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Review

Excess molar volumes of binary mixtures (an ionic liquid + water): A review

Indra Bahadur [a], Trevor M. Letcher [a], Sangeeta Singh [b], Gan G. Redhi [b], Pannuru Venkatesu [c], Deresh Ramjugernath [a,*]

[a] Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa
[b] Department of Chemistry, Durban University of Technology, P.O. Box 1334, Durban 4000, South Africa
[c] Department of Chemistry, University of Delhi, Delhi 110 007, India

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ABSTRACT

This review covers recent developments in the area of excess molar volumes for mixtures of {ILs (1) + H_2O (2)} where ILs refers to ionic liquids involving cations: imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium and ammonium groups; and anions: tetraborate, triflate, hydrogensulphate, methylsulphate, ethylsulphate, thiocyanate, dicyanamide, octanate, acetate, nitrate, chloride, bromide, and iodine. The excess molar volumes of aqueous ILs were found to cover a wide range of values for the different ILs (ranging from $-1.7\ cm^3 \cdot mol^{-1}$ to $1.2\ cm^3 \cdot mol^{-1}$). The excess molar volumes increased with increasing temperature for all systems studied in this review. The magnitude and in some cases the sign of the excess molar volumes for all the aqueous ILs mixtures, apart from the ammonium ILs, were very dependent on temperature. This was particularly important in the dilute IL concentration region. It was found that the sign and magnitude of the excess molar volumes of aqueous ILs (for ILs with hydrophobic cations), was more dependent on the nature of the anion than on the cation.

1. Introduction

Forty years ago a new class of solvents emerged which were called ionic liquids (ILs). They have unique physico-chemical properties which include negligible vapour pressures, non-flammability, high electrochemical stability and tune-ability [1]. The term IL refers to ionic salts which are molten at temperatures below 100 °C. They consist of cations such as quaternary ammonium, imidazolium, pyridinium, phosphonium, piperidinium, pyrrolidinium and morpholinium ions combined with anions such as chloride, bromide, acetate, tetrafluoroborate, alkylsulphate, nitrate, thiocyanate and bis(trifluoromethylsulfonyl)imide. It is their negligible vapour pressure which has caught the imagination of researchers and as a result these compounds are being explored as potential environmentally friendly solvents with the aim of replacing the volatile organic solvents (VOSs) which are so widely used in the chemical industry in separation processes, nuclear waste treatment, chemical synthesis and as catalysts. In particular, ILs are used in the important carbon–carbon bond Diels–Alder reaction [2]. Furthermore, ILs are finding a variety of applications in the field of electrochemistry, *e.g.*, rechargeable batteries, capacitors, photo-electrochemical cells, fuel cells, electroplating, electrocatalysis and electrosynthesis [3]. The numbers of possible ILs and their mixtures have been estimated to be of the order of 10^{18} and as each IL has its own unique set of properties, there is much scope for designing ILs for particular purposes. Ionic liquids have interesting solvent properties and some have the ability to dissolve cellulosic and other bio-materials. Their solubility properties have resulted in these compounds being called "designer solvents" [3–9].

To understand better the nature of ILs and to expand their applications, a detailed knowledge of the thermodynamic behaviour of ILs is essential [10,11]. In particular in view of the potential use of ILs as solvents, it is important to know the properties of ILs mixed with water or with organic solvents. To this end, a database of IL cation, anion and thermo-physical properties should be useful [12], and this is the *raison d'être* for this review, which involves excess molar volumes of ILs which are completely soluble in water. The IL cations discussed here include: 1-alkyl-3-methylimidazolium {abbreviated as [XMIM]}, where X is H (hydrogen) or M (methyl) or E (ethyl) or P (propyl) or B (butyl) or hex (hexyl) or O (octyl); *N*-alkylpyridinium (abbreviated as [Xpy]); tetraalkylammonium, {abbreviated as XN} where X is as above or hydroxyethyl (C_2H_4OH) or tris-2-hydroxyethylmethyl ammonium $(C_2H_4OH)_3NCH_3$; piperidinium, [Xpip]; *N*-alkylpyrrolidinium (abbreviated as [Xpyr]) and alkylmorpholinium (abbreviated as [Xmor]). These cat-

* Corresponding author. Tel.: +27 (31) 2603128; fax: +27 (31) 2601118.
E-mail address: ramjuger@ukzn.ac.za (D. Ramjugernath).

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ions are combined with either organic or inorganic anions, which include hydrogen sulphate [HSO_4], methyl sulphate [MSO_4], ethyl sulphate [ESO_4], tetrafluoroborate [BF_4], chloride [Cl], bromide [Br], dicyanamide [$N(CN)_2$], nitrate [NO_3], acetate [CH_3COO], diethyleneglycolmonomethyl ethylsulphate [$CH_3(OCH_2CH_2)_2OSO_3$], octanate [C_7CO_2], triflate [CF_3SO_3] or thiocyanate [SCN]. The ILs used in this review are given in table 1, together with abbreviation and chemical structure.

2. Volumetric properties of binary mixtures containing water and an IL

Volumetric properties of binary mixtures (density, excess and partial molar volumes) are complex properties because they depend not only on size, shape, and chemical nature of the components of a mixture [13,14], 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 [15]. All this is particularly relevant to mixtures of strongly hydrogen bonded water and an IL which is held together by coulombic forces.

The excess molar volume, V^E_m, for a binary mixture is defined as:

$$V^E_m = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2}, \quad (1)$$

and can be used as an indication of the interactions between the components of a binary mixture, in spite of its relative small magnitude. Typically the maximum magnitude of an excess molar volume of a binary mixture of organic liquids is less than 1 $cm^3 \cdot mol^{-1}$ which relates to a volume which is less than 0.5% of the total mixture. Excess volume data can also be used to predict (vapour + liquid) equilibria using appropriate EOS models [16].

The excess molar volume results tabulated in table 2, summarise the results for binary mixtures of an IL mixed with water. The results indicate the presence of competing effects: a positive excess molar volume is indicative of a weakening of the self-association of water (hydrogen bonds) or of the IL (ionic coulombic attraction or the Van der Waals association between the components (alkyl groups, for example) of the cation and anion; a negative effect could be due to associations between the IL and the water through ion – polar group attractions, bringing the different species closer together; a packing effect which can be negative (*e.g.* smaller molecules fitting in between larger molecules) or positive, with ill-fitting molecules mixed together). Very often, as we shall see in discussing the results in table 2, these competing effects can sometimes be better understood by looking at the partial molar volumes especially the partial molar volumes at infinite dilution.

In attempting to elucidate the interactions between ILs and water or an alkanol it is important to keep in mind the self-associations between: the IL moieties which can be (ion + ion) association and also Van der Waals associations between the floppy alkyl and other organic parts of the ILs; and the strong H-bonding between the H_2O molecules. The (ion + ion) association of the ILs is a function of the size of the ions. The larger the surface area of the ion the weaker will be its charge effect as the single charge will have to be smeared over a larger area. This influences the polarity of an IL and it has been verified by spectroscopic evidence that the polarity of ILs is dependant largely on the cation [17]. The reason for this is that in most ILs the cation with its floppy alkyl groups is usually larger than the anion. Any association between the IL and the H_2O must compete with the two relatively strong self-associations of ion-ion and the H-bonded water.

2.1. Excess molar volumes of ILs with water

Water, is the most common "green" solvent and many ILs are soluble or partially soluble in water. As a result water is often used as an extracting or curing agent for separating ILs from organic solvents. The addition of water to an IL has a major effect on the physical properties and hence on possible applications of ILs [18]. This review of data on excess molar volumes of aqueous solutions IL, considers only those ILs which are completely soluble in water.

2.1.1. Imidazolium ILs

2.1.1.1. 1,3-Dimethylimidazolium [MMIM]ILs. The excess molar volumes plotted against mole fraction for binary mixtures of imidazolium ILs mixed with water show positive, negative and sinusoidal shaped curves, indicating a competing set of phenomena. One common feature of all the mixtures of an imidazolium IL with water is the positive increase of the excess molar volume as the temperature is increased.

There have been two reported sets of data involving 1,3-dimethylimidazolium [MMIM] ILs; both relate to {[MMIM][MSO_4] (1) + H_2O (2)} [19,20].

Gómez *et al.* reported a double humped curve for V^E_m versus x_1 with maxima of 0.07 $cm^3 \cdot mol^{-1}$ (at $x_1 = 0.05$) and 0.02 (at $x_1 = 0.95$) and a minimum at −0.11 at $T = 298.15$ K (at $x_1 = 0.60$) and correlated the V^E_m results with refractive index, viscosity and excess Gibbs Free Energy data. Domanska *et al.* reported a sinusoidal curve with a maximum of 0.04 $cm^3 \cdot mol^{-1}$ (at $x_1 = 0.08$) and a minimum of 0.18 $cm^3 \cdot mol^{-1}$ (at $x_1 = 0.35$) and discussed their results in terms of theoretical models and partial molar excess quantities.

2.1.1.2. 1-Ethyl-3-methylimidazolium [EMIM]ILs. Mixtures of [EMIM][BF_4] with water show a positive excess volume with equimolar concentration values of 0.20 $cm^3 \cdot mol^{-1}$ and 0.30 $cm^3 \cdot mol^{-1}$ at $T = 293.15$ K and $T = 323.15$ K respectively [21]. The temperature effect is more pronounced in the dilute IL region than in the high IL concentration region. The positive V^E_m values, as a result of the mixing of the IL with H_2O could be a result of: a weakening of the IL self-association; a weakening of the H-bonded water self-association; or a packing effect with the large IL molecules not fitting into the network of H-bonded water. If this latter explanation was correct, one would expect the effect to weaken with increased temperature as a result of increased juggling of molecules. The fact that this effect is more pronounced at higher temperatures in the region of dilute IL concentration makes it reasonable to assume that the major effect is due to a weakening of the self-association of either or both components on mixing.

Positive V^E_m values (at $x_1 = 0.50$) were also found by Domanska *et al.* [22] for aqueous mixtures of [EMIM][SCN] with values 0.08 $cm^3 \cdot mol^{-1}$ and 0.27 $cm^3 \cdot mol^{-1}$ at $T = 298.15$ K and $T = 343.15$ K, respectively. Positive values were also obtained for {[EMIM][CF_3SO_3] (1) + H_2O (2)} where CF_3SO_3 is the triflate ion by Garcia-Miaja *et al.* [23] (0.12 $cm^3 \cdot mol^{-1}$ and 0.24 $cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$ at $T = 298.15$ K and $T = 318.15$ K, respectively) and Vercher *et al.* [24], (0.01 $cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$ at $T = 298.15$ K) and by Rodriguez *et al.* [25] (0.04 $cm^3 \cdot mol^{-1}$ and 0.39 $cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$ at $T = 278.15$ K and $T = 348.15$ K, respectively). However, the plot of V^E_m versus x_1 for the latter system at temperatures below $T = 300$ K shows distinct sinusoidal curves with minima at the low IL concentrations and maxima at high IL concentrations. These negative and positive V^E_m values indicate two very different processes. Again, the temperature effect was found to be more pronounced in the dilute IL region. At low IL concentrations the negative V^E_m values is indicative of an association between the few IL and the large number of H_2O molecules. This effect weakens as the temperature increases and as the concentration of the IL increases. At the other end of the composition scale (x_1 tending to (1) the V^E_m values are

TABLE 1
Names of the ionic liquids covered in this study together with abbreviation and chemical structure.

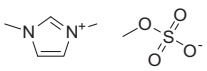
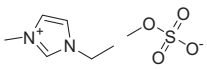
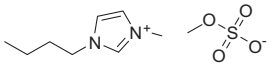
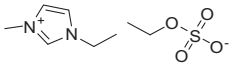
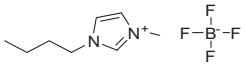
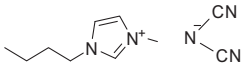
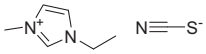
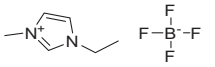
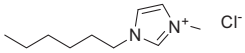
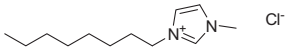
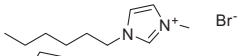
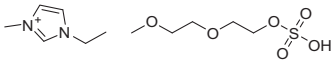
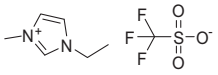
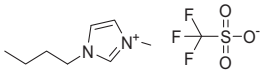
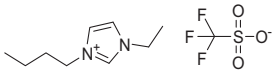
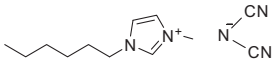
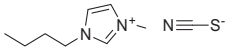
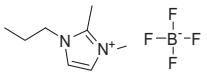
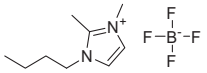
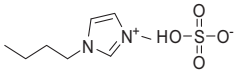
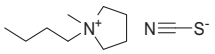
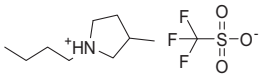
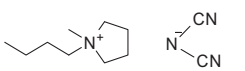
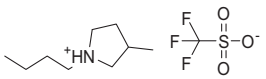
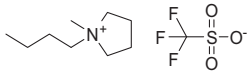
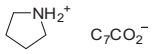
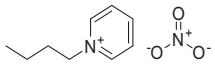
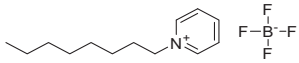
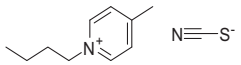
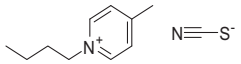
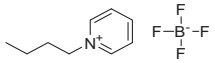
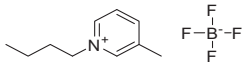
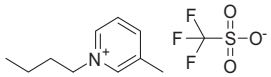
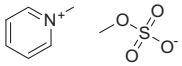
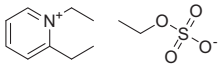
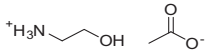
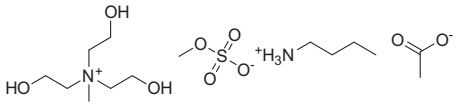
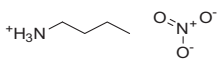
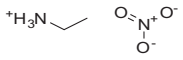
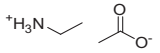
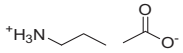
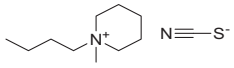
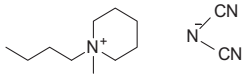
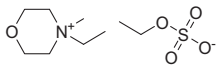
IL	Abbreviation	Structure
1,3-Dimethylimidazolium methylsulphate	[MMIM][MSO_4]	
1-Ethyl-3-methylimidazolium methylsulphate	[EMIM][MSO_4]	
1-Butyl-3-methylimidazolium methylsulphate	[BMIM][MSO_4]	
1-Ethyl-3-methylimidazolium ethylsulphate	[EMIM][[ESO_4]	
1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF_4]	
1-Butyl-3-methylimidazolium dicyanamide	[BMIM][$N(CN)_2$]	
1-Ethyl-3-methylimidazolium thiocyanate	[EMIM][SCN]	
1-Ethyl-3-methylimidazolium tetrafluoroborate	[EMIM][BF_4]	
1-Hexyl-3-methylimidazolium chloride	[HexMIM][Cl]	
1-Methyl-3-octylimidazolium chloride	[OMIM][Cl]	
1-Hexyl-3-methylimidazolium bromide	[HexMIM][Br]	
1-Ethyl-3-methylimidazolium	[EMIM]	
Diethyleneglycol monomethylethersulphate	[$CH_3(OCH_2CH_2)_2OSO_3$]	
1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	[EMIM][CF_3SO_3]	
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	[BMIM][CF_3SO_3]	
3-Butyl-1-ethylimidazolium trifluoromethanesulfonate	[BEIM][CF_3SO_3]	
1-Hexyl-3-methylimidazolium dicyanamide	[HexMIM][$N(CN)_2$]	
1-Butyl-3-methylimidazolium thiocyanate	[BMIM][SCN]	
1-Propyl-2,3-dimethylimidazolium tetrafluoroborate	[PMMIM][BF_4]	
1-*n*-Butyl-2,3-dimethylimidazolium tetrafluoroborate	[BMMIM][BF_4]	
1-Butyl-3-methylimidazolium hydrogensulphate	[BMIM][HSO_4]	
1-Butyl-1-methylpyrrolidinium thiocyanate	[BMpyr][SCN]	
1-Butyl-3-methylpyrrolidinium trifluoromethanesulfonate	[BMpyr][CF_3SO_3]	
1-Butyl-1-methylpyrrolidinium dicyanamide	[BMpyr][$N(CN)_2$]	
1-Butyl-3-methylpyrrolidinium trifluoromethanesulfonate	[BMpyr][CF_3SO_3]	

TABLE 1 (*continued*)

IL	Abbreviation	Structure
1-Butyl-1-methylpyrrolidinium Trifluoromethanesulfonate	[BMpyr][CF_3SO_3]	
Pyrrolidinium octanate	[pyr][C_7CO_2]	
1-Butylpyridinium nitrate	[Bpy][NO_3]	
1-Octylpyridinium tetrafluoroborate	[Opy][BF_4]	
1-Butyl-4-methylpyridinium thiocyanate	[BMpy][SCN]	
1-Butyl-pyridinium tetrafluoroborate	[Bpy][BF_4]	
1-Butyl-3-methylpyridinium tetra fluoroborate	[BMpy][BF_4]	
1-Butyl-3-methylpyridinium trifluoromethanesulfonate	[BMpy][CF_3SO_3]	
1-Methylpyridinium methylsulphate	[Mpy][MSO_4]	
1,2-Diethylpyridinium ethylsulphate	[EEpy][ESO_4]	
2-Hydroxyethylammonium acetate	[$C_2H_4OHNH_3$] [CH_3COO]	
Tris(2-hydroxyethyl) methylammonium Methylsulphate	[$(C_2H_4OH)_3NM$] [MSO_4]	
n-Butylammonium acetate	[BN][CH_3COO]	
n-Butylammonium nitrate	[BN][NO_3]	
Ethylammonium nitrate	[EN][NO_3]	
Ethylammonium acetate	[EN][CH_3COO]	
Propylammonium acetate	[PN][CH_3COO]	
1-Butyl-1-methylpipridinium thiocyanate	[BMpip][SCN]	
1-Butyl-1-methylpipridinium dicyanamide	[BMpip][$N(CN)_2$]	
1-Ethyl-1-methylmorpholinium ethylsulphate	[EMmor][ESO_4]	

positive and most likely due to the disruption of both or either of the self-association effects. This disruption is the dominant feature in this region and is obviously more important than the (IL + H_2O) association. As the IL molecules are very much larger (molar volumes of the order or 150 $cm^3 \cdot mol^{-1}$) than the molar volume of water (18 $cm^3 \cdot mol^{-1}$) and furthermore the concentration of the IL is very much larger than that of water in this concentration region, it is tantalizing to suggest that this positive effect is due to the disruption of the (IL + IL) association as any disruption of the water self-association would hardly be noticed. At this high IL concentration end of the concentration range the effect of temperature on the V^E_m is not as great as it is at the dilute IL end of the composition range – this again supports the idea that two very different effects are taking place at either end of the concentration range.

Negative V^E_m values at equimolar concentrations were found for: {[EMIM][ESO_4] (1) + H_2O (2)} of −0.37 $cm^3 \cdot mol^{-1}$ and −0.30 $cm^3 \cdot mol^{-1}$ at equimolar compositions at T = 293.15 K and T = 318.15 K respectively, as reported by Garcia-Miaja *et al.* [23]; by Gomez *et al.* [26] who reported results of −0.30 $cm^3 \cdot mol^{-1}$ and −0.22 $cm^3 \cdot mol^{-1}$ at equimolar compositions at T = 298.15 K and T = 328.15 K respectively; Lehman *et al.* [27] who reported −0.50 $cm^3 \cdot mol^{-1}$ at T = 298.15 K; and by Rodrigues and Brennecke

TABLE 2
Excess molar volumes at equimolar concentrations at various temperatures.

Ionic liquid	V_m^E/cm^3 · mol^{-1} at x_1 = 0.50		T/K	References
		Imidazolium based ILs		
[MMIM][MSO_4]	−0.12		298.15	[19]
[MMIM][MSO_4]	−0.02	Double hump	328.15	[19]
[MMIM][MSO_4]	−0.17	Sinusoidal	298.15	[20]
[EMIM][ESO_4]	−0.30		298.15	[26]
[EMIM][ESO_4]	−0.22	Sinusoidal	328.15	[26]
[EMIM][ESO_4]	−0.47		278.15	[25]
[EMIM][ESO_4]	−0.21	Sinusoidal	348.15	[25]
[EMIM][ESO_4]	−0.50		293.15	[27]
[EMIM][CF_3SO_4]	−0.57		278.15	[25]
[EMIM][CF_3SO_4]	−0.23		348.15	[25]
[EMIM][trifluoroacetic]	0.04	Sinusoidal	278.15	[25]
[EMIM][trifluoroacetic]	0.39		348.15	[25]
[EMIM][BF_4]	0.20		293.15	[21]
[EMIM][BF_4]	0.30		323.15	[21]
[EMIM][MSO_4]	−0.43		278.15	[28]
[EMIM][MSO_4]	−0.25	Sinusoidal	338.15	[28]
[EMIM][ESO_4]	−0.37		298.15	[23]
[EMIM] [ESO_4]	−0.30		318.15	[23]
[EMIM][ESO_4]	−0.44		283.15	[28]
[EMIM][ESO_4]	−0.23	Sinusoidal	343.15	[28]
[EMIM][CF_3SO_3]	0.12	Sinusoidal	298.15	[37]
[EMIM][CF_3SO_3]	0.24		318.15	[23]
[EMIM][CF_3SO_3]	0.01	Sinusoidal	278.15	[24]
[EMIM][CF_3SO_3]	0.33		338.15	[24]
[EMIM][SCN]	0.08		298.15	[22]
[EMIM][SCN]	0.27		343.15	[22]
[EMIM] [$CH_3(OCH_2$	−0.25		298.15	[29]
$CH_2)_2OSO_3$]	−0.22		313.15	[29]
[BMIM][BF_4]	0.38		298.00	[31]
[BMIM][BF_4]	0.48		298.15	[32]
[BMIM][BF_4]	0.65		333.15	[32]
[BMIM][BF_4]	0.13		298.00	[33]
[BMIM][BF_4]	0.37		303.15	[34]
[BMIM][BF_4]	0.81		353.15	[34]
[BMIM][HSO_4]	−0.46		303.15	[28]
[BMIM][HSO_4]	−0.32		343.15	[28]
[BMIM][MSO_4]	−0.50		283.15	[28]
[BMIM][MSO_4]	−0.28	Sinusoidal	343.15	[28]
[BMIM][MSO_4]	−0.35		298.15	[23]
BMIM][MSO_4]	−0.24		318.15	[23]
[BMIM][MSO_4]	−0.28		298.15	[20]
[BMIM][MSO_4]	−0.38		298.15	[30]
[BMIM][MSO_4]	−0.29		328.15	[30]
[BMIM][I]	0.35		298.15	[40]
[BMIM][I]	0.37		308.15	[40]
[BMIM][CF_3SO_3]	0.24		303.15	[37]
[BMIM][CF_3SO_3]	0.42		343.15	[37]
[BMIM][CF_3SO_3]	0.08	Sinusoidal	298.15	[23]
[BMIM][CF_3SO_3]	0.20		318.15	[23]
[BMIM][CF_3SO_3]	−0.04	Double hump	288.15	[35]
[BMIM][CF_3SO_3]	0.29		338.15	[35]
[BMIM][CF_3SO_3]	−0.02		288.15	[36]
[BMIM][CF_3SO_3]	0.10		308.15	[36]
[BMIM][SCN]	−0.06	Sinusoidal	298.15	[38]
[BMIM][SCN]	0.16		348.15	[38]
[BMIM][$N(CN)_2$]	0.09	Sinusoidal	288.15	[36]
[BMIM][$N(CN)_2$]	0.20		308.15	[36]
[PMMIM][BF_4]	0.44		298.15	[39]
[PMMIM][BF_4]	0.68		343.15	[39]
[BMMIM][BF_4]	0.40		298.00	[31]
[HexMIM][$N(CN)_2$]	0.02	Sinusoidal	288.15	[36]
[HexMIM][$N(CN)_2$]	0.14		308.15	[36]
[HexMIM][Cl]	−0.53		298.15	[41]
[HexMIM][Cl]	−0.48	Sinusoidal	348.15	[41]
[HexMIM][Br]	−0.04	Sinusoidal	293.15	[42]
[HexMIM][Br]	0.04	Double hump	333.15	[42]
[HexMIM][Br]	−0.15	Sinusoidal	298.15	[40]
[HexMIM][Br]	−0.12	Sinusoidal	308.15	[40]
[HexMIM][Cl]	−0.53		298.15	[40]
[HexMIM][Cl]	−0.49		308.15	[40]
[HexMIM][I]	0.87		298.15	[40]
[HexMIM][I]	0.95		308.15	[40]
[OMIM][Cl]	−0.56	Sinusoidal	298.15	[41]

TABLE 2 (*continued*)

Ionic liquid	V^E_m/cm^3 · mol^{-1} at x_1 = 0.50		T/K	References
[OMIM][Cl]	−0.40		348.15	[41]
[OMIM][Cl]	−0.56		298.15	[40]
[OMIM][Cl]	−0.52		308.15	[40]
[OMIM][Br]	−0.60	Sinusoidal	298.15	[40]
[OMIM][Br]	−0.48	Sinusoidal	308.15	[40]
[OMIM][I]	1.04		298.15	[40]
[OMIM][I]	1.14		308.15	[40]
[BEIM][CF_3SO_3]	−0.12	Sinusoidal	278.15	[35]
[BEIM][CF_3SO_3]	0.31		338.15	[35]
		Pyridinium based ILs		
[Mpy][MSO_4]	−0.07	Sinusoidal	288.15	[36]
[Mpy][MSO_4]	−0.01	Double hump	308.15	[36]
[EEpy][ESO_4]	−0.40		288.15	[36]
[EEpy][ESO_4]	−0.32		308.15	[36]
[Bpy][BF_4]	0.43		283.15	[43]
[Bpy][BF_4]	0.82		343.15	[43]
[Bpy][BF_4]	0.39		298.15	[44]
[Bpy][BF_4]	0.54		318.15	[44]
[Bpy][NO_3]	−0.75		298.00	[45]
[BMpy][CF_2SO_3]	−0.06		288.15	[36]
[BMpy][CF_2SO_3]	0.06		308.15	[36]
[BMpy][SCN]	− 0.06	Sinusoidal	298.15	[38]
[BMpy][SCN]	0.22		348.15	[38]
[Opy][BF_4]	0.32		283.15	[43]
[Opy] [BF_4]	0.64		343.15	[43]
		Pyrrolidinium based ILs		
[pyr][C_7CO_2]	−1.24		298.15	[48]
[pyr][C_7CO_2]	−1.52		328.15	[48]
[EMpyr][ESO_4]	−0.50		298.15	[47]
[EMpyr][ESO_4]	−0.05	Sinusoidal	343.15	[47]
[BMpyr][CF_3SO_3]	−0.09	Sinusoidal	278.15	[35]
[BMpyr][CF_3SO_3]	0.30		338.15	[35]
[BMpyr][CF_3SO_3]	−0.07	Sinusoidal	288.15	[30]
[BMpyr][CF_3SO_3]	0.06		308.15	[36]
[BMpyr][$N(CN)_2$]	−0.03	Sinusoidal	288.15	[36]
[BMpyr][NC_2N_2]	0.09		308.15	[48]
[BMpyr][$N(CN)_2$]	0.03	Sinusoidal	298.15	[46]
[BMpyr][$N(CN)_2$]	0.25		343.15	[46]
[BMpyr][SCN]	−0.17	Sinusoidal	298.15	[38]
[BMpyr][SCN]	0.06		348.15	[38]
[BMpyr][CF_3SO_3]	−0.07		288.15	[36]
[BMpyr][CF_3SO_3]	0.06		308.15	[36]
		Piperidinium based ILs		
[EMpip][ESO_4]	−0.61		298.15	[47]
[EMpip][ESO_4]	−0.42		343.15	[47]
[BMpip][SCN]	−0.05	Sinusoidal	298.15	[38]
[BMpip][SCN]	0.10		348.15	[38]
[BMpip][$N(CN)_2$]	−0.04	Sinusoidal	298.15	[46]
[BMpip][$N(CN)_2$]	0.22		343.15	[46]
		Morpholinium based ILs		
[EMmor][ESO_4]	−0.21		298.15	[47]
[EMmor][ESO_4]	−0.13	Sinusoidal	343.15	[47]
		Ammonium based ILs		
[$(C_2H_4OH)_3NM$][MSO_4]	−0.23		298.15	[52]
[EN][NO_3]	−0.45		298.00	[31]
[BN][CH_3COO]	−1.11		293.15	[49]
[BN][CH_3COO]	−1.11		313.15	[49]
[BN][NO_3]	−0.60		293.15	[49]
[BN][NO_3]	−0.50		313.15	[49]
[EN][CH_3COO]	−1.07		298.15	[50]
[PN][CH_3COO]	−1.20		298.15	[50]
[C_2H_4OHN][CH_3COO]	−0.74		288.15	[51]
[C_2H_4OHN][CH_3COO]	−0.70		323.15	[51]

[25] who reported −0.47 cm^3 · mol^{-1} and −0.21 cm^3 · mol^{-1} at equimolar compositions at T = 298.15 K and T = 328.15 K, respectively. Similar results were reported by Bhattacharjee *et al.* [28]} for the related system: {[EMIM][MSO_4] (1) + H_2O (2)} of −0.43 cm^3 - · mol^{-1} and −0.25 cm^3 · mol^{-1} at x_1 = 0.5, at T = 278.15 K and T = 338.15 K, respectively {reported by Bhattacharjee *et al.* [28]}; and for {[EMIM][$CH_3(OCH_2CH_2)SO_4$] (1) + H_2O (2)} of −0.25 cm^3 · mol^{-1} and −0.22 cm^3 · mol^{-1} at x_1 = 0.5, at T = 298.15 K and T = 313.15 K, respectively {reported by Bhujrajh and Deenadayalu, [29]}. The V^E_m {for the system {[EMIM][MSO_4] (1) + H_2O (2)} [28], and {[EMIM][ESO_4] (1) + H_2O (2)} [23,28] did show a sinusoidal curve for high temperatures (above T = 330.15 K) with positive values over a small range of concentration in the low IL concentration range (with a maximum value of 0.10 cm^3 · mol^{-1}). The positive values were probably due to the more dominant disruption of the H-bonded water at the higher temperatures. The negative values of

V^E_m could be due to (IL + water) association through H-bonding between the acid proton of H_2O and the O atoms in the $[SO_4]$ group or $[CH_3(OCH_2CH_2)SO_4]$ group. At the higher temperatures and at low IL concentrations the most prominent volume effect due to (IL + H_2O) association was overtaken by the volume effect of the disruption of the water self-association.

Rodriguez *et al.* [25] has reported the V^E_m for the aqueous solution, involving the IL 1-ethyl-3-methylimidazolium trifluoroacetic acid, {[EMIM][CF_3CO_2] (1) + H_2O (2)}. The results were negative, over the whole composition range, with equimolar composition values of $-0.57\ cm^3 \cdot mol^{-1}$ and $-0.23\ cm^3 \cdot mol^{-1}$ at $T = 278.15$ K and $T = 348.15$ K, respectively. The results show a strong association between H_2O and the IL probably through H-bonding with the acidic acetate group and the proton of H_2O. This result is in sharp contrast to the V^E_m values reported for the related aqueous solutions of 1-ethyl-3methylimidazolium trifluoromethane sulphate, which were positive above $T = 300$ K. The triflate ion is very much more hydrophobic than the trifluoroacetic acid ion (TFA) and does not form H-bonds with H_2O as does the TFA ion.

Looking at the effect of temperature on V^E_m we see that for all the aqueous [EMIM] systems the effect is much greater in the low IL concentration region than in the high IL concentration region. Two examples are: for {[EMIM][BF_4] (1) + H_2O (2)} system [21], the value of (dV^E_m/dT) at $x_1 = 0.90$ is $0.4 \times 10^{-3}\ cm^3 \cdot mol^{-1} \cdot K^{-1}$ and at $x_1 = 0.10$ is $4.6 \times 10^{-3}\ cm^3 \cdot mol^{-1} \cdot K^{-1}$; and for {[EMIM][$MSO_4$] (1) + H_2O (2)} system [28] the value of (dV^E_m/dT) at $x_1 = 0.90$ is $0.4 \times 10^{-3}\ cm^3 \cdot mol^{-1} \cdot K^{-1}$ and at $x_1 = 0.10$ is $5 \times 10^{-3}\ cm^3 \cdot mol^{-1} \cdot K^{-1}$. In both cases the difference in the temperature effects is greater than an order of magnitude. The process at the low IL concentration end is obviously very different to the process at the high IL concentration end.

2.1.1.3. 1-Butyl-3-methylimidazolium [BMIM]ILs. The V^E_m for the mixture {[BMIM][HSO_4] (1) + H_2O (2)} at equimolar concentrations is $-0.60\ cm^3 \cdot mol^{-1}$ and $-0.32\ cm^3 \cdot mol^{-1}$ at $T = 308.15$ K and $T = 343.15$ K, respectively, as reported by Bhattacharjee *et al.* [28]. For the mixture {BMIM][MSO_4] (1) + H_2O (2)} the reported V^E_m was $-0.50\ cm^3 \cdot mol^{-1}$ and $-0.28\ cm^3 \cdot mol^{-1}$ at $T = 283.15$ K and $T = 343.15$ K, respectively [28]}. The equimolar V^E_m vales for the mixture {[BMIM][MSO_4] (1) + H_2O (2)} was $-0.33\ cm^3 \cdot mol^{-1}$ and $-0.24\ cm^3 \cdot mol^{-1}$ at $T = 298.15$ K and $T = 318.15$ K, respectively, as reported by Garcia-Maija *et al.*, [23]. Gonzales *et al.* [30] and Domanska *et al.* [20] also reported on this system. Gonzales *et al.* [30] correlated their V^E_m results with refractive index, viscosity and excess Gibbs Free Energy data. The V^E_m values for the (1-butyl-3-methylimidazolium + water) mixtures follow a similar pattern to the (1-ethyl-3-methylimidazolium + water) mixtures, with the V^E_m for: {[BMIM][BF_4] (1) + H_2O (2)]} as reported by Malham *et al.* [31], Robello *et al.* [32], Navarro *et al.* [33] and Zhao *et al.* [34], being positive at all reported temperatures from $T = 278.25$ K to $T = 353.15$ K; {[BMIM][CF_3SO_3] (1) + H_2O (2)]}as reported by Garcia-Miaja *et al.* [23], Vercher *et al.* [35], Gonzales *et al.* [36] and Ge *et al.* [37], being positive at temperatures above $T = 308.15$ K and sinusoidal at temperatures below $T = 308.15$ K; {[BMIM][MSO_4] (1) + H_2O (2)]} as reported by Garcia-Miaja *et al.* [23] and Bhattacharjee *et al.* [28], being negative at low temperatures ($T = 283.15$ K) but sinusoidal at high temperature ($T = 343.15$ K), being largely negative but with a small positive region at low IL concentrations. Results for mixtures related to the latter system, fit a similar pattern as can be seen from: {[BMIM][HSO_4] (1) + H_2O (2)]}, as reported by Bhattacharjee *et al.* [28] being negative at temperature ranging from $T = 308.15$ K to $T = 343.15$ K and {[BMIM][MSO_4] (1) + H_2O (2)]}, reported by Garcia-Miaja *et al.*, [23] being negative at $T = 298.15$ K to $T = 318.15$ K. The results for the {[BMIM][SCN] (1) + H_2O (2)]} mixtures by Domanska *et al.* [38] also follow the same pattern as the [EMIM] related mixtures also reported by Domanska *et al.* [22] at the higher temperatures (for example at $T = 348.15$ K). However at the lower temperatures (such as at $T = 298.15$ K) the V^E_m values become sinusoidal (see figure 1). The V^E_m values for the aqueous dicyanamide, IL system, [BMIM][$N(CN)_2$] (1) + H_2O (2)] [36] showed a similar behaviour to the SCN system discussed above being positive at the higher temperature of $T = 308.15$ K and becoming sinusoidal at the lower temperature of $T = 288.15$ K (see figure 2).

The V^E_m values for a related systems {[BMMIM][BF_4] (1) + H_2O (2)}, reported by Malham *et al.* [31] and {[PMMIM][BF_4] (1) + H_2O (2)} by Ge *et al.* [39], like all the above-mentioned imidazolium ionic liquids containing the $[BF_4]$ ion, (such as [EMIM][BF_4] by Zhang *et al.* [21] and [BMIM][BF_4] by Malham *et al.* [31], Rebello *et al.* [32], Zhao *et al.* [34] are positive over the whole composition range at all the reported temperatures, $T = 278.15$ K to $T = 333.15$ K.

An interesting set of V^E_m s involving halogen anions has been reported by Sastry [40]. He measured seven systems and the first reported here is for {[BMIM][I] (1) + H_2O (2)}. For this system the V^E_m values are positive at all concentrations (V^E_ms at $x_1 = 0.5$ are $0.35\ cm^3 \cdot mol^{-1}$ and $0.37\ cm^3 \cdot mol^{-1}$ at $T = 298.15$ K and $T = 308.15$ K, respectively).

The associations taking place on mixing all of these [BMIM] type ILs with water can be explained using the same arguments as discussed for the [EMIM] type ILs above: the weakening of the association between the IL moieties (in the IL rich region) and the weakening of H-bonded water network in the dilute IL region results in a positive V^E_m effect for ILs containing the $[BF_4]$, [SCN], $[N(CN)_2]$, $[CH_3SO_3]$ and [I] ions; strong H-type bonded association between the IL and the H_2O molecules for ILs containing $[ESO_4]$, $[MESO_4]$, $[MSO_4]$, $[HSO_4]$ result in a negative V^E_m which in the dilute IL region is in competition with the positive effect of the breakdown of the H-bonded water structure, which dominates at the higher temperatures. An example of the latter effect is exemplified by the system: {[BMIM][MSO_4] (1) + H_2O (2)} reported by Bhattacharjee *et al.* [28] which is negative at low x_1 values and positive at concentrations $x_1 > 0.1$ at $T = 283.15$ K or {[EMIM][MSO_4] (1) + H_2O (2)} at $T = 338.15$ K [28] or {[EMIM][ESO_4] (1) + H_2O (2)} [28].

It does appear that the anion is the most important component in defining the sign and magnitude of the V^E_m on mixing water with an IL.

The V^E_m for the related triflate system {[BEIM][CF_3SO_3] (1) + H_2O (2)} reported by Vercher *et al.* [35] follow a very similar pattern to that of the system {[BMIM][CF_3SO_3] (1) + H_2O (2)} as reported by Garcia-Miaja *et al. et al.* [23] and by Vercher *et al.* [35] and also {[EMIM][CF_3SO_3] (1) + H_2O (2)} reported by Garcia-Miaja *et al.* [23] and by Vercher [24] with the V^E_m values being positive at the higher temperatures ($T = 338.15$ K) and sinusoidal at the lower temperatures with negative values in the low IL concentration range ($T = 298.15$ K). At even lower temperatures ($T = 278.15$ K) the negative V^E_m region increases and only at the high IL concentration region is it positive. At the higher temperatures the dissociation of the (H_2O + H_2O) and possibly the dissociation of the IL dominates, but at the lower temperatures the association of (IL + H_2O) dominates especially in the low IL concentration region.

2.1.1.4. 1-Hexyl-3-methylimidazolium [HexMIM]ILs. The V^E_m for the mixtures {[HexMIM][$N(CN)_2$] (1) + H_2O (2)} by Gonzales *et al.* [36] are positive ($0.14\ cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$) at $T = 308.15$ K, but sinusoidal ($0.02\ cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$) at $T = 288.15$ K and follows the trend of the related system {[BMIM][$N(CN)_2$] (1) + H_2O (2)} [36]. It confirms the idea that the anion dictates the basic sign and magnitude of the V^E_m (see figure 3).

The V^E_m for the mixture {[HexMIM][Cl] (1) + H_2O (2)} by Gomez *et al.* [41] are negative ($-0.53\ cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$) at $T = 298.15$ K, but sinusoidal ($-0.48\ cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$ at $T = 343.15$ K) being positive in the low IL concentration region

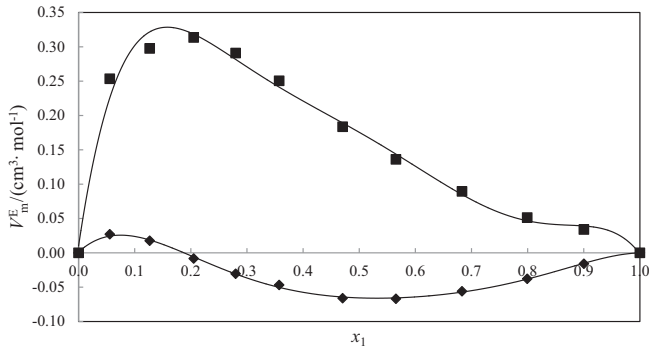


FIGURE 1. Excess molar volume V^E_m versus x_1 for the {[BMIM][SCN] (1) + water (2)} binary system at temperatures: ♦, 298.15 K; and ■, 348.15 K. The *solid lines* represent the smoothness of the data [38].

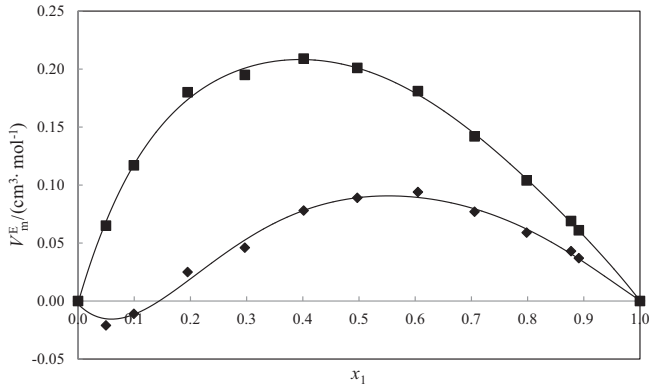


FIGURE 2. Excess molar volume V^E_m versus x_1 for the {[BMIM][N(CN)$_2$] (1) + water (2)} binary system at temperatures: ♦, 288.15 K; and ■, 308.15 K. The *solid lines* represent the smoothness of the data [36].

($x_1 < 0.15$). Sastry *et al.* [40] reported similar results on the same system (-0.53 cm$^3 \cdot$ mol^{-1} and -0.49 cm$^3 \cdot$ mol^{-1} at $T = 298.15$ K and $T = 308.15$ K, respectively) (see figure 4). This pattern is similar to that found in {[EMIM][MSO$_4$] (1) + H$_2$O (2)} and in {[BMIM][MSO$_4$] (1) + H$_2$O (2)} by Bhattacharjee *et al.* [28]. In this case, involving the [Cl] anion, the association between the water molecules and the anion (resulting in the negative V^E_m) is probable dictated by the small size of the anion (its volume is 15.7 cm$^3 \cdot$ mol^{-1}, which is even smaller than the H$_2$O molecule). This attraction is possibly, through H-bonding to the hydrophilic [Cl] ion. The positive region at low IL concentrations at the higher temperatures (above $T = 338.15$ K) is an indication that the (IL + H$_2$O) interaction weakens with increasing temperature and at these temperatures the (H$_2$O + H$_2$O) dissociation becomes the more dominant effect as far as V^E_m is concerned.

It is interesting to note that the V^E_m for {[HexMIM][Br] (1) + H$_2$O (2)} reported by Li *et al.* [42] at $T = 293.15$ K, is negative at low IL concentrations (minimum of -0.07 cm$^3 \cdot$ mol^{-1} at $x_1 = 0.30$ and positive with a maximum of 0.25 cm$^3 \cdot$ mol^{-1} at $x_1 = 0.81$). Furthermore Li *et al.* [42] measured V^E_m values at $T = 333.15$ K and produced a double humped curve (see figure 5), Sastry *et al.* [40] also reported on this system and also found a sinusoidal shaped curves, but not a double humped curve (at $x_1 = 0.5$, the V^E_m values were -0.15 cm$^3 \cdot$ mol^{-1} and -0.12 cm$^3 \cdot$ mol^{-1} at $T = 298.15$ K and $T = 308.15$ K, respectively). These results are very different to the system involving the [Cl] anion. Here the effect appears to be dictated by the dissociation of the IL molecule in the rich IL region and by the H-Br association in the dilute IL region. At the higher temperature of $T = 333.15$ K, the V^E_m is positive over the whole composition range and furthermore shows a double hump with maxima at $x_1 = 0.10$ (0.06 cm$^3 \cdot$ mol^{-1}) and at 0.80 (0.25 cm$^3 \cdot$ mol^{-1}) [42]. This does show just how complex these competing associations are. At the higher temperatures ($T = 333.15$ K) in the IL rich region, the dissociation of the IL dominates, but in the dilute IL region the dissociation of the H bonds in the water (positive effect) dominates; in between, the association of (IL + H$_2$O) becomes important. The latter association dominates at the lower temperature ($T = 293.15$ K); the results at $T = 293.15$ K and $T = 333.15$ K have been reproduced in figure 4.

An interesting follow up to the halogen results are the V^E_m results for {[HexMIM][I] (1) + H$_2$O (2)} which have been reported by Sastry *et al.* [40]. These results are positive over the whole concentration range (at $x_1 = 0.5$, the V^E_m values were 0.87 cm$^3 \cdot$ mol^{-1} and 0.95 cm$^3 \cdot$ mol^{-1} at $T = 298.15$ K and $T = 308.15$ K, respectively) and together with the {[HexMIM][Cl] and {[HexMIM]Br] form a sequence in magnitude and sign related to the halogen electronegativity: Cl, Br, I (see figure 4).

2.1.1.5. 1-Octyl-3-methylimidazolium [OMIM]ILs. The data for V^E_m {[OMIM][Cl] (1) + H$_2$O (2)} have been reported by Gomez *et al.* [41]. The results are very similar to the related system, also reported by Gomez *et al.* [41], of {[HexMIM][Cl] (1) + H$_2$O (2)} with $V^E_m = -0.56$ cm$^3 \cdot$ mol^{-1} at $x_1 = 0.5$ at $T = 298.15$ K and a sinusoidal graph at $T = 348.15$ K with an equimolar V^E_m value of -0.40 cm$^3 \cdot$ mol^{-1}. Similar results were obtained by Sastry *et al.* [40] (V^E_m at $x_1 = 0.5$ of -0.56 cm$^3 \cdot$ mol^{-1} and -0.52 cm$^3 \cdot$ mol^{-1} at $T = 298.15$ K and $T = 308.15$ K respectively). Sasty *et al.* [40] also measured the V^E_m for {[OMIM][Br] (1) + H$_2$O (2)} (V^E_m being sinusoidal and at $x_1 = 0.5$ of -0.60 cm$^3 \cdot$ mol^{-1}and -0.48 cm$^3 \cdot$ mol^{-1} at

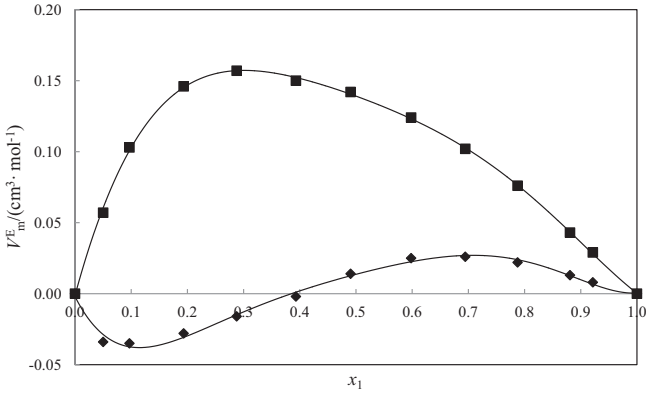


FIGURE 3. Excess molar volume V^E_m versus x_1 for the {[HexMIM][N(CN)$_2$] (1) + water (2)} binary system at temperatures: ♦, 288.15 K; and ■, 308.15 K. The *solid lines* represent the smoothness of the data [36].

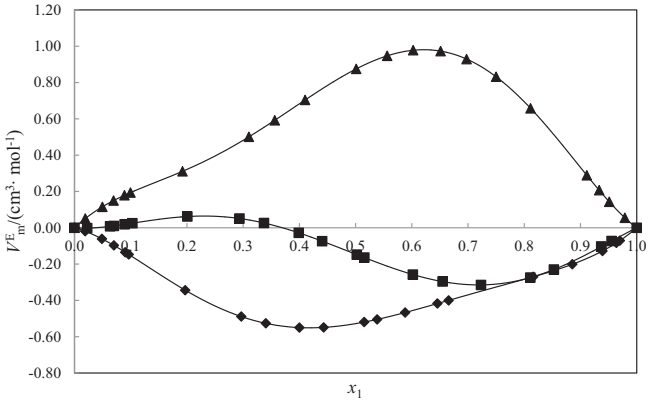


FIGURE 4. Excess molar volume V^E_m versus x_1 at 298.15 K: ♦, {[HexMIM][Cl] (1) + water (2)}; ■,{[HexMIM][Br] (1) + water (2)} and ▲,{[HexMIM][I] (1) + water (2)} binary systems. The *solid lines* represent the smoothness of the data [40].

T = 298.15 K and T = 308.15 K, respectively) and {[OMIM][I] (1) + H_2O (2)} (V^E_m at x_1 = 0.5 of 1.04 $cm^3 \cdot mol^{-1}$ and 1.14 $cm^3 \cdot mol^{-1}$ at T = 298.15 K and T = 308.15 K, respectively). These results follow the same trend as that found for the HexMIM][Cl], HexMIM][Br], HexMIM][I]. Again the imidazolium cation has little influence on the overall sign and magnitude of the V^E_m values.

Summing up the effect on V^E_m of mixing an imidazolium IL with water at the temperatures between T = 278 K and T = 348 K: the dominant positive effects are the weakening of the (IL + IL) association in the rich IL region and the dissociation of the H-bonded water network in the dilute IL concentration region. The dominant negative effect is due to the association of the polar water molecules with the anions, either through H bonding or through attraction of the polar water to a highly charged small ion. Competition between these effects gives rise to sinusoidal curves and even in one case a double humped curve.

2.1.2. Pyridinium [py]ILs

The volume changes V^E_m on mixing water with a pyridinium ionic liquid in general follow the pattern given by their imidazolium counterparts. The V^E_m values for {[Bpy][BF_4] (1) + H_2O (2)} reported by Mokhtarani *et al.* [43] and Garcia-Miaja *et al.* [44] are positive over the whole composition range for all temperatures in the range of T = 283.15 K (0.43 $cm^3 \cdot mol^{-1}$ at x_1 = 0.5) to T = 343.15 K (0.82 $cm^3 \cdot mol^{-1}$ at x_1 = 0.5) [43,44] as are the V^E_m values for the related system {[Opy][BF_4] (1) + H_2O (2)} [43] (see table 2). These values are higher than that seen for the imidazolium tetraborate ionic liquids, but follow the same positive V^E_m pattern. The V^E_m results for {[EEpy][ESO_4] (1) + H_2O (2)} by Gonzales *et al.* [36] and for {[BMpy][SCN] (1) + H_2O (2)} by Domanska *et al.* [38] (see table 2 and figure 6) again follow the pattern of the imidazolium ethylsulphate [28] and imidazolium thiosulphate [38] ILs, respectively. This again supports the idea that the anion dictates the sign and magnitude of the excess volume. The V^E_m for {[Mpy][MSO_4] (1) + H_2O (2)} reported by Gonzales *et al.* [36], are small (between 0 $cm^3 \cdot mol^{-1}$ and −0.08 $cm^3 \cdot mol^{-1}$) for temperatures between T = 288.15 K and T = 308.15 K, respectively. The small values are an indication of competing interactions which are of similar strength. This system {[Mpy][MSO_4] (1) + H_2O (2)} [36] ions of particular interest in that Gonzales *et al.* has reported a double hump V^E_m result at the higher temperature of T = 308.15 K being positive at either end of the concentration spectrum. This reflects the complex nature of the competing interactions with the (IL + H_2O) interaction contributing a negative effect to the overall volume which is similar but of opposite sign to the (H_2O + H_2O) and (IL + IL) dissociation effects. In the dilute IL region the competition is probably between the dissociation of the H-bonded water and the H-bonding between the water molecules and the O atoms of the SO_4 groups. In this dilute region, at temperatures of T = 288.15 K and also at T = 308.15 K the dissociation of water is more important. At the other end of the concentration range, the (IL + IL) dissociation contributes more to the overall excess volume than does the (IL + H_2O) association.

The V^E_m for {[Bpy][NO_3] (1) + H_2O (2)} as reported by Wang *et al.* [45] is large and negative with a value of −0.75 $cm^3 \cdot mol^{-1}$ (at x_1 = 0.5) at T = 298.15 K and points to a strong association of H_2O to the NO_3, probably through H-bonding.

2.1.3. Pyrrolidinium [pyr]ILs

The V^E_m for {[BMpyr][$N(CN)_2$] (1) + H_2O (2)} reported by Gonzales *et al.* [36] (see figure 7) and by Krolikowska *et al.* [46], follow the pattern of {[BMIM][$N(CN)_2$] (1) + H_2O (2)} [36], {[HMIM][$N(CN)_2$] (1) + H_2O (2)} [36] in that results at the high temperature of T = 343.15 K are positive at all compositions and at the low temperature of T = 288.15 K, the results are positive at the high IL concentration region but negative at the low IL concentrations.

The V^E_m for {[BMpyr][CF_3SO_3] (1) + H_2O (2)} by Vecher *et al.* [35] and by Gonzales *et al.* [36] also follow the pattern of related triflate IL systems, namely {[EMIM][CF_3SO_3] (1) + H_2O (2)} by Vecher *et al.* [24], {[BMIM][CF_3SO_3] (1) + H_2O (2)} Gonzales *et al.* [36] and Vecher *et al.* [35] and {[BEIM][CF_3SO_3] (1) + H_2O (2)} [35] in that at the relatively high temperature of T = 338.15 K values of V^E_m are positive at all compositions, and at the low temperature of T = 278.15 K the values are positive at the high IL concentration region, but negative at the low IL concentrations.

The values for V^E_m for {[BMpyr][SCN] (1) + H_2O (2)} by Domanska *et al.* [38] (see figure 8) also follow the pattern of related [SCN] IL systems, involving [BMIM][SCN] [38] and [BMpy][SCN] [38] in that at the relatively high temperature of T = 348.15 K, the V^E_m values are all positive at all compositions, apart from a narrow composition range close to x_1 = 1; and at the low temperature of T = 298.15 K the values are negative at all compositions apart from a narrow range of composition at dilute IL concentrations.

The V^E_m for {[EMpyr][ESO_4] (1) + H_2O (2)} reported by Krolikowska *et al.* [47] were negative over the whole concentration range (−0.50 $cm^3 \cdot mol^{-1}$ at x_1 = 0.5) at T = 298.15 K, and in this respect was similar to other [ESO_4] IL systems such as for the IL, [EMIM][ESO_4] [28] and [EMpip][ESO_4] [47]. At higher temperatures, the V^E_m values for {[EMpyr][ESO_4] (1) + H_2O (2)} showed a sinusoidal behaviour with a maximum of 0.42 $cm^3 \cdot mol^{-1}$ at x_1 = 0.8 and a minimum of −0.5 $cm^3 \cdot mol^{-1}$ at x_1 = 0.5.

These results again show that it is the anion of the IL that dictates the sign and magnitude of the excess volume on mixing an IL with water.

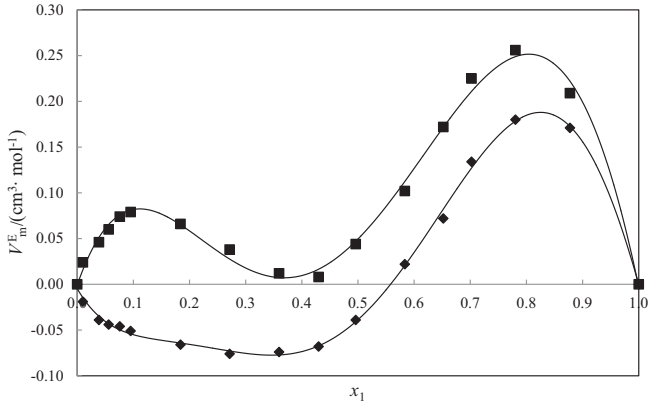


FIGURE 5. Excess molar volume V^E_m versus x_1 for the {[HexMIM][Br] (1) + water (2)} binary system at temperatures: ♦, 293.15 K; and ■, 333.15 K. The *solid lines* represent the smoothness of the data [42].

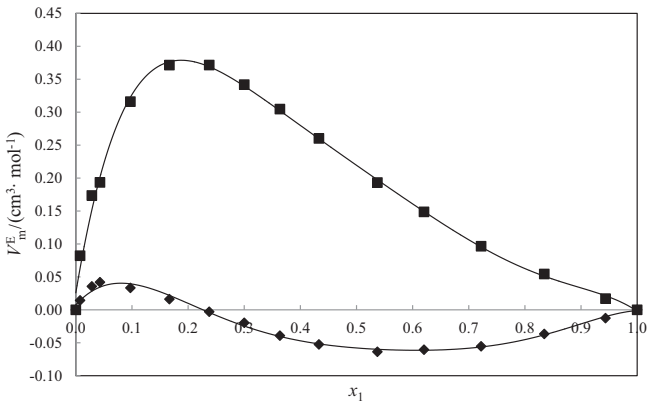


FIGURE 6. Excess molar volume V^E_m versus x_1 for the {[BMpy][SCN] (1) + water (2)} binary system at temperatures: ♦, 298.15 K; and ■, 348.15 K. The *solid lines* represent the smoothness of the data [38].

The V^E_m values for {[pyr][C_7CO_2] (1) + H_2O (2)} [48] are particularly interesting because of their magnitude; the V^E_m values at equimolar composition are $-1.24\ cm^3 \cdot mol^{-1}$ and $-1.52\ cm^3 \cdot mol^{-1}$ at $T = 298.15$ K and $T = 328.15$ K, respectively. The results indicate a particularly strong association between the IL and H_2O probably through H-bonding between the negative COO group and the relatively positive hydrogen atom of H_2O.

2.1.4. Piperidinium [pip]ILs

The piperidinium group (a six membered ring containing a N atom) is very similar to the pyrrolidinium group (a five membered ring containing a N atom) so it is not surprising that the V^E_m values for related compounds are very similar. This evidence is based on only two sets of data, but from all the other evidence we have seen for different ILs and their related compounds this comes as no surprise. The V^E_m for {[BMPIP][SCN] (1) + H_2O (2)} by Domanska *et al.* [38] (see figure 9) also follow the pattern of related [SCN] IL systems, namely {[BMpy][SCN] (1) + H_2O (2)} [38], {[BMpyr][SCN] (1) + H_2O (2)} [38] and {[BMIM][SCN] (1) + H_2O (2)} [38] in that at the relatively high temperature of $T = 348.15$ K, the V^E_m are positive for all compositions, and at the lower temperature of $T = 298.15$ K the values are positive over a small range of concentration at low IL concentration region, but negative over the remaining concentration range.

The V^E_m for {[BMpip][CF_3SO_3] (1) + H_2O (2)} reported by Krolikowska *et al.* [46] also follow the pattern of related triflate IL systems, namely {[EMIM][CF_3SO_3] (1) + H_2O (2)} by Vercher *et al.* [24], {[BMIM][CF_3SO_3] (1) + H_2O (2)} by Vecher *et al.* [35] and by Gonzales *et al.* [36] and {[BEIM][CF_3SO_3] (1) + H_2O (2)} [35] and in particular {[BMpyr][CF_3SO_3] (1) + H_2O (2)} [46] in that at the relatively high temperature of $T = 343.15$ K, the V^E_m are positive at all compositions, and at the low temperature of $T = 298.15$ K the values are positive at the high IL concentration region, but negative at the low IL concentrations.

The V^E_m for {[EMpip][ESO_4] (1) + H_2O (2)} reported by Krolikowska *et al.* [47] were negative over the whole concentration range, ($-0.60\ cm^3 \cdot mol^{-1}$ and $-0.42\ cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$ at $T = 298.15$ K and $T = 343.15$ K, respectively) also follow the pattern of related [ESO_4] IL system [28], especially at the lower temperatures ($T < 300$ K).

2.1.5. Morpholinium [mor]ILs

The V^E_m for {[EMmor][ESO_4] (1) + H_2O (2)} reported by Krolikowska *et al.* [47] were negative over the whole concentration range ($-0.21\ cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$) at $T = 298.15$ K, and in this respect was similar to other [ESO_4] IL systems such as for the IL, [EMIM][ESO_4] [28] and [EMpyr][ESO_4] [47] as discussed above. At

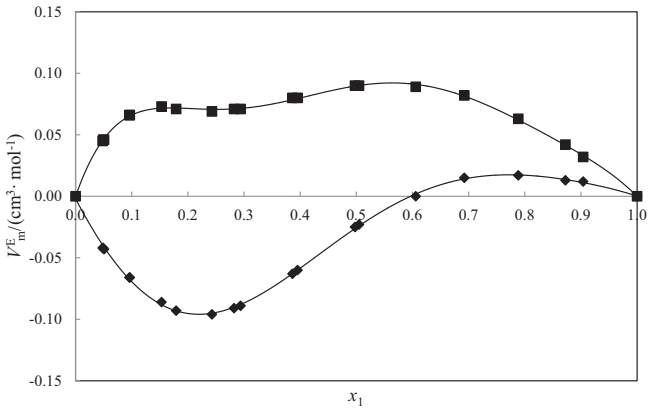


FIGURE 7. Excess molar volume V^E_m versus x_1 for the {[BMpyr][$N(CN)_2$] (1) + water (2)} binary system at temperatures: ♦, 288.15 K; and ■, 308.15 K. The *solid lines* represent the smoothness of the data [36].

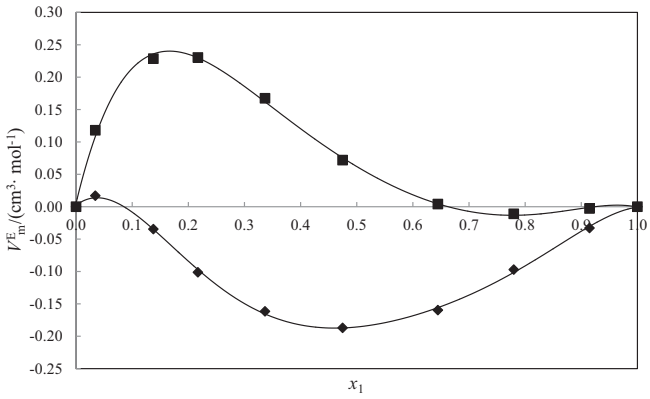


FIGURE 8. Excess molar volume V^E_m versus x_1 for the {[BMpyr][SCN] (1) + water (2)} binary system at temperatures: ♦, 298.15 K; and ■, 348.15 K. The *solid lines* represent the smoothness of the data [38].

higher temperatures the V^E_m for {[EMmor][ESO_4] (1) + H_2O (2)} showed a sinusoidal behaviour with a maximum of $0.02\ cm^3 \cdot mol^{-1}$ at $x_1 = 0.95$ and a minimum of $-0.13\ cm^3 \cdot mol^{-1}$ at $T = 343.15$ K. The related system involving {[EMpyr][ESO_4] also showed as sinusoidal curve with a maximum in the high IL concentration region.

2.1.6. Ammonium [N]ILs

Relatively few of the ammonium ionic liquids are soluble in water in all proportions and furthermore there are very few reported V^E_m values for aqueous solutions of [N] ionic liquids. Butyl ammonium acetate has been investigated by Xu *et al.* [49] and the V^E_m values for {[BN][CH_3COO] (1) + H_2O (2)}are negative over the whole composition range at $T = 293.15$ K ($-1.11\ cm^3 \cdot mol^{-1}$) and at $T = 313.15$ K ($-1.11\ cm^3 \cdot mol^{-1}$). The V^E_m results for the related systems of {[EN][CH_3COO] (1) + H_2O (2)} and {[PN][CH_3COO] (1) + H_2O (2)}, both by Hou *et al.* [50], are also negative over the whole composition range. At $T = 298.15$ K the values are $-1.07\ cm^3 \cdot mol^{-1}$ and $-1.20\ cm^3 \cdot mol^{-1}$ respectively. The effect of altering the alkyl group on the ammonium ion resulted in only a slight increase in the negative value of the excess molar volume. Again, the anion is the moiety that dictates the sign and magnitude of the V^E_m values. However, replacing the alkyl group on the ammonium ion with a hydrophilic group (C_2H_4OH) as reported by Alvarez *et al.* [51] in {[$C_2H_4(OH)NH_3$][CH_3COO] (1) + H_2O (2)} results in a more positive V^E_m compared to the previous three alkyl ammonium IL systems. The V^E_m values at $T = 288.15$ K and $T = 323.15$ K are $-0.74\ cm^3 \cdot mol^{-1}$ and $-0.70\ cm^3 \cdot mol^{-1}$, respectively. The stronger self-association of the (IL + IL) through H-bonding between the OH attached to the ethyl group on the N atom and the acidic acetate group would reduce the (IL + H_2O) association and thus a less negative excess volume. One other ammonium system with the hydrophilic cation, [$(C_2H_4OH)_3NM$] is the mixture {[$(C_2H_4OH)_3NM$][MSO_4] (1) + H_2O (2)} by Arce [52]. The equimolar V^E_m is $-0.25\ cm^3 \cdot mol^{-1}$ at $T = 298.15$ K and the curve is sinusoidal with a very small positive region in the high IL concentration region. Over most of the concentration region the (IL + H_2O) dominates but in the very concentrated IL region the breakdown and separation of the cation and anion of the IL is dominant.

2.2. Partial excess molar volumes

The partial excess molar volume gives a better picture of the interactions taking place in these mixtures. This is especially true at infinite dilution. At infinite dilution the partial excess molar volume at $x_1 = 0$, can be determined from a tangent drawn on the V^E_m versus x_1 graph at $x_1 = 0$. The tangent cuts the $x_1 = 1$ axis at a

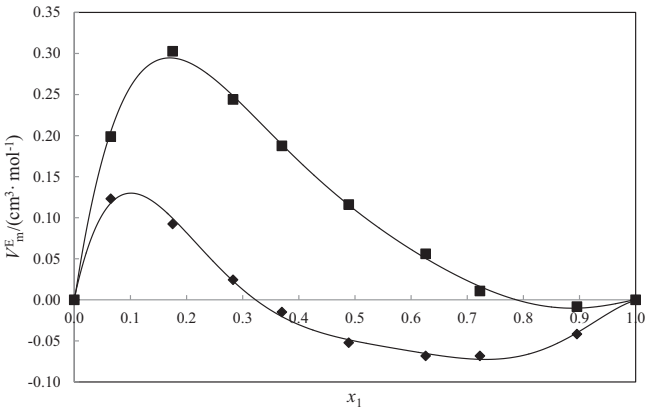


FIGURE 9. Excess molar volume V^E_m versus x_1 for the {[BMpip][SCN] (1) + water (2)} binary system at temperatures: ♦, 318.15 K; and ■, 348.15 K. The *solid lines* represent the smoothness of the data [38].

point and the distance between that point and the $V^E_m = 0$ on the $x_1 = 1$ axis is the excess partial molar volume at infinite dilution, $V^{E\infty}_m$. The value of $V^{E\infty}_m$ can be determined in the same way at the other end of the concentration scale [53]. The excess partial molar volume at infinite dilution for a component is the contribution, by that component at infinite dilution, to the excess volume. As an example, the partial molar excess volumes for {[EN][NO_3] (1) + H_2O (2)} at $T = 298.15$ K have been reported by Malham *et al.* [31]: at infinite dilution $V^{E\infty}_m = 82.8\ cm^3 \cdot mol^{-1}$ (the molar volume of [EN][NO_3] is $89.3\ cm^3 \cdot mol^{-1}$) and infinite dilution $V^{E\infty}_m = 16.7\ cm^3 \cdot mol^{-1}$ (the molar volume of H_2O is $18.0\ cm^3 \cdot mol^{-1}$). The results indicate the contribution each component makes to the overall excess volume which in this case will be a negative quantity.

The excess partial molar volumes at infinite dilution can readily be obtained from V^E_m as a function of x_1. If the V^E_m is summarised in terms of the Redlich–Kister equation:

$$V^E_m = x_1(1-x_1)[A + B(1-2x_1) + C(1-2x_1)^2 + \cdots], \quad (2)$$

$$V^{E\infty}_1 = \left[\partial V^E_m/\partial n_1\right] n_2 = \left[(\partial V^E_m/\partial x_1)(\partial V^E_m/\partial n_1) n_2\right]. \quad (3)$$

And at $x_1 = 0$

$$V^{E\infty}_1 = A + B + C + \cdots \quad (4)$$

And similarly $V^{E\infty}_2 = A - B + C - \cdots$ (5)

2.3. Effect of the groups attached to the IL cation

Evidence discussed above shows that different alkyl groups (hydrophobic in nature) attached to the IL cation, for mixtures of an IL mixed with water, has only a small effect on the overall V^E_m. This is true for imidazolium, pyridinium, pyrrolidinium, piperidinium and even ammonium ionic liquids. A bigger effect takes place when the alkyl group is replaced by a polar, hydrophilic group (compare the results by Alvarez *et al.*, [51] on aqueous solutions of [$(C_2H_4OH)NH_3$][CH_3COO] with the work on [EN][CH_3COO] and [PN][CH_3COO] by Xu *et al.* and Hou *et al.* respectively [49,50]. Work by Domanska *et al.* [38], who investigated the V^E_m for the aqueous mixtures of ILs made up of the anion [SCN] and cations [BMIM], [BMpy], BMpyr] and [BMPIP], showed very clearly that these cations played only a minor role in the magnitude and shape of the excess molar volume/composition curves. Work by Krolikowska *et al.* [46] and by Gonzales *et al.* [36] with aqueous solutions of ILs made up of the anion dicyanamide [$N(CN)_2$] with cations [BMpyr], [BMpip] and [BMIM], also showed that these cations played only a minor role. Yet another set of data by Vercher *et al.* [24,35]; by Gonzales *et al.* [36]; and Garcia-Miaja [23] on the triflate anion (CF_3SO_3) with cations [EMIM], [BMIM], [BEIM], [BMpy] and [BMpyr] further supports the fact the IL cation plays only a minor role in V^E_m. In all these works, apart from the one case (involving the IL 2-hydroxyethylammonium acetate), the groups which form part of the cation are all hydrophobic groups. From this one piece of evidence it is tempting to suggest that if polar and hydrophilic groups were attached to these cations, the results would be very different.

2.4. Effect of the anion

The anion is the dominant group as far as influencing the magnitude, shape and sign of the excess molar volume-composition curves for mixtures of an ionic liquid and water. This was evident for cations involving imidazolium (with anions [BF_4], [ESO_4], [MSO_4], [SCN], [CF_3SO_4], [$CH_3(OCH_3CH_2O)_2SO_4$], [$N(CN)_2$], [Cl], and [Br]), pyridinium (with anions [BF_4], [ESO_4], [MSO_4], [SCN], [CF_3SO_4], and [NO_3], pyrrolidinium (with anions [SCN], [CF_3SO_4], [$N(CN)_2$] and [C_7CO_2], piperidinium (with anions [SCN], [$N(CN)_2$]) and even ammonium (with anions [CH_3COO] and [NO_3]) groups. The ions containing many oxygen atoms ([ESO_4], [MSO4], [$CH_3(OCH_3CH_2O)_2SO_4$], [CH_3COO] and [NO_3]) result in negative V^E_m values especially at the lower temperatures while the more hydrophobic groups of [BF_4], [SCN], [CF_3SO_4], tend to result in positive V^E_m values especially at high temperatures.

2.5. Effect of temperature

The effect of temperature is most noticeable in the dilute IL region for all the imidazolium, pyridinium, pyrrolidinium, piperidinium IL mixtures with water. The change of V^E_m with temperature is much less in the high IL concentration region. This can be seen from the relevant partial molar volumes at infinite dilution, and also from the isobaric expansivity values. Domanska *et al.* [22] has published data on the isobaric expansivities for the system {EMIM][SCN] (1) + H_2O (2)} and the results show very clearly that in the low IL concentration region the value of α is orders of magnitude greater than it is in the high IL concentration region. These results support the comments we made at the end of Section 2.1.1.2. This, points to two different processes taking place at either end of the concentration spectrum. According to our hypothesis, the dominant process in the dilute IL concentration region is the breakdown of the H-bonded water network which competes with the (IL + H_2O) association. If the latter effect is stronger the excess volume is negative and vice versa. At the higher temperatures the former predominates and this could be due to the fact that the (IL + H_2O) association weakens as the temperature increases and so does the (H_2O + H_2O) interaction. These effects appear to be more temperature dependant than the effects dominating the high IL concentration region.

The change of V^E_m with temperature for the aqueous ammonium ionic liquid mixtures is small at both ends of the concentration spectrum – this too is an indication that the processes taking place in the aqueous ammonium mixtures is different to that taking place in the other IL mixtures. It could be a result of the cations of the ammonium ILs being smaller than cations of the IM, py, pyr and pip ILs. This would make the cation – anion association much stronger as the positive charge on the cation would be smeared over the much smaller ammonium surface area. The resultant higher charge per unit area on the cation might also allow the association of the polar water molecules adding another association (H_2O-[cation]) to compete with the H-bond-[anion] association.

2.6. Effect of ionic liquid composition

The relative amount of one component in a mixture dictates the interactions and in particular the very dilute solutions have very different interactions between the components than does a solution at $x_1 = 0.5$. It is for this reason that we have focused on the extreme concentrations in our attempt to understand the processes involved. The concentration of the V^E_m maximum or minimum does give some indication of the relative strength of the competing effects. For example, for the mixture {[$(C_2H_4OH)_3NCH_3$][CH_3SO_3] (1) + H_2O (2)} [52] the minimum 0.3 $cm^3 \cdot mol^{-1}$ is at $x_1 = 0.20$. This indicates that the association of H_2O with the hydrophilic anion is the dominant feature.

2.7. Double hump curves

Double hump V^E_m –composition curves for binary liquid mixtures are unusual in thermodynamics but not unknown; the cause is usually a set of competing interactions. In the aqueous IL systems discussed in this work there are a number of double humped systems. In a dilute IL region the competition would probably be between the break-down of the H-bonded water network and the association between the IL anion and the water molecules. In some cases the (IL + water) is the dominant feature (negative effect) and in other cases it is the (H_2O + H_2O) breakdown (positive effect) that is the dominant process. At the other end of the concentration spectrum, the IL-water interaction (negative) competes with the separation of the cation and anion (positive). In between these extreme concentrations one or other effect would dominate. As an example we consider the case of [BMpyr][$N(CN)_2$] at $T = 288.15$ K [42]. At low IL concentration ($x_1 < 0.1$) the V^E_m is slightly positive (0.02 $cm^3 \cdot mol^{-1}$) and at higher concentrations in becomes negative ($V^E_m = -0.02$ $cm^3 \cdot mol^{-1}$ at $x_1 = 0.5$) and even high IL concentrations, the value of V^E_m become positive again. The slightly stronger association of the water-$N(CN)_2$ is probably responsible for the small negative effect which is seen in the middle concentration ranges. This interaction probably competes with the two dissociation effects which dominate at either end of the concentration range resulting in positive V^E_m values. The overall effect, being small, indicates at least three interactions which are of similar strength.

2.8. Summing up of the possible processes taking place in aqueous IL mixtures

From the V^E_m evidence above the interactions between an IL and water are complex and no doubt involve many possible interactions which are likely to involve:

(a) (cation + anion) disassociation (a positive V^E_m effect)
(b) H-bond dissociation of water (a positive V^E_m effect)
(c) cation-H-bond (a negative but small effect)
(d) anion-H-bond association (a negative effect)
(e) packing effect
(f) breakdown of (cation + cation) interaction

The magnitude of the effect (a), involving the weakening of the coulombic interaction between the ILs (cation + anion), as a result of mixing with water, would depend on the size of the cation and also, to a certain extent, on the anion; the larger the size, the weaker the coulombic attraction. Usually for the systems discussed here, it is the cation which is large. This effect is prominent in aqueous mixtures of {IL (1) + H_2O (2)}, at the high IL concentrations for soluble IL involving imidazolium or pyridinium cations with the anions: [BF_4], [SCN], [$N(CN)_2$] and [CH_3SO_3], and especially at the higher temperatures ($T > 300$ K). These are the more hydrophobic anions.

The effect on V^E_m of the breakdown of the H-bonded network, {(b) type effect} as a result of mixing water with an IL, is perhaps the most important positive effect in the mixtures reported in this survey. It is responsible for the positive V^E_m of many of the systems, especially at the dilute IL end of the concentration spectrum. In some cases, where strong anion-H-bond interactions give rise to a negative V^E_m s over much of the composition range, this positive effect can dominate at the dilute IL concentration region. This is true for imidazolium or pyridinium or pyrrolidinium or piperidinium cations with the anion [SCN] and some mixtures involving [$N(CN)_2$] and for mixtures involving [EMIM][MSO4], [Mpy][MSO4], [HexMIM][Cl], [BMpy][CF_3SO_3], especially at the higher temperatures of $T > 300$ K.

The interaction between a hydrophilic anion and the proton of water (H-bond) {(c) in the above listing} is the most important of the negative effects in the mixtures discussed here. Negative V^E_m values are seen for the ILs involving imidazolium or pyridinium or pyrrolidinium or ammonium cations with hydrophilic anions containing O or Cl atoms such as [NO_3], [C_7COO], [MSO_4], [ESO_4], [$CH_3(OCH_2CH_2)_2SO4$], [HSO_4] and [CH_3COO]. The effect is seen at both ends of the concentration scale.

This H-bonding interaction is one of the factors that dictates whether an IL is soluble in water or not, hence the reason why so many of the mixtures in this compilation exhibit negative V^E_m values. Looking at the ILs that are not soluble in water, most involve very hydrophobic cations and anions such as in [HexMIM][BF_4] and [EMIM][PF_6] which are not soluble in water over the whole composition range.

The interaction between the cation and the proton of water {case (d) in the list above} for example in the case of 2-hydroxyethyl ammonium {$(C_2H_4OH)NH_3$} and tris-2-hydroxyethylmethyl ammonium {$(C_2H_4OH)_3NCH_3$} IL might well be important in contributing to the negative V^E_ms but with so many other associations to consider it is impossible to define.

The effect of packing {case (e) in the list above} is always important and must play some role in these interactions especially in the cases involving large molecules mixing with smaller molecules. This could give rise to a negative effect if one of the species fitted into voids unoccupied by the other species. It could have a role in the mixtures discussed here, but one would expect its effect to become more prominent with an increase of temperature, however this does not happen. Its role is possibly a minor one.

The last effect in the list above (f) is also possibly a minor effect. Its importance increases with increasing size and polarity of the cation groups. It could well play a role in the magnitude of the V^E_m of the 2-hydroxyethyl ammonium {$(C_2H_4OH)NH_3$} and tris-2-hydroxyethylmethyl ammonium {$(C_2H_4OH)_3NCH_3$} IL water mixtures as a result of H-bonding between the cations.

3. Conclusions

The outstanding features of the excess molar volumes of aqueous ILs is not only the wide range of values for the different ILs (from -1.7 $cm^3 \cdot mol^{-1}$ to 0.7 $cm^3 \cdot mol^{-1}$) but the large temperature effect which at equimolar concentrations was as high as $9 \cdot 10^{-3}$ $cm^3 \cdot mol^{-1} \cdot K^{-1}$ (for the IL [BMIM][BF_4]) [34]. Another important issue related to the excess molar volumes of aqueous ILs is the fact that for ILs with hydrophobic cations, the anion was the most important factor in defining the sign and magnitude of the excess molar volume.

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