Osmotic and apparent molar properties of binary mixtures alcohol + 1-butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid

Emilio J. González [a], Noelia Calvar [a], Ángeles Domínguez [b], Eugénia A. Macedo [a,*]

[a] LSRE – Laboratory of Separation and Reaction Engineering, Associated Laboratory LSRE/LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, s/n, Porto 4200-465, Portugal
[b] Advanced Separation Processes Group, Department of Chemical Engineering, University of Vigo, Campus Lagoas-Marcosende, 36310 Vigo, Spain

ARTICLE INFO

ABSTRACT

In this work, physical properties (densities and speeds of sound) for the binary systems {1-propanol, or 2-propanol, or 1-butanol, or 2-butanol, or 1-pentanol + 1-butyl-3-methylimidazolium trifluoromethanesulfonate} were experimentally measured from T = (293.15 to 323.15) K and at atmospheric pressure. These data were used to calculate the apparent molar volume and apparent molar isentropic compression which were fitted to a Redlich–Meyer type equation. This fit was used to obtain the corresponding apparent molar properties at infinite dilution. On the other hand, the osmotic and activity coefficients and vapor pressures of these binary mixtures were also determined at T = 323.15 K using the vapor pressure osmometry technique. The Extended Pitzer model of Archer was employed to correlate the experimental osmotic coefficients. From the parameters obtained in the correlation, the mean molal activity coefficients and the excess Gibbs free energy for the studied mixtures were calculated.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Nowadays, ionic liquids (ILs) are being demanded as replacements for the volatile organic solvents in many processes, due to their unique properties, which allow to reduce the environmental impact and to improve safety. The enormous range of possible anions and cations leads to many different ILs with different properties, making necessary the study of the behavior of such properties for the pure ILs and for their mixtures with solvents.

Systematic studies of thermodynamic properties of mixtures containing ILs will allow a better understanding of the behavior of these compounds in common solvents. In this way, acoustic and volumetric data are very helpful for the study of intermolecular interactions between the IL and solvent and for the development of specific thermodynamic models for this kind of systems. On the other hand, the osmotic and activity coefficients are useful to get a deeper knowledge about the nonideality of mixtures, especially about their thermodynamic behavior, and for testing the validity of usual thermodynamic tools. Some papers were found in literature [1,2] containing data of physical properties for the pure ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMim][TfO], but, to our knowledge, the experimental data reported in this work have not been previously determined.

In this paper, as a continuation of our ongoing work on acoustical, volumetric and osmotic properties of binary mixtures {alcohol + ionic liquid} [3–5], densities and speeds of sound data for the binary mixtures {1-propanol (1), or 2-propanol (1), or 1-butanol (1), or 2-butanol (1), or 1-pentanol (1) + 1-butyl-3-methylimidazolium trifluoromethanesulfonate (2)} are reported from T = (293.15 to 323.15) K and at atmospheric pressure. These data were used to calculate the corresponding apparent molar volumes and apparent molar isentropic compressions. These derived properties were fitted to a Redlich–Meyer type equation [6], and the apparent molar volumes and apparent molar isentropic compressions at infinite dilution were obtained. Moreover, osmotic and activity coefficients and vapor pressures of binary systems containing the above mentioned alcohols were determined at T = 323.15 K using the vapor pressure osmometry technique. The Extended Pitzer model modified by Archer [7,8] was adopted to represent the experimental data. The parameters of the Extended Pitzer model modified by Archer were used to calculate the mean molal activity coefficients and the excess Gibbs free energy for the studied binary mixtures.

2. Experimental section

2.1. Chemicals

The ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMim][TfO], was supplied by Iolitec GmbH

* Corresponding author. Tel.: +351 225081653; fax: +351 225081674.
  E-mail address: eamacedo@fe.up.pt (E.A. Macedo).

(Germany) with a purity higher than 0.99 by mass. In order to reduce its water content and volatile compounds, this compound was subjected to vacuum ($p = 2 \cdot 10^{-1}$ Pa) at moderate temperature ($T = 323.15$ K), and kept in a bottle under Argon atmosphere. The final water content, w_w, for this ionic liquid was 602 ppm.

1-Propanol and 2-propanol were purchased from VWR with a purity of 0.999 in mass fraction; 2-butanol was obtained from Fluka with a purity higher than 0.995 in mass fraction, and 1-butanol and 1-pentanol were supplied by Sigma–Aldrich with purities greater than 0.999 and 0.990 in mass fraction, respectively. Prior to their use, they were ultrasonically degassed and dried over molecular sieves type $4 \cdot 10^{-10}$ m, supplied by Aldrich. Then, the alcohols were kept in bottles under inert atmosphere in order to avoid absorption of moisture. Table 1 shows the density, ρ (in kg · m^{-3}), and speed of sound, u (in m · s^{-1}) data at $T = (293.15$ to $323.15)$ K for all the pure components together with the values found in literature for the same compounds at $T = 293.15$ K [1,2,9–12]. As it can be observed, the experimental data are in agreement with those found in the literature. The differences between experimental and literature may be attributed to the different water content or other impurities present in our or literature samples.

2.2. Apparatus and procedure

The water content of the pure ionic liquid was determined using a Metrohm 870 KF Titrino using Titran 2, supplied by Merck, as titrant.

The binary mixtures {alcohol (1) + [BMim][TfO] (2)} were gravimetrically prepared into stoppered bottles inside a glove box under inert atmosphere using a Mettler AX-205 Delta Range balance with an uncertainty of ±3 × 10^{-4} g. Before measurements, the samples were vigorously stirred in order to ensure a complete mixing of the chemicals.

Densities and speeds of sound measurements were carried out using an Anton Paar DSA-5000 M 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 manual instructions.

Finally, a Knauer K-7000 vapor pressure osmometer (VPO) with a temperature control of ±0.01 K was used to perform the measurements of vapor pressure osmometry. With this technique, the solution and the solvent droplets are placed directly 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 [13]. It is worth mentioning that special care was taken to keep the drop size and shape as constant as possible and equal on both thermistors. The uncertainty in the output of instrument was ±1 Ω.

3. Results and discussion

3.1. Apparent molar properties

Experimental density, ρ, and speed of sound, u, data for the binary systems {1-propanol (1), or 2-propanol (1), or 1-butanol (1), or 2-butanol (1), or 1-pentanol (1) + [BMim][TfO] (2)} from $T = (293.15$ to $323.15)$ K and atmospheric pressure are reported in table 2. The experimental data show that the density and the speed of sound decrease with temperature and increase with molality. The similar behavior was found in literature for alcoholic solutions of "classical" electrolytes such as lithium bromide, sodium bromide, sodium perchlorate, sodium tetraphenylborate, and tetraphenylphosphonium bromide [14,15]. Moreover, comparing the different systems studied in this work, at the same temperature, is also possible to observe that these physical properties decrease in the order: 1-pentanol > 1-butanol > 2-butanol ≅ 1-propanol > 2-propanol. This behavior was also obtained for the binary mixtures containing primary and secondary alcohols mixed with the ionic liquid 1-butyl-3-methylimidazolium dicyanamide, [BMim][dca] [5].

Density data were used to calculate the apparent molar volumes, V_ϕ, of [BMim][TfO] in the primary and secondary alcohols. This property was calculated using the following equation:

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

where M is the molar mass of [BMim][TfO] and is equal to 0.28829 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 for the binary systems {alcohol (1) + [BMim][TfO] (2)}, at the studied temperatures, are reported in table 2, and their variation with molality, at the three studied temperatures, are also plotted in figure S1, available in Supplementary data. As it can be observed, apparent molar volume increases

TABLE 1
Density, ρ, and speed of sound, u, of pure components at $T = (293.15$ to $323.15)$ K and at $p = 0.1$ MPa.

Compound	Supplier	Purity, mass fraction	ρ/(kg · m^{-3})				u/(m · s^{-1})			
			293.15 K		308.15 K	323.15 K	293.15 K		308.15 K	323.15 K
			Exp.	Lit.	Exp.	Exp.	Exp.	Lit.	Exp.	Exp.
[BMim][TfO]	Iolitec	>9.990	1303.7	1301.6[a] 1307.0[b]	1291.7	1279.9	1402.9	n.a.	1369.1	1336.5
1-Propanol	VWR	0.999	803.92	803.61[c]	791.84	779.33	1223.9	1223.17[d]	1172.6	1122.0
2-Propanol	VWR	>0.999	785.10	785.45[c]	772.31	758.70	1156.7	1157.8[e]	1104.1	1050.8
1-Butanol	Sigma–Aldrich	>0.999	809.54	809.56[c]	798.01	786.15	1256.2	1256.8[f]	1205.9	1155.7
2-Butanol	Fluka	>0.995	806.56	806.52[c]	794.00	780.50	1230.0	1230.1[f]	1175.8	1120.3
1-Pentanol	Sigma–Aldrich	>0.990	814.53	814.45[c]	803.52	792.15	1292.7	1293.45[d]	1242.4	1192.7

Standard uncertainty: ρ is ±0.03 kg · m^{-3}, u is ±0.3 m · s^{-1}.
[a] Reference [1].
[b] Reference [2].
[c] Reference [9].
[d] Reference [10].
[e] Reference [11].
[f] Reference [12].