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Procedia Engineering 42 (2012) 1383 – 1389

Procedia Engineering

www.elsevier.com/locate/procedia

20th International Congress of Chemical and Process Engineering CHISA 2012
25 – 29 August 2012, Prague, Czech Republic

Physical and excess properties for binary systems containing an alcohol and ionic liquid at T = 298.15 K

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Abstract

In this paper, density, speed of sound and refractive index of six binary systems (alcohol + ionic liquid) were measured, along the whole composition range, at T = 298.15 K and atmospheric pressure. The ionic liquids used in this work are constituted by different cations (pyridinium and pyrrolidinium), anions (trifluoromethanesulfonate and dicyanamide) and alkyl-side chain (propyl- and butyl-). From the experimental data, excess molar volumes, excess molar isentropic compressions and excess refractive index were calculated and satisfactorily fitted using the Redlich-Kister equation. The obtained results show that the physical and excess properties studied in this work are dependent on the structure of the ILs, especially on the anion.

Keywords: Density; speed of sound; refractive index; excess molar properties; ionic liquid; alcohol

1. Introduction

The ionic liquids (ILs) are relatively new substances and detailed knowledge of their physical properties is required to a better understanding of the behavior of these substances, pure or mixed with

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doi:10.1016/j.proeng.2012.07.531

other solvents, to find new applications or to design new technological processes. In this way, the density is necessary for developing equations of state and required for the design of different equipment, while the excess molar volume is of great importance when studying the nature of the molecular interactions present in mixtures. On the other hand, refractive index can be used as a measure of the electronic polarizability of a molecule and can provide useful information when studying the forces between molecules or their behavior in solution. [1]

In this work, density, speed of sound and refractive index for binary systems containing ethanol, or 1-propanol, mixed with the ionic liquids 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, [BMpy][NTf_2], or 1-methyl-3-propylpyridinium bis(trifluoromethylsulfonyl)imide, [PMpy][NTf_2], or 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMpyr][NTf_2], or 1-butyl-1-methylpyrrolidinium dicyanamide, [BMpyr][dca] were measured at T = 298.15 K and atmospheric pressure, and from them excess molar volumes, excess molar isentropic compressions and excess refractive index were calculated and fitted using the Redlich-Kister equation.

2. Experimental

The studied ionic liquids were supplied by IoLiTec (Germany) with purity higher than 99.0 %, by mass. Since the physical properties of ILs are sensitive to impurities and water content, prior their use, these compounds were subjected to vacuum ($p = 2 \cdot 10^{-1}$ Pa) at moderate temperature (T = 323.15 K) with the aim of reducing the water content and volatile compounds to negligible values. Once dried, the ILs were kept in a bottle under argon gas, and their purity was periodically checked by density measurements.

The binary mixtures were prepared by weighing known masses of ionic liquid and alcohol, injected into a stoppered glass vial. All samples were prepared immediately prior to measurements using a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3 \cdot 10^{-4}$ g. In order to avoid water adsorption, the ILs were manipulated inside a glove box under argon atmosphere.

Densities and speeds of sound of pure liquids and binary mixtures were measured using an Anton Paar DSA-5000M digital vibrating-tube densimeter, and refractive indices were determined using an automatic refractometer Abbemat-HP Dr. Kernchen. The experimental uncertainties for density and speed of sound are $\pm 3 \cdot 10^{-5}$ g·cm^{-3} and ±0.3 m·s^{-1}, respectively, and for the refractive index, the experimental uncertainty is $\pm 4 \cdot 10^{-5}$.

3. Results and Discussion

From the experimental data on density, speed of sound and refractive index, excess molar volumes, V^E, excess molar isentropic compressibilities, $\kappa_{S,m}^E$, and excess refractive index, n_D^E, were calculated and fitted using a Redlich-Kister type equation [2]. The variation of these magnitudes with the fraction of the alcohol is plotted in Figure 1 for the binary systems {alcohol (1) + ionic liquid} at T = 298.15 K.

The experimental densities were used to calculate the excess molar volume, V^E, of the mixture using the following equation:

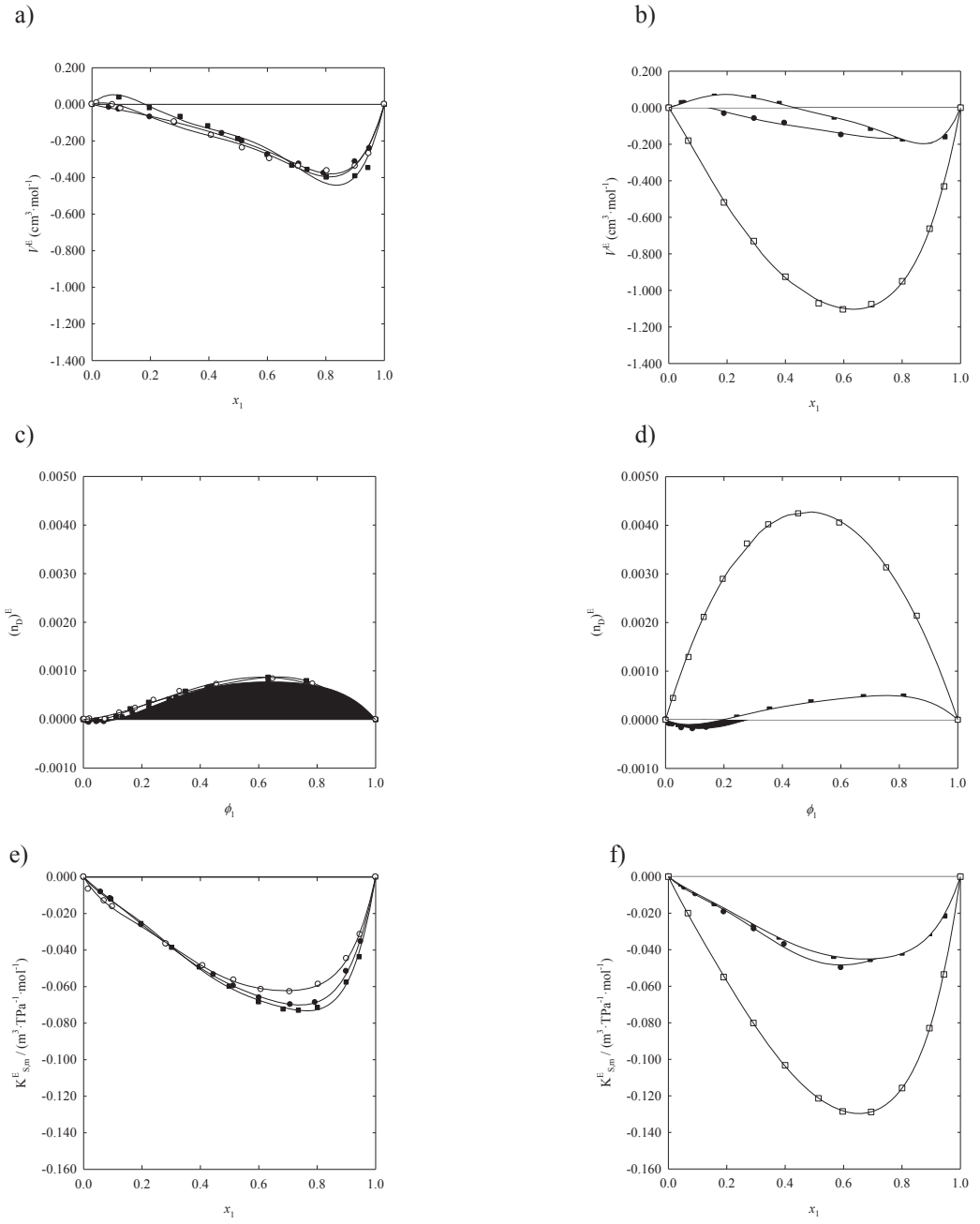

Fig. 1. Excess molar volumes, V^E, excess refractive index, n_D^E, and excess molar isentropic compressibilities, $K_{S,m}^E$, for the binary mixtures a), c) and e) ethanol (1) + ionic liquid (2); b), d) and f) 1-propanol (1) + ionic liquid (2) at T = 298.15 K. Ionic liquids: a) (●) [BMpyr][NTf_2], (■) [BMpy][NTf_2], (○) [PMpy][NTf_2], (□) [BMpyr][dca]

$$V^E = V_m - \sum_i x_i V_i^* \quad (1)$$

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

Regarding to the speed of sound, u, this property can be related to the isentropic compressibility, κ_s, by the Laplace equation, but to achieve agreement with the other properties, it is more appropriate to shift from the volume-intensive, κ_s, to the mole-intensive quantity, $K_{S,m}$, [3,4] calculated as follows:

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

where M_m is the molar mass of the mixture and $K_{S,m}$ is the molar isentropic compression.

The excess molar isentropic compression, $K_{S,m}^E$, is calculated by the next equation:

$$K_{S,m}^E = K_{S,m} - K_{S,m}^{id} \quad (3)$$

where $K_{S,m}^{id}$ is defined by the approach developed by Benson and Kiyohara:20

$$K_{S,m}^{id} = \sum_i x_i \left[K_{S,i}^* + T \frac{\left(E_{p,i}^*\right)^2}{C_{p,i}^*} \right] - T \left[\frac{\left(\sum_i x_i E_{p,i}^* \right)^2}{\sum_i x_i C_{p,i}^*} \right] \quad (4)$$

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 isobaric expansibility. The values for the pure ILs were calculated from their density data at the studied temperatures.

Regarding to refractive index, the excess squared refractive index, $(n_D^2)^E$, was selected for describing experimental refractive indices as a function of the composition at fixed *T* and *p*, according to the recommendations suggested by Reis et al. [33], who proposed the use of this excess magnitude instead of refractive index deviation to interpret the behavior of the refractive index of binary liquid mixtures.

Excess squared refractive index, $(n_D^2)^E$, was calculated using an equation defined by Buep [34] as:

$$\left(n_D^2\right)^E = n_D^2 - \left(n_D^2\right)^{id} = n_D^2 - \sum_i \varphi_i \left(n_{D,i}^*\right)^2 \quad (5)$$

The excess molar volume and excess molar isentropic compression at several temperatures were fitted to a Redlich-Kister22 type equation:

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^{M} B_p \left(x_i - x_j\right)^p \quad (6)$$

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 23.

The corresponding fitting parameters for each system, together with the standard relative deviation, σ, are given in Table 1. The equation used for the calculation of σ is the following:

$$\sigma = \left\{ \sum_{i}^{n_{dat}} \left((z - z_{cal}) / z_{cal} \right)^2 / n_{dat} \right\}^{1/2} \quad (7)$$

where z and z_{cal} are the values of the experimental and calculated property, and n_{dat} is the number of experimental points.

Table 1. Fitting parameters and standard relative deviations, σ, for the binary mixtures alcohol (1) + ionic liquid (2) at T = 298.15 K

Excess property	B_0	B_1	B_2	B_3	B_4	σ
			Ethanol + [BMpyr][NTf$_2$]			
V^{E} / cm^3·mol^{-1}	-0.792	-1.076	-1.310	-1.542	-0.922	0.072
$K^{E}_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	-0.235	-0.154	-0.117	-0.187	-0.141	0.021
n^{E}_{D}	0.0029	0.0016	-0.0004	0.0030	-	0.326
			Ethanol + [BMpy][NTf$_2$]			
V^{E} / cm^3·mol^{-1}	-0.705	-1.021	-1.907	-3.208	-	0.224
$K^{E}_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	-0.242	-0.166	-0.079	-0.228	-0.264	0.029
n^{E}_{D}	0.0030	0.0024	0.0019	-0.0003	-0.0044	0.225
			Ethanol + [PMpy][NTf$_2$]			
V^{E} / cm^3·mol^{-1}	-0.103	-0.619	-0.454	0.089	0.166	0.213
$K^{E}_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	-0.225	-0.128	-0.045	-0.108	-0.233	0.195
n^{E}_{D}	0.0032	0.0032	0.0032	-	-	1.199
			1-Propanol + [BMpyr][NTf$_2$]			
V^{E} / cm^3·mol^{-1}	-0.469	-0.488	-0.563	-0.649	0.606	0.198
$K^{E}_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	-0.184	-0.097	0.065	-0.005	-0.132	0.046
n^{E}_{D}	0.0013	0.0018	-0.0028	-	-	0.546
			1-Propanol + [BMpy][NTf$_2$]			
V^{E} / cm^3·mol^{-1}	-0.109	-0.756	0.061	-1.446	-1.741	0.104
$K^{E}_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	-0.164	-0.164	-0.164	-0.164	-0.164	0.044
n^{E}_{D}	0.0014	0.0016	0.0005	0.0024	-0.0006	0.337
			1-Propanol + [BMpyr][dca]			
V^{E} / cm^3·mol^{-1}	-4.173	-1.692	-1.372	-1.384	-	0.018
$K^{E}_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	-0.4782	-0.2492	-0.1278	-0.1586	-0.1286	0.010
n^{E}_{D}	0.0171	-0.0009	0.0016	-	-	0.030

As it can be observed in Figure 1, the systems present asymmetrical curves, which are quite common in mixtures containing two components with a large molar volume difference, as is indeed the case. The

influence of the cation, both in systems containing ethanol and containing 1-propanol, is relatively small, since although the minimum or maximum can shift, the values in the three excess properties studied are quite similar. The influence of the alkyl-side chain can be analyzed comparing the behavior of the systems containing [PMpy][NTf_2] and [BMpy][NTf_2]; this influence is also small, finding the highest differences in the excess molar isentropic compressibilities. From this figure it is also possible to conclude that the behavior of the excess properties of the binary systems containing ILs with a common anion ([NTf_2^-]) is quite similar and different from the mixture containing the IL with dicyanamide anion. This fact suggests that the chemical structure of the anion plays an important role on the shape of the excess properties curves, and therefore on the thermodynamic behavior of the studied systems.

The curves of V^E of the binary systems containing ILs with [NTf_2^-] anion are sinusoidal, while in the system 1-propanol (1) + [BMpyr][dca] (2) this curve is negative along the whole composition range. This latter system also presents the larger deviation from ideality.

Regarding to the values of the excess squared refractive index, it is possible to observe that for the systems alcohol (1) + [BMpyr][NTf_2] (2) or [BMpy][NTf_2] (2) they are negative at low volumentric fraction of alcohol, while for the systems containing the ILs [BMpy][NTf_2] and [BMpyr][dca] they are positive in the whole composition range, being again the system with [BMpyr][dca] that presenting the larger deviation from ideality.

All the studied systems show negative $K_{S,m}^E$ values in the whole composition range, showing a minimum at high concentration of alcohol. These negative values imply that these mixtures are less compressible than the corresponding ideal mixtures due to a closer approach of unlike molecules and stronger interaction between the components of the mixtures.

4. Conclusions

In this work, new data of density, speed of sound and refractive index for six binary systems containing the primary alcohols ethanol, or 1-propanol mixed with the ionic liquids [BMpy][NTf_2] or [PMpy][NTf_2] or [BMpyr][NTf_2] or [BMpyr][dca] were measured at T = 298.15 K and atmospheric pressure. From these experimental data, excess molar volumes, V^E, excess molar isentropic compressions, $K_{S,m}^E$, and excess refractive index, $(n_D^2)^E$, were calculated and satisfactorily fitted to a Redlich-Kister type equation.

The influence of the cation and of the alkyl-side chain on the excess properties is relatively small, since although the minimum or maximum can shift, the values in the three excess properties studied are quite similar. The behavior of the excess properties of the binary systems containing ILs with the anion [NTf_2^-] is quite similar and different from the mixture containing the IL with dicyanamide anion which is the mixture that exhibits the behavior farthest from ideality. These results show that the structure of the ILs plays an important role on the physical properties and on their corresponding excess magnitudes, especially the anion, which has a strong effect on the shape and values of the excess properties curves and therefore on the thermodynamic behavior of the studied systems.

Acknowledgements

N.C. and E.J.G acknowledge the financial support from FCT (Portugal) through their postdoctoral grants SFRH/BPD/37775/2007 and SFRH/BPD/70776/2010, respectively. P. Fernández is grateful to the Comisión Interministerial de Ciencia y Tecnología (Spain) for her FPI grant (BES-2011-050308). This work is partially supported by project PEst-C/EQB/LA0020/2011, financed by FEDER through COMPETE - Programa Operacional Factores de Competitividade and by FCT - Fundação para a Ciência e a Tecnologia.

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