



Correlation and modelling the thermodynamics properties of mixtures containing zinc (II) chloride-based deep eutectic solvent and alkanols with PC-SAFT EoS, and the Nomoto's relation

Ncomeka Mgxadeni^a, Ariel Hernández^b, Indra Bahadur^{a,*}, Faruq Mohammad^c, Ahmed Abdullah Soleiman^d

^a Department of Chemistry, Faculty of Natural and Agricultural Sciences, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^b Departamento de Ingeniería Industrial, Facultad de Ingeniería, Universidad Católica de la Santísima Concepción, Alonso de Ribera 2850, Concepción, Chile

^c Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

^d Department of Chemistry, Southern University and A&M College, Baton Rouge, LA 70813 USA

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ABSTRACT

In this work, the thermophysical characteristics of binary mixtures including alkanols and a deep eutectic solvent (DES) based on zinc (II) chloride (ZnCl_2) were examined. Densities (ρ), and speed of sounds (u) of binary mixtures of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 with methanol, ethanol, and propanol were measured at temperature between (293.15—313.15) K and at atmospheric pressure. DESs have attracted a lot of researchers because of their unique properties and prospective uses in various fields. The focus of this research was to better understand the behaviour of binary mixtures composed of ZnCl_2 -based DES and alkanols, with an emphasis on their thermophysical properties. Thermodynamic properties such as excess molar volumes, isentropic compressibilities, deviations in isentropic compressibilities, and intermolecular free length were evaluated and interpreted in terms of molecular interactions occurring in the mixtures. The excess molar volumes and deviation in isentropic compressibility of the mixture containing $[\text{ZnCl}_2][\text{acetic acid}]$ with methanol and ethanol were seen to be negative across all compositions and temperatures. Conversely, positive excess molar volumes were observed for the mixture containing $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 with propanol. The isentropic compressibility values demonstrate a direct relationship with the increase in temperature while maintaining a consistent composition throughout all examined binary mixtures. The intermolecular free length values also demonstrate a positive correlation with increasing temperatures. To deepen our comprehension, we used the Redlich-Kister equation with temperature-dependent parameters to establish a correlation between excess molar volumes and variations in compressibilities. This enabled us to gain valuable knowledge on the thermodynamic characteristics and mixing properties shown by these binary systems. Finally, the density of the mixtures composed of DES and 1-alkanol was correlated with PC-SAFT EoS, and Nomoto's relation was successfully used for the modelling of speed of sound as a predictive approach. This approach enhances the applicability of the findings in practical scenarios. This investigation not only enhances the fundamental comprehension of ZnCl_2 -based DES and alkanol combinations but also provides practical perspectives on their thermophysical characteristics, which may have implications for their potential implementation in diverse industrial sectors. The work presents novel discoveries and correlations, expanding the knowledge base in this domain. These findings contribute to the broader understanding of DES and alkanol mixtures, offering valuable insights for researchers and practitioners alike.

1. Introduction

Science and engineering use thermophysical properties to understand and predict the behaviour of materials and substances in many

different applications, ranging from heat transfer and fluid mechanics to material science [1,2]. These physical properties of a substance explain its behaviour in response to changes in temperature, pressure, or composition.

* Corresponding author.

E-mail address: bahadur.indra@nwu.ac.za (I. Bahadur).

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When these two types of compounds combine, they form binary mixtures that have distinct thermophysical characteristics. Thermophysical characteristics of DESs include certain crucial elements such as melting point, viscosity, density, thermal stability, heat capacity, and solubility [3]. Typically, DESs have lower melting points than their components, hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) [4]. The eutectic mixture forms a eutectic point, which is the composition at which the mixture has the lowest melting point. It is this property that allows DESs to be in a liquid state at room temperature or lower. DESs have greater viscosities than typical organic solvents. The strong hydrogen bonding interactions between the HBD and HBA components are responsible for the high viscosity [5]. The viscosity of DESs, on the other hand, may be modified by altering the composition or adding other components. The density of DESs changes according to the type of HBD and HBA used, as well as their concentrations [6] and is higher than that of ordinary organic solvents but lower than that of water [3]. Solubility and buoyancy are two qualities that may be affected by density. DESs are usually thermally stable across a large temperature range and can endure high temperatures without substantial degradation or decomposition, making them appropriate for high-temperature applications [7]. The type of HBD and HBA components, as well as their concentrations, impact the heat capacity of DESs [8]. When compared to organic solvents, DESs frequently have greater heat capabilities, which might be useful in heat transfer applications. DESs possess unique solvation properties due to their ionic nature and hydrogen bonding capabilities [8] and provide ideal solvents for a variety of applications since they can dissolve a large variety of molecules, including both polar and non-polar. For the development of new applications and the optimization of existing processes, it is crucial to understand these properties.

A new class of ionic liquids called Zinc (II) Chloride-Based DESs is created by combining a metal salt, such as Zinc (II) Chloride, with a hydrogen bond donor, such as primary alcohols, organic acids, or amides [9]. As per the literature, DESs have attracted attention because of their distinctive thermophysical characteristics and potential uses in a variety of fields, including chemical engineering, materials science, energy storage, separation science, catalysis, and electrochemistry [10]. DESs are a possible replacement for conventional organic solvents due to their outstanding solvation characteristics, low toxicity, and biodegradability. It has been noted that the DES $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4, which combines zinc chloride and acetic acid, has high solubility for a variety of organic molecules [10].

Alkanols, on the other hand, are organic molecules with a hydroxyl ($-\text{OH}$) group linked to an alkyl chain [11]. These compounds are widely employed as solvents because of their ability to dissolve a wide range of polar and nonpolar molecules. Alkanols are used in a variety of applications, including solvents, fuels, and the synthesis of compounds such as esters and ethers [12,13]. They are widely employed in the manufacture of beverages with alcohol, as well as antiseptics and disinfectants.

To the best of our knowledge, no thermophysical properties: density and speed of sound for the studied binary systems $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 with methanol, ethanol, and propanol have been measured at different temperatures ranging from 293.15 to 313.15 K and at atmospheric pressure. Furthermore, thermophysical properties were used to calculate excess molar volumes, isentropic compressibilities, deviations in isentropic compressibilities, and intermolecular length. The computed thermodynamic properties, such as excess molar volumes and deviations in isentropic compressibilities, have been effectively fitted to the Redlich-Kister equation [14]. Finally, density and speed of sound data have been modelled using PC-SAFT EoS and Nomoto's relation, respectively.

2. Experimental

2.1. Chemicals and materials

All the chemicals used in this study are analytical reagent grade and were obtained from Sigma-Aldrich; the results are shown in Table 1. The analysis of samples was conducted using Karl Fisher titration (831 Metrohm). The methanol exhibited a water content of 0.0003 mass percentage, while ethanol showed 0.0008, propanol had 0.0005, and acetic acid displayed 0.033 (Table 1). To avoid compositional variations due to solvent evaporation, all samples were prepared just before measurements. In the preparation of any of the sample mixtures, no additional purification procedures were used. All the solvents' purity was determined by comparing our previous measurements of densities and speed of sound (Table 2).

2.2. Apparatus and procedure

Our previous study described the preparation and formation of $[\text{ZnCl}_2][\text{acetic acid}]$ 1:4 DES [10]. The DSA 5000 M method's experimental procedure for determining the density and speed of sounds has been thoroughly explained in the literature [15–19]. The masses of the binary mixture components were measured via an OHAUS analytical balance with a precision of 0.0001 g. The pure liquids were placed in shelled vials to avoid evaporation during the preparation of the binary mixtures. Subsequently, the mixtures were shaken to ensure that all the samples were properly mixed. Binary mixtures were passed between two piezoelectric ultrasound transducers to measure sound velocity. The first transducer sends sound waves into the cavity filled with the sample, and the second transducer picks up those waves. The transducer generates a frequency of about 3 MHz. A temperature regulator built into the DSA-5000 M keeps the samples at a set temperature with a 0.02 K margin of uncertainty [20]. The outcomes are automatically preserved and exhibited on the TFT LCD on the apparatus. The apparatus facilitates the immediate printing and exportation of result data files through the utilization of a USB flash drive. A duly certified standard liquid was employed in the calibration of the instrument, and the outcomes were compared with a calibration certificate for the standard liquid, which encompassed a reference value. The density (ρ) and sound velocity (u) measurements of water were obtained after a series of measurements of the sample mixtures, which were conducted to ascertain the precision and reliability of the ρ and u measurements. Anton Paar's ISO 17025 calibration ensures the precise traceability of our apparatus to the International System of Units (SI). The establishment of traceability is the sole means by which one can ascertain the global comparability and accuracy of one's measurement outcomes. The uncertainties were estimated for density and speed of sound measurements within $0.0009 \text{ g}\cdot\text{cm}^{-3}$ and $2.63 \text{ m}\cdot\text{s}^{-1}$, respectively.

Table 1
Molecular mass, Suppliers, CAS number, and purity of chemicals.

Chemical name	Molecular mass (g/mol)	Supplier	Water content/%	CAS number	Mass fraction purity
Zinc chloride	136.30	Merck		7646-85-7	≥ 0.99
Acetic acid	60.05	Sigma-Aldrich	0.033	64-19-7	≥ 0.99
Methanol	32.04	Sigma-Aldrich	0.0003	67-56-1	≥ 0.99
Ethanol	46.07	Sigma-Aldrich	0.0008	64-17-5	≥ 0.99
Propanol	60.1	Sigma-Aldrich	0.0005	71-23-8	≥ 0.99

Table 2
Comparison of experimental and literature density, ρ , and speed of sound, u , of pure components at T = (293.15, 303.15, 308.15, 313.15, and 313.15) K.

T (K)	ρ (g cm ⁻³)		u (m s ⁻¹)	
	expt	Lit	expt	lit
Methanol				
293.15	0.7916	0.7961 [46]	1119.60	1119.00 [46]
		0.7913 [47]		1119.13 [47]
		0.7936 [48]		1106.63 [48]
		0.7914 [49]		
		0.7930 [44]		
		0.7926 [50]		1105.19 [50]
		0.7910 [51]		1119.60 [51]
		0.7912 [52]		
		0.7910 [53]		1120.00 [53]
		0.7819 [49]		
303.15	0.7822	0.7819 [47]	1087.20	1086.00[47]
		0.7819 [54]		1086.00[54]
		0.7846 [48]		1082.73 [48]
		0.7837 [50]		1088.73 [50]
		0.7824 [18]		1092.29 [18]
		0.7827 [55]		1088.26 [55]
		0.7836 [44]		
		0.7810 [56]		1085.89 [56]
		0.7820 [51]		1086.60 [51]
		0.7818 [52]		
308.15	0.7776	0.7820 [53]	1071.07	1087.00 [53]
		0.7772 [49]		
		0.7772 [47]		1069.70 [47]
		0.7779 [48]		1068.82 [48]
		0.7769 [50]		1070.82 [50]
		0.7771 [54]		1069.00 [54]
		0.7776 [18]		1077.90 [18]
		0.7779 [55]		1072.04 [55]
		0.7773 [56]		1074.00 [56]
		0.7771 [52]		
313.15	0.7727	0.7741 [44]	1055.00	
		0.7724 [47]		1053.57 [47]
		0.7724 [48]		1059.41 [48]
		0.7720 [51]		1054.20 [51]
		0.7725 [54]		1052.00 [54]
		0.7729 [18]		1065.03 [18]
		0.7732 [55]		1055.91 [55]
		0.7728 [56]		1052.00 [56]
		0.7723[52]		
		773.00 [53]		1055.00 [53]
Ethanol				
293.15	0.7896	0.7894 [57]	1160.37	
		0.7897 [47]		1161.00 [47]
		0.7894 [48]		1159.34 [48]
		0.7895 [49]		
		0.7895 [50]		1161.38 [50]
		0.7895 [58]		1162.30 [58]
		0.7895[44]		
		0.7896 [51]		1162.30 [51]
		0.7895[52]		
		0.7900 [53]		1162.00 [53]
303.15	0.7810	0.7808 [57]	1126.91	
		0.7810 [47]		1126.77 [47]
		0.7820 [48]		
		0.7808 [49]		
		0.7820 [50]		1129.01 [50]
		0.7810 [54]		1127.00 [54]
		0.7809 [58]		1128.90 [58]
		0.7810 [59]		
		0.7820 [60]		1128.00 [60]
		0.7809 [44]		
308.15	0.7723	0.7810 [51]	1109.94	1128.20 [51]
		0.7807 [52]		
		0.7810 [53]		1127.00 [53]
		0.7820 [56]		1128.00 [56]
		0.7764 [57]		
		0.7767 [47]		1109.87 [47]
		0.7778[50]		1099.74 [50]

Table 2 (continued)				
T (K)	ρ (g cm ⁻³)		u (m s ⁻¹)	
	expt	Lit	expt	lit
313.15	0.7701	0.7755 [54]	1093.40	1109.00 [54]
		0.7777 [60]		1098.00[60]
		0.7764 [52]		
		0.7777 [56]		1098.00 [56]
		0.7720 [57]		
		0.7723 [47]		1093.11[47]
		0.7732 [48]		1090.92 [48]
		0.7722 [49]		
		0.7732 [50]		1093.11 [50]
		0.7723 [54]		1089.00 [54]
		0.7722 [58]		1095.40 [58]
		0.7722 [59]		
		0.7736 [60]		1086.00 [60]
		0.7722 [44]		
		0.7720 [51]		1094.50 [51]
Propanol	0.8036	0.7721 [52]	1222.69	1094.00 [53]
		0.7720 [53]		1086.00 [56]
		0.7736 [56]		
		0.8036 [61]		
		0.8036 [47]		1223.12 [47]
		0.8037[50]		1196.64 [50]
		0.8038 [57]		
		803.75 [49]		
		0.8030 [62]		1224.30 [62]
		0.8039 [59]		
		0.8039 [44]		
		0.8036 [52]		
		0.8040 [53]		1226.00 [53]
		0.7955 [63]		
303.15	0.7956	0.7956 [47]	1188.88	1188.64 [47]
		0.7960 [55]		1189.26 [55]
		0.7956 [61]		
		0.7956 [57]		
		0.7957 [50]		1185.89 [50]
		0.7955 [49]		
		0.7960 [62]		1189.90 [62]
		0.7958 [44]		
		0.7956 [52]		
		0.7960 [53]		1191.00 [53]
		0.7915 [61]		
308.15	0.7916	0.7915 [47]	1171.93	1171.64 [47]
		0.7905 [50]		1170.01 [50]
		0.7919 [55]		1172.37 [55]
		0.7915 [57]		
		0.7915 [52]		
		0.7874 [63]		
313.15	0.7875	0.7874 [47]	1155.23	1154.88 [47]
		0.7874 [50]		1159.51 [50]
		0.7878 [55]		1155.53 [55]
		0.7874 [61]		
		0.7874 [57]		
		787.42 [49]		
		0.7880 [62]		1156.00 [62]
		0.7874 [59]		
		0.7876 [44]		
		0.7874 [52]		
		0.7880 [53]		1157.00 [53]

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 $U_c(x) = 0.0006$, $U_c(\rho) = 0.0009$ g cm⁻³, $U_c(u) = 2.63$ m s⁻¹, respectively (0.95 level of confidence).

2.3. Modelling of density and speed of sound

Gross and Sadowski proposed the PC-SAFT EoS [21,22] over twenty years ago. This equation of state proposes that the Helmholtz energy of the system is given by a sum of four terms: contribution for ideal gas, term related to hard chain, contribution related to dispersion forces, and term related to association contribution. In this work, we have used PC-SAFT EoS to compute the density of pure fluids and binary mixtures. On

the other hand, Nomoto’s relation was used for modelling the speed of sound for the binary mixtures as a predictive approach [23].

3. Results and discussion

3.1. Thermophysical properties

3.1.1. Density

The density was measured at T = (293.15, 303.15, 308.15, and 313.15) K and p = 0.1 MPa for the [ZnCl₂][acetic acid] 1:4 DES and their binary systems, and the results are shown in Table 3 and Fig S1. Fig. S1 shows density versus concentration plots of [ZnCl₂][acetic acid] 1:4 DES at various temperatures. The density of a solution depends on a variety of factors, such as the solute’s molar mass, its concentration, and its temperature and pressure [24]. In the instance of a DES, the density can also be influenced by the mole fraction of the solvent components. The density of the resulting solution increases as the mole fraction of the [ZnCl₂][acetic acid] 1:4 DES increases with the binary system of methanol, ethanol, and propanol. This implies that DES has a higher density than alcohols and that as more DES is added to the solution, the overall density increases. Binary mixtures of [ZnCl₂][acetic acid] 1:4 DES with methanol, ethanol, and propanol exhibit a decrease in density with increasing temperatures. This is most likely because, as the temperature increases, the molecules in the mixture gain energy and become more freely. The molecules become less closely packed because of the increased molecular motion, which lowers the density [25,26]. This increased molecular motion causes the molecules to be less tightly packed and results in a decrease in density.

3.1.2. Sound velocity

Speed of sound refers to the speed of sound waves as they pass through a medium, which is affected by temperature, pressure, and the medium’s properties [27,28]. The plots of speed of sound versus concentration of [ZnCl₂][acetic acid] 1:4 DES at investigated temperatures are given in Fig. S2 and Table 3. From Fig. S2, it can be observed that the speed of sounds decreases with temperature. This can be explained by the fact that as the temperature of a material increases, its molecules or atoms tend to move faster and collide more frequently. This leads to a reduction in the material’s stiffness or elasticity. As a result, the sound waves passing through the material encounter more resistance and take longer to propagate, leading to a decrease in the speed of sound. Sound velocity values increase as the mole fraction of the [ZnCl₂][acetic acid] 1:4 DES increases. It implies a direct link between the two, with increasing the mole fraction of the DES leading to an increase in sound speed [29].

3.2. Excess molar volumes

The excess molar volume is a thermodynamic property that measures the deviation of the mixture’s volume from its ideal behaviour and is calculated using a standard equation and the results shown in Fig. 1 and Table S1. The excess molar volumes are determined by various factors, including volume expansion and contraction effects as well as other elements like the chemical characteristics and concentration of the components, temperature, and pressure, which collectively influence both the magnitude and sign. Excess molar volumes are completely negative for [ZnCl₂][acetic acid] 1:4 with methanol or ethanol mixture at all temperatures evaluated and change sign from negative to positive for [ZnCl₂][acetic acid] 1:4 with propanol mixture. The $V_{m,min}^E$ occurred at $x_1 = 0.5560$ for methanol, $x_1 = 0.5559$ for ethanol and $x_1 = 0.3559$ for propanol to all temperatures. The $V_{m,max}^E$ occurred at $x_1 = 0.9523$ for propanol to all temperatures. The minimum excess molar volumes occurs when the components in the mixture form stable interaction with each other. It is simple to compute the excess molar volume by calculating the ratio between the actual volume of the mixture and the

Table 3
Density, ρ , speed of sound, u , isentropic compressibility and intermolecular free length, L_f , for the binary mixture { [ZnCl₂][acetic acid] 1:4 (x_1) + methanol, ethanol, and propanol (x_2)} at T = (293.15, 303.15, 308.15, and 313.15) K.

x_1	ρ /(g · cm ⁻³)	u /(m · s ⁻¹)	κ_s / (TPa ⁻¹) · 10 ⁻²	L_f (nm) · 10 ²
{[ZnCl ₂][acetic acid] 1:4 (x_1) + methanol (x_2)}				
T = 293.15				
0.0000	0.7916	1119.60	10.08	6.47
0.2096	0.9612	1193.02	7.31	5.51
0.3580	1.0697	1215.05	6.33	5.13
0.5560	1.1955	1259.34	5.27	4.68
0.6827	1.2670	1268.26	4.91	4.51
0.7705	1.3114	1277.17	4.67	4.41
0.8334	1.3411	1274.90	4.59	4.37
0.8827	1.3625	1273.75	4.52	4.33
0.9211	1.3784	1273.15	4.48	4.31
0.9524	1.3911	1272.90	4.44	4.29
0.9783	1.4014	1273.26	4.40	4.28
1.0000	1.4105	1272.58	4.38	4.26
T = 303.15				
0.0000	0.7822	1087.20	10.82	6.83
0.2096	0.9511	1162.23	7.78	5.79
0.3580	1.0587	1186.43	6.71	5.38
0.5560	1.1838	1235.08	5.54	4.88
0.6827	1.2554	1247.55	5.12	4.70
0.7705	1.3001	1247.59	4.94	4.61
0.8334	1.3294	1245.47	4.85	4.57
0.8827	1.3511	1244.60	4.78	4.54
0.9211	1.3671	1244.18	4.73	4.51
0.9524	1.3796	1244.02	4.68	4.49
0.9783	1.3899	1244.26	4.65	4.48
1.0000	1.3987	1243.46	4.62	4.46
T = 308.15				
0.0000	0.7776	1071.00	11.21	7.01
0.2096	0.9465	1147.12	8.03	5.93
0.3580	1.0537	1172.31	6.91	5.50
0.5560	1.1789	1222.94	5.67	4.99
0.6827	1.2499	1233.96	5.25	4.80
0.7705	1.2944	1233.00	5.08	4.72
0.8334	1.3239	1231.12	4.98	4.68
0.8827	1.3454	1230.18	4.91	4.64
0.9211	1.3614	1229.96	4.86	4.61
0.9524	1.3740	1229.75	4.81	4.59
0.9783	1.3843	1229.96	4.78	4.58
1.0000	1.3929	1229.14	4.75	4.57
T = 313.15				
0.0000	0.7727	1055.00	11.63	7.21
0.2096	0.9414	1132.36	8.28	6.08
0.3580	1.0486	1158.83	7.10	5.63
0.5560	1.1733	1212.04	5.80	5.09
0.6827	1.2444	1219.96	5.40	4.91
0.7705	1.2888	1218.57	5.23	4.83
0.8334	1.3184	1217.51	5.12	4.78
0.8827	1.3398	1215.97	5.05	4.75
0.9211	1.3558	1215.64	4.99	4.72
0.9524	1.3683	1215.56	4.95	4.70
0.9783	1.3787	1215.60	4.91	4.68
1.0000	1.3870	1211.72	4.91	4.68
{[ZnCl ₂][acetic acid] 1:4 (x_1) + ethanol (x_2)}				
T = 293.15				
0.0000	0.7896	1160.37	9.41	6.25
0.2084	0.9142	1200.62	7.59	5.61
0.3573	1.0057	1226.31	6.61	5.24
0.5559	1.1317	1240.51	5.74	4.88
0.6821	1.2120	1251.50	5.27	4.68
0.7694	1.2680	1259.93	4.97	4.54
0.8324	1.3076	1260.99	4.81	4.47
0.8819	1.3387	1262.91	4.68	4.41
0.9177	1.3610	1265.59	4.59	4.37

(continued on next page)

Table 3 (continued)

x_1	$\rho /(\text{g}\cdot\text{cm}^{-3})$	$u /(\text{m}\cdot\text{s}^{-1})$	$\kappa_s/(\text{TPa}^{-1})\cdot 10^{-2}$	$L_f(\text{nm})\cdot 10^2$
0.9520	1.3817	1268.16	4.50	4.32
0.9777	1.3973	1271.11	4.43	4.29
1.0000	1.4105	1272.58	4.38	4.26
T = 303.15				
0.0000	0.7810	1126.91	10.08	6.59
0.2084	0.9050	1168.08	8.10	5.91
0.3573	0.9960	1194.55	7.04	5.51
0.5559	1.1210	1212.92	6.06	5.11
0.6821	1.2012	1218.19	5.61	4.92
0.7694	1.2569	1229.71	5.26	4.76
0.8324	1.2961	1231.32	5.09	4.68
0.8819	1.3271	1233.80	4.95	4.62
0.9177	1.3493	1236.69	4.85	4.57
0.9520	1.3700	1239.38	4.75	4.52
0.9777	1.3856	1242.24	4.68	4.49
1.0000	1.3987	1243.46	4.62	4.46
T = 308.15				
0.0000	0.7723	1109.94	10.51	6.79
0.2084	0.8970	1151.80	8.40	6.07
0.3573	0.9881	1178.64	7.29	5.65
0.5559	1.1133	1197.94	6.26	5.24
0.6821	1.1939	1203.87	5.78	5.03
0.7694	1.2498	1214.60	5.42	4.88
0.8324	1.2895	1216.60	5.24	4.79
0.8819	1.3207	1219.29	5.09	4.73
0.9177	1.3431	1222.23	4.98	4.68
0.9520	1.3641	1225.09	4.88	4.63
0.9777	1.3797	1227.98	4.81	4.59
1.0000	1.3929	1229.14	4.75	4.57
T = 313.15				
0.0000	0.7634	1093.40	10.96	6.99
0.2084	0.8886	1135.61	8.73	6.24
0.3573	0.9796	1162.85	7.55	5.81
0.5559	1.1055	1183.04	6.46	5.37
0.6821	1.1863	1187.44	5.98	5.17
0.7694	1.2428	1199.58	5.59	5.00
0.8324	1.2829	1201.94	5.40	4.91
0.8819	1.3143	1204.89	5.24	4.84
0.9177	1.3367	1207.83	5.13	4.79
0.9520	1.3584	1210.97	5.02	4.73
0.9777	1.3739	1213.91	4.94	4.70
1.0000	1.3870	1214.97	4.88	4.67
{[ZnCl ₂][acetic acid] 1:4 (x_1) + propanol (x_2)}				
T = 293.15				
0.0000	0.8036	1222.69	8.32	5.88
0.2083	0.9025	1232.33	7.30	5.50
0.3575	0.9798	1240.45	6.63	5.25
0.5558	1.0941	1241.00	5.93	4.97
0.6820	1.1746	1243.87	5.50	4.78
0.7693	1.2344	1247.03	5.21	4.65
0.8334	1.2807	1251.59	4.98	4.55
0.8824	1.3176	1253.82	4.83	4.48
0.9211	1.3475	1259.81	4.68	4.41
0.9524	1.3727	1263.51	4.56	4.35
0.9783	1.3941	1267.34	4.47	4.31
1.0000	1.4132	1272.58	4.37	4.26
T = 303.15				
0.0000	0.7956	1188.88	8.89	6.19
0.2083	0.8936	1199.27	7.78	5.79
0.3575	0.9703	1208.25	7.06	5.51
0.5558	1.0832	1210.42	6.30	5.21
0.6820	1.1628	1213.75	5.84	5.01
0.7693	1.2221	1217.43	5.52	4.88
0.8334	1.2679	1222.33	5.28	4.77
0.8824	1.3044	1224.98	5.11	4.69
0.9211	1.3340	1230.92	4.95	4.62
0.9524	1.3588	1234.68	4.83	4.56

Table 3 (continued)

x_1	$\rho /(\text{g}\cdot\text{cm}^{-3})$	$u /(\text{m}\cdot\text{s}^{-1})$	$\kappa_s/(\text{TPa}^{-1})\cdot 10^{-2}$	$L_f(\text{nm})\cdot 10^2$
0.9783	1.3801	1238.50	4.72	4.51
1.0000	1.3987	1243.46	4.62	4.46
T = 308.15				
0.0000	0.7916	1171.93	9.20	6.35
0.2083	0.8892	1182.69	8.04	5.94
0.3575	0.9656	1191.98	7.29	5.65
0.5558	1.0784	1195.85	6.48	5.33
0.6820	1.1576	1198.75	6.01	5.13
0.7693	1.2167	1202.70	5.68	4.99
0.8334	1.2625	1207.76	5.43	4.88
0.8824	1.2988	1210.63	5.25	4.80
0.9211	1.3284	1216.52	5.09	4.72
0.9524	1.3531	1220.37	4.96	4.67
0.9783	1.3744	1224.25	4.85	4.61
1.0000	1.3929	1229.14	4.75	4.57
T = 313.15				
0.0000	0.7875	1155.23	9.52	6.52
0.2083	0.8847	1166.16	8.31	6.09
0.3575	0.9609	1175.76	7.53	5.80
0.5558	1.0734	1181.45	6.67	5.46
0.6820	1.1524	1183.89	6.19	5.26
0.7693	1.2113	1188.08	5.85	5.11
0.8334	1.2570	1193.31	5.59	4.99
0.8824	1.2933	1196.41	5.40	4.91
0.9211	1.3228	1202.24	5.23	4.83
0.9524	1.3474	1206.21	5.10	4.77
0.9783	1.3686	1210.46	4.99	4.72
1.0000	1.3870	1214.97	4.88	4.67

Standard uncertainties u are $u(T) = 0.02\text{ K}$, $u(p) = 0.04\text{ MPa}$, 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).

volume predicted by an ideal solution. If the excess molar volume is negative, then the mixture yields a smaller volume than the ideal volume. If the excess molar volume is positive, the mixture yields a larger volume [30,31].

The negative excess molar volume in the case of [ZnCl₂][acetic acid] 1:4 with methanol or ethanol suggests that the interactions between the components of the combination are higher than the interactions in an ideal solution. This behaviour is likely for mixtures of polar and non-polar components, such as [ZnCl₂][acetic acid] 1:4, with alcohols, as the polar components may form hydrogen bonds with the acetic acid and the non-polar components can interact with the zinc chloride through Van der Waals forces. The negative excess molar volume of [ZnCl₂][acetic acid] 1:4 with propanol at low mole fractions indicates that the interactions between the components are still greater than in an ideal solution. But as the mole fraction of propanol increases, the interactions between propanol molecules result in a positive excess molar volume. This tendency is common in combinations of components of varying sizes or shapes, since the packing of the molecules might become less effective as the mole fraction of one component increases.

In the binary mixtures containing [ZnCl₂][acetic acid] 1:4 DES with methanol, ethanol, or propanol, the values of excess molar volumes decrease with increasing temperature [32,33]. This phenomenon can be clarified by studying the interactions of the mixture's components. The components tend to be more closely packed together at low temperatures, and the attractive interactions between them are more severe. This causes a greater difference from the ideal molar volume, resulting in a greater excess molar volume value. As the temperature increases, the components gain thermal energy, and their attractive interactions lessen. This decreases the deviation from the ideal molar volume, resulting in a lower excess molar volume value. Factors such as the nature and extent of the intermolecular interactions between the components, the size and shape of the molecules, and the degree of solvation

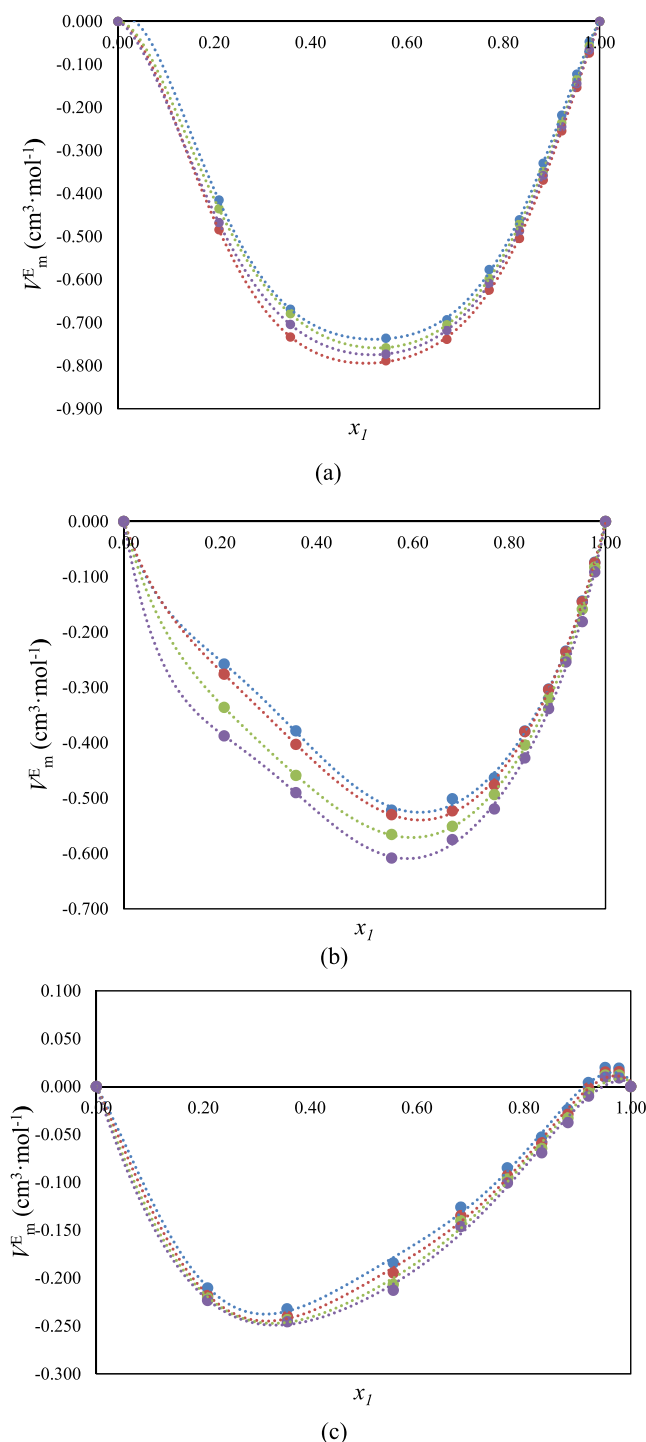


Fig. 1. Experimental excess molar volume and values calculated using Redlich-Kister model for the mixtures {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol (a), ethanol (b), and propanol (c)}. Circles represent the experimental data and lines represent the theoretical results. Colours: (blue) 293.15 K, (red) 303.15 K, (green) 308.15 K, (purple) 313.15 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the ions in the deep eutectic solvent can all influence it.

When methanol, ethanol, or propanol is added to the DES, the alkyl chain length of the alcohol increases from one to three carbon atoms. One expected result is that when the alcohol's alkyl chain length increases, the polarity of the DES decreases. This can happen because longer alkyl chains are less polar than shorter ones, causing the total

polarity of the combination to decrease. This change in polarity may influence the solubility of certain compounds in the mixture, especially those with higher polarity. Another impact of increasing the alkyl chain length is that it might enhance the mixture's hydrophobicity. This can happen because longer alkyl chains are more hydrophobic than shorter ones, increasing the total hydrophobicity of the combination. This may impair the mixture's ability to dissolve compounds, especially those that are more hydrophilic in nature.

3.3. Isentropic compressibility and excess isentropic compressibility

The isentropic compressibility values were calculated using the Newton-Laplace equation [34]. Excess isentropic compressibility is a thermodynamic property that characterizes the deviation of the compressibility of a mixture from that of an ideal mixture at the same temperature and pressure [35]. Tables 3 and Fig. 2 show the calculated values for isentropic compressibility and deviation in isentropic compressibility for binary mixtures of [ZnCl₂][acetic acid] 1:4 with methanol, ethanol, or propanol at all investigated temperatures.

From Table 3 at each temperature, it appears that the isentropic compressibility of a solution decreases with an increased concentration of [ZnCl₂][acetic acid] 1:4 with alcohols [36]. Isentropic compressibility refers to a substance's volume change under adiabatic conditions relative to pressure changes [37]. There are indications that the solution is more resistant to pressure variation when the concentration of [ZnCl₂][acetic acid] 1:4 with alcohols is increased.

The results reported in Table 3 show that the isentropic compressibility values increase with increasing temperature at a fixed composition for all examined binary mixtures. This is because as temperatures increase, the average kinetic energy of the molecules increases [38]. This causes them to move more vigorously and repel each other. As a result, the substance becomes more compressible, which means that it can be compressed more easily under the same pressure change.

According to the findings in Fig. 2 and Table S1, the deviation in isentropic compressibility values is negative for mixtures of [ZnCl₂][acetic acid] 1:4 with methanol or ethanol at all temperatures; however, they change the sign from negative to positive for mixtures of [ZnCl₂][acetic acid] 1:4 with propanol. A binary mixture is less compressible than an ideal mixture at the same temperature and pressure if the deviation in isentropic compressibility is negative [39]. This is because a mixture with a negative excess isentropic compressibility responds to changes in pressure with a smaller volume change than an ideal mixture [40]. This could also mean that the molecules of the mixture are more tightly packed together than the molecules of the individual components. This can happen when the components have strong interactions that reduce the free space available for compression. The $\Delta K_{s,min}$ occurred at $x_1 = 0.4000$ for methanol, ethanol, and propanol at all temperatures. The $\Delta K_{s,max}$ occurred at $x_1 = 0.9523$ for propanol at all temperatures. The minimum deviation at $x_1 = 0.4000$ indicates more consistent behaviour and maximum deviation could be due to interactions or phase behavior that caused the compressibility to be higher than expected.

The deviation in isentropic compressibility also points to the presence of potent intermolecular interactions in the mixture of alcohol and DES. Both the occurrence of ion-dipole interactions between the zinc chloride and the alcohol molecules and the hydrogen bonding between the carboxyl group of acetic acid and the oxygen atom of the alcohol could be responsible for these interactions [36]. This indicates that the mixture contains these alcohols, which results in a structure that is denser than would be predicted based on the compressibility of the individual components.

A positive deviation in isentropic compressibility occurs when a mixture has a higher compressibility than an ideal mixture. This behaviour is typically observed in mixtures with attractive intermolecular forces.

The effective volume available for molecular motion is diminished in

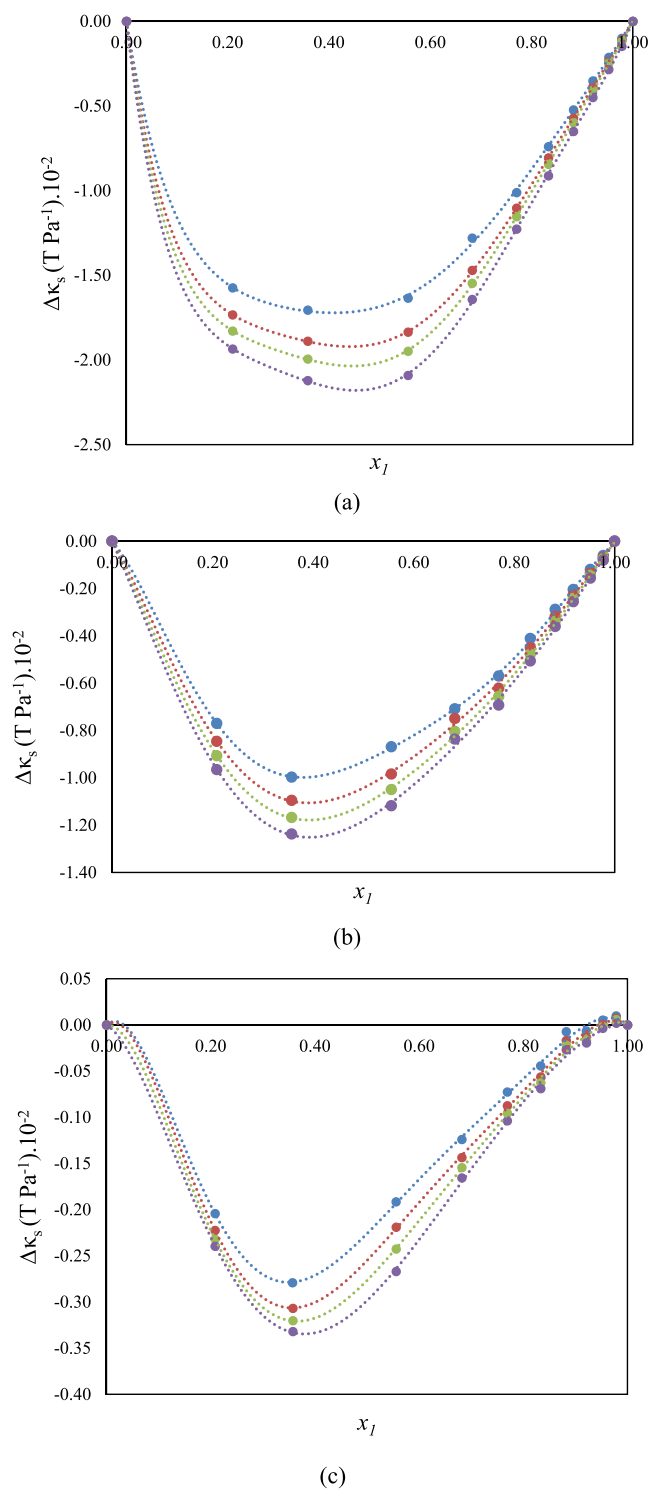


Fig. 2. Experimental excess isentropic compressibility and values calculated using Redlich-Kister model for the mixtures {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol (a), ethanol (b), and propanol (c)}. Circles represent the experimental data and lines represent the theoretical results. Colours: (blue) 293.15 K, (red) 303.15 K, (green) 308.15 K, (purple) 313.15 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

a mixture where there are attractive forces between its component molecules. Consequently, when the mixture is compressed under adiabatic (no heat exchange) conditions, the attractive forces lead to a higher degree of compression than in an ideal mixture. Positive excess

compressibility indicates a mixture that is more likely to be compressed at adiabatic temperatures [41]. Due to the reduced effective volume available for the molecules to move, intermolecular forces make compression easier since the molecules can come closer together more easily.

As temperatures increase, the excess isentropic compressibility values for methanol and ethanol binary mixtures become more negative [42]. In general, an increase in temperature leads to an increase in molecular motion, which increases the free volume available to molecules. As a result, the mixture's compressibility increases, and the excess isentropic compressibility becomes more negative.

The excess isentropic compressibility values are becoming more negative and less positive as temperature increases for binary mixtures of propanol. The specific behaviour of propanol binary mixtures with increasing temperature, resulting in more negative and less positive excess isentropic compressibility values, could be related to changes in molecular interactions within the mixture. Temperature-dependent variations in intermolecular forces, like hydrogen bonding, dipole-dipole interactions, or Van der Waals forces, can influence compressibility behavior.

3.4. Intermolecular free length

It is related to the size and shape of the molecules, as well as the intermolecular forces between them [43]. Intermolecular free length (L_f) for the binary mixture's values was calculated from Jacobson's empirical relation and isentropic compressibility [43].

Where K_j is the temperature-dependent Jacobson's constant given by $(93.875 + 0.375 T)10^{-8}$.

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

The mole fraction of [ZnCl₂][acetic acid] 1:4 DES increases as the intermolecular free length values decrease in Table 3 and Fig. 3. This is because introducing additional solvent molecules to a mixture can improve molecular interactions, resulting in tighter packing and a shorter average distance between molecules. The intermolecular free length values also increase as the temperature increases. This is because, at higher temperatures, the thermal energy of the molecules increases, causing them to move faster and take up more space. As a result, the average distance between molecules increases.

The intermolecular free length values of the binary systems decrease with the increase in the alkyl chain length of the alcohols (i.e., methanol < ethanol < propanol). This implies that as the alkyl chain length of the alcohols increases, the molecules become more closely packed, and the average distance between adjacent molecules decreases. This behavior is expected because longer alkyl chains increase the hydrophobicity of the alcohol molecules, which can lead to stronger interactions with the nonpolar components of the deep eutectic solvent. These interactions can cause the molecules to pack more tightly, resulting in shorter intermolecular free lengths.

3.5. Redlich-Kister correlation

The Redlich-Kister fitting parameters were calculated from Eq. (2) [14]:

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

where Z is the V_m^E or $\Delta\kappa_s$; x_1 is the mole fraction of the [ZnCl₂][acetic acid] 1:4; x_2 is the mole fraction of methanol, ethanol, and propanol; N is the degree of the polynomial expansion; and A_i is the Redlich-Kister parameters obtained for the system.

The root mean square deviation was calculated from Eq. (3)

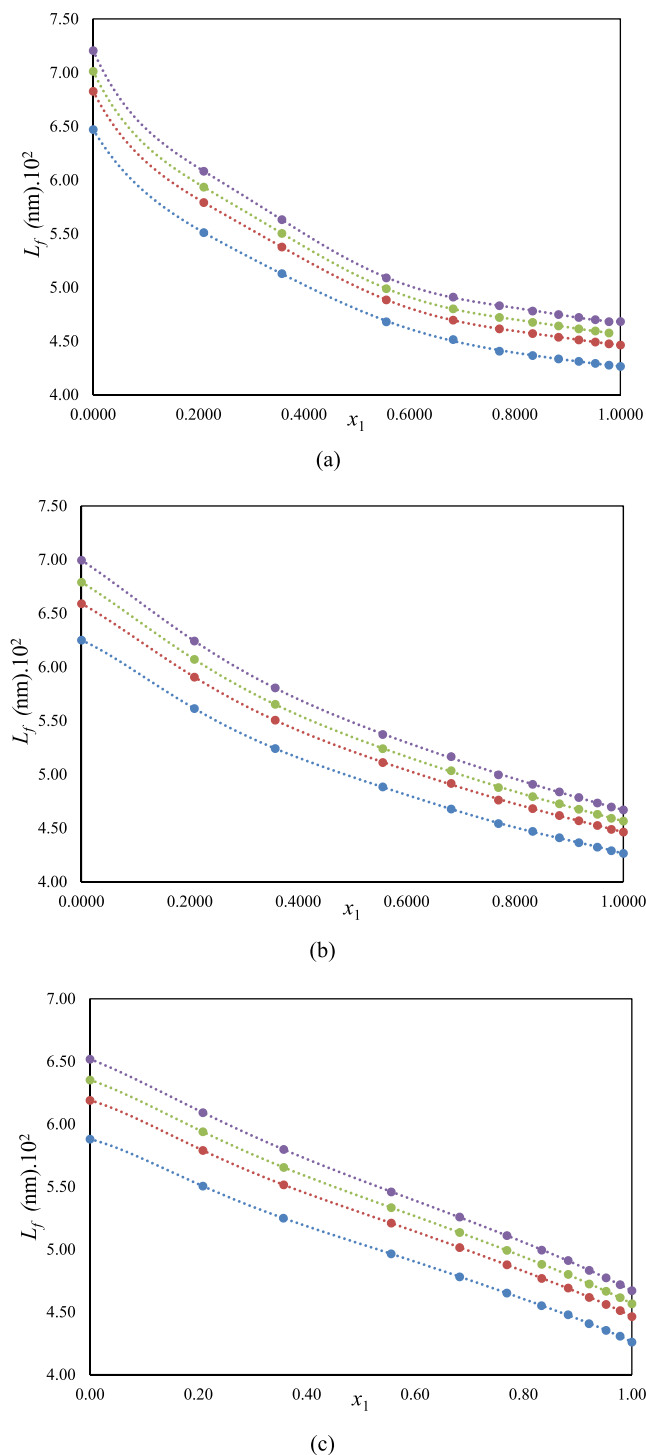


Fig. 3. Graphs of intermolecular free length L_f , of the binary mixtures of $\{[\text{ZnCl}_2][\text{acetic acid}] 1:4 (x_1) + \text{methanol (a), ethanol (b), and propanol (c)}\}$ at $T = (293.15, 303.15, 308.15, \text{ and } 313.15) \text{ K}$.

$$\sigma = \left(\frac{\sum_{i=1}^M (Z_{\text{exp}} - Z_{\text{cal}})^2}{M - k} \right)^{1/2} \quad (3)$$

where Z_{exp} , Z_{cal} , are the values of the experimental and computed V_m^E or $\Delta\kappa_s$ and M is the number of experimental data points and k is the number of coefficients used in the Redlich-Kister correlation, respectively.

The Redlich-Kister parameters and the root mean square deviation for all binary systems are given in Table 4. The Redlich-Kister fitting

Table 4

Redlich-Kister fitting parameters and root-mean-square deviation, σ , for the binary mixtures at $T = (293.15, 303.15, 308.15, \text{ and } 313.15) \text{ K}$.

	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
$\Delta\kappa_s / (\text{TPa}^{-1})$	σ	0.005	0.004	0.001	0.004
	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)}					
$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1})$	A_0	-1.967	-2.033	-2.200	-2.353
	A_1	-1.120	-1.045	-0.864	-0.907
	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
$\Delta\kappa_s / (\text{TPa}^{-1})$	σ	0.006	0.006	0.004	0.008
	A_0	-366.784	-419.959	-447.580	-478.286
	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
$\Delta\kappa_s / (\text{TPa}^{-1})$	σ	0.008	0.006	0.006	0.008
	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

Standard uncertainties u are $u(T) = 0.02 \text{ K}$, $u(p) = 0.04 \text{ MPa}$, 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).

smoothing polynomial was used to obtain the fitting parameters of the binary systems together with the standard deviations [44,45]. The Redlich-Kister smoothing equation was used successfully for the correlation of V_m^E and $\Delta\kappa_s$ data.

3.6. Results of PC-SAFT EoS and Nomoto's relation

All fluids were considered as self-associating with a 2B scheme, i.e., one positive site and one negative site. The fitted parameters of the alcohols were obtained from the literature [22]. The parameters for the $[\text{ZnCl}_2][\text{acetic acid}] 1:4$ were fit in this work and we have obtained: $m = 2.8419$.

$\sigma = 3.0000 \text{ \AA}$, $\frac{\epsilon}{k_B} = 299.9681 \text{ K}$, $\kappa^{AB} = 0.0296$, and $\frac{\epsilon^{AB}}{k_B} = 2023.8457 \text{ K}$. These parameters were optimized from Eq. (4):

$$OF = \sum_{i=1}^n \left(\frac{\rho_i^{\text{calc.}} - \rho_i^{\text{exp.}}}{\rho_i^{\text{exp.}}} \right)^2 \quad (4)$$

where n is the number of experimental points, the superscript *calc.* is

related to calculated value and the superscript *exp.* indicate the experimental value. The absolute average deviation in density was 0 %.

Table 5 shows the binary interaction parameters and the absolute average deviations for density and speed of sound. The results of PC-SAFT EoS are very good (the overall deviation for density was 0.27 %), and Nomoto's relation was able to correctly predict the speed of sound (the overall deviation was 1.05 %). Figs. 4 and 5 show the variation of density and speed of sound with mole fraction of DES for the DES (1) + methanol (2) mixture and the DES (1) + ethanol (2) mixture, respectively. Fig. 4 shows good agreement between experimental and theoretical density data, while Fig. 5 shows that the speed of sound predicted by Nomoto's relation is monotonically increasing over the entire mole fraction range.

4. Conclusion

This study demonstrates the assessment of the thermophysical properties of binary mixtures containing zinc chloride-based deep eutectic solvents and alkanols. It is observed that all of the investigated thermodynamic parameters show a significant effect on temperature, as these values (such as V_m^E , κ_s , $\Delta\kappa_s$, and L_f) were found to either decrease or increase with an increase in temperature. Across the full composition and temperature range, the combination including [ZnCl₂][acetic acid] 1:4 with methanol and ethanol consistently exhibited negative values for excess molar volumes and deviations in isentropic compressibility. Nevertheless, upon the mixture of propanol, the resulting blend exhibited affirmative excess molar volumes. A direct relationship between temperature and isentropic compressibility values was identified, with an increase in temperature leading to higher compressibility values. This association was evident in all the investigated binary mixtures, where the composition remained constant throughout the study. Furthermore, it was observed that the intermolecular free length values exhibited an increase in conjunction with an increase in temperature. PC-SAFT EoS correctly modelled the density of the binary mixtures (global deviation = 0.27 %), using and fitting parameters for each mixture, and the choice of Nomoto's relation was very suitable for the prediction of the speed of sound (global deviation = 1.05 %).

The significance of this research extends to the broader implications within the field. The investigation into the density and velocity of sound in binary mixtures comprising DES containing zinc (II) chloride and alkanols represents a significant and captivating field of research. Herein lie a multitude of perspectives and considerations that warrant exploration in forthcoming research endeavors within this domain. Future studies could delve deeper into specific interactions, explore different combinations of solvents and alkanols, and assess the applicability of these findings in industrial processes. Overall, this investigation lays a solid foundation for advancing our understanding of thermophysical properties in complex solvent mixtures and opens avenues for innovative applications in various scientific and industrial contexts.

Table 5

Fitted binary parameters and the absolute average deviation for liquid density and speed of sound for all the binary mixtures considered in this study.

Mixture	k_{ij}	%AAD ρ	%AAD u
DES (1) + methanol (2)	0.0094	0.26	1.84
DES (1) + ethanol (2)	0.0109	0.19	0.89
DES (1) + 1-propanol (2)	-0.0371	0.36	0.41
Overall		0.27	1.05

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 $U_c(x) = 0.0006$, $U_c(\rho) = 0.0009$ g·cm⁻³, $U_c(u) = 2.63$ m·s⁻¹, respectively (0.95 level of confidence).

$$\%AAD\rho = \frac{100}{n} \sum_{i=1}^n \left| \frac{\rho_i^{exp} - \rho_i^{calc.}}{\rho_i^{exp.}} \right|, \rho = \rho_{or}u, \text{ and } n \text{ is the number of points.}$$

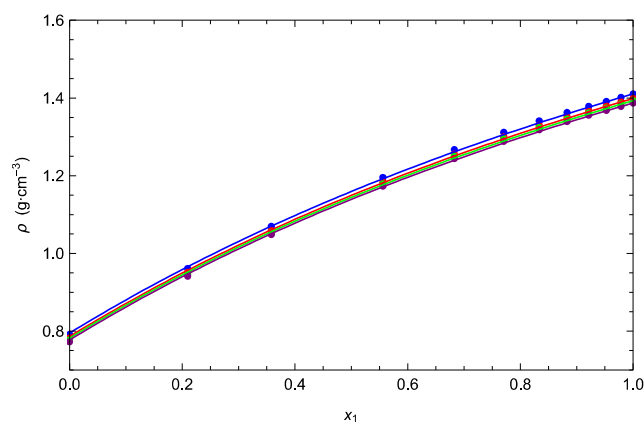


Fig. 4. Plot of the density for the {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol (x_2)} at 293.15 K (blue), 303.15 K (red), 308.15 K (green), 313.15 K (purple). The lines represent the results obtained with PC-SAFT EoS. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

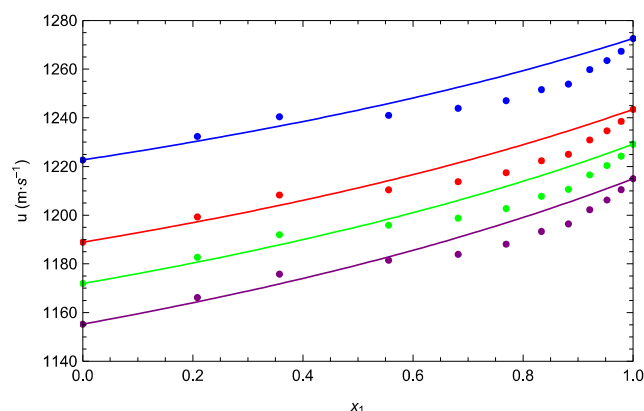


Fig. 5. Plot of the speed of sound for the {[ZnCl₂][acetic acid] 1:4 (x_1) + methanol (x_2)} mixture at 293.15 K (blue), 303.15 K (red), 308.15 K (green), 313.15 K (purple). The lines represent the results obtained with Nomoto's relation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Ethical approval

This study does not involve humans or animals.

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CRediT authorship contribution statement

Ncomeka Mgxadeni: Formal analysis, Data curation. **Ariel Hernández:** Methodology, Investigation. **Indra Bahadur:** Supervision, Conceptualization. **Faruq Mohammad:** Writing – original draft, Visualization, Validation. **Ahmed Abdullah Soleiman:** Writing – review & editing, Visualization, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2024.124155>.

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