Osmotic coefficients and apparent molar volumes of 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid in alcohols

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ABSTRACT

In this work, density for the binary mixtures of 1-hexyl-3-methylimidazolium trifluoromethanesulfonate in alcohols (1-propanol, or 2-propanol, or 1-butanol, or 2-butanol, or 1-pentanol) was measured at $T = 323.15$ K and atmospheric pressure. From this property, the corresponding apparent molar volumes were calculated and fitted to a Redlich–Meyer type equation. For these mixtures, the osmotic and activity coefficients, and vapor pressures of these binary systems were also determined at the same temperature using the vapor pressure osmometry technique. The experimental osmotic coefficients were modeled by the Extended Pitzer model of Archer. The parameters obtained in this correlation were used to calculate the mean molal activity coefficients and the excess Gibbs free energy for the studied mixtures.

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1. Introduction

Ionic liquids (ILs) are salts with a melting point lower than 100 °C. As it is known, these solvents have interesting properties, which make them attractive for a number of applications. Some of these properties are their negligible vapor pressure, their non-flammability, their chemical stability and their excellent solubility for organic and inorganic compounds. Due to their relative novelty, there is still a lack of experimental data, especially concerning physical properties and phase behavior, which becomes vital for the application of ILs in industrial processes or for developing thermodynamic models.

Studies of thermodynamic properties of mixtures containing ILs mixed with other compounds are crucial because they provide useful information to understand the behavior of these liquid salts in common solvents. As example, density and derived properties are usually required to develop specific thermodynamic models and they are also of great relevance in assessing intermolecular interactions between the ionic liquid and the solvent. The calculation of osmotic and activity coefficients allows to analyze the nonideality of mixtures, studying their thermodynamics, and to test the usu-

ally used thermodynamic tools. To date, most of the works are based on the study of physical properties of ILs in water, while the studies of non-aqueous mixtures containing ILs are still not abundant [1–5].

This paper is an extension of our studies on volumetric and osmotic properties of ILs in alcohols [6,7]. In this work, densities for the binary mixtures {1-propanol (1), or 2-propanol (1), or 1-butanol (1), or 2-butanol (1), or 1-pentanol (1) + 1-hexyl-3-methylimidazolium trifluoromethanesulfonate (2)} are reported at $T = 323.15$ K and atmospheric pressure. From these data, the corresponding apparent molar volumes were obtained and fitted to a Redlich–Meyer type equation [8]. On the other hand, a vapor pressure osmometry technique was used to obtain osmotic and activity coefficients and vapor pressures of the above mentioned binary mixtures. The Extended Pitzer model modified by Archer [9,10] was used for modeling the experimental data. Finally, the mean molal activity coefficients and the excess Gibbs free energy for the studied binary mixtures were calculated from the obtained parameters.

The ionic liquid studied in this work was selected in order to compare the experimental results obtained here with those previously published for the binary mixtures of 1-butyl-3-methylimidazolium trifluoromethanesulfonate in alcohols [7]. The comparison of these results allows evaluating the effect of the alkyl chain length of the cation on the properties reported in this work.

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To our knowledge, some papers containing physical property data for the pure ionic liquid were previously published [11–13]; nevertheless, the experimental data reported in this work were not previously determined.

2. Experimental section

2.1. Chemicals

The ionic liquid 1-hexyl-3-methylimidazolium trifluoromethanesulfonate, [HMim][TfO], was supplied by Iolitec GmbH (Germany) with a purity higher than 0.990 by mass. Prior to its use, this compound was dried under vacuum ($p = 2 \cdot 10^{-1}$ Pa; $T = 323.15$ K). The water content, w_w, for the dried ionic liquid was 520 ppm.

Alcohols were purchased in specialized companies. They were ultrasonically degassed and dried over molecular sieves type $4 \cdot 10^{-10}$ m, supplied by Aldrich, and kept in bottles under inert atmosphere to avoid moisture. For the chemicals used in this work, the supplier, purity, density (in kg · m³) and speed of sound (in m · s^{-1}) measured at $T = 323.15$ K are reported in table 1. In this table, density data found in the literature for the studied compounds were also included for comparison purpose [11,12,14,15].

2.2. Apparatus and procedure

A Metrohm 870 Karl Fischer Titrino was used to determine the water content of the pure ionic liquid. Titran 2, supplied by Merck, was used as titrant.

The binary mixtures were prepared by weighing using a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3 \cdot 10^{-4}$ g. All the samples were prepared into stoppered bottles inside a glove box under argon atmosphere. Then, the samples were vigorously stirred in order to get a complete mixing of the two components.

The determination of density and speed of sound (the latter only for pure components) was carried out using an Anton Paar DSA-5000M digital vibrating-tube densimeter with an uncertainty of ± 0.03 kg · m^{-3} and ± 0.3 m · s^{-1}, respectively. The combined expanded uncertainties ($k = 2$) for density and speed of sound are ± 0.06 kg · m^{-3} and ± 0.6 m · s^{-1}, respectively. This equipment has a temperature controller that keeps the samples at working temperature with a stability of ± 0.01 K. The apparatus was calibrated using Millipore quality water and air, according to the instructions manual.

A Knauer K-7000 vapor pressure osmometer (VPO) with a temperature control of ± 0.01 K was used for the determination of vapor pressures and osmotic and activity coefficients. With this technique, the solution and the solvent droplets are placed on two thermistors arranged in a Wheatstone bridge circuit so that the temperature increase can be measured very accurately as a function of the output voltage. The method and procedure are described in detail in a previous paper [16]. The drop size and shape should be maintained as constant as possible and equal on both thermistors to obtain reliable experimental data. The uncertainty in the output of the instrument was ± 1 Ω.

3. Results and discussion

3.1. Apparent molar volume

In this work, densities, ρ, for the binary systems of [HMim][TfO] in alcohols (1-propanol (1), or 2-propanol (1), or 1-butanol (1), or 2-butanol (1), or 1-pentanol (1)) were measured at $T = 323.15$ K and atmospheric pressure. The experimental data, which are reported in table 2, show that this physical property increases with molality, following a similar behavior to that presented by alcoholic solutions of "classical" electrolytes [17,18]. Moreover, density data decrease in the order: 1-pentanol > 1-butanol > 2-butanol $\cong$ 1-propanol > 2-propanol. This behavior was also observed for other {alcohol + ionic liquid} binary mixtures [6,7].

From densities of the binary mixtures, the apparent molar volumes, V_ϕ, of [HMim][TfO] in the studied alcohols were calculated as:

$$V_\phi = \frac{M}{\rho} - \frac{(\rho - \rho_0)}{m \cdot \rho \cdot \rho_0}, \tag{1}$$

where M is the molar mass of [HMim][TfO] and is equal to 0.31634 kg · mol^{-1}; ρ and ρ_0 are densities (in kg · m^{-3}) of mixture and pure alcohol, respectively; and m is molality of the ionic liquid (in mol · kg^{-1}). The standard uncertainties for the molality and the apparent molar volume are ± 0.001 mol · kg^{-1} and ± 0.04 m^3 · mol^{-1}, respectively. The V_ϕ data obtained for the binary systems reported in this work are also included in table 2, while the dependence of this magnitude with molality is plotted in figure 1. As it can be observed, apparent molar volume increases when m increases at low concentrations, and it remains practically constant at the highest studied concentrations. Shekaari and Armanfar [5] comment that this behavior can be due to that at infinite dilution, the apparent molar volume is unaffected by ion–ion interaction and it is a measure only of the ion–solvent interaction, while at high concentration the ion–ion interactions also play an important role.

On the other hand, the comparison of the V_ϕ values for the studied binary mixtures, plotted in figure 1, indicates that the experimental values follow the order: V_ϕ (2-propanol) < V_ϕ (1-propanol) $\cong$ V_ϕ (2-butanol) < V_ϕ (1-butanol) < V_ϕ (1-pentanol), indicating that apparent molar volume increases with the alcohol size.

TABLE 1

Supplier, purity (in mass fraction), density, ρ, and speed of sound, u, of pure components at $T = 323.15$ K and atmospheric pressure.

Compound	Supplier	Purity, mass fraction	$\rho/(\text{kg} \cdot \text{m}^{-3})$		$u/(\text{m} \cdot \text{s}^{-1})$
			Exp.	Lit.	Exp.
[HMim][TfO]	Iolitec	>9.990	1217.24	1220.0[a] 1220.11[b]	1327.2
1-Propanol	Sigma–Aldrich	⩾0.999	779.09	779.095[c]	1121.8
2-Propanol	VWR	0.999	758.63	758.71[d]	1050.9
1-Butanol	VWR	0.999	786.32	786.238[c]	1157.3
2-Butanol	Fluka	⩾0.995	780.40	780.515[c]	1120.2
1-Pentanol	Sigma–Aldrich	⩾0.990	792.14	792.166[c]	1192.9

Standard uncertainty: ρ is ± 0.03 kg · m^{-3}, u is ± 0.3 m · s^{-1}.
[a] Ref. [11].
[b] Ref. [12].
[c] Ref. [14].
[d] Ref. [15].