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Molecular interactions between ammonium-based ionic liquids and molecular solvents: current progress and challenges†

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In view of the spacious scope of structural information and the molecular interactions between ammonium-based ionic liquids (ILs) and molecular solvents in various applications including chemical and pharmaceutical that are crucial for all aspects of scientific community, the knowledge of the molecular mechanisms, in particular, the thermodynamic basis of the structure-breaking/making interactions as well as the packing effect of the molecular liquids is essential to understand the ion–ion and ion–solvent interactions that exist in the liquid mixtures. In this perspective, we describe how the thermodynamic parameters can be effectively used to gain valuable insights into molecular interactions between ammonium-based ILs and molecular solvents, which would be most useful in various industries. This perspective presents the thermophysical properties of pure ammonium-based ILs, then these properties of the mixtures of these ILs with other solvents, and reviews the correlation researches on the properties of these systems. Finally, this perspective also brings a brief overview on several studies accomplished in this area by various researchers.

1. Introduction

Thermophysical properties are the properties of a material or substance which affect the transfer and storage of heat, they may vary with the temperature, pressure and composition of the mixture.[1] The studies of composition dependence of the thermophysical properties are of high importance and primarily fundamental in all aspects for the scientific community, which can be a fruitful source of information regarding the macroscopic effects of the various types of intermolecular forces which are present in liquid mixtures.[2–4] The information on thermophysical properties is again essential in aiding with the basic understanding of solvent physical and chemical behavior, including their macroscopic and microscopic characteristics. This is a primary extensive factor that any researcher is required to evaluate and review before application or use of any material, as a search for the most eco-friendly and cost effective materials still poses a persisting challenge to researchers. The physiochemical properties of each material are of significance to aid in assimilation of the structure and property of the material and its correlations, which will enhance a predictive modeling.[5]

Mixed solvents enable the variation of excess/derived thermodynamic properties of liquids and their mixtures; therefore ion–ion and ion–solvent interactions have reached a high level of understanding in traditional chemistry and are of broad research interest. The contribution of thermophysical properties is sensitive to the entire range of interactions such as solute–solvent, solute–solute and solute–cosolvent.[4,6] Furthermore, these routine properties allow to draw information on the structure and interactions of mixed solvents.[4] Various attempts to understand and describe the thermodynamics of structural interactions have attracted considerable effort from both academicians and industrialists. Chemical industries have recognized the importance of the thermodynamic properties in design calculations involving chemical separations, heat transfer, mass transfer and fluid flow.[4,6,7] Obviously, a detailed structural model of interactions in liquid mixtures is necessary to explain and understand their properties.

The thermophysical properties of liquids have been studied extensively in the open literature, which have proven to be a very useful tool in elucidating the structural interactions among the components.[8–14] During the last few decades, large numbers of solvents have been used for numerous processes in academia by various researchers from all disciplines related to chemistry and in industry. Because of new environmental regulations, the challenge of using non-harmful solvents and conventional organic solvents has prompted a great development of innovative products to

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protect the environment. In this regard, ionic liquids (ILs) emerged as a new class of solvents considered for the replacement of volatile organic compounds in chemical and industrial processes to reduce both economic cost and environmental pollution.[15–22] ILs, as a class of eco-friendly solvents, are used in a wide range of commercial, industrial and incredible applications. These ILs are comprised of ions and are liquid at relatively close to room temperature and have novel and unique properties such as extremely low vapor pressure.[23–26] ILs combine alkyl-substituted imidazolium, ammonium, pyridinium, pyrrolidinium, piperidinium, phosphonium, pyrazolium, thiazolium, cholinium and sulfonium cations, amongst others, in combination with organic and inorganic anions such as chloride, bromide, acetate, nitrate, alkylsulfate, hexafluorophosphate, tetrafluoroborate, bis(trifluoromethylsulfonyl)imide, alkylsulfonate, tosylate, hydroxide, sulfate, phosphate and dicyanimide.[27–30] Physicochemical properties such as melting point, viscosity, density, hydrophobicity and so on of ILs are extremely sensitive towards the structure and nature of cations and anions, that can be finely tuned by simple modification of the ions of ILs.[31–33] Currently, there is fast-growing research on ILs in nearly every branch of the scientific community and a great interest in their multipurpose applications.

Significant and special attention has been applied from all disciplines of science and engineering towards the utilization of these newly emerging ILs mainly due to their unique, novel and specified properties such as high ionic mobility, good solubility in organic and inorganic solvents, nonflammability, high potential for recycling, extremely low vapor pressure, wide electrochemical window and high thermal stability.[17–22] Even just from the last decade, several comprehensive perspective articles and research papers have been published for more general details on aspects related to the history, synthesis, experimental design properties, commercial and technical applications of newly emerging materials of ILs.[34–51] These researches exhibit the great potential and significant application prospects of these ILs.

Among all the different families of ILs, ammonium-based ILs are recognized to display a significant role in chemical and biochemical processes. With the worldwide increasing demand for ILs, ammonium-based ILs are attracting increasing attention as eco-friendly co-solvents in a wide variety of research areas.[52–55] The specific and attractive properties of ammonium-based ILs may present clear advantages in different pharmaceutical and biomedical applications[56–58] and have prompted their use in batteries as electrolytes,[59–61] fuel cells,[62,63] nanotechnology,[64,65] polymerization reactions[66–68] as well as commercial and technical applications.[69–76] These ammonium-based ILs are currently used in secondary batteries and electrochemical intercalation of lithium into a natural graphite anode has been studied in presence of a trimethyl-*n*-hexylammonium quaternary ammonium-based IL.[77,78]

Varadhi Govinda

Dr Varadhi Govinda was awarded his PhD Degree in Physical Chemistry from the Department of Chemistry, Sri Venkateswara University, Tirupati, India. He is currently working as a Research Associate (RA) in the Department of Chemistry, University of Delhi, New Delhi, India. He was awarded a Meritorious Research Fellow (MRF) from University Grants Commission-Basic Scientific Research (UGC-BSR), New Delhi, India from 2012 to 2014. His research is focused on the thermophysical properties and transport properties of a novel class of ionic liquids, molecular solvents and their mixtures. He is a life member of the Indian Thermodynamics Society (ITS). He has received an award for the best research paper poster presentation at International Conference on Chemical Constellation Cheminar (C^3-2012), Department of Chemistry, Dr B. R. Ambedkar National Institute of Technology, Jalandhar, India, in the year 2012. In the same year, he was also awarded for the best research paper poster presentation at 7th National Conference on Thermodynamics of Chemical, Biological and Environmental Processes (TCBEP-2012) from Department of Chemistry, Sri Venkateswara University, Tirupati, India.

Pannuru Venkatesu

Dr Pannuru Venkatesu was awarded his PhD at Sri Venkateswara University, Department of Chemistry, Tirupati, Andhra Pradesh, India. At present he is a faculty member in the Department of Chemistry, University of Delhi, Delhi, India. He is a Fellow of Andhra Pradesh Akademi of Sciences, Andhra Pradesh, India. His research is focused on the thermodynamics of protein folding/unfolding in the presence of ionic liquids, osmolytes and denaturants, the behaviour of a polymer chain or ionic liquid in coexisting liquid phases, the influence of ionic liquids on thermoresponsive polymers and the thermodynamic and physicochemical properties of a novel class of liquids, ionic liquids and their mixtures. He is the author of 130 articles in scientifically reputed journals and 45 presentations at international conferences. In 2006, he was awarded Fast Track Young Scientist by the Department of Science and Technology (DST), New Delhi, India. In 2011, he received the Dr Arvind Kumar Memorial Award from the Indian Council of Chemists, India, and in 2013 he received the Professor Suresh C. Ameta award from the Indian Chemical Society, India. Another achievement is best research paper presentation award from Global Science and Technology Forum (GSTF), Singapore in 2013.

Furthermore, these ammonium-based ILs play an important and fundamental role in biomolecules and their processes, as they modify the strengths of the intra- and intermolecular interactions of biomolecules.[37–41] On the other hand, these ILs have been distinctly demonstrated as excellent biocompatible solvents for proteins and found to improve the stability and shelf life of several proteins[79–89] and as stabilizing solvents for several amino acids and model protein compounds.[90–95] The outcome of the research carried out by several researchers has explicitly elucidated that typically ammonium-based ILs act as biocompatible solvents for various biomolecules.

Despite numerous studies focusing on the application of ammonium-based ILs in the various aspects of scientific communities[96–114] however, limited discussion and no in-depth review on the subject of molecular interactions of ammonium-based ILs with molecular solvents has been published. In the view of the fast growing importance of these ammonium-based ILs, it is essential and desirable to assemble all the available thermophysical data for these ILs and their mixtures with molecular solvents in one place. Currently, great interest to investigate interactions and structures of binary mixtures of IL with molecular solvents is due to a variety of applications in various branches of industry. A detailed structural information of interactions in such systems is essentially required to explain and understand their properties. Therefore, this perspective is predominantly focusing on recent progress of experimental thermophysical properties of ammonium-based ILs with molecular solvents and we also illustrate comparisons between them in detail. Table S1 (ESI†) illustrates abbreviations and chemical structures of the commonly used ammonium-based ILs in referred to in this perspective.

In this perspective, we initially discuss various thermophysical properties such as densities (ρ), ultrasonic sound velocities (u), viscosities (η) and refractive indices (n_D) of ammonium-based ILs and their mixtures with molecular solvents, which are available in the open literature. We then discuss various excess/derived properties such as excess molar volume (V^E), deviation in isentropic compressibilities ($\Delta\kappa_s$), deviation in viscosities ($\Delta\eta$) and deviation in refractive indices (Δn_D) for ammonium-based ILs with molecular solvents. The ρ, u, η and n_D values for binary mixtures are used to calculate the excess/deviation properties of the mixtures by using standard equations.[115–118] The two sections are not mutually exclusive and whenever possible we have used currently available published data to describe and highlight the experimental criteria. We believe this discussion to be of interest not only from the point of view of solution thermodynamics, but also from the more general point of view of the physical chemistry of solutions.

Indra Bahadur

Dr Indra Bahadur was awarded his D Tech at Durban University of Technology, Department of Chemistry, Durban, South Africa. He has served as a post-doctoral fellow at several institutions in South Africa for five years. He had completed his first post-doctoral study at Department of Chemistry, Durban University of Technology, Durban, South Africa from 2011 to 2012, second post-doctoral study at School of Engineering, Chemical engineering, University of KwaZulu-Natal, Durban, South Africa from 2013 to 2014 and third post-doctoral study at Department of Chemistry, North-West University, Mafikeng Campus, Mmabotho, South Africa from 2014 to 2015. At present he is a faculty member in the Department of Chemistry, North-West University, Mafikeng Campus, Mmabotho, South Africa. His research is focused on the influence of ionic liquids on thermo-responsive polymers and the thermodynamic and physicochemical properties of a novel class of liquids, ionic liquids and their mixtures. Phase Equilibria of pure and multi component liquid mixtures. Absorption of gases in ionic liquids/co-solvents, Corrosion Science, Biofuels and Biomass. He is the author of 60 articles in scientifically reputed journals and 32 presentations at international conferences. In 2013, he was recognised as one of the top publishing Scientists by the Durban University of Technology Durban, South Africa. He has been awarded a fellowship from DST/NRF for his doctoral and post-doctoral studies.

2. Thermophysical properties of ammonium-based ionic liquids

Practically, the thermophysical properties of ammonium-based ILs mostly depend on the nature and structure of ions and the alkyl chain length of the cation. Table 1 summarizes the temperature dependence property of ρ values for a series of ammonium-based ILs published in the literature as a function of temperature. The ρ values for most of the ammonium-based ILs are approximately within the range of 0.947 to 1.460 g cm^{-3} (Table 1). The data in Table 1 explicitly elucidate that the ρ values significantly decrease as the temperature increases in all collected ILs from the literature.[103–105,115–202] Chhotaray and Gardas[126] point out that for ILs having the same anion, hydroxyl-ammonium ILs have higher ρ values as compared to simple ammonium ILs as can be seen from Table 1, which may be mainly due to the additional hydrogen bonding. Usually, a larger anion size leads to higher IL density whereas higher alkyl chain length cation leads to smaller IL density. On the other hand, ρ values decrease with increasing the cation alkyl chain length of ILs. With increasing the number of carbon atoms in the alkyl chain length of the cation, the change in investigated properties is very high from methyl to butyl group of ILs.

Ethylammonium nitrate (EAN) was the first reported and the most extensively studied IL in most of the scientific fields. Initially, Drummond's research group reported the ρ value of EAN is 1.2160 g cm^{-3} at 27 °C.[103,119] Later, there have been a large number of reports on the measurements of ρ at various temperatures which are readily available in the literature. However, from the available data it is not possible to derive the same value for this IL mainly because of the inconsistency

Table 1 Density (ρ) values of pure ammonium-based ILs at different temperatures from 20 to 40 °C

	Density (ρ/g cm^{-3})					
Ionic liquid	20 °C	25 °C	30 °C	35 °C	40 °C	Ref.
Ethylammonium nitrate [EAN]		1.2160[a]				103, 119
		1.21076				120
	1.21854	1.21523	1.21255	1.20918	1.20549	121
	1.21					122, 123
	1.2103	1.2060	1.2014	1.1965	1.1922	194
N-Propylammonium nitrate [PAN]		1.15035				120
	1.15582	1.15267	1.15003	1.14716	1.14431	121
	1.15					122
	1.16					123
N-Butylammonium nitrate [BAN]		1.10549				120
	1.11034	1.10775	1.10481	1.10107	1.06785	121
	1.10468	1.10152	1.09838	1.09526	1.09217	124, 125
Methylammonium formate [MAF]		1.0870[a]				119
Ethylammonium formate [EAF]		1.0390[a]				103, 119
Propylammonium formate [PAF]	0.99618	0.99347	0.99077	0.98809	0.98542	126
Butylammonium formate [BAF]		0.9680[a]				103, 119
Pentylammonium formate [PeAF]		0.9500[a]				126, 119
Ethylammonium propionate [EAP]		1.0180[a]				119
Ethylammonium butyrate [EAB]		0.9800[a]				119
Ethylammonium glycolate [EAG]		1.1890[a]				103, 119
Ethylammonium lactate [EAL]		1.1100[a]				119
n-Ethylammonium acetate [N2A]		1.01771				127
n-Propylammonium acetate [N3A]		0.96682				127
	0.98997	0.98691	0.98385	0.98077	0.97769	126
n-Butylammonium acetate [N4A]	0.95961	0.95644	0.95333	0.95015	0.94698	125, 128
Ethanolammonium nitrate [EOAN]		1.2650[a]				103, 119
	1.39					122
Ethanolammonium formate [EOAF]		1.1840[a]				103, 119
	1.04					122
Ethanolammonium acetate [EOAA]		1.1760[a]				103, 119
Diethylammonium formate [DEAF]		1.039[a]				103
Triethylammonium formate [TEAF]		1.028[a]				103
Diethanolammonium formate [DEOAF]		0.988[a]				103
2-Propanolammonium formate [2-POAF]		1.1440[a]				119
Ethanolammonium lactate [EOAL]		1.2280[a]				119
Ethylammonium hydrogen sulfate [EAHS]		1.4380[a]				119
2-Methylpropylammonium formate [2-MPAF]		0.9780[a]				119
2-Methylbutylammonium formate [2-MBAF]		0.9650[a]				119
Dimethylethylammonium formate [DMEAF]	1.03					122
2-Methoxyethylammonium nitrate [MEOEAN]		1.25324				120
3-Hydroxypropylammonium formate [3-HPAF]	1.14829	1.14584	1.14339	1.14095	1.13853	126
3-Hydroxypropylammonium acetate [3-HPAA]	1.11458	1.11202	1.10946	1.10391	1.10436	126
3-Hydroxypropylammonium trifluoroacetate [3-HPATFA]	1.31144	1.30781	1.30420	1.30058	1.29696	126
Diethylammonium acetate [DEAA]		1.02146	1.01652	1.01187	1.00714	129, 130, 192
Diethylammonium hydrogen sulfate [DEAS]		1.02839	1.02397	1.02054	1.01656	117, 130, 192
Triethylammonium acetate [TEAA]		1.01586	1.00958	1.00261	0.99743	129, 130, 192
Triethylammonium phosphate [TEAP]		1.12570	1.12468	1.12371	1.12237	131, 132
Triethylammonium hydrogen sulfate [TEAS]		1.14289	1.14183	1.14072	1.14002	130, 131, 192
Trimethylammonium acetate [TMAA]		1.05385	1.04987	1.04581	1.04170	132, 133, 192
Trimethylammonium phosphate [TMAP]		1.35361	1.35062	1.34759	1.34452	132, 133
Trimethylammonium hydrogen sulfate [TMAS]		1.46758	1.46357	1.46350	1.45563	132, 133, 192
Tetramethylammonium hydroxide [TMAH]		1.01797	1.01564	1.01321	1.01071	134–136, 196
Tetraethylammonium hydroxide [TEAH]		1.00881	1.00731	1.00396	1.00138	134–136, 196
Tetrapropylammonium hydroxide [TPAH]		0.99594	0.99360	0.99111	0.98576	134–136, 196
Tetrabutylammonium hydroxide [TBAH]		0.99358	0.99170	0.98962	0.98737	134–136, 196
Diallylammonium formate [DAAF]		0.93540		0.92680		137
Diallylammonium acetate [DAAA]		0.97840		0.96960		137
1-Hydroxyethylammonium formate [HEAF]		1.13990		1.13390		137
1-Hydroxyethylammonium acetate [HEAA]		1.15290		1.14730		137
1-Hydroxyethylammonium malonate [HEAMal]		1.33270		1.32550		137
2-Hydroxyethylammonium formate [2-HEAF]		1.17709				138
	1.18004	1.17649	1.17294	1.16939	1.16584	139
		1.0204				140, 141
2-Hydroxydiethylamonium formate [2-HDEAF]	1.19725	1.19404	1.19081	1.18755	1.18426	139
2-Hydroxytriethylamonium formate [2-HTEAF]		1.22186				139
2-Hydroxyethylammonium acetate [2-HEAA]	1.15187	1.14904	1.14622		1.14054	142
		1.1200				141
2-Hydroxyethylammonium lactate [2-HEAL]		1.2020				141

Table 1 (*continued*)

Ionic liquid	Density (ρ/g cm^{-3}) 20 °C	25 °C	30 °C	35 °C	40 °C	Ref.
Tri-(2-hydroxyethyl)ammonium acetate [THEAA]		1.120				141
Tri-(2-hydroxyethyl)ammonium lactate [THEAL]		1.222				141
2-(2-Hydroxyethoxy)ammonium formate [2,2-HEOAF]		1.133				141
2-(2-Hydroxyethoxy)ammonium acetate [2,2-HEOAA]		1.119				141
2-(2-Hydroxyethoxy)ammonium lactate [2,2-HEOAL]		1.149				141
3-Hydroxypropylammonium formate [3-HPAF]		1.15620		1.15080		137
3-Hydroxypropylammonium acetate [3-HPAA]		1.11700		1.11170		137
3-Hydroxypropylammonium malonate [3-HPAMal]		1.25590		1.24970		137
Bis(2-hydroxyethyl)ammonium formate [2-BHEAF]		1.21930		1.21340		137
Bis(2-hydroxyethyl)ammonium acetate [2-BHEAA]		1.17770		1.17130		137
			1.16862		1.16229	143, 144
	1.17385		1.16639		1.16012	145
	1.17320	1.17020	1.16710		1.16090	146
Bis(2-hydroxyethyl)ammonium malonate [DEAMal]		1.24090		1.23450		137
Bis(2-hydroxyethyl)ammonium propionate [2-BHEAP]	1.14270	1.13940	1.13610		1.12920	137
Tris(2-hydroxyethyl)ammonium acetate [2-TEAA]				1.17520		137
Tris(2-hydroxyethyl)ammonium malonate [2-TEAMal]		1.24660		1.23860		137
N-Methyl-2-hydroxyethylammonium formate [m-2-HEAF]		1.12825				148
N-Methyl-2-hydroxyethylammonium acetate [m-2-HEAA]		1.10083				148
N-Methyl-2-hydroxyethylammonium propionate [m-2-HEAPr]		1.07127				148
N-Methyl-2-hydroxyethylammonium butyrate [m-2-HEAB]		1.03924				148
		1.03340	1.03587		1.02914	149
N-Methyl-2-hydroxyethylammonium isobutyrate [m-2-HEAiB]		1.04337				148
N-Methyl-2-hydroxyethylammonium pentanoate [m-2-HEAP]		1.01621				148
Tris(2-hydroxyethyl)methylammonium methylsulfate [MTEOA][$MeOSO_3$]		1.34413				150
Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide		1.1039	1.1032	1.0966	1.09577	151–154
$[MOA]^+[Tf_2N]^-$			1.10228		1.09474	155
	1.10480	1.10101	1.09722	1.09343	1.08964	156
		1.1093	1.1051		1.0983	157
Trimethylbutylammonium bis(tifluoromethylsulfonyl)imide	1.3971	1.3927	1.3883	1.3840	1.3796	158
$[N_{1114}][Tf_2N]$	1.3984				1.3803	159
	1.3965		1.3876		1.3790	160
	1.3962		1.3874		1.3783	161
		1.3747	1.3686	1.3656	1.3614	162
		1.3940		1.3850		163
	1.3969		1.3875		1.3786	164
		1.3930				165, 166
	1.3987	1.3942	1.3898	1.3854	1.3810	167
Tributylmethylammonium bis(trifluoromethylsulfonyl)imide		1.2613				165
$[N_{4441}][Tf_2N]$	1.2673	1.2628	1.2584	1.2541	1.2499	167
			1.253			168
Triethyl(pentyl)ammonium bis(trifluoromethylsulfonyl)imide $[N_{2225}][Tf_2N]$		1.3215	1.3174	1.3132	1.3089	169
N-Hexyltriethylammonium bis(trifluoromethylsulfonyl)imide		1.2793	1.2754	1.2719	1.2676	162
$[N_{6,222}][Tf_2N]$	1.270					168
		1.2914	1.2874	1.2834	1.2795	169
	1.29291					170
	1.29332		1.28487		1.27645	171
N-Heptyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{7,222}][Tf_2N]$	1.27574		1.26736		1.25898	171
N-Octyltriethylammonium bis(trifluoromethylsulfonyl)imide		1.2512	1.2472	1.2429	1.2394	169
$[N_{8,222}][Tf_2N]$	1.25339					170
	1.25380		1.24560		1.23740	171
N-Decyltriethylammonium bis(trifluoromethylsulfonyl)imide		1.2181	1.2144	1.2108	1.2076	169
$[N_{10,222}][Tf_2N]$	1.22027		1.21226		1.20421	171
N-Dodecyltriethylammonium bis(trifluoromethylsulfonyl)imide		1.1911	1.1871	1.1831	1.1794	169
$[N_{12,222}][Tf_2N]$	1.19169					170
	1.19221		1.18437		1.17646	171
N-Tetradecyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{14,222}][Tf_2N]$	1.16897		1.16122		1.15342	171
Poly(*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl]-*N*-(2-methoxyethyl)ammonium) bis(fluorosulfonyl)imide ($[C_3ON_{MA,11}]FSI$)		1.34				68
Poly(*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl]-*N*-(2-methoxyethyl)ammonium) bis(fluorosulfonyl)imide ($[C_5O_2N_{MA,11}]FSI$)		1.31				68

Table 1 (*continued*)

Ionic liquid	Density (ρ/g cm^{-3}) 20 °C	25 °C	30 °C	35 °C	40 °C	Ref.
Poly(*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl]-*N*-[2-2-(2-methoxyethoxyethyl)ammonium)] bis(fluorosulfonyl)imide ([$C_7O_3N_{MA,11}$]FSI)		1.29				68
Poly(*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl]-*N*-(2-methoxyethyl)ammonium) bis(trifluorosulfonyl)imide ([$C_3ON_{MA,11}$]TFSI)		1.41				68
Poly(*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl]-*N*-[2-(2-methoxy)ethyl]ammonium) bis(trifluorosulfonyl)imide ([$C_5O_2N_{MA,11}$]TFSI)		1.38				68
Poly(*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl]-*N*-[2-(2-(2-methoxyethoxy)ethoxy)ethyl]ammonium) bis(trifluorosulfonyl)imide ([$C_7O_3N_{MA,11}$]TFSI)		1.36				68
Poly(*N*-(*n*-butyl)-*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl]ammonium) bis(fluorosulfonyl)imide ([$C_4N_{MA,11}$]FSI)		1.32				68
Poly(*N*-(*n*-butyl)-*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl]ammonium) bis(trifluoromethanesulfonyl)imide ([$C_4N_{MA,11}$]TFSI)		1.36				68
Poly(*N*,*N*-dimethyl-*N*-(*n*-butyl)-*N*-[2-(methacryloyloxy)ethyl]-*N*-(2-methoxyethyl)ammonium) bis(fluorosulfonyl)imide ([$C_7N_{MA,11}$]FSI)		1.22				68
Poly(*N*,*N*-dimethyl-*N*-(*n*-heptyl)-*N*-[2-(methacryloyloxy)ethyl]-*N*-(2-methoxyethyl)ammonium) bis(trifluorosulfonyl)imide ([$C_7N_{MA,11}$]TFSI)		1.30				68
(2-Hydroxyethyl)trimethylammonium bis(trifluoromethylsulfonyl)imide [N_{1112OH}][NTf_2]					1.51434	172
N,*N*,*N*-Trimethylammonium-*N*-butanoic acid bis(trifluoromethylsulfonyl)imide [$N4_{COOH}111$][Tf_2N]	1.5194				1.5016	159
(2-Hydroxyethyl)dimethylpropylammonium bis(trifluoromethylsulfonyl)imide [N_{1132OH}][Tf_2N]	1.4536		1.4445		1435.7	160
(2-Acetate)trimethylammonium bis(trifluoromethylsulfonyl)imide [$N_{1112OOCCH3}$][Tf_2N]	1.4869		1.4773		1.4680	160
Dimethyl(butyl)(isopropyl)ammonium bis(trifluoromethylsulfonyl)imide [N(4)113][Tf_2N]		1.3483	1.3457	1.3421	1.3378	162
Trimethyl(hexyl)ammonium bis(trifluoromethylsulfonyl)imide [N(6)111][Tf_2N]		1.3103	1.3078	1.3040	1.2995	162
Dimethyl(hexyl)(isopropyl)ammonium bis(trifluoromethylsulfonyl)imide [N(6)113][Tf_2N]		1.2846	1.2816	1.2775	1.2732	162
Trimethyl(decyl)ammonium bis(trifluoromethylsulfonyl)imide [N(10)111][Tf_2N]		1.2263	1.2222	1.2186	1.2147	162
Dimethyl(decyl)(isopropyl)ammonium bis(trifluoromethylsulfonyl)imide [N(10)113][Tf_2N]		1.2007	1.1977	1.1942	1.1908	162
Trioctyl(methyl)ammonium bis(trifluoromethylsulfonyl)imide [N(1)888][Tf_2N]		1.0823	1.0803	1.0773	1.0738	162
		1.1046		1.0972		163
	1.1113	1.1075	1.1035	1.0997	1.0960	173
Tributylhexylammonium bis(trifluoromethylsulfonyl)imide [$N_{4,4,4,6}$][NTf_2]	1.1954	1.1911	1.1868	1.1827	1.1786	173
Tributyloctylammonium bis(trifluoromethylsulfonyl)imide [$N_{4,4,4,8}$][NTf_2][$Bu_3OcN^+Tf_2N^-$]	1.120					168
N,*N*,*N*,*N*-Tetraethylammonium tetrafluoroborate [N_{2222}]BF_4	1.2204					174
N,*N*,*N*,*N*-Tetraethylammonium hexafluorophosphate [N_{2222}]PF_6	1.4395					174
N,*N*,*N*,*N*-Tetraethylammonium hexafluoroantimonate [N_{2222}]SbF_6	1.7152					174
N,*N*,*N*-Triethylbutylammonium tetrafluoroborate [N_{2224}]BF_4	1.1397					174
N,*N*,*N*-Triethylbutylammonium hexafluorophosphate [N_{2224}]PF_6	1.3662					174
N,*N*,*N*-Triethylbutylammonium hexafluoroantimonate [N_{2224}]SbF_6	1.6402					174
N,*N*,*N*-Triethylhexylammonium tetrafluoroborate [N_{2226}]BF_4	1.0935					174
N,*N*,*N*-Triethylhexylammonium hexafluorophosphate [N_{2226}]PF_6	1.3513					174
N,*N*,*N*-Triethylhexylammonium hexafluoroantimonate [N_{2226}]SbF_6	1.4882					174
N,*N*,*N*-Triethyloctylammonium tetrafluoroborate [N_{2228}]BF_4	1.0653					174
N,*N*,*N*-Triethyloctylammonium hexafluorophosphate [N_{2228}]PF_6	1.1902					174
N,*N*,*N*-Triethyloctylammonium hexafluoroantimonate [N_{2228}]SbF_6	1.4389					174
N,*N*-Diethyl-*N*-methyl-*N*-(*n*-propyl)ammonium bis(2,2,2-trifluoroethoxysulfonyl)imide (N_{1223}[TFESI])		2.07				175
N-(*n*-Butyl)-*N*,*N*-diethyl-*N*-methylammonium bis(2,2,2-trifluoroethoxysulfonyl)imide (N_{1224}[TFESI])		1.91				175

Table 1 (*continued*)

Ionic liquid	Density (ρ/g cm^{-3}) 20 °C	25 °C	30 °C	35 °C	40 °C	Ref.
N,*N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(2,2,2-trifluoroethoxysulfonyl)imide ($N_{122.1O2}$[TFESI])		1.99				175
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1, R^2, R^3 = C_2H_5)			1.25			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1, R^2 = C_2H_5; R^3 = CH_3)			1.26			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1 = C_2H_5; R^2, R^3 = CH_3)			1.27			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1 = C_4H_9; R^2, R^3 = CH_3)			1.24			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1 = C_6H_{13}; R^2, R^3 = CH_3)			1.21			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1 = C_7H_{15}; R^2, R^3 = CH_3)			1.19			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1 = C_8H_{17}; R^2, R^3 = CH_3)			1.18			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1 = C_9H_{19}; R^2, R^3 = CH_3)			1.17			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1 = $C_{10}H_{21}$; R^2, R^3 = CH_3)			1.15			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1 = $C_{11}H_{23}$; R^2, R^3 = CH_3)			1.14			176, 177
Trimethylbutylammonium bis(trifluorosulfonyl)imide [N_{1114}][TFSI]	1.41					178, 179
Methylethyldipropylammonium bis(trifluorosulfonyl)imide [N_{1233}][TFSI]	1.32					179
Dimethylethylpropylammonium bis(trifluorosulfonyl)imide [N_{1123}][TFSI]	1.39					179
Diethylmethylbutylammonium bis(trifluorosulfonyl)imide [N_{1224}][TFSI]	1.34					179
Diethylmethyltrifluorobutylammonium bis(trifluorosulfonyl)imide [N_{1224f}][TFSI]	1.46					179
Trimethylhexylammonium bis(trifluorosulfonyl)imide [N_{1116}][TFSI]	1.32					179
Trimethyloctylammonium bis(trifluorosulfonyl)imide [N_{1118}][TFSI]	1.26					179
Diethylmethylammonium trifluoromethanesulfonate ([N122][TfO])	1.292	1.284	1.277	1.270	1.262	180
Allyldimethylammonium trifluoromethanesulfonate ([N11a][TfO])	1.311	1.303	1.295	1.288	1.280	180
Dimethylpropylammonium trifluoromethanesulfonate [N113][TfO]	1.284	1.276	1.269	1.262	1.254	180
Allyldiethylammonium trifluoromethanesulfonate [N22a][TfO]	1.263	1.255	1.247	1.240	1.232	180
Diethylpropylammonium trifluoromethanesulfonate [N223][TfO]	1.229	1.222	1.215	1.208	1.201	180
Diallylmethylammonium trifluoromethanesulfonate [N1aa][TfO]	1.261	1.253	1.246	1.239	1.231	180
Dipropylmethylammonium trifluoromethanesulfonate [N133][TfO]	1.218	1.211	1.203	1.196	1.189	180
2-[2-Hydroxyethyl(methyl)amino]ethanol (MDEA)	1.0410	1.0374	1.0337	1.0302	1.0267	181
			1.03374		1.02672	182
Diisopropylethylammonium heptanoate [DIPEA][C_6COO]		0.8665				183
Diisopropylethylammonium octanoate [DIPEA][C_7COO]		0.8585				183
Trimethylpropylammonium [TMPA]	1.41585	1.41241	1.40807	1.40458	1.39879	184
Ethyl-(2-hydroxyethyl)dimethylammonium bromide [ehoedma][Br]		1.1018				185, 186
Butyl-(2-hydroxyethyl)dimethylammonium bromide [bhoedma][Br]		1.0670				185, 186
(2-Hydroxyethyl)dimethylpropylammonium bromide [hoedmpa][Br]		1.0827				185, 186
Hexyl-(2-hydroxyethyl)dimethylammonium bromide [hhoedma][Br]		1.0412				185, 186
Diisopropylmethylammonium formate [DIPMF]	1.002					187
Diisopropylmethylammonium acetate [DIPMA]	0.995					187
Diisopropylmethylammonium hydrogenebisfluoride [DIPMHF]	1.055					187
Diisopropylethylammonium formate [DIPEF]	1.015					187
Diisopropylethylammonium acetate [DIPEA]	0.982					187
Diisopropylethylammonium hydrogenebisfluoride [DIPEHF]	1.003					187
Diethanolamine formate [DEA][Of]		1.13				188

Table 1 (*continued*)

Ionic liquid	Density (ρ/g cm^{-3}) 20 °C	25 °C	30 °C	35 °C	40 °C	Ref.
Diethanolamine acetate [DEA][A]		1.22				188
Diethanolamine hydrogen sulfate [DEA][HSO_4]		1.21				188
Diethanolamine sulfamate [DEA][OSA]		1.45				188
Diethanolamine chloride [DEA][Cl]		1.24				188
Triethanolamine formate [TEtA][Of]		1.04				188
Rriethanolamine acetate [TEtA][A]		0.96				188
Di-*n*-propylamine formate [DPA][Of]		0.97				188
2-Hydroxyethyltrimethylammonium L-(+)-lactate [HE3MA][LAC]	1.14473	1.14139	1.13797	1.13460	1.13150	189
Tris(2-hydroxyethyl)methylammonium methylsulfate[3HEMA]MS	1.34662	1.34373	1.34087	1.33801	1.33517	189
N-Butyl-(*N*-hydroxyethyl)ammonium trifluoroacetate [BHEA][TFA]			1.20334	1.19807	1.19418	200
N-Butyl-(*N*-hydroxyethyl)ammonium nitrate [BHEA][NO_3]			1.11469	1.11158	1.10847	200
N-Methylcyclohexylammonium pentanoate [NMC][Pen]	0.96576	0.96221	0.95863	0.95501	0.95134	201
N-Methylcyclohexylammonium hexanoate [NMC][Hex]	0.95514	0.95165	0.94813	0.94456	0.94096	201
N-Methylcyclohexylammonium heptanoate [NMC][Hep]	0.94580	0.94218	0.93851	0.93481	0.93105	201
N-Methylcyclohexylammonium octanoate [NMC][Oct]	0.93859	0.93517	0.93173	0.92825	0.92474	201
2-(Dimethylamino)-*N*,*N*-dimethylethan-1-ammonium acetate [$N_{11\{2(N11)\}H}$][CH_3CO_2]	1.0091	1.0047	1.0004	0.9963	0.9919	202
N-Ethyl-*N*,*N*-dimethylammonium phenylacetate [N_{112H}][$C_7H_7CO_2$]	1.1025	1.0989	1.0954	1.0918	1.0883	202
3-(2-Allyldimethylammonio)ethyl-1-methyl-1-*H*-imidazol-3-ium di-dicyanamide		1.17734	1.17364		1.16756	211
3-(2-Allyldimethylammonio)ethyl-1-vinyl-1-*H*-imidazol-3-ium di-dicyanamide		1.18931	1.18668		1.18196	211

[a] At 27 °C.

and variability from one group to another (Table 1). For example, in 2012, Capelo *et al.*[121] reported that the ρ value for EAN is 1.21523 g cm^{-3} at 25 °C. In another study, very recently, Usula *et al.*[120] reported that the ρ value for EAN is 1.21076 g cm^{-3} at 25 °C. In another paper of Zarrougui *et al.*[194] obtained 1.2060 g cm^{-3} at 25 °C. Clearly, these three values are very different for same IL under the same experimental conditions. This discrepancy is mainly due to the purity, water content and the methodology. Interestingly, the ρ values significantly decrease as the temperature increases for EAN IL.[121,194]

In the extensive studies on the ρ values of the alkylammonium nitrate ILs, the observed ρ values decrease as the alkyl chain length of the cation increases (from ethyl to butyl), whereas, the addition of the methoxy group to the smaller alkyl chain, results in an increase of the ρ values.[120–125,194] This is mainly due to the difference in molecular mass and to the enhanced capability to provide polar–polar attractive interactions.[120] Moreover, this is due to increasing the alkyl chain length, with an increase in the average distance between ions and makes the formation of hydrogen bonds difficult; the enhanced repulsions arising from the greater size of the hydrocarbon chains prevents the ions from approaching at distances lower than required for hydrogen bonding.[121] Therefore, ILs with shorter alkyl chains are expected to be more hydrogen bonded and denser. A similar effect was observed that ρ values decrease when the alkyl chain length of the cation increases for alkylammonium formate ILs.[103,119,126] Similarly, Xu's research group observed that shorter alkyl chains of cation with acetate anion-based ILs are more dense than for higher alkyl chain of cation with the same anion.[125,127,128]

It was reported that nitrate anion-based IL have significantly higher denser than formate anion-based IL with alkylammonium cation.[103,116,117,119–126] The ρ values at 25 °C of the ethylammonium cation with different anions of ILs follow the order: EAN > EAG > EAL > EAF > EAP > EAA > EAB (Table 1). This order displays the highest ρ values due to the increased size of the anion with same cation. Amongst all ILs the acetate-based ILs show the lowest ρ values compared to nitrate or formate anion-based IL with the same cation.[103,119–125,128,141] On the other hand, Pinkert *et al.*[137] reported that acetate-based ILs are more dense than the formate anion-based IL with the same cation. Kurnia *et al.*[145] showed that ILs with lactate anion show higher ρ than acetate anion-based IL with the same cation. It appears that ρ of hydroxylammonium ILs showed high dependence on the molar mass of anion. More fundamentally, the ρ values of these ILs varied only little with changes in the structure of the anion and cation, though there was a clear trend that as the alkyl chain length of the cation or organic anion increased the density decreased a little, which was attributed to an increase in steric hindrance as the chains become more bulky.[119]

A comparison of ρ values between some of the ammonium-based ILs show that acetate anion-based ILs show significantly lower ρ values than sulfate and phosphate ions of ILs.[129–133] The sulfate or phosphate ions of ILs display the highest ρ values due to increased mass of phosphate or sulfate ions, respectively. As can be seen in Table 1, ρ values of ILs, possessing tetraalkyl-ammonium cation $[R_4N]^+$ with commonly used anion hydroxide $[OH]^-$, have been found to decrease with increase in the cation alkyl chain length from methyl to butyl.[134–136] This is mainly contributing to anion accommodation closer to the cation.

Apparently, ILs that possess a higher cation side chain is accompanied by lower ρ and the cation size was responsible for the alteration of the thermophysical properties of ILs.[134] Obviously, as mentioned before, the lower alkyl chain length cationic ILs are much dense than higher alkyl chain length ILs.[134] In contrast, Cota *et al.*[139] explicitly reported that the higher alkyl chain length of cation of ILs (2-hydroxytriethylammonium formate) (2-HTEAF), (ρ = 1.22186 g cm^{-3} at 25 °C) are more dense than lower alkyl chain length IL 2-hydroxyethylammonium formate (2-HEAF), (ρ = 1.17649 g cm^{-3} at 25 °C). For these types of ions of the ILs, the bulk cation develops lower steric hindrance influence than the linear anion and this fact may be observed in terms of higher values of ρ for those ILs of the lighter anion and the heavier cation.[139] Interestingly, Murugesan's research group[143–145] has reported three different ρ values for bis(2-hydroxyethyl)ammonium acetate (2-BHEAA) IL under the same experimental conditions (Table 1). The discrepancies in the ρ values of hydroxylammonium ILs when compared with the literature may be due to water content and method used to determine the value as well as the drying method involved.[145] Overall, results show that the ρ values of the ILs decrease with increasing the alkyl chain length of the cation. It has been shown that the smaller molecular volume of the alkyl branch of ammonium-based ILs is the primary cause of the higher ρ values.[180] Most importantly, it should be noted that the ρ values reported by different groups sometimes show significant discrepancy, this may caused by the impurities, especially water content.

Obviously, the majority of the literature shows the effect of the alkyl chain length of the cation on thermophysical properties of ILs. On the other hand, to see the effect of the anionic chain length of the ILs, Usula *et al.*[198] quite recently reported the ρ values of ethylammonium alkanoate (EAX, where X is methanoate, propanoate and butanoate) family ILs at 25 °C. The authors explicitly elucidated that the ρ values of pure EAX decrease as the alkyl chain length of anion increase. Analogously, Jacquemin *et al.*[183] observed that ρ values decrease when the alkyl chain length on the anion increases, for example ρ = 0.8665 g cm^{-3} for [DIPEA][C_6COO], which is obviously higher than for [DIPEA][C_7COO] (ρ = 0.8585 g cm^{-3}) under the same experimental conditions. The ρ values are strongly affected by the nature of the anion in the ammonium-based ILs.

The value of u is an important thermodynamic property of liquids and always chosen as a source to determine the molecular interactions. The knowledge of the ultrasonic studies of ammonium-based ILs and their mixtures are quite important to optimize the design of desirable ILs for several industrial processes. A database for the u of pure ammonium-based ILs is collected from many literatures covering all temperatures is included in Table 2. Practically, the u values of ILs mainly depend on the nature and structure of ions and the alkyl chain length of the cation of ILs. As can be seen in Table 2 the u values of ILs have been found to decrease with increasing the temperature.[117,121,126,129–136,139,189,192,193,196] Furthermore, the u values decrease as the cation alkyl chain length of ILs increases.[121,134–136] Apparently, ILs that possess higher cation side chains are accompanied by lower ρ and lower u. When the number of carbon atoms in the alkyl chain length of the cation is increased, the change in u is very high from methyl to propyl group of ILs.[135] Conversely, the u values increase as the cation alkyl chain length from diethylammonium (DEA^+) to triethylammonium (TEA^+) of ILs increases.[129,130]

Clearly, the results might imply that the cation size was responsible for the alteration of the u values of protic ILs. Additionally, Chhotaray and Gardas[126] observed that the u values increase with an increase with carbon chain length for anions in both ammonium and hydroxylammonium-based ILs with fixed cation, which can be attributed to the increase in spatial distance between molecules due to steric hindrance. A similar effect was observed for short aliphatic chain length of ILs, in which u values increase with increase in chain length in anions of ILs with fixed cation from 2-HEA (u = 1709.00 m s^{-1}) or 2-hydroxydiethylammonium formate [2-HDEAF], (u = 1798.54 m s^{-1}) to 2-HTEAF, (u = 1884.60 m s^{-1}).[139] It was demonstrated that nitrate anion-based ILs had significantly higher u values than formate anion-based ILs with alkylammonium cations.[121,126] Furthermore, acetate-based ILs show the lowest u values in comparison with nitrate or formate anion-based ILs, with the same cation (Table 2).[121,126,133,148] The ions of ILs have strong effects on the physicochemical properties, with the steric hindrance being a key factor for accommodation into a liquid structure. Cota *et al.*[139] pointed out that the degree of their influence depends on the nature of the cation, however, the influence of the anion residue is higher because of its linear and longer structure. This factor produces a higher distribution in terms of the accommodation of ions, which indicates that the bulk cation shows a lower steric hindrance influence than the linear anion.

The η data for ammonium-based ILs are of prime importance from the scientific point of view. The η of ammonium family ILs always increases as the alkyl chain on the cation is lengthened because of increased van der Waals interactions.[119,122,124,125,129–131,134,135,148] On the other hand, the η of *N*-propylammonium nitrate (PAN) is larger than that of *N*-butylammonium nitrate (BAN), while its conductivity is also larger than that of its longer chain homologue, reflecting the different mechanisms involved in mass and charge transport.[121] Temperature has a significant effect on the η values of ILs with ammonium-based ILs. As can be seen in Table 3, η values of ILs have been found to decrease with increasing the temperature. This temperature effect can be attributed to increased Brownian motion of the constituent molecules of ILs. The nature of the anion also affects the η of an IL, particularly through relative basicity and the ability to participate in hydrogen bonding. When the cation is kept constant, the η of an IL for the counter anions follow the order:[119] EAG > EAL > EAB > EAP > EAN > EAF.

It has been reported that acetate anion-based ILs show greater η values as compared to their formate or nitrate ILs (Table 3).[125,126,128,137,142] However, the η values of DEAA or TEAA are lower than DEAS or TEAS under the same experimental conditions.[129,130] Moreover, the η of ammonium-based ILs follow the order: TMAP > TMAS > TMAA. Obviously, the acetate anion IL shows lower η values than the phosphate or

Table 2 Ultrasonic sound velocity (u) values of pure ammonium-based ILs at different temperatures from 20 to 40 °C

Ionic liquid	Ultrasonic sound velocity (u/m s^{-1})					Ref.
	20 °C	25 °C	30 °C	35 °C	40 °C	
Ethylammonium nitrate [EAN]	1654	1647	1640	1633	1625	121
N-Propylammonium nitrate [PAN]	1592	1585	1577	1569	1562	121
N-Butylammonium nitrate [BAN]	1548	1540	1533	1524	1515	121
Propylammonium formate [PAF]	1553.06	1542.72	1532.43	1522.21	1511.96	126
Propylammonium acetate [PAA]	1517.12	1507.96	1497.08	1487.62	1477.02	126
3-Hydroxypropylammonium formate [3-HPAF]	1824.27	1816.35	1808.29	1800.45	1792.32	126
3-Hydroxypropylammonium acetate [3-HPAAc]	1779.78	1770.84	1761.87	1753.29	1745.22	126
3-Hydroxypropylammonium trifluoroacetate [3-HPATFAc]	1487.90	1476.51	1465.53	1454.92	1444.53	126
Diethylammonium acetate [DEAA]		1608	1604	1599	1584	129, 130
Diethylammonium hydrogen sulfate [DEAS]		1432	1408	1392	1374	117, 130
Triethylammonium acetate [TEAA]		1840	1824	1798	1784	129, 130
Triethylammonium phosphate [TEAP]		1794	1769	1757	1730	131, 132
Triethylammonium hydrogen sulfate [TEAS]		1874	1871	1866	1860	130, 131
Trimethylammonium acetate [TMAA]		1544	1514	1508	1490	132, 133, 193
Trimethylammonium phosphate [TMAP]		1672	1660	1661	1664	132, 133, 193
Trimethylammonium hydrogen sulfate [TMAS]		1564	1560	1556	1552	132, 133, 193
Tetramethylammonium hydroxide [TMAH]		1828	1817	1806	1795	134–136, 196
Tetraethylammonium hydroxide [TEAH]		1814	1803	1792	1781	134–136, 196
Tetrapropylammonium hydroxide [TPAH]		1801	1790	1779	1769	134–136, 196
Tetrabutylammonium hydroxide [TBAH]		1798	1788	1777	1767	134–136, 196
2-Hydroxyethylammonium formate [2-HEAF]		1719.59				138
	1727.27	1709.00	1695.81	1682.56	1670.14	139
2-Hydroxydiethylammonium formate [2-HDEAF]	1811.20	1798.54	1785.75	1774.08	1762.63	139
2-Hydroxytriethylammonium formate [2-HTEAF]		1884.60				139
2-Hydroxyethylammonium acetate [2-HEAA]	1803.21	1790.73	1779.04		1757.17	142
N-Methyl-2-hydroxyethylammonium formate [m-2-HEAF]		1815.3				133
N-Methyl-2-hydroxyethylammonium acetate [m-2-HEAA]		1794.8				148
N-Methyl-2-hydroxyethylammonium propionate [m-2-HEAPr]		1690				148
N-Methyl-2-hydroxyethylammonium butyrate [m-2-HEAB]		1614.6				148
N-Methyl-2-hydroxyethylammonium isobutyrate [m-2-HEAiB]		1611.3				148
N-Methyl-2-hydroxyethylammonium pentanoate [m-2-HEAP]		1548.8				148
Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide [MOA]$^+$[Tf$_2$N]$^-$		1260	1242	1230	1212	154
2-Hydroxyethyltrimethylammonium L-(+)-lactate [HE3MA][LAC]	1933	1910	1891	1873	1858	189
Tris(2-hydroxyethyl)methylammonium methylsulfate [3HEMA]MS	1975	1961	1949	1937	1925	189
N-Butyl-(*N*-hydroxyethyl)ammonium trifluoroacetate [BHEA][TFA]			1282.6	1270.0	1257.7	200
N-Butyl-(*N*-hydroxyethyl)ammonium nitrate [BHEA][NO$_3$]			1608.3	1595.7	1583.5	200
N-Methylcyclohexylammonium pentanoate [NMC][Pen]	1495.3	1475.7	1456.7	1438.2	1420.1	201
N-Methylcyclohexylammonium hexanoate [NMC][Hex]	1484.0	1464.9	1446.4	1428.2	1410.3	201
N-Methylcyclohexylammonium heptanoate [NMC][Hep]	1478.3	1458.5	1440.2	1422.2	1404.5	201
N-Methylcyclohexylammonium octanoate [NMC][Oct]	1471.6	1453.1	1435.0	1417.2	1399.5	201

hydrogen sulfate anion of ILs.[129,130,132,133] Generally, increasing anion size and cations with longer alkyl chains produce more viscous ILs due to stronger solvophobic and van der Waals interactions.[122,137] Similarly, cations with more localized charges produce more viscous liquids. Apparently, ILs that possess a higher cation side chain are accompanied by lower ρ, lower u and larger η.[135] The thermophysical properties of ILs mainly depend on the nature and structure of ions and the alkyl chain length of the cation.

The data in Table 4 show that the n_D values decrease with increasing the temperature for ammonium-based ILs.[121,143,145,155,167,189] In contrast, Alvarez *et al.*[149] reported that the n_D values of *N*-methyl-2-hydroxyethylammonium butyrate (m-2-HEAB) increase from 1.3650 at 15 °C to 1.3672 at 30 °C or 1.3741 at 40 °C. The reported n_D values of ammonium-based ILs increase as the alkyl chain on the cation increased[119,127,192] However, in 2012, Capelo *et al.*[121] found that the n_D value of PAN is larger than that of BAN. The authors concluded that for ILs with an odd number of carbons in the alkyl chain, the Abbe number increases slowly as the carbon number and so the material tends to be less dispersive, but data for longer alkyl chains are needed to clarify this tendency. PAN, which incorporates an odd number of alkyl groups in the cation alkyl chain, presents a lower Abbe number, and thus higher dispersive power than those of EAN and PAN.

The temperature dependence of conductivity of ammonium-based ILs is essential to understand since they are used for many applications in different fields, particularly in electrochemical processes.[119] Pinkert *et al.*[137] have systematically carried out conductivity studies for different alkyl chain length of cations with the same anion of ammonium-based ILs. They observed that conductivity values decrease as the alkyl chain length of the cation increases for acetate or malonate anion of ammonium-based ILs.[137] Interestingly, Cota *et al.*[139] have studied the conductivities for various alkyl chain length of cations with formate anion-based ammonium ILs. The authors reported that the lower alkyl chain length of cation of IL shows higher conductivity values than those with large alkyl chain length of cation of the ILs whereas the values increase with increasing the temperature. Overall, the conductivity values decrease with

Table 3 Viscosity (η) values of pure ammonium-based ILs at different temperatures from 20 to 40 °C

Ionic liquid	Viscosity (η/mPa s) 20 °C	25 °C	30 °C	35 °C	40 °C	Ref.
Ethylammonium nitrate [EAN]		32[a]				103, 119, 190
	35.9	32.4	29.6	27.9	25.2	122
	40.61	34.49	29.65	25.76	22.67	194
Propylammonium nitrate [PAN]		67				190
	89.3	75.4	64.8	53.6	47.5	122
n-Butylammonium nitrate [N4NO$_3$]	111.35	89.954	73.038	60.248	50.116	124, 125
Butylammonium thiocyanate [BASCN]		97				190
Methylammonium formate [MAF]		17[a]				119
Ethylammonium formate [EAF]		32[a]				103, 119
		23[a]				190
	23.1	20.7	17.3	14.5	10.1	122
Butylammonium formate [BAF]		70[a]				103, 119
Pentylammonium formate [PeAF]		78[a]				103, 119, 190
Ethylammonium propionate [EAP]		75[a]				119
Ethylammonium butyrate [EAB]		208[a]				119
Ethylammonium glycolate [EAG]		1200[a]				103, 119
Ethylammonium lactate [EAL]		803[a]				119
Propylammonium formate [PAF]	96.77	78.60	63.58	52.67	43.97	126
Propylammonium acetate [PAAc]	932.22	627.41	435.42	309.95	226.35	126
Ethanolammonium nitrate [EOAN]		113[a]				103, 119
Diethylammonium formate [DEAF]		5.4[a]				103
Triethylammonium formate [TEAF]		5.8[a]				103
Diethanolammonium formate [DEOAF]		494[a]				103
	156	114	91	78	69	122
2-Hydroxyethylammonium formate [2-HEAF]		105[a]				119
		118				142
2-Hydroxyethylammonium acetate [2-HEAA]		640				142
n-Butylammonium acetate [N4Ac]	771.69	546.348	397.170	294.586	222.241	125, 128
3-Hydroxypropylammonium formate [3-HPAF]	339.04	257.15	198.39	154.49	122.56	126
3-Hydroxypropylammonium acetate [3-HPAA]	4261.7	2827.01	1937.03	1348.55	970.90	126
3-Hydroxypropylammonium trifluoroacetate [3-PATFA]	1430.2	970.33	677.32	483.03	352.31	126
Ethanolammonium formate [EOAF]		220				119
Ethanolammonium acetate [EOAA]		701				119, 187
2-Propanolammonium formate [2-POAF]		854				119
Ethanolammonium lactate [EOAL]		1324				119
Ethylammonium hydrogen sulfate [EAHS]		128				119, 191
2-Methylpropylammonium formate [2-MPAF]		225				119
2-Methylbutylammonium formate [2-MBAF]		229				119, 191
Dimethylethylammonium formate [DMEAF]	9.8	8.7	6.3	5.1	4.6	122
Diethylammonium acetate [DEAA]		16.36	13.64	11.83	10.48	129, 130
Diethylammonium hydrogen sulfate [DEAS]		25.80	21.30	18.10	15.67	117, 130
Triethylammonium acetate [TEAA]		24.12	19.64	16.13	12.27	129, 130
Triethylammonium phosphate [TEAP]		64.27	57.10	49.45	38.26	131, 132
Triethylammonium hydrogen sulfate [TEAS]		235.0	153.0	138.0	108.0	130, 131
Trimethylammonium acetate [TMAA]		2.76	2.37	2.06	1.83	122, 123
Trimethylammonium phosphate [TMAP]		7.64	6.46	5.61	5.07	129, 130
Trimethylammonium hydrogensulfate [TMAS]		5.10	4.48	3.94	3.16	117, 130
Tetramethylammonium hydroxide [TMAH]		2.77	2.71	2.62	2.56	134, 135, 196
Tetraethylammonium hydroxide [TEAH]		4.94	4.72	4.43	4.27	134, 135, 196
Tetrapropylammonium hydroxide [TPAH]		6.10	6.01	5.88	5.66	134, 135, 196
Tetrabutylammonium hydroxide [TBAH]		6.69	6.49	6.29	6.13	134, 135, 196
Diallylammonium formate [DAAF]		2.45		1.92		137
Diallylammonium acetate [DAAA]		80.0		45.7		137
1-Hydroxyethylammonium formate [HEAF]		66.2		39.7		137
3-Hydroxypropylammonium formate [3-HPAF]		310		170		137
Bis(2-hydroxyethyl)ammonium formate [2-BHEAF]		951		518		137
2-Hydroxyethylammonium lactate [2-HEAL]		1200				141
Tri-(2-hydroxyethyl)ammonium acetate [THEAA]		342				141
Tri-(2-hydroxyethyl)ammonium lactate [THEAL]		455				141
2-(2-Hydroxyethoxy)ammonium formate [2,2-HEOAF]		371				141
2-(2-Hydroxyethoxy)ammonium acetate [2,2-HEOAA]		2893				141
2-(2-Hydroxyethoxy)ammonium lactate [2,2-HEOAL]		3040				141
Bis(2-hydroxyethyl)ammonium propionate [BHEAP]	740.28	480.18	322.17		157.97	147
Tris(2-hydroxyethyl)ammonium acetate [2-TEAA]				797		137
N-Methyl-2-hydroxyethylammonium formate [m-2-HEAF]		20.27				148
N-Methyl-2-hydroxyethylammonium acetate [m-2-HEAA]		103.06				148
N-Methyl-2-hydroxyethylammonium propionate [m-2-HEAPr]		215.06				148
N-methyl-2-hydroxyethylammonium butyrate [m-2-HEAB]		298.15				148
N-Methyl-2-hydroxyethylammonium isobutyrate [m-2-HEAiB]		163.08				148

Table 3 (*continued*)

Ionic liquid	Viscosity (η/mPa s) 20 °C	25 °C	30 °C	35 °C	40 °C	Ref.
N-Methyl-2-hydroxyethylammonium pentanoate [m-2-HEAP]		234.44				148
Tris(2-hydroxyethyl)methylammonium methylsulfate [MTEOA][$MeOSO_3$]		1236				150
Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide $[MOA]^+[Tf_2N]^-$	676.3		359.9		200.7	156
N-Hexyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{6,222}][Tf_2N]$	234.5	187.5	136.7	109.2	87.67	171
N-Heptyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{7,222}][Tf_2N]$	253.6	204.6	154.2	116.9	90.36	171
N-Octyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{8,222}][Tf_2N]$	288.4	238.7	178.9	134.7	103.1	171
N-Docyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{10,222}][Tf_2N]$	358.9	288.6	214.5	160.1	122.0	171
N-Dodecyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{12,222}][Tf_2N]$	410.0	321.6	249.2	203.1	152.7	171
N-Tetradecyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{14,222}][Tf_2N]$	490.3	401.1	293.6	236.5	176.1	171
Trimethylbutylammonium bis(tifluoromethylsulfony)limide	104				48	159
$[N_{1114}][Tf_2N]$	138		82.3		52.2	160
	142.5		86.5		55.3	161
Tributylmethylammonium bis(trifluoromethylsulfonyl)imide $[N_{4441}][Tf_2N]$			386			168
Triethyl(pentyl)ammonium bis(trifluoromethylsulfonyl)imide $[N_{2225}][Tf_2N]$		161.6	121.4	92.11	71.86	169
N-Hexyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{6,222}][Tf_2N]$		186.6	137.9	105.1	81.64	169
		167				168
N-Octyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{8,222}][Tf_2N]$		221.4	163.9	124.7	96.76	169
N-Decyltriethylammonium bis(trifluoromethylsulfonyl)imide $[N_{10,222}][Tf_2N]$		281.9	205.4	152.7	115.1	169
N-Dodecyltriethylammoniumbis(trifluoromethylsulfonyl)imide $[N_{12,222}][Tf_2N]$		311.8	227.6	167.7	137.8	169
(2-Hydroxyethyl)trimethylammonium bis(trifluoro-methylsulfonyl)imide $[N_{1112OH}][NTf_2]$					56.44	172
N,*N*,*N*-Trimethylammonium-*N*-butanoic acid bis[(trifluoromethyl)sulfonyl]imide $[N4_{COOH}111][Tf_2N]$	1750				49.3	159
(2-Hydroxyethyl)dimethylpropylammonium bis(trifluoromethylsulfonyl)imide $[N_{1132OH}][Tf_2N]$	160		92.7		58.1	160
(2-Acetate)trimethylammonium bis(trifluoromethylsulfonyl)imide $[N_{1112OOCCH3}][Tf_2N]$	309		162		90.7	160
Trioctylmethylammonium bis(trifluormethylsulfonyl)imide [N(1)888][Tf_2N]	877.56	619.64	446.75	328.50	246.02	173
Tributylhexylammonium bis(trifluoromethylsulfonyl)imide $[N_{4,4,4,6}][NTf_2]$	910.46	611.32	426.67	305.82	225.69	173
Tributyloctylammonium bis(trifluoromethylsulfonyl)imide $[Bu_3OcN^+Tf_2N^-]$		574				168
N,*N*-Diethyl-*N*-methyl-*N*-(*n*-propyl)ammonium bis(2,2,2-trifluoroethoxysulfonyl)imide (N_{1223}[TFESI])		267				175
N-(*n*-Butyl)-*N*,*N*-diethyl-*N*-methylammonium bis(2,2,2-trifluoroethoxysulfonyl)imide (N_{1224}[TFESI])		284				175
N,*N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(2,2,2-trifluoroethoxysulfonyl)imide ($N_{122.1O2}$[TFESI])		224				175
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1, R^2, $R^3 = C_2H_5$)			876			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1, $R^2 = C_2H_5$; $R^3 = CH_3$)			754			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides ($R^1 = C_2H_5$; R^2, $R^3 = CH_3$)			714			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides ($R^1 = C_4H_9$; R^2, $R^3 = CH_3$)			745			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides ($R^1 = C_6H_{13}$; R^2, $R^3 = CH_3$)			774			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides ($R^1 = C_7H_{15}$; R^2, $R^3 = CH_3$)			787			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides ($R^1 = C_8H_{17}$; R^2, $R^3 = CH_3$)			806			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides ($R^1 = C_9H_{19}$; R^2, $R^3 = CH_3$)			829			176, 177
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides ($R^1 = C_{10}H_{21}$; R^2, $R^3 = CH_3$)			840			176, 177

Table 3 (*continued*)

Ionic liquid	Viscosity (η/mPa s) 20 °C	25 °C	30 °C	35 °C	40 °C	Ref.
Trialkyl[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]ammonium bis(trifluoromethanesulfonyl)imides (R^1 = $C_{11}H_{23}$; R^2, R^3 = CH_3)			844			176, 177
Trimethylbutylammonium bis(trifluorosulfonyl)imide [N_{1114}][TFSI]	148	111				176, 177
Methylethyldipropylammonium bis(trifluorosulfonyl)imide [N_{1233}][TFSI]	155					179
Dimethylethylpropylammonium bis(trifluorosulfonyl)imide [N_{1123}][TFSI]	82					179
Diethylmethylbutylammonium bis(trifluorosulfonyl)imide [N_{1224}][TFSI]	161					179
Diethylmethyltrifluorobutylammonium bis(trifluorosulfonyl)imide [N_{1224f}][TFSI]	774					179
Trimethylhexylammonium bis(trifluorosulfonyl)imide [N_{1116}][TFSI]	205					179
Trimethyloctylammonium bis(trifluorosulfonyl)imide [N_{1118}][TFSI]	257					179
Diethylmethylammonium trifluoromethanesulfonate ([N122][TfO])			36.9			180
Allyldimethylammonium trifluoromethanesulfonate ([N11a][TfO])			28.8			180
Dimethylpropylammonium trifluoromethanesulfonate [N113][TfO]			33.2			180
Allyldiethylammonium trifluoromethanesulfonate [N22a][TfO]			51.0			180
Diethylpropylammonium trifluoromethanesulfonate [N223][TfO]			54.3			180
Diallylmethylammonium trifluoromethanesulfonate [N1aa][TfO]			38.5			180
Dipropylmethylammonium trifluoromethanesulfonate [N133][TfO]			48.7			180
2-[2-Hydroxyethyl(methyl)amino]ethanol (MDEA)			57.57		34.78	181
			57.69		34.79	182
Trimethyl propylammonium [TMPA]	98	74	65	57	48	184
Diisopropylmethylammonium formate [DIPMF]	25.0					187
Diisopropylmethylammonium acetate [DIPMAc]	32.2					187
Diisopropylmethylammonium hydrogenebisfluoride [DIPMHF]	100.0					187
Diisopropylethylammonium formate [DIPEF]	18.0					187
Diisopropylethylammonium acetate [DIPEA]	54.4					187
Diisopropylethylammonium hydrogenbisfluoride [DIPEHF]	81.1					187
Diethanolamine formate [DEA][Of]		28				188
Diethanolamine acetate [DEA][Ac]		336				188
Diethanolamine hydrogen sulfate [DEA][HSO_4]		>4356				188
Diethanolamine sulfamate [DEA][OSA]		720				188
Diethanolamine chloride [DEA][Cl]		305				188
Triethanolamine formate [TEtA][Of]		10				188
Triethanolamine acetate [TEtA][A]		11				188
Di-*n*-propylamine formate [DPA][Of]		19				188
2-Hydroxyethyltrimethylammonium L-(+)-lactate [HE3MA][LAC]	3942		1500		649	189
Tris(2-hydroxyethyl)methylammonium methylsulfate [3HEMA][MS]	1695		799		397	189
N-Butyl(*N*-hydroxyethyl)ammonium trifluoroacetate [BHEA][TFA]			211.7	171.1	135.3	200
N-Butyl(*N*-hydroxyethyl)ammonium nitrate [BHEA][NO_3]			272.1	202.9	154.0	200
2-(Dimethylamino)-*N*,*N*-dimethylethan-1-ammonium acetate [$N_{11\{2(N11)\}H}$][CH_3CO_2]	34.0	25.9	20.2	16.0	12.9	202
N-Ethyl-*N*,*N*-dimethylammoniumphenylacetate [N_{112H}][$C_7H_7CO_2$]	185.3	130.8	96.00	72.45	56.16	202

[a] At 27 °C.

increasing the alkyl chain length of the cation of ammonium-based ILs.[178–180]

3. Density data of mixtures for ammonium-based ILs with molecular solvents

The knowledge of ρ data of ILs + molecular solvents are fascinating from various chemical and technological points of view. In recent decades, considerable amount of data on the ρ values of ammonium-based ILs with molecular solvents are available. Very recently, Usula *et al.*[120] examined the ρ values for ammonium-based ILs with *N*-methyl-2-pyrrolidone (NMP) at 25 °C. They observed ρ values 1.12936 g cm^{-3} (at $x_{IL} \approx 0.5400$), 1.10572 g cm^{-3} (at $x_{IL} \approx 0.5510$), 1.08043 g cm^{-3} (at $x_{IL} \approx 0.5380$) or 1.14299 g cm^{-3} (at $x_{IL} \approx 0.4480$) for EAN, PAN, BAN or 2-methoxyethylammonium nitrate (MEOEAN) + NMP binary systems at 25 °C, respectively. The ρ values decrease as the alkyl chain length of the cation increases,

Table 4 Refractive indices (n_D) values of the pure ammonium-based ILs at different temperatures from 20 to 40 °C

Ionic liquid	Refractive indices (n_D) 20 °C	25 °C	30 °C	35 °C	40 °C	Ref.
Ethylammonium nitrate [EAN]		1.4524				119
	1.4538	1.4526	1.4515	1.4506	1.4488	121
N-Propylammonium nitrate [PAN]	1.4565	1.4554	1.4543	1.4529	1.4515	121
N-Butylammonium nitrate [BAN]	1.4542	1.4530	1.4516	1.4505	1.4485	121
		1.4458				124
Methylammonium formate [MAF]		1.4336				119
Ethylammonium formate [EAF]		1.4344				119
Butylammonium formate [BAF]		1.4422				119
Pentylammonium formate [PeAF]		1.4434				119
Ethylammonium propionate [EAP]		1.4358				119
Ethylammonium butyrate [EAB]		1.4398				119
Ethylammonium glycolate [EAG]		1.4692				119
Ethylammonium lactate [EAL]		1.4581				119
Ethylammonium acetate [N2A]		1.4345				127
Propylammonium acetate [N3A]		1.4405				127
n-Butylammonium acetate [N4A]		1.4426				128
Ethanolammonium nitrate [EOAN]		1.4400				119
Ethanolammonium formate [EOAF]		1.4705				119
Ethanolammonium acetate [EOAA]		1.4690				119
2-Propanolammonium formate [2-POAF]		1.4642				119
Ethanolammonium lactate [EOAL]		1.4702				119
Ethylammonium hydrogen sulfate [EAHS]		1.4489				119
2-Methylpropylammonium formate [2-MPAF]		1.4434				119
2-Methylbutylammonium formate [2-MBAF]		1.4462				119
2-Hydroxyethylammonium formate [2-HEAF]		1.4772				140
Bis(2-hydroxyethyl)ammonium acetate [2-BHEAA]			1.48008		1.47793	143
			1.43238		1.43029	145
N-Methyl-2-hydroxyethylammonium formate [m-2-HEAF]		1.4458				148
N-Methyl-2-hydroxyethylammonium acetate [m-2-HEAA]		1.4494				148
N-Methyl-2-hydroxyethylammonium propionate [m-2-HEAPr]		1.4534				148
N-methyl-2-hydroxyethylammonium butyrate [m-2-HEAB]		1.4549				148
			1.3672		1.3741	149
N-Methyl-2-hydroxyethylammonium isobutyrate [m-2-HEAiB]		1.4511				148
N-Methyl-2-hydroxyethylammonium pentanoate [m-2-HEAP]		1.4538				148
Tris(2-hydroxyethyl)methylammonium methylsulfate [MTEOA][$MeOSO_3$]		1.48489				150
Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide [MOA]$^+$[Tf_2N]$^-$			1.43656		1.43341	155
	1.4388		1.4359		1.4328	156
Trimethylbutylammonium bis(tifluoromethylsulfonyl)imide [N_{1114}][Tf_2N]		1.40806				165
Tributylmethylammonium bis(trifluoromethylsulfonyl)imide [N_{4441}][Tf_2N]		1.42614				165
Diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide [S_{221}][Tf_2N]	1.42452	1.42325	1.42168	1.42026	1.41886	167
Triethylsulfonium bis(trifluoromethylsulfonyl)imide [S_{222}][Tf_2N]	1.42765	1.42632	1.42472	1.42325	1.42185	167
Trimethylbutylammonium bis(trifluoromethylsulfonyl)imide [N_{4111}][NTf_2]	1.40945	1.40818	1.40676	1.40538	1.40405	167
Tributylmethylammonium bis(trifluoromethylsulfonyl)imide [N_{4441}][Tf_2N]	1.42787	1.42643	1.42491	1.42338	1.42194	167
N-Hexyltriethylammonium bis(trifluoromethylsulfonyl)imide [$N_{6,222}$][Tf_2N]		1.42567				170
		1.42599				171
N-Heptyltriethylammonium bis(trifluoromethylsulfonyl)imide [$N_{7,222}$][Tf_2N]		1.42708				171
N-Octyltriethylammonium bis(trifluoromethylsulfonyl)imide [$N_{8,222}$][Tf_2N]		1.42903				170
		1.42871				171
N-Docyltriethylammonium bis(trifluoromethylsulfonyl)imide [$N_{10,222}$][Tf_2N]		1.43169				171
N-Dodecyltriethylammonium bis(trifluoromethylsulfonyl)imide [$N_{12,222}$][Tf_2N]		1.43454				170
		1.43414				171
N-Tetradecyl-triethylammonium bis(trifluoromethylsulfonyl)imide [$N_{14,222}$][Tf_2N]		1.43587				171
2-Hydroxyethyltrimethylammonium L-(+)-lactate [HE3MA][LAC]		1.4828		1.47953		189
Tris(2-hydroxyethyl)methylammonium methylsulfate [3HEMA][MS]		1.4843		1.48210		189
Diethylammonium acetate [DEAA]		1.431				192
Diethylammonium hydrogen sulfate [DEAS]		1.422				192
Triethylammonium acetate [TEAA]		1.501				192
Triethylammonium hydrogen sulfate [TEAS]		1.516				192
Trimethylammonium acetate [TMAA]		1.392				192
Trimethylammonium hydrogen sulfate [TMAS]		1.406				192
N-Butyl-(*N*-hydroxyethyl)ammonium trifluoroacetate [BHEA][TFA]			211.7	171.1	135.3	200
N-Butyl-(*N*-hydroxyethyl)ammonium nitrate [BHEA][NO_3]			272.1	202.9	154.0	200
2-(Dimethylamino)-*N*,*N*-dimethylethan-1-ammonium acetate [$N_{11\{2(N11)\}H}$][CH_3CO_2]	34.0	25.9	20.2	16.0	12.9	202
N-Ethyl-*N*,*N*-dimethylammoniumphenylacetate [N_{112H}][$C_7H_7CO_2$]	185.3	130.8	96.00	72.45	56.16	202

except for MEOEAN + NMP, whereas the addition of the methoxy group to the smaller alkyl chain, results in an increase of ρ at equimolar concentration. This can be attributed perhaps due to the difference in molecular mass and to the improved

capability to polar–polar attractive interactions between the ions of ILs and NMP. This indicates that a long alkyl chain obstructs the compaction of these ILs, while the addition of a polar group in a short chain has an opposite effect, *i.e.* promotes a greater compaction of the ions of ILs.[120]

The ρ values have been reported for different alkyl chain cations of ammonium-based ILs with different anions such as acetate, sulfate, phosphate and hydroxyl ions with dimethyl sulfoxide (DMSO) at the temperature range from 25 to 40 °C over the entire composition range and the ρ values decreased as the temperature increased. The ρ values for various ammonium-based ILs with DMSO[117,129,131,133,134] at 25 °C are shown in Fig. 1a for comparison of the available data. The ρ values decreased for the mixtures of DEAA, TEAA, DEAS, TMAA, TPAH or TBAH with DMSO with increasing x_{IL} as shown in Fig. 1a. Conversely, the ρ values increased for TMAS or TEAS or TMAP with DMSO with increasing mole fraction of these ILs (Fig. 1a). In addition of TEAP with DMSO, the ρ values increased up to $x_{IL} \approx 0.8000$, later, the ρ values slightly decreased as the mole fraction of IL increased. TMAH or TEAH with DMSO mixture shows that the ρ value slightly increased up to $x_{IL} \approx 0.1000$, after that the values decreased with increasing the x_{ILs}.[134] The ρ values of ammonium-based ILs with DMSO showed the following order: TMAS > TMAP > TEAP > TEAS > TMAH > TMAA > TEAH > DEAS > DEAA > TPAH > TEAA > TBAH. The sulfate anion TMAS IL with DMSO shows higher density than acetate or phosphate anion of the ammonium-based IL with DMSO.[133]

The ρ values of the TMAS + DMSO mixture are higher, when compared to rest of the ILs with DMSO at the entire composition of ILs. The large ρ value of the TMAS + DMSO system is mainly due to stronger intermolecular interactions between ions of TMAS and DMSO. This mainly contributes to anion accommodating itself closer to the relatively larger cation of ILs. Therefore, large mass of the sulfate anion leads to higher ρ values as compared to the lower mass anions of the rest of the ILs.[131,133] The lower ρ of the TBAH + DMSO system indicates weaker intermolecular interactions between ions of TBAH and DMSO.[134] The ρ values generally decrease or increase depending on the variation in the interactions of cation or anion of ILs with DMSO molecules. The ρ values decrease with increasing the alkyl chain length in the cation with the same anion of ammonium-based ILs + DMSO at all studied temperatures. For instance, the acetate anion of DEAA shows higher ρ value with DMSO than acetate anion of TEAA with DMSO, and TMAP shows higher ρ value with DMSO than TEAP with DMSO. This can be attributed to that the smaller alkyl chain length of the cation with acetate anion of ammonium-based IL leads to stronger interactions with DMSO than higher alkyl chain length of ammonium-based IL.[129] The results reveal that ρ of hydroxyl group ammonium-based ILs with DMSO decrease as the alkyl chain length increases from methyl to butyl chain of ILs as shown in Fig. 1a. The ρ values of these mixtures follow the order: TMAH > TEAH > TPAH > TBAH, which reveals that the lower alkyl chain length of cation of ILs leads to higher density than higher alkyl chain length of the ILs.[134] These studies confirm that the ρ values are quite sensitive to the size of the cation of ammonium-based ILs and also the size of the anion.[134]

Fig. 1b displays a comparison among ammonium-based ILs with NMP at 25 °C. The results in this figure show that the ρ values of TMAS, TMAP, TEAS, TEAP or TMAA with NMP[132] systems significantly increased with increasing x_{IL}. The ρ values significantly increased for DEAS with NMP with increasing the x_{IL} at all temperatures, except for DEAS + NMP at 40 °C, in which the ρ values increased with increasing up to the $x_{IL} \approx 0.5400$, later the ρ values decreased up to $x_{IL} \approx 0.9300$ at 40 °C.[130]

The ρ values significantly decrease as the temperature increases for NMP with ammonium-based ILs due to weakening of the molecular interactions in the mixture. The ρ values of ammonium-based ILs with NMP follow order: TMAP > DEAS > TMAS > TEAS > TEAP > TMAA > DEAA > TMAH > TEAH > TPAH > TEAA > TBAH (Fig. 1b) at 25 °C. The maximum or minimum ρ values are obtained for TMAP or TBAH with NMP at 25 °C, respectively. The phosphate anion with (TMA^+) shows higher ρ values with NMP than sulfate, acetate or hydroxyl anion with the same cation (TMA^+) of ammonium-based ILs with NMP, which indicates that the highest ρ values due to increased size of the phosphate ion than acetate, hydroxyl or sulfate ions of ILs. It has been revealed that the ρ values for the mixtures of TEAA or TEAS with NMP are lower than those for the mixture of DEAA or

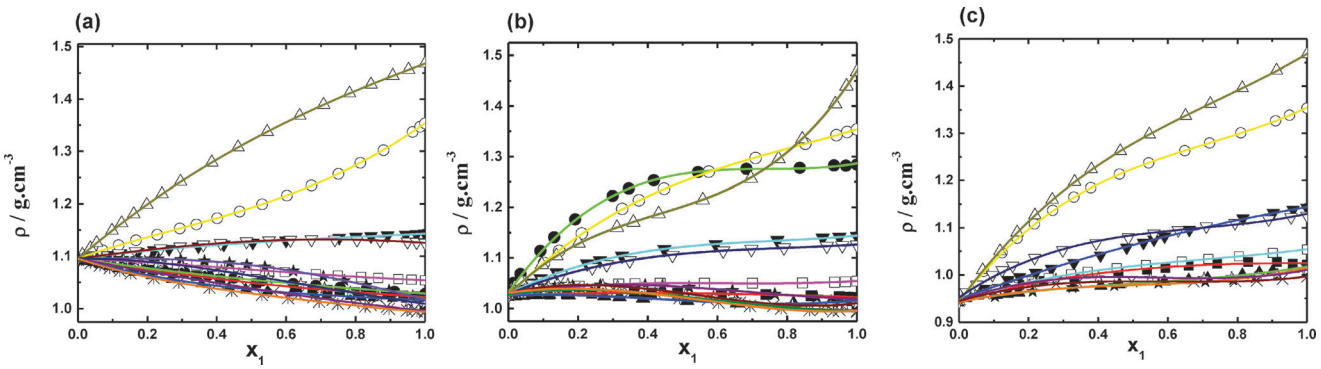

Fig. 1 Comparison among the available literature density (ρ) data for mixtures of ammonium-based ILs + (a) DMSO;[117,129,131,133,134] (b) NMP;[130,132,135] (c) DMF[116,136,193] as a function of the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (○) TMAP; (△) TMAS; (▽) TEAP; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

DEAS with NMP under the same experimental conditions. The TEAP + NMP system has lower ρ values as compared with TMAP + NMP at all studied temperatures. This can be attributed to that the lower alkyl chain length of cation of TMAP IL leads to higher density than the higher alkyl chain length of TEAP IL.[132] Clearly, the lower alkyl chain length of cation ILs with NMP are denser than the higher alkyl chain length of ILs with NMP.[135]

By analogy, the ρ values for TMAS, TMAP, TMAA, TEAH, TPAH or TMAH with *N*,*N*-dimethylformamide (DMF) mixtures increased with increasing concentrations of the ILs[136,193] and the ρ values decreased with increasing temperatures. From Fig. 1c, the ρ values of all ammonium-based ILs with DMF follows the order: TMAS > TMAP > TEAP > TEAS > TMAA > DEAA > TEAH > TPAH > TMAH > TEAA.[116,136,193] It can be seen in Fig. 1c that the higher and lower ρ values are found for TMAS and TEAA ILs with DMF at 25 °C, respectively. Among them, the acetate anions of ILs systems show lower ρ than sulfate, phosphate or hydroxyl anion of ILs. The sulfate and phosphate anion of ILs with DMF show the highest ρ values due to increased density of the anions of ILs than acetate anion of IL.[193] Clearly, Fig. 1c shows that the ρ values of TEAA with DMF were lower when compared to those for DEAA with DMF.[116] In contrast, the ρ values of the TEAH with DMF mixtures were higher as compared to the ρ values for the mixtures of TMAH or TPAH + DMF.[136] Usually, ρ values decrease with increasing length of alkyl chain in a cation, however, on the contrary, here ρ values increase with increasing the alkyl chain length of IL. Generally, ρ values of the ILs containing the same cation increase with increasing molecular mass of associated anion.[137] In this regard Fredlake and co-authors clearly pointed out that anions are small enough to easily occupy a position closer to the relatively large cation.[203] The variation in ρ values between ILs (fixed cation) with various anion systems can be explained by the different sizes of the anions associated with same cation.[193] In this context, the ρ values in Fig. 1c show that the ρ values of TMAS + DMF system are higher than those for TMAP, TMAA or TMAH + DMF systems under the same experimental condition. The sulfate anion is found to lead to higher densities with DMF, lower values are found for hydroxyl or acetate anion and moderate densities for phosphate with the same cation in the DMF system. These observations indicate that the anion of ILs plays a key role in ρ values of the mixtures. The ρ value decrease or increase depending on the variation in the interactions of cation or anion of ammonium-based ILs with DMF molecules.

It is noteworthy to compare the ρ values of all ammonium-based ILs with these polar solvents (DMSO, NMP and DMF), presented in the literature (Fig. 1). The ρ values of DMSO + ammonium-based ILs roughly ranges within 0.99488 to 1.45601 g cm^{-3}. The ρ data of NMP with same ILs range from 0.99507 to 1.43941 g cm^{-3}. Furthermore, the range of these ILs with DMF is 0.95239 to 1.43304 g cm^{-3}. These studies distinctly demonstrate that the ρ values of DMSO with these ILs are higher than those of NMP or DMF with these same ILs. Amongst all investigated ammonium-based ILs, the sulfate anion ammonium-based ILs show highest ρ values, the acetate ILs show the lowest ρ values and hydroxide and phosphate ILs show moderate ρ values.

From Fig. 1a, the sulfate, acetate and phosphate anion of ammonium-based ILs with lower size of alkyl chain length of cation groups show higher ρ values as compared to larger size of alkyl chain length of cation with DMSO (TEAS < TMAS, TEAA < DEAA and TEAP < TMAP) except DEAS and TEAS, where DEAS < TEAS. The same trend is observed for these anions of the ammonium-based ILs with NMP or DMF (Fig. 1b and c). In general, hydroxide anion ammonium-based IL with DMSO or NMP systems show lower ρ than the sulfate, acetate or phosphate anion groups of ammonium-based IL (Fig. 1a and b). However, in contrast, acetate anions of ammonium-based ILs with DMF show lower ρ than hydroxide, sulfate and phosphate anion of ammonium-based IL with DMF (Fig. 1c). The literature clearly shows that the hydroxyl groups of ILs with DMSO (0.99488 to 1.45601 g cm^{-3}) are more dense than those of NMP (0.99507 to 1.43941 g cm^{-3}) and DMF (0.95239 to 1.43304 g cm^{-3}).

Xu *et al.*[124] measured the ρ values of *n*-butylammonium nitrate ($N4NO_3$) with alkanols at different temperatures from 20 to 40 °C and they found ρ values of 1.03655 g cm^{-3} (at $x_{IL} \approx 0.5015$), 1.00957 g cm^{-3} (at $x_{IL} \approx 0.5005$), 0.99396 g cm^{-3} (at $x_{IL} \approx 0.4995$) or 0.97869 g cm^{-3} (at $x_{IL} \approx 0.4955$) at 25 °C for $N4NO_3$ with methanol, ethanol, propanol or butanol at equivalent composition, respectively. The ρ values are decreased for $N4NO_3$ with methanol to butanol, which indicates that the molecular interactions decrease between the ions of $N4NO_3$ and methanol to butanol due to increasing $-CH_2$ groups from methanol to butanol.[124] It has been shown that the ρ values for $N4NO_3$ + alkanols decrease as temperature increases.[124]

Further research demonstrated that the observed ρ values were decreased for 2-HEAF with water, methanol or ethanol systems with decreasing the mole fraction IL and with increasing temperature.[138] The ρ values are 1.15583 g cm^{-3} (at $x_{IL} \approx 0.4920$), 1.07254 g cm^{-3} (at $x_{IL} \approx 0.5000$) or 1.03738 g cm^{-3} (at $x_{IL} \approx 0.5000$) were observed for 2-HEAF with water, methanol or ethanol at 25 °C, respectively.[138] The ρ values of 2-HEAF with methanol or ethanol are lower than 2-HEAF + water, which indicates that the ion-pair interactions decrease between the ions of 2-HEAF and methanol or ethanol due to the presence of $-CH_2$ groups in methanol or ethanol.[138] Alvarez *et al.*[142] demonstrated that the 2-hydroxyethylammonium acetate (2-HEAA) + water mixture (1.13755 g cm^{-3} at $x_{IL} \approx 0.5016$) shows higher ρ values than 2-HEAA + methanol (1.05674 g cm^{-3} at $x_{IL} \approx 0.4825$) or ethanol (1.02643 g cm^{-3} at $x_{IL} \approx 0.4946$), which indicates that 2-HEAA IL may form more hydrogen bonding with water than methanol or ethanol, respectively.[142]

Taib *et al.*[144] have investigated the ρ values for 2-BHEAA with water or monoethanolamine (MEA) systems over the temperature range 30 to 80 °C. The ρ values for 2-BHEAA + water or MEA systems were decreased with increasing temperature. The ρ values were 1.16060 g cm^{-3} (at $x_{IL} \approx 0.4659$) or 1.10844 g cm^{-3} (at $x_{IL} \approx 0.5000$) for 2-BHEAA with water or MEA at 30 °C, respectively. Consequently, here also 2-BHEAA + water system is more dense than 2-BHEAA + MEA. The ρ values were obtained for 2-BHEAA + methanol or ethanol or 1-propanol binary mixtures over the entire mole fraction range of IL and at

different temperatures.[146] The ρ data are 1.10081 g cm^{-3} (at $x_{IL} \approx 0.5034$), 1.07217 g cm^{-3} (at $x_{IL} \approx 0.5048$) or 1.06054 g cm^{-3} (at $x_{IL} \approx 0.5224$) for 2-BHEAA + methanol, ethanol or 1-propanol at 20 °C, respectively. The ρ values decreased from methanol to propanol with 2-BHEAA. Furthermore, the ρ values of water with 2-BHEAA are higher than ρ values of 2-BHEAA with alkanols, which indicates that 2-BHEAA shows stronger interactions with water than alkanols due to water being more polar than alkanols.[144,146]

In addition, Kurnia *et al.*[147] systematically investigated the ρ values for bis(2-hydroxyethyl)ammonium propionate, (2-BHEAP) with methanol, ethanol or 1-propanol mixtures over the entire mole fraction range of IL at different temperatures from 20 to 50 °C. They observed ρ values of 1.0824 g cm^{-3} (at $x_{IL} \approx 0.5038$) or 1.0583 g cm^{-3} (at $x_{IL} \approx 0.5084$) or 1.0412 g cm^{-3} (at $x_{IL} \approx 0.5009$) for 2-BHEAP with methanol, ethanol or 1-propanol at 20 °C, respectively. Higher ρ values are obtained for 2-BHEAP + methanol than for the ethanol or propanol system at 20 °C. This can be revealed as due to formation of stronger ion-pair interactions between the ions of 2-BHEAP and methanol than 2-BHEAP with ethanol or propanol.[147]

Fig. 2 shows a comparison among five literature sources, to see the anion effect of ILs with water or alkanols. The results in Fig. 2 of ammonium-based ILs with various solvents show that the ρ values increase with increasing the IL concentration. The data in Fig. 2a indicate that the ρ value of ILs with water follows the order at equimolar composition: 2-BHEAA > 2-HEAF > 2-HEAA. As can be seen from this order, the ρ values of 2-BHEAA + water are much higher than 2-HEAA + water under similar conditions.[142,144] On the other hand, the ρ values of the formate anion show higher values than the acetate anion with the same cation of [2-HEA].

It is revealed from Fig. 2b that the ρ values are higher for the bis(2-hydroxyethyl)ammonium group of ILs such as 2-BHEAA and 2-BHEAP than 2-hydroxyethylammonium group of ILs at lower concentrations of ILs in methanol. The ρ values of formate anion of 2-HEAF + methanol shows larger value than acetate anion of 2-HEAA + methanol. Conversely, acetate anion of 2-BHEAA + methanol shows larger ρ values than propionate anion of 2-BHEAP + methanol. This can be attributed to that the ion-pair interactions are decreased with increasing the size of anion in the same cation groups 2-HEA or 2-BHEA with methanol.[138,142,146,147] As expected, a systematic decrease of ρ values with increasing the alkyl chain length of alkanols is seen. In other words, the 2-BHEAP IL with alkanols show lower ρ values in comparison to the 2-BHEAA IL with alkanols, which indicates that maybe the 2-BHEAA forms stronger molecular interactions with alkanols than 2-BHEAP due to structural effects of the solvents.[144,146,147]

In another study, Alvarez *et al.*[149] reported the ρ values of 0.99260 g cm^{-3} (at $x_{IL} \approx 0.5027$), 0.97657 g cm^{-3} (at $x_{IL} \approx 0.4930$) or 0.96889 g cm^{-3} (at $x_{IL} \approx 0.4912$) for *N*-methyl-2-hydroxyethylammonium butyrate (m-2-HEAB) with methyl acetate, ethyl acetate or propyl acetate at 35 °C, respectively. The ρ values of these mixtures were increased with decreasing of the mole fraction of IL. The m-2-HEAB with methyl acetate system shows higher ρ values as compared to m-2-HEAB with ethyl acetate or propyl acetate. The results can be explicitly elucidated that the ρ values of this m-2-HEAB in esters decrease from methyl to propyl acetate. This can be perhaps attributed to the lower size of methyl ester, which occupies less volume than ethyl or propyl esters, respectively.[149]

In 2012, Bahadur *et al.*[151] explored the ρ values for binary systems containing methyltrioctylammonium bis(trifluoromethylsulfonyl)imide, ([MOA]$^+$[Tf$_2$N]) IL with alkanols at different temperatures. The ρ values are 1.0676 g cm^{-3} (at $x_{IL} \approx 0.4824$), 1.0728 g cm^{-3} (at $x_{IL} \approx 0.5343$) or 1.0667 g cm^{-3} (at $x_{IL} \approx 0.5045$) for ([MOA]$^+$[Tf$_2$N]$^-$) + 2-propanol, +1-butanol or +2-butanol system at 25 °C, respectively. They found that the ρ values decrease with an increase in the temperature.[151] Significantly, the –CH$_3$ group position not show much effect on butanol structures. Moreover, Deenadayalu and co-workers[152] have obtained the ρ values for binary systems [MOA]$^+$[Tf$_2$N]$^-$ with methyl acetate or ethyl acetate over the entire composition range at different temperatures under atmospheric pressure. The ρ values are 1.09050 g cm^{-3} (at $x_{IL} \approx 0.5029$) or 1.07970 g cm^{-3} (at $x_{IL} \approx 0.4848$) for [MOA]$^+$[Tf$_2$N]$^-$ with methyl acetate or ethyl acetate at 25 °C, respectively. According to Deenadayalu *et al.*[152] the ρ values decreased from methyl acetate to ethyl acetate with this IL at all studied temperatures. The ρ values increased with

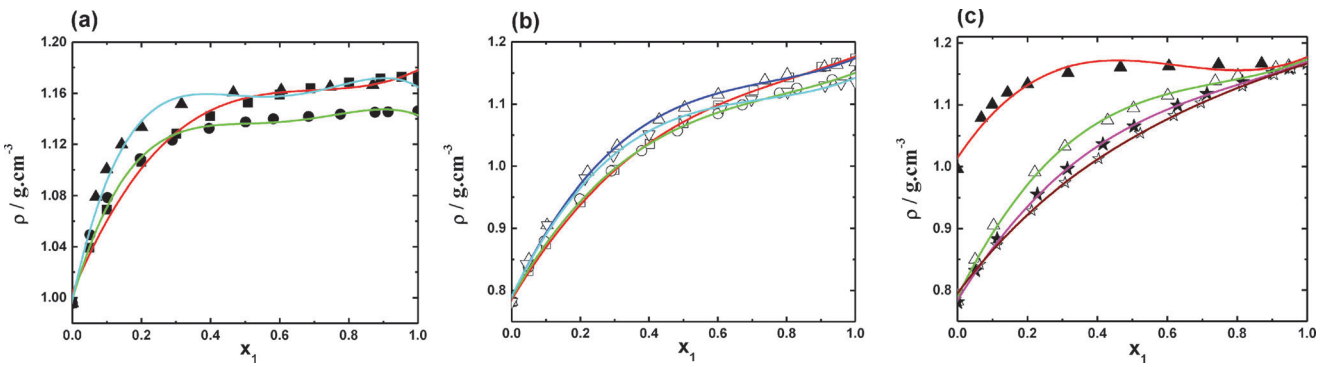

Fig. 2 Plots of density (ρ) for mixtures of ammonium-based ILs + solvents as a function of the mole fraction (x_1) of IL; (a) (■) 2-HEAF + water;[138] (●) 2-HEAA + water;[142] (▲) 2-BHEAA + water;[144] (b) (□) 2-HEAF + methanol;[138] (○) 2-HEAA + methanol;[142] (△) 2-BHEAA + methanol,[146] (▽) 2-BHEAP + methanol;[147] (c) (▲) 2-BHEAA + water;[144] (△) 2-BHEAA + methanol;[146] (★) BHEAA + ethanol[146] and (☆) 2-BHEAA + propanol[146] at 30 °C.

increasing the concentration of x_{IL} and decreased with increasing temperature.

Later, in another work, Bahadur *et al.*[154] have observed ρ values 0.84470 g cm^{-3} (at $x_{IL} \approx 0.4006$) or 0.93510 g cm^{-3} (at $x_{IL} \approx 0.4006$) for $[MOA]^+[Tf_2N]^-$ IL + ethanol or ethyl acetate system at 25 °C, respectively. From their results, one can see that the ρ values of ($[MOA]^+[Tf_2N]^-$) IL + ethanol are lower than $[MOA]^+[Tf_2N]^-$ IL + ethyl acetate at all studied temperatures. This indicates higher dispersive interactions between ester and ($[MOA]^+[Tf_2N]^-$) IL system than in the ethanol and $[MOA]^+[Tf_2N]^-$ system.[151–154] The ρ values are 1.08870 g cm^{-3} (at $x_{IL} \approx 0.5362$), 1.08020 g cm^{-3} (at $x_{IL} \approx 0.5145$) or 1.07620 g cm^{-3} (at $x_{IL} \approx 0.5240$) for ($[MOA]^+[Tf_2N]^-$) with methanol, ethanol or propanol at 25 °C, respectively.[157] Sibiya and Deenadayalu,[157] found that the ρ values of this ($[MOA]^+[Tf_2N]^-$) IL with lower alkanols are higher than with higher alkanols. The difference in ρ values of ($[MOA]^+[Tf_2N]^-$) can be attributed that the variation in the interactions between the IL and alkanol. The IL with the larger alkanol exhibits lower densities than smaller alkanols due to the nonpolar nature increasing from lower alkanols to higher alkanols.[151,157]

Very recently, Brennecke's research group[158] investigated the ρ values for butyltrimethylammonium bis(trifluoromethylsulfonyl)imide, $[N_{1114}][NTf_2]$ IL with ethanol, propanol or DMF at various temperatures from 20 to 60 °C. This group confirmed that the ρ of the mixtures decreased as the temperature and the mole fraction of the ethanol, propanol or DMF increase. The ρ values are 1.28930 g cm^{-3} (at $x_{IL} \approx 0.4969$), 1.26940 g cm^{-3} (at $x_{IL} \approx 0.5004$) or 1.29280 g cm^{-3} (at $x_{IL} \approx 0.4922$) for $[N_{1114}][NTf_2]$ IL with ethanol, propanol or DMF at 25 °C, respectively. The $[N_{1114}][NTf_2]$ + DMF system shows higher ρ values than $[N_{1114}][NTf_2]$ + alkanol. Machanová *et al.*[170] evaluated the ρ values for variation in the cation alkyl chain length of ammonium-based ILs with the same $[Tf_2N]$ anion with methanol at different temperatures. The authors observed that the ρ values decreased as the temperature and the mole fraction of these ILs increased with methanol. The ρ values are 1.24000 g cm^{-3} (at $x_{IL} \approx 0.5064$), 1.2050 g cm^{-3} (at $x_{IL} \approx 0.4914$) or 1.1563 g cm^{-3} (at $x_{IL} \approx 0.5075$) for $[N_{6,222}][Tf_2N]$, $[N_{8,222}][Tf_2N]$ or $[N_{12,222}][Tf_2N]$ + methanol at 25 °C, respectively. The results reveal that the ρ of these ILs with methanol, following the order: $[N_{6,222}][Tf_2N] > [N_{8,222}][Tf_2N] > [N_{12,222}][Tf_2N]$. This can be attributed that the lower alkyl chain length cation ILs are much denser than higher alkyl chain length ILs. Therefore, the $[N_{6,222}][Tf_2N]$ IL shows more hydrogen bonding with methanol than $[N_{8,222}][Tf_2N]$ or $[N_{12,222}][Tf_2N]$.[170]

Recently, Domańska and co-workers[172] obtained the ρ values for $[N_{1114}][NTf_2]$ with 1,2-propanediol, 1,2-butanediol or 2,3-butanediol as well as for (2-hydroxyethyl)trimethylammonium bis(trifluoromethylsulfonyl)imide, $[N_{1112OH}][NTf_2]$ IL in 1,2-propanediol, 1,3-propanediol or 1,5-pentanediol at different temperatures from 50 to 80 °C. The ρ date of the mixtures decreased with increase in temperature and as the mole fraction of the ILs increased. The influence of the cation $[N_{1114}]^+$ *vs.* $[N_{1112OH}]^+$ of the IL is evident on the values of ρ for the ILs systems. The ρ of the pure IL and mixtures are much higher for $[N_{1112OH}][Nf_2T]$ as compared with $[N_{1114}][Nf_2T]$.[172] The introduction of the hydroxyl group instead of the ethyl group in the molecule increases the internal hydrogen bonding and changes the physicochemical properties of the ILs.[172]

The ρ values for diisopropylethylammonium heptanoate, $[DIPEA][C_6COO]$ or diisopropylethylammonium octanoate, $[DIPEA][C_7COO]$ with water at 25 °C have been reported.[183] The ρ values are 0.88990 g cm^{-3} (at $x_{IL} \approx 0.5007$) or 0.87740 g cm^{-3} (at $x_{IL} \approx 0.5050$) for $[DIPEA][C_6COO]$ or $[DIPEA][C_7COO]$ with water at 25 °C, respectively. Here, the ρ values of $[DIPEA][C_7COO]$ with water is less as compared to $[DIPEA][C_6COO]$ with water at the entire composition range. This can be explicitly revealed in terms of more ion-pair interaction between the ions of $[DIPEA][C_7COO]$ IL and water than $[DIPEA][C_6COO]$ and water.[183] Also, the ρ values of $[DIPEA][C_6COO]$ with acetonitrile are higher than of $[DIPEA][C_7COO]$. The ρ values are 0.85710 g cm^{-3} (at $x_{IL} \approx 0.5021$) or 0.85000 g cm^{-3} (at $x_{IL} \approx 0.5050$) for $[DIPEA][C_6COO]$ or $[DIPEA][C_7COO]$ with acetonitrile at 25 °C, respectively. From these reports, clearly one can see that the ρ values of these ILs with water systems are more dense than with acetonitrile systems.[183]

Moreover, our research group reported that the ρ values increased for DEAA, TEAA, DEAS, TEAS, TMAA or TMAS and different alkyl cations with same hydroxide anion of ILs with water as the concentrations of the IL is increased at 25 °C[192,196] and is illustrated in Fig. 3. The increase in ρ values for these ILs with water mixtures were possibly due to increase in the ion-pair interactions between IL and water. The ρ values of the ILs in water follow the order: TMAS > DEAS > TEAS > TMAA > DEAA > TEAA, which indicates that the lower alkyl chain length of cation of ILs leads to higher densities than higher alkyl chain length of ILs. Here, the ρ values of DEAA + water is higher than TEAA + water as well as the ρ values of DEAS + water is higher than TEAS + water. This can be attributed to an increase in dispersive interactions in ILs with increase in chain length, resulting in a nanostructural organization in polar and nonpolar regions. The nonpolar regions show a buildup of alkyl chains whereas the polar groups contain the cationic head

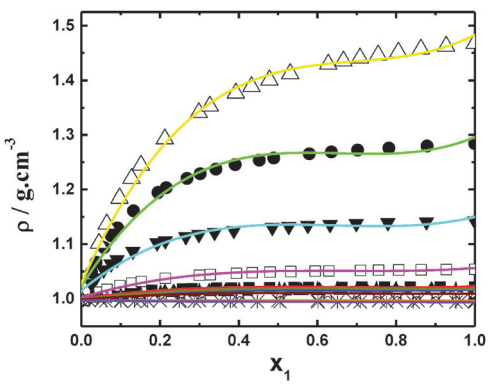

Fig. 3 Comparison among the available literature density (ρ) for mixtures of ammonium-based ILs + water[192,196] as a function of the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (△) TMAS; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

groups and the anions. When we increase the chain length of cation, the nonpolar regions increase and take up more and more space, and as a result lower overall ρ in higher alkyl chain length of ILs.[192] Meanwhile, acetate-based ILs display lower ρ values than the corresponding sulfate-based ILs due to the ionic species and the increased molecular mass of the anion of IL.[192]

Recently, our research group also measured ρ values for common hydroxide anion salts of various tetraalkylammonium-based ILs with water at various temperatures from 25 to 40 °C under atmospheric pressure.[196] The ρ values of these systems decreased with increasing temperature. As can be seen Fig. 3, the ρ values of the ILs with water follow the order: TMAH > TEAH > TPAH > TBAH, which shows that the lower alkyl chain length of cation of ILs gives higher densities than larger alkyl chain length of ILs. This may be due to the ion–ion pair interactions decreasing with increasing size of alkyl chain length of cation of the ILs.[196] Overall, amongst all ammonium-based ILs (Fig. 3), the sulfate anion of IL shows highest ρ values with water, lower ρ values are found for the hydroxyl anion of IL and moderate ρ values for acetate anion of IL with water system.[192,196]

Very recently, Zarrougui *et al.*[194] found the ρ values for EAN with water. The ρ values decreased when the temperature was increased for both pure ILs and mixtures. As can be seen in Fig. 4, the ρ value of 1.09589 g cm^{-3} (at $x_{IL} \approx 0.5011$) for $N4NO_3$ + water[125] system is lower than those for EAN + water, 1.1795 g cm^{-3} (at $x_{IL} \approx 5300$) at 25 °C, which is a result of difference in the polarity of ILs and may also be due to steric hindrance caused by the larger size of *n*-butylammonium cation of $N4NO_3$ IL than ethylammonium cation of EAN.[125,194]

In 2013, Hou *et al.*[127] examined the ρ values for ethylammonium acetate (N2A) or propylammonium acetate (N3A) + water systems with x_{IL} at 25 °C. Results clearly revealed that the ρ values of N2A or N3A + water systems abruptly increased up to $x_{ILs} \approx 0.2000$ or 0.1000, respectively. Later, the ρ values decreased with increasing the x_{ILs}. This is due to a decrease in the ion pair interactions between ions of N2A or N3A with water. From Fig. 4, the ρ values of acetate anion of ammonium-based ILs with water show the following order: N2A > N3A > N4A.[125,127] From this order, it can be observed that the ρ values of acetate anion of these ammonium-based ILs with water decreased with increasing the alkyl chain length of cation of these ILs.[125,127] The ρ values of nitrate anion of IL with water are large as compared to acetate anion of IL with water, which indicates increased polar interactions between the nitrate anion of IL and water than acetate anion of ILs.[125,127]

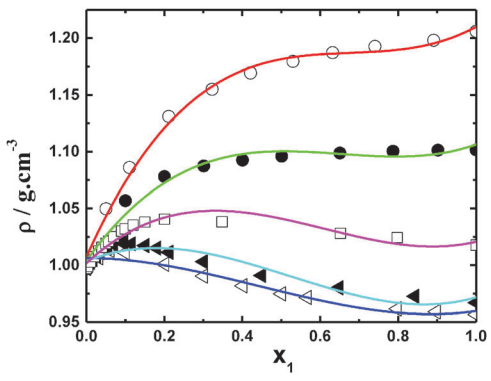

Fig. 4 Comparison among the available literature density (ρ) for mixtures of ammonium-based ILs (a) (○) EAN + water;[194] (●) $N4NO_3$ + water;[125] (□) N2A + water;[127] (◀) N3A + water[127] and (◁) N4A + water[125] at 25 °C as a function of the mole fraction (x_1) of IL.

4. Ultrasonic sound velocity data of mixtures for ammonium-based ILs with molecular solvents

The *u* data give direct and precise information about the molecular interactions of the mixtures. The thermophysical property of *u* is also another important source to gather information about the properties of different solvents and their mixtures. The thermodynamic properties of the *u* data of ILs with polar solvents have attracted attention from many industrial and academic communities. The *u* values have been schematically studied with varying cations and anions of ammonium-based ILs with DMSO at different temperatures from 25 to 40 °C and over the entire mole fraction of IL.[117,129,131,133,134] The *u* values for various ammonium-based ILs comprising different cations and anions with DMSO at 25 °C are represented in Fig. 5a for comparison of the available data.

The *u* values increased for the all ammonium-based ILs with DMSO[117,129,131,133,134] with increasing the mole fraction of IL at all studied temperatures, except for DEAS, DEAA or TEAA + DMSO systems (Fig. 5a). Of the latter, the DEAS + DMSO system shows that the *u* values decreased with increasing the mole fraction of DEAS up to 0.8306. At mole fraction >0.8306, the *u* values slightly increased.[117] The magnitude of equimolar *u* data of ammonium-based ILs with DMSO at 25 °C showed the following order: TEAA > TBAH > TPAH > TEAH ≈ TEAS > TEAP > TMAH > DEAA > TMAP > TMAS > TMAA > DEAS. Very interestingly, amongst all ILs, the higher and lower *u* values were observed for the acetate anion of $[TEA]^+$ and sulfate anion of $[DEA]^+$ of ILs with DMSO. The *u* values slightly increase when the alkyl substituent size of the cation increases with different kinds of anions containing ammonium-based ILs with DMSO (Fig. 5a). Moreover, the small size of (DEA^+) with acetate, sulfate anions of ILs lead to lower *u* values with DMSO, when compared to large size of (TEA^+) with same anions of the ILs with DMSO at 25 °C (Fig. 5a).

Overall, increases or decreases of the *u* data depend on the diffences in the interactions of cation or anion of ILs with DMSO molecules. In the case of hydroxide anion of ammonium-based ILs with DMSO, we have observed a reversal in the *u* data above the $x_{ILs} \approx 0.5000$. Here, the small size of TMAH + DMSO system shows higher *u* data than those for large size of TEAH, TPAH or TBAH + DMSO systems. This can be revealed as due to structural effects, because of hetero-associations decreasing with increasing size of cations from tetramethyl- to tetrabutylammonium-based ILs with DMSO at higher concentration.[134]

The *u* data established for the ILs with NMP are displayed in Fig. 5b for comparison of the available data at 25 °C. The temperature-dependent *u* values of all ammonium-based ILs

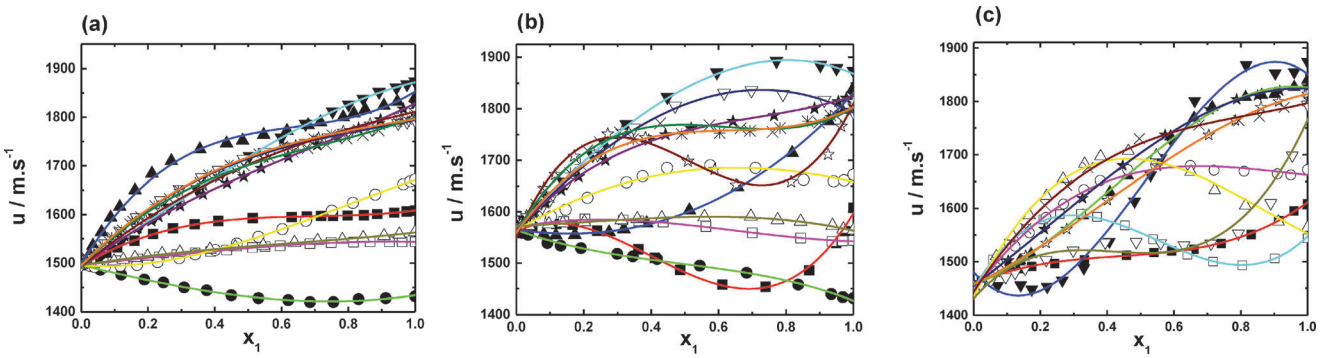

Fig. 5 Comparison among the available literature ultrasonic sound velocity (u) for mixtures of ammonium-based ILs + (a) DMSO;[117,129,131,133,134] (b) NMP;[130,132,135] (c) DMF[116,136,193] as a function of the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (○) TMAP; (△) TMAS; (▽) TEAP; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

with NMP[130,132,135] show different behavior for each system as can be seen in Fig. 5b. The u values roughly increased for the DEAA + NMP system up to $x_{IL} \approx 0.1700$, later, the values of u decreased with increasing the x_{IL} up to ≈ 0.7400; finally a sharp increase occurs above $x_{IL} \approx 0.7400$. The u values sharply increased with increasing mole fraction of TEAA with NMP. On the other hand, the values of u were decreased with increasing the mole fraction of DEAS in the NMP system at all studied temperatures.[130] In the case of TEAS + NMP system, u data increased up to $x_{IL} \approx 0.7700$ and then the observed u values slightly decrease up to $x_{IL} \approx 0.9900$ at all studied temperatures.[130] The u data sharply decreased as the temperature increases for TEAA, DEAS and TEAS + NMP systems, except for DEAA + NMP system at $x_{IL} \approx 0.5000$.[130]

Furthermore, the u significantly increased for TMAA, TMAS or TEAP + NMP systems up to $x_{ILs} \approx 0.1700$, ≈ 0.6000 or ≈ 0.6200, respectively. Afterwards, the u values decreased with increasing the mole fraction of TMAA, TMAP or TEAP,[132] whereas for the TMAP + NMP system, the u values increased as the concentration of TMAP increases with NMP up to $x_{IL} \approx 0.6000$, later, the u values approximately decreased and finally u values slightly increased at $x_{IL} > 0.9000$.[132] It has already been noted that for the TMAH + NMP system, observed u values were increased when x_{IL} increases in the mixture at all studied temperatures.[135] The opposite behavior was observed for the TEAH, TPAH or TBAH with NMP systems, in which, the u values sharply increased up to $x_{ILs} \approx 0.3000$, ≈ 0.5000 or ≈ 0.5000, respectively. Afterwards, the u data approximately decreased with increasing the x_{ILs} in the mixture and eventually increased for $x_{ILs} > 0.8000$, at all experimental temperatures.[135] Most importantly, it has been noted that the u values increase for hydroxide anion-based ammonium ILs up to $x_{IL} \approx 0.3000$.

The u values of mixtures of ammonium-based ILs with DMF[116,136,193] are presented in Fig. 5c from the various sources of the literature. From the close observation of Fig. 5c, it is clearly seen that the u values monotonically increased for the mixture of DEAA or TEAA with DMF at 25 °C. On the other hand, the TEAS + DMF system shows that the u values were decreased with increasing the mole fraction of TEAS up to ≈ 0.2000, later the u values sharply increased with increasing the mole fraction of TEAS in DMF. Furthermore, the u data increased with mole fraction of TEAP + DMF system up to ≈ 0.5000 and the u values slightly decreased up to $x_{IL} \approx 0.8000$ and eventually u data increased with increasing concentration of TEAP in DMF.[116]

On the other hand, the u values were also systematically studied with acetate, sulfate and phosphate anions with fixed cation (TMA^+) of ILs with DMF systems.[193] As can be seen in Fig. 5c, the anionic u effect is most obvious, since we have used a common cation, resulting in extensively higher u data for the larger anion size of IL systems.[193] Therefore, this result demonstrates that the influence of the anion significantly affected ammonium family IL–solvent interactions. The results in Fig. 5c show that the u of TMAP with DMF at 25 °C rapidly increases with the increasing up to $x_{IL} \approx 0.4000$, later the u values slightly increased. On the other hand, in the case of TMAS with DMF, there was a rapid increase in u values up to $x_{IL} \approx 0.4300$, later the u values suddenly decreased up to $x_{IL} \approx 0.9900$ at 25 °C.[193] Fascinating results were seen in the case of TMAA for which its u values rapidly enhance a $x_{IL} \approx 0.2000$; further a decrease was noted up to $x_{IL} \approx 0.8000$ and later the u values sharply increased up to $x_{IL} \approx 0.9800$.[193]

As seen from the results in Fig. 5c, the u data were found to increase with increasing the mole fraction of TMAH, TEAH and TPAH ILs with DMF.[136] In the case of TPAH IL the u value at 30 °C is higher than that at 25 °C, while a decrease was noted when higher mole fraction was reached. This may be due to self interaction taking place between the TPAH and DMF molecules at 30 °C.[136] As seen from the results in Fig. 5c, it is clear that there is no regular order in the values of u for hydroxide-based ILs with DMF and this may be due to the large steric hindrance in the bulky groups, which tends to resist crowding more than smaller groups. TPAH exhibits higher u values up to $x_{IL} \approx 0.5800$ than TMAH or TEAH with DMF at 25 °C. Later, the u data of TPAH + DMF system sharply decreased from 0.6000 to 0.9800 mol fraction of TPAH and obviously the u values were lower than those of TMAH or TEAH with DMF. This is a somewhat surprising result, since one would expect at first view that, as the side chain length increases, the overall contribution will generally increase. This shows that there is a significant effect of ρ on u; as ρ increases, u also increased.[136]

To characterize the type and magnitude of the molecular interactions between ions of ILs with solvents, further research carried out by Iglesias *et al.*[138] show the *u* values for 2-HEAF with water, methanol or ethanol. From these results, the *u* data evidently show a fascinating maximum trend (at scarcely equimolar compositions for water and low solvent composition for alcohols) at any temperature. For all the systems, the temperature dependence was the same and the *u* values increased with decreasing temperature. Here, 2-HEAF with water system shows a sigmoid tendency for *u* data. From Fig. 6a, the *u* data of 2-HEAF IL with these solvents shows the following order: ethanol < methanol < water at 30 °C.[138]

Later, the *u* data was reported for 2-HEAA with water, methanol or ethanol as a function of composition at three temperatures by Alvarez *et al.*[142] These reports have shown a stronger inflection at dilute (2-HEAA + water) mixtures, which is a very different shape than for 2-HEAA + methanol or ethanol mixtures at all studied temperatures.[142] As seen in Fig. 6b, the *u* data of 2-HEAA with these solvents shows the following order: ethanol < methanol < water. From these observations, it is clearly revealed that the *u* data of acetate anion with (2-HEA$^+$) of IL with these solvent systems are showing higher values than those for formate anion with (2-HEA$^+$) of IL with these solvent systems. This can be attributed that the small size of formate anion with (2-HEA$^+$) of IL may lead to stronger interactions with water, methanol or ethanol, than the larger sized acetate anion with the same cation of IL.[138,142]

It has been revealed that the ([MOA]$^+$[Tf$_2$N]$^-$) + ethanol system shows higher *u* value than ([MOA]$^+$[Tf$_2$N]$^-$) + ethyl acetate at $x_{IL} \approx 0.4006$ under the same experimental conditions.[154] Meanwhile, Sibiya and Deenadayalu[157] have measured *u* values for ([MOA]$^+$[Tf$_2$N]$^-$) IL with methanol, ethanol or 1-propanol at 25 °C over the entire composition range of IL. From these results, it was found that the *u* data increased as the alcohol chain length increases. The increased *u* data values indicate that there is a decrease in squeeze between the unlike component molecules in the mixture.[157] Very interestingly, both reports show similar *u* data for ([MOA]$^+$[Tf$_2$N]$^-$) IL + ethanol at the entire composition range of IL.[154,157]

The cation and anion characteristics greatly affect the thermophysical properties in water, in this context, Umapathi *et al.*[192] have systematically studied that both size of the ions of ILs and water content, based on the *u* values of the ammonium-based ILs with water, and the results are shown in Fig. 7 at 25 °C over the entire mole fraction range of ILs. From Fig. 7, the *u* data of these ILs with water systems follow the order: TEAS > TEAA > DEAA > TMAS > TMAA > DEAS. From these results, it can be conveyed that the same anion with large size of alkyl chain length of cation of IL with water system has higher *u* values than those for same anion with small size of alkyl chain length of cation of ILs with water. Moreover, the same cation with small size of anion of IL with water system shows higher *u* values than compared to the same cation with large size anion of IL with water.[192] The effects of the length of the cation alkyl chains in the aqueous solution of ammonium-based ILs are interesting, in this regard, very recently the *u* data were reported for fixed hydroxide anion with different alkyl chain length of ammonium-based ILs with water as a function of IL concentration at various temperatures by our research group.[196] For the sake of the clarity of presentation and to see the effect of cation, we have included the *u* values of these systems in Fig. 7. As illustrated in Fig. 7, we have also observed that the *u* values

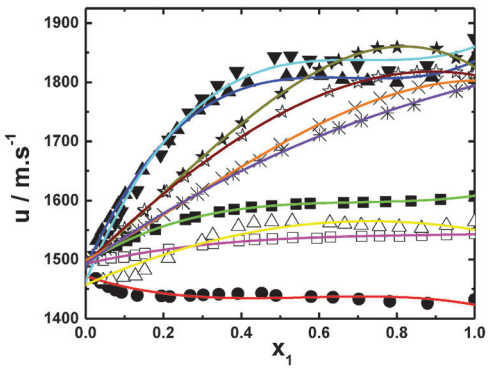

Fig. 7 Ultrasonic sound velocity (*u*) for mixtures of ammonium-based ILs + water[192,196] as a function of the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (△) TMAS; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

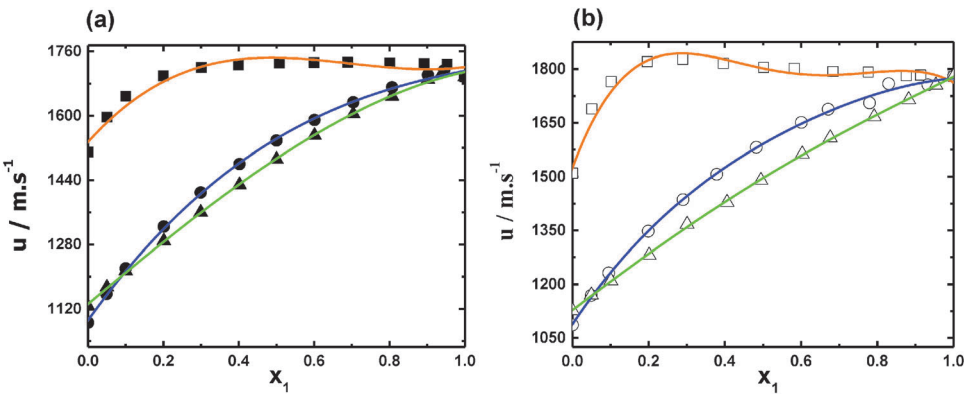

Fig. 6 Plots of ultrasonic sound velocity (*u*) for mixtures of ammonium-based ILs + solvents as a function of the mole fraction (x_1) of IL; (a) 2-HEAF[138] + water (■); + methanol (●); + ethanol (▲); (b) 2-HEAA[142] + water (□); + methanol (○) and + ethanol (△) at 30 °C.

increased with concentration of ILs. The order of u data of this hydroxide anion of different cationic alkyl chain length of ILs with water is: TMAH > TEAH > TPAH > TBAH. This can be attributed that the interaction of water is became stronger with decreasing in the size of alkyl chain length of cation of ILs. This may be due to the stronger molecular interactions decreasing with increasing size of alkyl chain length of the cation of ammonium-based ILs with water.[196]

The u values at equimolar concentration for all aqueous ammonium-based ILs systems fall in the order: TEAS > TEAA > TMAH > TEAH > TPAH > TBAH > DEAA > TMAA > TMAS > DEAS. Here, (TEA^+) of ILs shows higher u values than (DEA^+) of ILs. Sulfate anion with (TEA^+) of IL display higher u values than acetate anion with (TEA^+) of IL. Conversely, sulfate anion with (DEA^+) of IL do not display much greater u values than acetate anion with (DEA^+) of IL. With regard to the (TMA^+), the u values of $[OH]^-$ of ILs are higher than those for acetate or sulfate anions of ILs with the same cation. To conclude, the u values of these ammonium-based ILs with water are governed by both ion size and attractive interaction, such as hydrogen boding between ions of ILs and water molecules.

5. Viscosity data of mixtures for ammonium-based ILs with molecular solvents

The understanding of the η of the ILs is of prime importance from both the scientific and industrial point of view as it plays a major role in chemical process design and development. Ammonium-based ILs are generally highly viscous liquids and fall into the range 25–2900 mPa s. The higher η values are disadvantages for some industrial applications. Nonetheless, the addition of molecular solvents decreases the η of the ILs. In this section, we will discuss the available information on the η data of ammonium-based ILs with molecular solvents. In 2013, Smith *et al.*[122] obtained the zero shear η data for nitrate–nitrate and nitrate–formate mixtures of ILs systems such as ethanol-ammonium nitrate (EtAN) + EAN, PAN; ethylammonium formate (EAF) + EtAN, EAN or PAN and PAN + EAN systems, respectively. Surprisingly, one can explicitly observe that the addition of small amounts of EAF IL comprising of nitrate–formate IL systems increased the η data for all nitrate anion ILs as compared to nitrate–nitrate ions of ILs. Amongst these, the higher η data was found for EtAN + EAF mixture and lower η data for EAN + EAF. In order to interpret the observed results we must consider the effects of both the H-bond network and the solvophobic nano-structure as well as chemical additional effects between the ions of ILs systems.[122] The η values observed for $N4NO_3$ with methanol, ethanol, 1-propanol or 1-butanol have been measured at different temperatures from 20 to 40 °C and over the whole composition range of IL.[124] Fig. 8 shows the η values of $N4NO_3$ with methanol, ethanol, 1-propanol or 1-butanol for comparison of the available data of $N4NO_3$ with water[125] at 25 °C. The η values of $N4NO_3$ with alkanols are in the following order: methanol < ethanol < 1-propanol < 1-butanol. This order clearly shows that increasing the alkyl chain length from methanol to 1-butanol led to increased η values at given temperature. The η values of $N4NO_3$ with alkanols are decreased with increasing the temperature. Thus, these η values entirely depended on the nature of IL and solvents.[124]

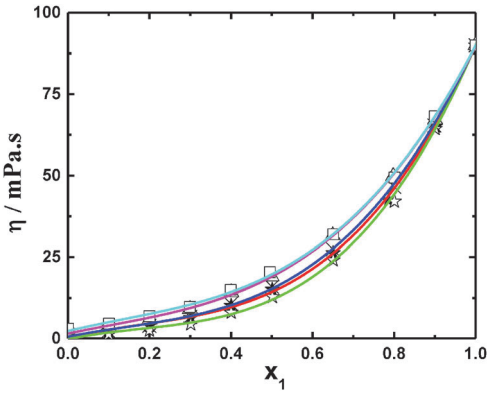

Fig. 8 Comparison among the available literature viscosity (η) for mixtures of ammonium-based ILs + water[125] and alkanols[124] as a function of the composition expressed in the mole fraction (x_1) of IL; (★) $N4NO_3$ + water;[125] (☆) $N4NO_3$ + methanol;[124] (×) $N4NO_3$ + ethanol;[124] (△) $N4NO_3$ + 1-propanol[124] and (□) $N4NO_3$ + 1-butanol[124] at 25 °C.

Moreover, the η values were reported for the N4A or $N4NO_3$ + water mixtures at the studied temperatures from 20 to 40 °C under atmospheric pressure.[125] The η values of these mixtures increased abruptly with increasing the x_{IL} and decreased with temperature increases. It should be noted that the η values of N4A + water system are higher than $N4NO_3$ + water system under similar conditions. It is found that the pure N4A is more viscous than pure $N4NO_3$.[125] Since N4A or $N4NO_3$ have the same cation, the variation in η is related to the size and basicity of the two anions. Obviously, the basicity of acetate is stronger than that of nitrate, there are more obvious interactions between cation and acetate in N4A than those between cation and nitrate in $N4NO_3$.[125] From Fig. 8, the η values of $N4NO_3$ with water system are higher than those for $N4NO_3$ with methanol and lower than $N4NO_3$ with ethanol, 1-propanol or 1-butanol, respectively. This can be attributed that the intermolecular interactions between the ions of $N4NO_3$ with water are lower by nitrate anion of ammonium-based ILs with methanol and higher than with ethanol, 1-propanol or 1-butanol.[124,125]

Subsequently, Xu *et al.*[128] have measured η values for binary mixtures of N4A with methanol, ethanol, *n*-propanol or *n*-butanol at different temperatures from 20 to 40 °C and over the whole composition range of IL. From Fig. 9, the η values of N4A with alkanols are in the following order: ethanol > *n*-propanol > methanol > *n*-butanol. Overall, the η values of N4A with water are larger than those for N4A with alkanols, which indicates stronger hydrogen bonding formed between the acetate anion of N4A and water as compared to alkanols.[125,128]

Quite recently, the η values were reported for the binary mixtures of EAN with water over the entire molar fraction range at various temperatures ranging from 20 to 45 °C and under atmospheric pressure.[194] The η of EAN + water system decreased with increasing the temperature and increased with

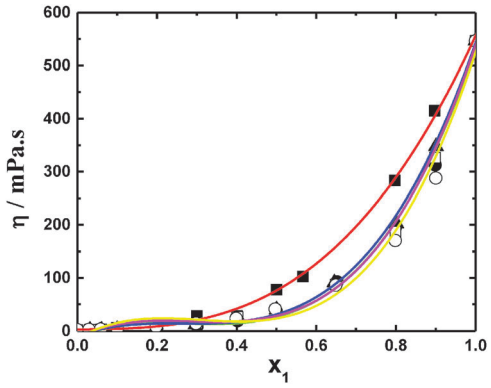

Fig. 9 Comparison among the available literature viscosity (η) for mixtures of ammonium-based ILs + water[125] and alkanols[128] as a function of the mole fraction (x_1) of IL; (■) N4A + water;[125] (●) N4A + methanol;[128] (▲) N4A + ethanol;[128] (□) N4A + 1-propanol[128] and (○) N4A + 1-butanol[128] at 25 °C.

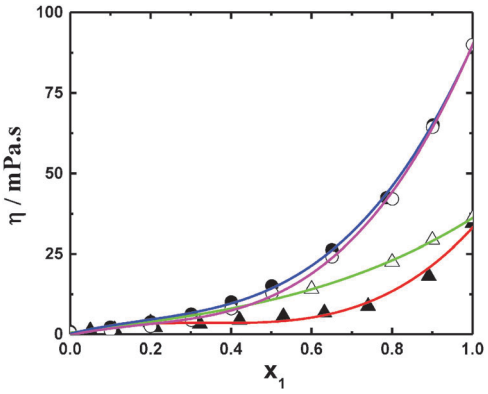

Fig. 10 Viscosity for mixtures of ammonium-based ILs + water or methanol as a function of the mole fraction (x_1) of IL; (▲) EAN + water;[194] (△) EAN + methanol;[205] (●) $N4NO_3$ + water[125] and (○) $N4NO_3$ + methanol[124] at 25 °C.

increasing the concentration of IL. Thus, these results revealed that the addition of 36 mol% of water decreases η by 50% relative to pure EAN at 20 °C. This can be attributed that formation of hydrogen bonds between EAN ions and water.[194] On the other hand, addition of the water molecules weakens the solvation of the ions of EAN by strong coulombic and hydrogen bond interactions between ions of opposite charges which leads to the decrease of η values with increasing the temperature. At water-rich concentration, the η data of mixtures shows a slight change with increasing up to $x_{IL} \approx 0.2000$, and later rapidly increased the $x_{IL} > 0.2000$.[194] In 2010, Litaeim and Dhahbi systematically studied the η values for EAN with different organic solvents such as dimethyl carbonate (DMC) and formamide (FA) over the whole composition range and at a temperature range from 20 to 40 °C.[204] The η data of these systems were decreased with increasing temperature due to the rise in the fluidity of ions of IL by the increasing kinetic energy of the molecules. At fixed temperature, the results show an increase in η with increasing IL concentration. This is due to the fact that with increasing of IL concentration, the number of collisions between the molecules increased, resulting in a loss of kinetic energy. Therefore, the molecules tend to stick together which increases η.[204]

On the other hand, Chagnes *et al.*[205] measured η values for EAN with methanol at various temperatures from 20 to 55 °C. From these results, the authors observed two kinds of behavior: one is the increase in the temperature is responsible for a decrease in methanol solution η values for $x_{IL} > 0.6000$, whereas at lower content in IL, $x_{IL} < 0.6000$, an increase in temperature leads to a surprisingly small increase in η values of this system.[205] The results show that the EAN with methanol system shows higher η values than those for EAN + water, + DMC or + FA systems, which indicates that EAN may be forming more hydrogen bonding with methanol than those for water, DMC or FA due to the less polar nature of methanol.[194,204,205] Overall, as seen in Fig. 10, the EAN IL shows higher η values with methanol as compared to water. Moreover, the $N4NO_3$ IL shows higher η values with water as compared to methanol. This discrepancy in η data of nitrate anion of ammonium-based ILs is dependent on the polarity and shape of IL as well as nature of water or methanol solvent in the mixture.

In 2011, Kurnia and Mutalib measured the η values for 2-BHEAP + methanol, ethanol or 1-propanol at various temperatures from 20 to 50 °C.[147] The η values were increased with increasing the x_{IL} and decreased with increasing temperature. From these results, one can be clearly seen that the η data for 2-BHEAP are higher than those for methanol, ethanol or 1-propanol and the η values decrease with increasing mole fraction of alcohol. The η data for 2-BHEAP with alkanols increased as the chain length of alkanols increases due to the ion–dipole interactions and packing effects of polar 2-BHEAP being stronger with lower chain length of alkanols. In this context, 2-BHEAP + methanol system shows lower η values than 2-BHEAP + ethanol and 2-BHEAP + propanol at all studied temperatures.[147]

Domańska and co-workers[172] systematically studied the η values for $[N_{1114}][NTf_2]$ with 1,2-propanediol, 1,2-butanediol or 2,3-butanediol and for $[N_{1112OH}][NTf_2]$ with 1,2-propanediol, 1,3-propanediol or 1,5-pentanediol as a function of IL concentration at different temperatures from 50 to 80 °C and ambient pressure. The authors observed that η values of ILs are larger than those of alkanediols.[172] The η values of these systems decrease with increasing the temperature. The η values of the systems increase as x_{IL} increases, except for $[N_{1112OH}][NTf_2]$ + 1,5-pentanediol system, in which the η values decrease up to $x_{IL} \approx 0.3153$, later the η values increase with mole fraction of IL above 0.3153. As a result the η values of the pure IL and mixtures are much higher for $[N_{1112OH}][NTf_2]$ in comparison with $[N_{1114}][NTf_2]$. The introduction of the hydroxyl group instead of the ethyl group in the molecule increases the internal hydrogen bonding.[172]

The difference of the zero-shear η values of [DIPEA][C_6COO] and [DIPEA][C_7COO] with water or acetonitrile at 25 °C and over the entire x_{ILs} has been reported.[183] The maximum of zero-shear η values were obtained between the $x_{ILs} \approx 0.2000$ to 0.9000 for these systems. From these results clearly it can be seen that water affects more strongly the rheological behaviors of studied systems than does acetonitrile. In the acetonitrile

systems, zero-shear η values were obtained up to a maximum at $x_{CH_3CN} \approx 0.2000$. The maximum zero-shear η values were 13.50 mPa s or 14.82 mPa s in the case of mixtures containing [DIPEA][C_6COO] or [DIPEA][C_7COO] with acetonitrile, respectively. In the case of water, the maximum zero-shear η values were obtained at $x_{H_2O} \approx 0.9000$. The maximum zero-shear η values are 43.71 mPa s or 52.36 mPa s in the case of mixtures containing [DIPEA][C_6COO] or [DIPEA][C_7COO] with water as a function of composition, respectively. These reports explicitly reveal that the zero-shear η values are increased with increasing the carboxylate alkyl chain length of these ILs from m = 6 to 7.[183]

Furthermore, our research group systematically demonstrated the temperature dependence of η values for ammonium-based ILs with DMSO at different temperatures from 25 to 40 °C over the whole composition range of ILs.[117,129,131,133,134] The η values of all ILs with DMSO were decreased as the temperature increases. Fig. 11a shows the η values of all ILs with DMSO for comparison of the available data at 25 °C. As depicted in Fig. 11a, DEAA, DEAS, TEAA, TEAS, TEAP, TMAS or TMAP + DMSO systems clearly show that the η values rapidly increased with increasing x_{IL} with DMSO whereas in the case of TMAA + DMSO, the η values slightly increased up to $x_{IL} \approx 0.7000$ and then decrease slightly with increasing the x_{IL}. These reports explicitly demonstrated that the strong coulombic interactions between the ions of ILs are strengthened upon mixing with DMSO, leading to a lower mobility of ions which is partially based on smaller sizes of ions of ILs. This means that the strong coulombic interactions between anion and cation are weakened at higher concentration of TMAA that leads to a decrease in η.

The η values of ammonium-based ILs with DMSO follow the order: TEAS > TEAP > TMAA > DEAS > TEAA > DEAA > TBAH ≈ TMAP > TPAH > TMAS ≈ TEAH > TMAH (Fig. 11a). As can be seen in this order, the TEAS + DMSO system shows higher η values amongst all ammonium-based ILs with DMSO. This can be attributed to strengthening of coulombic interactions between the ions of TEAS + DMSO. We have anticipated the reason for the rise of η in the case of TEAS that the size of anion is large enough to facilitate the interactions between DMSO and ions of TEAS IL. The highest η of the TEAS containing (TEA^+) can be explained by strong molecular interactions due to hydrogen bonding. On the other hand, we have seen lower η values for TMAH with DMSO, which indicates that the TMAH containing the (TMA^+) can show weaker hydrogen bonding interactions with DMSO; due to the large gap in the size of anion and cation of TMAH the interactions are not enough to enhance the η values. Actually, a low molecular weight of IL has lower η values in which the cation has sufficient side chain mobility.

Kavitha *et al.*[130,132,135] also reported that the η values for ammonium-based ILs with NMP and the values of η values of all ammonium-based ILs with NMP are shown in Fig. 11b as a function of IL concentration at 25 °C. The η values of ILs with NMP decreased with increasing temperature. The η values increased with increasing mole fraction of DEAA or TEAA + NMP at all investigated temperatures.

The η values of all ammonium-based ILs with NMP systems are in the following order: TEAS > DEAS > TEAP > TMAP > TEAA > DEAA > TMAS > TBAH > TPAH > TEAH > TMAA > TMAH. Furthermore, at a given temperature, the η value of the sulfate anion of ammonium-based IL + NMP is found to be higher than that of acetate anion of IL + NMP system. Evidently, the η values increased with increasing the anion size due to the increase in the internal resistance, for mobility of the ammonium-based ILs.[130] Furthermore, the η value of the TMAH + NMP mixture was found to be lower than those of the TEAH, TPAH or TBAH + NMP systems. Evidently, the η values increased with increasing the number of carbon atoms in the alkyl chain and likely was influenced by cation size. However, in the case of TPAH or TBAH with NMP, the coulombic interactions strengthened as x_{IL} increases, and thereby the η was high at all investigated concentrations. We have suspected the reason for the high η in the case of TPAH or TBAH is that the size of cation is large enough to facilitate the interactions between anion and cation instead of between IL and NMP. On the other hand, due to the large gap in the size of anion and cation of TMAH the interactions are not large enough to enhance the η values.[135]

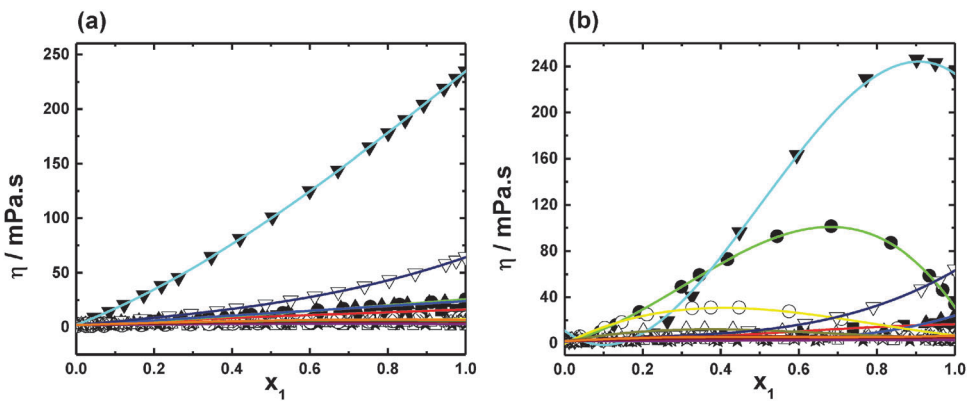

Fig. 11 Comparison among the available literature viscosity (η) for mixtures of ammonium-based ILs + (a) DMSO;[117,129,131,133,134] (b) NMP[130,132,135] as a function of the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (○) TMAP; (△) TMAS; (▽) TEAP; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

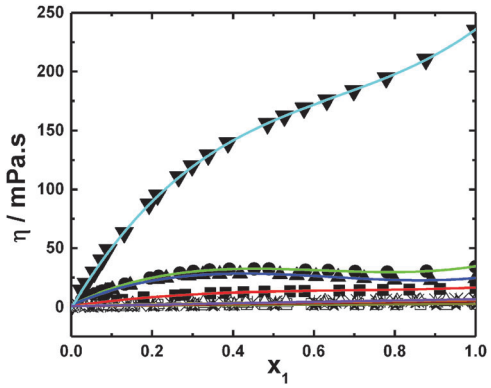

Fig. 12 Viscosity (η) for mixtures of ammonium-based ILs + water[192,196] as a function of the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (△) TMAS; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

Very recently, the η values were studied by our research group to explain the effect of water on the various anions and cations of ammonium-based ILs.[192,196] The values of η for the all ammonium-based ILs with water are illustrated in Fig. 12 as a function of the mole fraction of ILs. It was quite clear that IL + water mixtures are less viscous than pure ILs, though they are more viscous than water.[192] From Fig. 12, the η values for acetate and sulfate anions of ammonium-based ILs + water follow the order: TEAS > DEAS > TEAA > DEAA > TMAS > TMAA. Clearly, one can be seen that the acetate-based ILs systems were showing lower η values than the corresponding sulfate-based ILs systems under the same experimental conditions.[192] The anionic η effect and their ionic nature are most obvious in the liquid mixture, as a result the higher η for sulfate-based IL systems indicate stronger interactions with water as compared to acetate-based IL systems. For all the investigated systems with a common anion, the η values increased with the increase of the alkyl side chain length of the cation. This trend is due to an increase on the van der Waals interactions between the alkyl side chains of the cations and on the proportion of the charged species in the overall mixtures.[192]

Subsequently, we have reported the η values for a series of ILs possessing tetraalkylammonium cation $[R_4N]^+$ with fixed $[OH^-]$ anion of ILs with water as a function of IL concentrations at various temperatures from 25 to 40 °C.[196] Apparently, the η data of each IL system with water was shown to increase with increasing the x_{ILs}, whereas η data decrease as the temperature increases for all the systems. The η data of hydroxide anion of all ammonium-based ILs with water are also included in Fig. 12 as a function of IL concentrations at 25 °C. The data in Fig. 12 indicates that the η data of the ILs follow the order: TMAH < TEAH < TPAH < TBAH. The η values increase with increasing alkyl side chain length of the cation of ILs.[196] Finally, this result has been interpreted by the fact that the strong coulombic interaction between the ions of ammonium-based ILs are strengthening upon mixing with the water leading to a low mobility of the ions of ILs.[192,196]

6. Refractive index data of mixtures for ammonium-based ILs with molecular solvents

The n_D can be used as a measure of the electronic polarizability of a molecule and can provide useful information about the interaction between molecules. For most of substrates, the values of n_D decrease by increasing temperature due to the interactions between molecules decreasing as the temperature increases, as is illustrated in Table 4. The values of Δn_D are useful to understand the molecular interactions between the two or more components of mixtures. An accurate n_D data for ILs with molecular solvents are still scarce. In the context, Hou *et al.*[127] systematically studied that the n_D values for N2A or N3A IL + water systems as a function of concentration of ILs at 25 °C. The n_D values of N2A or N3A + water systems were increased with increasing the x_{ILs}. The observed n_D values were 1.4294 (at $x_{IL} \approx 0.6519$) or 1.4362 (at $x_{IL} \approx 0.6475$) for N2A or N3A + water systems at 25 °C, respectively. As seen in Fig. 13, the n_D values increased as the alkyl chain length of the cation of ILs increases with water mixtures. This can be attributed that the difference in molecular mass and to the improved capability to polar–polar attractive interactions between the ions of ILs and water.[127]

On the other hand, Xu *et al.*[128] measured the n_D values for N4A IL + methanol, ethanol, *n*-propanol or *n*-butanol systems and results are illustrated in Fig. 14 as a function of x_{IL} at 25 °C. The n_D values of these systems were increased with increasing x_{IL}. The n_D values were 1.4212 (at $x_{IL} \approx 0.4995$), 1.4219 (at $x_{IL} \approx 0.5005$), 1.4236 (at $x_{IL} \approx 0.4970$) or 1.4256 (at $x_{IL} \approx 0.4970$) for N4A + methanol, ethanol, *n*-propanol or *n*-butanol systems at 25 °C. The increase in the n_D values of N4A was observed with increasing the chain length of alkanols, which indicates that the molecular size of the solvents follow this order: methanol < ethanol < *n*-propanol < *n*-butanol, reflecting the most notable packing efficiency between ions of N4A and alkanols.[128]

Further, the n_D data have been measured for m-2-HEAB over the whole composition range of esters at different temperatures at 101.3 kPa.[149] The n_D data of m-2-HEAB with these ester systems are depicted in Fig. 15 and the n_D values increased with

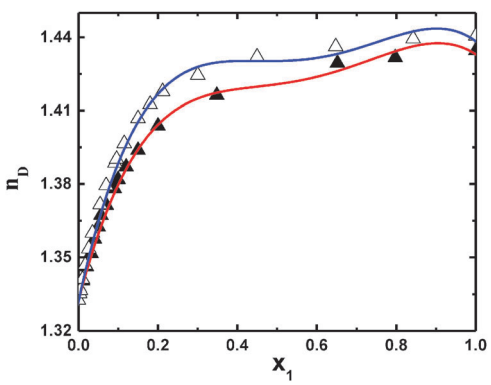

Fig. 13 Refractive indices (n_D) for mixtures of ammonium-based ILs + water[127] as a function of the mole fraction (x_1) of IL; (▲) N2A and (△) N3A at 25 °C.

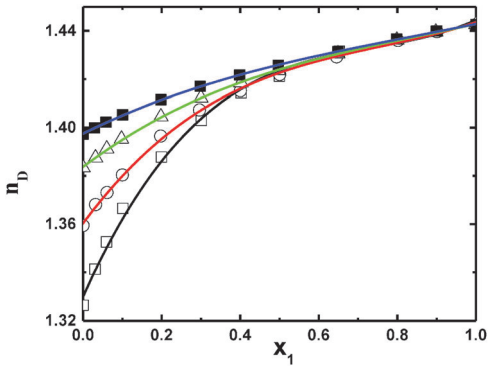

Fig. 14 Refractive indices (n_D) for mixtures of N4A IL + alkanols[128] as a function of the mole fraction (x_1) of IL; (□) methanol; (○) ethanol; (△) *n*-propanol and (■) *n*-butanol at 25 °C.

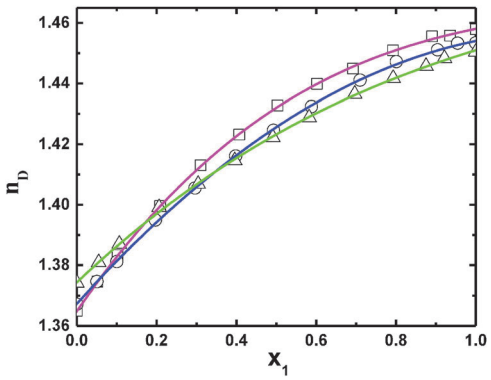

Fig. 15 Refractive indices (n_D) for mixtures of ammonium-based ILs + esters[149] as a function of the mole fraction (x_1) of IL; (□) methyl acetate; (○) ethyl acetate and (△) propyl acetate.

increasing x_{IL}. The data in Fig. 15 indicate that the n_D value of IL with esters follow the order at equimolar composition: methyl acetate > ethyl acetate > propyl acetate. The observed n_D data were 1.4327 (at $x_{IL} \approx 0.5027$), 1.4246 (at $x_{IL} \approx 0.4930$) or 1.4222 (at $x_{IL} \approx 0.4912$) for m-2-HEAB with methyl acetate, ethyl acetate or propyl acetate, respectively. The m-2-HEAB with methyl acetate system shows higher n_D data as compared to m-2-HEAB with ethyl acetate or propyl acetate. This is due to the increasing the size of ester from methyl to butyl increasing the volume on the surface of m-2-HEAB.[149]

In 2013, Li *et al.*[174] reported the n_D values for ammonium-based ILs, which share a homologous series of cations $(CH_3CH_2)_3N^+(C_nH_{2n+1})$ with n = 2, 4, 6, 8 and a variety of anions, such as BF_4^-, PF_6^- or SbF_6^- with trifluoromethanesulfonic acid (TFSA) at different mass fraction (w, w = mass of ILs/(mass of IL + mass of TFSA)) ranging from 0.00 to 0.60 at 20 °C at atmospheric pressure. The n_D values of these systems increased pseudo-linearly with increasing over the studied mass range of ILs. It was clearly shown that the elongation of alkyl chain of the cation had a positive effect on the n_D values of a binary mixture of TFSA and ILs with fixed mass fraction.[174] On the other hand, in the case of the same cation with different anions, PF_6^- salts of all ammonium-based ILs with TFSA show higher n_D values as

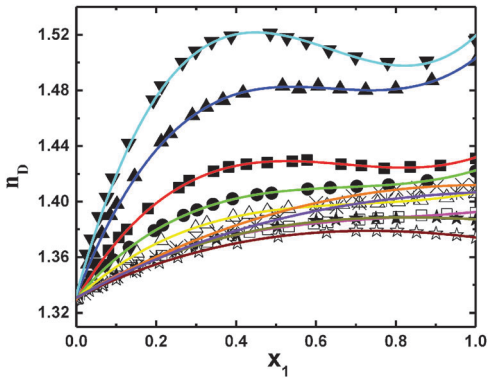

Fig. 16 Refractive indices (n_D) for mixtures of ammonium-based ILs + water[192,196] as a function of the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (△) TMAS; (★) TMAH; (☆) TEAH; (×) [TPAH] and (*) TBAH at 25 °C.

compared to SbF_6^- and BF_4^- salts at mass faction ≥ 0.3, whereas the BF_4^- of ammonium-based shown maximum n_D values at mass fraction ≤ 0.2.

Recently, Umapathi *et al.*[192] have systematically studied the n_D values for ammonium-based IL with water at 25 °C over the whole composition range of IL. As can be seen in Fig. 16, the n_D values of these ILs with water systems increased with increasing composition of IL, except DEAA, TEAA or TEAS with water systems. Fig. 16 reveals that the n_D values increased for DEAA, TEAA or TEAS + water systems up to $x_{ILs} \approx 0.5700$, ≈0.5500 or ≈0.4800, respectively. Later, the n_D values slightly decreased with increasing the mole fraction of IL for these systems. This may be due to diminished ion–ion pair interactions between the IL and water and also self-interaction between the ions of IL. From Fig. 16, the n_D values of all ILs with water follow the order: TEAS > TEAA > DEAA > DEAS > TMAS > TMAA. This order clearly shows that sulfate anion with same cation ILs show larger n_D values as compared to the corresponding acetate-based IL mixtures, except (DEA^+) of ILs. The highest n_D values are due to the ion arrangements and an efficient packing of ions of ILs.

Very recently, our research group examined the n_D values for $[OH]^-$ anion of ammonium-based ILs with water at different temperatures from 25 to 40 °C under the whole composition range of IL.[196] The n_D values of these systems increased with increasing x_{ILs}. However, Fig. 16 reveals that the n_D values of TMAH or TEAH + water systems increased up to $x_{IL} \approx 0.9000$ or ≈0.8000, respectively. Later, the n_D values slightly decreased with increasing the mole fraction of these ILs with water. Interestingly, TEAH + water system shows n_D values slightly lower as compared to TPAH or TBAH after $x_{IL} \approx 0.9000$, because the + inductive effect (+I effect) of short alkyl chain length of cation ILs was weaker than that of large alkyl chain length of cation ILs at these x_{IL} with water. This indicates that the lower +I effect of TEAH leads to weaker interactions with water as compared to greater +I of other ILs such as TPAH or TBAH at high x_{IL}. The order of n_D values for hydroxide anion of all ammonium-based ILs with water is as follows: TPAH > TBAH > TMAH > TEAH. This is attributed to that the n_D values

of these systems do not follow a regular trend. From Fig. 16, it is observed that the sulfate anion of ammonium-based ILs with water systems show higher n_D values than acetate and hydroxide anions of ammonium-based ILs with water. The highest n_D values of sulfate anion of ammonium-based ILs with water system is due to the higher arrangement and packing efficiencies of sulfate anions of ammonium-based ILs on the water surface as compared to acetate and hydroxide anions of ammonium-based ILs with water.[192,196]

7. Excess molar volume data for ammonium-based ILs with molecular solvents mixtures

Excess properties have traditionally been of great importance in ascertaining a better understanding of molecular interaction between solvents. The volumetric properties of binary mixtures are complex properties because they depend not only on size, shape and chemical nature of the components of a mixture, but also on the solute + solute, solvent + solvent, solute + solvent interactions, and on structural effects arising from interstitial accommodation due to differences in molar volume and free volume between solution components. Among the several excess thermodynamic properties, excess molar volumes (V^E), deviation in isentropic compressibilities ($\Delta\kappa_s$), deviation in viscosities ($\Delta\eta$) and deviation in refractive indices (Δn_D) are some of the most important for design of any equipment in industrial as well as theoretical studies. The V^E is a very useful parameter for technological processes of a reaction. Excess volume at infinite dilution can be used for understanding the molecular interactions such as hydrogen bonding interactions, dipole–dipole interactions, dipole-induced effects, van der Waals forces and structural effects involved between compounds in mixtures.[4,115–117] The thermophysical parameter of V^E study is helpful for characterizing the structure and properties of solutions comprising components in the mixtures. Thus, the excess thermodynamic properties are extensively used to study the deviation of real liquid mixtures from ideality.

Excess volume of mixing can be defined as the difference between the volume of mixing of a real mixture and the value corresponding to the ideal mixture at the same conditions of temperature, pressure and composition. Nonetheless, V^E can be interpreted into three terms, namely physical, chemical and structural effects.[4] The volume changes occur because of the combination of the following factors such as differences of energy in the intermolecular interaction between like and unlike molecules, formation of new chemical species, hydrogen bonding and differences in size and shape of the components and structural changes such as in the correlation of molecular orientations. The physical effects involve dispersion forces and non-specific interactions in the mixture, adding positive contributions to V^E.[4] The chemical and specific interactions result in decrease in volume, which includes charge-transfer type forces and other complex forming interactions between the two species, thereby these chemical effects contribute negative values to V^E.[4,7] The structural effects that arise from the geometrical fitting of one component into the others are due to the different molar volumes and free volumes of pure components, and add negative contributions to V^E. Throughout the years of research a vast amount of information concerning the V^E of ILs with molecular solvents is available in the open literature. In this context, we have taken ammonium-based ILs with molecular solvent mixtures, to explicitly explore the importance of design process of industrial instruments, engineering process and to understand the molecular interactions in solution chemistry. The relative position between the anion and cation comprising the bulk IL solution is one of the most important structural factors that determine the physical and chemical properties of particular ILs in the mixture. There is much discussion in the literature concerning the evaluation and prediction of excess properties of ammonium-based ILs with molecular solvents, as will be discussed in forthcoming sections. This perspective focuses especially on the recent progress and perspectives in the molecular interactions of ammonium-based ILs with molecular solvents based on V^E.

7.1. Excess molar volume data of mixtures for ammonium-based ILs with water

The most dipolar protic molecules such as water usually exhibit strong localized interactions with the anions or cations of ILs because it is a polar covalent molecule and it has a slight positive and slight negative charge on opposite ends. When the IL is added to water it will disrupt the water structure which is strongly self-associated by hydrogen bonds which form a three-dimensional network. In this section, we can attempt to elucidate the molecular interactions of water with ammonium-based ILs. Few studies have been reported in the literature on the composition dependence of thermophysical properties of water with ammonium-based ILs across the entire range of mole fractions.

In extensive work on V^E of ammonium-based ILs with water, Xu[125] has observed negative V^E values for both binary mixtures as N4A or $N4NO_3$ IL with water mixtures over the whole composition range at several temperatures. The negative V^E values decrease with increasing the temperature for N4A or $N4NO_3$ with water over the whole composition range and at atmospheric pressure. The negative V^E values of these ILs indicate formation of strong molecular interactions (such as hydrogen bonding, electrostatics interactions) with water molecules. It is more interesting that both N4A and $N4NO_3$ in water mixtures have minimum V^E values at around $x_{IL} \approx 0.3000$ under the same experimental conditions. The values of $V^E = -1.343\ cm^3\ mol^{-1}$ (at $x_{IL} \approx 0.2999$) for N4A + water system were more negative than those for $N4NO_3$ + water system, $V^E = -0.563\ cm^3\ mol^{-1}$ (at $x_{IL} \approx 0.3009$), which may be attributed the strong interactions between the ions of N4A and water or significant packing efficiency.[125] The presence of acetate anion of N4A may be involved in the formation of stronger H-bonding with water molecules than nitrate anion of $N4NO_3$ due to the difference between the nature of ions of N4A and $N4NO_3$ as well as the basicity of acetate anion which is larger than that of nitrate anion. Roughly at the same time, Hou *et al.*[127] have also

found negative V^E values for the binary systems of N2A or N3A IL with water at 25 °C. The minimum negative V^E values -1.182 cm^3 mol^{-1} for N2A + water or -1.413 cm^3 mol^{-1} for N3A + water were located at $x_{IL} \approx 0.3481$ or $x_{IL} \approx 0.3001$, respectively, at 25 °C. However, the V^E values of N3A + water system are more negative than those for N2A + water system at the same conditions, which shows stronger interactions of ions of N3A with water than for N2A in water. Interactions between like molecules lead to increased V^E values, while negative contributions to V^E arise from interaction between unlike molecules such as ion–dipole and hydrogen bonding, or structural effects such as packing effects. However, the interactions or packing efficiency between unlike molecules in the binary system are higher for N3A in water than those N2A in water.

For the sake of comparison, for the interactions between the acetate or nitrate anion-based ILs with water, the available V^E data[125,127,194] for the acetate and nitrate anion-based ILs with water at 25 °C are shown in Fig. 17. As depicted in Fig. 17, the negative values of $V^E = -1.343$ cm^3 mol^{-1} (at $x_{IL} \approx 0.2999$) for N4A + water, -1.413 cm^3 mol^{-1} (at $x_{IL} \approx 0.3001$) for N3A + water and -0.182 cm^3 mol^{-1} (at $x_{IL} \approx 0.3481$) for N2A + water are found to decrease with decreasing of alkyl chain length from N4A to N2A in aqueous solution at 25 °C, except in the mixture N3A with water. Interestingly, N3A + water mixture exhibits higher negative V^E values as compared to other ILs with water systems. It is well known that variation in alkyl chain length of cation in ILs causes changes in interaction with water by dipole–dipole interactions, and forms hydrogen bonded complexes or hetero-associates. Overall, the negative V^E values of water with acetate anion-based ILs are larger than those for nitrate anion of $N4NO_3$ IL in water, which indicates that stronger intermolecular interactions are formed by acetate anion of ammonium-based ILs with water than by nitrate anion of ammonium-based ILs.[125,127]

Very recently, Zarrougui *et al.*[194] have reported the negative V^E values for EAN IL with water except for high concentration of EAN at several temperatures. For comparison, we have calculated V^E values from the densities of mixtures of EAN + water from the Zarrougui data, and included this in Fig. 17. Negative V^E values are exhibited for this mixture up to $x_{IL} \approx 0.7000$, later increasing concentration of IL in water system, then the negative V^E enters to positive deviation (Fig. 17). The observed V^E values present a minimum at $x_{IL} \approx 0.2000$ and maximum at $x_{IL} \approx 0.8000$ and the minimum decreases and the maximum increases when the temperature increases. On the other hand, the negative V^E values -0.563 cm^3 mol^{-1} at $x_{IL} \approx 0.3000$ for $N4NO_3$ + water[125] system are slightly higher than those for EAN in water ($V^E = -0.387$ cm^3 mol^{-1} at $x_{IL} \approx 2000$), which is due to the difference in the polarity of ions of ILs. Finally, we can verify negative contributions of systems from packing efficiency of the both EAN and $N4NO_3$ ILs with water due to steric hindrance.[125,194]

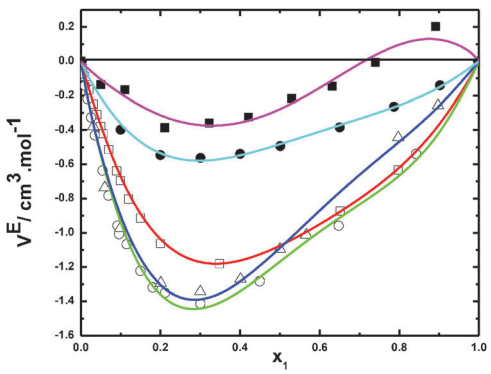

Fig. 17 Plots of excess molar volume (V^E) for mixtures of ILs + water as a function of the mole fraction (x_1) of IL; (□) N2A;[127] (○) N3A;[127] (△) N4A;[125] (●) $N4NO_3$[125] and (■) EAN[194] at 25 °C.

Iglesias *et al.*[138] have observed negative V^E values for 2-HEAF IL with water at different temperatures from 15 to 50 °C. The minimum negative V^E value of -0.413 cm^3 mol^{-1} (at $x_{IL} \approx 0.3990$) is obtained for 2-HEAF + water mixture at 25 °C. From these results, the most negative V^E values were observed for 2-HEAF with water at almost equimolar compositions and under the lowest temperature. This fact indicates that as the increased kinetics of the water molecules produce an increase of the potency of the hydrogen bond, this diminishes the ion–dipole interaction between the ions of ILs.[138]

In 2011, Alvarez *et al.*[142] have found negative V^E values for 2-HEAA IL with water at a temperatures range from 15 to 50 °C and over the whole composition range. The values of V^E (-0.854 cm^3 mol^{-1} at 20 °C) show a minimum at $x_{IL} \approx 0.7106$ of water mixture at all studied temperatures, which exhibits stronger ion solvent interactions formed with 2-HEAA, due to stronger hydrogen bonds and higher dipole interactions. The negative deviation becomes more with increasing temperature from 15 to 50 °C for this mixture. The negative V^E values of these systems are contributing to a contraction in volume of IL when water is dominant. Therefore, we can reveal from their reports, the binary mixture of water with 2-HEAA could be classified as a contractive mixture when 2-HEAA is added to water, this effect may be strengthened by the ions of 2-HEAA.[142] Later, Taib *et al.*[144] reported V^E values for the binary mixtures of 2-BHEAA + water at several temperatures from 30 to 80 °C as a function of IL concentration. The V^E values are negative for 2-BHEAA with water over the whole composition range and the large V^E value -1.016 cm^3 mol^{-1} was observed at $x_{IL} \approx 0.3159$. The absolute negative values of V^E are found to increase with an increasing of temperature of this mixture.

Fig. 18 explains the V^E values of 2-HEAF, 2-HEAA or 2-BHEAA with water over the entire composition range of IL at 30 °C for comparison. The reports show that the minimum values of $V^E = -0.832$ cm^3 mol^{-1} (at $x_{IL} \approx 0.2894$) for 2-HEAA + water[142] and -1.016 cm^3 mol^{-1} (at $x_{IL} \approx 0.3159$) for 2-BHEAA[144] + water at 30 °C. Clearly, the minimum V^E value of 2-BHEAA + water is higher than 2-HEAA + water. These results demonstrated that water interacts with 2-BHEAA by dipole–dipole interactions, and form some hydrogen bonded complexes or hetero-associates more so than with 2-HEAA. The results in Fig. 18 reveal negative V^E values -0.409 cm^3 mol^{-1}, -0.832 cm^3 mol^{-1} or -1.016 cm^3 mol^{-1} for 2-HEAF, 2-HEAA or 2-BHEAA with water at $x_{IL} \approx 0.3990$, ≈ 0.2894 or ≈ 0.3159 at 30 °C, respectively. Among them, the less negative V^E values are obtained for formate anion than those for acetate anion

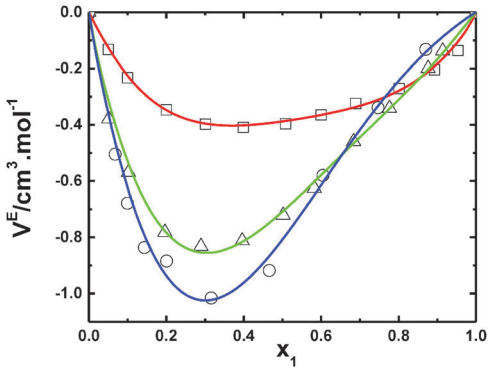

Fig. 18 Plots of excess molar volume (V^E) for mixtures of ILs + water as a function of the mole fraction (x_1) of IL; (□) 2-HEAF;[138] (△) 2-HEAA[142] and (○) 2-BHEAA[144] at 30 °C.

of the same cation (2-HEA$^+$) of IL with water. This indicates that the formate anion interacts more weakly with water than acetate anion with water. On the other hand, acetate anion of 2-BHEAA IL in water shows more negative V^E values. The more negative V^E values reveal that a more efficient packing or attractive interaction occurred when 2-BHEAA is mixed with water as compared to 2-HEAF or 2-HEAA. The interactions between the water molecules and the ions of these ILs are due to ion–dipole interactions. This will reduce the hydrogen bonding between the cation and anion in the ILs, which contribute to the negative V^E values.

In 2008, Arce *et al.*[150] obtained negative V^E values for tris-(2-hydroxyethyl)methylammonium methylsulfate, [MTEOA][MeOSO$_3$] with water over the whole composition range of IL except at high mole fractions of IL. The minimum around V^E = −0.350 cm^3 mol^{-1} (at $x_1 \approx 0.2556$) of this IL with water suggests formation of hydrogen bonding between water and ions of [MTEOA][MeOSO$_3$].[150]

It was demonstrated that negative V^E values are observed for [DIPEA][C$_6$COO] or [DIPEA][C$_7$COO] ILs with water over the whole composition range of ILs.[183] The minimum negative V^E values −3.470 cm^3 mol^{-1} (at $x_{IL} \approx 0.1980$) or −3.530 cm^3 mol^{-1} (at $x_{IL} \approx 0.2908$) were observed for the mixture [DIPEA][C$_6$COO] or [DIPEA][C$_7$COO] with water at 25 °C, respectively. Here, the V^E values of [DIPEA][C$_7$COO] with water is higher as compared to [DIPEA][C$_6$COO] with water at the entire composition range of IL.[183] Furthermore, V^E diminished with increasing the anion alkyl chain length of IL, and this effect may be explained by the increase of the apolar part on the anion; increase of the carboxylate alkyl chain length of these ammonium-based ILs from m = 6 to 7 did not affect strongly on the V^E of the mixture. Thus, these values completely depended on the nature of ILs and water. In another study, very recently, Usula *et al.*[198] also observed negative V^E values for EAM, EAP or EAB with water at 25 °C over the whole composition range. All these systems show a minimum at x_{IL} in the range 0.3000–0.3500. Apparently, the V^E data do not follow the alkyl chain length of the anion of ILs.[198]

Quite recently, Umapathi *et al.*[192] observed negative V^E values for binary mixtures of ammonium-based ILs such as DEAA, TEAA, DEAS, TEAS, TMAA or TMAS with water over the entire range of composition ILs at 25 °C under atmospheric pressure. The negative V^E values = −0.164 cm^3 mol^{-1} (at $x_{IL} \approx 0.4000$) for DEAA + water obviously higher than those for TEAA + water, (V^E = −0.051 cm^3 mol^{-1} at $x_{IL} \approx 0.4000$). Subsequently, the negative V^E values −0.583 cm^3 mol^{-1} (at $x_{IL} \approx 0.4000$) for DEAS + water is also higher than those for TEAS + water, V^E = −0.204 cm^3 mol^{-1} (at $x_{IL} \approx 0.4000$). From these results, the V^E values become less negative with higher alkyl length of the ILs in water under the entire experimental conditions. The less negative V^E values for (TEA$^+$) mixture indicates that higher alkyl chain molecules decrease the hydrogen bonding tendency between (TEA$^+$) with water as compared to (DEA$^+$). Also, the negative V^E value −0.213 cm^3 mol^{-1} (at $x_{IL} \approx 0.3900$) of acetate anion of TMAA is lower than sulfate anion (V^E = −0.266 cm^3 mol^{-1} at $x_1 \approx 0.4700$) of TMAS with water. Overall, the aforesaid results show ILs can form hydrogen bonding to water molecules. From these reports, one can conclude that lower alkyl chain length of cation of ILs are showing stronger molecular interactions with water than higher alkyl chain length of ILs. These results indicate that moderate steric hindrance of the alkyl chain in (TEA$^+$) of ILs with water as compared to (DEA$^+$) of ILs with water molecules.[192]

Furthermore, very recently, our research group observed negative V^E values for hydroxide anion of different alkyl chain length cation of ammonium-based ILs with water as a function of x_{IL} at different temperatures from 25 to 40 °C.[196] The V^E values become more negative with increasing temperature from 25 to 40 °C for all the mixtures and the V^E values are negative in the whole concentration region with a minimum $x_{ILs} \approx 0.5000$, 0.5500, 0.6600 or 0.4500 for TMAH, TEAH, TPAH or TBAH with water, respectively. On the basis of V^E values, it can be concluded that the order of the interactions for ILs with water follow the sequence: TMAH > TEAH > TPAH > TBAH. This order explicitly elucidates that the lower cation alkyl chain length of the ILs interact more strongly with water than those with longer alkyl chains. This is probably due to the larger steric hindrance of the long alkyl chain in TPAH or TBAH with water as compared to TMAH or TEAH with water.[196]

The higher alkyl chain length of cation of ILs decreased the hydrogen bonding tendency between TPAH or TBAH with water because of its structural effects. Thus, it is important to note that the nature of interactions between the IL + water system was highly dependent on the size and nature of the ions of the ILs.[196] For sake of clarity and comparison between the ammonium-based ILs interactions with water, we have displayed V^E data of the two sources[192,196] in Fig. 19. At equimolar composition, the V^E data of these ammonium-based ILs with water follow the order: DEAS > TMAS > TMAA > TEAS > TMAH > TEAH > DEAA > TPAH > TBAH > TEAA. From Fig. 19, amongst the sulfate anion-based ILs shows the more negative V^E values with water than those for the acetate or hydroxide anion-based ILs system. This can be attributed that a more efficient packing or attractive interactions occur when these ILs are mixed with water. The more negative V^E values suggest the formation of stronger association interactions between the ions of IL and water.[192,196]

Overall, the V^E values for ammonium-based ILs with water are negative over the whole composition range except for the

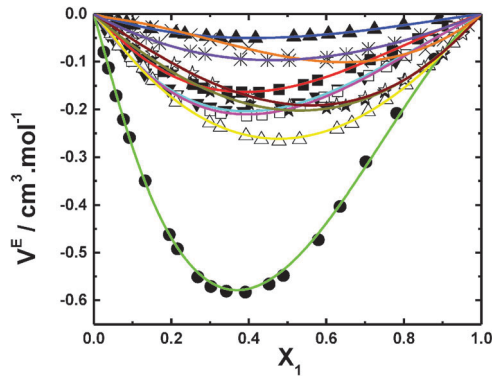

Fig. 19 Plots of excess molar volume (V^E) for mixtures of ILs + water[192,196] as a function of the mole fraction (x_{IL}) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (△) TMAS; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

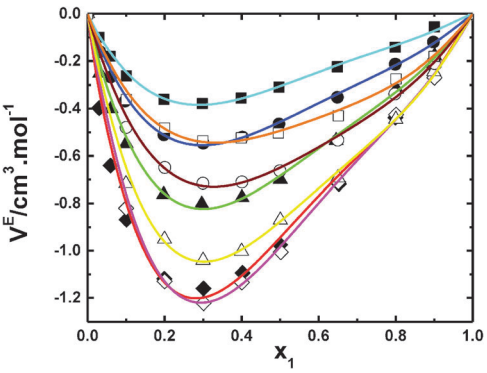

Fig. 20 Plots of excess molar volume (V^E) for mixtures of ILs + alkanols[124,128] as a function of the mole fraction (x_{IL}) of IL; N4A[124] + methanol (◆); + ethanol (▲); + 1-propanol (●) and + 1-butanol (■); $N4NO_3$[128] + methanol (◇); + ethanol (△); + 1-propanol (○) and 1-butanol (□) at 25 °C.

EAN + water system.[194] The positive V^E values are observed for EAN + water system at higher mole fraction of IL. Therefore, it is important to note that the nature of interactions in IL with water system is highly dependent on the nature of ions of ILs.

7.2. Excess molar volume data of mixtures for ammonium-based ILs with alkanols

Most ILs are polar liquids and formed by proton transfer from a Brønsted acid to a Brønsted base.[206] These are used in many chemical processes and electrochemical applications due to strong self-association by hydrogen bonding with polar solvents such as alkanols. Whilst, alkanols are polar liquids, strongly self-associated by hydrogen bonding, the extent of this differs depending on chain length and position of the OH-group in alkanols.[207–209] For the alkanols, which are highly associated in the pure state, breaking of the H-bonds followed by specific interactions occurs upon mixing with highly polar solvents.[210] An exhaustive survey of the literature has shown that a number of research articles have been reported by researchers on the volumetric properties of ammonium-based ILs with alkanols and the results significantly differ from each other.

Xu *et al.*[124] reported the V^E values for $N4NO_3$ IL with alkanols such as methanol, ethanol, 1-propanol or 1-butanol at different temperatures from 20 to 40 °C and the V^E values are negative over the entire composition range of IL. The minimum negative V^E values are −1.222 cm^3 mol^{-1} (at $x_{IL} \approx 0.3012$), −1.041 cm^3 mol^{-1} (at $x_{IL} \approx 0.2999$), −0.716 cm^3 mol^{-1} (at $x_{IL} \approx 0.2994$) and −0.536 cm^3 mol^{-1} (at $x_{IL} \approx 0.2993$) for $N4NO_3$ with methanol, ethanol, 1-propanol and 1-butanol at 25 °C, respectively. The order of negative V^E values is in the sequence: 1-butanol < 1-propanol < ethanol < methanol, which indicates that the V^E values decrease as the chain length of the alkanol increases. Consequently, the same authors have observed negative V^E values of −1.160 cm^3 mol^{-1} (at $x_{IL} \approx 0.3010$), −0.803 cm^3 mol^{-1} (at $x_{IL} \approx 0.2965$), −0.547 cm^3 mol^{-1} (at $x_{IL} \approx 0.3002$) and −0.379 cm^3 mol^{-1} (at $x_{IL} \approx 0.2981$) for N4A[128] with methanol, ethanol, propanol or butanol at 25 °C, respectively. Fig. 20 summarizes the V^E values of $N4NO_3$ or N4A + alkanols at 25 °C over the whole composition range of ILs, which are available in the literature.[124,128] The results show that the negative V^E values of $N4NO_3$ with alkanols (methanol to 1-butanol) are higher than those for N4A with the same alkanols (methanol to 1-butanol), which indicates that the difference in the polarity of ions of ILs and alkanols are highly associated with ILs. Finally, it can be assumed that the negative contributions of binary systems, are mainly due to the packing efficiency such as accommodation of organic molecules (alkanols) in the interstices of the IL networks and the interactions such as ion–dipole and hydrogen bonding between the alkanols and ions of ILs. Moreover, the larger negative V^E values show that the increased ability of stronger hydrogen bonding between the ions of $N4NO_3$ with alkanols than ions of N4A with alkanols is due to nitrate anion being of more polar nature than acetate anion. Meanwhile, the negative V^E values −0.563 cm^3 mol^{-1} (at $x_{IL} \approx 0.3009$) for $N4NO_3$ with water[125] are lower than those for $N4NO_3$ with alkanols, except in butanol.[124] On the other hand, the negative V^E values for N4A with water[125] (V^E = −1.343 cm^3 mol^{-1} at $x_{IL} \approx 0.2999$) are higher than those for N4A with all alkanols.[128] It is more interesting to note that the minimum V^E values are around at $x_{IL} \approx 0.3000$ for N4A or $N4NO_3$ with water or alkanol mixtures under the same experimental conditions (Fig. 20). In the case of water, stronger interactions are found with N4A than $N4NO_3$, but this is the opposite in the case of alkanols. This may lead to the variations in the molecular interactions between the ions of these ILs with water or alkanols.

Negative V^E values for 2-HEAF were measured with methanol or ethanol almost at equimolar compositions.[138] The minimum V^E values are −1.157 cm^3 mol^{-1} (at $x_{IL} \approx 0.2990$) for methanol + 2-HEAF and −0.984 cm^3 mol^{-1} (at $x_{IL} \approx 0.4020$) for ethanol + 2-HEAF at 25 °C. Alvarez *et al.*[142] observed the V^E values are negative for 2-HEAA IL with methanol or ethanol at 15 to 50 °C and over the whole composition range of ILs under atmospheric pressure. The negative V^E values −1.308 cm^3 mol^{-1} (at $x_{IL} \approx 0.2900$) for 2-HEAA + methanol are higher than 2-HEAA + ethanol, V^E = −1.003 cm^3 mol^{-1} (at $x_{IL} \approx 0.4057$) at 20 °C, which indicates a contraction in volume. These reports show a considerable decrease in the V^E data of 2-HEAA + alkanols being

more negative than those of 2-HEAA + water ($V^E = -0.854$ cm^3 mol^{-1} at $x_{IL} \approx 0.2894$) at 20 °C.[142] This behavior can be explained by the high dielectric constant of water and the filling of hydroxylic solvents into the interstices of the ILs network, and the ion–dipole interactions are the main factors controlling the strong contractive trend and ion–dipole interactions in the mixture. Here, the 2-HEAA IL with methanol shows higher V^E values than those in ethanol. On the other hand, 2-HEAF + methanol system shows lower V^E values than those in the mixture of 2-HEAF + ethanol. This can be obviously understood by that 2-HEAA formed stronger interactions with methanol than ethanol, in contrast, 2-HEAF IL shows a weaker interaction with methanol than ethanol, which indicates that the differences in the nature of ions of these ILs and structural effects of unlike molecules in the mixture.[138,142]

In 2011, Kurnia *et al.*[146] obtained negative V^E values for 2-BHEAA IL with methanol, ethanol or 1-propanol and the negative V^E values increase with raising the temperature for all three systems over the entire mole fraction range. The negative V^E values of 2-BHEAA + methanol ($V^E = -1.149$ cm^3 mol^{-1} at $x_1 \approx 0.3000$) are higher than those in ethanol ($V^E = -1.085$ cm^3 mol^{-1} at $x_1 \approx 0.3000$) or in 1-propanol ($V^E = -0.907$ cm^3 mol^{-1} at $x_1 \approx 0.4000$). Therefore, methanol interacts more strongly with this IL than ethanol or 1-propanol. From these reports, it is seen that the strength of ion–dipole interactions of 2-BHEAA decrease with increasing the chain length of the alkanols, which was indicated by a decrease in negative V^E values from methanol to 1-propanol.[146] Additionally, the same authors have investigated the V^E value for the same alkanol with 2-BHEAP at 20 to 50 °C.[147] From their results almost the same negative V^E values are observed for 2-BHEAA or 2-BHEAP with the same alkanol (Fig. 21).[146,147] Therefore from these results one can observe that the anion (A or P) does not influence the V^E values of these systems (Fig. 21). The minimum negative V^E values are -1.156 cm^3 mol^{-1} (at $x_{IL} \approx 0.2957$), -1.0927 cm^3 mol^{-1} (at $x_{IL} \approx 0.3168$) or -0.9145 cm^3 mol^{-1} (at $x_{IL} \approx 0.4017$) for 2-BHEAP with methanol, ethanol or propanol at 20 °C, respectively. The negative V^E values for 2-BHEAP with alkanols (from methanol to propanol) mixtures decrease as the chain length of alkanol increases due to the ion–dipole interactions and packing effects of 2-BHEAP with methanol being stronger than for the higher chain length alkanols.[147]

The values of $V^E = -1.149$ cm^3 mol^{-1} (at $x_{IL} \approx 0.3070$) for 2-BHEAA + methanol[146] are lower than those for 2-HEAA + methanol[142] ($V^E = -1.308$ cm^3 mol^{-1} at $x_{IL} \approx 0.3000$) at 20 °C. In contrast, the values of $V^E = -1.085$ cm^3 mol^{-1} (at $x_{IL} \approx 0.3140$) for 2-BHEAA + ethanol[146] are higher than those for 2-HEAA with ethanol[142] ($V^E = -1.003$ cm^3 mol^{-1} at $x_{IL} \approx 0.4000$). Upon addition of these ILs to methanol or ethanol, the higher or lower negative V^E values of the mixtures of 2-HEAA with methanol or ethanol, and *vice versa* with 2-BHEAA are probably due to steric hindrance from 2-HEAA with methanol or ethanol by contrast with the bridging group in 2-BHEAA with methanol or ethanol. This implies that the ion–dipole interactions and packing effects are stronger in methanol systems than in the higher alkanol (ethanol or 1-propanol) systems.[147]

Moreover, Arce *et al.*[150] reported negative V^E values for [MTEOA][MeOSO$_3$] IL + ethanol at 25 °C and the system leads to a minimum around -1.700 cm^3 mol^{-1} at $x_{IL} \approx 0.4000$. In 2012, Bahadur *et al.*[151] found negative to positive V^E values for ([MOA]$^+$[Tf$_2$N]$^-$) IL with 2-propanol, 1-butanol or 2-butanol binary mixtures from 20 to 40 °C. The sign and magnitude of V^E value depend on the strength of hydrogen bonding of alkanols in their pure state and ions of ILs in the mixture. Later, increase the mole fraction of IL, ($x_{IL} \approx 0.4824$, 0.6385 or 0.5045 for 2-propanol, 1-butanol or 2-butanol, respectively) the V^E values become positive due to the dissociation of the hydrogen bonding in these alkanols. This can be attributed to weaker intermolecular interactions formed between the ions of ILs and alkanols with a rise in the concentration of ILs.[151] In another work, Bahadur *et al.*[154] have explicitly explained the apparent molar volume, $V_\varnothing$ for the binary mixture of ([MOA]$^+$[Tf$_2$N]$^-$) IL with ethanol. The $V_\varnothing$ values also increase with increases of concentration of ILs, which indicates that may be stronger intermolecular interactions are formed between the ions of ([MOA]$^+$[Tf$_2$N]$^-$) with ethanol in the mixture.[154]

Sibiya *et al.*[157] have obtained positive to negative V^E values for ([MOA]$^+$[Tf$_2$N]$^-$) with methanol whereas negative to positive V^E values were found for ([MOA]$^+$[Tf$_2$N]$^-$) with ethanol or 1-propanol at various temperatures from 25 to 40 °C. Similarly, the authors have also observed negative to positive V^E values for this IL with 2-propanol, 1-butanol or 2-butanol.[151] As can be seen from the results in Fig. 22, it is very interesting to note that the V^E values were observed to be positive in methanol for ([MOA]$^+$[Tf$_2$N]$^-$) mole fraction up to $x_{IL} \approx 0.7084$, further increasing the mole fraction of IL, these values are become negative. In other words, the V^E values are negative up to $x_{IL} \approx 0.1731$ or ≈ 0.1146 for ethanol or propanol with ([MOA]$^+$[Tf$_2$N]$^-$), respectively. Later, the V^E values become positive with increase in the mole fraction of IL. It can be concluded that the negative V^E values are due to the alkanols tending to fill the interstices of the IL and the ion–dipole interaction between organic molecular liquids and the IL. The positive V^E values are due to the dissociation of the hydrogen bonding in the alkanol being

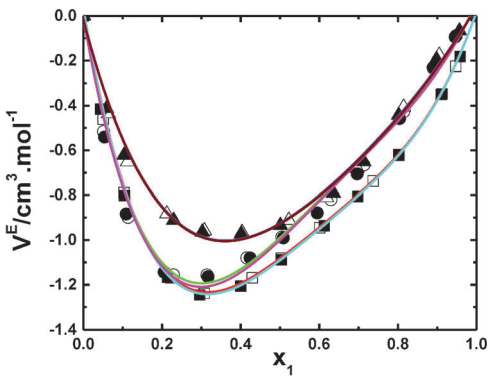

Fig. 21 Plots of excess molar volume (V^E) for mixtures of ILs + alkanols[146,147] as a function of the mole fraction (x_{IL}) of IL; 2-BHEAA[146] + methanol (□); + ethanol (○) and + 1-propanol (△); 2-BHEAP[147] + methanol (■); + ethanol (●) and + 1-propanol (▲) at 30 °C.

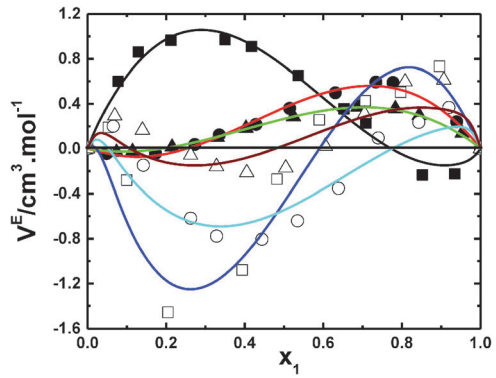

Fig. 22 Plots of excess molar volume (V^E) for mixtures of ILs + alkanols[151,157] as a function of the mole fraction (x_{IL}) of IL; ([MOA]$^+$[Tf$_2$N]$^-$) + methanol (■); + ethanol (●); + 1-propanol (▲); + 2-propanol (□); + 1-butanol (○) and + 2-butanol (△) at 25 °C.

greater than intermolecular bond formation between ions of ([MOA]$^+$[Tf$_2$N]$^-$) and alkanol.[157] As the alkyl chain length of the alkanol increases it was observed that the minimum values are shifted to maximum for ethanol or propanol from lower mole fraction of IL to higher mole fraction of IL and it was reversed in methanol. The reverse trend for ([MOA]$^+$[Tf$_2$N]$^-$) + ethanol or 1-propanol system is possibly due to having an additional –CH$_2$ group that changes the intermolecular interactions, an opposite effect to that of the IL + methanol system.[157] A similar conclusion can be drawn from the same authors for ([MOA]$^+$[Tf$_2$N]$^-$) with 2-propanol, 1-butanol or 2-butanol.[151]

Very recently, Brennecke and co-workers[158] have observed negative V^E values for [N$_{1114}$][NTf$_2$] IL with ethanol or propanol at several temperatures. The negative V^E values (−0.311 cm^3 mol^{-1} at $x_{IL} \approx 0.1237$) of [N$_{1114}$][Tf$_2$N] + ethanol were higher than those for [N$_{1114}$][Tf$_2$N] + propanol (−0.103 cm^3 mol^{-1} at $x_{IL} \approx 0.0502$) under the same experimental conditions. The negative V^E values increase with increasing the temperature. A study on the influence of the alkyl chain length in *N*-alkyltriethylammonium bis(trifluoromethylsulfonyl)imide ILs, [N$_{R,222}$][Tf$_2$N] (R = 6, 8 or 12) on V^E of methanol mixtures were carried out from 10 to 65 °C within intervals of 5 °C.[170] The excess properties of mixtures showed that the physical (van der Waals) and chemical (H-bonds) contributions caused the contraction of the volume of the mixtures. Here, in all three studied systems such as [N$_{6,222}$][Tf$_2$N], [N$_{8,222}$][Tf$_2$N] or [N$_{12,222}$][Tf$_2$N] with methanol, the V^E values show very small deviations from ideality, however in an S-shaped curve corresponding to partly negative and partly positive deviations from the ideal mixture because the presence of large alkyl group composition of ILs leading to differing chemical and physical contributions.[170] These pure ILs may be found to form organized structures similar to that on a molecular level due to intermolecular interactions, particularly coulombic and van der Waals forces.[170]

Domańska *et al.*[172] have obtained positive V^E values for [N$_{1114}$][NTf$_2$] with 1,2-propanediol, 1,2-butanediol or 2,3-butanediol as well as observing positive V^E values for [N$_{1112OH}$][NTf$_2$] IL with 1,2-propanediol, 1,3-propanediol or 1,5-pentanediol at different temperatures from 50 to 80 °C over the entire composition range. The maximum values of V^E = 0.611 cm^3 mol^{-1} (at $x_{IL} \approx 0.4700$), 0.496 cm^3 mol^{-1} (at $x_{IL} \approx 0.3700$) and 0.584 cm^3 mol^{-1} (at $x_{IL} \approx 0.4400$) are observed for [N$_{1114}$][NTf$_2$] IL in 1,2-propanediol, 1,2-butanediol and 2,3-butenediol at 50 °C, respectively. Furthermore, the maximum V^E values (V^E = 0.339 cm^3 mol^{-1} at $x_{IL} \approx$ 0.4100; 0.486 cm^3 mol^{-1} at $x_{IL} \approx 0.4300$ and 0.570 cm^3 mol^{-1} at $x_{IL} \approx 0.4900$) have been found for [N$_{1112OH}$][NTf$_2$] with 1,2-propanediol, 1,3-propanediol and 1,5-pentanediol at 50 °C, respectively.[172] From these results, one can see that the values of V^E for [N$_{1114}$][NTf$_2$] + 1,2-propanediol are two times higher than those for [N$_{1112OH}$][NTf$_2$] + 1,2-propanediol at 50 °C. This is due to the presence of an additional hydroxyl group in the [N$_{1112OH}$][NTf$_2$] IL, resulting in stronger interaction of the [N$_{1112OH}$]$^+$ cation with 1,2-propanediol and better packing effects. On the other hand, the V^E data for [N$_{1114}$][NTf$_2$] become more positive with 1,2-propanediol than 1,2-butanediol or 2,3-butanediol.[172] This is due to the presence of diol-alkanols containing –OH groups controlling internally hydrogen bond strength on ILs from 1,2-propanediol to 2,3-butanediol. The authors observed that the V^E data for [N$_{1114}$][NTf$_2$] become more positive in the following order: 1,2-butanediol < 2,3-butanediol < 1,2-propanediol. Whereas, the V^E values for [N$_{1112OH}$][NTf$_2$] increase in the following order: 1,2-propanediol < 1,3-propanediol < 1,5-pentanediol. This may be attributed to the dominance of a steric effect, due to the presence of increase in –CH$_2$ groups from 1,2-propanediol to 1,5-pentanediol. Moreover, the presence of methyl groups also decrease the association due to the steric effect. The interaction between unlike molecules decreases with an increase of the chain length of alkanediols, especially for [N$_{1112OH}$][NTf$_2$].[172] Negative V^E values have been found for tetraalkylammonium hydroxide ILs such as TPAH or TBAH with isomers of butanol (1-butanol, 2-butanol and 2-methyl-2-propanol) at the temperature range from 20 to 40 °C except for the TBAH + 2-butanol system at 25 to 40 °C, here positive V^E values are observed for this system.[197] These negative V^E values reveal that a more efficient packing or attractive interactions takes place between the ions of these ILs and butanol isomers. On the other hand, the observed positive V^E values for TBAH + 2-butanol at higher temperature show that there exist no specific interactions between the ions of TBAH and 2-butanol.[197]

Here, the overall V^E data for all ammonium-based ILs with alkanol systems such as methanol, ethanol, 1-propanol and 1-butanol reveal that the observed V^E data were negative, which becomes more negative in the order, 1-butanol < 1-propanol < ethanol < methanol. This is indicating that the V^E data decrease as the chain length of the alkanol increases, whereas negative to positive V^E data are observed for certain ILs such as ([MOA]$^+$[Tf$_2$N]$^-$) with 1-alkanols and 2-alkanols. In contrast, positive V^E data are observed for [N$_{1114}$][NTf$_2$] and [N$_{1112OH}$][NTf$_2$] with diols such as 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 2,3-butanediol and 1,5-pentanediol over the entire composition range of IL. On the other hand, the negative V^E data of ammonium-based ILs with alkanols decreased with increasing the alkyl chain length of alkanols and increased with increasing the temperature over the entire composition range of IL.

Thus, the negative or positive V^E values of ammonium-based ILs with alkanols depend on the variation in the interactions between the ions of ammonium-based ILs and alkanols.

7.3. Excess molar volume data of mixtures for ammonium-based ILs with esters

In this section, we will discuss the available data on V^E for ammonium-based ILs with esters. Alvarez *et al.*[149] reported positive to negative V^E values for m-2-HEAB IL with methyl acetate at 15 °C or ethyl acetate at 30 °C or propyl acetate at 40 °C. This research group suggested the V^E values increase with increasing of alkyl chain length of esters, from methyl acetate to propyl acetate, showing the ability of the alkyl chain to fill the holes of the new structure ionic liquid–ester.[149] The minimum V^E = −0.341 cm^3 mol^{-1} (at $x_{IL} \approx 0.4072$), −0.407 cm^3 mol^{-1} (at $x_{IL} \approx 0.3982$) or −0.961 cm^3 mol^{-1} (at $x_{IL} \approx 0.4912$) for m-2-HEAB IL + methyl acetate, ethyl acetate or propyl acetate, respectively. The minimum V^E, could be due to the formation of hydrogen bonds between esters and ions of m-2-HEAB at high concentration of IL. From this result, one can explicitly explain that dissociation of the ions in m-2-HEAB at lower concentrations of esters, which is indicating the presence of significant intermolecular dipole–dipole interactions by ions of IL. On the other hand, the carbonyl group of ester containing oxygen is more electronegative than carbon and forms a partially charged dipole.[149] Overall, positive to negative V^E values observed for m-2-HEAB with methyl acetate, ethyl acetate or propyl acetate at different temperatures. In another study, Deenadayalu *et al.*[152] have found negative V^E values (V^E = −1.397 cm^3 mol^{-1} at $x_{IL} \approx 0.5029$ or −1.579 cm^3 mol^{-1} at $x_{IL} \approx 0.5450$ at 25 °C) for ($[MOA]^+[Tf_2N]^-$) IL with methyl acetate or ethyl acetate, respectively.

7.4. Excess molar volume data of mixtures for ammonium-based ILs with DMF, DMSO and NMP solvents

A considerable amount of work on the thermophysical properties of ammonium-based ILs with highly polar solvents has been explicitly elucidated by various research groups. Recently, Usula *et al.*[120] have systematically studied the volumetric properties of a series of the alkylammonium nitrate (XAN) family ILs such as EAN, PAN, BAN and MEOEAN ILs with NMP at 25 °C to see the cationic chain length effect on the thermophysical properties. Negative V^E values were found for all XAN with NMP system, which indicates the presence of strong attractive interactions between ions of XAN ILs and NMP molecules. The V^E values have a broad minimum at the composition around ≈0.3000 mole fraction of all ILs and V^E curves are not affected by the alkyl chain length of the cation of the ILs, since the negative V^E values are almost the same as a function of concentration of ILs.[120] On the other hand, the negative V^E values for MEOEAN + NMP (−0.730 cm^3 mol^{-1} at $x_{IL} \approx 0.3000$) are lower than XAN with NMP systems (−0.920 cm^3 mol^{-1}, −0.980 cm^3 mol^{-1} or −0.930 cm^3 mol^{-1} for EAN, PAN or BAN with NMP respectively, at $x_{IL} \approx 0.3000$). These results show the reduction of volume is smaller than those obtained for the other XAN + NMP systems, that indicates that addition of a polar group, such as methoxy, prevents the compaction of the mixture.[120]

It is noteworthy to compare the V^E data of ammonium-based ILs with highly polar solvents such as DMF, DMSO and NMP. In this context, negative V^E values have been obtained for DEAA + DMF[116] at 25 °C, + DMSO[129] or NMP[130] at various temperatures from 25 to 40 °C. The negative V^E = −1.766 cm^3 mol^{-1} (at $x_{IL} \approx 0.7418$) or −0.208 cm^3 mol^{-1} (at $x_{IL} \approx 0.2100$) or −0.721 cm^3 mol^{-1} (at $x_{IL} \approx 0.4856$) for DEAA with DMF or DMSO or NMP at 25 °C, respectively. Among them, the negative V^E data of DEAA + DMF was higher than DEAA + DMSO or NMP systems. The more negative V^E revealed that a more efficient packing or attractive interaction occurred when DEAA was mixed with DMF. Furthermore, Attri *et al.*[116] and Govinda *et al.*[129] have observed positive V^E values for TEAA with DMF, and DMSO, respectively from 25 to 40 °C. In contrast, Kavitha *et al.*[130] reported negative to positive V^E values for TEAA + NMP under the same experimental conditions. The positive V^E = 1.686 cm^3 mol^{-1} (at $x_{IL} \approx 0.6600$) or 0.480 cm^3 mol^{-1} (at $x_{IL} \approx 0.4831$) for TEAA + DMF or DMSO at 25 °C, respectively. The positive V^E values for TEAA + DMF or DMSO, suggest that the factors responsible for expansion in volumes are dominant over the entire composition range of IL in the mixture. Furthermore, the observed positive values show that there exist no specific interactions between unlike molecules and also the compact structure of the DMF or DMSO because of dipolar association has been broken by ions of TEAA IL.[116,129] Negative V^E values were observed up to $x_{IL} \approx 0.3200$, later the positive V^E values were observed on further increasing the concentration of TEAA in NMP.[130] This indicates that interactions between TEAA and NMP decrease as the concentration of the TEAA increases. Moreover, the V^E values are positive for TEAA-rich compositions and negative for NMP-rich compositions for TEAA + NMP system at all investigated temperatures.[130] However, the decrease in the magnitude of the negative V^E values with an increase in IL composition can be attributed to the decrease of hydrogen bonding between the ions of TEAA and NMP.[130]

Negative V^E values are reported for DEAS with DMSO[117] or NMP[130] at different temperatures from 25 to 40 °C, over the entire range of composition. The negative V^E = −0.249 cm^3 mol^{-1} (at $x_{IL} \approx 0.4494$) for DEAS + DMSO is lower than those for DEAS + NMP (V^E = −9.057 cm^3 mol^{-1} at $x_{IL} \approx 0.3452$) under the same experimental conditions. Subsequently, positive V^E values were observed for TEAS with DMF[116] or DMSO[131] except with NMP[130] at all studied temperatures, in which negative V^E deviation was observed for TEAS + NMP. From these results, the authors found that the negative V^E = −0.249 cm^3 mol^{-1} (at $x_{IL} \approx 0.4494$) for DEAS + DMSO and positive V^E values 0.356 cm^3 mol^{-1} (at $x_{IL} \approx 0.4202$) for TEAS + DMSO at 25 °C. This may be attributed to strong interactions between the ions of DEAS and DMSO as well as the dominance of the steric effect, due to the presence of increasing alkyl groups from diethyl to triethyl in the cation of these ILs.[117,131] Clearly, the negative V^E data of DEAS + NMP are higher than TEAS + NMP at 25 °C. This indicates that the molecular interactions between the ions of DEAS and NMP are stronger than the ions of TEAS and NMP, owing to the steric hindrance in TEAS.[130] The observed negative V^E values are −2.091 cm^3 mol^{-1} (at $x_{IL} \approx 0.2171$), −1.414 cm^3 mol^{-1}

(at $x_{IL} \approx 0.6728$) or -2.252 cm^3 mol^{-1} (at $x_{IL} \approx 0.4000$) for TEAP + DMF, + DMSO or + NMP at 25 °C, respectively.[116,131,132] This sequence shows that TEAP interacts more strongly with NMP than DMF or DMSO. This implies that ion–dipole interactions and packing effects of TEAP with NMP are stronger than in DMF or in DMSO.

Govinda *et al.*[134] and Kavitha *et al.*[135] have observed negative V^E values for TMAH + DMSO or NMP at various temperatures from 25 to 40 °C, respectively, whereas Attri *et al.*[136] reported negative to positive V^E values for this IL + DMF. The V^E values for TEAH + DMSO were negative at all the ranges of composition[134] whereas the V^E value showed opposite behavior from negative to positive deviation for TEAH with NMP[135] or DMF[136] under the same experimental conditions. In the same studies, the authors observed negative V^E values for TPAH with DMSO, NMP or DMF, except for TPAH + DMF at lower temperature. Analogously, negative V^E values are observed for TBAH with DMSO ($V^E = -2.096$ cm^3 mol^{-1} at $x_{IL} \approx 0.4429$) or + NMP ($V^E = -3.750$ cm^3 mol^{-1} at $x_{IL} \approx 0.3600$) at 25 °C, respectively. From these reports, the TPAH and TBAH ILs show V^E values with polar solvents in the following order: NMP > DMSO > DMF. This can be attributed that the formation of stronger hydrogen bonding interactions between the ions of these ILs and NMP as compared to DMSO or DMF.

Further research demonstrated that negative V^E data are observed for TMAA + DMSO[133] and DMF[193] at various temperatures from 25 to 40 °C over the whole composition range of IL. Later, Kavitha *et al.*[132] reported that the V^E data for TMAA + NMP are almost always negative in the entire range of composition, except for TMAA rich concentrations at all temperatures, in which slightly positive values are obtained at rich composition of ILs. The negative V^E values are -1.099 cm^3 mol^{-1} (at $x_{IL} \approx 0.3220$), -1.209 cm^3 mol^{-1} (at $x_{IL} \approx 0.3100$) or -0.414 cm^3 mol^{-1} (at $x_{IL} \approx 0.3408$) for TMAA with DMF, NMP or DMSO at 25 °C, respectively. Among them, the V^E data of TMAA + NMP is higher than DMF or DMSO with TMAA. In addition, negative V^E values were obtained for TMAP + NMP[132] or DMF[193] at 25 °C. In contrast, Govinda *et al.*[133] reported positive V^E values for TMAP + DMSO at 25 °C. As per these results, one can conclude that the more negative V^E values of TMAP is due to phosphate anion showing strong interactions with NMP or DMF. Furthermore, the observed high positive values show that there are no specific interactions between unlike molecules and the compact structure of the DMSO as the dipolar association is broken by ions of TMAP in DMSO. The variation in the V^E values indicate that may be differences of structural arrangements of polar solvents and the nature of the ions. As a result, the sign and magnitude of V^E obviously depend on the nature of the ions as well as the solvent polarity.

Negative V^E values are found for TMAS with DMSO[133] or DMF[193] at various temperatures from 25 to 40 °C and over the entire composition range of IL. On the other hand, Kavitha *et al.*[132] observed negative to positive V^E values for TMAS + NMP at different temperatures from 25 to 40 °C. The sign and magnitude of V^E value depend on the strength of hydrogen bonding of polar solvents such as DMSO or DMF or NMP, in their pure state and with ions of TMAS in the mixture. According to these reports, we have delineated the more negative V^E values of TMAP, containing phosphate anion, shows stronger interactions in the order NMP > DMF > DMSO as compared to acetate or sulfate anions of TMAA or TMAS ILs, respectively. These may be a result of the variation in the molecular interactions of ions of these ILs and polar solvents such as NMP, DMF or DMSO.[132,133,193]

It is worthwhile to compare the V^E data of all alkylammonium-based ILs with polar solvents such as DMSO, NMP and DMF, thereby, in the present perspective, we have shown the V^E data of ammonium-based ILs with these polar solvents at 25 °C, in Fig. 23. As can be seen in Fig. 23a, the TEAH + DMSO mixture exhibits higher negative V^E values as compared to all ammonium-based ILs with DMSO, which indicates the formation of strong hydrogen bonding between the hydroxyl anion of (TEA^+) and DMSO. The large negative V^E data of TEAH + DMSO system is due to the strong + inductive effect (+I) that is produced by the longer alkyl chain. The +I effect is lower in TMAH when compared to the TEAH, because of the shorter alkyl chain length.[134] At the same time, we note that the TBAH + DMSO system shows a larger negative V^E than TEAH + DMSO as per the +I effect. To rationalise this, when increasing the alkyl chain length from TEAH to TBAH, this leads to variation in the hydrogen bonding between the cation

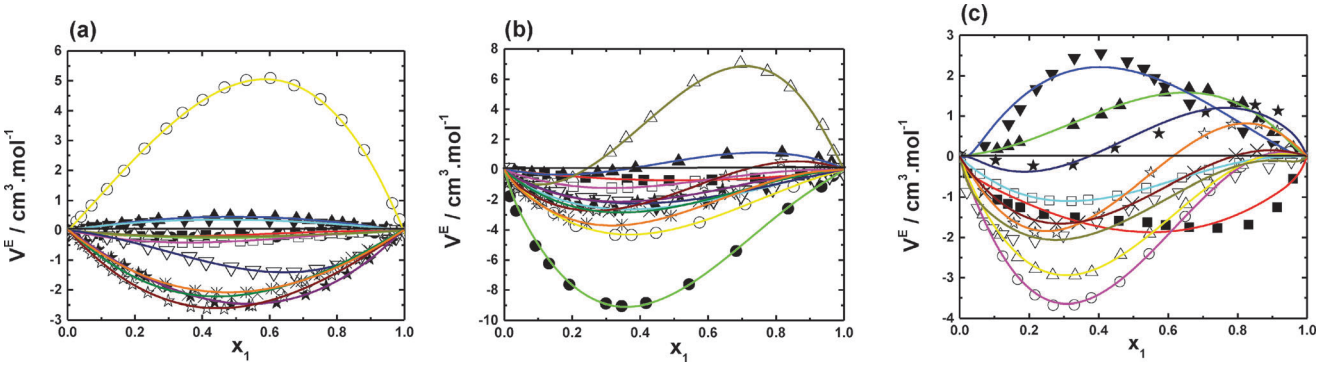

Fig. 23 Plots of excess molar volume (V^E) for mixtures of ILs + (a) DMSO;[117,129,131,133,134] (b) NMP;[130,132,135] and (c) DMF[116,136,193] as a function of the mole fraction (x_{IL}) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (○) TMAP; (△) TMAS; (▽) TEAP; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C which are available from the literature.

and the anion of ILs with DMSO. These results clearly demonstrate that higher alkyl chain molecules decrease the hydrogen bonding tendency due to moderate steric hindrance in TBAH IL, since TBAH + DMSO system shows less negative V^E than the TEAH + DMSO system. Apparently, the TMAP + DMSO system shows more positive V^E values and TEAA or TEAS ILs show slightly positive V^E values with DMSO. At equimolar composition, the negative V^E data of the remaining ammonium-based ILs with DMSO follow the order: TEAH > TMAH > TPAH > TBAH > TEAP > TMAA > TMAS > DEAS > DEAA. The results in Fig. 23a show that the hydroxide anion of ammonium-based ILs show more negative V^E data with DMSO as compared to acetate, sulfate and phosphate anion of ammonium-based ILs. The more negative V^E data of hydroxide anion of ILs indicate the IL strongly interacts with DMSO as compared to acetate, sulfate and phosphate anion of ILs.

As can be seen in Fig. 23b, these all ILs are showing the negative V^E values with NMP, except at higher mole fractions of TMAS, TEAA or TEAH, in which positive V^E values were observed. The interactions of TMAS, TEAA or TEAH with NMP systems are dissociated with increasing concentration of these ILs with NMP. At equimolar composition, the V^E data of all ammonium-based ILs with NMP follow the order: DEAS > TMAP > TBAH > TPAH > TEAH > TMAH > TEAS > TEAP > TMAA > DEAA > TEAA > TMAS. From this order, the minimum (DEAS) and maximum (TMAS) V^E data are observed for sulfate anion of ammonium-based ILs with NMP and moderate V^E data for phosphate, hydroxide and acetate anions of ammonium-based ILs. The discrepancies of the V^E data of sulfate anion of (DEA^+) and (TEA^+) ILs with NMP indicate that steric hindrance in the structures of these ILs. The small size (DEA^+) of the IL shows stronger hydrogen bonding interactions with NMP as compared to large size (TEA^+) of IL due to the structural effects.

We have explicitly illustrated the V^E data for ammonium-based ILs with DMF in Fig. 23c. Negative V^E data are observed for DEAA, TMAA, TMAP, TMAS or TEAP with DMF over the entire composition of IL. The order of the negative V^E data of these ILs with DMF is TMAP > TMAS > TEAP > DEAA > TMAA. The negative V^E data reveal that more efficient packing or attractive interactions take place when these ILs added with DMF. The results in Fig. 23c show that negative to positive V^E data are observed for TMAH, TEAH or TPAH + DMF systems, which indicates that the more polar DMF forms hydrogen bonding with ions of these ILs at lower concentrations, while the other part of the DMF resonating structure (non-hydrogen bonding) interacts more strongly with increasing the concentration of TMAH, TEAH or TPAH with DMF. TEAA or TEAS + DMF systems show positive V^E data at whole concentrations of IL in the mixture. The positive V^E data of these ILs with DMF follow the order: TEAS > TEAA. This can be attributed that weaker molecular interactions between the ions of these ILs and DMF. Eventually, the deviation in V^E data (negative or positive) of all ammonium-based ILs with these polar solvents from ideality obviously depends on the variation in the interactions of the cation or anion of ILs with molecular solvents.

Overall, it is clear that different phenomena of the V^E values are observed for the ammonium-based ILs with the differing molecular solvents. As mentioned earlier, the type of interactions apparently depends on the nature of the ions of ILs and structural arrangements of the solvents. Naturally, it seems that both cation and anion play a significant role in the V^E data of ammonium-based ILs with polar solvents. Negative and positive deviations from ideal behavior are seen, which indicates that fascinating results are obtained for structure-based and temperature dependent properties of ammonium-based ILs with polar solvents. The established structure-based properties of these ILs enhance our knowledge on the molecular interactions between the ions ILs and polar solvents and reveal that ILs offer many opportunities for exploration of various scientific fields.

8. Deviation in isentropic compressibility data of mixtures for ammonium-based ILs with molecular solvents

The $\Delta\kappa_s$ values have been extensively used to study physicochemical behavior and molecular interactions of a variety of liquid mixtures. In recent years there has been considerable progress in the experimental investigation of ammonium-based ILs with molecular solvents. These studies have proven to be a very useful tool in elucidating the structural interactions among the components which are of great importance in helping to understand the nature and extent of the patterns of molecular aggregation that exist in liquid mixtures. In 2008, Iglesias *et al.*[138] reported negative $\Delta\kappa_s$ values for 2-HEAF with water, methanol or ethanol. On the other hand, Alvarez *et al.*[142] demonstrated negative $\Delta\kappa_s$ values for 2-HEAA with water, methanol or ethanol. The $\Delta\kappa_s$ values of 2-HEAF or 2-HEAA with water, methanol or ethanol systems are shown in Fig. 24 at 30 °C. The negative $\Delta\kappa_s$ values imply that solvent molecules around the solute are less compressible than the solvent molecules in the bulk solutions. As can be seen in Fig. 24, the negative $\Delta\kappa_s$ values for 2-HEAF with these solvents are in the following order: methanol > ethanol > water. The negative

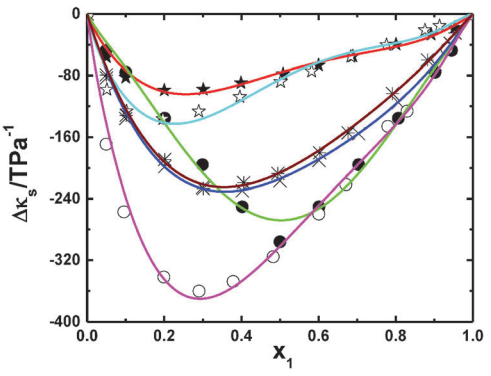

Fig. 24 Plots of deviation in isentropic compressibility ($\Delta\kappa_s$) for mixtures of ILs + water, methanol or ethanol as a function of the mole fraction (x_1) of IL; 2-HEAF[138] + water (★); + methanol (●) and + ethanol (×); 2-HEAA[142] + water (☆); + methanol (○) and + ethanol (*) at 30 °C.

$\Delta\kappa_s$ data of 2-HEAF + methanol system is higher than for 2-HEAF + ethanol or + water systems, which indicates that may be stronger ion–dipole interactions formed between ions of 2-HEAF and methanol than ethanol or water. From Fig. 24, the negative $\Delta\kappa_s$ values of 2-HEAA + these solvent systems is in the following order: methanol > ethanol > water. A similar trend can be drawn from these solvents with 2-HEAF by Iglesias *et al.*[138] From these results, it can be observed that the $\Delta\kappa_s$ data of acetate anion of (2-HEA^+) of IL with water, methanol or ethanol systems are higher as compared to formate anion of (2-HEA^+) of IL with water or methanol or ethanol. This can be attributed to that the large size acetate anion may form weaker interactions with water, methanol or ethanol than the smaller formate anion of this cation of IL.[138,142]

Sibiya *et al.*[157] obtained negative $\Delta\kappa_s$ values for ($[\text{MOA}]^+[\text{Tf}_2\text{N}]^-$) IL with methanol, ethanol or 1-propanol except at higher mole fraction of ILs. The negative $\Delta\kappa_s$ values are -42.7 TPa^{-1} (at $x_{IL} \approx 0.4000$) for 1-propanol, -108.0 TPa^{-1} (at $x_{IL} \approx 0.5000$) for ethanol or -146.0 TPa^{-1} (at $x_{IL} \approx 0.4000$) for methanol. The decrease in compressibility is due to stronger interaction between components of mixtures due to the proximity of unlike molecules. Thus, the negative $\Delta\kappa_s$ values indicate that may be due to the association of the hydrogen bonding in the alkanols being greater than ion pair bonding formation between the ions of ILs and the alkanols. On the other hand, Attri *et al.*[197] have found negative $\Delta\kappa_s$ values for TPAH and TBAH ILs with butanol isomers such as 1-butanol, 2-butanol and 2-methyl-2-propanol at various temperatures from 25 to 40 °C except for TBAH + butanol isomers systems in higher concentration region of IL at higher temperatures, which might be due to the reduced attractive interaction between the ions of TBAH and butanol isomers at higher concentration.[197]

Recently, Venkatesu and co-workers examined the $\Delta\kappa_s$ values for ammonium-based ILs + water systems and the values are negative for all the compositions range of IL at 25 °C.[192,196] For clarity of presentation, we have illustrated the $\Delta\kappa_s$ values of ammonium family ILs with water in Fig. 25 at 25 °C. As can be seen in this figure the fitting curves are asymmetric and present a minimum which is obtained in the water-region at $x_{IL} \approx 0.3000$ to 0.4500. The negative $\Delta\kappa_s$ values are attributed to the strong dispersive interactions due to the solvation of the ions in the solution. A strong intermolecular interaction through charge transfer, dipole–induced dipole and dipole–dipole interactions, interstitial accommodation and orientational ordering lead to a more compact structure which contributes to negative deviation in $\Delta\kappa_s$ values. The negative $\Delta\kappa_s$ values of the ILs with water imply that solvent molecules around the solute are less compressible than the solvent molecules in the bulk solutions. The algebraic values of $\Delta\kappa_s$ for ammonium-based ILs with water fall in the order: TEAS > TEAA ≥ TMAS > TMAH > TEAH > DEAS > DEAA ≥ TPAH > TBAH > TMAA. From this order, these results explicitly reveal that different phenomena of $\Delta\kappa_s$ were observed for the various ILs with water. As can be seen from this order, the $\Delta\kappa_s$ values for sulfate-based IL (TMA^+ or TEA^+) with water systems are higher than those for acetate or hydroxide-based ILs with water. The lower $\Delta\kappa_s$ values of acetate-based ILs with water serves as further evidence that the interactions between acetate-based ILs with water are weaker than those between sulfate or hydroxide-based ILs.[192,196] In other words, in the case of hydroxide anion with various cation groups of ammonium-based ILs with water, the $\Delta\kappa_s$ values follow the order: TMAH > TEAH > TPAH > TBAH. From this order, it can be clearly observed that the intermolecular interactions decrease with increasing alkyl chain length of cation of ILs. The more negative $\Delta\kappa_s$ values for methyl cation of ILs serve as further evidence that the interactions between small sizes of methyl cation ILs with water are stronger than in the higher alkyl cation chain ILs.[196]

Negative $\Delta\kappa_s$ values are reported for DEAA with DMSO[129] at 25 °C, whereas the $\Delta\kappa_s$ data show an inversion in the sign from negative to positive for DEAA with NMP[130] or DMF[116] under the same experimental conditions. The inversion from negative to positive deviation suggests that the interaction between DEAA and NMP or DMF decreases as the concentration of the IL increases. As the concentration of the IL increases the $\Delta\kappa_s$ enters into positive deviation, which suggests a loss of dipolar association of the components. Later, Attri *et al.*[116] and Govinda *et al.*[129] observed the $\Delta\kappa_s$ values were negative for TEAA with DMF or DMSO, respectively, while Kavitha *et al.*[130] obtained positive $\Delta\kappa_s$ values for TEAA in NMP over the entire composition range of ILs at 25 °C.

Furthermore, positive and negative $\Delta\kappa_s$ values have been reported for DEAS + DMSO[117] and DEAS + NMP[130] at 25 °C. The variation in $\Delta\kappa_s$ values may be attributed to that the interactions of DEAS with NMP are stronger than DMSO. In addition, negative $\Delta\kappa_s$ values have been observed for TEAS in NMP[130] or DMSO[131] at 25 °C, while an inversion in the sign of $\Delta\kappa_s$ from positive to negative is observed for TEAS + DMF.[116] Subsequently, an inversion in the sign of the $\Delta\kappa_s$ values from negative to positive was obtained for TEAP with DMF[116] at 25 °C, whereas negative $\Delta\kappa_s$ values were observed for TEAP with NMP[132] or DMSO[131] at 25 °C. From these results, TEAP IL shows stronger dispersive interactions with DMSO or NMP than with DMF.[116,131,132]

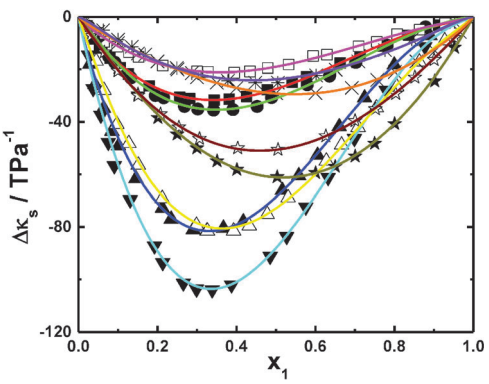

Fig. 25 Plots of deviation in isentropic compressibility ($\Delta\kappa_s$) data for mixtures of ILs + water[192,196] as a function of the mole fraction (x_{IL}) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (△) TMAS; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

Moreover, the $\Delta\kappa_s$ values were measured for hydroxyl anion with different tetraalkyl chain length of cation ammonium-based ILs such as TMAH, TEAH, TPAH and TBAH with DMSO,[134] NMP[135] or DMF[136] at various temperatures, to see the effect of variation in the alkyl cationic chain length on the interaction between the ions of ILs and polar solvents. The $\Delta\kappa_s$ values were found to be negative for these ILs with these polar solvents except the TEAH + NMP system, whereas the $\Delta\kappa_s$ values have observed an inversion in the sign from negative to positive for the TEAH + NMP system. This can be attributed that the presence of strong hydrogen bonding interactions between the hydroxyl group of ILs and polar part of DMSO, NMP or DMF. From these results, it can be seen that the $\Delta\kappa_s$ data were decreased with increasing alkyl chain length of IL, which indicates that formation of the stronger hydrogen-bonding interactions weakening with increasing the size of alkyl chain length of the cation with hydroxyl anion of ammonium-based ILs.[134–136]

Negative $\Delta\kappa_s$ values are reported for acetate anion of (TMA^+) with DMF,[193] DMSO[133] or NMP,[132] except at higher concentration of TMAA + DMF at 25 °C. However, the phosphate anion with same (TMA^+) shows anomalous results with these polar solvents. TMAP shows negative $\Delta\kappa_s$ data with DMF[193] or NMP[132] and positive value with DMSO.[133] Furthermore, the $\Delta\kappa_s$ data for TMAS + DMF[193] or DMSO[133] were found to be negative over all ranges of composition of IL, whereas the $\Delta\kappa_s$ value shows an inversion in the sign from negative to positive deviation for TMAS with NMP[132] system under the same experimental conditions. The inversion of sign of $\Delta\kappa_s$ values of TMAS + NMP reveal that the molecular interactions become weaker with increasing concentration of IL due to steric hindrance formed at high concentration of large size sulfate anion in TMAS than for other small anions such as acetate and phosphate of TMAA or TMAP ILs with NMP. The negative $\Delta\kappa_s$ values of these ILs with DMF follow the order: TMAA < TMAP < TMAS. The more negative $\Delta\kappa_s$ values of TMAS + DMF system indicates stronger intermolecular interaction between the ions of TMAS and DMF than TMAA or TMAP with DMF.[193] The positive $\Delta\kappa_s$ values of TMAP + DMSO indicate weaker interactions between the ions of TMAP and DMSO. Among the all ILs, acetate anion of IL shows stronger interactions with DMF, NMP or DMSO than phosphate or sulfate anions of ILs.[132,133,193]

Fig. 26 depicts the $\Delta\kappa_s$ data of ammonium-based ILs with DMSO, NMP and DMF at 25 °C obtained from various literature sources.[116,117,129–136,193] As can be seen in Fig. 26a, all the ammonium-based IL systems show negative $\Delta\kappa_s$ data with DMSO, except DEAS or TMAP + DMSO systems, which exhibit positive $\Delta\kappa_s$ values in the entire composition range of IL. At equimolar composition, the negative $\Delta\kappa_s$ data of ammonium-based ILs with DMSO follow the order: TEAA > TEAP > TEAS > TBAH ≈ TEAH > TPAH > TMAH > TMAS > DEAA > TMAA. From these results, the acetate anion of ammonium-based ILs show more negative $\Delta\kappa_s$ data than sulfate, hydroxide or phosphate anions of ammonium-based ILs. The more negative $\Delta\kappa_s$ data of acetate anion of ILs implies that they strongly interact with DMSO as compared to sulfate, hydroxide or phosphate anion of ILs. The maximum and minimum negative $\Delta\kappa_s$ are observed for TEAA and TMAA with DMSO systems at 25 °C, respectively. On the other hand, the positive $\Delta\kappa_s$ data of ammonium-based ILs with DMSO follow the order: DEAS > TMAP. In another study, ammonium-based ILs such as DEAA, TMAS, TEAH or TPAH show an inversion in sign in the $\Delta\kappa_s$ data from negative to positive with NMP with increasing the mole fractions of ILs at 25 °C (Fig. 26b).[130,132,135] As can be seen in Fig. 26b, negative $\Delta\kappa_s$ data are observed for DEAS, TEAS, TMAA, TMAP, TEAP, TBAH or TMAH + NMP systems whereas positive $\Delta\kappa_s$ values were obtained for TEAA with NMP over the entire composition range and approaches a maximum at $x_{IL} \approx 0.5100$. At equimolar composition, the negative $\Delta\kappa_s$ data of ILs with NMP follow the order: TEAP > TMAP > TBAH > TMAH > DEAS > TEAS > TMAA. From this order, the phosphate anion of ammonium-based ILs with NMP show more negative $\Delta\kappa_s$ data as compared to hydroxide, sulfate or acetate anions of ammonium-based ILs with NMP. The more negative $\Delta\kappa_s$ data implies that phosphate anion of ILs more strongly interacts with NMP as compared to hydroxide, sulfate or acetate anions of ammonium-based ILs. It is interesting to note that TEAA IL interacts more strongly with DMSO (Fig. 26a) whereas the same IL interacts very weakly with NMP (Fig. 26b) under the similar experimental conditions. Furthermore, it is also of note that TEAA interacts very strongly with DMSO compared to the interaction with DMF (Fig. 26c).

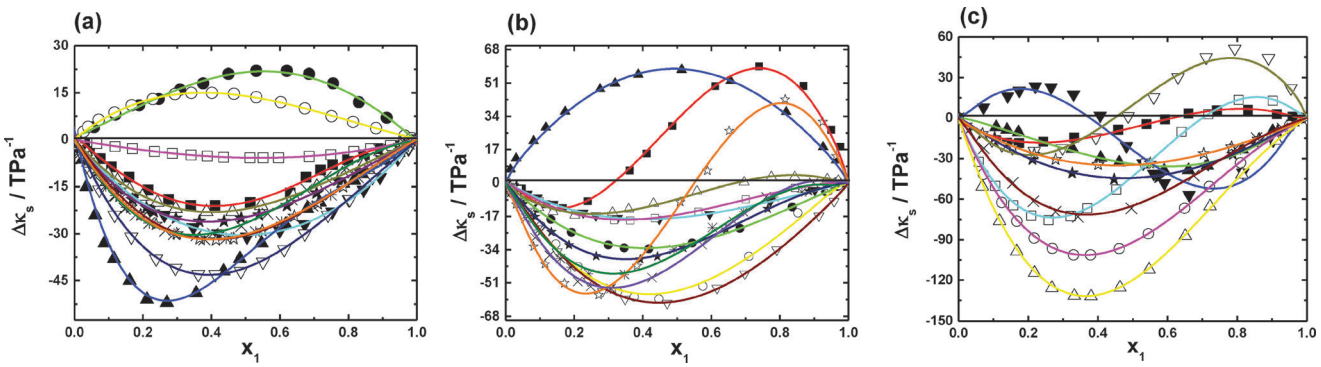

Fig. 26 Plots of deviation in isentropic compressibility ($\Delta\kappa_s$) for mixtures of ILs + (a) DMSO,[117,129,131,133,134] (b) NMP[130,132,135] and (c) DMF[116,136,193] as a function of the composition expressed in the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (○) TMAP; (△) TMAS; (▽) TEAP; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

The TMAS + DMF system shows highest negative $\Delta\kappa_s$ values among all of the ILs because attractive interactions are higher between the ions of TMAS and DMF than other ILs with DMF. Interestingly, the TEAS + DMF system shows positive to negative $\Delta\kappa_s$ values as can be seen in Fig. 26c, whereas TMAA, DEAA or TEAP + DMF systems are showing negative to positive $\Delta\kappa_s$ data. At equimolar composition, the order of $\Delta\kappa_s$ data of these ILs with DMF is: TMAS > TMAP > TPAH > TMAH > TEAH > TEAA. This implies that the sulfate anion of (TMA^+) of ammonium-based ILs show stronger interaction with DMF as compared to acetate or hydroxide anions of ammonium-based ILs. The observed negative $\Delta\kappa_s$ values of ILs with DMF are higher as compared to NMP and DMSO. The more negative $\Delta\kappa_s$ data demonstrate that they may be a dependency on the nature of the ions of ILs and DMF solvent. From these results, one can point out that the intermolecular interactions depend on variation in the size of cation and anion of ILs and nature of the molecular solvents.

Overall, the $\Delta\kappa_s$ values of ammonium family ILs with molecular solvents elucidate the clear phenomena of molecular interactions between the ions of ILs and molecular solvents. Negative $\Delta\kappa_s$ values are observed for all ammonium-based ILs with water, alkanols, DMSO, NMP or DMF over the entire composition range of IL except, DEAA, TEAH or TMAS + NMP systems and TEAP, TMAA or DEAA + DMF, in which systems negative to positive $\Delta\kappa_s$ values are observed, whereas positive $\Delta\kappa_s$ values are obtained for TMAP or DEAS + DMSO and TEAA + NMP systems. The observed $\Delta\kappa_s$ values of the ammonium family ILs with molecular solvent systems are highly dependent on the size and shape of the ions of ILs and nature of the solvents. As mentioned earlier, the type of interactions apparently depends on the nature of the ions of ILs and structural arrangements of the solvents. Consequently, these results thoroughly depend on the both the interaction of the cation or anion of ammonium-based IL with molecular solvent.

9. Deviation in viscosity data of mixtures for ammonium-based ILs with molecular solvents

The $\Delta\eta$ data are needed in all the situations involving fluid flow, such as in irrigation, power generation and in the most chemical industries. Consequently, η and its deviations are of vital importance for industrial and academic communities. Besides it is very useful in solution chemistry to understanding the molecular interactions between unlike molecules in the mixture.

9.1. Deviation in viscosity data of mixtures for ammonium-based ILs with water

The influence of temperature and the composition of molecular solvent on $\Delta\eta$ data of ammonium-based ILs are very interesting and important, and obviously provide information on the molecular interactions of the binary mixtures. An adequate knowledge of $\Delta\eta$ of ammonium family ILs with molecular solvents is essentially required to clarify the nature of molecular interactions between ILs with solvents. In this context, to understand the effect of anion on the $\Delta\eta$ data, Xu[125] has systematically studied $\Delta\eta$ data of *n*-butylammonium cation containing acetate and nitrate anions of ILs such as N4A and $N4NO_3$ ILs with water over the whole concentration range of ILs at various temperatures. Negative $\Delta\eta$ data were reported for these two ILs with water systems and $\Delta\eta$ data become less negative with increasing temperature.

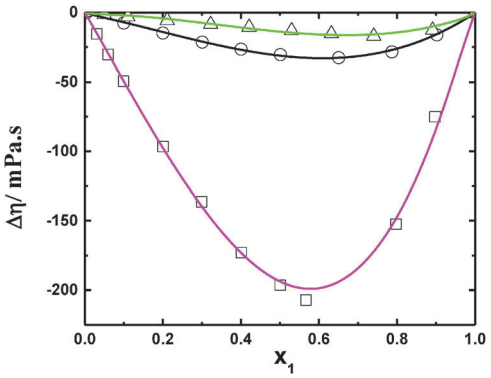

Fig. 27 Comparison among the available literature for deviation in viscosity ($\Delta\eta$) for mixtures of ammonium-based ILs + water as a function of the mole fraction (x_1) of IL, (○) $N4NO_3$;[125] (□) N4A[125] and (△) EAN[194] at 25 °C.

Furthermore, Zarrougui *et al.*[194] have observed negative $\Delta\eta$ values ($\Delta\eta = -20$ mPa s at $x_{IL} \approx 0.7500$) for EAN IL with water over the entire concentration of IL. The negative $\Delta\eta$ values of $N4NO_3$ in water are higher than those for EAN in water, which indicates the formation of weaker hydrogen bonding interactions between the ions of $N4NO_3$ ILs with water as compared to the EAN + water system.[125,194] This is mainly due to the steric hindrance of alkyl chain groups in $N4NO_3$. Fig. 27 shows a comparison for available $\Delta\eta$ data for $N4NO_3$, N4A or EAN with water at 25 °C. The minimum $\Delta\eta$ values are −207 mPa s (at $x_{IL} \approx 0.5666$) and −32 mPa s (at $x_{IL} \approx 0.6506$) for N4A or $N4NO_3$ + water at 25 °C, respectively. These results clearly show that the $\Delta\eta$ data is more affected with anions of *n*-butylammonium cation of ILs, which indicates that the interactions become weaker between the ions of N4A + water than for the $N4NO_3$ + water system due to weakening of the dipolar association by N4A IL. Fig. 27 clearly reveals that acetate anion of ammonium-based IL with water system shows higher negative $\Delta\eta$ data as compared to nitrate anion of ammonium-based ILs with water. On the other hand, the nitrate anion of the both ILs, EAN + water system shows lower negative values than those for the $N4NO_3$ + water system. The variation in the $\Delta\eta$ data of these ILs with water may be dependent on the nature of ions of ILs and polarity of water.[125,194]

Recently, Umapathi *et al.*[192] have measured $\Delta\eta$ values for DEAA, TEAA, DEAS, TEAS, TMAA and TMAS ILs with water at 25 °C over the entire composition range of ILs and they observed positive $\Delta\eta$ values for these systems, as can be seen in Fig. 28. A broad maximum of $\Delta\eta$ data for all mixtures was observed at region of IL ≈ 0.3000 to 0.3400. The positive $\Delta\eta$ data of these ILs with water followed the order: TEAS > DEAS > TEAA > DEAA > TMAS > TMAA. These results reveal that the highest $\Delta\eta$ values were observed for TEAS with water, this may

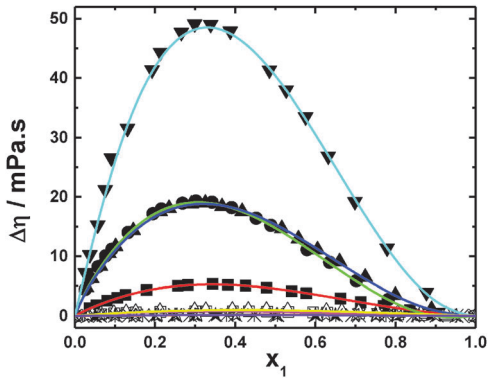

Fig. 28 Plots of deviations in viscosity ($\Delta\eta$) for mixtures of ILs + water[192,196] as a function of the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (○) TMAP; (△) TMAS; (▽) TEAP; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

be due to the formation of strong dispersive interactions between the ions of TEAS with water as compared with the rest of the ILs with water.[192] Furthermore, this order explicitly elucidates that the $\Delta\eta$ values increased with increasing the size of alkyl chain length of cation with the same anion of ILs. The sulfate anions of ILs + water systems show higher $\Delta\eta$ values than those for acetate anion ILs + water mixtures, mainly due to that variation in η values of pure ILs are caused mostly on the conformational changes in the structural interactions and ion–ion pair interactions, size and also shape of the components.[192]

Very recently, our research group found positive $\Delta\eta$ data for TMAH, TEAH, TPAH or TBAH with water at all studied temperatures.[196] The positive $\Delta\eta$ data increased for all ILs with water as the temperature increases, which can be attributed to the hydrogen bonding between water molecules and ILs. When the temperature increases, the interactions become acutely reduced because of the dissociation of ions of the ILs. The $\Delta\eta$ data of these ILs with water at 25 °C are also included in Fig. 28. The order of $\Delta\eta$ data for these ILs with water is: TMAH > TEAH > TPAH > TBAH. From these results, the $\Delta\eta$ data slightly decrease with increasing the alkyl chain length in the cations of ILs, which leads to the decreasing in the interactions from methyl to butyl in the ammonium-based ILs with water.[196] Overall, the $\Delta\eta$ values of all ammonium-based ILs with water systems follows the order: TEAS > DEAS > TEAA > DEAA > TMAS > TMAA ≥ TMAH > TEAH > TPAH > TBAH. From this order amongst all ILs, the sulfate anion of (TEA^+) of IL shows highest positive $\Delta\eta$ values with water and hydroxide anion of (TBA^+) of IL shows lowest positive $\Delta\eta$ values with water.

The use of an IL mixture is one approach to address electrochemical system viscosities issues, in this context, Smith *et al.*[122] have observed positive $\Delta\eta$ values for EAN, EtAN or PAN with EAF. The positive values indicate a strong hydrogen bonding network between the cationic and anionic groups of ammonium ILs. Here, the EtAN + EAF system shows more positive value than PAN or EAN which indicates that stronger ion-pair interactions are formed between the polar group in the cation of EtAN and formate anion of EAF. The positive $\Delta\eta$ values indicate enhanced intermolecular interactions with increasing the alkyl chain length from ethylammonium to propylammonium ILs. On the other hand, negative $\Delta\eta$ values were reported for EAN + PAN and EAN + EtAN mixtures. Later, an inversion from negative to positive $\Delta\eta$ values were observed for EtAN + PAN.[122] Overall, these results show stronger intermolecular interactions in the presence of the mixing nitrate ion of ILs to formate ion of ILs than nitrate anion of ILs. The mixtures containing both nitrate and formate anions have increased resistance to flow, due to the differences in hydrogen bonding capacity of the anions. Mixing of cations can give rise to complex behavior due to the offsetting effects of hydrogen bonding and solvophobic nanostructure formation.[122]

9.2. Deviations in viscosity data of mixtures for ammonium-based ILs with DMSO and NMP

The $\Delta\eta$ data of binary mixtures of ILs with polar solvents clearly depends on the structure of the solvent and the IL cations. Furthermore, for a given cation, the $\Delta\eta$ data is highly correlated with the size and the nature of the anion. The $\Delta\eta$ data of all ammonium-based ILs with DMSO or NMP are collected from the available literature[117,129–135] in Fig. 29. The results in this figure show that $\Delta\eta$ values for DEAA + DMSO at 25 °C are

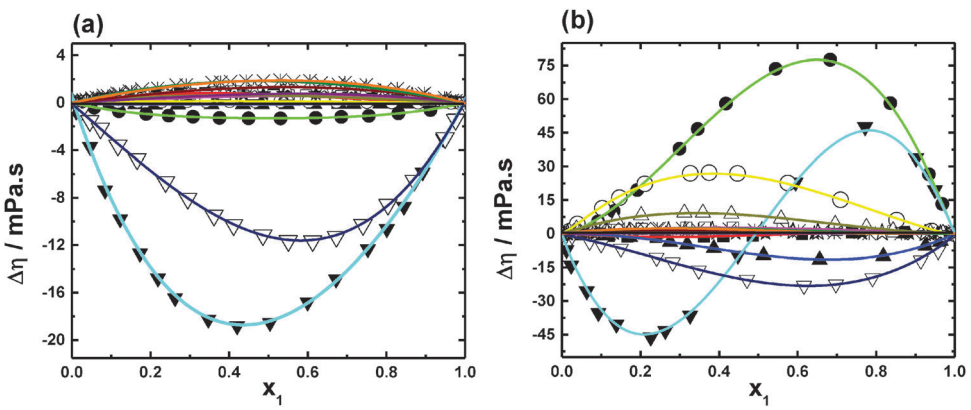

Fig. 29 Plots of deviation in viscosity ($\Delta\eta$) for mixtures of ILs + (a) DMSO[117,129,131,133] and (b) NMP[130,132,135] as a function of the mole fraction (x_1) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (○) TMAP; (△) TMAS; (▽) TEAP; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

positive (Fig. 29a) whereas the $\Delta\eta$ values are reversed from negative to positive deviation for DEAA + NMP (Fig. 29b). The positive $\Delta\eta$ values of DEAA + DMSO system indicate that the coulombic interactions are stronger with increasing the concentration of IL with DMSO.[129] Later, negative $\Delta\eta$ values were found for TEAA with DMSO[129] or NMP[130] at 25 °C over the whole composition range of IL. The negative $\Delta\eta$ values can be attributed to weakened interactions between the ions of this IL with DMSO or NMP. By increasing the composition of ILs the interactions become very weak due to the dipolar association being broken by the ions TEAA in DMSO or NMP, as well as the dissociation of the ion-pairs in TEAA IL.

The $\Delta\eta$ values are negative (−1.3 mPa s at $x_{IL} \approx 0.5306$) for DEAS + DMSO[117] whereas the $\Delta\eta$ values are positive (77.5 mPa s at $x_{IL} \approx 0.6829$) for DEAS + NMP[130] at 25 °C. Interestingly, temperature influences strongly on the $\Delta\eta$ values of the DEAS + DMSO system, as temperature increases, the deviations are reduced and even reach positive $\Delta\eta$ values for this system at 55 °C.[117] On the other hand, negative $\Delta\eta$ values (−46.2 mPa s at $x_{IL} \approx 0.2259$) or (−18.8 mPa s at $x_{IL} \approx 0.4202$) were reported for TEAS + NMP[130] or DMSO[131] at 25 °C, respectively. The DEAA IL shows the positive $\Delta\eta$ values with DMSO whereas negative $\Delta\eta$ values are reported for TEAA with DMSO at all temperatures.[129] In other words, the $\Delta\eta$ values are found to be less negative for DEAA + NMP than TEAA + NMP system at all investigated temperatures.[130] These observations clearly reveal that the $\Delta\eta$ values approach the positive $\Delta\eta$ values with decreasing the alkyl chain length of ammonium-based ILs with these solvents. Consequently, Govinda *et al.*[131] and Kavitha *et al.*[132] reported negative $\Delta\eta$ values for TEAP with DMSO or NMP at all studied temperatures. In fact, the temperature influences strongly on the $\Delta\eta$ values of all ammonium-based ILs with these solvents. As the temperature increases, the deviations are reduced over the complete mole fraction range for TEAP IL with DMSO or with NMP.[131,132]

The results in Fig. 29, TMAA or TMAS with NMP[132] and DMSO[133] show positive $\Delta\eta$ values. The reported positive $\Delta\eta$ values are 26.0 mPa s (at $x_{IL} \approx 0.3800$) or 0.6 mPa s (at $x_{IL} \approx 0.5500$) for TMAA with NMP or DMSO at 25 °C, respectively, which indicates NMP interacts more strongly with TMAA than DMSO. The positive $\Delta\eta$ values are observed (9.0 mPa s at $x_{IL} \approx 0.3100$) for TMAS + NMP or (0.7 mPa s at $x_{IL} \approx 0.3800$) for TMAS + DMSO at 25 °C, respectively. Similarly, positive $\Delta\eta$ values were reported for TMAP + NMP or DMSO systems over the whole composition of IL. The maximum $\Delta\eta$ values (28.0 mPa s at $x_{IL} \approx 0.4400$) for TMAP + NMP and (0.2 mPa s at $x_{IL} \approx 0.4000$) for TMAP + DMSO were obtained. From these reports, one can be explicitly see that TMAP shows more positive $\Delta\eta$ values with NMP or DMSO than TMAA or TMAS. This can be attributed to that the phosphate anion of (TMA^+) forms stronger hydrogen bonding with NMP or DMSO than acetate or sulfate anions with (TMA^+) of ILs.[132,133] Interestingly, from these systems, NMP + TMAA, TMAS or TMAP mixtures show higher $\Delta\eta$ values than those of DMSO + these ILs.

Apparently, it is interesting to see the influence of alkyl chain length of cation with fixed anion on the ammonium-based ILs with DMSO or NMP. In this context, the hydroxide, [OH^-] anion with tetraalkylammonium cation [R_4N^+] (R is methyl, ethyl, propyl or butyl) of ammonium-based ILs with DMSO[134] or NMP[135] systems show positive $\Delta\eta$ values at all investigated temperatures and over the entire composition range of ILs. However, except at higher composition of TBAH, slightly negative values were observed for the TBAH + NMP system.[135] The temperature strongly influences on the $\Delta\eta$ values of these [R_4N^+][OH^-] ILs with DMSO or NMP. It is obvious that the $\Delta\eta$ values increase with increasing the temperatures for all four systems TMAH, TEAH, TPAH or TBAH + DMSO.[134] Conversely, as the temperature increases the $\Delta\eta$ values were decreased for TMAH, TEAH, TPAH or TBAH + NMP mixtures.[135] This is mainly due to structural arrangement polarity of the molecular solvents and also size and shape of the molecules. The positive deviation for these systems indicates strong interaction between the ammonium-based ILs and polar solvents. Furthermore, the positive $\Delta\eta$ values for these ammonium family IL systems indicate that the η values of associates formed between unlike molecules are relatively higher than those of the pure components. The highest $\Delta\eta$ values were observed for TBAH with DMSO[134] or NMP[135] while lower values were observed for TMAH with NMP at all temperatures.

Clearly, the $\Delta\eta$ values of these ammonium-based ILs with DMSO or NMP were found to increase with increasing alkyl chain length of cation (from methyl to butyl). The positive $\Delta\eta$ value (0.73 mPa s at $x_{IL} \approx 0.5500$) of TMAH + DMSO system is higher than those for TMAH + NMP (0.22 mPa s at $x_{IL} \approx 0.5186$) system at 25 °C. However, the $\Delta\eta$ values of TEAH + DMSO (1.33 mPa s at $x_{IL} \approx 0.5047$) are lower than those of TEAH + NMP (1.43 mPa s at $x_{IL} \approx 0.5089$). On the other hand, the $\Delta\eta$ values of TPAH (1.78 mPa s at $x_{IL} \approx 0.5000$) or TBAH (1.80 mPa s at $x_{IL} \approx 0.5500$) + DMSO are lower than those for TPAH (2.40 mPa s at $x_{IL} \approx 0.3000$) or TBAH (2.25 mPa s at $x_{IL} \approx 0.3000$) + NMP at all studied temperatures.[134,135] Therefore, the $\Delta\eta$ value depends on molecular interactions as well as on the size and the shape of the molecules. A comparison between the $\Delta\eta$ values of these ILs with DMSO and NMP suggest that there is a difference arising from the alkyl chain length of cation in ammonium-based ILs with common hydroxide anion, leading to variation in the hydrogen bonding between the ions of ILs as a function of alkyl chain length of cation.

Fig. 29a, clearly reveals that the $\Delta\eta$ values of all ammonium-based ILs with DMSO are positive, except DEAS, TEAA, TEAS or TEAP ILs with DMSO. This can be explicitly explained in that the positive deviation of these ILs with DMSO, is due to the formation of strong coulombic interactions such as dipole–dipole interactions, van der Waals interaction or hydrogen bonding between the ions of these ILs with DMSO. On the other hand, negative $\Delta\eta$ data were observed for DEAS, TEAA, TEAS or TEAP with DMSO, which indicates a decreased hydrogen bonding tendency between the component molecules in the mixture due to structural effects.[117,129,131,133] At equimolar composition, the positive $\Delta\eta$ values of these ILs with DMSO follows the order: TBAH ≥ TPAH > TEAH > TMAH > DEAS > TMAA ≥ TMAP. From this order, the hydroxide anion of

ammonium-based ILs with DMSO show more positive $\Delta\eta$ values as compared to sulfate, phosphate or acetate anions of ammonium-based ILs with DMSO. The negative $\Delta\eta$ values of these ILs with DMSO follow the order: TEAS > TEAP > DEAA > TEAA. The more negative $\Delta\eta$ values imply that sulfate anion of ammonium-based ILs weakly interacts with DMSO as compared to phosphate or acetate anions of ammonium-based ILs. The graphical representations in Fig. 29b show positive $\Delta\eta$ data observed for DEAS, TMAA, TMAP, TMAS, TMAH, TEAH, TPAH or TBAH with NMP at 25 °C. The order of positive $\Delta\eta$ data these ILs with NMP: DEAS > TMAA ≈ TMAP > TMAS > TPAH ≥ TBAH > TEAH > TMAH. From this order, the more positive $\Delta\eta$ data of DEAS + NMP system suggests that the ions of DEAS IL formed more associations with NMP molecules than those of other ILs with NMP. In other words, negative $\Delta\eta$ data are found for TEAA or TEAP with NMP over the entire composition range whereas DEAA or TEAS systems show a change in sign from negative to positive $\Delta\eta$ data with NMP at all temperatures.[130,132,135] The change from negative to positive deviation of DEAA or TEAS + NMP system shows that the interaction between ions of these ILs and NMP are increasing as the concentration of the ILs increases in the mixture.

Interestingly, from Fig. 29b, the TMAP + NMP system shows positive $\Delta\eta$ values whereas negative $\Delta\eta$ values are obtained for the TEAP + NMP system, which indicates a stronger interaction between phosphate anion with (TMA^+) of IL with NMP than the same anion with (TEA^+) of IL due to increasing in the size from trimethyl to triethyl of cations of these ILs with NMP.

9.3. Deviation in viscosity data of mixtures for ammonium-based ILs with alkanols

Apparently, it is interesting to see the alkyl chain length effect of alkanol on the $\Delta\eta$ of alkanols with ammonium family ILs, in this context, in 2013, Xu *et al.*[124] have systematically measured $\Delta\eta$ values over the whole concentration range of $N4NO_3$ IL with alcohols such as methanol, ethanol, propanol or butanol. Negative $\Delta\eta$ values were found for all binary systems at all investigated temperatures. The authors explained that the negative $\Delta\eta$ values of these binary mixtures are due to the van der Waals interactions dominating, which indicates that the network structure of $N4NO_3$ is destroyed when the alkanols were added.[124] The minimum $\Delta\eta$ data for all mixtures occurs at concentration of IL around ≈0.6500. The $\Delta\eta$ values of $N4NO_3$ with alkanols follows the sequence: methanol < ethanol < 1-propanol ≈ 1-butanol. This indicates increasingly destroyed structure of $N4NO_3$ from methanol to butanol due to increased $-CH_2$ groups. The temperature influenced highly $\Delta\eta$ values of $N4NO_3$ + alkanol mixtures, however the observed minimum in $\Delta\eta$ are found to be almost constant and independent of the temperatures and the $\Delta\eta$ values become less negative with increasing the temperatures for these mixtures.[124] Later, the negative $\Delta\eta$ values for N4A with these alkanols were also reported over the whole composition range of IL at various temperatures by the same research group.[128] A minimum value in $\Delta\eta$ was reached with a mole fraction of N4A near to 0.7000 for all the systems. Overall, from these results, the negative $\Delta\eta$ values of N4A are higher than those for $N4NO_3$ with these all alkanols. It has been shown that alkanols interact more with ions of $N4NO_3$ than those for ions of N4A IL.[124,128]

It is interesting to note that the $\Delta\eta$ values of $N4NO_3$ + water[125] (−32.6 mPa s at x_{IL} ≈ 0.6505) are lower than $N4NO_3$ (−34.6 mPa s at x_1 ≈ 0.6507) + methanol and higher than those for $N4NO_3$ + ethanol (−31.4 mPa s at x_{IL} ≈ 0.6501), + propanol (−27.5 mPa s at x_{IL} ≈ 0.6495) or + butanol (−27.5 mPa s at x_{IL} ≈ 0.6508) at 25 °C.[124] Similarly, the $\Delta\eta$ data of N4A with water are lower than N4A with alkanols at 25 °C.[125,128] This can be explained by stronger interactions of $N4NO_3$ or N4A with water than methanol as well as interactions becoming weaker between the ions of $N4NO_3$ or N4A with alkanols from methanol to butanol, due to increasing nonpolar nature.[124,125,128]

In another work, the negative $\Delta\eta$ values for 2-BHEAP IL with methanol or ethanol or 1-propanol over the whole composition range of ILs were observed by Kurnia *et al.*[147] The negative $\Delta\eta$ values are −103.6 mPa s (at x_{IL} ≈ 0.5038), −92.5 mPa s (at x_{IL} ≈ 0.5084) or −83.6 mPa s (at x_{IL} ≈ 0.5009) for 2-BHEAP with methanol, ethanol or 1-propanol at 20 °C, respectively. The negative $\Delta\eta$ values of 2-BHEAP with alkanols mixtures follow the order: methanol > ethanol > 1-propanol. The $\Delta\eta$ values are less negative as the temperature increases and also the values decrease with increasing in alkanol chain length from methanol to 1-propanol due to the higher difference in viscosity of pure compounds.[147]

Recently, Domańska *et al.*[172] systematically obtained negative $\Delta\eta$ values for $[N_{1114}][NTf_2]$ IL with 1,2-propanediol, 1,2-butanediol or 2,3-butanediol and also negative $\Delta\eta$ values for $[N_{1112OH}][NTf_2]$ IL with 1,2-propanediol, 1,2-butanediol or 1,5-pentanediol with the entire composition range of ILs at various temperatures. It was observed that the $\Delta\eta$ data for $[N_{1114}][NTf_2]$ became more negative in the following order: 1,2-butanediol > 1,2-propanediol > 2,3-butanediol with very small differences between alkanediols, while for $[N_{1112OH}][NTf_2]$ values of $\Delta\eta$ decrease in the following order: 1,2-propanediol > 1,3-propanediol > 1,5-pentanediol. The interaction between unlike molecules decreases with an increase in the chain length of alkanediols, which is seen for $[N_{1112OH}][NTf_2]$. The $\Delta\eta$ data also show the influence of the position of hydroxyl group in the alkanediol molecules. From these results, it can be observed that the $\Delta\eta$ values decreased with increasing chain length of alkanediols due to weakening of the molecular interactions between unlike molecules. However, the $\Delta\eta$ values for $[N_{1112OH}][NTf_2]$ + diol-alkanols are higher than those for $[N_{1114}][NTf_2]$ + diol-alkanols. The relative position of the –OH groups within diol-alkanols molecule affects the intermolecular interaction.[172] The relative position of the –OH groups within the alcohol molecule affected the mutual solubility so altering the miscibility and interactions with the ILs.[172] The influence of the cation of the IL showed much higher interaction between unlike molecules for $[N_{1112OH}]^+$. This is undoubtedly the result of a better packing effect and of the hydrogen bonding between the hydroxyl group in the cation and the diol-alkanols.[172]

Overall, the $\Delta\eta$ values for some of ammonium-based ILs with alkanol systems are negative over the entire composition range. The $\Delta\eta$ values are particularly strong in dilute solutions

of alkanols in the ammonium-based ILs. The negative $\Delta\eta$ data of all ammonium-based ILs with alkanol systems decreased sharply as the temperature increases. However, positive $\Delta\eta$ data were obtained for mixtures of ammonium-based ILs.[122] The negative to positive $\Delta\eta$ values are observed for EtAN with PAN system at EtAN-rich composition.[122] Consequently, the interactions between the nitrate anions of ammonium-based ILs in the mixtures are highly dependent on the nature of ions of ammonium-based ILs. Overall, acetate, sulfate, phosphate and hydroxide anions of all ammonium-based ILs show more positive $\Delta\eta$ data with DMSO or NMP at all studied temperatures.[117,129–135] Studies on $\Delta\eta$ values of ammonium-based ILs with the molecular solvents have shown that the choice of anion or cation has strongly influenced the molecular interactions between unlike molecules.

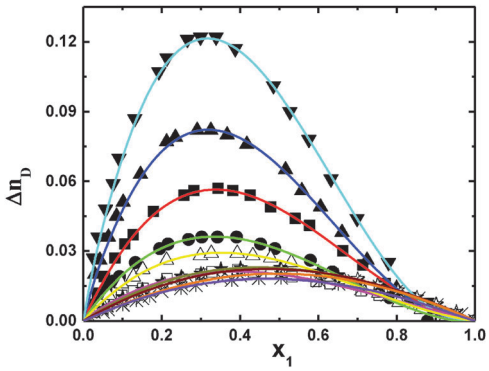

Fig. 30 Plots of deviation in refractive indices (Δn_D) data for mixtures of ILs + water[192,196] as a function of the mole fraction (x_{IL}) of IL; (■) DEAA; (●) DEAS; (▲) TEAA; (▼) TEAS; (□) TMAA; (△) TMAS; (★) TMAH; (☆) TEAH; (×) TPAH and (*) TBAH at 25 °C.

10. Deviation in refractive index data of mixtures for ammonium-based ILs with molecular solvents

The Δn_D of ammonium-based ILs with molecular solvents will be the final part of the current perspective. Very few data of Δn_D of ammonium-based ILs with molecular solvents are available in the open literature. The values of Δn_D are useful to understand the molecular interactions between two or more components in the mixtures. To understand the molecular interactions between the ILs and water, in 2013, Hou *et al.*[127] studied the positive Δn_D values for acetate anion of ethyl and propylammonium-based ILs with water at 25 °C over the whole composition range. A maximum value in Δn_D of two binary systems was reached approximately at $x_{IL} \approx 0.2500$. The Δn_D values of N3A + water system are higher than those for the N2A + water system. Clearly, the increase in the chain length of the cation leads to more positive Δn_D values, which indicates that the stronger interactions of ions of N3A with water are higher than for the ions of the N2A + water system.

Our research group reported positive Δn_D values for acetate and sulfate anions with alkyl cations of ammonium-based ILs such as DEAA, TEAA, DEAS, TEAS, TMAA and TMAS with water over the whole composition range of ILs at 25 °C[192] and results are shown in Fig. 30. The positive values can be explained by strong attractive interactions between ions of ILs and water. The maximum positive values existed in the IL region $x_{IL} \approx$ 0.3000–0.4000. The absolute Δn_D values followed in the order: TEAS > TEAA > DEAA > DEAS > TMAS > TMAA. The order shows that Δn_D values increase with increasing chain length of the cation and higher Δn_D values are observed for mixtures containing (TEA^+) than for mixtures with (DEA^+). The observed Δn_D values of the TEAS + water system show higher Δn_D values whereas the lowest Δn_D values are observed for TMAA + water system. The variation in the Δn_D data demonstrate that the interactions between the unlike component molecules in the mixture depend on the nature of the cation and anion of ILs and water molecules.[192]

Very recently, the temperature dependence of Δn_D values was measured for hydroxide anion salts of ammonium-based ILs with water systems by our research group at various temperatures from 25 to 40 °C over the entire composition range of IL.[196] The observed positive Δn_D values decreased as the temperature increases. The positive Δn_D values of these systems are also included in Fig. 30 for comparison of Δn_D values of various ammonium families ILs with water. The positive Δn_D values slightly decreased with increasing alkyl chain length of the cation of these ILs. In Fig. 19, the negative V^E values of these systems decreased with increasing alkyl chain length in cation of ILs. This is mainly due to less free volume available than in an ideal solution, which indicates a strong correlation between V^E and Δn_D values for all the studied systems. We have observed negative V^E values corresponding to positive Δn_D values; the minimum or maximum of both values existing at almost the same x_{IL}. Overall, our experimental results explicitly elucidate that there is hydrogen bonding between ions of these ILs and water.[192,196] From Fig. 30, the Δn_D values of all ammonium-based ILs with water mixtures follow the order: TEAS > TEAA > DEAA > DEAS > TMAS > TMAA ≈ TMAH > TEAH > TPAH ≈ TBAH. From this order, the large cation alkyl chain length of the ILs interact with water more strongly than those with lower alkyl chain length. However, the nature of interactions between the IL + water system was highly dependent on the nature of the ions of ILs.[192,196]

An interesting study explored the positive Δn_D values for N4A IL + methanol, + ethanol, + *n*-propanol or *n*-butanol over the whole concentration range of IL.[128] The positive Δn_D values are (0.042, 0.023, 0.011 or 0.006) for N4A + methanol, ethanol, propanol or butanol around the $x_{IL} \approx 0.3000$ at 25 °C, respectively. The Δn_D values of N4A with alkanol mixtures follow the order: methanol > ethanol > *n*-propanol > *n*-butanol. This can be revealed as due to increasing hydrogen bonding interactions from methanol to butanol in the presence of ions of N4A ILs, because of decreasing in the nature of polarity from methanol to *n*-butanol.[128]

In 2013, Alvarez *et al.*[149] have reported the positive Δn_D values for m-2-HEAB IL with methyl acetate, ethyl acetate or propyl acetate over the entire mole fraction range. The m-2-HEAB + methyl acetate system shows maximum Δn_D values (0.021 at $x_{IL} \approx 0.6000$) and 0.015 or 0.011 for ethyl acetate or propyl acetate around $\approx$0.5000 mole fraction of ILs, respectively. However, the Δn_D values decrease with increasing of alkyl chain length of ester, *i.e.*, from methyl acetate to propyl acetate at all experimental conditions, which indicates that the nature of interactions in m-2-HEAB IL with ester systems are clearly dependent on the nature of the ions of this IL and nature of ester. The maximum Δn_D values observed for m-2-HEAB with methyl acetate system compared to m-2-HEAB with ethyl acetate or propyl acetate systems, explicitly reveals that may be stronger hydrogen bonding interaction involved between ions this IL and methyl acetate than ethyl acetate or propyl acetate, *i.e.*, decrease the H-bonding with increasing the alkyl chain length of esters with m-2-HEAB.[149]

11. Effect of alkyl chain length on thermophysical properties of ammonium family ILs with molecular solvents

The effect of the alkyl chain length was systematically observed on thermophysical properties such as ρ, u, η and n_D values of different cationic alkyl chain length with various anions of all ammonium-based ILs with different types of molecular solvents. The ρ values are decreased with increasing alkyl chain length of cation with the same anion of ILs with solvents except MEOEAN + NMP. For $[N_{n,222}][Tf_2N]$, the order of the ρ values with methanol is: $[N_{6,222}][Tf_2N] > [N_{8,222}][Tf_2N] > [N_{12,222}][Tf_2N]$. For N_nA systems, the ρ values of acetate anion of ammonium-based ILs with water were in the following order: N2A > N3A > N4A. On the other hand, the ρ values were measured for acetate, sulfate, phosphate and hydroxide anions with different types of alkyl chain length cation of ammonium family ILs with polar solvents such as DMSO, NMP, DMF or water. The ρ values decrease for these mixtures with increasing alkyl chain length in the cation of ammonium-based ILs with the same anion of ILs. The majority of the literature shows the effect of the alkyl chain length of the cation of ammonium-based ILs with molecular solvents on the thermophysical properties. However, the influences of anionic chain length on the thermophysical properties are scarcely investigated. The ρ values of ILs decreased as the alkyl chain length of anion increase.[183,198] The ρ values are strongly affected by the nature of the anion of the ammonium-based ILs. The effect of the alkyl chain length is also observed on the u values of ammonium-based ILs with molecular solvents. The u values increase with increasing alkyl chain length of cation with the same anion of all ammonium-based ILs in polar solvents. However, for some special cases, the u values of ammonium-based ILs do not follow this trend, *i.e.*, in the case (TMA^+), (TEA^+), (TPA^+) or (TBA^+) with (OH^-) of ILs, we have observed contrary behavior in u values for these ILs above the $x_{ILs} \approx 0.5000$, the order of u values: TMAH > TEAH > TPAH > TBAH. NMP or DMF was observed to show contrary behavior in u values of hydroxide anion-based ammonium ILs with increasing the alkyl chain length.

Overall, the η values were strongly affected by alkyl chain length of cation of ILs as well as the nature of the solvent. The η values are increased with increasing the alkyl chain length of cation with the same anion of all ammonium-based ILs in polar solvents. For instance, the order of η values of ammonium-based ILs with water, DMSO or NMP: TEAS > DEAS, TEAA > DEAA or TBAH > TPAH > TEAH > TMAH. The order of η values of nitrate anion with various alkyl chain length cation of ammonium-based ILs with water shows: EAN < $N4NO_3$ and with methanol: EAN > $N4NO_3$. For [DIPEA][C_6COO] or [DIPEA][C_7COO] with water or acetonitrile systems, the η values are increased with increasing the carboxylate alkyl chain length of these ILs from m = 6 to 7. On the other hand, the n_D values are increased with increasing alkyl chain length of cation with same anion of ILs in the molecular solvents. In this regard, the n_D values increased for m-2-HEAB with increasing the alkyl chain length of esters from methyl acetate to butyl acetate. The order of n_D values of acetate anion with various alkyl chain length cation of ammonium-based ILs with water is: N3A > N2A. Furthermore, the n_D values are increased for N4A with increasing the chain length of alkanols, which indicates that the molecular size of the solvents follow this trend: *n*-butanol > *n*-propanol > ethanol > methanol. In the case of acetate or sulfate anion, the n_D values are increased with increasing the alkyl chain length cation of ammonium-based ILs with water in the following order: TEAS > DEAS, TEAA > DEAA. For hydroxide anion with varying alkyl chain length of cation of ILs, however, the n_D values of these systems do not follow the regular trend.

12. Effect of alkyl chain length on V^E, $\Delta\kappa_s$, $\Delta\eta$ and Δn_D of ammonium family ILs with molecular solvents

The effect of the alkyl chain length strongly affected the V^E values of the ammonium-based ILs with molecular solvent systems. The negative V^E values of nitrate anion of ammonium-based ILs with water systems are increased with increasing the alkyl chain length of ILs. The order of V^E values of nitrate anion ILs with water: $N4NO_3$ > EAN. On the other hand, it was observed that negative V^E values changes irregularly with an increase of the alkyl chain length. For NnA systems, the large size of N3A IL with water system shows more negative values as compared to small size of N2A + water, except N4A. The order of V^E values: N3A > N4A > N2A. In the case of acetate, sulfate or hydroxide anions of ammonium-based ILs with water, the observed negative V^E values decreased with increasing the alkyl chain length of cation of ILs; *i.e.*, DEAA > TEAA, DEAS > TEAS or TMAH > TEAH > TPAH > TBAH. For $N4NO_3$ or N4A, the negative V^E values are decreased as the chain length of the alkanol increases. The order of

negative V^E values of $N4NO_3$ or N4A with alkanols: methanol > ethanol > 1-propanol > 1-butanol. The order of negative V^E values of 2-BHEAP with alkanols: methanol > ethanol > 1-propanol. In this case of $[N_{R,222}][Tf_2N]$ with methanol systems, the negative V^E values are decreased as the chain length of cation of IL increases, *i.e.*, $[N_{6,222}][Tf_2N] > [N_{8,222}][Tf_2N] > [N_{12,222}][Tf_2N]$. For nitrate anion of ammonium-based ILs with NMP, it was summarized irregularly in negative V^E values, with the order: PAN > BAN > EAN > MEOEAN. The alkyl chain affect is higher on the V^E values of acetate, sulfate and hydroxide anion with different cations of ammonium-based ILs in DMSO or NMP systems. The order of V^E values: DEAA > TEAA, DEAS > TEAS or TEAH > TMAH > TPAH > TBAH except for NMP with hydroxide anion of IL, in which more negative V^E values are observed as alkyl chain length increases, the order of V^E values: TBAH > TPAH > TEAH > TMAH. Furthermore, negative V^E values are increased with the increasing the anion alkyl chain length of ILs, the order of V^E values: $[DIPEA][C_7COO] > [DIPEA][C_6COO]$ with water. Overall, in most of the cases, the negative V^E values of ammonium-based ILs with molecular solvents are decreased with increasing the alkyl chain length of cation of ammonium-based ILs, which might due to structural effects.

Furthermore, we have systematically observed the effect of alkyl chain length on $\Delta\kappa_s$ values of all ammonium-based ILs with polar solvents. Overall, the $\Delta\kappa_s$ values are decreased with increasing the alkyl chain length of the solvent, for example, ($[MOA]^+[Tf_2N]^-$) with alkanol systems, the order of $\Delta\kappa_s$ values: 1-methanol > ethanol > propanol. Moreover, the observed $\Delta\kappa_s$ values are increased with increasing the alkyl chain length of the cation with same anion of ammonium family ILs with molecular solvents: TEAA > DEAA, TEAS > DEAS, TEAP > TMAP or TBAH > TPAH ≈ TEAH > TMAH.

On the other hand, the $\Delta\eta$ values of nitrate anion of ammonium-based ILs with water systems are increased with decreasing the alkyl chain length of ILs. The order of $\Delta\eta$ values of nitrate anion ILs with water: EAN > $N4NO_3$. For acetate or sulfate anion of ammonium-based ILs with water containing $\Delta\eta$ values were increased as alkyl chain length increases. The $\Delta\eta$ values of these ILs with water follow the order: TEAS > DEAS or TEAA > DEAA. In other words, this behavior is opposite that found for hydroxide anion on increasing the tetraalkyl chain length of ammonium-based ILs. The order of $\Delta\eta$ values for these ILs with water, TMAH > TEAH > TPAH > TBAH. However, the alkyl chain length effect is more marked for the $\Delta\eta$ values of ammonium-based ILs with DMSO systems. The $\Delta\eta$ values of these ILs are increasing as the alkyl chain length increases. Furthermore, the $\Delta\eta$ values of all ammonium-based ILs with NMP systems are not depending on the alkyl chain length of the cation of IL.

Moreover, the effect of the alkyl chain length was studied on the Δn_D values of all ammonium-based ILs with molecular solvents. The Δn_D values are increased with increasing alkyl chain length of cation with the same anion of ILs in polar solvent. In this context, N3A > N2A, TEAS > DEAS or TEAA > DEAA. It was observed that the Δn_D values irregularly with elongation of the alkyl chain length with hydroxide anion of ammonium-based ILs, with the following order: TMAH > TEAH > TPAH > TBAH.

13. Effect of temperature on thermophysical properties and derived properties of ammonium family ILs with molecular solvents

The effect of the temperature was also dependent on the properties such as ρ, u, η and n_D values of all ammonium-based ILs in molecular solvents. Overall, the ρ or u values decrease with increasing the temperature for the most of ammonium-based ILs with polar solvent systems. In this context, the ρ or u values of nitrate, formate, propionate, acetate, sulfate, phosphate, hydroxide or $[Tf_2N]^-$ anions with various type cations of ammonium-based ILs with molecular solvent systems are decreased as the temperature increases. Amongst, few ILs with solvent systems ρ or u values decrease non-linearly as temperature increases, due to weakening the molecular interactions with increasing the temperature.

The η values decrease as temperature increases for $N4NO_3$, N4A or 2-BHEAP with alkanols; EAN, $N4NO_3$ or N4A + water and EAN + DMC or FA mixtures. Furthermore, $[N_{1114}][NTf_2]$ and $[N_{1112OH}][NTf_2]$ with diol systems show that η values decrease with increasing the temperature. The η values of acetate, sulfate, phosphate or hydroxide anions with various alkyl chain length of ammonium-based ILs with DMSO or NMP are decreased as the temperature increases. On the other hand, the n_D values of hydroxide anion with different types of tetraalkyl cations of ammonium-based ILs with water decrease as the temperature increases.

The objective of this study was to provide information regarding the thermophysical properties of different anions and cations of ammonium family ILs with molecular solvents at various temperatures. The negative V^E values increase with increasing the temperature for 2-HEAF or 2-BHEAA + water; N4A or $N4NO_3$ + alkanols; 2-HEAF, 2-HEAA, 2-BHEAA or 2-BHEAP + methanol and ethanol; 2-BHEAA or 2-BHEAP + propanol; TMAH, TEAH, TPAH or TBAH + water; DEAS, DEAA + DMSO (except TEAA + DMSO system), in which the observed positive V^E values decrease as temperature increases. The negative V^E values decrease as temperature increases for EAN + water system up to $x_{IL} \approx 0.4000$, later the negative V^E values increase with increasing the temperature for this system. Finally, this system provides positive V^E values with increasing the temperature at high concentration of IL except for 45 °C. The negative V^E values decrease with increasing the temperature for N4A or $N4NO_3$ + water; 2-HEAA + water. The variation of V^E values with temperature might be attributed to the increasing/decreasing the hydrogen bonding effect between the ions of ILs and solvents. From these reports, the molecular interactions, however, strongly depends on the temperature as well as the composition of IL.

The temperature dependence should be observed on $\Delta\kappa_s$ values of ammonium-based ILs with molecular solvents. The $\Delta\kappa_s$ values decrease with increasing the temperature for these

ammonium-based ILs systems. The condition of low temperatures helps the IL to establish a more intense packing with solvent due to the lower dipole–dipole interactions. These $\Delta\kappa_s$ values are negative for all ammonium-based ILs with solvents, except for these ILs such as DEAS, TEAA or TMAP with molecular solvents. The influence of decreasing temperature produces lower negative $\Delta\kappa_s$ values observed for all ammonium-based ILs.

The $\Delta\eta$ values increased with increasing the temperature for ammonium-based ILs with molecular solvents. Interestingly, temperature influences strongly the $\Delta\eta$ values of DEAS + DMSO system, as temperature increases, the deviations are reduced and even reach positive $\Delta\eta$ values for this system. Overall, acetate, sulfate, phosphate and hydroxide anion of ammonium-based ILs show more positive $\Delta\eta$ values with molecular solvents as the temperature increases. Eventually, we have observed that the temperature effect on the $\Delta\eta$ values of ammonium-based ILs with the molecular solvents through the choice of anion or cation influence on the molecular interactions between the unlike molecules. Besides, the Δn_D values also increased with increasing the temperature for ammonium-based ILs with molecular solvents.

14. Specific observations of solution properties (V^E, $\Delta\kappa_s$, $\Delta\eta$ and Δn_D) for ammonium-based ILs with molecular solvents

The interpretation of the derived properties such as V^E, $\Delta\kappa_s$, $\Delta\eta$ and Δn_D from various available literature are really interesting, since they are sometimes showing strong correlation between them while sometimes inconsistency in results are also observed. Considering the fact that similar factors have opposite effects on the V^E and $\Delta\eta$. The literature shows that negative V^E values and a positive $\Delta\eta$ values are observed for some of the ammonium-based ILs and with different molecular solvents.[134,150,192,196] However, this conclusion is not observed in some of the mixtures of ammonium-based ILs with solvents.[124,128] On the other hand, it should be noted that the observed negative V^E values correspond to positive Δn_D values for some of the mixtures of ammonium family ILs with the solvents.[127,128,143,149,192,196] Obviously, the sign and the magnitude of these properties are mainly depending on the size and shape of the ions of the ILs as well as the nature of molecular solvents.

15. Conclusions

In this perspective, we have discussed the various studies on thermophysical properties of ammonium-based ILs with the intent of explaining their behavior in molecular solvents. We have highlighted the knowledge gained and the challenges that are multifactorial from the available thermophysical results and data analysis. Recent advances that are related to molecular interactions of ammonium-based ILs with molecular solvents and data analysis together have contributed to considerable progress, considering all of the published studies carried out in the past decade. We conclude that the recent successes of these studies are a harbinger of what one can expect in the future. The thermophysical characterization of ammonium-based ILs and molecular solvents have revealed their broad range of applications through the intermolecular interactions, which have been found to be very sensitive to simple structural modifications. The thermophysical properties of ILs mainly depend on the nature and structure of ions and the alkyl chain length of the cation of ILs, anions as well as nature of the solvent. The effect of mixing different anions and cations of ILs has also been examined with increasing temperature. The effect of alkyl chain length of cation of ILs was also studied in terms of the thermophysical properties. As expected, the ρ and u values decrease whereas η and n_D values increase upon increasing the alkyl chain length of the IL and decrease as temperature increases for these ILs with molecular solvents. Finally, fascinating results are obtained for structure-based and temperature dependent properties of ammonium-based ILs with molecular solvents. The structure-based properties of ILs and structural arrangements of ions of ILs suggest many more aspects for exploration of various scientific fields. These thermophysical properties of ammonium family ILs with molecular solvents will undoubtedly provide valuable and unique knowledge on the molecular interactions and the structural arrangement of ions of ILs for a large-scale commercial applications and basic research.

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