination of optimal solvent for entrainer in azeotropic extractive distillation or liquid-liquid extraction procedures, particularly when dealing with systems that encompass azeotropes or mixtures with similar boiling points.

$$S_{ij,s}^{\infty} = \frac{\gamma_i^{\infty}}{\gamma_j^{\infty}} \quad (3.31)$$

and

$$k_j^{\infty} = \frac{1}{\gamma_j^{\infty}} \quad (3.32)$$

The variables i and j are used to denote the two solutes that are intended to be separated. If the selectivity value exceeds 1, it signifies that a solvent possesses the necessary characteristics to function as an entrainer in extractive distillation. In the context of this study, the term "solvent" specifically pertains to DESs [217, 219]. The solute's dissolution in the solvent can be quantified by the solvent's capacity, denoted as, k_j^{∞} as expressed in equation 3.32.

3.10. Calculation of uncertainty

The law of propagation of uncertainties is a widely used methodology in scientific and engineering measurements to determine uncertainties in computed quantities. It considers various uncertainties, including the inherent limitations of measurement apparatus and the reproducibility of observed values. Constraints on accuracy and precision in instruments contribute to the collective indeterminacy of quantified magnitudes. Repeatability in measurements refers to the inherent variability observed when multiple measurements are conducted under identical conditions. The law of propagation of uncertainties sets up an accurate mathematical framework for measuring the spread of uncertainty in input quantities through mathematical equations, which leads to the calculated result. The 1994 work by Taylor, Barry N., and Chris E. Kuyatt is expected to be a useful guide for using

the law of propagation of uncertainties correctly. It gives detailed explanations, mathematical expressions, and real-life examples for figuring out uncertainties and how they spread in mathematical calculations [219]. The equation for determining uncertainties is presented herein.

$$u(\theta) = \sqrt{\sum_{j=1}^y \left[\frac{\partial \theta}{\partial x_i} u(x_i) \right]^2} \quad (3.33)$$

Let θ be the computed variable (specifically, γ_{13}^{∞} in this context), y denotes the number of independent variables, and x_i represents the independent variable used in the computation of θ . Given the inherent nature of type, we must consider its property of repeatability. Let us consider a distribution consisting of q repetitions. The error, denoted as u_r , can be determined by evaluating the standard deviation.

$$u_r(\theta) = \sigma = \sqrt{\frac{1}{n-1} \sum_{j=1}^q (\theta_j - \bar{\theta})^2} \quad (3.34)$$

where, $\bar{\theta}$ is the mean value of a θ and θ_j is the j th repetition.

3.11. Density

Density is a fundamental physical property that quantifies the mass of a substance in relation to its volume. The symbol ρ (rho) is frequently used to represent this quantity. The density of a material is a quantitative measure that characterizes the degree of particle or molecular packing within the substance. By dividing the mass of a given substance by its corresponding volume, one can express the concept of density mathematically [220].

$$\rho = \frac{m}{v} \quad (3.35)$$

In the given context, the variables m and v symbolize the quantities of mass and volume, respectively. The International System of Units (SI) designates kilograms per cubic meter (kg/m^3) as the standard unit for measuring density. However, alternative units commonly employed include grams per cubic centimeter (g/cm^3) and pounds per cubic inch (lb/in^3).

The density of pure liquids is a thermodynamic property that is dependent on temperature. It can be mathematically represented as:

$$\rho = kT + m' \quad (3.36)$$

Density is a crucial metric in thermodynamics, indicating the compression of matter within a specific volume. High density indicates a large mass within a smaller volume, while low density indicates a reduced mass dispersed across an expanded volume. The consideration of densities and other volumetric properties of liquid mixtures holds significant importance in a multitude of industrial applications and theoretical calculations. The thermodynamic properties of liquid mixtures offer crucial insights into the behavior and traits of these systems, enabling engineers and scientists to effectively devise processes and enhance conditions.

3.12. Excess molar volume

Excess molar volume is a thermodynamic characteristic that quantifies the difference between the volume of a mixture and the volume predicted by the volumes of its individual pure components. It can be quantified as the magnitude of alterations in the molecular interplay and configuration of the combination in relation to its components in their pure states [221].

The excess molar volume, symbolized as V_m^E , is characterized as:

$$V_m^E = V_{mixture} - \sum_{i=1}^N x_i V_i^0 \quad (3.37)$$

where, $V_{mixture}$ is the volume of the mixture, n is the number of components, x_i is the mole fraction of component i , and V_i^0 is the molar volume of component i .

Excess molar volumes can be determined through experimental means employing diverse techniques, including density measurements, vibrating tube densitometry, and pycnometry [17]. The experimental techniques employed in this study entail the measurement of the density or volume of both the mixture and its individual components. Subsequently, the excess molar volume is determined by applying the formula. The experimental data presented herein offer valuable insights into the behavior of the mixture and can aid in comprehending the fundamental factors that contribute to the observed volume changes. The investigation and prediction of excess molar volumes are facilitated through the utilization of theoretical models, such as equations of state or molecular simulation methods [222-224]. These models incorporate molecular characteristics, intermolecular interactions, and other pertinent variables to compute the anticipated alterations in volume that occur during the process of mixing. Nevertheless, because of the complex nature of molecular interactions, these models frequently necessitate approximations and simplifications, and their precision may fluctuate depending on the specific system being investigated.

According to Handa's in 1979 description of the processes, there are a variety of factors that can affect excess molar volumes when mixing two liquids [225]. There are several crucial factors that should be taken into consideration:

- **Molecular interactions:** The size and shape of the molecules present in each liquid can have an impact on the packing arrangement after mixing. For instance, when the intermolecular forces in two liquids exhibit similarity, such as both being either polar or nonpolar, they have a greater tendency to mix in a more favorable manner. This favorable mixing leads to the observation of smaller excess molar volumes. Conversely, disparate intermolecular forces can result in greater magnitudes of excess molar volumes.
- **Molecular size and shape:** The packing arrangement upon mixing can be influenced by the size and shape of the molecules present in each liquid. When molecules possess comparable sizes and shapes, their ability to interlock in a more optimal manner leads to reduced excess molar volumes. The opposite is true when the molecules are very different from one another in terms of size or shape. This can make it harder for them to arrange themselves in a close-packed way, which can lead to more extra molar volumes.
- **Intermolecular attractions:** Besides the forces between molecules, certain attractions like hydrogen bonds or dipole-dipole interactions can also influence extra molar volumes. If the two liquids possess molecules that can establish strong intermolecular attraction, it is possible for the excess molar volume to be decreased. On the other hand, the presence of weaker or nonexistent intermolecular attractions can be a contributing factor to the increase in excess molar volumes.
- **Structural effects:** The presence of structural effects in liquids, such as molecular asymmetry or the incorporation of functional groups, can affect excess molar volumes. The observed effects can be attributed to variations in molecular arrangement and orientation, resulting in deviations from ideal mixing characteristics.
- **Temperature and pressure:** Variations in temperature and pressure have the potential to exert an impact on the excess molar volumes. The excess molar volume may exhibit a decrease as temperatures increase, which can be attributed to increased molecular motion and improved mixing. On the other hand, it is worth noting that at elevated pressures, excess molar volume could potentially exhibit an increase because of alterations in molecular arrangement and the influence of compression.

3.13. Speed of sound

The determination of sound velocity (u) in various liquid media, such as ionic liquids, deep eutectic solvents, and organic solvents, is a highly advantageous method for investigating the molecular interactions within these substances and acquiring essential equilibrium thermodynamic information. The term "sound velocity," also referred to as the "speed of sound" or "acoustic velocity," pertains to the rate at which sound waves propagate within a given medium [226-228].

The determination of sound velocity in liquids provides valuable insights into the physical and chemical properties of these substances [229]. Through the utilization of sound velocity measurements, researchers are able to acquire valuable insights pertaining to molecular interactions, including intermolecular forces, hydrogen bonding, and associated phenomena [230]. The mentioned interactions are of paramount importance in influencing the behavior and characteristics of the liquid system being studied.

Sound velocity measurements have been applied in various significant domains, including [231]:

- Thermodynamic studies: Measurements of sound velocity offer valuable information regarding the compressibility, density, and adiabatic compressibility of liquids, thereby contributing to a comprehensive understanding of their thermodynamic properties. The provided data can be utilized for the computation of thermodynamic properties, including isentropic compressibility, isothermal compressibility, and specific heat capacity.
- Molecular interactions: The velocity of sound is modulated by intermolecular interactions within the liquid medium. Through the examination of changes in sound velocity in relation to concentration or temperature, scholars can acquire valuable knowledge regarding the characteristics and intensity of various interactions, including solute-solvent interactions, association/dissociation phenomena, and phase transitions.
- Solution behavior: Measurements of sound velocity can yield valuable insights into the characteristics of solutions, such as their phase diagrams, critical phenomena, and excess properties. The provided data facilitates comprehension of the mixing characteristics, compatibility, and phase separation in binary and multicomponent systems.
- Kinetic studies: The measurement of sound velocity in liquids can be employed as a means to examine the dynamics of various processes, including diffusion, reaction rates, and relaxation phenomena. The velocity at which acoustic waves travel within a given medium can yield significant insights into the kinetics of molecular phenomena.

3.14. Isentropic compressibility

Isentropic compressibility, represented by the symbol K_S , is a thermodynamic property that describes the behavior of a substance or mixture in response to variations in pressure. Nevertheless, its relevance is limited to the compressibility of a substance under conditions of constant entropy (isentropic conditions), rather than directly affecting the molecular interactions in binary liquid mixtures.

This condition remains valid when the velocity (u) is measured using a low-frequency generator, such as the DSA 5000 M transducer, which operates at approximately 3 MHz [232]. However, for frequencies exceeding 100 MHz, the dominant factors affecting sound waves are velocity dispersion and absorption [232-234].

The Newton-Laplace equation serves as the fundamental framework for experimentally determining the isentropic compressibilities of liquid mixtures. The Newton-Laplace equation is utilized in the determination of the isentropic compressibility of liquid mixtures. This equation establishes a connection between the measured velocity of a fluid at a low frequency (such as 3 MHz) and its density.

The equation known as the Newton-Laplace equation is presented as follows:

$$K_S = \frac{1}{\rho u^2} \quad (3.38)$$

3.15 Deviation in isentropic compressibility

The isentropic compressibility deviation for binary mixtures refers to the alteration in compressibility between an actual solution and an ideal one [235, 236]. This deviation can be determined using equation (3.39).

$$\Delta K_S = K_S - \sum_i^n x_i K_{s,i} \quad (3.39)$$

where, x_i and $K_{s,i}$ denote the mole fraction and isentropic compressibility of component i correspondingly.

It should be emphasized that excess isentropic compressibility is a diverse characteristic that is influenced by various factors, including composition, intermolecular interactions, molecular size, shape, temperature conditions, pressure, phase behavior, and concentration range. The quantification of the deviation in isentropic compressibility can be accomplished by comparing the isentropic compressibility of a real fluid with that of an ideal gas under identical conditions. A fluid that

demonstrates greater compressibility in comparison to an ideal gas is characterized as having a positive deviation. On the other hand, in the event that the actual fluid demonstrates a reduced level of compressibility in comparison to the theoretical gas, it is characterized as displaying a negative deviation. A positive deviation in isentropic compressibility is often seen in fluids that have strong intermolecular interactions or molecules that are attracted to each other. These intermolecular forces induce a higher degree of compressibility in the fluid compared to that of an ideal gas under identical conditions. On the other hand, fluids with weaker interactions between molecules or molecules that push against each other have a negative deviation in isentropic compressibility. This leads to a lower compressibility compared to an ideal gas.

3.16. Intermolecular free length

Intermolecular free length is the average distance between two dissimilar molecules' surfaces [237]. Researchers can gain insights into intermolecular forces in mixtures by measuring them. Intermolecular forces are classified into attractive and repulsive forces, which arise from interactions between molecules and neighboring particles. Attractive forces pull molecules together, while repulsive forces push them apart. The value of intermolecular free length is influenced by the strength of these forces. Understanding these forces is crucial for understanding the behavior and properties of mixtures, such as stability, solubility, and phase behavior.

Intermolecular interactions like van der Waals forces, hydrogen bonds, or electrostatic interactions are what describe the attractive forces in a mixture. The center of attraction, or the point where attractive forces originate, contributes to the stability and cohesion of the system. Repulsive forces arise from overlapping electron clouds or other factors that result in mutual repulsion. The distance between the surfaces of molecules is crucial in determining the strength of these repulsive forces.

Calculating the exact distances between molecules in a mixture can be challenging due to the complex nature of molecular interactions. However, theoretical models and computational methods, such as molecular dynamics simulations, can provide insights into these distances. Understanding the interplay between attractive and repulsive forces and the distances between molecules is important in various fields, such as chemistry, physics, and materials science, as it allows for the prediction of properties and behaviors of mixtures, such as solubility, phase transitions, and viscosity.

Jacobson's theory of free length has been employed for the computation of the intermolecular free length [238, 239]. The intermolecular free length can be determined by establishing a connection between Jacobson's empirical relation and isentropic compressibility, as expressed in the following equation:

$$L_f = k_j (K_s)^{\frac{1}{2}} \quad (3.40)$$

The symbol k_j represents Jacobson's constant, which is dependent on temperature. It can be expressed as $k_j = (93.875 + 0.375 T) \times 10^{-8}$.

3.17 Correlation and prediction for measured thermophysical properties

3.17.1 Density

The PC-SAFT EoS equation of state can be expressed using the Helmholtz energy represented as (A), which comprises four components: the contribution from an ideal gas (A^{id}), a component related to hard-chain interactions (A^{hc}), interactions resulting from dispersion forces (A^{disp}), and association contribution (A^{assoc}). As a result, the PC-SAFT EoS equation of state can be denoted as equation 3.41:

$$A = A^{id} + A^{hc} + A^{disp} + A^{assoc} \quad (3.41)$$

The equation of state (EoS) relies on five adjustable parameters for pure fluids: the number of segments (m), segment diameter (σ), depth of pair potential energy (ϵ/k_B), association energy of interaction (ϵ^{AB}/k_B), and effective volume of interaction (κ^{AB}) [240, 241]. To account for hydrogen bonding interactions among molecules of the same type and different molecules, an association scheme must be employed. Alcohols are self-associating using a 2B scheme, signifying one positive site in the hydrogen atom and one negative site in the oxygen atom. Conversely, the DES is considered a pseudo-pure component with two association sites (2B scheme) to facilitate self-association between the HBA and the HBD of the DES, forming a hydrogen bond. Consequently, in binary mixtures, cross-association between DES and alcohol is considered, stemming from the HBA and HBD interactions. On the other hand, for binary mixtures, the following mixing rules are imperative:

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (3.42)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} (1 - k_{ij}) \quad (3.43)$$

$$\epsilon^{A_i B_j} = \frac{1}{2} (\epsilon^{A_i B_i} + \epsilon^{A_j B_j}) \quad (3.44)$$

$$\kappa^{A_i B_j} = \sqrt{\kappa^{A_i B_i} \kappa^{A_j B_j}} \left[\frac{\sqrt{\sigma_i \sigma_j}}{(\sigma_i + \sigma_j)/2} \right]^3 \quad (3.45)$$

Therefore, k_{ij} is the binary interaction parameter and can be obtained by fitting experimental density data for binary mixtures.

3.17.2 Speed of sound

Schaaff's collision factor theory (SCFT) [242] and Nomoto's relation (NR) [242] were employed to model the speed of sound in binary mixtures.

According to SCFT, equation 3.46 provides the expression for the speed of sound.

$$u = \rho u_{\infty} (x_1 s_1 + x_2 s_2) (x_1 B_1 + x_2 B_2) \quad (3.46)$$

The molar density of the mixture, calculated using the PC-SAFT EoS, can be noted as ρ , while $u_{\infty} = 1600$ m/s, s_i ($i = 1, 2$) represents the space filling factor of components i in the mixture. We also have the experimental speed of sound for the pure fluid and the molar density of the pure fluid, which are obtained using the PC-SAFT EoS. Further, x_i ($i = 1, 2$) is the liquid mole fraction, and B_i ($i = 1, 2$) corresponds to the actual volume of the molecule per mole of component i , which is determined by equation 3.47:

$$B_i = N_A m_i \frac{\pi}{6} d_i^3 \quad (3.47)$$

with N_A , the Avogadro constant. On the other hand, equation 3.48 gives the speed of sound from NR:

$$u = \left(\frac{x_1 D_1 + x_2 D_2}{\frac{x_1}{\rho_1} + \frac{x_2}{\rho_2}} \right)^3, \quad D_i = \frac{1}{\rho_i} u_i^{1/3} \quad (3.48)$$

where D_i , ρ_i , and u_i , stand for the molar speed of sound, the molar density of the pure fluid obtained with PC-SAFT, and the experimental speed of sound for the pure fluid, respectively.

3.18. Correlation of derived thermodynamic properties

3.18.1 Redlich-kister polynomial

The Redlich-Kister smoothing polynomial was employed to fit thermodynamic properties such as excess molar volume and deviation in isentropic compressibility data [243]. The Redlich-Kister fitting parameters were computed utilizing the equation presented herein.

$$Z = x_1 x_2 \sum_{i=0}^N A_i (2x - 1)^i \quad (3.49)$$

Let Z be a variable that represents the substance or compound possessing a distinct property indicated by either ν_m^E or $\Delta \kappa_s$ value. The mole fraction of $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 and $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 is indicated by x_1 . The mole fraction of methanol, ethanol, and propanol is expressed by x_2 and the Redlich-Kister parameters, denoted A_i , are computed for this system, where N symbolizes the order degree of the polynomial expansion.

$$\sigma = \left(\frac{\sum_i^m (Z_{\text{exp}} - Z_{\text{cal}})}{M - k} \right)^{1/2} \quad (3.50)$$

Z_{exp} , Z_{cal} , represent the experimental and calculated values ν_m^E or $\Delta \kappa_s$. M denotes the number of experimental data points, and k represents the number of coefficients used in the Redlich-Kister correlation.

EXPERIMENTAL METHODS

4.1. Chapter overview

This section presented a comprehensive account of the materials, experimental setup, procedures, and techniques employed for the measurement of the IDACs and binary mixtures as well as address the process of preparing DESs and their characterization. Furthermore, discussion on the uncertainties pertaining to the experimental parameters and variables are provided.

4.2. Materials

The Table 4.1 below provides a summary of the organic solutes. The manufacturer stated that the samples used in this study were of analytical grade and had mass purities ranging from (97.00 to 99.99) %. Due to the advantageous nature of the gas-liquid chromatography technique, which allows for the separation of impurities during measurements, no additional purification of solutes was conducted.

Table 4. 1: Solute specifications: supplier, mass fraction purity, analysis method and CAS number.

Solutes	Supplier	Mass fraction purity	Analysis method	CAS No.
2,2-Dimethylbutane	Merck	≥ 0.99	GC	75-83-2
<i>n</i> -Pentane	Sigma-Aldrich	≥ 0.99	GC	109-66-0
<i>n</i> -Hexane	Sigma-Aldrich	≥ 0.99	GC	110-54-3
<i>n</i> -Heptane	Sigma-Aldrich	≥ 0.99	GC	142-82-5
<i>n</i> -Octane	Sigma-Aldrich	≥ 0.99	GC	17252-77-6
<i>n</i> -Nonane	Merck	≥ 0.99	GC	111-84-2
<i>n</i> -Decane	Merck	≥ 0.99	GC	124-18-5
1-Pentene	Sigma-Aldrich	≥ 0.99	GC	109-67-1
1-Hexene	Sigma-Aldrich	≥ 0.99	GC	592-41-6
1-Heptene	Sigma-Aldrich	≥ 0.99	GC	592-76-7
Non-1-ene	Fluka	≥ 0.99	GC	124-11-8
Dec-1-ene	Fluka	≥ 0.99	GC	872-05-9
Cyclohexene	Merck	≥ 0.99	GC	110-83-8
Cyclohexane	Merck	≥ 0.99	GC	110-82-7
Cyclooctane	Merck	≥ 0.99	GC	292-64-8
1-Pentyne	Sigma-Aldrich	≥ 0.99	GC	627-19-0
Hex-1-yne	Sigma-Aldrich	≥ 0.97	GC	693-02-7
Hept-1-yne	Sigma-Aldrich	≥ 0.98	GC	628-71-7
Benzene	Sigma-Aldrich	≥ 0.99	GC	71-43-2
Toluene	Sigma-Aldrich	≥ 0.99	GC	108-88-3
Ethylbenzene	Sigma-Aldrich	≥ 0.99	GC	100-41-4
<i>o</i> -Xylene	Sigma-Aldrich	≥ 0.99	GC	95-47-6
<i>m</i> -Xylene	Sigma-Aldrich	≥ 0.99	GC	108-38-3
<i>p</i> -Xylene	Sigma-Aldrich	≥ 0.99	GC	106-42-3

Methanol	Sigma-Aldrich	≥ 0.99	GC	67-56-1
Ethanol	Sigma-Aldrich	≥ 0.99	GC	64-17-5
Propanol	Sigma-Aldrich	≥ 0.99	GC	71-23-8
Butanol	Sigma-Aldrich	≥ 0.99	GC	71-36-3
THF	Sigma-Aldrich	≥ 0.99	GC	109-99-9
Thiophene	Sigma-Aldrich	≥ 0.99	GC	110-02-1
Acetonitrile	Sigma-Aldrich	≥ 0.99	GC	75-05-8
Acetone	Sigma-Aldrich	≥ 0.99	GC	67-64-1
MEKP	Sigma-Aldrich	≥ 0.99	GC	1338-23-4
Water	Merck	≥ 0.99	GC	7732-18-5
Zinc chloride	Merck	≥ 0.99	GC	7646-85-7
Phosphoric acid	Sigma-Aldrich	≥ 0.99	GC	7664-38-2
Acetic acid	Sigma-Aldrich	> 0.99	GC	64-19-7

4.3. Helium

The carrier gas employed for gas-liquid chromatography applications was an inert gas (helium), which was procured from Afrox South Africa (Pty) Ltd. The helium was contained in a cylinder with a volume of 9.1 m^3 , and its temperature and pressure were maintained at 20°C and 1 atm, respectively. The helium gas was guaranteed to possess a minimum purity level of 99.99%, as certified by the supplier. The impurities present in the sample are primarily comprised of moisture, oxygen, nitrogen, and methane, with concentrations below 10.5 parts per million (ppm).

4.4. DESs preparation

The DESs were prepared using varying molar ratios, specifically $[\text{ZnCl}_2][\text{acetic acid}]$ at ratios of 1:2 or 1:4, and $[\text{ZnCl}_2][\text{phosphoric acid}]$ at ratios of 1:2 or 1:2.5. The preparation procedure consisted of combining zinc chloride with the corresponding HBDs, such as acetic acid and phosphoric acid, within a sealed glass vial. This mixture was then stirred using a magnetic stirring bar placed on a heated plate, maintaining a temperature of $(40\text{--}90)^\circ\text{C}$ for a duration of 6 to 8 hours. The solution was agitated until it achieved a state of uniformity and lack of colour, after which it was permitted to reach ambient temperature. This procedure facilitates the acquisition of a more concentrated and purified DES. To maintain the stability of the DES and prevent the introduction of moisture, a hermetically sealed enclosure was employed for the storage of the prepared DES. The moisture content in the DES was quantified utilizing a Karl-Fischer auto titrator, a device designed to measure the water content present in each sample. According to the passage, the moisture content of the prepared DESs did not exceed $310.10^{-6} \%$ by mass percentage, suggesting a relatively low moisture content.

4.5. Characterization of DESs

The density and sound velocity of the DESs under investigation were measured using an Anton Paar (DSA 5000 M) instrument. Prior to performing DESs property tests, a calibration procedure involved

calculating the density and sound speed of ultra-pure water at a specific temperature. The surface tension was also measured using a tensiometer (Attention Sigma 703D, Biolin Scientific, China). Table 4.2 displays all the data, which were obtained at 298.15 K and at 101.3 kPa [7, 30].

Table 4. 2: Experimental density (ρ), sound velocity (u), and surface tension (γ) of the DESs utilized in this investigation at a temperature of 298.15 K and under atmospheric pressure.

Solvent	ρ (g/cm ³)	Mole ratio	u (m/s)	γ (mN/m)
[ZnCl ₂][acetic acid]	1.7119	1:2	1284.75	24.10
[ZnCl ₂][acetic acid]	1.4819	1:4	1254.38	17.63
[ZnCl ₂][phosphoric acid]	1.9854	1:2	1507.98	57.11
[ZnCl ₂][phosphoric acid]	1.9390	1:2.5	1527.35	56.80

Fourier transform infrared spectroscopy (FTIR) is a technique used to analyze the molecular composition of a sample based on its absorption and transmission of infrared light [244, 245]. The FTIR spectrum would exhibit absorption bands related to its functional groups and molecular vibrations. FTIR spectra of phosphoric acid, acetic acid, zinc chloride, [ZnCl₂ + acetic acid] 1:2 or 1:4 and [ZnCl₂ + phosphoric] 1:2 or 1:2.5 were acquired using an FTIR spectrometer (Alpha II FT-IR, Bruker South Africa (Pty) Ltd) under ambient conditions. The spectrums were measured with a resolution of a 4.0 cm⁻¹, encompassing wavelengths from 500 cm⁻¹ to 4000 cm⁻¹.

Acetic acid's FTIR spectrum often has numerous distinct peaks. Absorption bands associated with the C-H stretching vibrations of methyl (CH₃) and methylene (CH₂) groups were found in the fingerprint area at 2900-3000 cm⁻¹. There is also a prominent peak about 1710 cm⁻¹, which corresponds to the C=O stretching vibration of the carboxylic acid group (COOH). Another distinguishing trait is the existence of a wide O-H stretching band between 2500 and 3300 cm⁻¹ [12].

Zinc chloride is an inorganic compound that occurs as a white crystalline solid [246]. Characteristic absorption bands connected to its chemical vibrations were seen in its FTIR spectra. A broad band around 3500-3200 cm⁻¹, indicates the stretching vibration of hydrogen-bonded O-H groups (water of crystallization) and is due to the presence of water molecules as ZnCl₂ tends to absorb moisture from the atmosphere [247]. A sharp band around 1600 cm⁻¹, corresponds to the bending vibration of water molecules. Bands in the range of 1000-500 cm⁻¹, represent the stretching and bending vibrations of the Zn-Cl bonds [248].

The phosphoric acid (H₃PO₄) FTIR spectrum has a broad band around 3000-2500 cm⁻¹, indicating the stretching vibration of the O-H bonds [30, 247]. A band around 1200-1000 cm⁻¹, represents the stretching vibration of the P = O bond [247, 249]. Bands in the range of 900-700 cm⁻¹, correspond to the stretching and bending vibrations of the P-O bonds [247].

When $[\text{ZnCl}_2 + \text{acetic acid}]$ 1:2 or 1:4 and $[\text{ZnCl}_2 + \text{phosphoric}]$ 1:2 or 1:2.5 are combined to form a DES, the resulting FTIR spectrum exhibits a combination of the characteristic peaks from both components. The peaks related to Zn-Cl bonds in zinc chloride are present, indicating the persistence of the ZnCl_2 component in the DES. Furthermore, peaks belonging to acetic acid functional groups, such as the C-H stretching vibrations and the C=O stretching vibration of the carboxylic acid group, are apparent. When compared to the pure components, the presence of DESs may cause the individual peaks to be broad or shift due to interactions.

The FTIR spectrum of this combination shows the combined features of ZnCl_2 and phosphoric acid. A combination of the absorption bands found for ZnCl_2 and phosphoric acid, as described earlier, was detected. Changes in the intensity or position of certain bands because of probable interactions or complex formation between ZnCl_2 and phosphoric acid molecules.

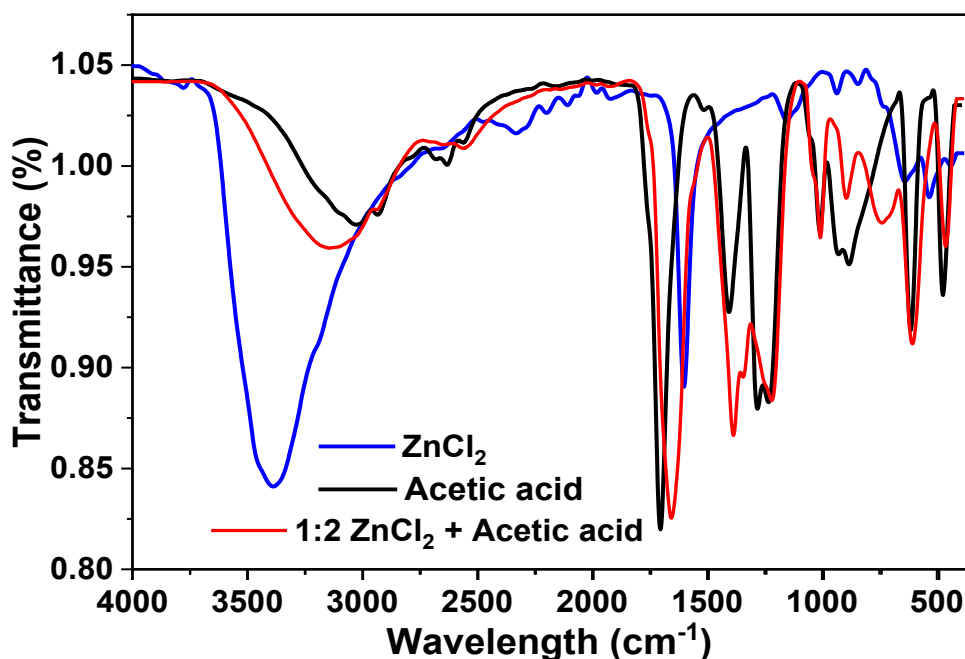


Figure 4. 1: FTIR spectra for pure zinc chloride and acetic acid including [zinc chloride + acetic acid] 1:2 deep eutectic solvent.

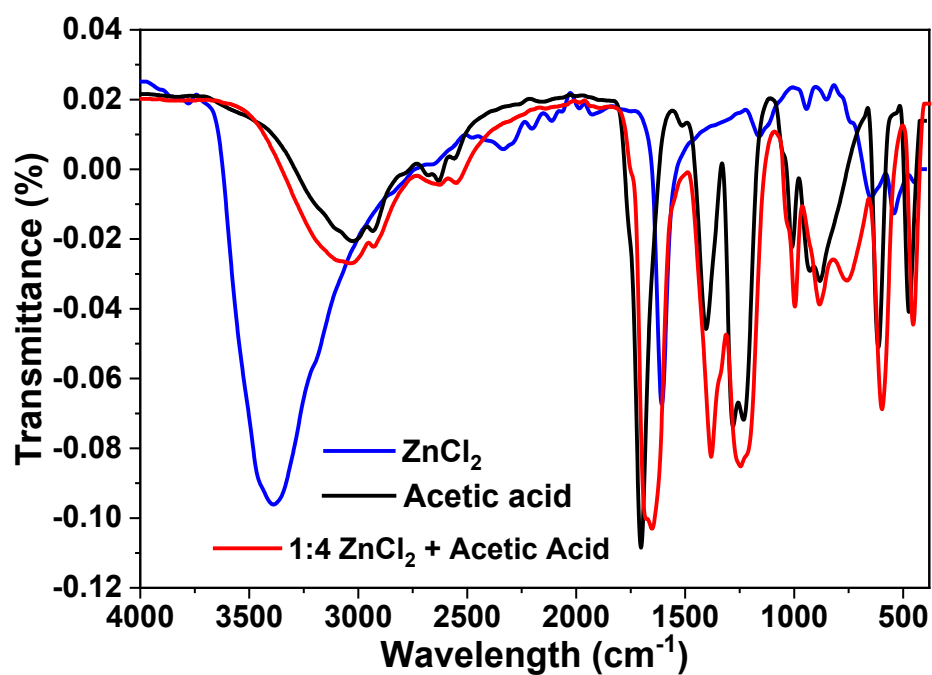


Figure 4. 2: FTIR spectra for pure zinc chloride and acetic acid including [zinc chloride + acetic acid] 1:4 deep eutectic solvent.

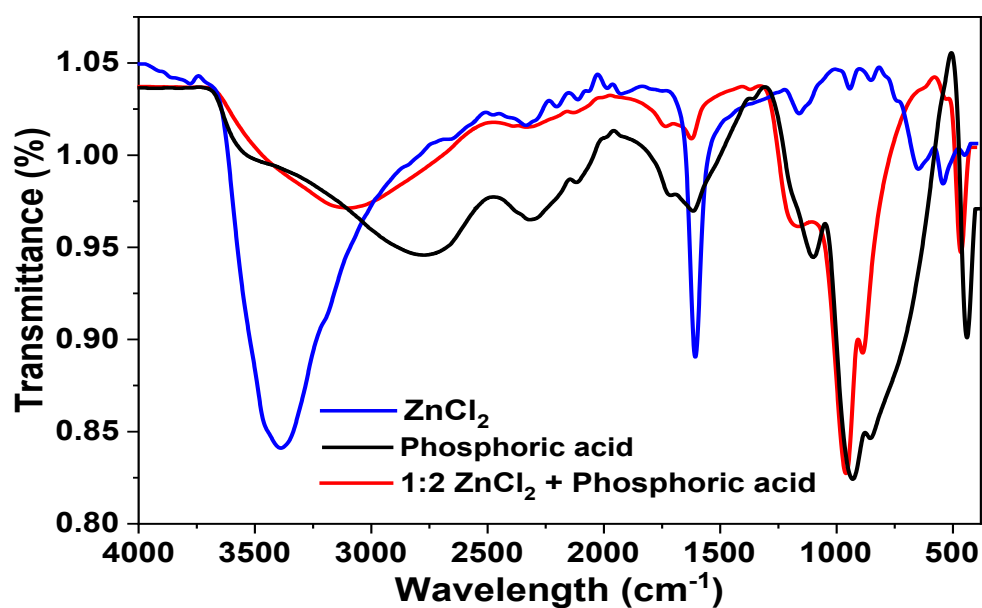


Figure 4. 3: FTIR spectra for pure zinc chloride and phosphoric acid including [zinc chloride + phosphoric acid] 1:2 deep eutectic solvent.

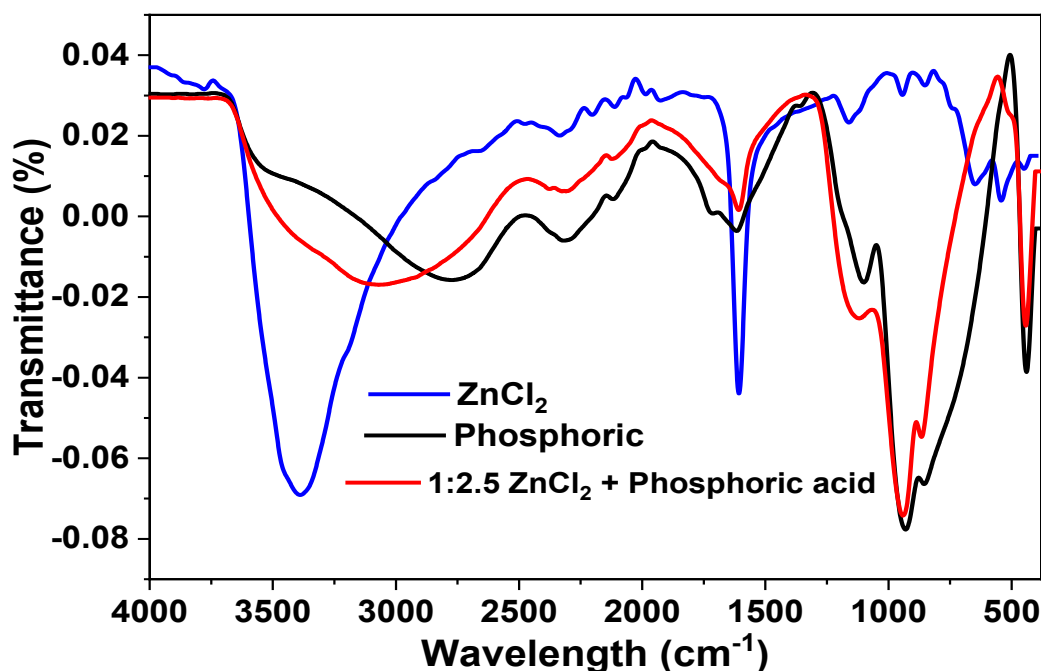


Figure 4. 4: FTIR spectra for pure zinc chloride and phosphoric acid including [zinc chloride + phosphoric acid] 1:2.5 deep eutectic solvent.

Thermogravimetric analysis (TGA) is an analytical method used to quantify the change in mass of a specimen when exposed to different temperature conditions [250]. This resource offers insights into the thermal stability, composition, and breakdown characteristics of several compounds. TGA involves subjecting a small amount of material to heat at a consistent pace while simultaneously monitoring its weight. The specimen is often positioned in a crucible and subjected to high temperatures within a furnace. As the temperature rises, the sample experiences a range of thermal phenomena, including evaporation, sublimation, decomposition, and oxidation. The change in weight of the specimen is documented in relation to temperature or time, and the corresponding data is captured in the thermogram. The thermogram has the capability to provide insights about the thermal stability of the samples.

Differential scanning calorimetry (DSC) is a thermal analysis method used for the purpose of characterizing the thermal properties and behavior of a given material [251]. This technique quantifies the thermal energy transfer occurring between a sample and its surroundings with respect to either temperature or time. In the context of DSC, it is customary to position the reference material and the sample in distinct cells inside the instrument. Both cells are exposed to an identical temperature program, which includes both heating and cooling. Any disparity in heating between the sample and the reference is then quantified. When a sample experiences a phase transition, such as melting, crystallization, glass transition, or chemical reaction, it exhibits heat absorption or release.

The thermal stabilities of DESs were studied using a Mettler Toledo TGA system, and a differential scanning calorimetry (using SDT Q600 V20.9 Build 2D) was used for thermogravimetric analysis. The samples were placed in TGA aluminum pans, and the analysis were conducted under a nitrogen atmosphere with a carrier gas flow rate of 50 mL/min. The temperature was ramped from room temperature to 900 °C at a heating rate of 10 °C/min.

The TGA results reveal interesting insights into the effect of varying the amount of acetic acid in $[\text{ZnCl}_2][\text{acetic acid}]$ mixtures on the stability of the resulting compounds (refer Figure 4.5). Specifically, an increase in the acetic acid content within the 1:4 molar ratio exhibits a slight decrease in stability. This observation implies that the balance of components within this ratio is crucial, and deviations can impact stability.

In contrast, when comparing $[\text{ZnCl}_2][\text{phosphoric acid}]$ mixtures at 1:2 and 1:2.5 ratios, only a marginal difference in stability is noted (refer Figure 4.5). This finding suggests that the relationship between $[\text{ZnCl}_2][\text{phosphoric acid}]$ may be less sensitive to variations in their proportions compared to the $[\text{ZnCl}_2][\text{acetic acid}]$ system.

Significantly, the comparison between acetic and phosphoric acid as hydrogen-bond donors indicates that the latter confers higher stability. This implies that the nature of the hydrogen-bonding interactions plays a pivotal role in determining the stability of the resulting compounds.

An intriguing observation is made in the weight loss below 100 °C, primarily attributed to trapped water in the acetic acid HBD [252]. This phenomenon underscores the importance of considering the presence of water molecules in the analysis of these compounds, especially in the acetic acid-containing systems.

Further differentiating between the acetic acid ratios, the 1:4 ratio exhibits a higher weight loss compared to the 1:2 ratio. This discrepancy suggests that the amount of acetic acid within the mixture directly influences the thermal properties, potentially leading to increased volatility or decomposition.

In contrast, the weight loss for phosphoric acid is noted to be less significant when compared to acetic acid HBD. This indicates that the phosphoric acid-containing systems may be more thermally stable, further supporting its role as a more stabilizing hydrogen-bond donor in these mixtures.

The TGA results highlight the sensitivity of the stability of zinc chloride-containing compounds to variations in the amount and type of hydrogen-bond donors. The higher stability associated with phosphoric acid suggests its potential as a more favorable component in these systems compared to acetic acid. However, careful consideration of ratios is crucial, as observed in the differences between the 1:2 and 1:2.5 ratios.

The solvents that was used in the experiment are referred to as DESs, and examined their properties with a focus on their melting temperatures. The findings indicate the displayed melting temperatures as follows: $[\text{ZnCl}_2][\text{acetic acid}]$ 1:2 had a melting temperature of 10 °C, $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 had a melting temperature of 12 °C, $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2 had a melting temperature of 29 °C, and $[\text{ZnCl}_2][\text{acetic acid}]$ 1:2.5 had a melting temperature of 30 °C [30]. It is worth noting that these temperatures are lower than the melting points of the individual components used in creating these DESs which confirm the preparation of DESs.

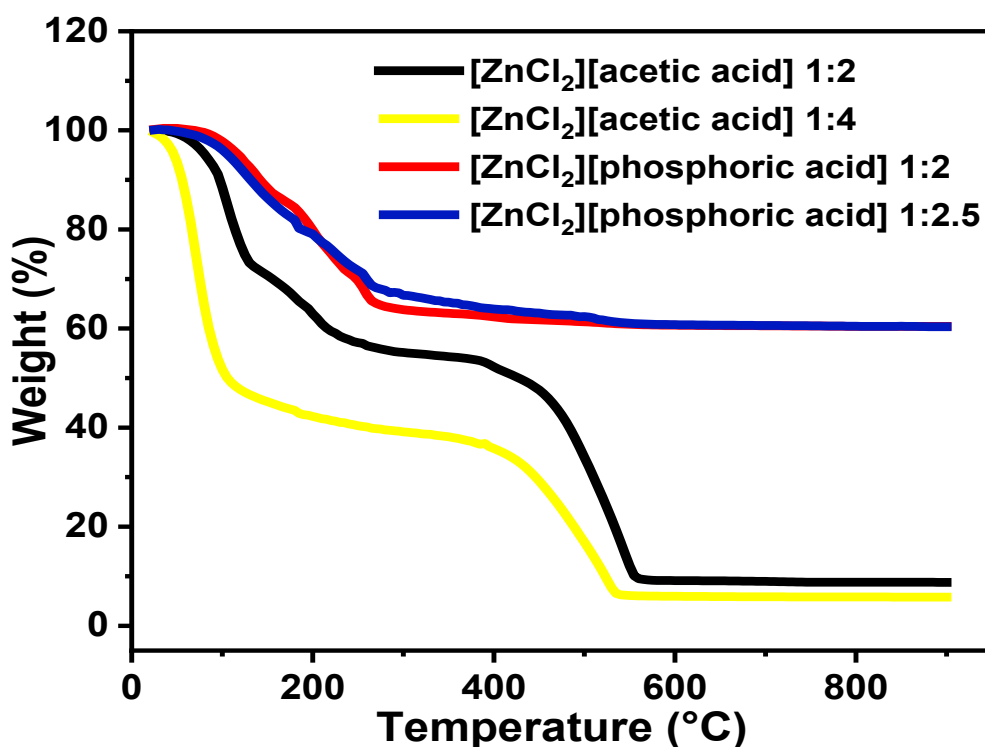


Figure 4. 5: Thermogram showing the thermal stability of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:2 , 1:4 and $[\text{ZnCl}_2]$ + $[\text{phosphoric acid}]$ 1:2 and 1:2.5 deep eutectic solvents.

4.6. Activity coefficient techniques

These methodologies hold significant value within the realm of thermodynamics and are employed to gain insights into the characteristics exhibited by solutions when solute concentrations are relatively low. These data sources offer significant information for a range of applications, including the selection of solvents, separation techniques, and the development of chemical processes. In this section, we delve into two prominent techniques: Inert gas stripping and differential ebulliometer and evaluate their strengths and limitations compared to other methodologies.

4.6.1. Inert gas stripping technique

This methodology involves the separation of a volatile solute from a non-volatile solvent through the utilization of an inert gas. Analytical techniques, such as gas chromatography, are employed to

quantify the solute concentration in the gas phase. The activity coefficient at infinite dilution can be determined by comparing the concentration of the solute in the gas phase to its known concentration in the liquid phase [253, 254]. This method offers precise measurements of activity coefficients but requires sophisticated equipment like gas chromatographs. It's effective for volatile solutes but less suitable for non-volatile or highly viscous solvents. Compared to other techniques like vapor-pressure methods, it provides more direct activity coefficient data but may be labor-intensive and costly.

4.6.2. Differential ebulliometer technique

The methodology entails the quantification of the vapor-liquid equilibrium of a binary mixture across varying temperatures. The temperature at which the vapor phase above a liquid mixture has an identical composition to the liquid phase can be determined using a differential ebulliometer. The activity coefficient at infinite dilution may be determined by utilizing the mole fraction of the solute in the liquid phase and the total pressure [255]. This technique is robust for studying phase equilibria but requires precise temperature control and calibration. It's advantageous for non-volatile solutes and can provide data across a wide range of concentrations. However, compared to methods like isothermal titration calorimetry, it may have limitations in high-pressure systems or with complex mixtures.

Tumba (2009) detailed other techniques and methods such as the headspace analysis method, indirect headspace chromatography, dew point method, and Rayleigh distillation method [204]. The headspace analysis method and indirect headspace chromatography quantify solute concentrations in the vapor phase above a liquid mixture. These techniques offer insights into volatile solute behavior and can be useful for activity coefficient determinations. They are efficient for volatile solutes but may not directly determine activity coefficients at infinite dilution. They provide complementary data to other techniques but may have limitations for non-volatile solutes or complex mixtures. The dew point method determines activity coefficients by measuring the dew point of a binary mixture at various compositions. It's effective for studying phase equilibria and can provide data for activity coefficient calculations. This method offers insights into phase equilibria but may require precise experimental conditions. It's suitable for both volatile and non-volatile solutes but may be limited by the complexity of the mixture. The Rayleigh distillation method quantifies activity coefficients based on the distillation behavior of a binary mixture. It's effective for studying volatile solute behavior and can provide data for activity coefficient calculations. This method offers insights into distillation behavior but may require complex experimental setups. It's suitable for volatile solutes but may have limitations for non-volatile solutes or complex mixtures.

4.6.3. Equipment description for activity coefficient measurements

The equipment utilized for determining activity coefficients was significant and consisted of the following:

Analytical balance (OHAUS)

Ultrasonic water bath

Vacuum pump

Karl-Fischer auto titrator

Soap bubble flow meter

1 m long, 4.1 mm diameter stainless steel column

Rotary evaporator with water bath

Digital barometer

SHIMADZU GC-2014 Gas-chromatography coupled with thermal conductivity detector (TCD)

4.6.4. Gas-liquid chromatography

Gas-liquid chromatography is a prevalent technique in the field of analytical chemistry, initially introduced by Kojima in 1956 [169]. In the realm of ascertaining activity coefficients at infinite dilution, GLC can be employed to quantify the relative concentrations of the solute within a binary mixture. GLC is a technique that facilitates the separation of compounds by exploiting their differential distribution between a gaseous phase (referred to as the mobile phase) and a liquid phase (known as the stationary phase) within a column. The column is commonly coated with a stationary phase material that establishes interactions with the analytes present in the sample mixture. The separation and detection of various compounds can be achieved by manipulating the temperature of the column.

The GLC method has demonstrated its efficacy and efficiency in determining retention data, especially for solutes that are volatile in nature. The applicability of the system has been expanded to encompass medium volatility compounds through recent modifications and improvements [256]. In typical industrial separation processes, solvents are commonly applied as a coating within the column and are carefully regulated in terms of temperature to achieve consistent and replicable outcomes. The application of GLC in the determination of infinite dilution activity coefficients for non-volatile solvents is constrained by the volatilization of solutes, rendering it more appropriate for the examination of volatile solutes.

The measurements conducted using GLC have been reported to exhibit relative uncertainties ranging from approximately 3% to 5%, as stated by researchers [257-259]. To mitigate potential harm to the

solid support material utilized as the stationary phase, various strategies have been employed by researchers. These include the utilization of pre-coiled stainless-steel columns [171] and pre-coiled glass columns [260]. Ensuring a consistent column temperature is of utmost importance to attain results that can be replicated with accuracy. The extensive utilization of GLC and its ongoing enhancements render it a flexible instrument applicable in diverse research and industrial contexts.

4.7. Mechanism of DES in the stationary phase

Gas chromatography [73] is a scientific method employed for the purpose of separating and analyzing minute molecules in their gaseous state. The process entails the introduction of the sample molecules into a column, where they undergo partitioning between a stationary phase in liquid form and a mobile phase in gaseous form. In the context of GLC, it is customary to employ helium as the mobile phase [261]. Figure 4.6 displays a schematic representation of this phenomenon.

The stainless-steel column, measuring 1 meter in length and 4.1 millimeters in diameter, contained the stationary phase that was prepared as described in Section 4.7.2. The selection of the stationary phase in GC is contingent upon the desired separation, with options including both nonpolar and polar phases. Polydimethylpolysiloxane is frequently employed as the primary constituent in nonpolar commercial gas chromatography [73] stationary phases. Conversely, polar phases typically employ polyethylene glycol (PEG) as the primary component [262].

The unique selectivity and tunability of DESs have garnered significant attention in the field of GC. Utilizing DESs as either polar or nonpolar phases allows for a variety of applications, providing versatility in separation processes. Prior to its utilization as a stationary phase in GC analysis, a DESs necessitates a coating procedure within the capillary. The coating procedure necessitates the selection of a stationary phase that possesses solubility in a solution, which can subsequently undergo evaporation [263].

After the application of the DES, it is necessary to subject the column to a conditioning process at temperatures that do not exceed the maximum operating temperature. The conditioning process serves the purpose of eliminating impurities and preventing degradation of the column, thereby preserving its performance [264].

During GC analysis, the analytes, characterized as small molecules with a size of approximately 0.1 nm, undergo partitioning between the stationary and mobile phases, facilitating their separation by exploiting variations in chemical structure and hydrogen bonding interactions. DESs demonstrate selectivity as stationary phases in GC owing to their distinctive chemical composition and the presence of both hydrogen bond donors and acceptors.

When choosing DESs to be utilized as stationary phases in gas chromatography, it is necessary to consider specific properties. The properties encompass attributes such as exceptional stability, appropriate viscosity, favorable wettability, suitable polarity, and other characteristics that are compatible with GC. Furthermore, the attainment of precise and efficient separations in gas chromatography analysis is contingent upon the presence of selectivity and high efficiency [265].

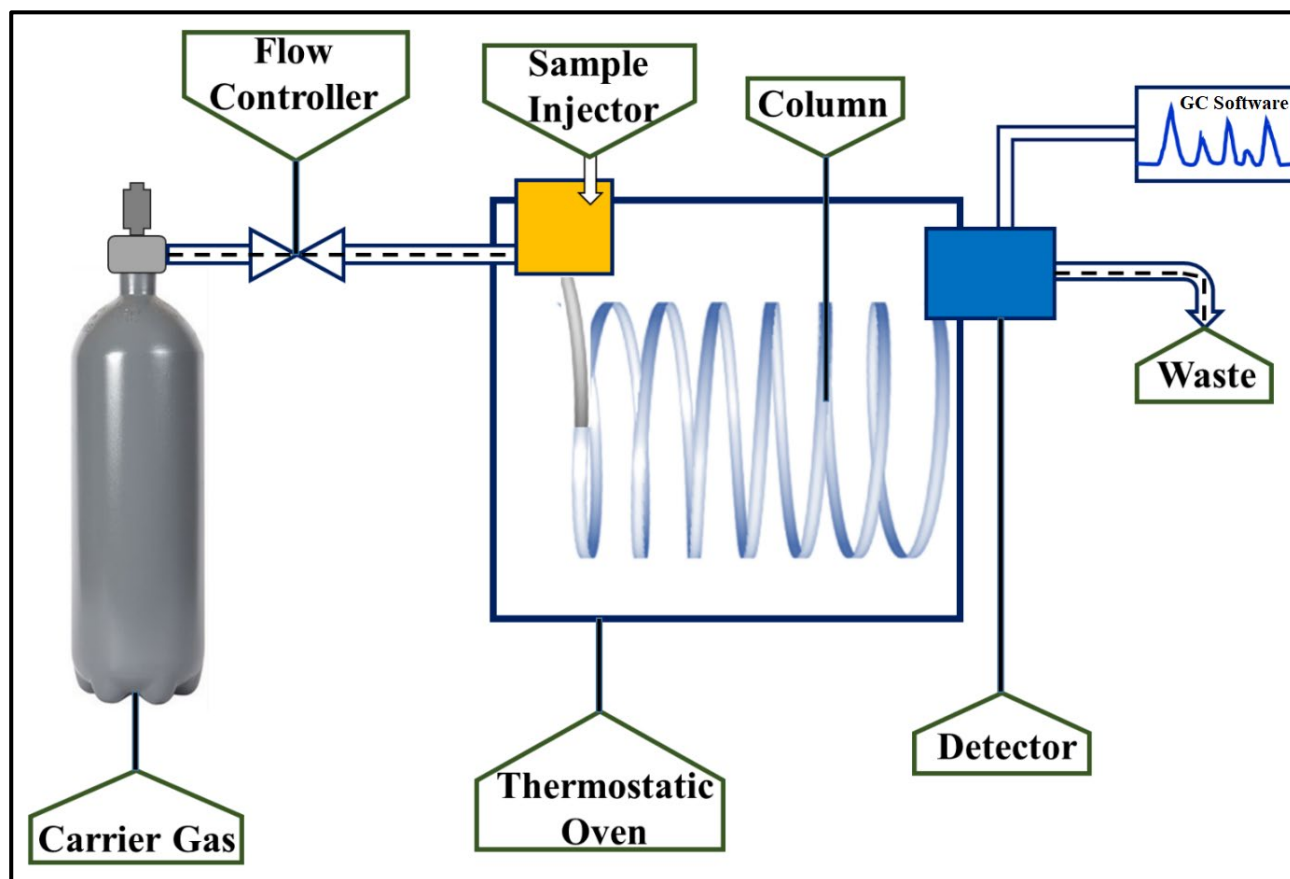


Figure 4. 6: A typical schematic diagram of a gas liquid chromatography [6].

4.7.1 Method for GLC technique

The methodology required for the GLC technique has been extensively documented in various scholarly sources [180, 204, 256, 257]. A detailed account of the procedure employed, along with any pertinent modifications, will be provided in a comprehensive manner.

Solvent purification

- **Purification:** The DESs underwent purification under low vapor pressure conditions of 6×10^{-3} Pa (Pascal) at a temperature of 343 K (Kelvin) for a duration of 10 hours. The primary objective of this purification procedure was to eliminate any possible impurities from the DES, thereby guaranteeing their purity for subsequent analytical investigations.

- **Sealing:** Following the purification process, the flask containing the purified DES was sealed tightly using parafilm, a commonly employed thin plastic film utilized for the purpose of sealing laboratory vessels. This procedural measure serves to inhibit the introduction of any extraneous impurities into the flask.
- **Insulation:** Following the parafilm sealing, insulation tape was used to further secure the flask and provide additional protection against potential leaks or contamination. The insulation tape acts as an extra barrier to maintain the integrity of the system.
- **Desiccator:** The closed container, containing the sealed flask with the DESs and silica gel crystals, was kept in a desiccator. A desiccator is a sealed container used to create a controlled environment with low humidity. It helps to maintain a dry atmosphere, further reducing the chances of moisture or other contaminants affecting the DESs.
- **Water content determination:** The Karl-Fischer auto titrator was employed for the purpose of evaluating the water content present in the purified DESs. The Karl-Fischer method is a commonly utilized technique in the field of analytical chemistry for a precise determination of water content in each sample. The auto-titrator is a mechanized apparatus that carries out the process of titration, enabling accurate and efficient measurement of water content.

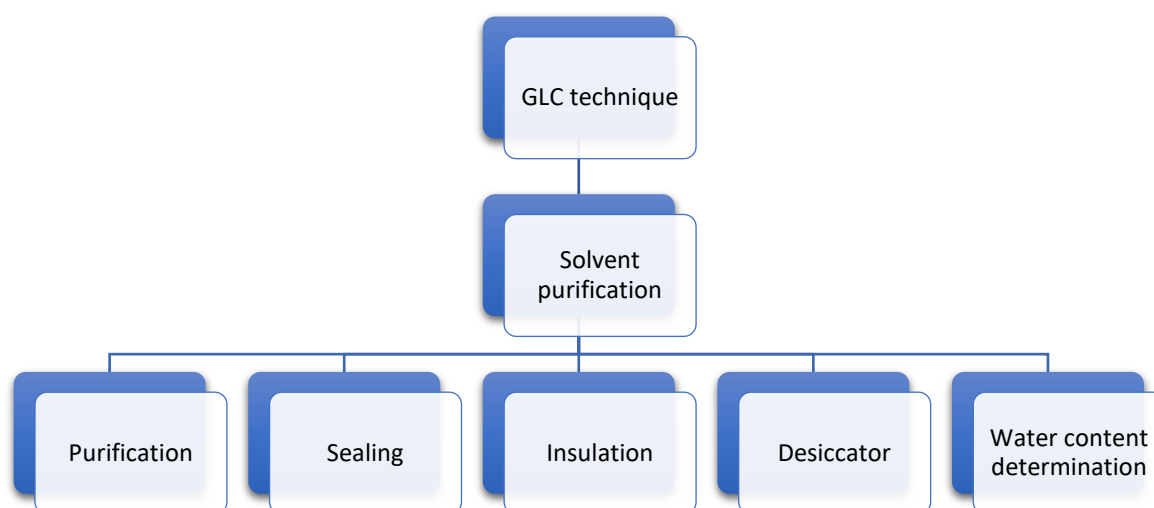


Figure 4. 7: Solvent purification

4.7.2. Preparation of the stationary phase

The present study focuses on the development of a stationary phase for chromatography through the utilization of DES in combination with a solid support material. The following is an analysis of the sequential procedures:

- Weighing the solid support material: The mass of the solid support material is determined through the application of an analytical mass balance, which exhibits a precision level of 0.0001 g. This step is crucial to obtain precise measurements for the subsequent calculations.
- Weighing the DES with solid support material: The mass of the DES is determined by weighing it in a flask that is already filled with the solid support material. The rapid execution of this process helps to reduce the risk of moisture infiltration, as such infiltration has the potential to adversely impact the characteristics and performance of the DESs.
- Addition of dichloromethane or methanol: To achieve a homogeneous distribution of the DES in the chromosorb (stationary phase), the addition of dichloromethane or methanol is employed, depending on the compatibility of the DES with the volatile organic solvent used to achieve the homogeneity between DES and chromosorb.
- Rotary evaporation: The method of rotary evaporation is utilized for the purpose of removing the volatile organic solvent (specifically dichloromethane or methanol) that has been introduced into the stationary phase. The process of rotary evaporation capitalizes on the inherent property of solvents with low boiling points, enabling their efficient elimination and resulting in the retention of the intended stationary phase.
- Weighing the mass of the stationary phase: Once the volatile solvent has undergone evaporation, the mass of the stationary phase, consisting of the solid support material combined with the DES, is measured to ascertain its corresponding mass. This measurement facilitates the precise determination of the quantity of stationary phase utilized.
- DES concentration onto the column: The stated mass of the DES is reported to fall within the range of 25-33%. The concentration range mentioned is deemed sufficiently high to inhibit the adsorption of undesired compounds onto the chromatography column, thereby guaranteeing the successful separation of the desired compounds during chromatographic analysis.

4.7.3. Preparation of the column

Steps for cleaning the stainless-steel column.

- Straightening the column: The stainless-steel column underwent manual straightening using a bench vice and was subsequently uncurled by hand. This procedure entailed the physical manipulation of the column to eliminate any bends or deformations and restore it to a straight form.
- Removing previous material content: The material content that was previously present within the column was taken out. The dispersion of the entire material was accomplished through the application of a ½-inch steel rod to the column. It appears that the steel rod was plausibly introduced into the column and employed to displace the preceding substance.
- Cleaning the column: After removing the previous material, the column was cleaned.
 - The cleaning process involved multiple steps:
 - Hot soapy water: The column underwent a cleaning process utilizing hot soapy water to eliminate any dirt, residue, or contaminants present on its surface.
 - Rinsing with water: Subsequently, the column was subjected to a water rinse to eliminate the soapy solution and residual impurities.
- Drying with acetone: To ensure complete drying, the column was dried using acetone, which evaporates quickly and leaves no residue.
- Final cleaning with compressed air: A stream of compressed air was directed through the column for a period of 10 to 20 minutes. This step was likely executed to guarantee the elimination of any residual moisture present within the column, resulting in its cleanliness and dryness.

4.7.4. Loading of the column

- Cleaning the column: Start with a clean and empty column. Ensure that there are no impurities or remnants from previous experiments.
- Inserting glass wool: Position a modest quantity of glass wool at the distal end of the column. Glass wool serves as a barrier that prevents the movement of the stationary phase during the loading procedure.
- Weighing the column: Following the insertion of the glass wool, proceed to measure the weight of the column. This measurement yields the initial mass of the column prior to the introduction of the stationary phase.
- Setting up the column: Clamp the column in a vertical position by utilizing a burette stand. This practice guarantees stability throughout the packing procedure.

- Connecting a vacuum rubber tube: Securely affix a rubber tube designed for vacuum applications to a flask, and subsequently establish a connection between the opposite end of the tube and the sealed base of the column. The utilization of a vacuum facilitates the generation of suction, thereby aiding in the consistent and compact arrangement of the column.
- Loading the stationary phase: Carefully introduce the prepared stationary phase material into the column. To enhance the packing process, it is recommended to utilize a steel rod measuring $\frac{1}{2}$ inch in diameter to gently strike the column. The application of a beating motion facilitates the settling of the stationary phase material and enhances the uniform distribution within the column.
- Sealing the second opening: After the stationary phase has been loaded, proceed to seal the second opening of the column by inserting an additional glass wool plug. The utilization of a glass wool plug serves the purpose of effectively securing the stationary phase in its designated position throughout the subsequent stages of the process.
- Calculating the mass of the loaded stationary phase: Weigh the column again, considering both ends are now sealed with glass wool. The mass difference between the fully packed column and the empty column (including glass wool plugs at both ends) represents the mass of the stationary phase that has been loaded into the column.

4.7.5. Conditioning and installation of the column

- Manual coiling: The packed column underwent manual coiling, whereby it was shaped into a coiled configuration that was presumably suitable for accommodation within the chromatography instrument.
- Insertion and conditioning: Subsequently, the coiled column was introduced into the GLC oven. Conditioning is the procedural step of preparing the column for analysis by purging it with a carrier gas. In this instance, the carrier gas employed is helium, with a flow rate of 30 ml/min.
- Temperature and duration: The conditioning procedure were carried out at a temperature of 90°C for a duration of 14 hours. The extended process of conditioning facilitates the achievement of stability and the elimination of contaminants from the column.



Figure 4. 8: A diagram showing a packed column inserted in GLC [260].

- Fully Packed Column: The column was completely packed with fine particles. This implies that the stationary phase is comprised of solid particles that serve as support for the liquid phase.
- High pressure drops: Due to the complete packing of the column, there is a significant increase in pressure drop within the column. This pertains to the resistance experienced by the carrier gas when passing the densely packed collection of particles.
- Coated particles: A liquid phase envelops the particles within the densely packed column. The liquid phase plays a crucial role in the separation of analytes in chromatographic analysis.
- Compound capacity: The fully packed column has a higher compound capacity, meaning it can accommodate more analytes for separation compared to other column types.
- Thermal conductivity detector (TCD): The utilization of the described packed column is frequently observed in conjunction with a thermal conductivity detector. The TCD is widely employed in gas chromatography to identify variations in thermal conductivity resulting from the existence of diverse compounds within the analyzed sample.

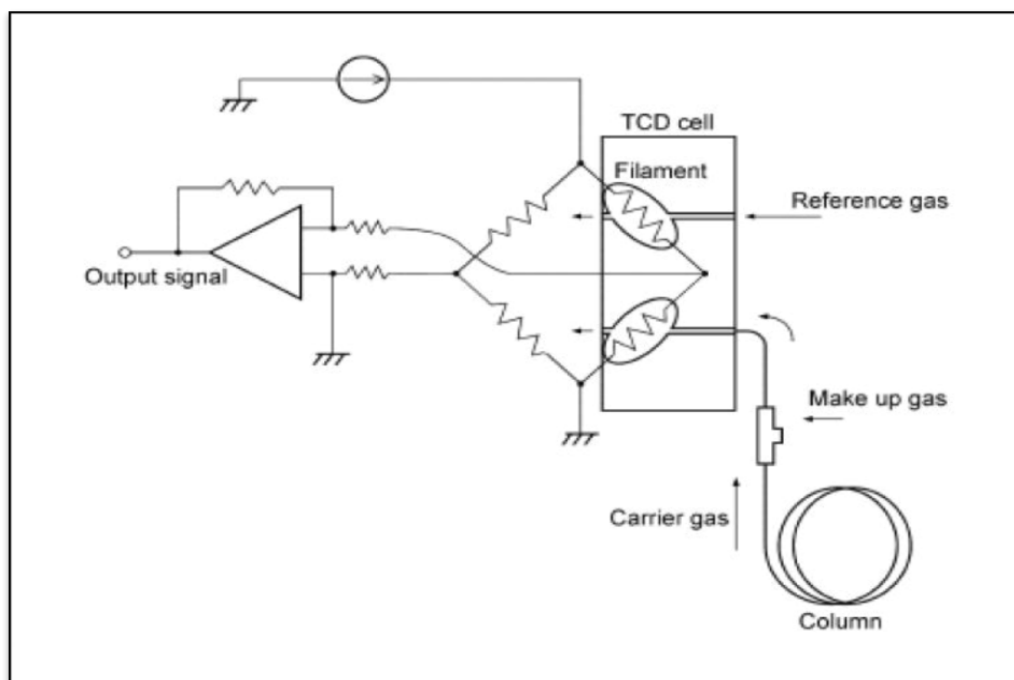


Figure 4. 9: Schematic diagram of a Shimadzu TCD is shown as given by (Shimadzu Asia Pacific Pty. Ltd in 2006) [266].

4.7.6. Measurements

- **Temperature:** The measurements were conducted over a temperature range of 313.15 K to 353.15 K, with intervals of 10 K.
- **Pressure:** The pressure during the measurements was consistently maintained at a constant value of 101 kPa.
- **Injection Volume:** The range of manually injected solute volumes into the GLC system varied between 0.2 μL and 0.3 μL .
- **Measurements:** The GLC system employed internal sensors to quantitatively assess the drop in pressure occurring within the column as well as to monitor the temperature and retention time of the solutes. The parameters play a pivotal role in the analysis of the separation and identification of constituents within a mixture through chromatography.
- **Pressure correction:** The measurements considered the atmospheric pressure by using a digital barometer. Pressure correction calculations are often necessary to account for any deviations caused by variations in atmospheric pressure.

4.8. Thermophysical measurements and instrumentation

4.8.1 Density analyser

The apparatus generally consists of a U-shaped tube that is filled with the sample intended for analysis. The U-tube is subsequently exposed to an electromagnetic force, resulting in its vibration.

The density of a sample can be determined by measuring the frequency and period of vibration of a U-tube that is packed with the sample. The relationship between the fundamental frequency of vibration in a U-tube and the mass of the system, which includes the sample, is direct. The density meter quantifies the frequency or period of oscillation in the U-tube and employs this data to determine the density of the sample. An accurate determination of density can be achieved by obtaining precise measurements of the frequency or period, as the fundamental frequency of vibration is dependent on the mass of the system [267]. The utilization of this technique is widespread across diverse sectors, including the chemical, pharmaceutical, and petroleum industries, wherein accurate density assessments are imperative for the purposes of quality assurance and process supervision.

The density, ρ , is determined by calculating the ratio of the period of oscillation of the U-tube to that of the reference oscillator:

$$\rho = KA \times Q^2 \times f_1 - KB \times f_2 \quad (4.1)$$

KA, KB are the constants associated with the apparatus

Q is the quotient of the U-tube's oscillation period to the reference oscillator's oscillation period.

f_1, f_2 are the correction terms for temperature, viscosity, and non-linearity.

The density value is shown on the liquid crystal display (LCD) panel. The DSA 5000 M is connected to a computer that is equipped with software capable of storing all recorded density data. The provided image depicts the density and sound velocity meter (DSA 5000 M).

4.8.2. Sound velocity analyser

The apparatus employs a cell made of stainless steel and functions by employing the pulse-echo technique, wherein a short ultrasound pulse is transmitted through the core of the sample. The velocity of sound was determined at a frequency of approximately 3-megahertz (MHz) in this instance. This specific technique has demonstrated a high level of effectiveness in yielding precise density measurements. When an ultrasound pulse encounters an obstacle or impedance within the sample, a fraction of the pulse is reflected, while the remaining fraction continues to propagate through the sample [268]. The equipment can convert the time interval between the emission of the pulse and the reception of the echo into a distance measurement by means of recording [269].

To determine the sound velocity, the sample is positioned within a sound velocity measurement cell, which is encompassed by an ultrasonic transmitter on one side and a receiver on the opposite side. The transmitter generates sound waves with a pre-established duration throughout the sample. The

determination of the velocity of sound, symbolized as u , entails the use of the duration of sound waves and the spatial separation between the transmitter and receiver.

$$u = \frac{l \times (1 + 1.6 \times 10^{-5} \times \Delta T)}{\frac{P_s}{512} - A \times f_s} \quad (4.2)$$

In the given equation, l represents the initial distance traveled by the sound waves, ΔT denotes the deviation in temperature from the reference value of 278.15 K, P_s signifies the period of oscillation of the received sound waves, "A" represents the apparatus constant for sound velocity, and f_s denotes the correction term associated with temperature. The measurement was conducted at a frequency of 3 MHz.

The density and velocity of sound are highly dependent on temperature, necessitating the use of thermostated measuring cells equipped with Peltier elements.

The DSA 5000M is characterized by its notable precision in density measurements. The DSA 5000 M instrument is equipped with cutting-edge digital density and sound velocity measuring technology, which is considered to be the most sophisticated in the world.

- (i) The measurement of the U-tube's oscillation period is conducted using optical pickups.
- (ii) The utilization of two integrated Pt 100 platinum thermometers, in conjunction with the incorporation of Peltier elements, facilitates the achievement of a remarkably precise thermostetting of the sample.
- (iii) A thermobalance is employed as an auxiliary reference oscillator, offering extended stability and facilitating accurate measurements across the entire temperature range of the instrument. This is achieved through a single adjustment at $T = 293.15$ K.
- (iv) Errors associated with viscosity can be effectively addressed throughout the entire range of viscosity by first measuring the damping effect of the viscous sample and then applying a mathematical correction to determine the density value.
- (v) Enhanced precision can be achieved by making specific modifications to the standards employed for substances with high viscosity and high density.

One of the main sources of measurement errors encountered when utilizing a density and sound velocity meter is the presence of gas bubbles within the measuring cells. In order to mitigate the occurrence of gas bubbles, Anton Paar density meter 5000M has implemented two novel characteristics:

Filling check: The instrument employs an advanced analysis of its oscillation pattern to automatically detect gas bubbles in the density measuring cell, subsequently issuing a cautionary message. U-View: The density measuring cell can be visually examined for gas bubbles by utilizing a real-time camera equipped with a zoom function. The specifications pertaining to the DSA 5000 M are presented in Table 4.3.

Table 4. 3: The DSA 5000 M certain specifications.

Measuring range density	0 to 3 g/cm ³
Measuring range sound velocity	1000 to 2000 m/s
Measuring range temperature	273.15 to 343.15 K (32 to 158 °F)
Pressure range	0 to 3 bar (0 to 44 psi)
Repeatability density	0.000001 g/cm ³
Repeatability sound velocity	0.1 m/s
Repeatability temperatures	273.151 K (0.002 °F)
Measuring time per sample	1 to 4 minutes
Sample volume	approx. 3 ml
Ambient air pressure sensor	yes
Reference oscillator	yes
Automatic bubble detection	yes
Visual check of the density measuring cell	camera

4.8.3 Characteristics of DSA 5000 M

4.8.3.1 Accuracy

The DSA 5000 M instrument is outfitted with cutting-edge digital density and sound velocity measurement technology, which is the most advanced in the world, where:

- Measurement of the U-tube's oscillation period is conducted using optical pickups.
- Utilization of two integrated Pt 100 platinum thermometers in conjunction with the Peltier elements facilitates highly accurate regulation of the sample's temperature.

- Thermo balance is an auxiliary reference oscillator that offers extended stability and facilitates accurate measurements across the entire temperature range of the instrument, requiring only a single adjustment at 20 degrees Celsius.

4.8.3.2 Error detection

Gas bubbles present in the measuring cells constitute a significant source of measurement errors when employing a density and sound velocity meter. To mitigate the occurrence of gas bubbles, Anton Paar density meter 5000 M implemented two novel characteristics.

- Filling check: The gas bubble detection in the density measuring cell is accomplished through an automated process wherein the instrument utilizes sophisticated analysis of its oscillation pattern. Subsequently, a warning message is generated to alert the user to the presence of gas bubbles.
- U-view: By employing a camera equipped with real-time capabilities and a zoom function, it becomes possible to visually examine the U-tube for the presence of gas bubbles within the density measuring cell.

4.8.3.3 User interface

The touch screen's user interface makes it possible to carry out operations in a way that is both simple and straightforward, making it useful for both daily applications and scientific study. The user interface facilitates the following functionalities:

- (i) The density and sound velocity values obtained from measurements can be automatically converted into concentration values for a wide range of substances that are pre-programmed in the factory. The instrument has the capability to be programmed with specific substances as needed.
- (ii) To function effectively in demanding industrial environments, the DSA 5000 M can be operated using a set of durable soft keys as an alternative to the touch-screen interface.
- (iii) The DSA 5000 M has the capability to establish connections with external input devices such as a keyboard, computer mouse, or bar code reader.

4.8.4 Preparation of binary mixtures

The binary mixtures were prepared in order to include the whole spectrum of mole fractions. The masses of the components of the binary mixtures were measured using an OHAUS analytical balance, manufactured by OHAUS, NJ, USA. This balance has a precision of ± 0.0001 g. The uncertainties in mole fraction, were $= 0.0006$. The binary mixtures were generated by introducing the individual pure liquids into vials in order to minimize evaporation. Subsequently, the mixtures were vigorously

shaken to achieve complete sample mixing and homogeneity. To ensure consistency in composition, the preparation of each combination was carried out promptly before conducting measurements of density and speed of sound. This approach aims to prevent any discrepancies in composition that may arise from the evaporation of the solvent.

4.9. Experimental setup and procedure for density and speed of sound measurements

This study outlines the experimental setup and procedures employed to measure density and speed of sound utilizing an Anton Paar DSA 5000M vibrating U-tube densimeter. The following is a concise overview of the main points:

- **Measurement precision:** The temperatures obtained from the experiment are measured with a precision of ± 0.02 K. The density is measured with a precision of plus or minus $0.000005 \text{ g}\cdot\text{cm}^{-3}$, and the speed of sound is measured with a precision of plus or minus $0.01 \text{ m}\cdot\text{s}^{-1}$.
- **Cleaning process:** The measuring cell of the DSA 5000M undergoes a cleaning process using ethanol (liquid 1), followed by drying with acetone (liquid 2), facilitated by the automatic Xsample 452 Module. The aforementioned cleaning procedure is executed subsequent to every individual measurement.
- **Rinsing process:** The act of rinsing ethanol (referred to as liquid 1) facilitates the dissolution of any residual sample material present within the measuring cell. Acetone, referred to as liquid 2, is commonly employed for the purpose of rinsing and possesses high volatility and solubility in liquid 1. The liquid 1 is eliminated through rinsing, and the cell is subsequently subjected to a stream of dry air in order to speed up the drying procedure.
- **Calibration:** Following the cleaning process, the instrument undergoes calibration utilizing ultra-pure water and ambient air to ascertain the precision of the density measurement.
- **Sample handling:** The preparation of binary mixtures involves the placement of the mixture into vials, which are subsequently sealed using caps. The vials are positioned within a magazine containing 48 slots on the Xsample 452 instrument. The DSA 5000M system subsequently uses automated means to identify this arrangement. Subsequently, the sample changer proceeds to transfer the binary solutions contained within each vial into the measuring cell.
- **Bubble detection:** The instrument utilizes a novel analysis technique of oscillation patterns in order to identify and locate gas bubbles within the measuring cell. A cautionary message is generated in the event that bubbles are detected. A camera equipped with real-time capabilities and a zoom function can be employed for the purpose of visually inspecting gas bubbles on an external personal computer.

- Rinse and dry: Following each measurement, the measuring cell undergoes an automated rinsing and cleaning process involving two rinsing liquids, namely ethanol and acetone, followed by a subsequent drying step.
- Results display: The instrument's LED display and pre-installed software provide simultaneous presentation of the density and speed of sound measurements.
- Projected measurement error: The anticipated uncertainties associated with the measurements of temperature, density, and sound velocity are expected to be within the range of ± 0.02 K, ± 0.0009 g·cm⁻³, and ± 2.63 m·s⁻¹, respectively.

4.10. Systems studied in this work

To obtain the pure solutes, their properties were determined and compared to existing literature data. In this study, the binary mixtures {[ZnCl₂][acetic acid] 1:4 or [ZnCl₂][phosphoric acid] 1:2.5 + methanol or ethanol or propanol} were investigated at different temperatures (293.15, 303.15, 308.15, and 313.15) K and at a constant pressure of 0.1 MPa using the DSA 5000M. The research focused on determining several thermodynamic properties, including excess molar volumes, isentropic compressibility, intermolecular free length, and deviation in isentropic compressibility, using density and speed of sound measurements. These properties were determined using the equations provided in Chapter 3. By investigating these thermodynamic properties, the research aimed to understand the behavior of the binary mixtures at different temperatures and compositions.

Table 4. 4: Experimental and literature comparison of pure component density, ρ , and speed of sound, u , at T = (293.15, 303.15, 308.15, 313.15, and 313.15) K and at 0.1 MPa.

T (K)	ρ (g·cm ⁻³)		u (m·s ⁻¹)	
	Expt	Lit	Expt	Lit
Methanol				
293.15	0.7916	0.7961 [270]	1119.60	1119.00 [270]
		0.7913 [271]		1119.13 [271]
		0.7936 [272]		1106.63 [272]
		0.7914 [273]		
		0.7930 [274]		
		0.7926 [275]		1105.19 [275]
		0.7910 [276]		1119.60 [276]
		0.7912 [277]		
		0.7910 [278]		1120.00 [278]
		0.7819 [273]		
303.15	0.7822	0.7819 [271]	1087.20	1086.00 [271]
		0.7819 [279]		1086.00 [279]
		0.7846 [272]		1082.73 [272]
		0.7837 [275]		1088.73 [275]
		0.7824 [280]		1092.29 [280]
		0.7827 [281]		1088.26 [281]
		0.7836 [274]		

Table 4.4 continued

T (K)	ρ (g cm ⁻³)		u (m s ⁻¹)		ρ (g cm ⁻³)		u (m s ⁻¹)	
	Lit	Expt			Lit	Expt		
308.15	0.7776	0.7810 [282]			1071.07	1085.89 [282]		
		0.7820 [276]				1086.60 [276]		
		0.7818 [277]						
		0.7820 [278]				1087.00 [278]		
		0.7772 [273]						
		0.7772 [271]				1069.70 [271]		
		0.7779 [272]				1068.82 [272]		
		0.7769 [275]				1070.82 [275]		
		0.7771 [279]				1069.00 [279]		
		0.7776 [280]				1077.90 [280]		
		0.7779 [281]				1072.04 [281]		
		0.7773 [282]				1074.00 [282]		
		0.7771 [277]						
		0.7741 [274]						
313.15	0.7727	0.7724 [271]			1055.00	1053.57 [271]		
		0.7724 [272]				1059.41 [272]		
		0.7720 [276]				1054.20 [276]		
		0.7725 [279]				1052.00 [279]		
		0.7729 [280]				1065.03 [280]		
		0.7732 [281]				1055.91 [281]		
		0.7728 [282]				1052.00 [282]		
		0.7723 [277]						
		773.00 [278]				1055.00 [278]		
		Ethanol						
		0.7894 [283]						
293.15	0.7896	0.7897 [271]			1160.37	1161.00 [271]		
		0.7894 [272]				1159.34 [272]		
		0.7895 [273]						
		0.7895 [275]				1161.38 [275]		
		0.7895 [284]				1162.30 [284]		
		0.7895 [274]						
		0.7896 [276]				1162.30 [276]		
		0.7895 [277]						
		0.7900 [278]				1162.00 [278]		
		0.7808 [283]						
		0.7810 [271]				1126.77 [271]		
		0.7820 [272]						
		0.7808 [273]						
		0.7820 [275]				1129.01 [275]		
303.15	0.7810	0.7810 [279]			1126.91	1127.00 [279]		
		0.7809 [284]				1128.90 [284]		
		0.7810 [285]						
		0.7820 [286]				1128.00 [286]		
		0.7809 [274]						
		0.7810 [276]				1128.20 [276]		
		0.7807 [277]						
		0.7810 [278]				1127.00 [278]		
		0.7820 [282]				1128.00 [282]		
		0.7764 [283]						
		0.7767 [271]				1109.87 [271]		
		0.7778 [275]				1099.74 [275]		
		0.7755 [279]				1109.00 [279]		
		0.7777 [286]				1098.00 [286]		
		0.7764 [277]						
308.15	0.7723				1109.94			

Table 4.4 continued

T (K)	ρ (g cm ⁻³)		u (m s ⁻¹)	
	Lit	Expt	Lit	Expt
313.15	0.7701	0.7777 [282]	1093.40	1098.00 [282]
		0.7720 [283]		
		0.7723 [271]		1093.11 [271]
		0.7732 [272]		1090.92 [272]
		0.7722 [273]		
		0.7732 [275]		1093.11 [275]
		0.7723 [279]		1089.00 [279]
		0.7722 [284]		1095.40 [284]
		0.7722 [285]		
		0.7736 [286]		1086.00 [286]
		0.7722 [274]		
		0.7720 [276]		1094.50 [276]
		0.7721 [277]		
		0.7720 [278]		1094.00 [278]
		0.7736 [282]		1086.00 [282]
Propanol				
293.15	0.8036	0.8036 [287]	1222.69	
		0.8036 [271]		1223.12 [271]
		0.8037 [275]		1196.64 [275]
		0.8038 [283]		
		803.75 [273]		
		0.8030 [288]		1224.30 [288]
		0.8039 [285]		
		0.8039 [274]		
		0.8036 [277]		
		0.8040 [278]		1226.00 [278]
303.15	0.7956	0.7955 [289]	1188.88	
		0.7956 [271]		1188.64 [271]
		0.7960 [281]		1189.26 [281]
		0.7956 [287]		
		0.7956 [283]		
		0.7957 [275]		1185.89 [275]
		0.7955 [273]		
		0.7960 [288]		1189.90 [288]
		0.7958 [274]		
		0.7956 [277]		
308.15	0.7916	0.7960 [278]	1171.93	1191.00 [278]
		0.7915 [287]		
		0.7915 [271]		1171.64 [271]
		0.7905 [275]		1170.01 [275]
		0.7919 [281]		1172.37 [281]
		0.7915 [283]		
		0.7915 [277]		
313.15	0.7875	0.7874 [289]	1155.23	
		0.7874 [271]		1154.88 [271]
		0.7874 [275]		1159.51 [275]
		0.7878 [281]		1155.53 [281]
		0.7874 [287]		
		0.7874 [283]		
		787.42 [273]		
		0.7880 [288]		1156.00 [288]
		0.7874 [285]		
		0.7876 [274]		
		0.7874 [277]		

Standard uncertainties u are $u(T) = 0.02$ K, $u(p) = 0.04$ MPa, and the combined expanded uncertainties Uc in mole fraction, density, and speed of sound were $Uc(x) = 0.0006$, $Uc(\rho) = 0.0009$ g·cm⁻³, $Uc(\underline{u}) = 2.63$ m·s⁻¹, respectively (0.95 level of confidence).

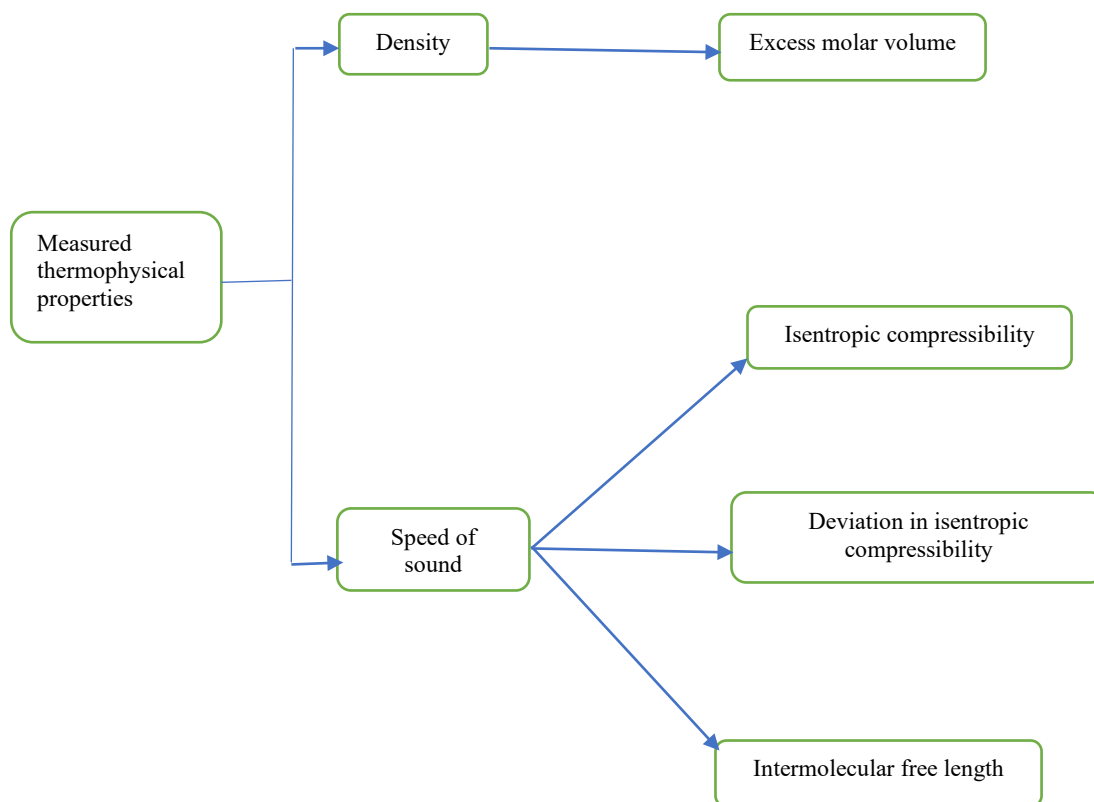


Figure 4. 10: Categorization of thermophysical and thermodynamic characteristics.

RESULTS AND DISCUSSION

5.1 Infinite dilution activity coefficient of {[ZnCl₂][acetic acid 1:2 or 1:4] and [ZnCl₂][phosphoric acid 1:2 or 1:2.5]}

Infinite dilution activity coefficients of 34 solutes, which describes their partitioning between helium gas as the carrier and an extracting solvent composed of {[ZnCl₂][acetic acid] 1:2 or 1:4} and {[ZnCl₂][phosphoric acid] 1:2 or 1:2.5}, has been calculated using retention data obtained through gas liquid chromatography technique. The outcomes of this analysis are presented in Tables 5.1-5.2, aligned with their respective temperatures. These values were determined over a range of temperatures, specifically from $T = (313.15 \text{ to } 353.15) \text{ K}$, with an increment of 10 K.

Table 5. 1: Average γ_{13}^{∞} (the solute is be denoted as component 1, and the solvent as component 3) for the solutes in the deep eutectic solvent [ZnCl₂][acetic acid] at 1:2 molar ratios and at five different temperatures for the standard state of the solutes hypothetical liquid at zero pressure ^a.

Solute	Average γ_{13}^{∞} values				
	$T = 313.15 \text{ K}$	$T = 323.15 \text{ K}$	$T = 333.15 \text{ K}$	$T = 343.15 \text{ K}$	$T = 353.15 \text{ K}$
2,2-dimethylbutane	42.88	51.48	57.78	67.21	79.47
<i>n</i> -Pentane	30.59	33.58	37.45	47.18	52.39
<i>n</i> -Hexane	74.03	91.38	102.7	114.3	142.9
<i>n</i> -Heptane	113.8	131.7	148.6	156.5	188.7
<i>n</i> -Octane	154.4	162.5	188.1	223.3	237.8
<i>n</i> -Nonane	233.5	254.8	279.8	301.3	337.0
<i>n</i> -Decane	333.2	380.5	416.3	460.4	481.8
1-Pentene	41.97	45.68	49.2	56.34	64.9
1-Hexene	102.3	107.6	114.2	121.4	134.6

1-Heptene	170.0	182.6	184.2	194.8	196.6
1-Nonene	203.9	222.2	226.6	248.8	280.5
1-Decene	254.7	274.8	291.0	310.3	330.2
Cyclohexene	68.90	74.78	73.87	83.71	91.01
Cyclohexane	47.50	54.51	64.11	71.24	80.10
Cyclooctane	125.8	141.7	164.8	187.4	232.8
1-Pentyne	50.22	52.78	55.30	57.74	61.02
1-Hexyne	87.52	92.70	97.14	98.01	98.20
1-Heptyne	149.6	155.8	166.7	173.9	178.2
Benzene	143.3	152.4	161.3	169.2	180.7
Toluene	151.1	159.8	170.7	179.5	188.3
Ethylbenzene	176.0	185.4	192.6	200.9	209.6
m-Xylene	182.8	190.9	198.7	207.7	213.7
p-Xylene	176.9	190.2	196.6	204.6	208.9
o-Xylene	172.9	181.0	187.9	195.7	203.4
Methanol	0.620	0.530	0.460	0.400	0.350
Ethanol	0.830	0.710	0.590	0.510	0.450
Propanol	1.060	0.910	0.830	0.730	0.670
Butanol	1.360	1.240	1.090	0.970	0.870
THF	0.180	0.240	0.310	0.440	0.790
Acetonitrile	0.890	0.770	0.590	0.450	0.340
Thiophene	129.8	139.9	145.6	165.6	186.9
Acetone	0.650	0.600	0.550	0.520	0.490
MEKP	1.450	1.240	1.100	0.970	0.830
Water	0.410	0.440	0.480	0.540	0.600

^a Standard uncertainties u are $u(\gamma_{13}^{\infty}) = 5 \%$, $u(T) = 0.02 \text{ K}$

Table 5. 2: Average γ_{13}^{∞} (the solute is denoted as component 1, and the solvent as component 3) for the solutes in the deep eutectic solvent $[\text{ZnCl}_2][\text{acetic acid}]$ at 1:4 molar ratios and at five different temperatures: for the standard state of solutes hypothetical liquid at zero pressure ^a.

Solutes	Average value γ_{13}^{∞}				
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K	T = 353.15 K
2,2-dimethylbutane	70.82	77.63	83.86	91.68	100.28
<i>n</i> -Pentane	55.93	62.65	66.67	74.88	82.59
<i>n</i> -Hexane	113.16	116.79	124.94	134.44	142.43
<i>n</i> -Heptane	169.71	181.91	190.20	199.76	206.16
<i>n</i> -Octane	212.28	226.05	236.50	252.16	265.10
<i>n</i> -Nonane	235.42	255.78	275.89	287.99	296.15
<i>n</i> -Decane	287.92	311.66	320.40	338.47	357.64
1-Pentene	73.46	80.15	87.27	100.68	104.95
1-Hexene	105.98	116.65	124.13	137.08	146.29
1-Heptene	189.39	210.59	225.62	246.50	261.42
1-Nonene	213.05	240.89	257.67	286.76	302.37
1-Decene	250.46	276.52	292.10	323.84	334.93
Cyclohexene	143.33	152.82	166.45	184.65	198.60
Cyclohexane	142.37	155.16	151.67	161.76	167.55
Cyclooctane	183.81	193.49	205.26	214.24	215.85
1-Pentyne	53.68	59.70	65.99	74.14	84.15
1-Hexyne	93.76	103.58	116.69	134.76	152.19
1-Heptyne	138.51	161.41	178.86	200.96	232.84
Benzene	129.67	142.24	154.25	170.95	189.57
Toluene	146.42	161.32	176.77	192.24	208.50
Ethylbenzene	187.83	208.78	228.67	244.33	255.58
<i>m</i> -Xylene	201.23	220.73	241.06	259.08	276.57
<i>p</i> -Xylene	192.62	210.88	230.45	246.83	265.03
<i>o</i> -Xylene	179.46	193.32	212.64	227.75	241.79
Methanol	0.55	0.50	0.45	0.41	0.38
Ethanol	0.64	0.59	0.54	0.49	0.45
Propanol	0.76	0.72	0.66	0.60	0.54

Butanol	0.93	0.86	0.79	0.73	0.66
THF	0.08	0.10	0.12	0.15	0.17
Acetonitrile	1.94	1.55	1.21	0.98	0.84
Thiophene	124.32	146.47	161.86	182.62	195.19
Acetone	3.56	2.84	2.29	1.83	1.48
MEKP	7.86	5.89	4.53	3.71	3.02
Water	0.33	0.40	0.48	0.56	0.65

^a Standard uncertainties u are $u(\gamma_{13}^{\infty}) = 5\%$, $u(T) = 0.02\text{ K}$

Table 5. 3: Physical quantities of γ_{13}^{∞} (the solute is be denoted as component 1, and the solvent as component 3) for the solutes in $[\text{ZnCl}_2][\text{phosphoric acid}]$ at 1:2 molar ratios and at five different temperatures: for the standard state of the solutes hypothetical liquid at zero pressure ^a.

Solutes	Average γ_{13}^{∞} values				
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K	T = 353.15 K
2,2-dimethylbutane	73.48	78.95	84.60	89.84	93.99
<i>n</i> -Pentane	58.76	63.67	67.45	70.44	74.32
<i>n</i> -Hexane	96.96	101.0	108.2	114.9	125.4
<i>n</i> -Heptane	129.8	138.1	145.8	156.6	167.2
<i>n</i> -Octane	151.6	158.9	166.3	181.3	193.3
<i>n</i> -Nonane	169.5	176.9	185.6	189.6	203.4
<i>n</i> -Decane	200.7	207.4	211.5	220.6	228.4
1-Pentene	48.04	49.74	52.21	53.84	55.60
1-Hexene	69.23	74.17	81.50	87.14	91.43
1-Heptene	113.3	120.8	130.2	137.8	147.0
1-Nonene	163.9	168.4	174.9	180.4	181.9
1-Decene	176.5	190.7	197.6	201.4	205.4
Cyclohexene	55.20	57.29	60.15	63.62	67.04
Cyclohexane	83.09	84.42	91.83	98.51	103.7
Cyclooctane	141.4	152.0	157.0	169.2	180.9
1-Pentyne	34.19	36.75	41.12	44.85	47.37

1-Hexyne	69.78	75.97	82.46	89.58	96.30
1-Heptyne	109.6	118.6	130.0	143.9	156.0
Benzene	94.09	98.92	104.3	110.8	115.8
Toluene	105.6	111.1	120.1	127.8	135.3
Ethylbenzene	134.0	142.3	150.2	159.2	168.5
m-Xylene	128.2	136.6	145.6	152.3	160.1
p-Xylene	122.6	130.0	139.5	147.4	155.2
o-Xylene	116.4	124.1	132.2	141.5	151.2
Methanol	0.230	0.240	0.260	0.293	0.300
Ethanol	0.291	0.315	0.322	0.342	0.371
Propanol	0.422	0.451	0.471	0.500	0.532
Butanol	0.563	0.583	0.622	0.641	0.663
THF	5.510	4.533	3.431	2.663	2.371
Acetonitrile	0.261	0.212	0.193	0.182	0.170
Thiophene	78.46	97.68	120.6	159.7	219.5
Acetone	13.91	9.010	6.000	4.301	3.244
MEKP	21.62	19.85	18.26	17.34	16.73
Water	0.331	0.332	0.341	0.383	0.412

^a Standard uncertainties u are $u(\gamma_{13}^{\infty}) = 5 \%$, $u(T) = 0.02 \text{ K}$

Table 5. 4: Average γ_{13}^{∞} (the solute is be denoted as component 1, and the solvent as component 3) for the solutes in the deep eutectic solvent $[\text{ZnCl}_2][\text{phosphoric acid}]$ at 1:2.5 molar ratios and at five different temperatures: for the standard state of the solutes hypothetical liquid at zero pressure

^a.

Solutes	Average γ_{13}^{∞} values				
	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K	T = 353.15 K
2,2-dimethylbutane	64.04	68.81	73.74	78.30	81.92
<i>n</i> -Pentane	51.21	55.49	58.79	61.40	64.78
<i>n</i> -Hexane	84.50	88.05	93.41	100.2	109.3
<i>n</i> -Heptane	113.2	120.4	127.1	136.5	145.7

<i>n</i> -Octane	132.1	138.5	144.9	158.0	168.5
<i>n</i> -Nonane	147.7	154.2	161.8	165.2	177.2
<i>n</i> -Decane	174.9	180.7	184.3	192.3	199.1
1- Pentene	41.87	43.35	45.51	46.93	48.47
1-Hexene	60.34	64.65	71.03	75.95	79.69
1-Heptene	98.73	105.3	113.5	120.1	128.1
1-Nonene	142.8	146.8	152.5	157.3	158.6
1-Decene	153.8	166.2	172.2	175.5	178.9
Cyclohexene	48.11	49.93	52.43	55.45	58.43
Cyclohexane	72.42	73.58	80.03	85.85	90.34
Cyclooctane	123.2	132.5	136.9	147.5	157.7
1-Pentyne	29.80	32.04	35.84	39.09	41.29
1-Hexyne	60.82	66.21	71.86	78.07	83.93
1-Heptyne	95.53	103.4	113.3	125.4	135.9
Benzene	82.00	86.21	90.86	96.54	100.9
Toluene	92.00	96.79	104.6	111.4	117.9
Ethylbenzene	116.8	124.0	131.5	138.7	146.9
m-Xylene	111.6	119.0	126.9	132.7	139.6
p-Xylene	106.9	113.3	121.6	128.4	135.3
o-Xylene	101.4	108.1	115.2	123.3	131.8
Methanol	0.200	0.212	0.232	0.252	0.263
Ethanol	0.252	0.273	0.281	0.301	0.330
Propanol	0.364	0.392	0.413	0.440	0.461
Butanol	0.493	0.510	0.544	0.562	0.582
THF	4.812	3.951	2.991	2.321	2.067
Acetonitrile	0.221	0.181	0.170	0.162	0.149
Thiophene	68.38	85.13	105.1	139.2	191.3
Acetone	12.12	7.850	5.230	3.753	2.831
MEKP	18.85	17.30	15.92	15.11	14.59
Water	0.293	0.292	0.301	0.331	0.360

^a Standard uncertainties *u* are $u(Y_{13}^{\infty}) = 5 \%$, $u(T) = 0.02 \text{ K}$.

The results shown in Tables 5.1–5.4 demonstrate that the investigated solutes, namely alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, and thiophene, exhibit noticeably elevated activity coefficients at infinite dilution. In the context of solutes, the term "standard state" refers to a hypothetical liquid state under the condition of zero pressure. The data shown in Tables 5.1–5.4 illustrate that the activity coefficients at infinite dilution for the solutes examined, namely alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, and thiophene, display a notably higher magnitude compared to the other solutes. The activity coefficients at infinite dilution quantifies the extent of solute-solvent interactions in the presence of very low solute concentrations. This statement elucidates the extent to which the solute's interactions with the solvent may be classified as either weak or strong. This observation implies that solutes have less interactions with the solvent when present in low quantities. The increased activity coefficients suggest that the solutes, including alkanes, cycloalkanes, alkenes, aromatics, and thiophene, exhibit reduced interactions with the solvent. In other terms, it may be seen that they exhibit reduced solubility or exhibit decreased interactions between solvent and solute.

The values of γ_{13}^{∞} (which may represent some property or parameter) for a series of solutes increase as the number of carbon atoms in the solutes increases. It suggests that as you add more carbon atoms to the solute molecules, the values of γ_{13}^{∞} increase.

This trend is attributed to the fact that as you increase the number of carbon atoms of a molecule, it can lead to the following effects:

- **Closer Positive and negative charges:** If the solute molecules have positive and negative charges (dipoles), adding more carbon atoms can cause these charges to be distributed differently. The charges may become closer to each other within the molecule, which can affect the overall polarity and dipole moment of the molecule.
- **Smaller dipole moment:** The proximity of positive and negative charges might result in a reduction in the dipole moment of the molecule. The dipole moment quantifies the extent of charge separation between positive and negative charges inside a given molecule. A reduced dipole moment signifies a decreased level of polarity in the molecule.
- **Reduced polarity:** A smaller dipole moment typically corresponds to reduced polarity. Polarity is a measure of how unevenly electrons are distributed in a molecule, leading to the presence of partial positive and negative charges. As the charges become closer, the molecule becomes less polar.

An increase in γ_{13}^{∞} may be a consequence of these changes in the molecular structure and properties. It suggests that as you add more carbon atoms to the solute molecules, they become less polar and have smaller dipole moments, which could affect their interaction with other molecules or their behavior in a particular chemical or physical context.

The alcohols, water, and acetonitrile have γ_{13}^{∞} values lower than other organic solutes. This suggests that they have strong dipole-dipole interactions with polar DES, making them more soluble in such solvents. Alkenes like 1-hexene have smaller γ_{13}^{∞} values than alkanes like *n*-hexane with the same carbon number. Non-polar solutes demonstrate elevated activity coefficients at infinite dilution levels in contrast to polar solutes. This implies that solutes lacking polarity exhibit decreased solubility within the DES. The differentiation mentioned is ascribed to the inherent capacity of polar molecules to readily interact with hydrogen bond donors, such as acetic and phosphoric acid HBD, which are found within DESs. This observation suggests that polar solutes exhibit enhanced solubility within the investigated deep eutectic solvents.

Infinite dilution activity coefficients of $[\text{ZnCl}_2][\text{acetic acid}]$ at a 1:4 molar ratio are generally higher, except for certain solutes such as *n*-decane, 1-decene, 1-heptyne, benzene, toluene, alcohols, THF, and water, when compared to the 1:2 molar ratio of $[\text{ZnCl}_2][\text{acetic acid}]$. This suggests that the interactions between zinc chloride and acetic acid components lead to increased activity coefficients for most solutes in the system at the 1:4 molar ratio. Simultaneously, for $[\text{ZnCl}_2][\text{phosphoric acid}]$, the infinite dilution activity coefficients at a 1:2 molar ratio are higher than those at a 1:2.5 molar ratio, indicating that the 1:2 molar ratio of $[\text{ZnCl}_2][\text{phosphoric acid}]$ provides a less favorable environment for solute interactions compared to the 1:2 molar ratio.

Both systems involve the same DESs, but with variations in molar ratios and mass percent loading of the stationary phase. In the case of $[\text{ZnCl}_2][\text{acetic acid}]$, the stationary phase at a 1:4 molar ratio contains 31.3% acetic acid, while at the 1:2 molar ratio, the loading is slightly lower at 29.86%. This difference in loading may contribute to the observed variations in activity coefficients. Similarly, for $[\text{ZnCl}_2][\text{phosphoric acid}]$, the stationary phase at a 1:2 molar ratio has a loading of 30.95%, whereas the 1:2.5 molar ratio system has a higher loading of 31.98%. This difference in mass percent loading likely influences solute interactions within the column, leading to the observed variations in infinite dilution activity coefficients between the two molar ratios [7, 30]. To give an example of alkanes in acetic acid HBD, decane ($\gamma_{13}^{\infty} = 357.64$) at $T = 353.15$ K for the DES prepared at a 1:4 and ($\gamma_{13}^{\infty} = 481.80$) at $T = 353.15$ K for the DES prepared at a 1:2 molar ratio. The highest γ_{13}^{∞} values are observed for *n*-decane (228.4 for $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2 and 199.1 for $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 at 353.15 K), indicating it is less soluble in DES. This variation is attributed to the ratio of hydrogen

bond acceptors to hydrogen bond donors, which also affects the yield. This means that the solutes can interact with and filled in the spaces of the deep eutectic solvents that were studied. The percentage loading of the solvent on the column plays an essential role in separation as it reveals the efficiency of the entrainer as well as the extraction expenses involved in a particular separation. Both DESs revealed that they better separate at lower percentage loading of the DES on the column, and this favours the extraction process, showing that low amounts of solvent would be required in the separation.

5.2. Thermodynamics functions at infinite dilution of [ZnCl₂][acetic 1:2 or 1:4] and [ZnCl₂][phosphoric acid 1:2 or 1:2.5]

The nature of interactions between DESs and solutes can also be analyzed by examining excess thermodynamic parameters ($\Delta H_1^{E,\infty}$, $\Delta S_1^{E,\infty}$ and $\Delta G_1^{E,\infty}$) calculated at infinite dilution. The Van't Hoff relation was employed to determine the values of entropies and enthalpies at infinite dilution [257]. Tables 5.5–5.7 present the thermodynamic properties at infinite dilution for all the solutes.

Table 5. 5: Physical quantities of limiting partial molar enthalpies $\Delta H_1^{E,\infty}$, Gibbs energies $\Delta G_1^{E,\infty}$ and entropies $T_{ref}\Delta S_1^{E,\infty}$ for solutes in the investigated DES [ZnCl₂][acetic acid] at a 1:2 molar ratio and at a reference temperature $T_{ref} = 323.15$ K.

Solute	$\Delta H_1^{E,\infty}$ (kJ · mol ⁻¹)	$\Delta G_1^{E,\infty}$ (kJ · mol ⁻¹)	$T_{ref}\Delta S_1^{E,\infty}$ (kJ · mol ⁻¹)
2,2-dimethylbutane	-13.8	10.6	-24.4
<i>n</i> -Pentane	-12.9	9.44	-22.4
<i>n</i> -Hexane	-14.2	12.1	-26.3
<i>n</i> -Heptane	-10.9	13.1	-23.9
<i>n</i> -Octane	-10.9	13.7	-24.5
<i>n</i> -Nonane	-8.32	14.9	-23.2
<i>n</i> -Decane	-8.53	15.9	-24.5
1- Pentene	-9.89	10.3	-20.2
1-Hexene	-5.98	12.6	-18.6
1-Heptene	-6.04	13.9	-20.0
1-Nonene	-8.27	14.5	-22.8
1-Decene	-5.20	15.2	-20.4
Cyclohexene	-6.11	11.6	-17.7
Cyclohexane	-13.8	10.7	-24.5
Cyclooctane	-11.1	13.5	-24.6
1-Pentyne	-2.82	10.9	-13.7
1-Hexyne	-2.67	12.2	-14.8
1-Heptyne	-3.52	13.5	-17.1
Benzene	-5.23	13.5	-18.7
Toluene	-5.13	13.6	-18.8
Ethylbenzene	-3.96	14.0	-17.9
m-Xylene	-3.66	14.1	-17.8

p-Xylene	-3.76	14.1	-17.9
o-Xylene	-3.71	13.9	-17.7
Methanol	13.3	-1.70	15.0
Ethanol	14.1	-0.920	15.0
Propanol	10.3	-0.260	10.6
Butanol	10.4	-0.570	9.90
THF	-33.1	-3.850	-29.2
Acetonitrile	22.5	-0.710	23.2
Thiophene	-8.21	13.28	-21.5
Acetone	6.66	-1.37	8.03
MEKP	12.4	0.580	11.8
Water	-8.66	-2.18	-6.48

^aStandard uncertainties u are $u(y_{13}^{\infty}) = 5 \%$, $u = 0.02$ K.

Table 5. 6: Limiting partial molar enthalpies $\Delta H_1^{E,\infty}$, Gibbs energies $\Delta G_1^{E,\infty}$ and entropies $T_{\text{ref}} \Delta S_1^{E,\infty}$ for solutes in the investigated deep eutectic solvent [ZnCl₂][acetic acid] at 1:4 molar ratio and at reference temperature $T_{\text{ref}} = 323.15$ K.

Solutes	$\Delta H_1^{E,\infty}$ (kJ · mol ⁻¹)	$\Delta G_1^{E,\infty}$ (kJ · mol ⁻¹)	$T_{\text{ref}} \Delta S_1^{E,\infty}$ (kJ · mol ⁻¹)
2,2-dimethylbutane	-7.73	11.69	-19.42
<i>n</i> -Pentane	-8.80	11.12	-19.92
<i>n</i> -Hexane	-5.51	12.79	-18.30
<i>n</i> -Heptane	-4.46	13.98	-18.44
<i>n</i> -Octane	-5.09	14.56	-19.66
<i>n</i> -Nonane	-5.35	14.90	-20.25
<i>n</i> -Decane	-4.75	15.43	-20.18
1-Pentene	-8.67	11.78	-20.45
1-Hexene	-7.42	12.79	-20.21
1-Heptene	-7.40	14.37	-21.77
1-Nonene	-8.07	14.74	-22.81
1-Decene	-6.82	15.11	-21.93
Cyclohexene	-7.73	13.51	-21.24
Cyclohexane	-3.38	13.55	-16.94
Cyclooctane	-3.92	14.15	-18.07
1-Pentyne	-10.25	10.99	-21.23
1-Hexyne	-11.31	12.47	-23.78
1-Heptyne	-11.57	13.66	-25.23
Benzene	-8.66	13.32	-21.98
Toluene	-8.12	13.66	-21.78
Ethylbenzene	-7.15	14.35	-21.50
<i>m</i> -Xylene	-7.33	14.50	-21.83
<i>p</i> -Xylene	-7.34	14.38	-21.72
<i>o</i> -Xylene	-7.01	14.14	-21.15
Methanol	8.50	-1.88	10.38
Ethanol	8.10	-1.44	9.54
Propanol	7.86	-0.90	8.75
Butanol	7.71	-0.41	8.12

THF	-17.94	-6.20	-11.74
Acetonitrile	19.65	1.17	18.47
Thiophene	-10.37	13.40	-23.77
Acetone	20.16	2.80	17.36
MEKP	21.92	4.77	17.16
Water	-15.69	-2.49	-13.20

^a Standard uncertainties u are $u(y_{13}^{\infty}) = 5 \%$, $u(T) = 0.02 \text{ K}$.

Table 5. 7: Physical quantities of limiting partial molar enthalpies $\Delta H_1^{E,\infty}$, Gibbs energies $\Delta G_1^{E,\infty}$ and entropies $T_{ref}\Delta S_1^{E,\infty}$ for solutes in the investigated DES $[\text{ZnCl}_2][\text{phosphoric acid}]$ at 1:2 molar ratio and at reference temperature $T_{ref} = 323.15 \text{ K}$.

solute	$\Delta H_1^{E,\infty} (\text{kJ}\cdot\text{mol}^{-1})$	$\Delta G_1^{E,\infty} (\text{kJ}\cdot\text{mol}^{-1})$	$T_{ref}\Delta S_1^{E,\infty} (\text{kJ}\cdot\text{mol}^{-1})$
2,2-dimethylbutane	-5.74	10.9	-16.6
<i>n</i> -Pentane	-5.27	10.3	-15.6
<i>n</i> -Hexane	-5.89	11.5	-17.4
<i>n</i> -Heptane	-5.79	12.4	-18.2
<i>n</i> -Octane	-5.67	12.8	-18.4
<i>n</i> -Nonane	-4.05	13.0	-17.1
<i>n</i> -Decane	-2.94	13.5	-16.4
1-Pentene	-3.43	9.63	-13.1
1-Hexene	-6.62	10.7	-17.3
1-Heptene	-6.01	12.0	-18.0
1-Nonene	-2.57	12.9	-15.5
1-Decene	-3.33	13.2	-16.6
Cyclohexene	-4.53	10.0	-14.5
Cyclohexane	-5.47	11.1	-16.5
Cyclooctane	-5.51	12.6	-18.1
1-Pentyne	-7.85	8.81	-16.7
1-Hexyne	-7.45	10.8	-18.2
1-Heptyne	-8.26	11.9	-20.2
Benzene	-4.86	11.5	-16.3
Toluene	-5.86	11.8	-17.6
Ethylbenzene	-5.25	12.5	-17.7
<i>m</i> -Xylene	-5.11	12.3	-17.5
<i>p</i> -Xylene	-5.50	12.2	-17.7
<i>o</i> -Xylene	-6.02	12.1	-18.1
Methanol	-6.29	-4.63	-1.65
Ethanol	-6.07	-4.02	-2.05
Propanol	-5.49	-3.03	-2.46
Butanol	-4.01	-2.32	-1.69
THF	20.4	3.19	17.2
Acetonitrile	8.31	-5.06	13.4
Thiophene	-23.4	11.4	-34.8
Acetone	33.6	5.04	28.6
MEKP	5.98	7.16	-1.17

Water	-5.74	-3.86	-1.87
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^a Standard uncertainties u are $u(y_{13}^{\infty}) = 5 \%$, $u(T) = 0.02 \text{ K}$

Table 5. 8: Limiting partial molar enthalpies $\Delta H_1^{E,\infty}$, Gibb's energies $\Delta G_1^{E,\infty}$ and entropies $T_{\text{ref}} \Delta S_1^{E,\infty}$ for solutes in the investigated deep eutectic solvent $[\text{ZnCl}_2][\text{phosphoric acid}]$ at 1:2.5 molar ratio and at reference temperature $T_{\text{ref}} = 323.15 \text{ K}$.

solute	$\Delta H_1^{E,\infty} (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta G_1^{E,\infty} (\text{kJ} \cdot \text{mol}^{-1})$	$T_{\text{ref}} \Delta S_1^{E,\infty} (\text{kJ} \cdot \text{mol}^{-1})$
2,2-dimethylbutane	-5.15	11.4	-16.5
<i>n</i> -Pentane	-5.27	10.8	-16.1
<i>n</i> -Hexane	-6.23	12.0	-18.3
<i>n</i> -Heptane	-5.87	12.9	-18.8
<i>n</i> -Octane	-5.67	13.3	-18.9
<i>n</i> -Nonane	-4.05	13.5	-17.6
<i>n</i> -Decane	-2.94	13.9	-16.9
1- Pentene	-3.43	10.1	-13.6
1-Hexene	-6.62	11.2	-17.8
1-Heptene	-6.01	12.5	-18.5
1-Nonene	-2.57	13.4	-15.9
1-Decene	-3.33	13.7	-17.1
Cyclohexene	-4.53	10.5	-15.0
Cyclohexane	-5.47	11.6	-17.0
Cyclooctane	-5.51	13.1	-18.6
1-Pentyne	-7.85	9.31	-17.1
1-Hexyne	-7.45	11.3	-18.7
1-Heptyne	-8.26	12.5	-20.7
Benzene	-4.85	11.9	-16.8
Toluene	-5.86	12.3	-18.1
Ethylbenzene	-5.25	12.9	-18.2
<i>m</i> -Xylene	-5.11	12.8	-17.9
<i>p</i> -Xylene	-5.50	12.7	-18.2
<i>o</i> -Xylene	-6.02	12.6	-18.6
Methanol	-6.12	-4.15	-1.97
Ethanol	-5.92	-3.52	-2.40
Propanol	-5.41	-2.53	-2.88
Butanol	-3.96	-1.82	-2.14
THF	20.4	3.69	16.7
Acetonitrile	8.52	-4.56	13.1
Thiophene	-23.4	11.9	-35.3
Acetone	33.6	5.54	28.1
MEKP	5.99	7.66	-1.67
Water	-5.51	-3.37	-2.14

^a Standard uncertainties u are $u(y_{13}^{\infty}) = 5 \%$, $u(T) = 0.02 \text{ K}$.

Figures 5.1–5.16 depict the logarithm of γ_{13}^{∞} values, derived from the natural logarithm, in relation to the reciprocal of absolute temperatures across all solutes.

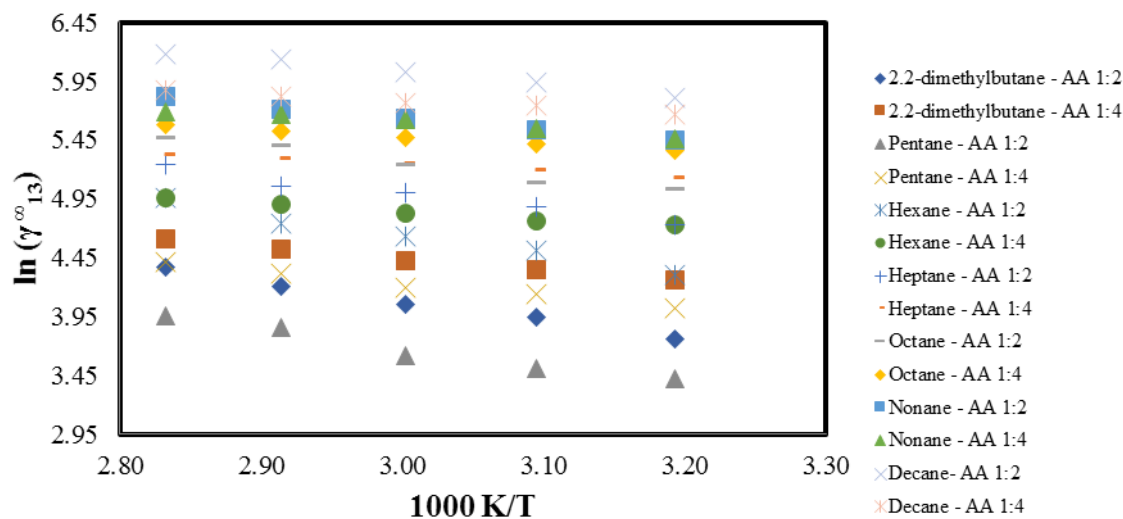


Figure 5. 1: Plot of $\ln \gamma_{13}^{\infty}$ against $1/T$ for the alkanes in the [ZnCl₂][acetic acid] (AA) 1:2 or [[ZnCl₂][acetic acid] (AA) 1:4] DESs at $T = (313.15\text{--}353.15)$ K.

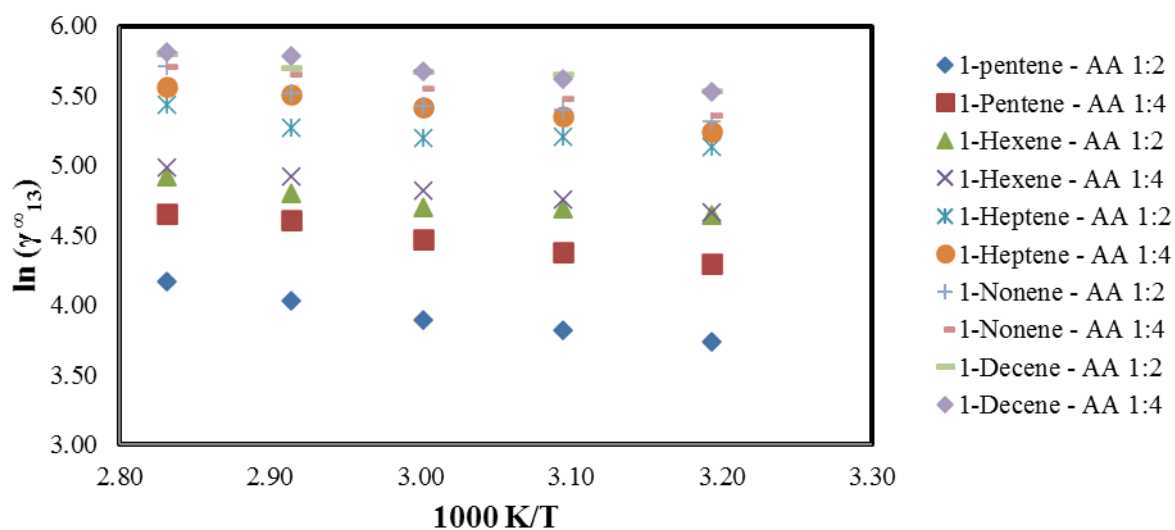


Figure 5. 2: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for alkenes in [ZnCl₂][acetic acid] (AA) 1:2 or [[ZnCl₂][acetic acid] (AA) 1:4] DESs at $T = (313.15\text{--}353.15)$ K.

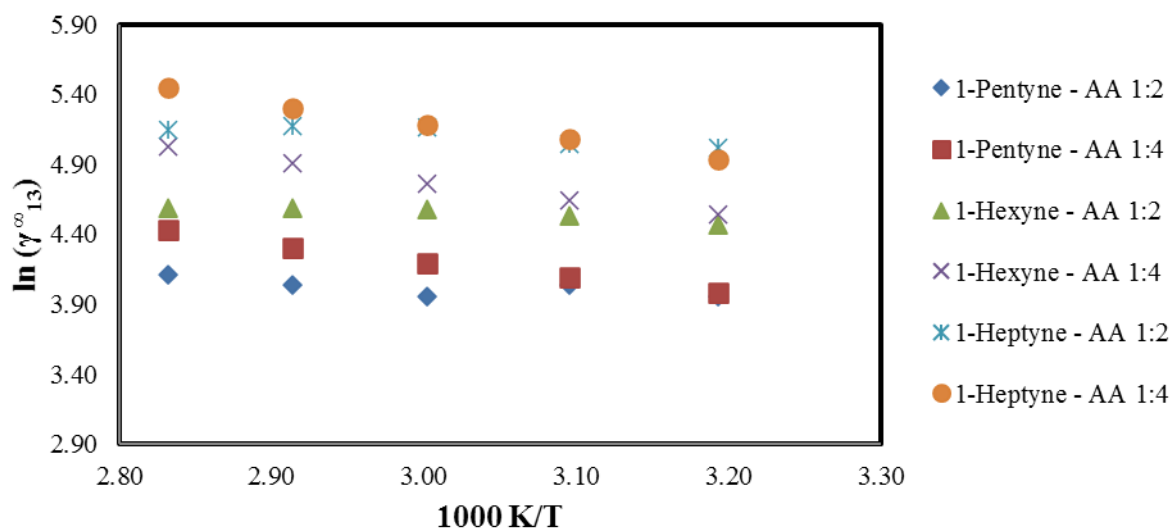


Figure 5. 3: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for alkynes in the $[\text{ZnCl}_2][\text{acetic acid}]$ (AA) 1:2 or $[[\text{ZnCl}_2][\text{acetic acid}]]$ (AA) 1:4 DESs at $T = (313.15\text{--}353.15)$ K.

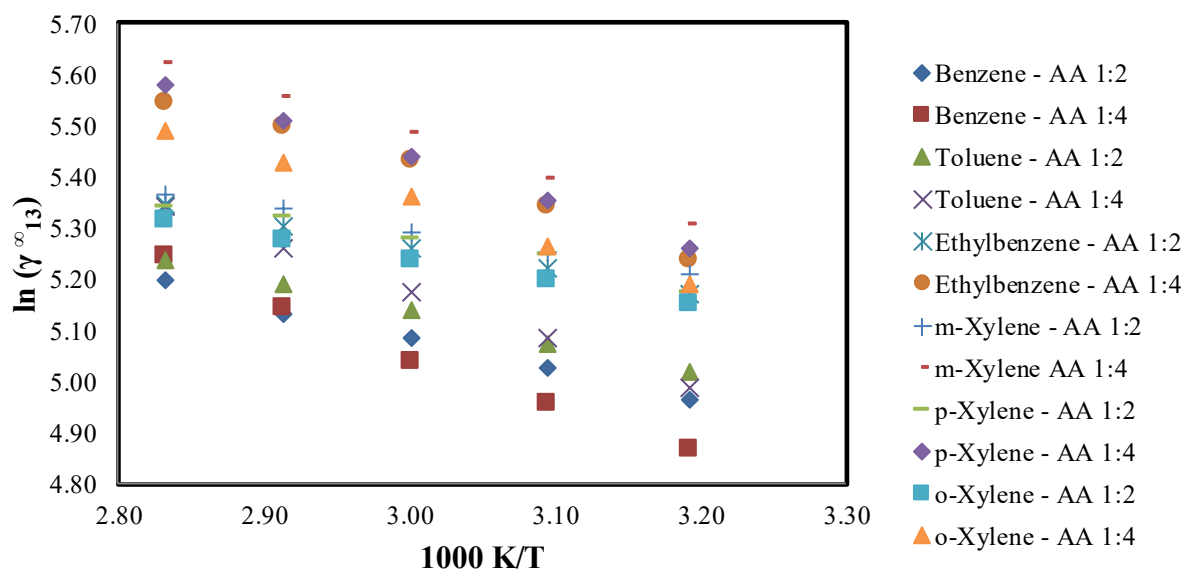


Figure 5. 4: A graph of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for aromatic hydrocarbons in the $[\text{ZnCl}_2][\text{acetic acid}]$ (AA) 1:2 or $[[\text{ZnCl}_2][\text{acetic acid}]]$ (AA) 1:4 DESs at $T = (313.1\text{--}353.15)$ K.

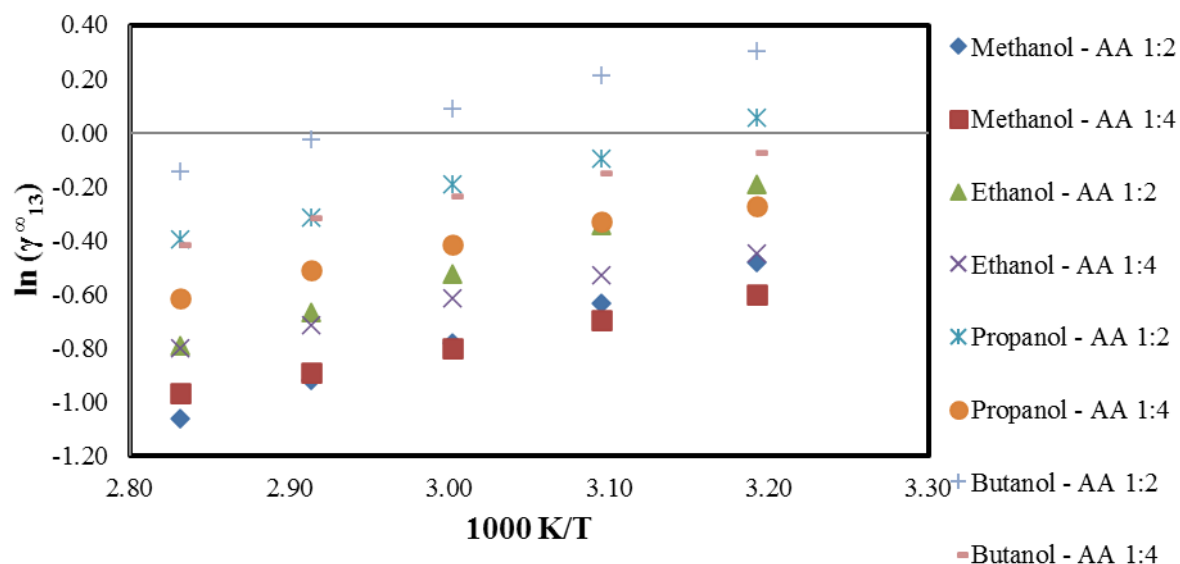


Figure 5. 5: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for alcohols in the $[\text{ZnCl}_2][\text{acetic acid}]$ (AA) 1:2 or $[[\text{ZnCl}_2][\text{acetic acid}]$ (AA) 1:4] DESs at $T = (313.15\text{--}353.15)$ K.

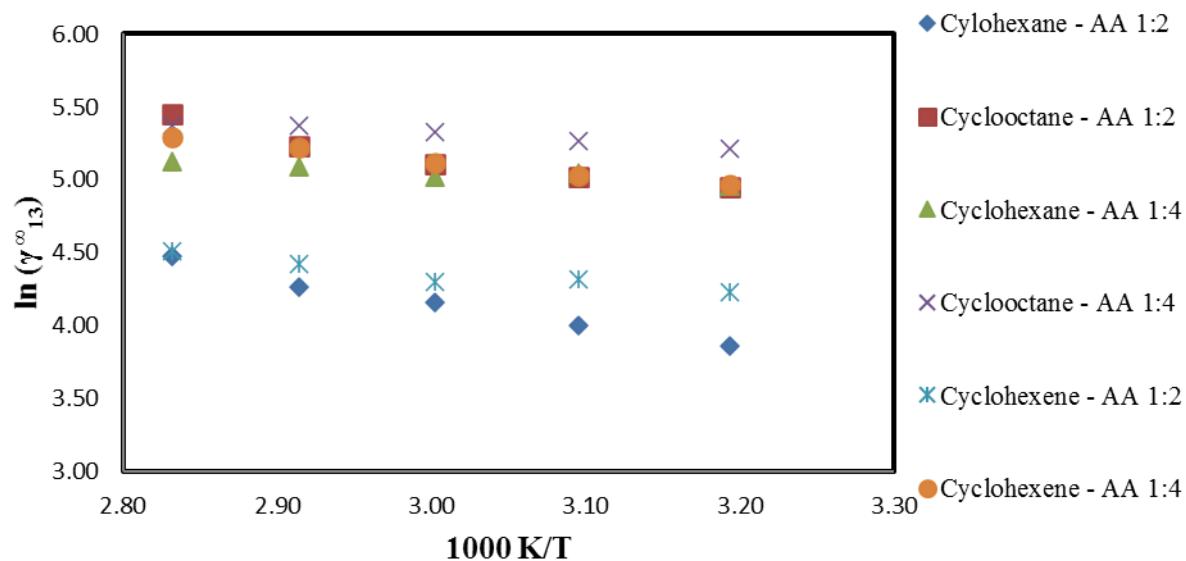


Figure 5. 6: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for cycloalkanes and cycloalkenes in $[\text{ZnCl}_2][\text{acetic acid}]$ (AA) 1:2 or $[[\text{ZnCl}_2][\text{acetic acid}]$ (AA) 1:4] DESs at $T = (313.15\text{--}353.15)$ K.

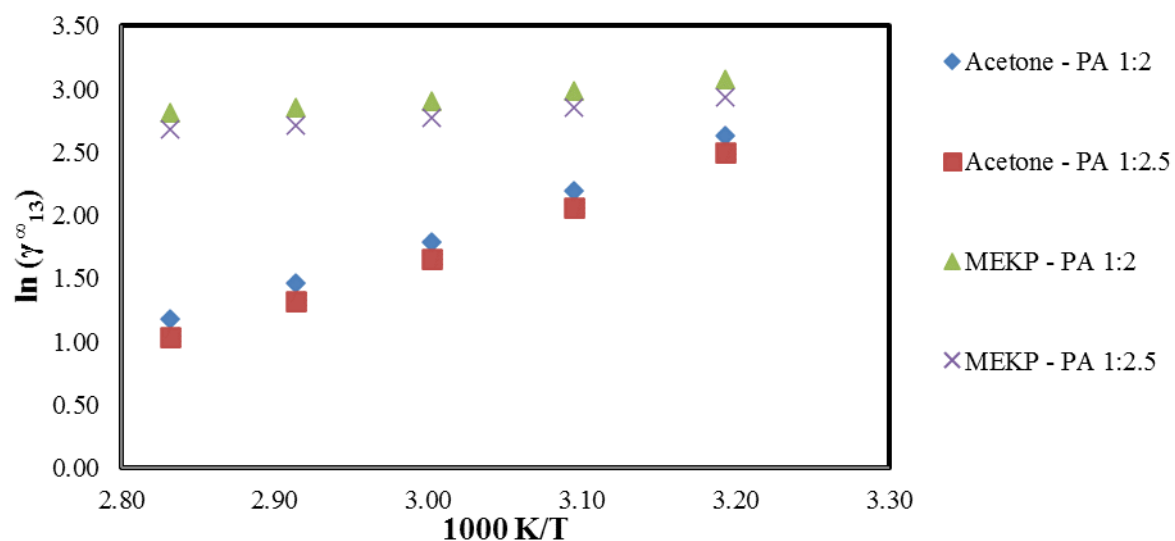


Figure 5. 7: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for ketones in the zinc chloride + acetic acid (AA) 1:2 or zinc chloride + acetic acid (AA) 1:4] DESs at $T = (313.15\text{--}353.15)$ K.

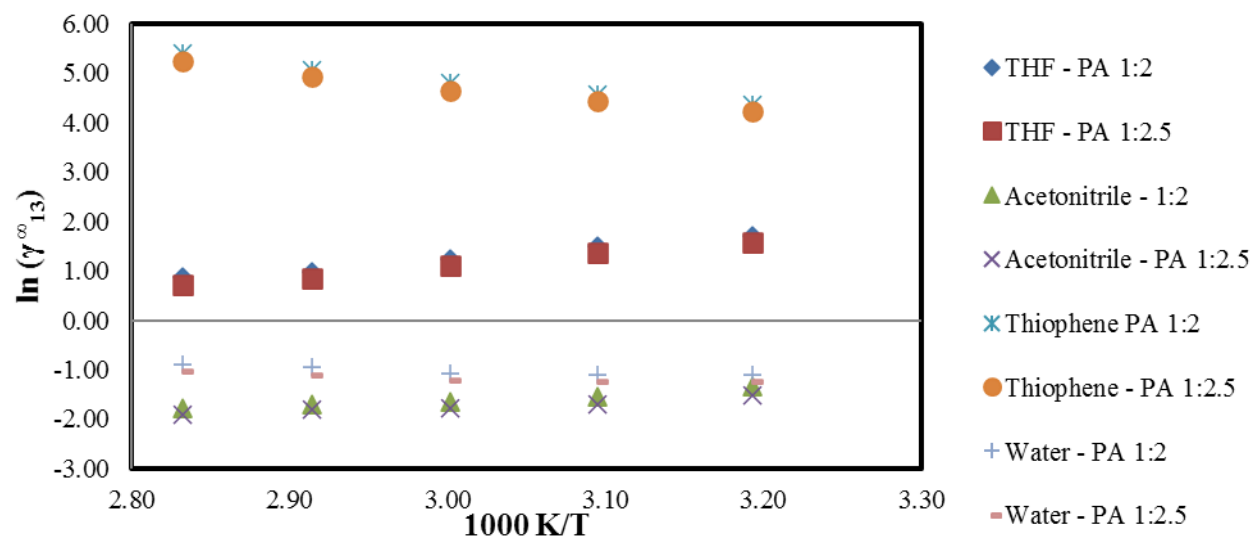


Figure 5. 8: Plot of $\ln \gamma_{13}^{\infty}$ against $1/T$ for THF, acetonitrile, thiophene, and water in the zinc chloride + acetic acid (AA) 1:2 or zinc chloride + acetic acid (AA) 1:4] DESs at $T = (313.15\text{--}353.15)$ K.

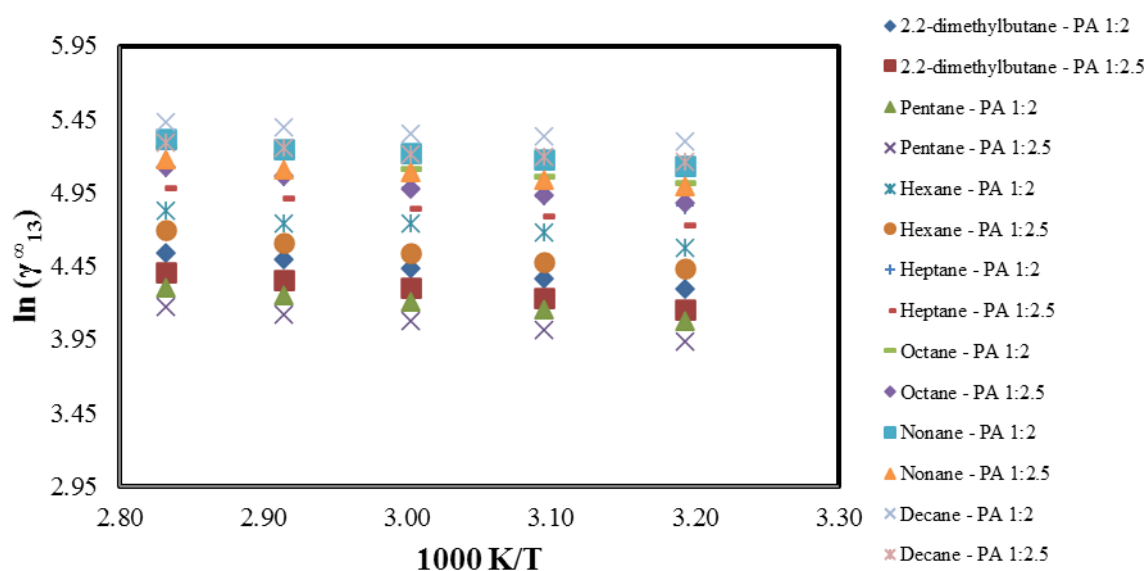


Figure 5. 9: Plot of $\ln \gamma_{13}^{\infty}$ against $1/T$ for the alkanes in the [ZnCl₂][phosphoric acid] (PA) 1:2 or [ZnCl₂][phosphoric acid] (PA) 1:2.5] DESs at $T = (313.15\text{--}353.15)$ K.

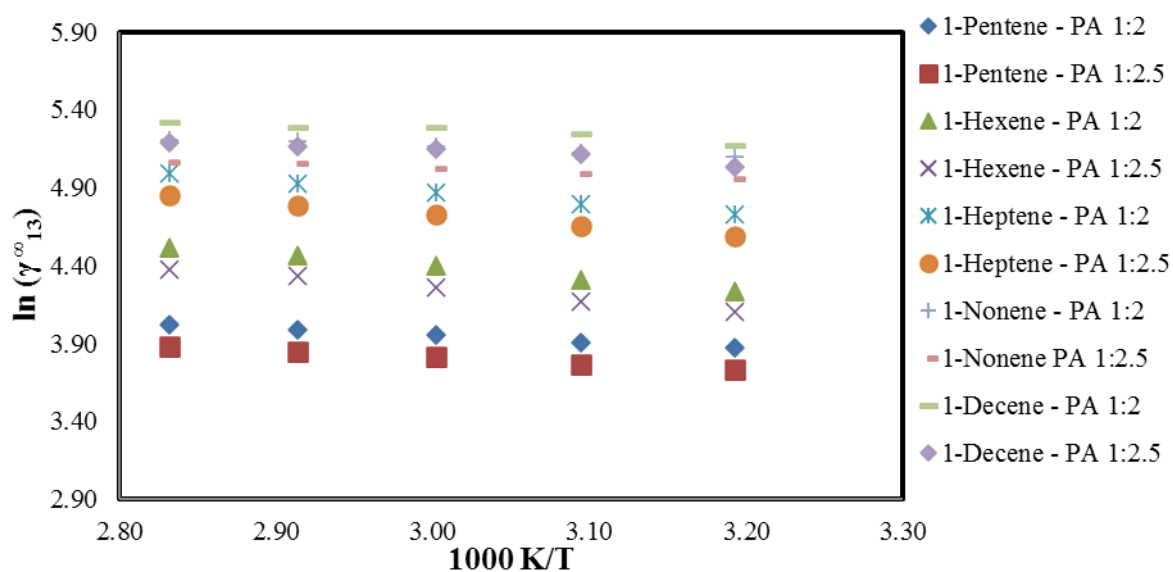


Figure 5. 10: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for alkenes in the [ZnCl₂][phosphoric acid] (PA) 1:2 or [ZnCl₂][phosphoric acid] (PA) 1:2.5] DESs at $T = (313.15\text{--}353.15)$ K.

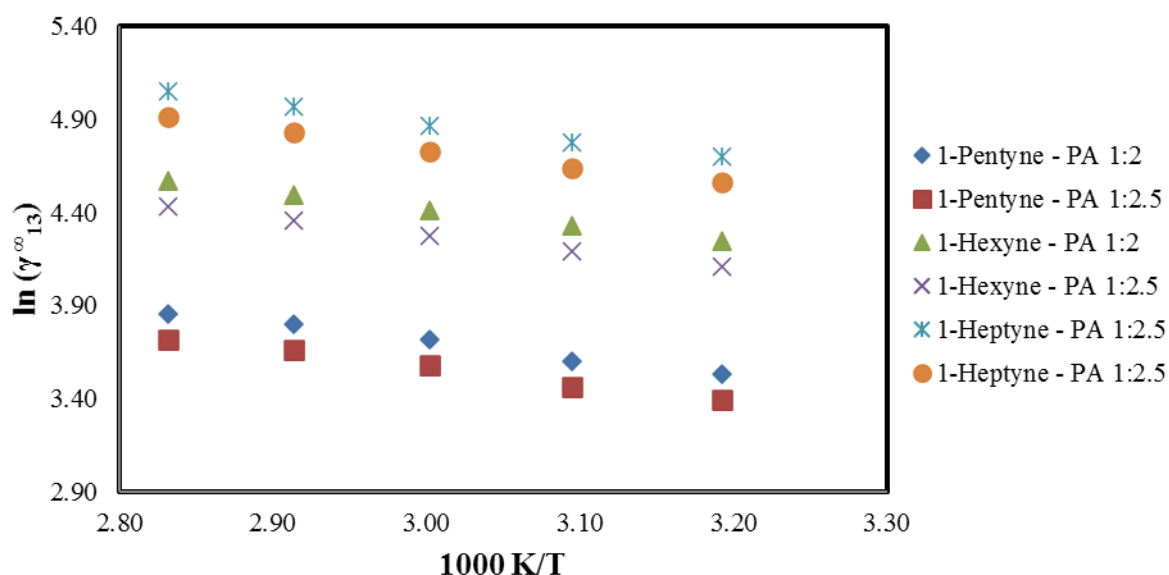


Figure 5. 11: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for alkynes in the $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2 or $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2.5] DESs at $T = (313.15\text{--}353.15)$ K.

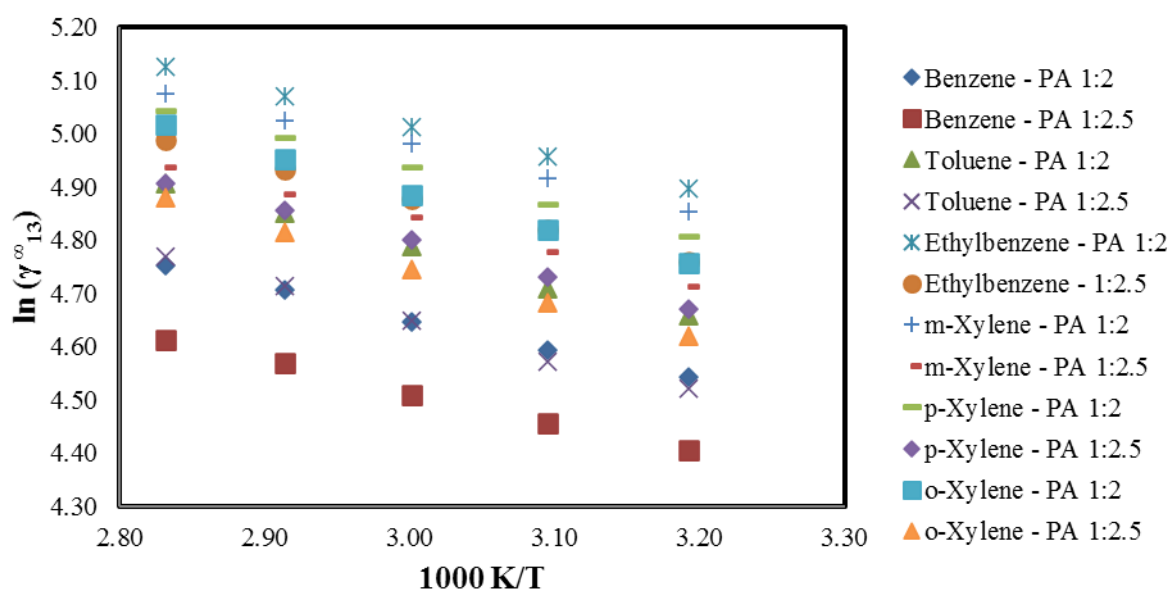


Figure 5. 12: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for aromatic hydrocarbons in the $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2 or $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2.5] DESs at $T = (313.15\text{--}353.15)$ K.

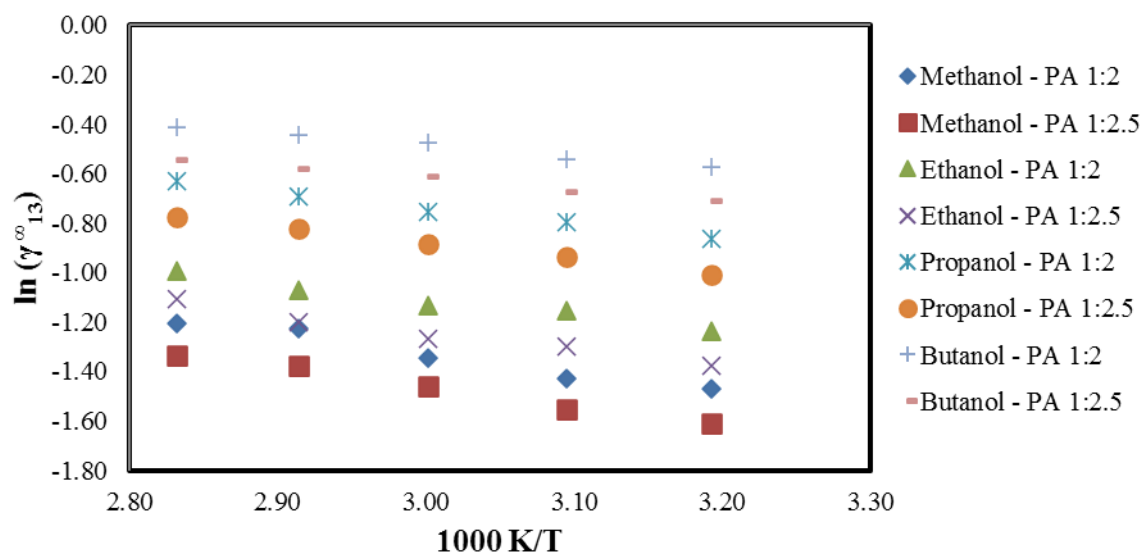


Figure 5. 13: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for alcohols in the $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2 or $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2.5] DESs at $T = (313.15\text{--}353.15)$ K.

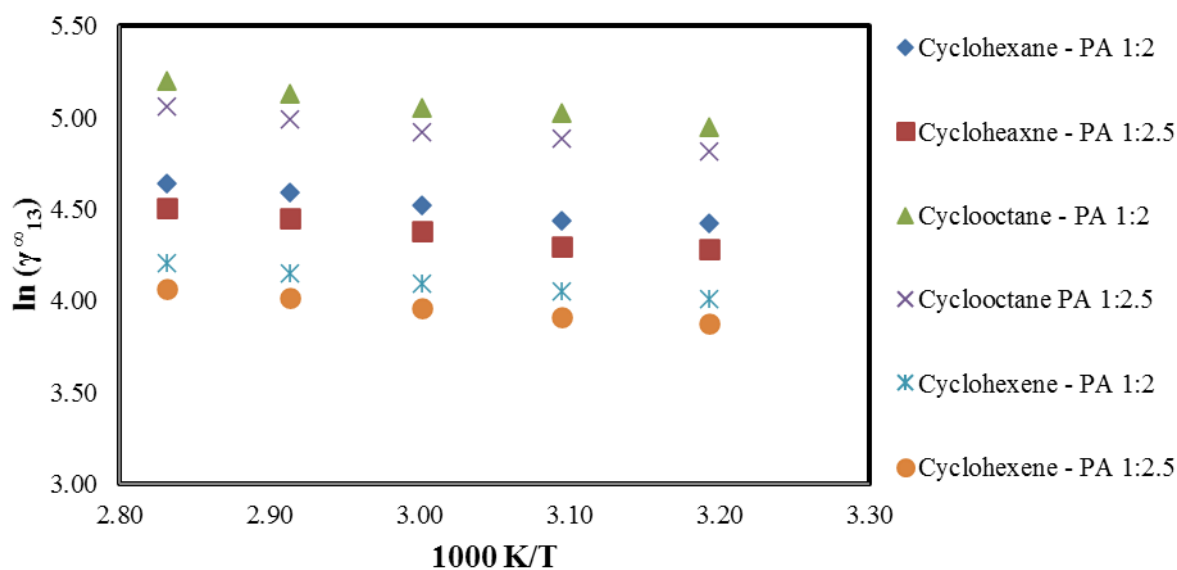


Figure 5. 14: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for cycloalkanes and cycloalkenes in the $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2 or $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2.5] DESs at $T = (313.15\text{--}353.15)$ K.

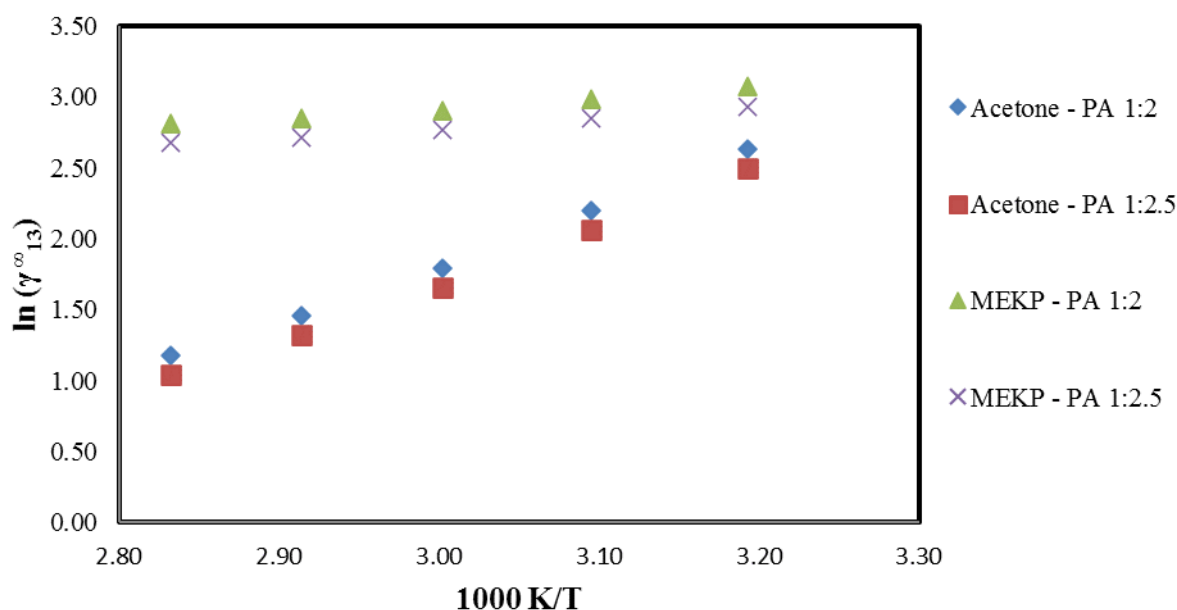


Figure 5. 15: Plot of $\ln \gamma_{13}^{\infty}$ versus $1/T$ for ketones in the $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2 or $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2.5] DESs at $T = (313.1\text{--}353.15)$ K.

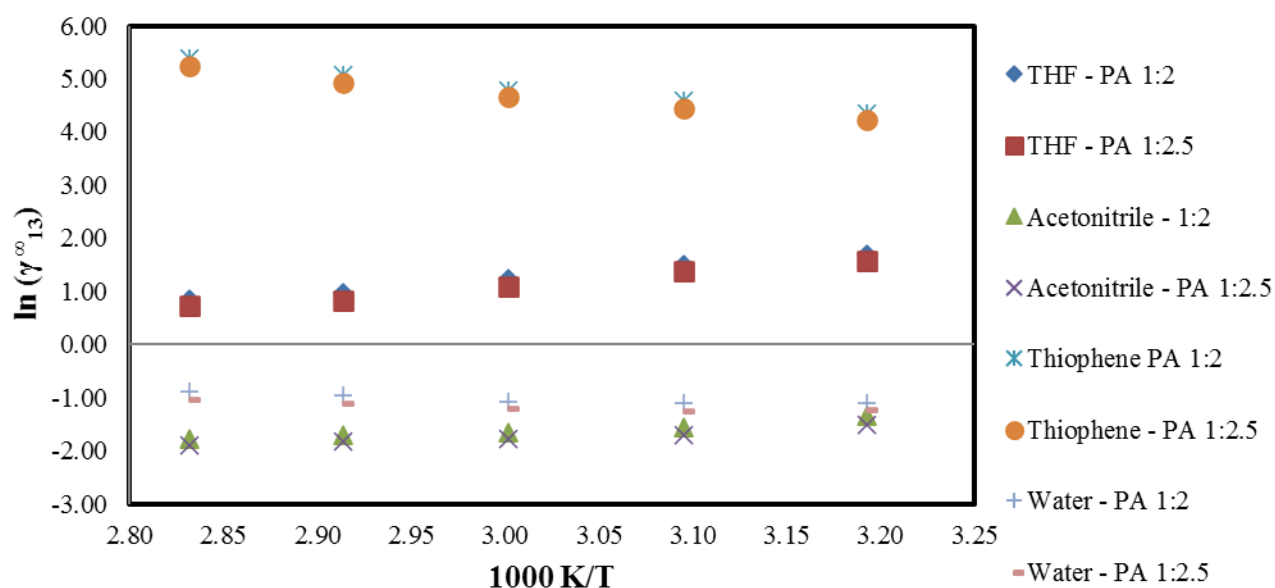


Figure 5. 16: Plot of $\ln \gamma_{13}^{\infty}$ against $1/T$ for THF, acetonitrile, thiophene, and water in the $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2 or $[\text{ZnCl}_2][\text{phosphoric acid}]$ (PA) 1:2.5] DESs at $T = (313.15\text{--}353.15)$ K.

The partial excess enthalpies exhibit a predominantly negative trend, except for methyl ethyl ketone peroxide (MEKP), acetone, acetonitrile, and alcohols in the $[\text{zinc chloride} + \text{acetic acid}]$ 1:2 or 1:4] DESs [7, 30]. The same trend was observed in Tables 5.7 and 5.8 of the $[\text{zinc chloride} + \text{phosphoric acid}]$ 1:2 or 1:4], except for acetone, acetonitrile, MEKP, and tetrahydrofuran (THF) [7, 30]. The positive values of $\Delta H_1^{E,\infty}$ shows that the values of γ_{13}^{∞} for these solutes decrease with an increase in

temperature. It indicates that the enthalpy change for the solute-solvent interaction increases with an increase in temperature. This indicates that there is an exothermic dissolving mechanism occurring due to the formation of hydrogen bonds between the substances and a particular solvent, or DES. In other words, as the temperature increases, the dissolution of these solutes becomes more energetically favorable due to hydrogen bonding. The presence of negative $\Delta H_1^{E,\infty}$ values suggests that the strength of interactions between solute and solvent molecules surpasses the strength of interactions between solute molecules themselves when the solution is infinitely diluted. Also, the presence of negative $\Delta H_1^{E,\infty}$ values indicate a reduction in the γ_{13}^∞ values of these solutes as temperatures increase.

The alterations in entropy and enthalpy exhibit a direct correlation with the variation in Gibbs free energy for any given process. When the Gibbs free energy exhibits a negative value, it signifies that the mechanism possesses a thermodynamic driving force that propels it in the forward direction. The Gibbs free energies exhibit positive magnitudes, indicating a positive deviation from Raoult's law. The change in entropy ($\Delta S_1^{E,\infty}$) and enthalpy ($\Delta H_1^{E,\infty}$) exhibits a profound interconnection with modifications in Gibbs free energy ($\Delta G_1^{E,\infty}$) within the context of a given process. The presence of negative values in both Table 5.5 and Table 5.6 of $\Delta G_1^{E,\infty}$ was noted except for alcohols, THF, acetonitrile, acetone, and water. Based on Tables 5.7 and 5.8, all $\Delta G_1^{E,\infty}$ values were positive except for water, acetonitrile, and alcohols. When the change in Gibbs free energy exhibits a negative value, it signifies that the process possesses a thermodynamic drive to proceed in a forward direction. This also indicates a more favorable dissolution, leading to suboptimal outcomes. The presence of negative $\Delta G_1^{E,\infty}$ values may be attributable to the phenomenon of electron delocalization, which enables the formation of hydrogen bonds between hydrogen and DES. Negative $\Delta G_1^{E,\infty}$ values indicate that the solute dissolves readily in the solvent. The mention of delocalized electrons and hydrogen bonds suggests that in cases where $\Delta G_1^{E,\infty}$ is negative, there may be favorable intermolecular interactions between the solute and solvent. Delocalized electrons can lead to stronger interactions, and hydrogen bonding is a well-known interaction that can enhance solubility.

The activity coefficients at infinite dilution exhibit values below unity, indicating a negative deviation from the principles of Raoult's law.

The increasing order of the highest $\Delta G_1^{E,\infty}$ values is demonstrated in Table 5.5 as follows: cycloalkene, specifically cyclohexene, < alkenes, such as 1-decene, < aromatic hydrocarbons, like m and p-xylene, < alkanes, including decane, < thiophene, < cycloalkane, like cyclooctane, < alkynes, such as 1-heptyne. This order is further illustrated in Table 5.6: thiophene < cycloalkene, specifically cyclohexene, < alkynes, like 1-heptyne, < cycloalkane, such as cyclooctane, < aromatic hydrocarbon, such as m-xylene, < alkenes, including 1-decene, < alkanes, like decane. Table 5.7 presents the

increasing order of $\Delta G_1^{E,\infty}$ values as follows: cyclohexene < thiophene < alkynes, like 1-heptyne, < aromatic hydrocarbon, < ethylbenzene, < cycloalkane, such as cyclooctane, < alkenes, including 1-decene, < alkanes, like decane. Lastly, Table 5.8 exhibits the increasing order of the highest $\Delta G_1^{E,\infty}$ values as follows: cycloalkene, specifically cyclohexene, < thiophene < alkynes, such as 1-heptyne, < aromatic hydrocarbon, like ethylbenzene, < cycloalkane, such as cyclooctane, < alkenes, including 1-decene, < alkanes, like decane.

Positive $\Delta G_1^{E,\infty}$ values suggest that the process of dissolving these solutes in the solvent is not favorable from a thermodynamic perspective. Also, these positive values of $\Delta G_1^{E,\infty}$ may result in inadequate miscibility between the solvent and solute. It means positive $\Delta G_1^{E,\infty}$ values suggest that the solvent and solute do not mix well, leading to poor solubility or immiscibility. This is because the system is not thermodynamically favorable for solute to undergo dissolution in the solvent.

In the Tables 5.5 and 5.6, it is noteworthy that the $\Delta S_1^{E,\infty}$ values exhibit a predominantly negative trend, except for alcohols, acetone, acetonitrile, and MEKP. The $\Delta S_1^{E,\infty}$ values in Tables 5.7 and 5.8 are negative except for THF, acetonitrile, and acetone. Negative values are an indicative of solute arrangements within the voids of DESs, whereas positive values signify the breaking of hydrogen bonds. When $\Delta S_1^{E,\infty}$ is negative, it indicates that the system is becoming more orderly, or in the context of solvation, the solute molecules are arranging themselves in a more structured manner in the solvent. This could happen due to the formation of strong intermolecular forces, such as hydrogen bonds, between the solute and solvent molecules. On the other hand, positive $\Delta S_1^{E,\infty}$ values often indicate an increase in disorder, which might be associated with the breaking of hydrogen bonds or other interactions between solute and solvent molecules. In this case, the solute is disrupting the solvent structure. Some solvents, like THF, acetonitrile, and acetone, have positive $\Delta S_1^{E,\infty}$ values. This could suggest that in these solvents, the solute is breaking hydrogen bonds or other intermolecular interactions between the solute and solvent molecules, leading to an increase in disorder.

5.3. Separation capability based on selectivity's and capacities

Table 5.9 displays the selectivity and capacity measurements for the deep eutectic solvents under investigation, as well as relevant data from the literature regarding ionic liquids, sulfolane, and organic solvents, all at a temperature of 323.15 K. This data pertains to the separation challenges examined in this study, including the systems benzene/ethanol, cyclohexane/ethanol, octane/acetonitrile, ethylbenzene/butanol, and heptane/butanol.

Table 5. 9: Selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) at T = 323.15 K, the state of infinite dilution examined in deep eutectic solvents [ZnCl₂ + acetic acid 1:2 or 1:4 or phosphoric 1:2 or 1:2.5] for various separation.

Solvent abbreviation	Selectivities (S_{ij}^{∞})				Capacities (k_j^{∞})				References
	benzene/ethanol	cyclohexane/ethanol	ethylbenzene/butanol	octane/acetonitrile	heptane/butanol	ethanol	butanol	acetonitrile	
[ZnCl ₂ + acetic acid] 1:4	241.09	155.60	242.77	145.84	211.52	1.69	1.16	0.65	This work
[ZnCl ₂ + acetic acid] 1:2	214.60	77.87	149.50	211.00	106.20	1.41	0.81	1.30	This work
[ZnCl ₂ + phosphoric acid] 1:2	314.00	268.0	244.10	749.50	237.30	4.72	1.72	4.17	This work
[ZnCl ₂ + phosphoric acid] 1:2.5	315.79	269.52	243.14	765.19	236.08	3.66	1.96	5.52	This work
[BMIM][Cl] + [Gly]	13.75	92.37	34.13	-	135.92	0.68	0.40	0.15	[116]
Hdiol	4.81	12.67	8.08	39.4	25.83	0.752	0.95	4.00	[290]
[4C ₃ NBr][Hdiol] 1:2	3.92	21.21	-	-	-	1.92	-	-	[120]
[C ₄ H ₁₂ NCl][EG] 1:2	139.70	8.19	-	-	-	0.46	-	-	[118]
[4C ₁ NCl][GLY] 1:2	69.93	15.87	-	-	-	0.32	-	-	[119]
[[4C ₁ H ₁ NCl][Hdiol]	20.64	5.51	-	-	-	0.58	-	-	[117]
[P ₆₆₆₁₄][DCA]	1.59	2.17	1.36	-	3.22	2.79	2.25	1.67	[291]
[C ₂ OHMIM][C ₄ F ₉ SO ₃]	2.79	11.01	-	65.80	-	0.72	-	1.08	[292]
[BMPYR][DCA]	2.67	-	3.93	166.17	85.45	1.90	1.15	1.50	[293]
[HMIM][Cl]	13.25	128.34	19.73	89.73	254.59	4.24	0.86	2.59	[294]
[DDA][ClO ₄]	1.00	3.58	-	3.58	-	2.01	-	1.84	[295]
[DDA][BF ₄]	1.11	3.06	-	3.06	-	2.13	-	0.83	[295]
[HMMIM][BF ₄]	1.18	1.31	.43	118.62	16.99	0.76	0.37	1.85	[296]
[OMMIM][BF ₄]	5.45	36.89	1.67	16.59	9.50	0.68	0.38	0.51	[297]
Sulfolane	0.87	7.18	1.13	-	11.55	0.382	0.23	-	[298]

For the separation problems under consideration, the selectivity values vary when using different combination of [ZnCl₂] and either acetic acid or phosphoric acid as follows: benzene/ethanol > octane/acetonitrile > ethylbenzene/butanol > heptane/butanol > cyclohexane/ethanol for [ZnCl₂][acetic acid], and octane/acetonitrile > benzene/ethanol > cyclohexane/ethanol > ethylbenzene/butanol > heptane/butanol for [ZnCl₂][phosphoric acid]. Specifically, the selectivity achieved in the study for heptane/butanol using [zinc chloride + acetic acid] 1:2 is lower (S_{ij}^{∞} = 106.20) compared to [BMIM][Cl] + [Gly] (S_{ij}^{∞} = 135.92) [116] and (1-hexyl-3-methylimidazolium

chloride) [HMIM][Cl] ($S_{ij}^{\infty} = 254.59$) [294]. Meanwhile, the selectivity for the separation involving heptane/butanol is ($S_{ij}^{\infty} = 237.29$) for [zinc chloride + phosphoric acid] 1:2 and is also lower than [HMIM][Cl] ($S_{ij}^{\infty} = 254.59$) [294].

In the findings, the results indicate that the [zinc chloride + acetic acid] 1:2 for ethylbenzene/butanol and heptane/butanol and [zinc chloride + acetic acid] 1:4 for octane/acetonitrile systems, prove ineffective in the separations. This ineffectiveness arises from the low capacity values, despite a high level of selectivity. However, when using [ZnCl₂][phosphoric acid], the selectivity and capacity values, as presented in Table 5.9, are acceptable and high for the separation of benzene/ethanol, cyclohexane/ethanol, and octane/acetonitrile. This suggests that phosphoric acid as a hydrogen bond donor yields higher selectivity's and capacities compared to acetic acid for the same separation problems, highlighting the significant impact of hydrogen bond donors on the separation processes. These findings indicate the potential applicability of [ZnCl₂][phosphoric acid] (1:2 and 1:2.5) in industrial separation processes.

The study of DESs as possible extracting solvents shows that the DES made with phosphoric acid at a 1:2 and 1:2.5 molar ratios can be used to separate azeotropes. This is evident from their high selectivity values and, more importantly, their capacity values, which suggest that smaller amounts of these solvents would be needed compared to other DESs and ILs described in the literature. Both prepared DESs prove to be effective in the selected industrial extraction problems.

The phosphoric acid's central atom exhibits an uneven distribution of charges, resulting in increased polarity. This heightened polarity enhances its interactions with ethanol, butanol, and acetonitrile, making them stronger. This also applies to acetic acid, which contains double-bonded oxygen that is more electronegative. Additionally, lower selectivity values observed in [ZnCl₂][acetic acid] are attributed to the dipole moment in the C-O bond, which induces positive and negative charges, resulting in interactions with alkanes and aromatic hydrocarbons.

5.4. Thermophysical and thermodynamics properties of DESs binary mixtures

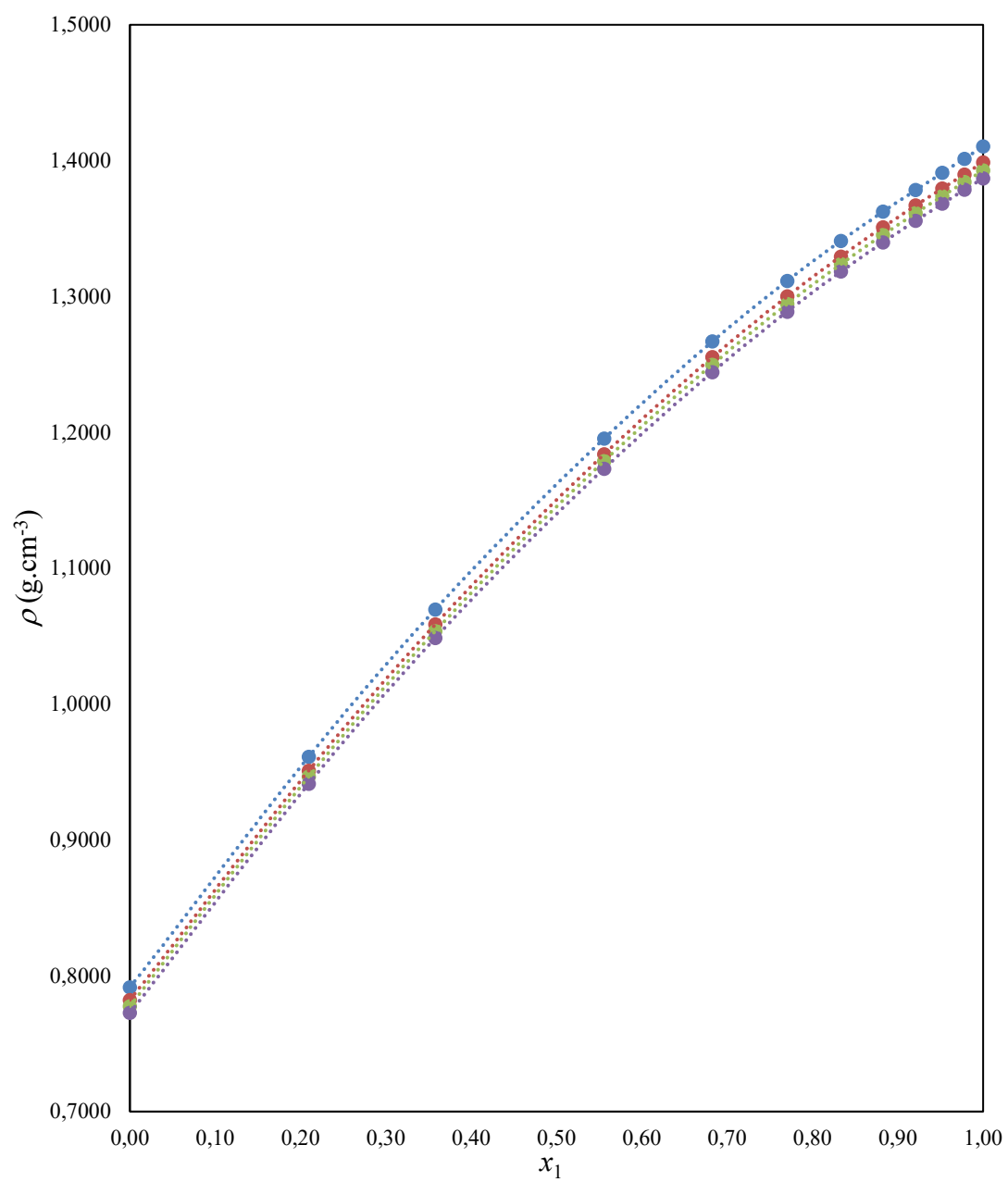
This study examined the binary mixtures {[ZnCl₂][acetic acid] 1:4 or [ZnCl₂][phosphoric acid] 1:2.5 + methanol or ethanol or propanol} at various temperatures (293.15, 303.15, 308.15, and 313.15) K and at constant pressure of 0.1 MPa using DSA 5000M. The main goal of the study was to find out different thermodynamic properties, like intermolecular free length, deviation in isentropic compressibility, excess molar volumes, and isentropic compressibility. These properties were determined through the utilization of density and speed of sound measurements. Using the equations from Chapter 3, it was possible to determine these properties in question. The objective of this study was to gain insight into the behavior of binary mixtures under varying temperatures and compositions

through an investigation of their thermodynamic properties. The data holds significant potential for a range of applications, including but not limited to process design, optimization, and elucidating the fundamental molecular interactions within the mixtures.

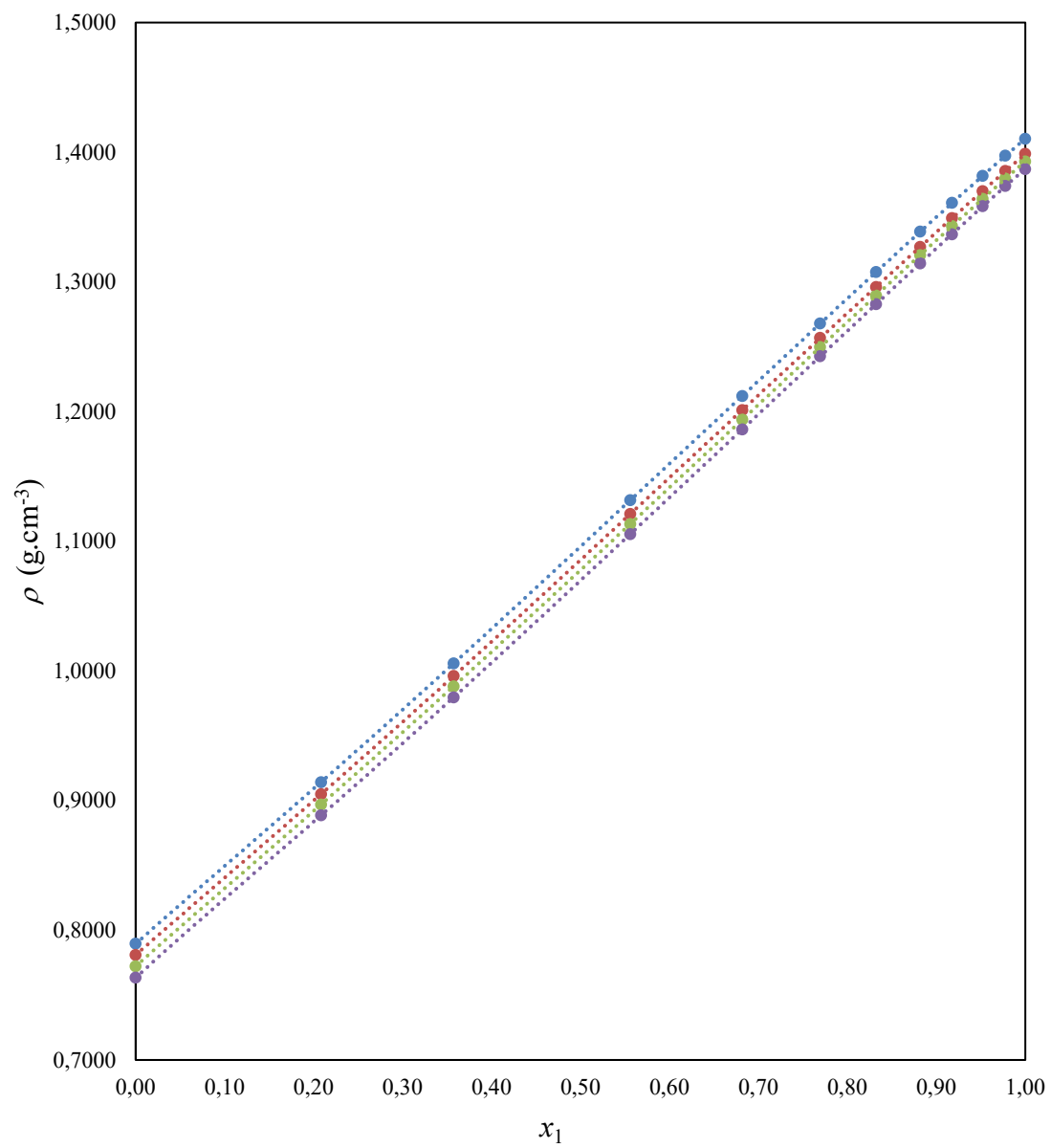
5.4.1 Thermophysical properties of [ZnCl₂][acetic acid] 1:4 and [ZnCl₂][phosphoric acid] 1:2.5 + methanol, or ethanol, or propanol

The density of the [ZnCl₂][acetic acid] 1:4 and [ZnCl₂][phosphoric acid] 1:2.5 DESs and their binary systems were measured at four different temperatures (293.15, 303.15, 308.15, and 313.15) K and at a pressure of 0.1 MPa. The obtained results are presented in Table 5.10 and Figure 5.17, which illustrate the relationship between density and concentration for the [ZnCl₂][acetic acid] 1:4 DES at various temperatures. These observations are also shown in Table 5.11 and Figure 5.17 for [ZnCl₂][phosphoric acid] 1:2.5. The correlation between composition and density is a crucial principle in comprehending the physical properties of substances and finds extensive application in scientific and technical domains. It plays a significant role in the development of materials suited for objectives and in the examination of the attributes shown by natural materials [299]. The mole fraction of the solvent constituents may have an impact on the density of a solution, such as in the case of DES. The density of the resultant solution exhibits an increase as the mole fraction of the [ZnCl₂][acetic acid] 1:4 and [ZnCl₂][phosphoric acid] 1:2.5 DESs increases within the binary system, including methanol, ethanol, and propanol. This suggests that the density of DES is higher compared to alcohols, and when the quantity of DES in the solution expands, the total density also increases.

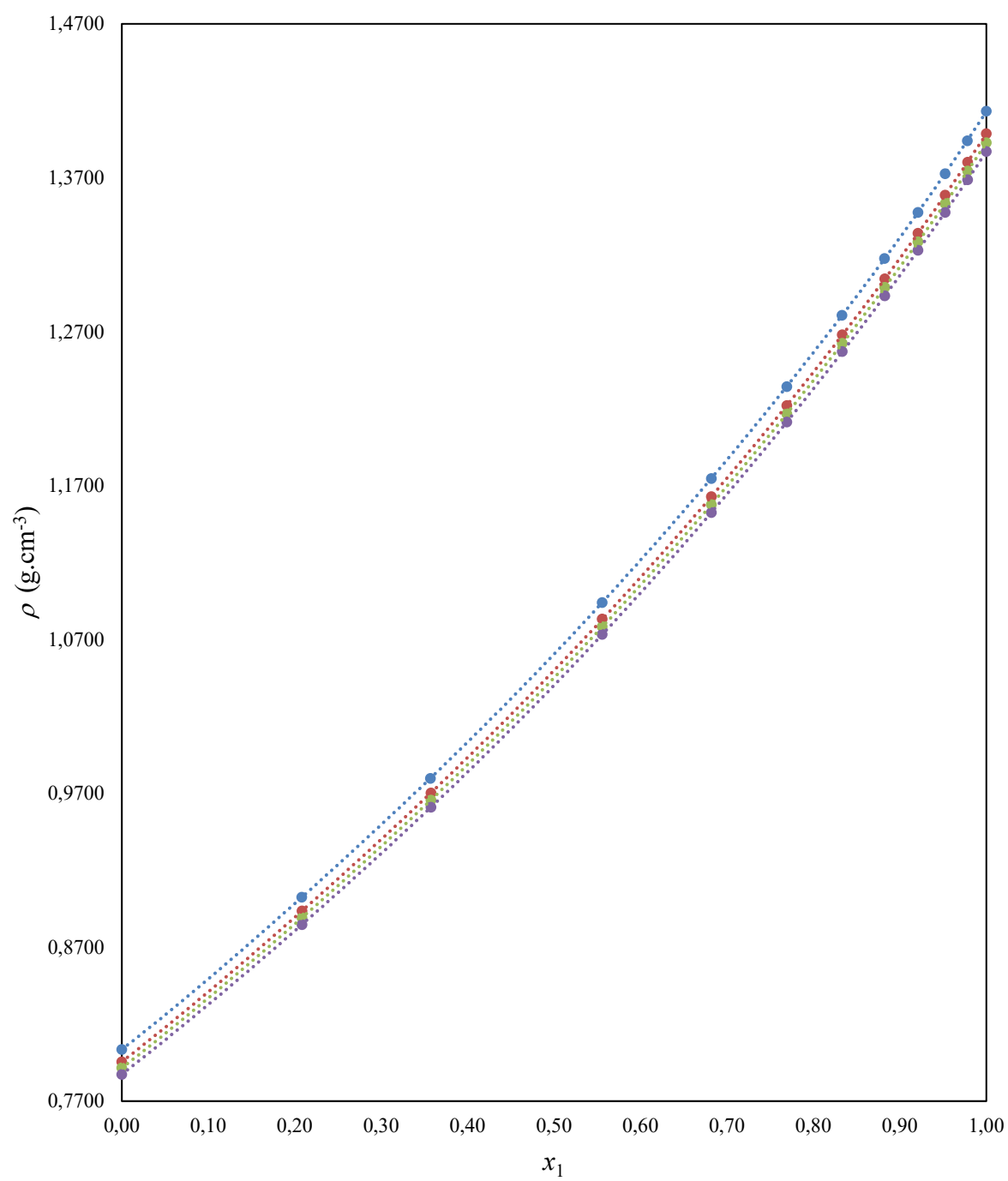
The density of binary mixtures containing [ZnCl₂][acetic acid] 1:4 and [ZnCl₂][phosphoric acid] 1:2.5 DESs with methanol, ethanol, and propanol decreases as the temperature increases. This phenomenon may be attributed to the fact that, with an increase in temperature, the molecules within the mixture experience an elevation in energy levels, leading to enhanced molecular mobility. The density decreases because of increased molecular motion, leading to a reduction in the degree of molecular packing [300, 301]. The increased molecular motion induces a reduction in molecular packing density, leading to a fall in overall density.



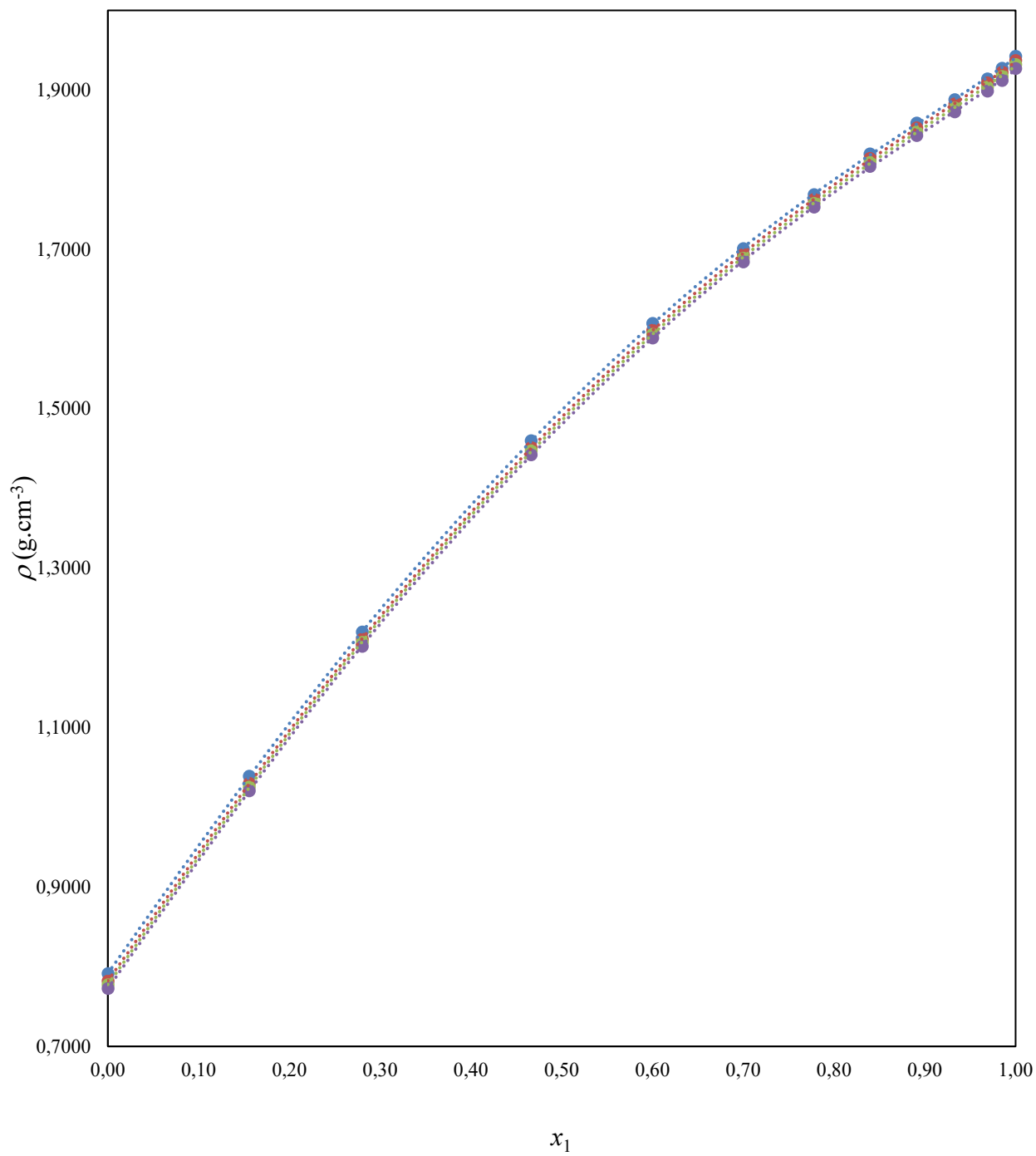
(a)



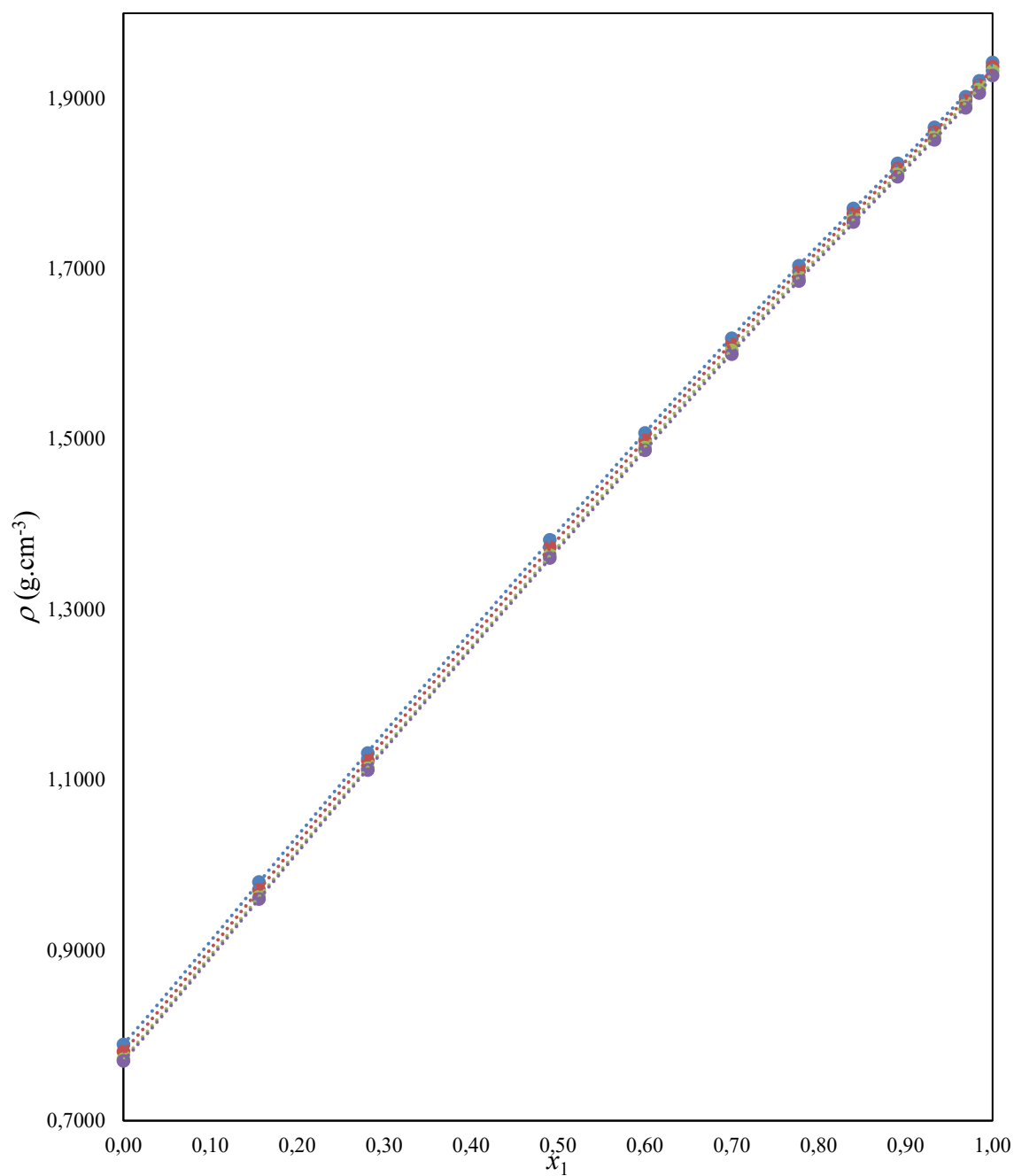
(b)



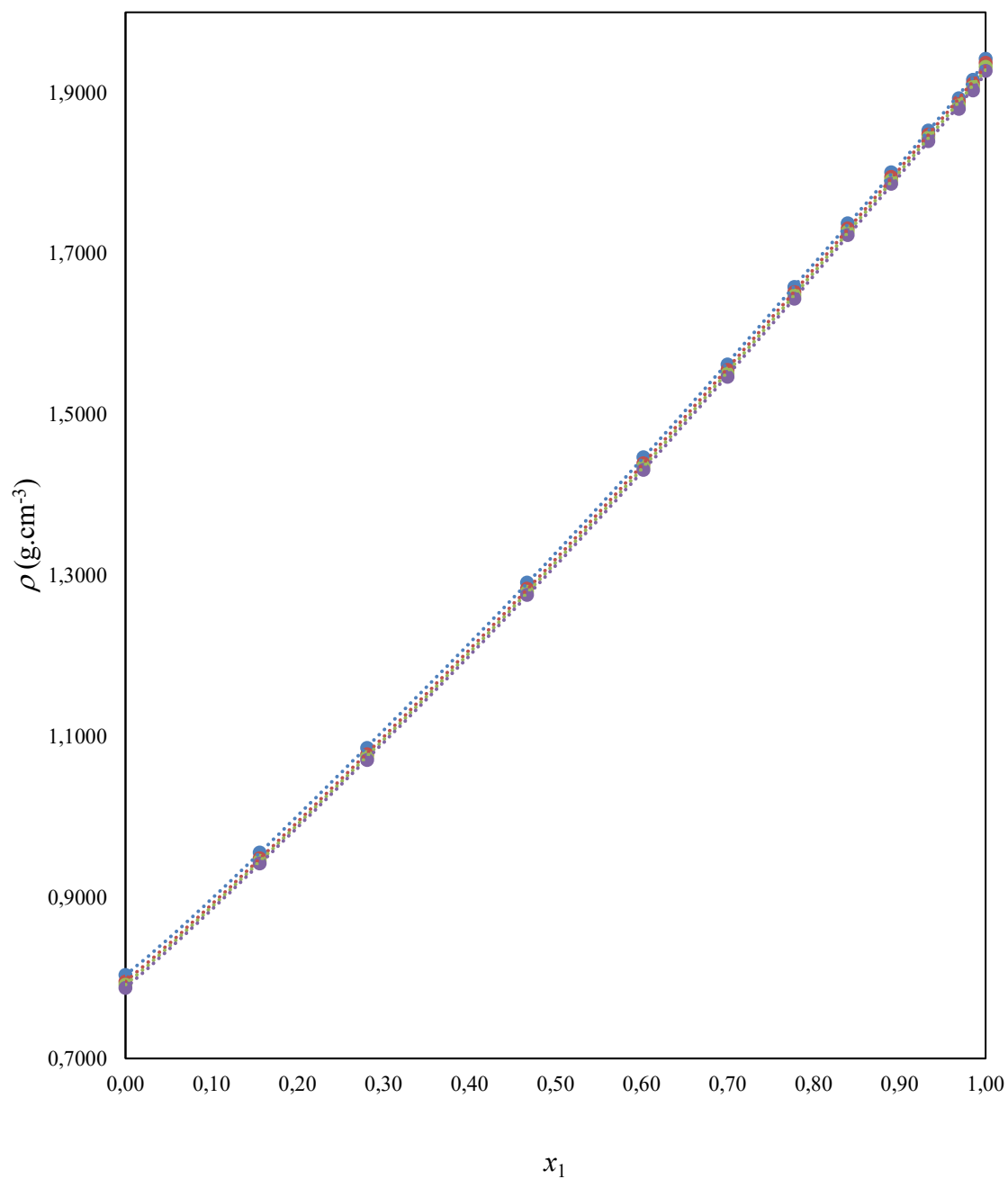
(c)



(d)



(e)



(f)

Figure 5. 17: Experimental densities of the binary mixture of {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol (a), ethanol (b), and propanol (c)} and {[ZnCl₂][phosphoric acid] 1:2.5 + methanol (d), ethanol (e), and propanol (f)} at 293.15 K (blue), 303.15 K (red), 308.15 K (green), and 313.15 K (purple).

Table 5. 10: Density, ρ , speed of sound, u , of the binary mixtures {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol or ethanol or propanol (x_2)} at T = (293.15, 303.15, 308.15, and 313.15) K

x_1	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$
{[ZnCl ₂][acetic acid] 1:4 (x_1) + methanol (x_2)}				
T = 293.15 K		T = 303.15 K		
0.0000	0.7916	1119.60	0.7822	1087.20
0.2096	0.9612	1193.02	0.9511	1162.23
0.3580	1.0697	1215.05	1.0587	1186.43
0.5560	1.1955	1259.34	1.1838	1235.08
0.6827	1.2670	1268.26	1.2554	1247.55
0.7705	1.3114	1277.17	1.3001	1247.59
0.8334	1.3411	1274.90	1.3294	1245.47
0.8827	1.3625	1273.75	1.3511	1244.60
0.9211	1.3784	1273.15	1.3671	1244.18
0.9524	1.3911	1272.90	1.3796	1244.02
0.9783	1.4014	1273.26	1.3899	1244.26
1.0000	1.4105	1272.58	1.3987	1243.46
T = 308.15 K		T = 313.15		
0.0000	0.7776	1071.00	0.7727	1055.00
0.2096	0.9465	1147.12	0.9414	1132.36
0.3580	1.0537	1172.31	1.0486	1158.83
0.5560	1.1789	1222.94	1.1733	1212.04
0.6827	1.2499	1233.96	1.2444	1219.96
0.7705	1.2944	1233.00	1.2888	1218.57
0.8334	1.3239	1231.12	1.3184	1217.51
0.8827	1.3454	1230.18	1.3398	1215.97
0.9211	1.3614	1229.96	1.3558	1215.64
0.9524	1.3740	1229.75	1.3683	1215.56
0.9783	1.3843	1229.96	1.3787	1215.60
1.0000	1.3929	1229.14	1.3870	1211.72
{[ZnCl ₂][acetic acid] (x_1) 1:4 + ethanol (x_2)}				
T = 293.15 K		T = 303.15 K		
0.0000	0.7896	1160.37	0.7810	1126.91
0.2084	0.9142	1200.62	0.9050	1168.08

Table 5.10 continued

x_1	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$
0.3573	1.0057	1226.31	0.9960	1194.55
0.5559	1.1317	1240.51	1.1210	1212.92
0.6821	1.2120	1251.50	1.2012	1218.19
0.7694	1.2680	1259.93	1.2569	1229.71
0.8324	1.3076	1260.99	1.2961	1231.32
0.8819	1.3387	1262.91	1.3271	1233.80
0.9177	1.3610	1265.59	1.3493	1236.69
0.9520	1.3817	1268.16	1.3700	1239.38
0.9777	1.3973	1271.11	1.3856	1242.24
1.0000	1.4105	1272.58	1.3987	1243.46
T = 308.15 K			T = 313.15 K	
0.0000	0.7723	1109.94	0.7634	1093.40
0.2084	0.8970	1151.80	0.8886	1135.61
0.3573	0.9881	1178.64	0.9796	1162.85
0.5559	1.1133	1197.94	1.1055	1183.04
0.6821	1.1939	1203.87	1.1863	1187.44
0.7694	1.2498	1214.60	1.2428	1199.58
0.8324	1.2895	1216.60	1.2829	1201.94
0.8819	1.3207	1219.29	1.3143	1204.89
0.9177	1.3431	1222.23	1.3367	1207.83
0.9520	1.3641	1225.09	1.3584	1210.97
0.9777	1.3797	1227.98	1.3739	1213.91
1.0000	1.3929	1229.14	1.3870	1214.97
{[ZnCl ₂][acetic acid] 1:4 (x_1) + propanol (x_2)}				
T = 293.15 K			T = 303.15 K	
0.0000	0.8036	1222.69	0.7956	1188.88
0.2082	0.9025	1232.33	0.8936	1199.27
0.3569	0.9798	1240.45	0.9703	1208.25
0.5556	1.0941	1241.00	1.0832	1210.42
0.6820	1.1746	1243.87	1.1628	1213.75
0.7692	1.2344	1247.03	1.2221	1217.43
0.8332	1.2807	1251.59	1.2679	1222.33
0.8822	1.3176	1253.82	1.3044	1224.98
0.9208	1.3475	1259.81	1.3340	1230.92

Table 5.10 continued

x_1	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$
0.9523	1.3727	1263.51	1.3588	1234.68
0.9781	1.3941	1267.34	1.3801	1238.50
1.0000	1.4132	1272.58	1.3987	1243.46
T = 308.15 K			T=313.15 K	
0.0000	0.7916	1171.93	0.7875	1155.23
0.2082	0.8892	1182.69	0.8847	1166.16
0.3569	0.9656	1191.98	0.9609	1175.76
0.5556	1.0784	1195.85	1.0734	1181.45
0.6820	1.1576	1198.75	1.1524	1183.89
0.7692	1.2167	1202.70	1.2113	1188.08
0.8332	1.2625	1207.76	1.2570	1193.31
0.8822	1.2988	1210.63	1.2933	1196.41
0.9208	1.3284	1216.52	1.3228	1202.24
0.9523	1.3531	1220.37	1.3474	1206.21
0.9781	1.3744	1224.25	1.3686	1210.46
1.0000	1.3929	1229.14	1.3870	1214.97

Standard uncertainties u are $u(T) = 0.02$ K, $u(p) = 0.04$ MPa, and the combined expanded uncertainties U_c in mole fraction, density, and speed of sound were $U_c(x) = 0.0006$, $U_c(\rho) = 0.0009 \text{ g} \cdot \text{cm}^{-3}$, $U_c(u) = 2.63 \text{ m} \cdot \text{s}^{-1}$, respectively (0.95 level of confidence).

Table 5. 11: Density, speed of sound, u , of the binary mixture {[ZnCl₂][phosphoric acid] 1:2.5 + methanol or ethanol or propanol} at T = (293.15, 303.15, 308.15, and 313.15) K.

x_1	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$
{[ZnCl ₂][phosphoric acid] 1:2.5 (x_1) + methanol (x_2)}				
T = 293.15 K			T = 303.15 K	
0.0000	0.7916	1119.60	0.7822	1087.20
0.1558	1.0390	1200.13	1.0300	1172.75
0.2802	1.2200	1302.70	1.2110	1280.96
0.4663	1.4600	1413.26	1.4516	1397.17
0.6001	1.6072	1439.82	1.5985	1424.85
0.7001	1.7012	1459.11	1.6937	1444.85
0.7779	1.7690	1477.73	1.7628	1463.82
0.8395	1.8200	1492.58	1.8142	1478.82
0.8909	1.8587	1505.30	1.8528	1491.58

0.9329	1.8880	1515.69	1.8827	1501.99
0.9688	1.9141	1523.76	1.9090	1510.01
0.9849	1.9274	1528.77	1.9223	1515.01
1.0000	1.9424	1537.77	1.9372	1520.24

T = 308.15 K

T = 313.15

0.0000	0.7776	1071.07	0.7727	1055.00
0.1558	1.0254	1159.10	1.0208	1145.58
0.2802	1.2070	1269.96	1.2020	1259.18
0.4663	1.4473	1388.81	1.4424	1380.77
0.6001	1.5937	1417.46	1.5890	1410.20
0.7001	1.6890	1437.87	1.6843	1430.97
0.7779	1.7580	1457.00	1.7532	1450.28
0.8395	1.8093	1472.08	1.8044	1465.44
0.8909	1.8479	1484.87	1.8430	1478.26
0.9329	1.8777	1495.27	1.8727	1488.65
0.9688	1.9039	1503.29	1.8989	1496.67
0.9849	1.9172	1508.28	1.9122	1501.66
1.0000	1.9321	1513.47	1.9271	1506.81

{[ZnCl₂][phosphoric acid] 1:2.5 (x_1) + ethanol (x_2)}

T = 293.15 K

T = 303.15 K

0.0000	0.7896	1160.37	0.7810	1126.91
0.1559	0.9801	1235.88	0.9713	1201.47
0.2810	1.1316	1322.11	1.1230	1295.41
0.4904	1.3818	1408.50	1.3732	1389.45
0.6000	1.5073	1418.87	1.4985	1401.44
0.6999	1.6185	1443.33	1.6114	1427.67
0.7771	1.7035	1464.41	1.6971	1448.72
0.8397	1.7710	1481.15	1.7650	1467.00
0.8906	1.8238	1496.19	1.8179	1482.46
0.9331	1.8660	1509.52	1.8605	1495.77
0.9690	1.9021	1521.68	1.8973	1507.95
0.9845	1.9205	1526.43	1.9155	1512.69
1.0000	1.9424	1537.77	1.9372	1520.24

T = 308.15 K

T = 313.15 K

Table 5.11 continued

x_1	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$
	T = 293.15 K	T = 303.15 K	T = 293.15 K	T = 303.15 K
0.0000	0.7723	1109.94	0.7701	1093.40
0.1559	0.9629	1220.15	0.9602	1201.91
0.2810	1.1140	1295.98	1.1118	1279.60
0.4904	1.3639	1379.43	1.3605	1369.43
0.6000	1.4902	1392.74	1.4869	1384.12
0.6999	1.6041	1419.89	1.5999	1412.17
0.7771	1.6896	1441.45	1.6858	1434.26
0.8397	1.7586	1460.02	1.7549	1453.12
0.8906	1.8119	1475.69	1.8082	1468.98
0.9331	1.8553	1489.03	1.8514	1482.37
0.9690	1.8927	1501.23	1.8889	1494.59
0.9845	1.9111	1505.97	1.9063	1499.34
1.0000	1.9321	1513.47	1.9271	1506.81
{[ZnCl ₂][phosphoric acid] 1:2.5 (x_1) + propanol (x_2)}				
	T = 293.15 K		T = 303.15 K	
0.0000	0.8036	1222.69	0.7956	1188.88
0.1558	0.9560	1263.35	0.9486	1232.26
0.2807	1.0860	1295.98	1.0778	1267.99
0.4668	1.2915	1342.65	1.2840	1319.67
0.6021	1.4471	1380.63	1.4396	1361.01
0.6998	1.5624	1411.58	1.5554	1394.06
0.7777	1.6586	1439.81	1.6522	1423.86
0.8395	1.7377	1464.18	1.7314	1449.25
0.8903	1.8012	1485.18	1.7956	1470.88
0.9333	1.8530	1503.67	1.8480	1489.71
0.9687	1.8931	1521.20	1.8884	1506.58
0.9851	1.9162	1523.81	1.9113	1509.90
1.0000	1.9424	1537.77	1.9372	1520.24
	T = 308.15 K		T=313.15 K	
0.0000	0.7916	1171.93	0.7875	1155.23
0.1558	0.9454	1216.62	0.9422	1201.06

Table 5.11 continued

x_1	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$	$\rho /(\text{g} \cdot \text{cm}^{-3})$	$u /(\text{m} \cdot \text{s}^{-1})$
	T = 293.15 K	T = 303.15 K	T = 293.15 K	T = 303.15 K
0.2807	1.0743	1253.92	1.0709	1239.92
0.4668	1.2797	1308.15	1.2761	1296.77
0.6021	1.4355	1351.22	1.4312	1341.50
0.6998	1.5510	1385.39	1.5468	1376.80
0.7777	1.6478	1415.97	1.6441	1408.16
0.8395	1.7275	1441.89	1.7232	1434.61
0.8903	1.7913	1463.84	1.7869	1456.88
0.9333	1.8441	1482.87	1.8398	1476.11
0.9687	1.8841	1499.28	1.8798	1491.97
0.9851	1.9072	1503.17	1.9028	1496.62
1.0000	1.9321	1513.47	1.9271	1506.81

Standard uncertainties u are $u(T) = 0.02$ K, $u(p) = 0.04$ MPa, and the combined expanded uncertainties Uc in mole fraction, density, and speed of sound were $Uc(x) = 0.0006$, $Uc(\rho) = 0.0009 \text{ g} \cdot \text{cm}^{-3}$, $Uc(u) = 2.63 \text{ m} \cdot \text{s}^{-1}$, respectively (0.95 level of confidence).

The speed of sound in a gas or liquid is contingent upon a multitude of parameters, including the density and compressibility of the medium [302, 303]. Temperature, pressure, and the characteristics of the medium all have an impact on this velocity. Figure 5.18 and Table 5.10 present the correlation between the speed of sound and the concentration of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 DES at various temperatures. Figure 5.18 and Table 5.11 present a mixture of $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 DES. Based on the data shown in Figure 5.18, it is evident that there is a decrease in the speed of sound as the temperature increases. The impact of rising temperatures cause molecules or atoms inside a material to have more kinetic energy, which results in higher velocities and a corresponding rise in collision frequency, may help to explain this phenomenon. Consequently, there is a decrease in the stiffness or elasticity of the material. Thus, the sound waves that traverse the substance experience increased opposition and undergo a longer propagation process, resulting in a reduction in the velocity of sound.

The speed of sound exhibits an increase when the mole fraction of the $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 and $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 DESs increases. This statement suggests a clear correlation between the two variables, since the increase in the mole fraction of the DES results in a corresponding increase in the speed of sound [304].

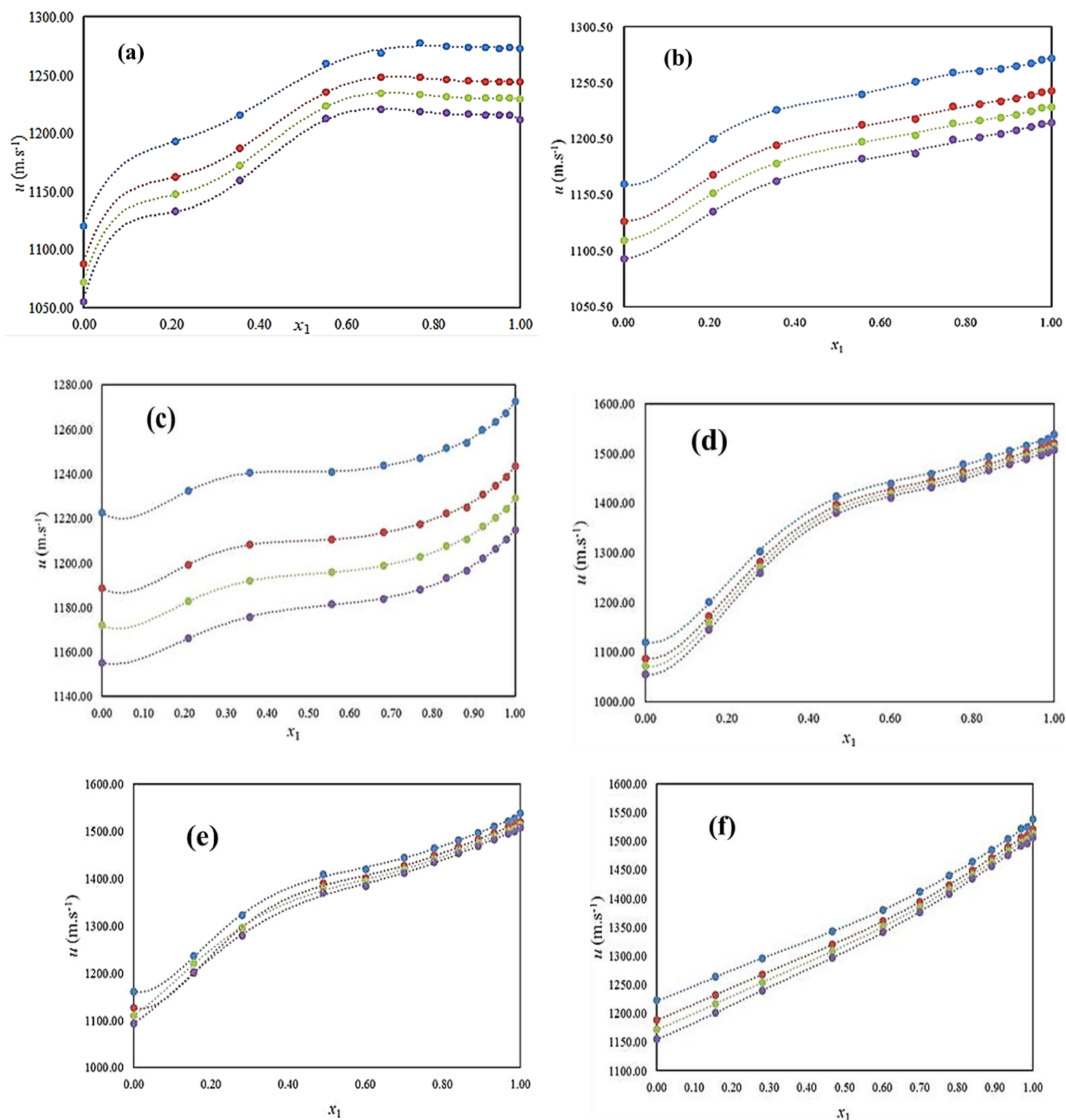


Figure 5. 18: Experimental speed of sound, u , of the binary mixtures of $\{[\text{ZnCl}_2][\text{acetic acid}] \text{ 1:4 (} x_1 \text{) + methanol (a), ethanol (b), and propanol (c)}\}$ and $\{[\text{ZnCl}_2][\text{phosphoric acid}] \text{ 1:2.5 + methanol (d), ethanol (e), and propanol (f)}\}$ at 293.15 K (blue), 303.15 K (red), 308.15 K (green), and 313.15 K (purple).

The excess molar volume (V_m^E) is a thermodynamic parameter that quantifies the deviation of the volume of a mixture from that of an ideal mixture [305, 306]. The term "deviation" refers to the

disparity between the measured molar volume of a mixture and the molar volume that would be expected in an ideal mixture. The excess molar volume is a thermodynamic characteristic that quantifies the deviation of the volume of a mixture from its ideal behavior, as illustrated in Figure 5.19 and Table 5.12 for $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 and Table 5.13 for $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5. The excess molar quantities of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 with methanol or ethanol were observed to be consistently negative throughout the examined temperatures. However, the sign of the excess molar volumes changes from negative to positive when $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 is mixed with propanol and $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 binary systems [11, 12].

Across the complete range of mole fractions of DES, spanning various temperatures and binary systems under investigation, it was observed that both negative and positive values were obtained for the calculated excess molar volume [11, 12]. At higher concentrations of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 is mixed with propanol and $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 DES as a function of mole fraction exhibit positive excess molar volume values. If the excess molar volume exhibits a negative value, the resulting combination will possess a volume that is less in comparison to the ideal volume. If the excess molar volume exhibits a positive value, it may be inferred that the resulting mixture will possess a greater volume [11, 307].

The observed negative excess molar volume in the $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 mixture with methanol or ethanol indicates that the intermolecular interactions between the constituents of the mixture are stronger than those expected in an ideal solution. This behavior can be observed in mixtures including both polar and non-polar components, such as $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 with alcohols. The polar components have the potential to establish hydrogen bonds with acetic acid, while the non-polar components may interact with zinc chloride via Van der Waals forces. The observed negative excess molar volume of the $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 and propanol mixture and $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 DES binary systems at low mole fractions suggests that the intermolecular interactions between the components are stronger than what would be expected in a perfect solution. However, when the mole fraction of propanol with $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 and propanol mixture and $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 DES binary systems increases, the intermolecular interactions among propanol molecules lead to a positive excess molar volumes. This phenomenon is often seen in mixtures composed of components with different sizes or shapes, since the arrangement of molecules may become less efficient as the mole fraction of one component grows.

As the temperature increases, the values of excess molar volumes in the binary solutions containing $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 and $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 DESs with methanol, ethanol, or propanol decrease [308, 309]. By examining how the mixture's constituent parts interact, this phenomenon can be clarified. At low temperatures, the components are more strongly attracted to one another and are

often packed closer together. This results in a larger excess molar volume value because there is a larger deviation from the optimum molar volume. The components gain thermal energy as the temperature increases, which decreases their attractive interactions. This lowers the value of the excess molar volume by reducing the deviation from the ideal molar volume. The type and strength of the intermolecular interactions between the constituents, the size and shape of the molecules, and the level of ion solvation in the deep eutectic solvent are just a few factors that can affect it.

The alcohol's alkyl chain length increases from one to three carbon atoms when methanol, ethanol, or propanol are added to the DES. One anticipated outcome is a decrease in the polarity of the DES with an increase in the length of the alcohol's alkyl chain. This may occur because the combination's overall polarity is decreasing because longer alkyl chains are less polar than shorter ones. Certain chemicals, especially those with higher polarity, may become less soluble in the mixture because of this shift in polarity. Increasing the length of the alkyl chain may also have the effect of making the mixture more hydrophobic. This is possible because the combination's overall hydrophobicity is increased by the longer alkyl chains' greater hydrophobicity than that of their shorter counterparts. This could make it more difficult for the mixture to dissolve substances, particularly those with a higher hydrophilic content.

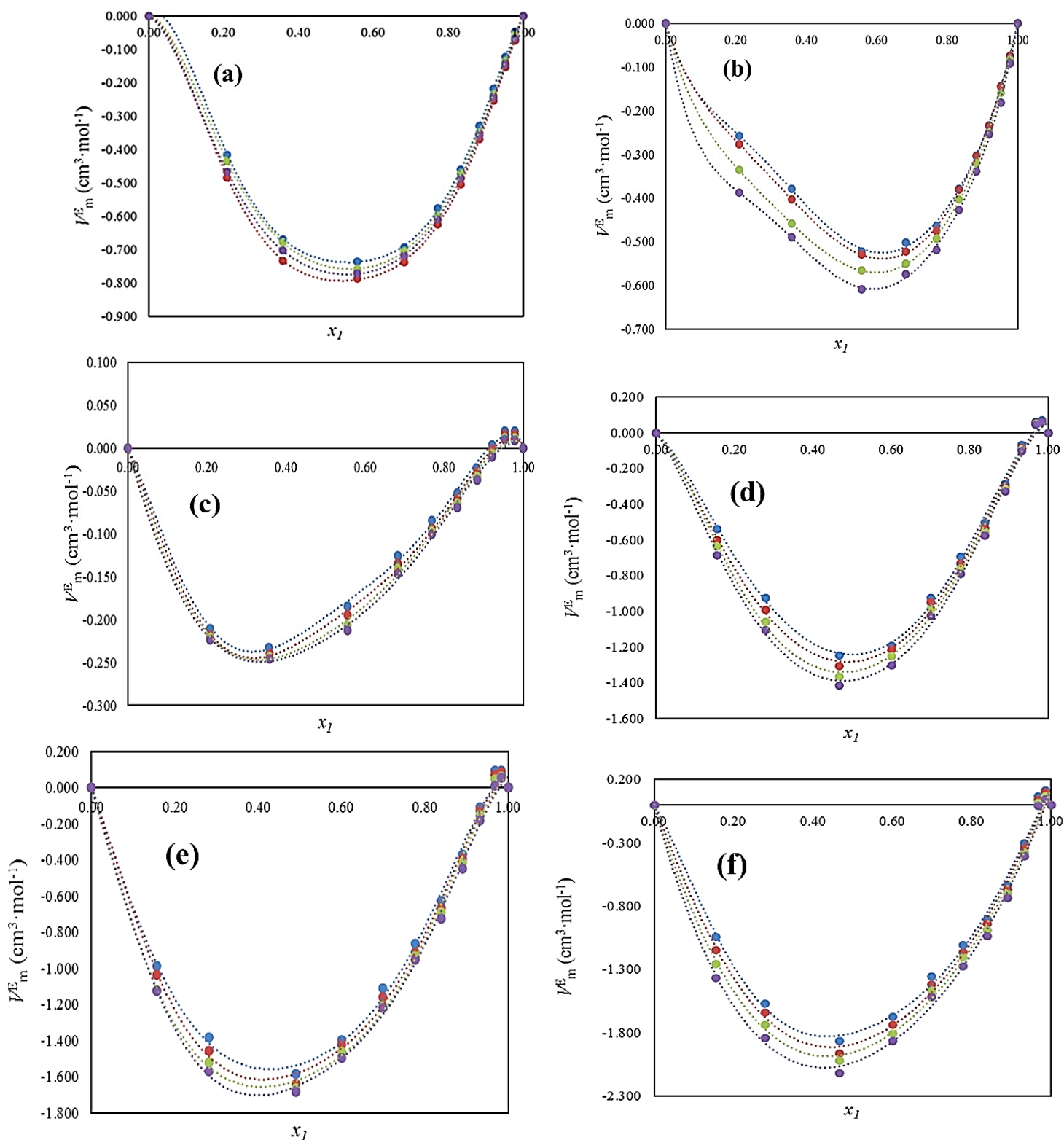


Figure 5.19: Experimental excess molar volume, V_m^E , and values calculated using the Redlich-Kister model for the mixtures $\{[\text{ZnCl}_2][\text{acetic acid}] 1:4 (x_1) + \text{methanol (a), ethanol (b), and propanol (c)}\}$ and $\{[\text{ZnCl}_2][\text{phosphoric acid}] 1:25 (x_1) + \text{methanol (d), ethanol (e), and propanol (f)}\}$. Circles represent the experimental data, while the solid lines were generated using a Redlich-Kister smoothing 6th-order polynomial. Colours: (blue) 293.15 K, (red) 303.15 K, (green) 308.15 K, and (purple) 313.15 K.

Table 5. 12: Excess molar volumes, V_m^E , isentropic compressibility K_s , and excess isentropic compressibility ΔK_s , and intermolecular free length L_f , for the binary mixtures { {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol, ethanol or propanol (x_2)} at T = (293.15, 303.15, 308.15, and 313.15) K.

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$K_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta K_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
{[ZnCl ₂][acetic acid] 1:4 (x_1) + methanol (x_2)}				
T = 293.15 K				
0.0000	0.000	10.08	0.00	6.47
0.2096	-0.415	7.31	-1.57	5.51
0.3580	-0.669	6.33	-1.71	5.13
0.5560	-0.736	5.27	-1.63	4.68
0.6827	-0.693	4.91	-1.28	4.51
0.7705	-0.577	4.67	-1.01	4.41
0.8334	-0.461	4.59	-0.74	4.37
0.8827	-0.330	4.52	-0.52	4.33
0.9211	-0.218	4.48	-0.35	4.31
0.9524	-0.123	4.44	-0.21	4.29
0.9783	-0.047	4.40	-0.10	4.28
1.0000	0.000	4.38	0.00	4.26
T = 303.15 K				
0.0000	0.000	10.82	0.00	6.83
0.2096	-0.435	7.78	-1.73	5.79
0.3580	-0.679	6.71	-1.89	5.38
0.5560	-0.758	5.54	-1.84	4.88
0.6827	-0.705	5.12	-1.47	4.70
0.7705	-0.598	4.94	-1.10	4.61
0.8334	-0.471	4.85	-0.81	4.57
0.8827	-0.349	4.78	-0.57	4.54
0.9211	-0.236	4.73	-0.39	4.51
0.9524	-0.135	4.68	-0.24	4.49
0.9783	-0.057	4.65	-0.11	4.48
1.0000	0.000	4.62	0.00	4.46
T = 308.15 K				
0.0000	0.000	11.21	0.00	7.01

Table 5.12 continued

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta \kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
0.2096	-0.468	8.03	-1.83	5.93
0.3580	-0.704	6.91	-1.99	5.50
0.5560	-0.773	5.67	-1.95	4.99
0.6827	-0.718	5.25	-1.55	4.80
0.7705	-0.609	5.08	-1.15	4.72
0.8334	-0.487	4.98	-0.84	4.68
0.8827	-0.358	4.91	-0.60	4.64
0.9211	-0.245	4.86	-0.41	4.61
0.9524	-0.144	4.81	-0.25	4.59
0.9783	-0.066	4.78	-0.12	4.58
1.0000	0.000	4.75	0.00	4.57
T = 313.15 K				
0.0000	0.000	11.63	0.00	7.21
0.2096	-0.484	8.28	-1.93	6.08
0.3580	-0.733	7.10	-2.12	5.63
0.5560	-0.788	5.80	-2.09	5.09
0.6827	-0.738	5.40	-1.64	4.91
0.7705	-0.624	5.23	-1.23	4.83
0.8334	-0.504	5.12	-0.91	4.78
0.8827	-0.369	5.05	-0.65	4.75
0.9211	-0.254	4.99	-0.45	4.72
0.9524	-0.153	4.95	-0.28	4.70
0.9783	-0.074	4.91	-0.15	4.68
1.0000	0.000	4.91	0.00	4.68
{[ZnCl ₂][acetic acid] 1:4 (x_1) + ethanol (x_2)}				
T = 293.15 K				
0.0000	0.000	9.41	0.00	6.25
0.2084	-0.258	7.59	-0.77	5.61
0.3573	-0.378	6.61	-1.00	5.24
0.5559	-0.522	5.74	-0.87	4.88
0.6821	-0.501	5.27	-0.71	4.68
0.7694	-0.463	4.97	-0.57	4.54
0.8324	-0.379	4.81	-0.41	4.47

Table 5.12 continued

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta \kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
0.8819	-0.303	4.68	-0.29	4.41
0.9177	-0.234	4.59	-0.20	4.37
0.9520	-0.144	4.62	-0.12	4.32
0.9777	-0.074	4.43	-0.06	4.29
1.0000	0.000	4.38	0.00	4.26
T = 303.15 K				
0.0000	0.000	10.08	0.00	6.59
0.2084	-0.276	8.10	-0.85	5.91
0.3573	-0.403	7.04	-1.10	5.51
0.5559	-0.530	6.06	-0.98	5.11
0.6821	-0.523	5.61	-0.75	4.92
0.7694	-0.476	5.26	-0.62	4.76
0.8324	-0.380	5.09	-0.45	4.68
0.8819	-0.304	4.95	-0.32	4.62
0.9177	-0.236	4.85	-0.23	4.57
0.9520	-0.145	4.75	-0.13	4.52
0.9777	-0.075	4.68	-0.07	4.49
1.0000	0.000	4.62	0.00	4.46
T = 308.15 K				
0.0000	0.000	10.51	0.00	6.79
0.2084	-0.336	8.40	-0.91	6.07
0.3573	-0.459	7.29	-1.17	5.65
0.5559	-0.566	6.26	-1.05	5.24
0.6821	-0.551	5.78	-0.80	5.03
0.7694	-0.494	5.42	-0.66	4.88
0.8324	-0.404	5.24	-0.48	4.79
0.8819	-0.320	5.09	-0.34	4.73
0.9177	-0.248	4.98	-0.24	4.68
0.9520	-0.159	4.88	-0.14	4.63
0.9777	-0.083	4.81	-0.07	4.59
1.0000	0.000	4.75	0.00	4.57
T = 313.15 K				
0.0000	0.000	10.96	0.00	6.99

Table 5.12 continued

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta \kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
0.2084	-0.387	8.73	-0.97	6.24
0.3573	-0.490	7.55	-1.24	5.81
0.5559	-0.608	6.46	-1.12	5.37
0.6821	-0.575	5.98	-0.84	5.17
0.7694	-0.519	5.59	-0.69	5.00
0.8324	-0.427	5.40	-0.51	4.91
0.8819	-0.338	5.24	-0.36	4.84
0.9177	-0.254	5.13	-0.26	4.79
0.9520	-0.181	5.02	-0.16	4.73
0.9777	-0.091	4.94	-0.08	4.70
1.0000	0.000	4.88	0.00	4.67
{[ZnCl ₂][acetic acid] 1:4 (x_1) + propanol (x_2)}				
T = 293.15 K				
0.0000	0.000	8.32	0.00	5.88
0.2082	-0.210	7.30	-0.20	5.50
0.3569	-0.232	6.63	-0.28	5.25
0.5556	-0.184	5.93	-0.19	4.97
0.6820	-0.126	5.50	-0.12	4.78
0.7692	-0.085	5.21	-0.07	4.65
0.8332	-0.053	4.98	-0.04	4.55
0.8822	-0.024	4.83	-0.01	4.48
0.9208	0.004	4.68	-0.01	4.41
0.9523	0.020	4.56	0.01	4.35
0.9781	0.019	4.47	0.01	4.31
1.0000	0.000	4.37	0.00	4.26
T = 303.15 K				
0.0000	0.000	8.89	0.00	6.19
0.2082	-0.218	7.78	-0.22	5.79
0.3569	-0.240	7.06	-0.31	5.51
0.5556	-0.195	6.30	-0.22	5.21
0.6820	-0.135	5.84	-0.14	5.01
0.7692	-0.093	5.52	-0.09	4.88
0.8332	-0.059	5.28	-0.06	4.77

Table 5.12 continued

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta \kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
0.8822	-0.029	5.11	-0.02	4.69
0.9208	-0.001	4.95	-0.01	4.62
0.9523	0.015	4.83	0.00	4.56
0.9781	0.016	4.72	0.01	4.51
1.0000	0.000	4.62	0.00	4.46
T = 308.15 K				
0.0000	0.000	9.20	0.00	6.35
0.2082	-0.221	8.04	-0.23	5.94
0.3569	-0.243	7.29	-0.32	5.65
0.5556	-0.207	6.48	-0.24	5.33
0.6820	-0.140	6.01	-0.15	5.13
0.7692	-0.097	5.68	-0.10	4.99
0.8332	-0.064	5.43	-0.06	4.88
0.8822	-0.033	5.25	-0.02	4.80
0.9208	-0.006	5.09	-0.02	4.72
0.9523	0.012	4.96	0.00	4.67
0.9781	0.012	4.85	0.01	4.61
1.0000	0.000	4.75	0.00	4.57
T = 313.15 K				
0.0000	0.000	9.52	0.00	6.52
0.2082	-0.223	8.31	-0.24	6.09
0.3569	-0.246	7.53	-0.33	5.80
0.5556	-0.213	6.67	-0.27	5.46
0.6820	-0.146	6.19	-0.17	5.26
0.7692	-0.101	5.85	-0.10	5.11
0.8332	-0.069	5.59	-0.07	4.99
0.8822	-0.038	5.40	-0.03	4.91
0.9208	-0.010	5.23	-0.02	4.83
0.9523	0.010	5.10	0.00	4.77
0.9781	0.009	4.99	0.00	4.72
1.0000	0.000	4.88	0.00	4.67

Standard uncertainties u are $u(T) = 0.02$ K, $u(p) = 0.04$ MPa, and the combined expanded uncertainties Uc in mole fraction, density, and speed of sound were $Uc(x) = 0.0006$, $Uc(\rho) = 0.0009 \text{ g} \cdot \text{cm}^{-3}$, $Uc(\underline{u}) = 2.63 \text{ m} \cdot \text{s}^{-1}$, respectively (0.95 level of confidence).

Table 5. 13: Excess molar volumes, V_m^E , isentropic compressibility K_s , and excess isentropic compressibility ΔK_s , and intermolecular free length L_f , for the binary mixtures $\{[\text{ZnCl}_2][\text{phosphoric acid}] \text{ 1:2.5 } (x_1) + \text{methanol, ethanol, or propanol } (x_2)\}$ at $T = (293.15, 303.15, 308.15, \text{ and } 313.15) \text{ K}$.

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$K_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta K_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
{[ZnCl ₂][phosphoric acid] (x_1) 1:2.5+ methanol (x_2)}				
T = 293.15 K				
0.0000	0.000	10.08	0.00	6.47
0.1558	-0.539	6.68	-2.16	5.27
0.2802	-0.927	4.83	-3.03	4.48
0.4663	-1.249	3.43	-2.96	3.77
0.6001	-1.196	3.00	-2.34	3.53
0.7001	-0.925	2.76	-1.79	3.39
0.7779	-0.692	2.59	-1.34	3.28
0.8395	-0.504	2.47	-0.98	3.20
0.8909	-0.288	2.37	-0.67	3.14
0.9329	-0.069	2.31	-0.40	3.09
0.9688	0.063	2.25	-0.17	3.06
0.9849	0.070	2.22	-0.08	3.04
1.0000	0.000	2.18	0.00	3.01
T = 303.15 K				
0.0000	0.000	10.82	0.00	6.83
0.1558	-0.601	7.06	-2.42	5.51
0.2802	-0.991	5.03	-3.38	4.66
0.4663	-1.306	3.53	-3.28	3.90
0.6001	-1.215	3.08	-2.58	3.64
0.7001	-0.952	2.83	-1.98	3.49
0.7779	-0.733	2.65	-1.49	3.38
0.8395	-0.536	2.52	-1.09	3.30
0.8909	-0.301	2.43	-0.74	3.23
0.9329	-0.086	2.35	-0.45	3.18
0.9688	0.052	2.30	-0.20	3.15
0.9849	0.062	2.27	-0.10	3.12
1.0000	0.000	2.23	0.00	3.10
T = 308.15 K				

Table 5.13 continued

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta \kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
0.0000	0.000	11.21	0.00	7.01
0.1558	-0.637	7.26	-2.56	5.64
0.2802	-1.062	5.14	-3.57	4.75
0.4663	-1.368	3.58	-3.45	3.96
0.6001	-1.253	3.12	-2.72	3.70
0.7001	-0.988	2.86	-2.08	3.54
0.7779	-0.760	2.68	-1.57	3.43
0.8395	-0.556	2.55	-1.15	3.34
0.8909	-0.315	2.45	-0.78	3.28
0.9329	-0.094	2.38	-0.48	3.23
0.9688	0.049	2.32	-0.21	3.19
0.9849	0.061	2.29	-0.10	3.17
1.0000	0.000	2.26	0.00	3.15
T = 313.15 K				
0.0000	0.000	11.63	0.00	7.21
0.1558	-0.686	7.46	-2.71	5.77
0.2802	-1.106	5.25	-3.76	4.84
0.4663	-1.417	3.64	-3.63	4.03
0.6001	-1.301	3.16	-2.86	3.76
0.7001	-1.028	2.90	-2.19	3.60
0.7779	-0.790	2.71	-1.65	3.48
0.8395	-0.578	2.58	-1.20	3.39
0.8909	-0.329	2.48	-0.82	3.33
0.9329	-0.102	2.41	-0.50	3.28
0.9688	0.046	2.35	-0.23	3.24
0.9849	0.060	2.32	-0.11	3.22
1.0000	0.000	2.29	0.00	3.19
{[ZnCl ₂][phosphoric acid] 1:2.5 (x_1) + ethanol (x_2)}				
T = 293.15 K				
0.0000	0.000	9.41	0.00	6.25
0.1559	-0.988	6.68	-1.60	5.27
0.2810	-1.383	5.06	-2.32	4.58
0.4904	-1.583	3.65	-2.21	3.89

Table 5.13 continued

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta \kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
0.6000	-1.398	3.30	-1.77	3.70
0.6999	-1.111	2.97	-1.38	3.51
0.7771	-0.866	2.74	-1.05	3.37
0.8397	-0.624	2.57	-0.76	3.27
0.8906	-0.372	2.45	-0.52	3.19
0.9331	-0.109	2.35	-0.31	3.13
0.9690	0.094	2.27	-0.13	3.07
0.9845	0.095	2.23	-0.05	3.05
1.0000	0.000	2.18	0.00	3.01
T = 303.15 K				
0.0000	0.000	10.08	0.00	6.59
0.1559	-1.036	6.74	-2.12	5.39
0.2810	-1.454	5.09	-2.78	4.68
0.4904	-1.637	3.67	-2.56	3.98
0.6000	-1.420	3.31	-2.06	3.78
0.6999	-1.162	2.98	-1.61	3.58
0.7771	-0.912	2.75	-1.24	3.44
0.8397	-0.665	2.58	-0.91	3.34
0.8906	-0.394	2.46	-0.64	3.25
0.9331	-0.126	2.36	-0.40	3.19
0.9690	0.071	2.28	-0.20	3.13
0.9845	0.086	2.24	-0.11	3.11
1.0000	0.000	2.23	0.00	3.10
T = 308.15 K				
0.0000	0.000	10.51	0.00	6.79
0.1559	-1.122	6.98	-2.25	5.53
0.2810	-1.518	5.34	-2.85	4.84
0.4904	-1.665	3.85	-2.61	4.11
0.6000	-1.463	3.46	-2.10	3.90
0.6999	-1.211	3.09	-1.64	3.68
0.7771	-0.931	2.85	-1.25	3.53
0.8397	-0.692	2.67	-0.91	3.42
0.8906	-0.413	2.53	-0.63	3.33

Table 5.13 continued

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta \kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
0.9331	-0.151	2.43	-0.38	3.27
0.9690	0.043	2.34	-0.17	3.21
0.9845	0.058	2.31	-0.08	3.18
1.0000	0.000	2.26	0.00	3.15
T = 313.15 K				
0.0000	0.000	10.86	0.00	6.96
0.1559	-1.128	7.21	-2.32	5.67
0.2810	-1.570	5.49	-2.96	4.95
0.4904	-1.685	3.92	-2.74	4.18
0.6000	-1.495	3.51	-2.21	3.96
0.6999	-1.220	3.13	-1.72	3.74
0.7771	-0.955	2.88	-1.31	3.59
0.8397	-0.725	2.70	-0.96	3.47
0.8906	-0.449	2.56	-0.66	3.38
0.9331	-0.181	2.46	-0.40	3.31
0.9690	0.010	2.37	-0.18	3.25
0.9845	0.053	2.33	-0.09	3.23
1.0000	0.000	2.29	0.00	3.19
{[ZnCl ₂][phosphoric acid] (x_1) 1:2.5 + propanol (x_2)}				
T = 293.15 K				
0.0000	0.000	8.32	0.00	5.88
0.1558	-1.044	6.55	-0.81	5.22
0.2807	-1.569	5.48	-1.12	4.77
0.4668	-1.866	4.30	-1.16	4.22
0.6021	-1.673	3.63	-1.00	3.88
0.6998	-1.358	3.21	-0.81	3.65
0.7777	-1.109	2.91	-0.64	3.48
0.8395	-0.905	2.68	-0.48	3.34
0.8903	-0.632	2.52	-0.33	3.23
0.9333	-0.302	2.39	-0.20	3.15
0.9687	0.067	2.28	-0.09	3.08
0.9851	0.111	2.25	-0.02	3.06
1.0000	0.000	2.18	0.00	3.01

Table 5.13 continued

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta \kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
T = 303.15 K				
0.0000	0.000	8.89	0.00	6.19
0.1558	-1.151	6.94	-0.91	5.47
0.2807	-1.638	5.77	-1.25	4.99
0.4668	-1.963	4.47	-1.31	4.39
0.6021	-1.740	3.75	-1.13	4.02
0.6998	-1.418	3.31	-0.92	3.78
0.7777	-1.164	2.99	-0.73	3.59
0.8395	-0.942	2.75	-0.55	3.44
0.8903	-0.666	2.57	-0.39	3.33
0.9333	-0.338	2.44	-0.24	3.24
0.9687	0.038	2.33	-0.11	3.17
0.9851	0.096	2.29	-0.04	3.14
1.0000	0.000	2.23	0.00	3.10
T = 308.15 K				
0.0000	0.000	9.20	0.00	6.35
0.1558	-1.257	7.15	-0.97	5.60
0.2807	-1.737	5.92	-1.33	5.10
0.4668	-2.025	4.57	-1.39	4.48
0.6021	-1.806	3.82	-1.21	4.09
0.6998	-1.465	3.36	-0.98	3.84
0.7777	-1.206	3.03	-0.78	3.64
0.8395	-0.994	2.78	-0.59	3.49
0.8903	-0.704	2.61	-0.42	3.38
0.9333	-0.380	2.47	-0.26	3.29
0.9687	0.013	2.36	-0.12	3.22
0.9851	0.064	2.32	-0.04	3.19
1.0000	0.000	2.26	0.00	3.15
T = 313.15 K				
0.0000	0.000	9.52	0.00	6.52
0.1558	-1.371	7.36	-1.03	5.73
0.2807	-1.843	6.07	-1.41	5.21
0.4668	-2.118	4.66	-1.48	4.56

Table 5.13 continued

x_1	$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$\Delta \kappa_s / (\text{TPa}^{-1}) \cdot 10^{-2}$	$L_f (\text{nm}) \cdot 10^2$
0.6021	-1.866	3.88	-1.28	4.16
0.6998	-1.522	3.41	-1.05	3.90
0.7777	-1.273	3.07	-0.83	3.70
0.8395	-1.037	2.82	-0.63	3.55
0.8903	-0.737	2.64	-0.44	3.43
0.9333	-0.410	2.49	-0.27	3.34
0.9687	-0.011	2.39	-0.12	3.27
0.9851	0.045	2.35	-0.05	3.24
1.0000	0.000	2.29	0.00	3.19

Standard uncertainties u are $u(T) = 0.02$ K, $u(p) = 0.04$ MPa, and the combined expanded uncertainties Uc in mole fraction, density, and speed of sound were $Uc(x) = 0.0006$, $Uc(\rho) = 0.0009 \text{ g} \cdot \text{cm}^{-3}$, $Uc(\underline{u}) = 2.63 \text{ m} \cdot \text{s}^{-1}$, respectively (0.95 level of confidence).

The isentropic compressibility values were determined by using the Newton-Laplace equation [310]. The isentropic compressibility was computed using the Newton-Laplace equation mentioned in Chapter 3. The concept of isentropic compressibility, κ_s , refers to the quantification of a substance's susceptibility to compression in the absence of heat exchange [13]. Tables 5.12 and Figure 5.20 provide the computed values pertaining to isentropic compressibility for binary mixtures including $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 when mixed with methanol, ethanol, or propanol throughout all the examined temperatures. Table 5.13 and Figure 5.20 show the findings of isentropic compressibility for the binary systems of $[\text{ZnCl}_2][\text{phosphoric acid}]$ in a molar ratio of 1:2.5 with methanol, ethanol, or propanol at various temperatures. The findings are graphically shown in Figure 5.20, illustrating the relationship between the mole fractions of $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 and the corresponding temperatures. Based on the data shown in Figure 5.20, it can be seen that the isentropic compressibility of a solution exhibits a decreasing trend when the concentration of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 with alcohol increases, with the same trend as $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5. The concept of isentropic compressibility pertains to the change in volume of a material in response to variations in pressure under adiabatic conditions [311]. There are indications suggesting that increasing the concentration of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 and $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 with alcohol enhances the solution's resistance to pressure change.

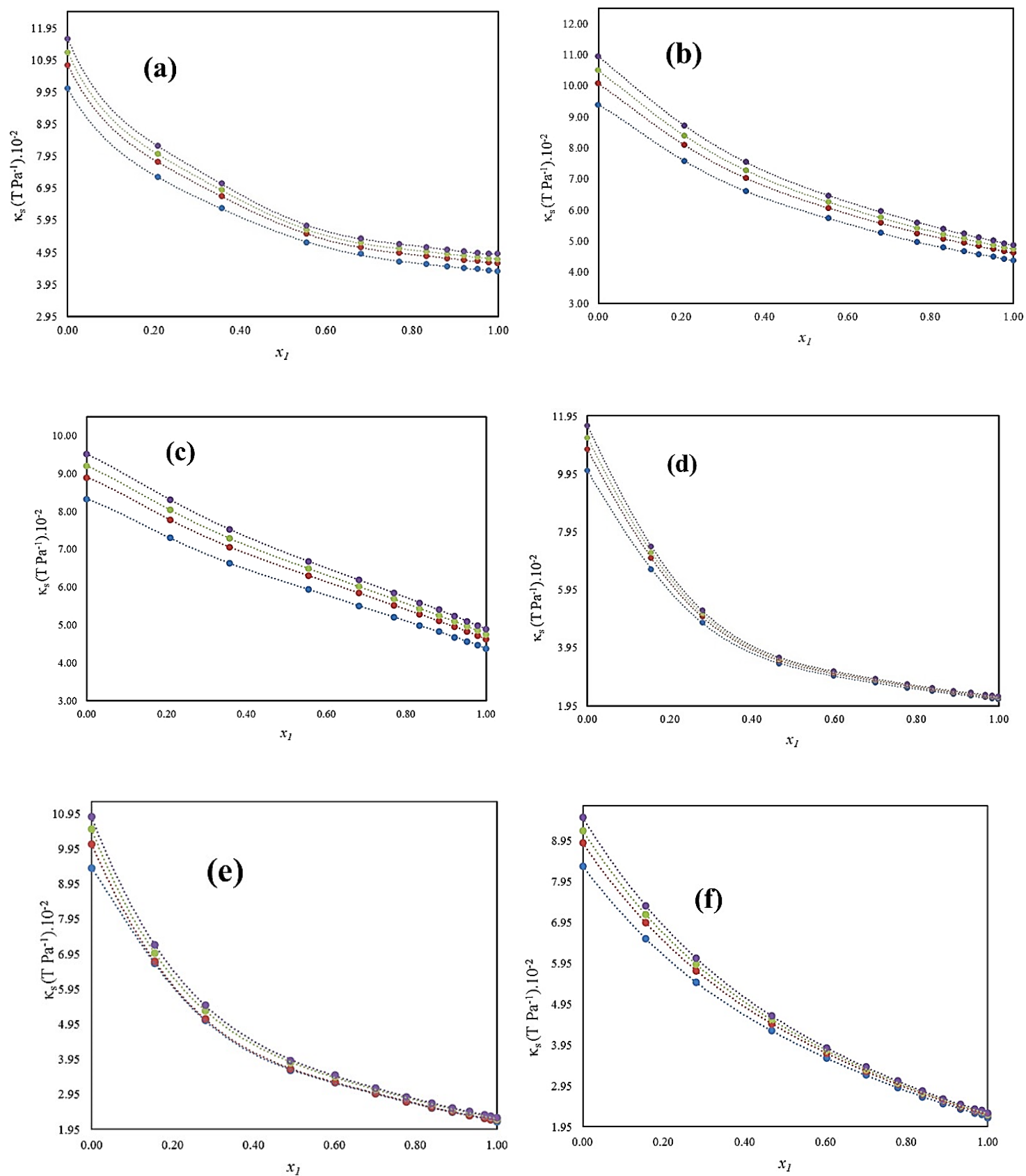


Figure 5.20: Calculated isentropic compressibility, of the binary mixtures of of $\{[\text{ZnCl}_2][\text{acetic acid}] 1:4 + \text{methanol (a), ethanol (b), and propanol (c)}\}$ and $\{[\text{ZnCl}_2][\text{phosphoric acid}] 1:2.5 + \text{methanol$

(d), ethanol (e), and propanol (f)} at 293.15 K (blue), 303.15 K (red), 308.15 K (green), 313.15 K (purple).

The ΔK_s is a measure of the deviation from ideal behavior in a mixture of two or more components. It is defined as the difference between the isentropic compressibility of the mixture and the isentropic compressibility that would be expected if the mixture behaved ideally [14, 15]. Calculated binary combinations exhibited negative values of deviation in isentropic compressibility, as shown in Tables 5.12 and 5.13, and Figure 5.21; however, they changed the sign from negative to positive for mixtures of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 with propanol. A binary mixture exhibits reduced compressibility compared to an ideal mixture under identical temperature and pressure conditions, provided that the deviation in isentropic compressibility is negative [312]. This phenomenon can be attributed to the fact that a mixture exhibiting negative excess isentropic compressibility displays a reduced magnitude of volume change in response to the pressure variations when compared to an ideal mixture [313]. This could also imply that the intermolecular forces between the molecules in the mixture are stronger, resulting in a higher degree of molecular packing compared to the individual components. This phenomenon can occur when the constituents exhibit strong intermolecular forces, thereby diminishing the available volume for compression.

The observed deviation in isentropic compressibility indicates the existence of strong intermolecular forces within the selected alcohols and DES mixtures. The presence of ion-dipole interactions between zinc chloride and alcohol molecules, as well as hydrogen bonding between the carboxyl group of acetic acid, the hydroxyl group of phosphoric acid, and the oxygen atom of the alcohol, may contribute to these interactions [140, 314]. This observation suggests that the concoction comprised these alcohol compounds, leads to a molecular arrangement that exhibits a higher density than anticipated solely from the compressibility characteristics of the individual constituents.

A positive deviation in isentropic compressibility is observed when a mixture exhibits a greater compressibility in contrast to that of an ideal mixture. This behavior is commonly observed in mixtures exhibiting cohesive intermolecular interactions. The effective volume for molecular motion experiences reduction in a mixture wherein intermolecular attractive forces are present among its constituent molecules. Therefore, when the concoction is subjected to adiabatic (without heat exchange) circumstances, the intermolecular forces result in a greater level of compression compared to that of an ideal mixture. A positive excess compressibility value signifies a mixture that exhibits a greater capacity for compression under adiabatic conditions [315]. As a result of the decreased effective volume accessible for the molecules to traverse, the presence of intermolecular forces facilitates the process of compression, as the molecules can readily approach one another in an easier manner.

The introduction of a longer-alkyl-chain alcohol into the DES has the potential to enhance the negative deviation in isentropic compressibility. This is due to the increased flexibility that the longer chain imparts to the DES molecules, thus leading to an expansion of the free volume. However, there is a chance that other factors, such as the formation of hydrogen bonds between the alcohol and DES, will lessen this impact and reduce the amount of space that is available.

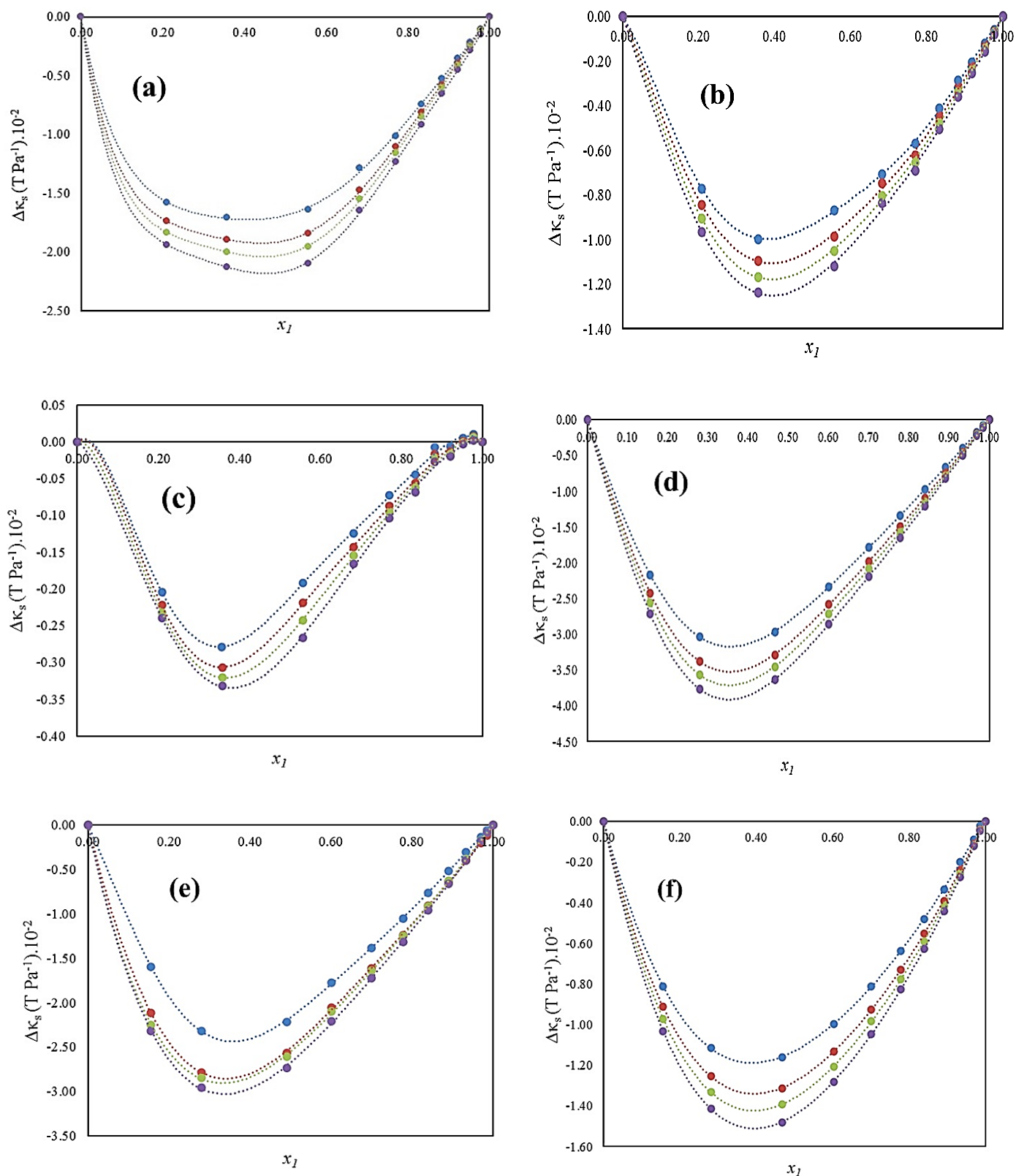


Figure 5. 21: Calculated excess isentropic compressibility, $\Delta\kappa_s$, of the binary mixtures of $\{[\text{ZnCl}_2][\text{acetic acid}] \text{ 1:4} + \text{methanol (a), ethanol (b), and propanol (c)}\}$ and $\{[\text{ZnCl}_2][\text{phosphoric acid}] \text{ 1:2.5} + \text{methanol (a), ethanol (b), and propanol (c)}\}$. Circles represent the experimental data,

while the solid lines were generated using a Redlich-Kister smoothing 6th-order polynomial. Colours: (blue) 293.15 K, (red) 303.15 K, (green) 308.15 K, (purple) 313.15 K.

The intermolecular free length of a binary mixture is a parameter that quantifies the average separation between molecules within the mixture [18]. The term often referred to as the mean-free path denotes the average distance that separates collisions. The calculation of the speed of sound in a mixture is dependent on the mixture's density and compressibility. The intermolecular free length in a binary mixture may be used to ascertain the features that result from the interplay of attracting and repulsive interactions. Additionally, it exhibits a straightforward linear relationship with the mole fraction of the deep eutectic solvent among the distinct molecular species.

The mole fraction of $[\text{ZnCl}_2]$ [acetic acid] 1:4 and $[\text{ZnCl}_2]$ [phosphoric acid] 1:2.5 DESs exhibits an upward trend as the values for intermolecular free length decrease, as shown by the data presented in Tables 5.12 and Table 13 as well as Figure 5.22. The justification for adding more solvent molecules to a mixture is based on the potential enhancement of molecular interactions, leading to increased molecular packing density, and reduced intermolecular distances. The values of intermolecular free length also exhibit an increase with increasing temperatures. This phenomenon may be attributed to the fact that elevated temperatures result in an increase in the molecules' thermal energy, accelerating their motion and expanding their spatial occupation. Consequently, there is an increase in the average intermolecular distance.

The intermolecular free length values of the binary systems exhibit a decreasing trend as the alkyl chain length of the alcohols increases, namely in the order of methanol < ethanol < propanol. This suggests that with an increase in the alkyl chain length of the alcohols, there is a corresponding increase in molecular packing, leading to a reduction in the average distance between neighboring molecules. The observed behavior may be attributed to the rise in hydrophobicity of alcohol molecules as the length of the alkyl chains increases. This enhanced hydrophobicity facilitates stronger interactions between the alcohol molecules and the nonpolar constituents of the deep eutectic solvent. These interactions have the potential to induce a higher degree of molecular packing, leading to a reduction in intermolecular free lengths.

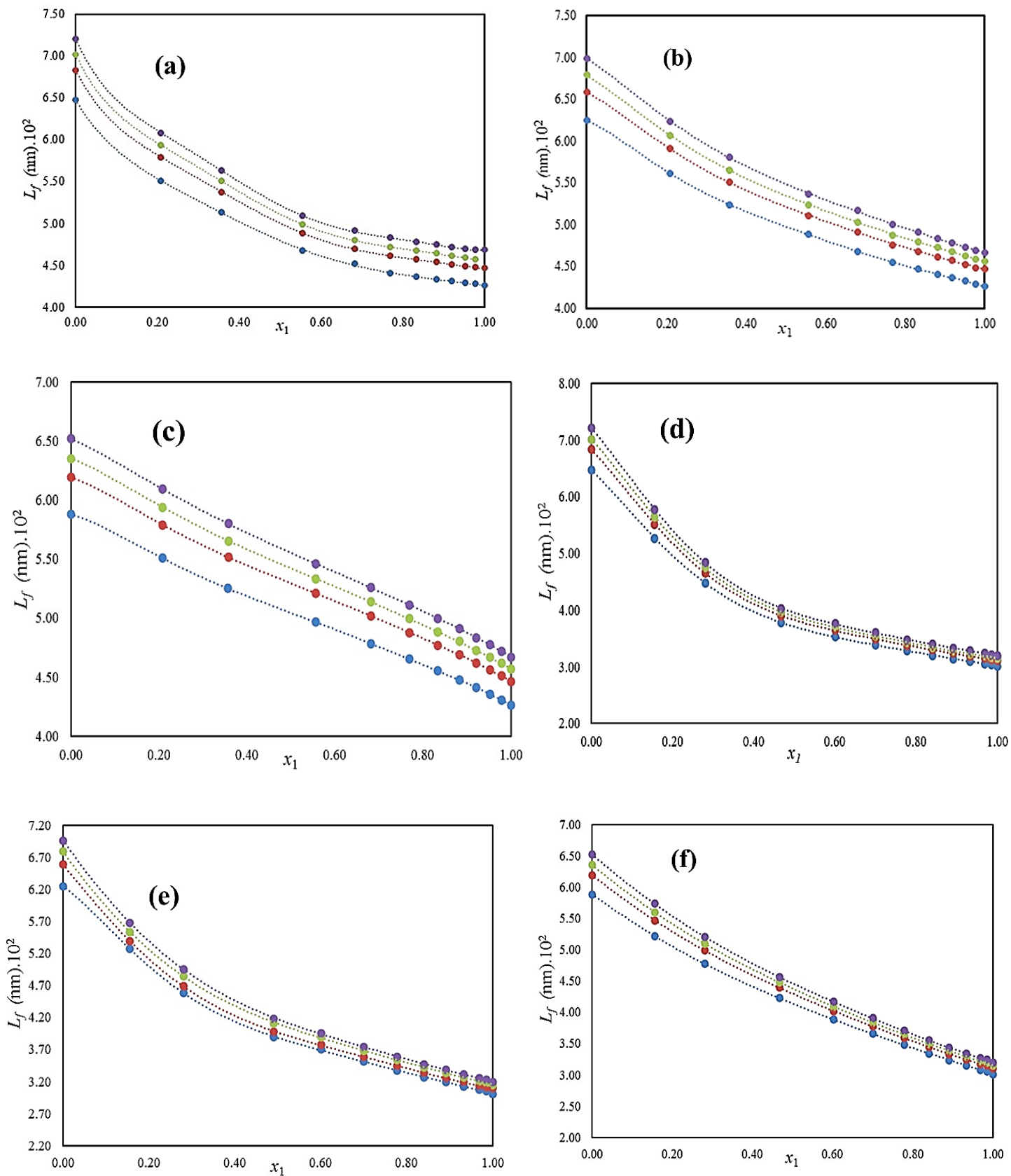


Figure 5.22: Plot of intermolecular free length L_f of the binary mixtures of {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol (a), ethanol (b), and propanol (c)} and {[ZnCl₂][phosphoric acid] 1:2.5 (x_1) +

methanol (d), ethanol (e), and propanol (f)} at 293.15 K (blue), 303.15 K (red), 308.15 K (green), and 313.15 K (purple).

Thermodynamic properties, specifically excess molar volumes and deviations in isentropic compressibility, were systematically determined through the analysis of thermophysical properties such as densities and speed of sound. These thermodynamic properties were then fitted to the Redlich-Kister equation, a widely used polynomial model for representing excess properties in binary systems.

In Tables 5.14 and 5.15, the calculated thermodynamic properties for both binary systems exhibited low standard deviations, indicating a robust correlation between the experimental and fitted values. The application of the Redlich-Kister model successfully captured the non-ideal behavior within the systems, providing a reliable representation of the excess molar volumes and isentropic compressibility deviations. This robust correlation underscores the accuracy and effectiveness of the chosen thermodynamic model in describing the behavior of the studied systems.

Table 5. 14: Redlich-Kister fitting parameters and root-mean-square deviation, σ , for the binary mixtures of {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol, ethanol or propanol (x_2)} at T = (293.15, 303.15, 308.15, and 313.15) K.

	A_i	293.15 K	303.15 K	308.15 K	313.15 K
{[ZnCl ₂][acetic acid] 1:4 (x_1) + methanol (x_2)}					
$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	A_0	-2.931	-2.952	-3.083	-3.175
	A_1	-0.233	-0.230	-0.263	-0.144
	A_2	-1.124	-1.378	-0.957	-1.116
	A_3	-1.365	-1.268	-0.850	-1.203
	A_4	3.578	3.356	2.326	2.548
	σ	0.005	0.004	0.001	0.004
$\Delta\kappa_s / (\text{TPa}^{-1})$	A_0	-684.189	780.341	-811.264	-870.834
	A_1	201.889	163.481	174.858	185.115
	A_2	128.736	70.954	161.760	267.412
	A_3	152.263	544.464	535.290	535.260
	A_4	-968.834	-781.288	-999.280	-1252.360
	A_5	780.341	258.902	407.405	492.432
	σ	1.247	0.162	0.149	0.725
{[ZnCl ₂][acetic acid] 1:4 (x_1) + ethanol (x_2)}					
	A_0	-1.967	-2.033	-2.200	-2.353
	A_1	-1.120	-1.045	-0.864	-0.907

$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	A_2	0.069	-0.223	-0.341	-0.184
	A_3	0.620	0.540	0.622	1.141
	A_4	-1.126	-0.661	-0.903	-1.910
	σ	0.006	0.006	0.004	0.008
	A_0	-366.784	-419.959	-447.580	-478.286
$\Delta\kappa_s / (\text{TPa}^{-1})$	A_1	172.094	216.681	224.609	252.105
	A_2	-277.280	-21.099	-28.854	55.374
	A_3	50.314	-248.261	-212.060	-334.885
	A_4	633.855	36.012	51.381	-161.548
	A_5	-468.842	189.835	136.142	384.958
	σ	0.642	1.429	1.291	1.683
{ZnCl ₂ }[acetic acid] 1:4 (x_1) + propanol (x_2)}					
$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	A_0	-0.760	-0.823	-0.948	-0.887
	A_1	0.450	0.628	0.450	0.513
	A_2	-0.646	-0.777	-0.086	-0.372
	A_3	0.713	0.203	0.434	0.401
	A_4	1.111	1.414	-0.364	0.684
	σ	0.008	0.006	0.006	0.008
$\Delta\kappa_s / (\text{TPa}^{-1})$	A_0	-88.978	-101.050	-111.616	-121.433
	A_1	107.958	115.340	114.059	114.277
	A_2	-52.787	-41.678	14.405	80.007
	A_3	-74.076	-94.329	-120.355	-162.351
	A_4	226.225	211.508	89.920	-46.269
	A_5	-78.702	-63.040	29.698	159.787
	σ	0.498	0.476	0.457	0.434

Table 5. 15: Redlich-Kister fitting parameters and root-mean-square deviation, σ , for the binary mixtures of {[ZnCl₂][phosphoric acid] 1:2.5 (x_1) + methanol, ethanol or propanol (x_2)} at T = (293.15, 303.15, 308.15, and 313.15) K and at 0.1 MPa.

	A_i	293.15 K	303.15 K	308.15 K	313.15 K
{ZnCl ₂ }[phosphoric acid] 1:2.5 (x_1) + methanol (x_2)}					
	A_0	-5.07206	-5.26356	-5.47790	-5.67405
	A_1	1.11783	1.57197	1.86950	1.85065

$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	A_2	3.31712	3.18079	2.85763	2.91990
	A_3	-7.85922	-9.40623	-9.82714	-9.54857
	A_4	-1.50922	-2.02911	-1.34595	-1.78171
	A_5	13.45640	15.3887	15.33090	15.57230
	σ	0.04	0.03	0.03	0.03
	A_0	-1132.500	-1254.040	-1318.250	-1386.930
$\Delta\kappa_s / (\text{TPa}^{-1})$	A_1	858.914	953.387	1007.220	1063.230
	A_2	-224.958	-279.539	-315.135	-346.553
	A_3	-525.784	-523.722	-530.085	-535.836
	A_4	240.408	281.329	319.688	340.506
	A_5	264.726	198.853	178.180	171.008
	σ	0.30	0.20	0.21	0.21
{ZnCl ₂ }[phosphoric acid] 1:2.5 (x_1) + ethanol (x_2)}					
$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	A_0	-6.37255	-6.54092	-6.65878	-6.74921
	A_1	3.62630	3.85315	3.45799	3.63169
	A_2	2.29619	1.42293	0.67025	0.02265
	A_3	-14.29770	-14.46340	-10.92830	-10.54310
	A_4	-3.47987	-2.38689	-1.95530	-0.72741
	A_5	23.50000	23.03660	18.92860	16.74900
$\Delta\kappa_s / (\text{TPa}^{-1})$	σ	0.04	0.03	0.03	0.03
	A_0	-869.944	-967.325	-1026.040	-1075.680
	A_1	689.901	758.244	788.543	815.719
	A_2	-179.625	-222.794	-277.463	-260.598
	A_3	-637.011	-672.840	-346.946	-392.202
	A_4	282.290	432.633	-165.468	-171.300
$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	A_5	361.356	215.931	541.947	568.046
	σ	0.75	0.84	0.97	0.98
{ZnCl ₂ }[phosphoric acid] 1:2.5 (x_1) + propanol (x_2)}					
$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	A_0	-7.44748	-7.81260	-8.04266	-8.38092
	A_1	4.04380	4.08689	4.06453	4.39982
	A_2	2.44647	3.32402	2.71992	2.49836
	A_3	-19.95160	-19.94770	-18.16330	-18.41450
	A_4	-4.69736	-7.43701	-7.61441	-8.34188
	A_5	28.52820	29.84090	27.68890	28.32440

	σ	0.08	0.07	0.07	0.06
	A_0	-452.966	-513.048	-544.757	-578.875
	A_1	211.866	225.124	236.304	251.020
	A_2	-75.668	-74.705	-81.628	-84.082
$\Delta\kappa_s / (\text{TPa}^{-1})$	A_3	-130.578	-109.677	-106.056	-119.775
	A_4	11.465	-13.902	-15.678	-23.425
	A_5	185.052	151.786	151.223	172.576
	σ	0.80	0.58	0.58	0.54

The parameters necessary for modeling alcohols in PC-SAFT were acquired from the literature [241]. When dealing with DESs, considered a pseudo-pure fluid, the parameters were adjusted only with experimental den

$$FO = \sum_{i=1}^{n_p} \left(\frac{\rho_i^{calc.} - \rho_i^{exp.}}{\rho_i^{exp.}} \right)^2 \quad (5.1)$$

sities, utilizing the objective function as defined in equation 5.1:

where n_p is the number of experimental points, ρ is the density, *calc.* is calculated using PC-SAFT EoS, and *exp.* is experimental. On the other hand, the absolute average deviation was calculated as equation 5.2:

$$\%AAD\varphi = \frac{100}{n_p} \sum_{i=1}^n \frac{|\varphi_i^{exp.} - \varphi_i^{calc.}|}{\varphi_i^{exp.}} \quad (5.2)$$

where φ is density or speed of sound. The fitted parameters of the alcohols were obtained from the literature [241]. The parameters for $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 were fitted in this work, and we have obtained: $m = 2.8419$, $\sigma = 3.0000 \text{ \AA}$, $\frac{\varepsilon}{k_B} = 299.9681 \text{ K}$, $\kappa^{AB} = 0.0296$, and $\frac{\varepsilon^{AB}}{k_B} = 2023.8457 \text{ K}$. The absolute average deviation in density was 0%.

The parameters obtained in $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 were $m = 2.100$, $\sigma = 3.5436 \text{ \AA}$, $\frac{\varepsilon}{k_B} = 772.4355 \text{ K}$, $\kappa^{AB} = 0.003297$, and $\frac{\varepsilon^{AB}}{k_B} = 4276.8451 \text{ K}$. The absolute average deviation in density was 0.05%.

Table 5.16 presents the binary interaction parameters along with the absolute average deviations for density and speed of sound. The PC-SAFT EoS yielded highly satisfactory results with an overall

deviation of 0.27% for density. Nomoto's relation accurately predicted the speed of sound with an overall deviation of 1.05%.

Table 5. 16: Fitted binary parameters and the absolute average deviation for liquid density and speed of sound for {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol, ethanol or propanol (x_2)} in the temperature range of 293.15 K to 313.15 K and at 0.1 MPa.

Mixture	k_{ij}	%AAD ρ	%AAD u
[ZnCl ₂][acetic acid] 1:4 (1) + methanol (2)	0.0094	0.26	1.84
[ZnCl ₂][acetic acid] 1:4 (1) + ethanol (2)	0.0109	0.19	0.89
[ZnCl ₂][acetic acid] 1:4 + 1- propanol (2)	-0.0371	0.36	0.41
Overall		0.27	1.05

The positive values for k_{ij} can be found in Table 5.17 for all the mixtures. Table 5.17 also provides information on the deviation in density and speed of sound using the SCFT and NR methods. Based on the findings, it can be observed that PC-SAFT successfully correlates the experimental densities with the mole fraction, with an overall deviation of 0.27%. Regarding the speed of sound, both equations accurately predict the experimental data. However, in the case of the binary mixtures comprising [ZnCl₂][phosphoric acid] 1:2.5 + 1-propanol, the NR method (with a deviation of 0.32%) demonstrates a lower error compared to the SCFT method (with a deviation of 1.99%), despite its relative simplicity.

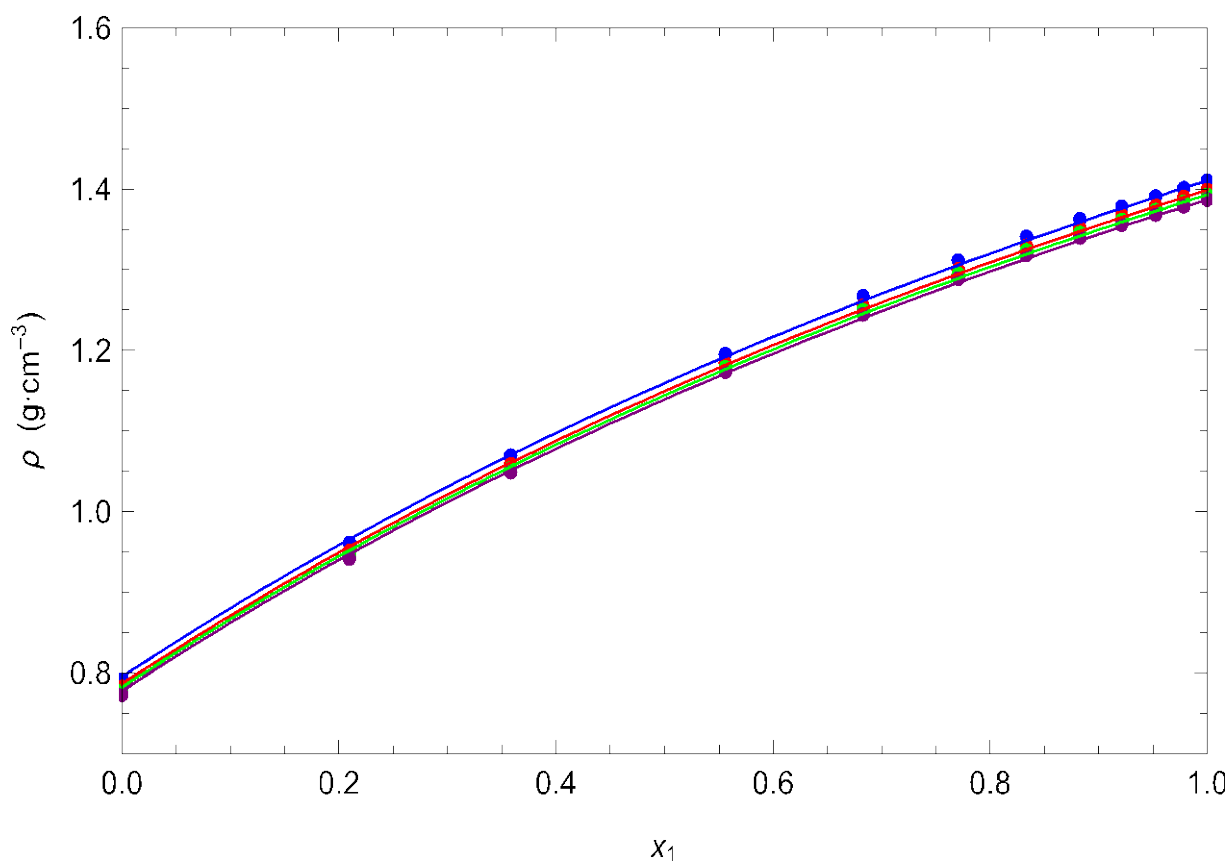
Table 5. 17: Binary parameters and absolute average deviation for liquid densities and speed of sound for {[ZnCl₂][phosphoric acid] 1:2.5 (x_1) + methanol, ethanol or propanol (x_2)} in the temperature range of 293.15 K to 313.15 K and at 0.1 MPa.

Mixture	k_{ij}	%AAD ρ	%AAD u	
			PC-SAFT + SCFT	PC-SAFT + NR
[ZnCl ₂][phosphoric acid] 1:2.5 (1) + methanol (2)	0.3521	0.18	0.62	1.63
[ZnCl ₂][phosphoric acid] 1:2.5 (1) + ethanol (2)	0.2552	0.31	0.74	2.01

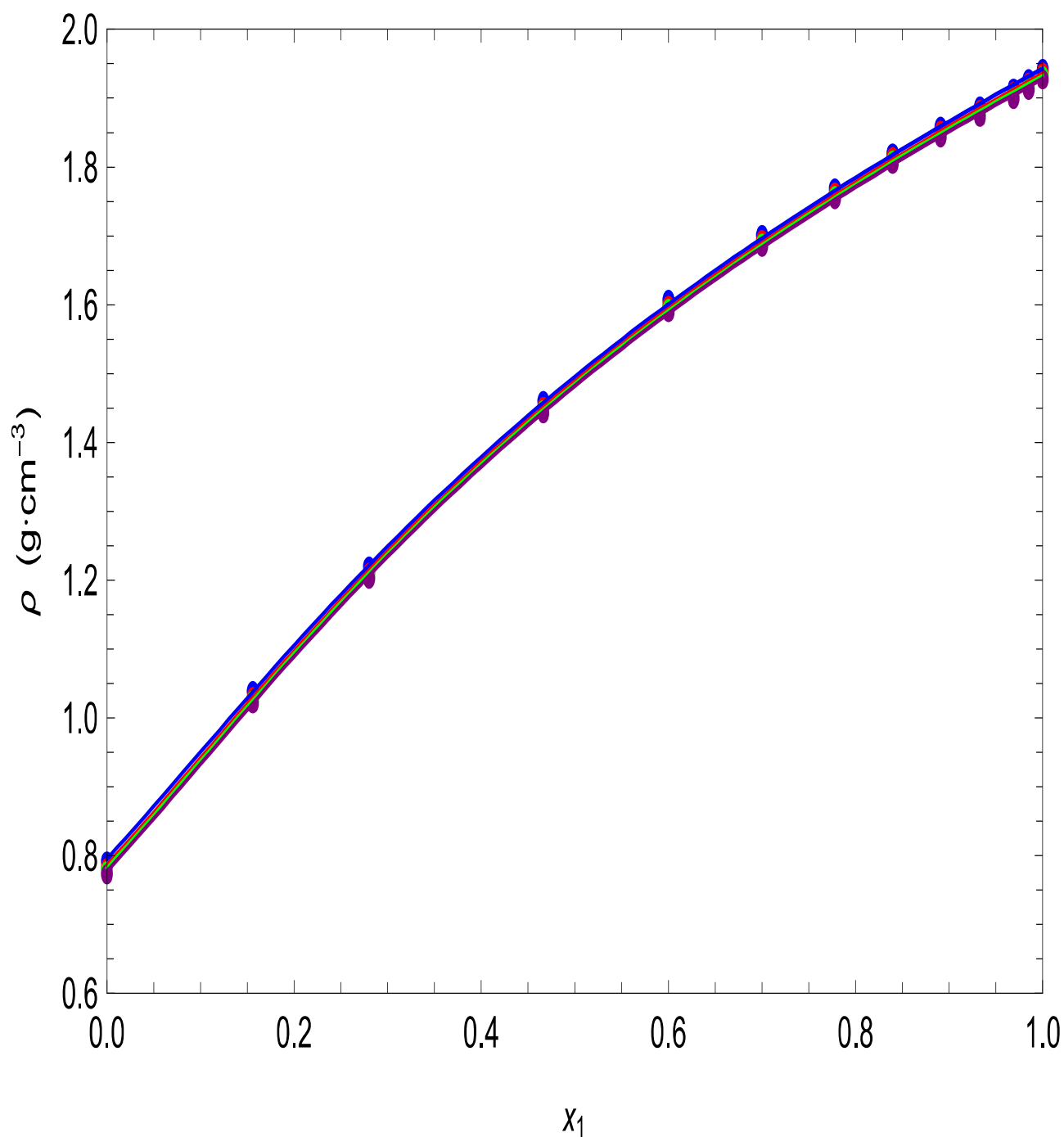
[ZnCl ₂][phosphoric acid] 1:2.5 (1) + 1-propanol (2)	0.0775	0.32	1.99	0.32
Overall	0.27		1.12	1.32

Figures 5.23 and 5.24 depict the variation of density and speed of sound as a function of the mole fraction of DES for the [ZnCl₂][acetic acid] 1:4 DES (1) + methanol (2) mixture and [ZnCl₂][acetic acid] 1:4 DES (1) + ethanol (2) mixture, respectively. In figure 5.23, the experimental and theoretical density data exhibit strong agreement. On the other hand, Figure 5.24 illustrates that the speed of sound, as predicted by Nomoto's relationship, consistently increases across the entire range of mole fractions.

Finally, some graphic results are illustrated in Figures 5.23 and 5.24. As depicted in Figure 5.23, the results with $k_{ij} = 0.3521$ for [ZnCl₂][phosphoric acid] 1:2.5 + methanol systems, showing good results in correlation of the densities. From Figure 5.23, the most effective experimental speed of sound correlation for the DES + ethanol mixture was achieved using the PC-SAFT EoS + SCFT approach.

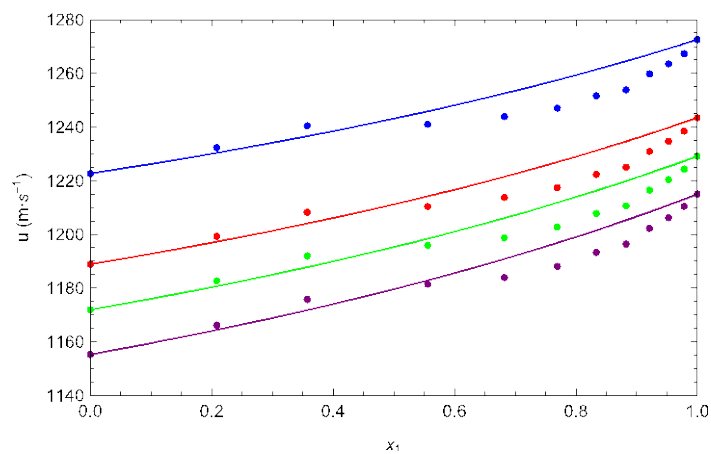


(a)

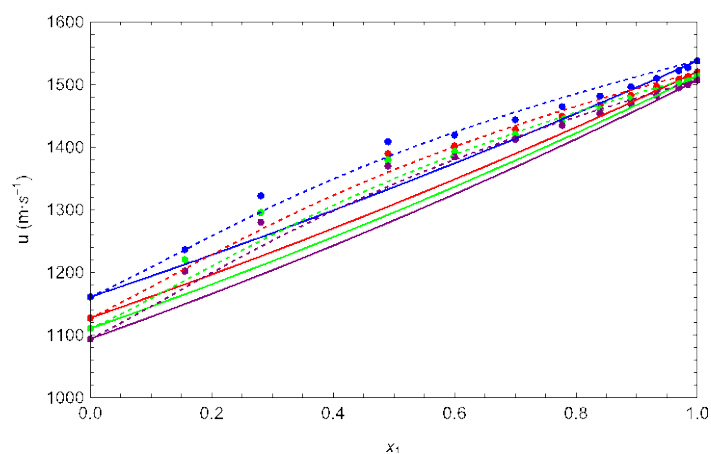


(b)

Figure 5.23: Plot of the densities for the (a) {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol (x_2)} and (b) {[ZnCl₂][phosphoric acid] 1:2.5 + methanol} at different temperatures as a function of the composition expressed in the mole fraction at 293.15 K (blue), 303.15 K (red), 308.15 K (green), and 313.15 K (purple). The lines were generated using PC-SAFT EoS.



(a)



(b)

Figure 5. 24: Plot of the speed of sound for the (a) {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol (x_2)} and (b) {[ZnCl₂][phosphoric acid] 1:2.5 (x_1) + ethanol (x_2)} at different temperatures as a function of the composition expressed in the mole fraction of [ZnCl₂][phosphoric acid] at 293.15 K (blue), 303.15 K (red), 308.15 K (green), and 313.15 K (purple). The continuous lines are results obtained with PC-SAFT + NR, and the segmented lines are results obtained with PC-SAFT + SCFT.

CONCLUSION AND RECOMMENDATIONS

The primary goal of this research was to perform experimental analysis aimed at exploring the separation capabilities, intermolecular interactions, and impact of temperature in DES mixtures when combined with volatile organic solvents. The intermolecular interactions were further characterized by calculating thermodynamic properties under conditions of infinite dilution, including enthalpies, entropies, and Gibbs free energies. The research focused on addressing separation challenges by evaluating selectivity and capacity.

This study initially screened four DESs for potential industrial use in extraction processes, which were as follows:

- [ZnCl₂][acetic acid] at a ratio of 1:2
- [ZnCl₂][acetic acid] at a ratio of 1:4
- [ZnCl₂][phosphoric acid] at a ratio of 1:2
- [ZnCl₂][phosphoric acid] at a ratio of 1:2.5

To obtain solute retention time and calculate the infinite dilution activity coefficient, gas-liquid chromatography employed for 34 polar and non-polar organic solutes in the DESs at five different temperatures under atmospheric pressure.

The calculated γ_{13}^{∞} values indicated that non-polar solutes had low solubility in DESs compared to polar solutes, suggesting stronger interactions between the solute and DES for polar solutes. Additionally, partial molar excess enthalpies for the same solutes by examining the temperature dependence of $\ln \gamma_{13}^{\infty}$, were computed and discussed these results in terms of molecular interactions.

Regarding the separation performance, the findings showed that [ZnCl₂][Acetic acid] (1:2) exhibited higher selectivity and capacity results for benzene/ethanol, cyclohexane/ethanol, and octane/acetonitrile systems, indicating its potential for industrial separation processes. On the other hand, the [zinc chloride + acetic acid] 1:4 exhibits better separation performance for benzene/ethanol, cyclohexane/ethanol, ethylbenzene/butanol, and heptane/butanol. However, [ZnCl₂][Phosphoric acid] (1:2 and 1:2.5) emerged as the most promising solvent for replacing conventional solvents due to its superior separation parameters (capacities and selectivity's) for components with close boiling points.

Despite the promise of the DESs based on phosphoric acid, there are certain challenges, such as corrosion caused by phosphoric acid in some industrial applications, that might limit its suitability for solving industrial separation problems.

Additionally, the study explored the molecular interactions between DESs and various alcohols. These DESs consisted of:

- $[\text{ZnCl}_2][\text{acetic acid}]$ in a 1:4 ratio with methanol, ethanol, or propanol.
- $[\text{ZnCl}_2][\text{phosphoric acid}]$ in a 1:2.5 ratio with methanol, ethanol, or propanol.

The research focused on determining the thermophysical properties of these binary mixtures of $[\text{ZnCl}_2][\text{phosphoric acid}]$ or $[\text{ZnCl}_2][\text{acetic acid}]$ with methanol, ethanol, and propanol at different temperatures (293.15, 303.15, 308.15, and 313.15) K. To confirm the occurrence of intermolecular interactions within these mixtures, various thermodynamically relevant parameters such as density and speed of sound were used to calculate parameters like, V_m^E , K_S , ΔK_S , and L_f .

For $[\text{ZnCl}_2][\text{acetic acid}]$ with methanol and ethanol, negative excess molar volumes were observed across all compositions and temperature ranges, indicating strong intermolecular interactions between dissimilar molecules. However, negative and positive excess molar volumes were found for $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 mixed with propanol and $[\text{ZnCl}_2][\text{phosphoric acid}]$ with methanol, ethanol, or propanol at higher mole fractions, suggesting volume expansion and the disruption of hydrogen bonds in self-associated alcohol molecules.

The excess molar volumes for the 1:4 ratio of $[\text{ZnCl}_2][\text{acetic acid}]$ with methanol or ethanol consistently showed negative values across the range of temperatures studied. However, the excess molar volumes transitioned from negative to positive when these mixtures were combined with propanol and in $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 binary systems.

The study further highlighted that ion-solvent and solute-solvent interactions dominated over self-interactions, such as solvent-solvent and ion-ion or solute-solute interactions. Additionally, temperature had a significant impact on all investigated thermodynamic parameters, as their values (including V_m^E , K_S , ΔK_S , and L_f) were found to either decrease or increase with rising temperature. Redlich-Kister smoothing expression was effectively employed to correlate excess molar volumes and deviation in isentropic compressibility calculated in the study and found good correlation. Additionally, the calculated combinations displayed negative deviations in isentropic compressibility for $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 with methanol or ethanol, and $[\text{ZnCl}_2][\text{phosphoric acid}]$ 1:2.5 with methanol, ethanol, and propanol. Notably, this sign change from negative to positive was observed in mixtures of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 with propanol. PC-SAFT EoS was employed to simulate

[ZnCl₂][phosphoric acid] 1:2.5 and [ZnCl₂][acetic acid] 1:4 DESs along with alcohol using a 2B scheme. The [ZnCl₂][phosphoric acid] 1:2.5 DES parameters, which were successfully determined as a pseudo-pure fluid were successfully obtained with a deviation of 0.05% for the density. When considering the overall deviation in density of the mixtures, it was 0.27% using PC-SAFT EoS. The most accurate prediction for the speed of sound was achieved with SCFT, with an overall deviation of 1.12%. Parameter fitting was performed for each mixture, and the selection of Nomoto's relation proved highly suitable for predicting the speed of sound, with an overall deviation of 1.05%.

Research on the infinite dilution activity coefficients and thermo-physical properties of DES mixtures is an active and evolving field. While significant progress has been made, there are still several gaps and areas where further research is needed. Some of these include:

- **Expanded database:** A broader database of experimental data for infinite dilution activity coefficients and thermo-physical properties of DES mixtures is needed. Many DESs are novel and unique, and more data is essential to better understanding their behavior.
- **DES composition effects:** Research should delve deeper into how the composition of DES mixtures affects their infinite dilution activity coefficients and thermo-physical properties. Understanding how different components interact and influence these properties is crucial for designing and optimizing DESs for various applications.
- **Temperature dependency:** Most experimental data available focuses on a limited temperature range. Investigating the temperature-dependent behavior of DES mixtures is vital in predicting their performance under different conditions and improving their thermodynamic models.
- **Solvent-solute interactions:** More research is needed to understand the specific interactions between solutes and the constituents of DESs. This includes both experimental and computational studies to provide insights into the molecular-level mechanisms governing solute-DES interactions.
- **Predictive models:** Developing accurate predictive models for infinite dilution activity coefficients and thermo-physical properties of DES mixtures would be highly valuable. These models should consider not only composition and temperature but also the influence of impurities and trace components that can affect DES properties.
- **Application-based research:** It is very important to learn more about how infinite dilution activity coefficients and thermophysical properties affect certain DES applications. This can include studies on their use as solvents, extractants, electrolytes, and more in various fields such as green chemistry, energy storage, and separation processes.

- **Safety and environmental impact:** Research should also address the safety and environmental aspects of DESs. This includes evaluating the toxicity and biodegradability of DES mixtures, which are crucial considerations for their practical use.
- **Standardization:** Establishing standardized experimental procedures and reporting guidelines for measuring infinite dilution activity coefficients and thermo-physical properties of DES mixtures would facilitate data comparison and promote consistency in research findings
- **Scale-up studies:** Conducting studies on a larger scale to assess the feasibility of using DES mixtures in industrial applications are necessary. This includes evaluating their performance, stability, and cost-effectiveness under practical conditions.

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