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Excess Molar Volumes and Partial Molar Volumes of Binary Systems (Ionic Liquid + Methanol or Ethanol or 1-Propanol) at T = (298.15, 303.15 and 313.15) K

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ABSTRACT

Excess molar volumes have been evaluated from density measurements over the entire composition range for binary systems of an ionic liquid (IL) and an alcohol at T = (298.15, 303.15 and 313.15) K. The IL is 1-butyl-3-methylimidazolium methylsulphate $[BMIM]^+[MeSO_4]^-$ and the alcohols are methanol, ethanol or 1-propanol. The Redlich-Kister smoothing polynomial equation was used to fit the excess molar volume data and the partial molar volumes were determined from the Redlich-Kister coefficients. For all the systems studied, the excess molar volumes were negative over the entire composition range at all temperatures. The results are interpreted in terms of the alcohol chain length and the intermolecular interactions.

KEYWORDS

Density, excess molar volume, partial molar volume, ionic liquid, alcohol.

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1. Introduction

An ionic liquid (IL) is defined as a salt with a melting temperature below the boiling point of water. Most of the salts identified in the literature as ILs are liquid at room temperature, and often at substantially lower temperatures. They usually consist of a large asymmetric organic cation coupled with a generally smaller weakly-coordinating anion.

ILs are being explored as possible environmentally benign solvents because of their negligible vapour pressures and as potential replacement solvents for volatile organic compounds (VOCs) currently used in industry. Implementation of ionic liquids in industry could lead to a reduction in VOC emissions and to a more cost-effective use of starting materials because ionic liquids are recyclable.[1–3]

The other main benefits of ILs are favourable solvation behaviour, high stability to air and moisture, and a wide electrochemical window. For successful and large-scale use of ILs, an intensive and systematic investigation of their physico-chemical properties is necessary. The precise numerical values of these properties are of significance in the design and control of the chemical processes involving the ILs.[2]

In solutions of ionic liquids, the structure and interaction of ions determine the unique properties of these solutions.[2]

Thermodynamic properties, including activity coefficients at infinite dilution and excess molar volumes, V_m^E, are also required for the development of reliable predictive models for systems containing ionic liquids. To this end, a database of IL cation, anion and thermo-physical properties should be useful.[3]

In this work the V_m^E were determined for the ionic liquid, 1-butyl-3-methylimidazolium methylsulphate $[BMIM]^+[MeSO_4]^-$ and an alcohol (methanol, ethanol or 1-propanol) over the entire composition range at T = (298.15, 303.15 and 313.15) K. The results are discussed in terms of intermolecular interactions. The Redlich-Kister smoothing polynomial equation was used to fit the excess molar volume data. The partial molar volumes were calculated from the Redlich-Kister correlation coefficients.

This work is a continuation of our research group's work on the thermodynamic properties of ILs.[4–10] The objective is to contribute to a data bank of thermodynamic properties of binary mixtures of ILs and to investigate the relationship between the ionic structure of the IL and the density of the binary mixture, in order to establish principles for the molecular design of suitable ILs for chemical separation processes.

The structure of the ionic liquid used in this work is presented in Fig. 1.

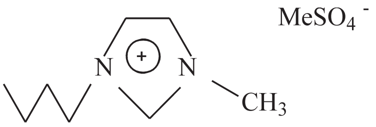

Figure 1 Structure of the IL (1-butyl-3-methylimidazolium methylsulphate).

2. Experimental

2.1. Materials

The chemicals, suppliers, purity, and the literature and experimental densities (ρ) are given in Table 1. The densities of the pure liquids and the mixtures were determined at T = (298.15, 303.15 and 313.15) K and at atmospheric pressure. The IL, methanol and ethanol were used without any further purification. 1-Propanol was first dried with magnesium turnings and then distilled before being used.[11] The purity of the pure solvents was also determined by comparison of the experimental density values with literature density values where available.[11]

The water content in all chemicals was determined by a Karl Fischer coulometer (Metrohm 831, Herisau, Switzerland). Mass percent water contents were 0.0024, 0.0016, 0.0061 and 0.0023 in the IL, methanol, ethanol and 1-propanol, respectively.

2.2. Apparatus and Procedure

The densities were measured with an Anton Paar (Graz, Austria) DMA 38 vibrating U-tube densimeter. The densimeter

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Table 1 Pure compound specifications: suppliers, purities, literature and experimental densities at *T* = (298.15, 303.15, and 313.15) K.

Chemical	Supplier	Purity/mole fraction	ρ/g cm^{-3}			
			Literature	Experimental		
			T = 298.15 K	*T* = 298.15 K	*T* = 303.15 K	*T* = 313.15 K
Methanol	Sigma-Aldrich	0.999	0.78637 [a]	0.7862	0.7836	0.7748
Ethanol	Riedel-de Haën	0.998	0.7852 [a]	0.7854	0.7821	0.7739
1- Propanol	Merck	0.995	0.79960 [a]	0.7994	0.7962	0.7884
$[\text{BMIM}]^+ [\text{MeSO}_4]^-$	Sigma- Aldrich	0.999	1.2124 [b]	1.2120	1.2023	1.1975

[a] Reference 11.
[b] Reference 3.

consists of a built-in thermostat controller capable of maintaining temperature precisely to ± 0.01 K and measuring density to ±0.0001 g cm^{-3}.

The binary mixtures were prepared by transferring the pure liquids via a syringe into stoppered bottles to prevent evaporation. An Ohaus (Pine Brook, NJ, USA) mass balance was used to determine the mass of each component. The mass balance has a precision of 0.0001 g. The mixtures were shaken in order to ensure complete homogeneity of the two compounds, since the ionic liquid is slightly viscous. To avoid formation of bubbles inside the vibrating tube of the densimeter, injection was done slowly. For a different temperature, the instrument had to be switched off and reset to the required temperature with the solution in the U-tube.

The densimeter was calibrated by measuring the density of ultra-pure water supplied by SH Calibration Service GmbH, Graz, Austria, and dried air at the same temperature.

The experimental technique was assessed by determining the excess molar volumes for the test system (toluene + cyclohexane) at *T* = 298.15 K and comparing them with the literature values.[13] The differences between experimental and literature V_m^E were within the experimental error. The experimental uncertainty in V_m^E is ± 0.007 cm^3 mol^{-1}.[12]

3. Results and Discussion

The excess molar volumes of the studied systems were calculated from the experimental density values, using Equation (1)

$$V_m^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \qquad (1)$$

where x_1 and x_2 are mole fractions, M_1 and M_2 are molar masses, ρ_1 and ρ_2 are the densities of the pure components, where 1 and 2 refer to the IL and the alcohol respectively, and ρ is the density of the mixture.

The Redlich-Kister polynomial (a smoothing equation) was used to fit the calculated excess molar volumes, using a commercial software program (MathCAD) (www.mathcad.com). The error between the experimental and the calculated excess molar volume values and the coefficients of the smoothing polynomial equation (2) was determined.

$$V_m^E/\text{cm}^3\ \text{mol}^{-1} = (1-x)\sum_{i=0}^{N} A_i(2x-1)^i \qquad (2)$$

where A_i is the polynomial coefficient and *N* is the polynomial degree. The densities and excess molar volumes of the systems are given in Tables 2 to 4.

The graphs of excess molar volumes for the binary systems studied versus the mole fraction of the IL over the whole compo-

Table 2 Densities and excess molar volumes for ionic liquid (x_1) + methanol (x_2) at *T* = (298.15, 303.15 and 313.15) K.

x_1	ρ/g cm^{-3}	V_m^E/cm^3 mol^{-1}	x_1	ρ/g cm^{-3}	V_m^E/cm^3 mol^{-1}
$[\text{BMIM}]^+[\text{MeSO}_4]^-$ (x_1) + methanol (x_2)					
T = 298.15 K					
0.0533	0.8905	–0.308	0.5589	1.1628	–0.936
0.1131	0.9638	–0.644	0.6518	1.1775	–0.771
0.1936	1.0329	–0.914	0.7169	1.1858	–0.617
0.2651	1.0748	–1.057	0.7935	1.1944	–0.432
0.3228	1.1002	–1.100	0.8510	1.1997	–0.291
0.4386	1.1371	–1.094	0.9206	1.2058	–0.147
T = 303.15 K					
0.0533	0.8841	–0.407	0.5589	1.1575	–1.321
0.1131	0.9596	–0.695	0.6518	1.1717	–1.171
0.1936	1.0294	–1.101	0.7169	1.1794	–0.987
0.2651	1.0713	–1.318	0.7935	1.1871	–0.754
0.3228	1.0964	–1.406	0.8510	1.1921	–0.571
0.4386	1.1325	–1.444	0.9206	1.1975	–0.353
T = 313.15 K					
0.0533	0.8740	–0.321	0.5589	1.1535	–1.531
0.1131	0.9504	–0.629	0.6518	1.1680	–1.405
0.1936	1.0207	–1.022	0.7169	1.1758	–1.227
0.2651	1.0630	–1.225	0.7935	1.11833	–0.957
0.3228	1.0890	–1.355	0.8510	1.1880	–0.720
0.4386	1.1270	–1.520	0.9206	1.1930	–0.424

Table 3 Densities and excess molar volumes for ionic liquid (x_1) + ethanol (x_2) at T = (298.15, 303.15 and 313.15) K.

x_1	ρ/g cm^{-3}	V_m^E/cm^3 mol^{-1}	x_1	ρ/g cm^{-3}	V_m^E/cm^3 mol^{-1}
$[BMIM]^+[MeSO_4]^-$ (x_1) + ethanol (x_2)					
T = 298.15 K					
0.0738	0.8814	–0.202	0.6223	1.1533	–0.524
0.1547	0.9573	–0.403	0.7231	1.1731	–0.415
0.2046	0.9950	–0.508	0.8249	1.1896	–0.281
0.3165	1.0560	–0.615	0.8877	1.1983	–0.173
0.4056	1.0926	–0.647	0.9424	1.2052	–0.079
0.5095	1.1256	–0.619			
T = 303.15 K					
0.0738	0.8771	–0.214	0.6223	1.1460	–0.698
0.1547	0.9520	–0.418	0.7231	1.1652	–0.568
0.2046	0.9893	–0.537	0.8249	1.1810	–0.385
0.3165	1.0500	–0.713	0.8877	1.1895	–0.276
0.4056	1.0862	–0.775	0.9424	1.1960	–0.141
0.5095	1.1187	–0.767			
T = 313.15 K					
0.0738	0.8694	–0.236	0.6223	1.1414	–0.844
0.1547	0.9445	–0.427	0.7231	1.1609	–0.729
0.2046	0.9819	–0.533	0.8249	1.1768	–0.535
0.3165	1.0437	–0.767	0.8877	1.1851	–0.377
0.4056	1.0806	–0.869	0.9424	1.1915	–0.210
0.5095	1.1134	–0.859			

sition range are shown in Figs. 2 to 4.

The excess molar volumes for all the systems studied are negative for the entire composition range and at all temperatures, which indicates that a more efficient packing and/or attractive interaction occurred when the ionic liquid and the alcohol were mixed.[12]

From Figs. 2–4 in can be seen that the curves are slightly skewed to the alcohol-rich region, similar to the results obtained by Pereiro[1] and Domanska.[3] The skewing of the curves is due to the greater differences in the molar volumes of the ionic liquid and the alcohol.[14]

The excess molar volumes become less negative in the order methanol < ethanol < 1-propanol. The $V_{m,min}^E$ values at T = 298.15 K are –1.100 cm^3 mol^{-1} at x_1 = 0.3228, –0.647 cm^3 mol^{-1} at x_1 = 0.4056 and –0.235 cm^3 mol^{-1} at x_1 = 0.4756, for methanol, ethanol or 1-propanol, respectively. The $V_{m,min}^E$ and the comparison of the results obtained in this work with those obtained by Pereiro[1] and Domanska[3] are shown in Table 5. Our results are close to those of Domanska[3] but less close to those of Pereiro.[1] The minimum of the V_m^E curve shifted from methanol (0.3228) to 1-propanol (0.4756). This trend in V_m^E values is attributed to greater association between the IL and the alcohol and to a pack-

Table 4 Densities and excess molar volumes for ionic liquid (x_1) + 1-propanol (x_2) at T = (298.15, 303.15 and 313.15) K.

x_1	ρ/g cm^{-3}	V_m^E/cm^3 mol^{-1}	x_1	ρ/g cm^{-3}	V_m^E/cm^3 mol^{-1}
$[BMIM]^+[MeSO_4]^-$ (x_1) + 1-propanol (x_2)					
T = 298.15 K					
0.1011	0.8978	–0.099	0.5862	1.1293	–0.223
0.1258	0.9175	–0.121	0.6708	1.1508	–0.190
0.2100	0.9752	–0.176	0.7775	1.1740	–0.139
0.2639	1.0060	–0.205	0.8542	1.1885	–0.100
0.3556	1.0500	–0.230	0.9168	1.1897	–0.064
0.4756	1.0957	–0.235	0.9600	1.1992	–0.059
T = 303.15 K					
0.1011	0.8933	–0.094	0.5862	1.11212	–0.227
0.1258	0.9128	–0.124	0.6708	1.1423	–0.193
0.2100	0.9698	–0.194	0.7775	1.1650	–0.133
0.2639	1.0001	–0.221	0.8542	1.1792	–0.090
0.3556	1.0434	–0.248	0.9168	1.1897	–0.055
0.4756	1.0883	–0.251	0.9600	1.1964	–0.023
T = 313.15 K					
0.1011	0.8858	–0.097	0.5862	1.1156	–0.257
0.1258	0.9054	–0.129	0.6708	1.1371	–0.248
0.2100	0.9626	–0.187	0.7775	1.1600	–0.179
0.2639	0.9931	–0.213	0.8542	1.1743	–0.124
0.3556	1.0368	–0.246	0.9168	1.1848	–0.067
0.4756	1.0822	–0.260	0.9600	1.1916	–0.037

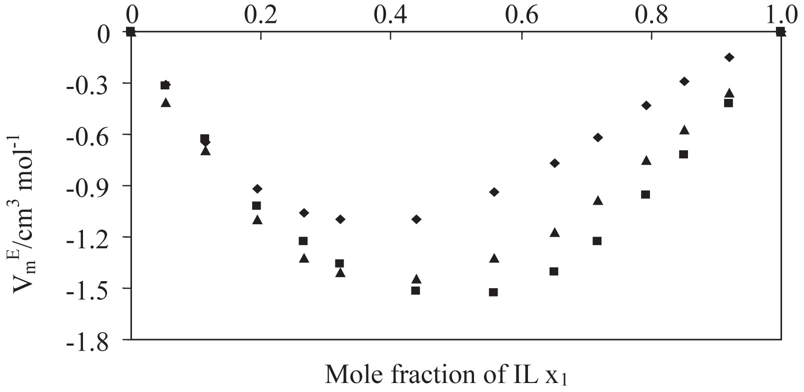

Figure 2 Plot of excess molar volumes V_m^E of binary mixtures of [BMIM]$^+$[MeSO$_4$]$^-$ (x_1) + methanol (x_2) against mole fraction of ionic liquid: ◆ at T = 298.15 K; ▲ at T = 303.15 K; ■ at T = 313.15 K.

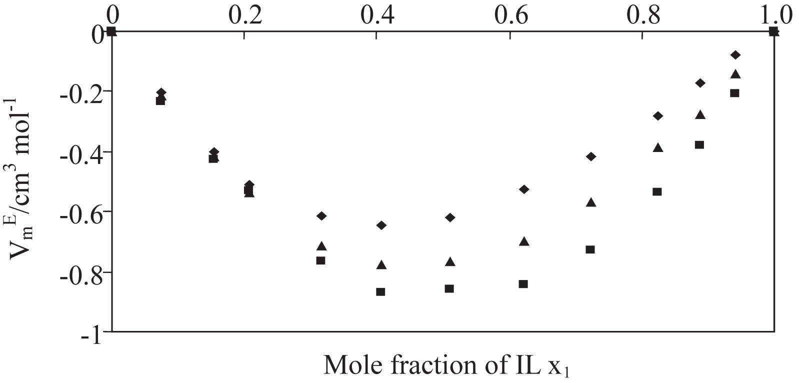

Figure 3 Plot of excess molar volumes V_m^E of binary mixtures of [BMIM]$^+$[MeSO$_4$]$^-$ (x_1) + ethanol (x_2) against mole fraction of ionic liquid: ◆ at T =298.15 K; ▲ at T = 303.15 K; ■ at T = 313.15 K.

ing effect; the latter effect decreases with an increase in alcohol chain length. The interactions between the IL and the alcohol are stronger than in the pure components, resulting in the V_m^E values being negative due to the size of the alcohol molecule, which allows for more efficient packing with the larger IL molecule.[1]

From the results, the V_m^E values increase with increase in the alcohol chain length for a specific temperature and decrease with an increase in temperature in the same order as above.

Pereiro determined V_m^E of the binary mixtures of [BMIM]$^+$[MeSO$_4$]$^-$ + ethanol and found that the V_m^E decreased when the temperature was increased for the system studied.[1] Domanska determined V_m^E of the binary mixtures of [BMIM]$^+$[MeSO$_4$]$^-$ + methanol and ethanol and found that the V_m^E increased with an increase in alcohol chain length for the system studied,[3] in both cases similar to our results.

The standard deviation $\sigma(V_m^E)$ is defined as:

$$\sigma(V_m^E) = \left[\sum_{i=1}^{N} (V_m^E \exp - V_m^E \mathrm{cal})^2/(n-k)\right]^{1/2} \qquad (3)$$

where n is the number of experimental points and k is the number of coefficients used in the Redlich-Kister correlation.[14] The standard deviations obtained for binary mixtures (ionic liquid + methanol or ethanol or 1-propanol) at T = (298.15, 303.15 and 313.15) K are presented in Table 6, together with the correlation coefficients.

The partial molar volume is the contribution that a component makes to the total volume of the mixture. The partial molar volume can be a positive or a negative quantity although the molar volume can only be positive. The partial molar volumes of component 1 in a binary mixture will vary as the composition of

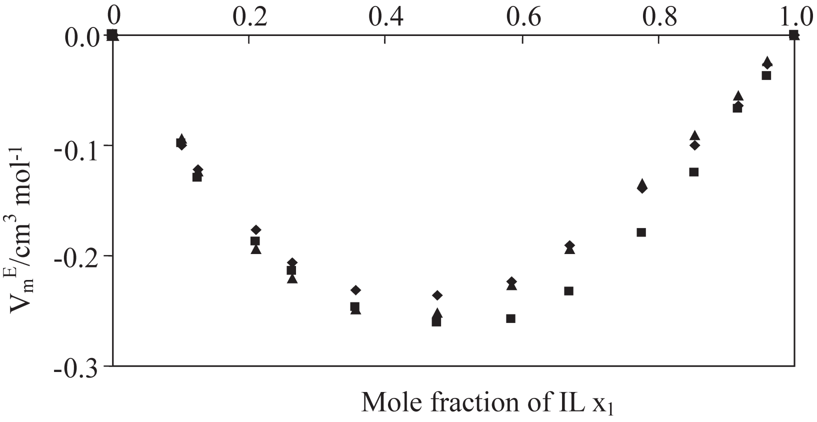

Figure 4 Plot of excess molar volumes V_m^E of binary mixtures of [BMIM]$^+$[MeSO$_4$]$^-$ (x_1) + 1-propanol (x_2) against mole fraction of ionic liquid: ◆ at T = 298.15 K; ▲ at T = 303.15 K; ■ at T = 313.15 K.

Table 5 The minimum excess molar volumes, V_m^E, at T = (298.15, 303.15 and 313.15) K and the comparison of the results obtained in this work with those obtained by Pereiro[1] and by Domanska.[3]

	System	$V^E_{m,min}$/cm^3 mol^{-1}		
		T = 298.15 K	T = 303.15 K	T = 313.15 K
Pereiro [a]	$[BMIM]^+[MeSO_4]^-$ + ethanol	–0.706	–0.746	
Domanska [b]	$[BMIM]^+[MeSO_4]^-$ + methanol	–1.133		
Domanska [b]	$[BMIM]^+[MeSO_4]^-$ + ethanol	–0.662		
This work	$[BMIM]^+[MeSO_4]^-$ + methanol	–1.100	–1.444	–1.531
	$[BMIM]^+[MeSO_4]^-$ + ethanol	–0.647	–0.775	–0.869
	$[BMIM]^+[MeSO_4]^-$ + 1-propanol	–0.235	–0.251	–0.260

[a] Reference 1.
[b] Reference 3.

Table 6 The coefficients A_i, partial molar volumes at infinite dilution and standard deviations obtained for ionic liquid $[BMIM]^+[MeSO_4]^-$ + (a) methanol, (b) ethanol, (c) 1-propanol at T = (298.15, 303.15 and 313.15) K.

(a)

T/ K	A_o	A_1	A_2	A_3	A_4	$V^\infty_{m,1}$/cm^3 mol^{-1}	$V^\infty_{m,2}$/cm^3 mol^{-1}	σ/cm^3 mol^{-1}
298.15	–4.104	–2.585	–0.545	–0.152	0.663	–6.723	–1.249	0.011
303.15	–5.647	–2.158	–0.452	0.681	–0.084	–7.660	–4.706	0.021
313.15	–6.2	–0.154	0.103	–0.572	0.267	–6.556	–5.104	0.017

(b)

298.15	–2.473	–1.035	–0.475	0.306	0.993	–2.684	–1.226	0.005
303.15	–3.108	–0619	0.197	0.512	0.164	–2.854	–2.64	0.006
313.15	–3.551	0.095	0.146	0.427	–0.193	–3.076	–4.12	0.017

(c)

298.15	–0.908	–0.099	–0.676	–0.399	1.424	–0.658	0.338	0.025
303.15	–0.975	–0.309	–0.368	–0.03	1.035	–0.647	0.031	0.013
313.15	–1.028	0.149	–0.844	–0.637	1.697	–0.663	0.313	0.018

the binary mixture changes because the immediate environment surrounding molecules of component 1 changes. The intermolecular forces acting between molecules therefore changes, resulting in a change in the partial molar volumes.

The partial molar volume of component 1 is given by:

$$V^\infty_{m,1} = \left(\frac{\partial V^E_m}{\partial n_1}\right)_{p,T,n_2} = \left(\frac{\partial V^E_m}{\partial x_1}\right)_{p,T,n_2} \text{cm}^3\,\text{mol}^{-1} \qquad (4)$$

where $\left(\frac{\partial V^E_m}{\partial x_1}\right)$ is related to the Redlich-Kister polynomial given in equation (2).

The partial molar volumes at infinite dilution, $V^\infty_{m,i}$, were calculated from the Redlich-Kister polynomial values as follows:

$$V^E_{m,1} = [A_0 + A_1 + A_2 + A_3 + A_4] \qquad (5)$$

and

$$V^E_{m,2} = [A_0 - A_1 + A_2 - A_3 + A_4] \qquad (6)$$

where A_i are the coefficients of expansion of the Redlich-Kister polynomial.[15]

The partial molar volumes at infinite dilution, $V^\infty_{m,1}$, increase as the alcohol chain length increases. The results obtained for $V^\infty_{m,1}$ are all negative at all temperatures. The partial molar volume data become less negative in the following order: methanol < ethanol < 1-propanol. The results obtained for $V^\infty_{m,2}$ are negative at all temperature for the (ionic liquid + methanol or ethanol) system, and are positive at all temperatures for the (ionic liquid + 1-propanol) system.[14] The partial molar volumes at infinite dilution for the IL, $V^\infty_{m,1}$, are more negative than the partial molar volumes at infinite dilution, $V^\infty_{m,2}$, of the alcohol. This is because not all hydrogen bonds are broken with a small amount of IL present.[3] For the (IL+1-propanol) system the partial molar volumes at infinite dilution for $V^\infty_{m,2}$ of the alcohol are positive at all temperatures, indicating that the dissociation effect is greater than any association effect, i.e. the hydrogen bonding in the pure state for 1-propanol is weaker than for methanol and ethanol.

The $V^\infty_{m,1}$ and $V^\infty_{m,2}$ results are presented in Table 6(a–c).

4. Conclusions

The results obtained from this study reveal that the negative V_m^E values observed for ($[BMIM]^+[MeSO_4]^-$ + methanol or ethanol or 1-propanol) mixtures can be explained by the strong hydrogen bonding effects between unlike molecules. An increase in alcohol chain length resulted in an increase in the values of V_m^E, while an increase in temperature resulted in a decrease in V_m^E.

The partial molar volumes at infinite dilution, $V^\infty_{m,1}$ and $V^\infty_{m,2}$, of the ionic liquid and the alcohol indicate the strength of pure component hydrogen bonds. An increase in $V^\infty_{m,1}$ values was observed with an increase in alcohol chain length.

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