



Effect of the temperature on the physical properties of the pure ionic liquid 1-ethyl-3-methylimidazolium methylsulfate and characterization of its binary mixtures with alcohols



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ABSTRACT

Experimental density, speed of sound, refractive index and viscosity data of the pure ionic liquid 1-ethyl-3-methylimidazolium methylsulfate, [EMim][MSO₄], were measured as a function of temperature from $T = (293.15 \text{ to } 343.15) \text{ K}$, every 5 K, and atmospheric pressure. Density, speed of sound and refractive index data were satisfactorily correlated with a linear equation, while viscosity data were fitted to the Vogel–Fulcher–Tamman (VFT) equation. Besides, from the experimental density values, the thermal expansion coefficient, α , was calculated. Furthermore, density and speed of sound for the binary systems of {methanol, or ethanol, or 1-propanol, or 2-propanol, or 1-butanol, or 1-pentanol + [EMim][MSO₄]} were experimentally determined over the whole composition range, at $T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$ and $p = 0.1 \text{ MPa}$. These properties were used to calculate the corresponding excess molar volumes and excess molar isentropic compressions, which were satisfactorily fitted to the Redlich–Kister equation. Finally, a comparison with available literature data was also carried out and the obtained results are discussed in terms of interactions and structure factors in these binary mixtures.

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1. Introduction

The use of ionic liquids (ILs) in separation processes is receiving increasing attention as a novel alternative to conventional organic solvents due to their unique properties, such as high thermal stability, large liquid-state temperature range, high ionic conductivity, negligible vapour pressure, non-flammability and miscibility with compounds having very wide range of polarities. Besides, they are known as “design solvents” because it is possible to perform different combinations of anion–cation which lead to a large number of ILs with different physico-chemical properties. This versatility of ILs presents multiple applications in different fields. The design of industrial processes and new products based on ILs can only be achieved when their thermophysical properties are adequately known. Furthermore, it is interesting to study the interactions between ILs with other molecular solvents, among which are alcohols. These data are relevant for modelling purposes as thermodynamic models are very necessary in the stage of process design. Therefore, the study of the interactions of the studied IL

with several alcohols was carrying out in this work, with the aim to understand better the behaviour of binary mixtures {ILs (1) + alcohol (2)}. Several alcohols were selected as example of molecules with hydroxyl as functional group.

In the last years, alhylsulfate-based ILs are being widely studied [1–8]. The pure IL 1-ethyl-3-methylimidazolium methylsulfate, [EMim][MSO₄], was chosen taking into account the following characteristics: (i) it is easily synthesized in an atom-efficient and halide-free way at reasonable cost, (ii) it is a compound with a low melting point and relatively low viscosity, and (iii) it presents an anion with a low toxicity in comparison with other ILs. Taking into account all these aspects, the physical properties (density, speed of sound, refractive index and dynamic viscosity) have been determined for pure [EMim][MSO₄] at $T = (293.15 \text{ to } 343.15) \text{ K}$, every 5 K, and atmospheric pressure. Experimental density data were used to calculate the thermal expansion coefficient. Density, speed of sound and refractive index data for the pure IL were fitted to a linear equation while the Vogel–Fulcher–Tamman (VFT) equation [9–11] was used to correlate the experimental viscosity data. On the other hand, densities and speeds of sound for the binary mixtures {methanol, or ethanol, or 1-propanol, or 2-propanol, or 2-butanol, or 1-pentanol + [EMim][MSO₄]} were also measured at

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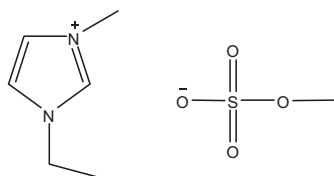


FIGURE 1. Structure of the ionic liquid 1-ethyl-3-methylimidazolium methylsulfate.

$T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$. These experimental data were used to calculate excess molar volumes, and excess molar isentropic compressions, whose values were fitted to the Redlich–Kister equation [12].

To our knowledge, five works about physical properties of the pure IL studied in this work [1–5] and its binary mixtures with alcohols [2] were found in the literature.

2. Experimental section

2.1. Chemicals

The pure ionic liquid [EMim][MSO₄] was supplied by Iolitec GmbH (Germany) while the studied alcohols were purchased from different suppliers. The ionic structure of the studied ionic liquid is shown in figure 1. The supplier, purity and experimental density and refractive index values of each component used in this work are reported in table 1, at $T = 298.15 \text{ K}$ and atmospheric pressure. Density and refractive data found in literature [1–5,13–18] for the studied chemicals are also included in this table in order to compare the experimental data reported in this work with those previously published by other authors. In table 1 it can be observed that the properties data for pure alcohols agree quite well with the literature values, while some discrepancies were observed for density data of pure IL, which will be discussed in the following section.

Due to the significant influence of the water and volatile compounds content over the physical properties of the IL and its binary mixtures with alcohols, it is necessary to reduce them to negligible

values. Therefore, the pure ionic liquid was dried with stirring at moderate temperature ($T = 343.15 \text{ K}$) and under vacuum ($p = 0.2 \text{ Pa}$) for at least 48 h prior to its use. Once dried, the water content of [EMim][MSO₄] was 501 ppm, which was determined using the Karl Fischer method.

Alcohols were degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich. Then, they were kept in bottles under inert atmosphere (argon gas) without any other treatment.

2.2. Apparatus and procedure

Density and speed of sound were measured using an Anton Paar DSA-5000M digital vibrating tube densimeter with an uncertainty of $\pm 3 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ and $\pm 1 \text{ m} \cdot \text{s}^{-1}$, respectively. This equipment has a temperature controller that keeps the samples at working temperature with an uncertainty of $\pm 0.01 \text{ K}$. This densimeter was calibrated by measuring Millipore quality water and air, according to the manual instructions. Moreover, the equipment automatically corrects the effect of viscosity on density, and also detects the presence of bubbles in the cell.

The experimental refractive indices were determined using an automatic refractometer Abbemat-HP Dr. Kernchen with an uncertainty in the measurements of $\pm 4 \cdot 10^{-5}$. The apparatus was checked by measuring Millipore quality water and pure solvents before each series of measurements according to the manual of instructions. This equipment also has a temperature controller that keeps the samples at working temperature, and its uncertainty is $\pm 0.01 \text{ K}$.

Kinematic viscosities were determined with an automatic viscosimeter Lauda PVS1 using a Ubbelohde microcapillary of $0.7 \cdot 10^{-3} \text{ m}$ diameter with an uncertainty in the experimental measurements of $\pm 0.03 \text{ mPa} \cdot \text{s}$. The microcapillaries were maintained in a D20KP LAUDA thermostat with an uncertainty of $\pm 0.01 \text{ K}$. The equipment is connected to a control unit PVS1 (Processor Viscosity System) that is a PC-controlled instrument for the precise measurements of the fall time, using standardized glass capillaries. The microcapillaries were calibrated and credited by the company.

The water content of the pure ionic liquid was measured with a Mettler Toledo C20 Coulometric KF Titrator using Coulomat CG and

TABLE 1
Supplier, purity, density, ρ , and refractive index, n_D , for the pure components at $T = 298.15 \text{ K}$ and atmospheric pressure.

Compound	Supplier	Purity, mass fraction	$\rho / (\text{g} \cdot \text{cm}^{-3})$		n_D	
			Exp.	Lit.	Exp.	Lit.
[EMim][MSO ₄]	Iolitec	>0.990	1.28081	1.2629 ^a 1.2880 ^b 1.2861 ^c 1.2860 ^d 1.2878 ^e	1.48125	n.a.
methanol	Panreac	>0.999	0.78710	0.7870 ^f	1.32649	1.32652 ^g
ethanol	Merck	>0.999	0.78552	0.78533 ^h	1.35907	1.35941 ^g
1-propanol	Sigma-Aldrich	0.999	0.80050	0.80009 ^h	1.38286	1.38370 ^g
2-propanol	Prolabo	0.999	0.78167	0.78126 ^g	1.37523	1.3752 ^g
2-butanol	Fluka	≥ 0.995	0.80282	0.8028 ⁱ	1.39487	1.3949 ^f
1-pentanol	Aldrich	≥ 0.99	0.81099	0.81094 ^j	1.40774	1.4077 ^k

^a [1].

^b [2].

^c [3].

^d [4].

^e [5].

^f [13].

^g [14].

^h [15].

ⁱ [16].

^j [17].

^k [18].

Coulomat AG, supplied by Sigma–Aldrich, as cathodic and anodic titrants, respectively.

Finally, all binary mixtures were prepared by weighing using a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3 \cdot 10^{-4}$ g. The uncertainties on the mole fraction of the prepared mixtures were estimated to be $1 \cdot 10^{-4}$. In order to avoid variations in composition due to evaporation of solvent or pickup of water by the ionic liquid, all samples were prepared immediately prior to measurements into stoppered bottles.

For the determination of the heat capacity of the pure IL, the sapphire method was the adopted technique, using a Mettler Toledo DSC, model DSC822^e, with Mettler-Toledo STAR^e software, version 9.3, with an uncertainty in experimental measurements of heat capacity of $\pm 1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and an uncertainty in temperature of $\pm 0.1 \text{ K}$. These data were measured in order to calculate the excess molar isentropic compressions for the binary mixtures {alcohol + ionic liquid} at the studied temperatures.

3. Results and discussion

3.1. Pure ionic liquid

The physical properties, density, ρ , speed of sound, u , refractive index, n_D , and kinematic viscosity, ν , were experimentally measured for pure [EMim][MSO₄] ionic liquid from $T = (293.15 \text{ to } 343.15) \text{ K}$, every 5 K, and atmospheric pressure. The obtained results are summarized in [table S1, available as Supporting Information](#).

A linear relationship was used to express the dependence with temperature for density, speed of sound and refractive index:

$$z = a + bT, \quad (1)$$

TABLE 2

Fitting parameters of equation (1) together with the correlation coefficient squared, R^2 , and the standard relative deviation, σ , for the density, ρ , speed of sound, u , and refractive index, n_D for the pure ionic liquid [EMim][MSO₄].

	a	b	R^2	σ
$\rho/\text{g} \cdot \text{cm}^{-3}$	1.4823	$-6.760 \cdot 10^{-4}$	0.9999	$5.06 \cdot 10^{-5}$
$u/\text{m} \cdot \text{s}^{-1}$	2447	-2.3191	0.9998	$2.69 \cdot 10^{-4}$
n_D	1.5587	$-2.598 \cdot 10^{-4}$	0.9999	$5.21 \cdot 10^{-5}$

where z is ρ , u or n_D , T is the absolute temperature in K, and a and b are the fitting parameters, given in [table 2](#). Standard relative deviation, σ , of the experimental physical properties data from their fitting values was calculated as:

$$\sigma = \left\{ \sum_i^{n_{\text{dat}}} \left(\frac{(Z - Z_{\text{cal}})}{Z_{\text{cal}}} \right)^2 / n_{\text{dat}} \right\}^{1/2}, \quad (2)$$

where z and z_{cal} are the values of experimental and calculated physical property, respectively, and n_{dat} is the number of the experimental points. The σ values are also shown in [table 2](#). In [figure 2](#), the influence of temperature on these physical properties is plotted. As it can be observed, all the studied properties decrease as the temperature increases.

The change of the molar volume with temperature can be expressed through the coefficient of thermal expansion, $\alpha_p = -(\partial \ln \rho / \partial T)_p = -(1/\rho)(\partial \rho / \partial T)_p$. The derivative of ρ with respect to temperature is a constant, according to equation (1). The inverse of ρ is a function of temperature, which for this ionic liquid is rather small (see [table 2](#)). Therefore, the thermal coefficient is dependent on temperature, but the change of its value is so small in the studied range, that it can be considered negligible and accordingly the thermal coefficient constant. It can be calculated

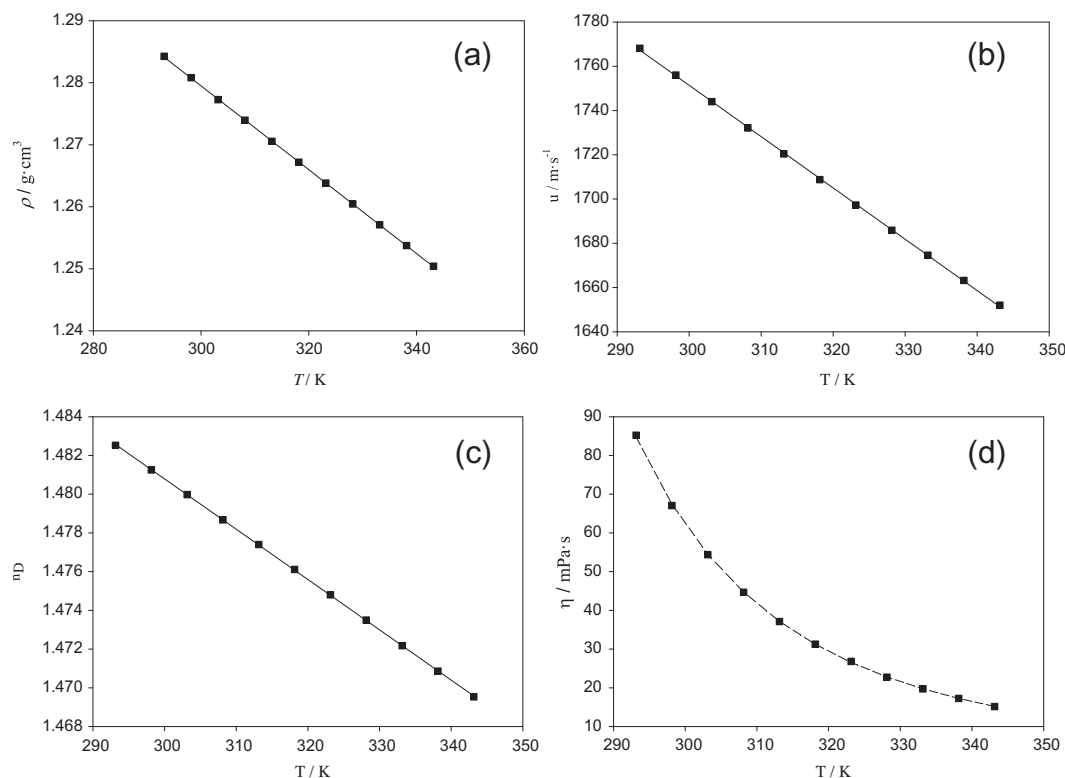


FIGURE 2. Physical properties of pure [EMim][MSO₄] ionic liquid against temperature: (a) density, ρ , (b) speed of sound, u , (c) refractive index, n_D , and (d) dynamic viscosity, η . Symbols: (■) this work, (—) linear fitting and (- - -) VFT equation.

from the experimental density data over the temperature range studied, being its value of $5.33 \cdot 10^{-4} \text{ K}^{-1}$. This value agrees with the data previously reported by Wang *et al.* [1] and Tomé *et al.* [2], whose values are $5.28 \cdot 10^{-4}$ and $5.92 \cdot 10^{-4} \text{ K}^{-1}$, respectively. The obtained coefficient of thermal expansion for [EMim][MSO₄] is in similar order of magnitude than other ILs previously investigated, suggesting a thermal behaviour practically independent of the ionic nature and temperature [19,20].

Furthermore, the experimental kinematic viscosities were used to calculate the corresponding dynamic viscosities, η , using the following equation:

$$\eta = \nu \cdot \rho. \quad (3)$$

The dynamic viscosity values, η , were fitted using the Vogel–Fulcher–Tamman (VFT) equation [9–11]:

$$\eta = A \cdot \exp(k/(T - T_0)), \quad (4)$$

where A (in $\text{mPa} \cdot \text{s}$), k (in K) and T_0 (in K) are adjustable parameters. The values of these parameters are 0.1688, 813.00 and 162.43, respectively. The standard relative deviation, σ , calculated from equation (2) is 0.004 indicating that the VFT equation provides a good description of the experimental data. This result is the expected since, this equation provides the best fit for those ionic liquids that present cations with certain symmetry in its structure [19,21], as in our case.

As shown in figure 2, the temperature dependence of the dynamic viscosity values presents convex curve profile. It can also be observed that the dynamic viscosity decreases significantly with temperature at low temperatures and achieves a moderate descent when the temperature increases.

A comparison of the experimental data with those previously reported by other authors was carried out. From figure 3a, it is possible to observe that our experimental density data are in agreement with data obtained by other authors [1–5], being the maximum deviation of 0.62% for the reported data by Tomé *et al.* [2]. Regarding the density data reported by Wang *et al.* [1], a high deviation is observed (1.43%). These differences can be attributed to impurities in the IL such as water which decrease density values. Moreover, a comparison of viscosity data was also included in figure 3b. As it can be seen in this figure, the viscosity data reported by Costa *et al.* [4] present larger differences with our experimental data at low temperatures, while an increase of temperature decreases these differences. A maximum deviation of 17.6% was observed at $T = 298.15 \text{ K}$.

Finally, the molar isobaric heat capacities, C_p , for [EMim][MSO₄], which are necessary to calculate the excess molar isentropic com-

pressibility, $K_{S,m}^E$, were determined at $T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$, through a thermal analysis. The obtained values are $(331.48, 340.77 \text{ and } 346.99) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively. Unlike the other physical properties studied in this work, C_p values increase with the temperature. This result agrees with other results found in the literature [22–25].

3.2. Binary mixtures

Prior to the measurements of density, ρ and speed of sound, u , of the binary mixtures [EMim][MSO₄] with methanol, ethanol, 1-propanol, 2-propanol, 2-butanol and 1-pentanol, several mixtures were prepared in order to determine the miscibility range. The obtained results show that [EMim][MSO₄] is completely miscible with all the studied alcohols.

Values of the density, ρ , and speed of sound, u , of the binary mixtures {alcohol (1) + [EMim][MSO₄]} at $T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$ and atmospheric pressure are listed in tables S2–S7, included as Supporting Information.

The experimental density data were used to calculate the corresponding excess molar volumes, V^E , which were obtained using the following expression:

$$V^E = V_m - \sum_i x_i V_i^*, \quad (5)$$

where V_m is the molar volume of the mixture, and x_i and V_i^* represent the molar fraction and the molar volume of component i , respectively.

Furthermore, using the experimental density and speed of sound data for the studied mixtures, the values of the isentropic compressibility, κ_s , were obtained by the Laplace equation:

$$\kappa_s = -V_m^{-1} (\partial V_m / \partial p)_S = \rho^{-1} u^{-2} = V_m / (M_m u^2), \quad (6)$$

where M_m is the molar mass of the mixture.

To achieve agreement with the other thermodynamic quantities, it is appropriate to shift from the volume-intensive κ_s to the mole-intensive quantity $K_{S,m}$, [26,27] calculated as follows:

$$K_{S,m} = -(\partial V_m / \partial p)_S = V_m \kappa_s = V_m^2 / (M_m u^2), \quad (7)$$

where $K_{S,m}$ is the molar isentropic compression.

The excess molar isentropic compression, $K_{S,m}^E$, is obtained from the following equation:

$$K_{S,m}^E = K_{S,m} - K_{S,m}^{id}, \quad (8)$$

where $K_{S,m}^{id}$ is defined by the approach developed by Benson and Kiyohara [28]:

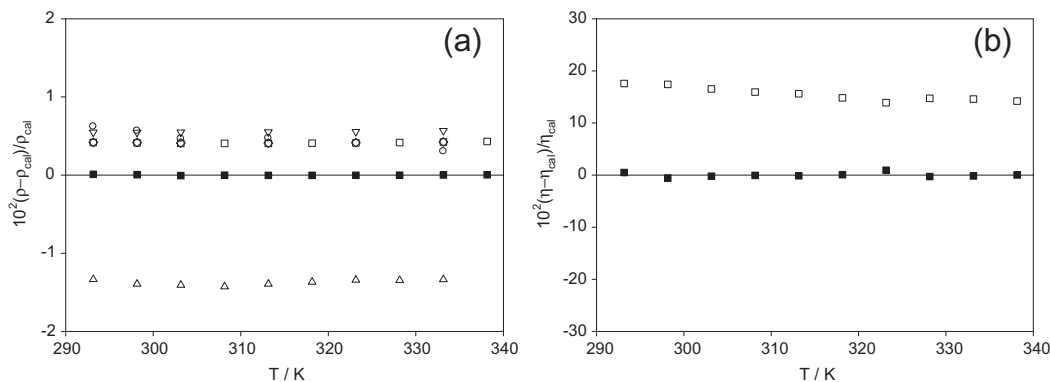


FIGURE 3. (a) Relative deviations between the density data obtained in this work using equation (1), ρ_{cal} , and reported in the literature, ρ , as a function of temperature, (b) relative deviations between the viscosity data obtained in this work using VFT equation, η_{cal} , and reported in the literature, η , as function of temperature. Symbols: (■) this work, (△) from reference [1]; (○) from reference [2], (◇) from reference [3], (□) from reference [4], (▽) from reference [5].

$$K_{S,m}^{id} = \sum_i x_i \left[K_{S,i}^* + T \frac{(E_{p,i}^*)^2}{C_{p,i}^*} \right] - T \left[\frac{\left(\sum_i x_i E_{p,i}^* \right)^2}{\sum_i x_i C_{p,i}^*} \right], \quad (9)$$

where $K_{S,i}^*$ is the product of the molar volume, V_i^* , and the isentropic compressibility, $\kappa_{S,i}^*$, of the pure component i . The molar isobaric expansion of pure component i , $E_{p,i}^*$, is the product of the molar volume and the coefficient of thermal expansion, $\alpha_{p,i}$, and $C_{p,i}^*$ is the molar isobaric heat capacity of the pure component i .

As commented above, the $\alpha_{p,i}$ for [EMim][MSO₄] ionic liquid was considered a temperature-independent constant and its value is $5.33 \cdot 10^{-4} \text{ K}^{-1}$, while the $C_{p,i}^*$ data were experimentally determined at $T = (288.15, 298.15 \text{ and } 308.15) \text{ K}$ and they were previously reported in the above section. For the studied alcohols, the values for $\alpha_{p,i}$ and $C_{p,i}^*$ were taken from literature [13]. The calcu-

lated values of excess molar volumes, V^E , and excess molar isentropic compression, $K_{S,m}^E$, are also included in tables S2–S7, included as Supporting Information.

The binary excess properties at the studied temperatures were satisfactorily fitted to a Redlich–Kister type equation [12]:

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^M B_p (x_i - x_j)^p, \quad (10)$$

where ΔQ_{ij} is the excess property, x is the mole fraction, B_p is the fitting parameter and M is the degree of the polynomial expansion, which was optimized using the F -test [29]. The corresponding fitting parameters of the Redlich–Kister equation for the studied temperatures, together with the corresponding standard relative deviations, σ , are given in tables 3–5.

TABLE 3

Adjustable parameters of the Redlich–Kister equation (equation (10)) and standard relative deviations, σ , for the different properties of the binary {alcohol (1) + [EMim][MSO₄] (2)} at $T = 288.15 \text{ K}$.

Excess property	B_0	B_1	B_2	B_3	B_4	σ
<i>Methanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−3.353	−2.303	−1.232	−2.425	−2.759	0.057
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0378	−0.0269	−0.0173	−0.0327	−0.0300	0.022
<i>Ethanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−3.203	−1.341	−1.481	−1.091	−0.233	0.029
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0428	−0.0234	−0.0121	−0.0151	−0.0124	0.014
<i>1-Propanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−2.376	0.010	−0.063	−0.442	−1.209	0.022
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0347	−0.0115	−0.0060	−0.0076	−0.0059	0.012
<i>2-Propanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−3.113	0.147	0.158	−0.991	−1.357	0.019
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0466	−0.0162	−0.0088	−0.0106	−0.0071	0.010
<i>2-Butanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−1.696	1.128	−0.473	−0.851	−0.722	0.044
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0370	−0.0071	−0.0070	−0.0059	−0.0037	0.011
<i>1-Pentanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−1.019	0.864	−0.276	0.664	−1.052	0.054
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0220	0.0010	−0.0063	−0.0021	−0.0019	0.012

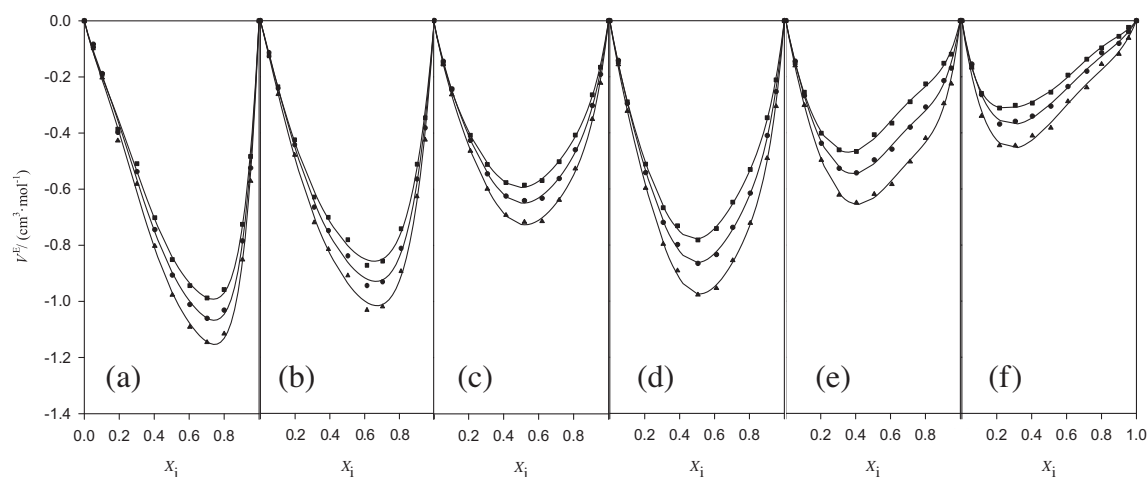
TABLE 4

Adjustable parameters of the Redlich–Kister equation (equation (10)) and standard relative deviations, σ , for the different properties of the binary {alcohol (1) + [EMim][MSO₄] (2)} at $T = 298.15 \text{ K}$.

Excess property	B_0	B_1	B_2	B_3	B_4	σ
<i>Methanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−3.573	−2.487	−1.372	−2.862	−2.758	0.071
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0430	−0.0306	−0.0198	−0.0385	−0.0364	0.032
<i>Ethanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−3.439	−1.523	−1.666	−1.387	−0.094	0.029
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0493	−0.0277	−0.0152	−0.0189	−0.155	0.013
<i>1-Propanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−2.598	−0.103	−0.079	−0.733	−1.145	0.021
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0403	−0.0145	−0.0073	−0.0095	−0.0082	0.011
<i>2-Propanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−3.447	−0.027	0.136	−1.377	−1.450	0.026
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0544	−0.0205	−0.0111	−0.0144	−0.0107	0.011
<i>2-Butanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−2.051	1.050	−0.504	−1.378	−0.812	0.044
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0441	−0.0103	−0.0092	−0.0086	−0.0051	0.010
<i>1-Pentanol (1) + [EMim][MSO₄] (2)</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	−1.206	1.091	−0.606	0.144	−0.450	0.044
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	−0.0266	−0.0003	−0.0067	−0.0027	−0.0033	0.010

TABLE 5Adjustable parameters of the Redlich–Kister equation (equation (10)) and standard relative deviations, σ , for the different properties of the binary {alcohol (1) + [EMim][MSO₄] (2)} at $T = 308.15$ K.

Excess property	B_0	B_1	B_2	B_3	B_4	σ
		Methanol (1) + [EMim][MSO ₄] (2)				
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-3.855	-2.678	-1.484	-3.158	-3.037	0.069
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	-0.0489	-0.0347	-0.0226	-0.0457	-0.0435	0.033
		Ethanol (1) + [EMim][MSO ₄] (2)				
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-3.738	-1.696	-1.885	-1.589	-0.148	0.029
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	-0.0565	-0.0325	-0.0184	-0.0235	-0.0194	0.014
		1-Propanol (1) + [EMim][MSO ₄] (2)				
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-2.903	-0.229	-0.075	-0.882	-1.352	0.021
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	-0.0468	-0.0181	-0.0091	-0.0120	-0.0105	0.011
		2-Propanol (1) + [EMim][MSO ₄] (2)				
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-3.894	-0.234	0.110	-1.645	-1.819	0.025
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	-0.0635	-0.0257	-0.0141	-0.0188	-0.0145	0.011
		2-Butanol (1) + [EMim][MSO ₄] (2)				
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-2.535	0.909	-0.575	-1.739	-1.085	0.035
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	-0.0525	-0.0142	-0.0116	-0.0117	-0.0073	0.009
		1-Pentanol (1) + [EMim][MSO ₄] (2)				
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-1.479	1.306	-0.948	-0.003	-0.439	0.065
$K_{S,m}^E/(\text{m}^3 \cdot \text{TPa}^{-1} \cdot \text{mol}^{-1})$	-0.0319	-0.0017	-0.0077	-0.0041	-0.0042	0.010

**FIGURE 4.** Excess molar volumes, V^E , for the binary {alcohol (1) + [EMim][MSO₄] (2)} mixtures at the studied temperatures (a) methanol, (b) ethanol, (c) 1-propanol, (d) 2-propanol, (e) 2-butanol and (f) 1-pentanol. Symbols: (■) $T = 288.15$ K; (●) 298.15 K; (▲) 308.15 K; and (—) Redlich–Kister fitting.

Furthermore, the excess molar volumes, V^E , and the excess molar isentropic compressions, $K_{S,m}^E$, against the molar fraction of alcohols, x_1 , as well as the Redlich–Kister fits, at the three studied temperatures are plotted in figures 4 and 5, respectively.

From these data, it is possible to observe that V^E and $K_{S,m}^E$ values are negative over the whole composition range, showing asymmetrical curves, which are quite common in this kind of systems which contain components with a large molar volume difference. The V^E is affected by the intermolecular forces between the components of the mixtures, and by the packing due to the differences in size and shape of molecules. Therefore, the negative V^E values can be attributed to strong interactions between the studied alcohols and [EMim][MSO₄] ionic liquid. Moreover, the small studied alcohols fit well into the free volume between the relatively large ions of the ionic liquid, resulting in these negative V^E values. As it can be seen in figure 4, an increase of alcohol chain length leads to less negative values of this excess property. Moreover, it is possible to observe that V^E curves present a minimum at high values of alcohol molar fraction, x_1 , in the short alcohols (methanol and

ethanol) while the minimum shift to smaller values of x_1 when the alcohol chain increases. This behavior was also reported by other authors [30–37].

Regarding the influence of temperature on the studied excess properties, the V^E values for the alcoholic mixtures reported in this study become more negative when the temperature increases, as it can be also seen in figure 4. This behaviour is quite usual for this kind of mixture, it can be associated with a special “iceberg structure” of the hydroxyl group of short molecules, and to the intense modifications that this structure undergoes as a function of composition and temperature in polar media, as previously reported by Iglesias *et al.* [38].

Furthermore, the mixture containing methanol is the one which presents a larger deviation from ideality, suggesting that the position of the hydroxyl group and the short length chain appears to play an important role on the interactions between the ionic liquid and the alcohol and, therefore, also on the excess molar volume.

As it can be observed in figure 5, similar conclusions were found in the variation of $K_{S,m}^E$ vs. x_1 , with the exception of the binary

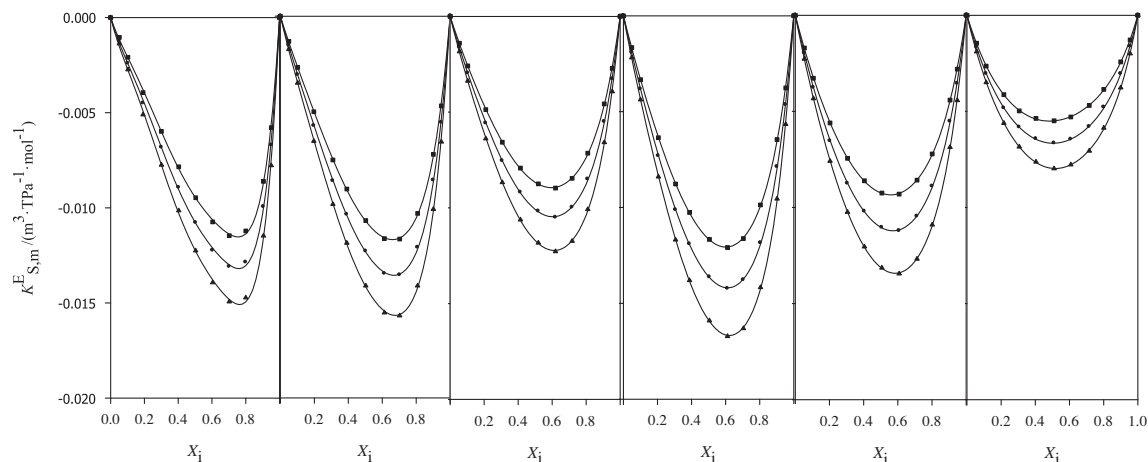


FIGURE 5. Excess molar isentropic compressions, $K_{S,m}^E$, for the binary {alcohol (1) + [EMim][MSO₄] (2)} mixtures at the studied temperatures (a) methanol, (b) ethanol, (c) 1-propanol, (d) 2-propanol, (e) 2-butanol and (f) 1-pentanol. Symbols: (■) $T = 288.15$ K; (●) 298.15 K; (▲) 308.15 K; and (—) Redlich–Kister fitting.

mixture 2-propanol + [EMim][MSO₄] which showed more deviation from ideality in this excess property.

4. Conclusions

In this work density, refractive index, speed of sound and dynamic viscosity of high purity [EMim][MSO₄] have been determined from $T = (293.15$ to $343.15)$ K. As expected, these properties decrease as temperature increases. The VFT equation was satisfactorily used to fit experimental viscosities vs. temperature while the rest of studied properties were fitted as a function of temperature to a linear equation.

Moreover, densities and speeds of sound for the binary mixtures {methanol (1), or ethanol (1), or 1-propanol (1), or 2-propanol (1), or 2-butanol (1), or 1-pentanol (1) + [EMim][MSO₄] (2)} were also measured over the whole composition range at $T = (288.15, 298.15$ and $308.15)$ K and atmospheric pressure. From these experimental data, the excess molar volume, and excess molar isentropic compression were calculated and these data were satisfactorily fitted to Redlich–Kister equation. Excess molar volume and excess isentropic compression show a similar behavior. Both properties are negative over the whole composition range. Moreover, both excess properties deviate more from ideality as the temperature increases.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2014.01.030>.

Literature cited

- [1] J.-Y. Wang, F.-Y. Zhao, Y. Min Liu, X.-L. Wang, Y.-Q. Hu, *Fluid Phase Equilib.* 305 (2011) 114–120.
- [2] L.I.N. Tomé, P.J. Carvalho, M.G. Freire, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, R.L. Gardas, *J. Chem. Eng. Data* 53 (2008) 1914–1921.
- [3] J. Jacquemin, P. Goodrich, W. Jiang, D.W. Rooney, C. Hardacre, *J. Phys. Chem. B* 117 (2013) 1938–1949.
- [4] A.J.L. Costa, J.M.S.S. Esperança, I.M. Marrucho, L.P.N. Rebelo, *J. Chem. Eng. Data* 56 (2011) 3433–3441.
- [5] L.E. Ficke, R.R. Novak, J.F. Brennecke, *J. Chem. Eng. Data* 55 (2010) 4946–4950.
- [6] J.D. Holbrey, W.M. Reichert, R.P. Swatloski, G.A. Broker, W.R. Pitner, K.R. Seddon, R.D. Rogers, *Green Chem.* 4 (2002) 407–413.
- [7] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, *J. Chem. Thermodyn.* 45 (2012) 68–74.
- [8] M. Alvarez-Guerra, A. Irabien, *Green Chem.* 13 (2011) 1507–1516.
- [9] H. Vogel, *Phys. Z.* 22 (1921) 645–646.
- [10] G.S. Fulcher, *J. Am. Ceram. Soc.* 8 (1925) 339–355.
- [11] O. Tammann, W.Z. Hesse, *Anorg. Allg. Chem.* 156 (1926) 245–257.
- [12] O. Redlich, A.T. Kister, *Ing. Eng. Chem.* 40 (1948) 345–348.
- [13] C.L. Yaws, *Chemical Properties Handbook*, McGraw-Hill, New York, 1999.
- [14] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic Solvents*, Wiley, New York, 1986.
- [15] E. Gómez, N. Calvar, E.A. Macedo, A. Domínguez, *J. Chem. Thermodyn.* 45 (2012) 9–15.
- [16] I. Bahadur, N. Deenadayalu, Z. Tywabi, S. Sen, T. Hofman, *J. Chem. Thermodyn.* 49 (2012) 24–38.
- [17] U. Domanska, M. Laskowska, *J. Solution Chem.* 38 (2009) 779–799.
- [18] E. Rilo, S. Freire, L. Segade, O. Cabeza, C. Franjo, E. Jiménez, *J. Chem. Thermodyn.* 35 (2003) 839–850.
- [19] R.G. Seoane, S. Corderi, E. Gómez, N. Calvar, E.J. González, E.A. Macedo, A. Domínguez, *Ind. Eng. Chem. Res.* 51 (2012) 2492–2504.
- [20] A.B. Pereiro, H.I.M. Veiga, J.M.M.S. Esperança, A. Rodríguez, *J. Chem. Thermodyn.* 41 (2009) 1419–1423.
- [21] O.O. Okoturo, T.J. VanderNoot, *J. Electroanal. Chem.* 568 (2004) 167–181.
- [22] J. Troncoso, C.A. Cerdeiriña, Y.A. Sanmamed, L. Romani, L.P.N. Rebelo, *J. Chem. Eng. Data* 51 (2006) 1856–1859.
- [23] A.A. Strechan, Y.U. Paulechka, A.G. Kabo, A.V. Blokhin, G.J. Kabo, *J. Chem. Eng. Data* 52 (2007) 1791–1799.
- [24] Y.H. Yu, A.N. Soriano, M.H. Li, *Thermochim. Acta* 482 (2009) 42–48.
- [25] A.F. Ferreira, P.N. Simões, A.G.M. Ferreira, *J. Chem. Thermodyn.* 45 (2012) 16–27.
- [26] G. Douhéret, M.I. Davis, J.C.R. Reis, M.J. Blandamer, *Chem. Phys. Chem.* 2 (2001) 148–161.
- [27] G. Douhéret, M.I. Davis, J.C.R. Reis, I.J. Fjellanger, M.B. Vaage, H. Holiand, *Chem. Phys. Chem.* 4 (2002) 6034–6042.
- [28] G.C. Benson, O. Kiyohara, *J. Chem. Thermodyn.* 11 (1979) 1061–1064.
- [29] P.R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969.
- [30] E. Vercher, A.V. Orchillés, P.J. Miguel, A. Martínez-Andreu, *J. Chem. Eng. Data* 52 (2007) 1468–1482.
- [31] E.J. González, L. Alonso, A. Domínguez, *J. Chem. Eng. Data* 51 (2006) 1446–1452.
- [32] E.J. González, B. González, N. Calvar, A. Domínguez, *J. Chem. Eng. Data* 52 (2007) 1641–1648.
- [33] E. Gómez, B. González, N. Calvar, E. Tojo, A. Domínguez, *J. Chem. Eng. Data* 51 (2006) 2096–2102.

- [34] A. Heintz, D. Klasen, J.K. Lehmann, C. Wertz, J. Solution Chem. 34 (2005) 1135–1144.
- [35] A. Arce, E. Rodil, A. Soto, J. Solution Chem. 35 (2006) 63–78.
- [36] U. Domanska, A. Pobudkowska, A. Wisniewska, J. Solution Chem. 35 (2006) 311–334.
- [37] J. Lachwa, P. Morgado, J.M.S.S. Esperança, H.J.R. Guedes, J.N. Lopes, L.P.N. Rebelo, J. Chem. Eng. Data 51 (2006) 2215–2221.
- [38] M. Iglesias, A. Torres, R. Gonzalez-Olmos, D. Salvatierra, J. Chem. Thermodyn. 40 (2008) 119–133.

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