PHYSICAL PROPERTIES OF BINARY MIXTURES: IONIC LIQUIDS + ALCOHOLS

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ABSTRACT

Information on the interactions between ionic liquids and molecular solvents are essential for the understanding of the function of ionic liquids in related procedures, and excess properties are sensitive probe for studying these interactions. In this paper, physical properties such as densities and speeds of sound of the binary systems containing 1–propyl–4–methylpyridiniumbis(trifluoromethylsulfonil)imide and 1-propyl–4–methylpyridiniumbis(trifluoromethylsulfonil)imide, ethanol and propanol, over the whole composition range were measured at T=(298.15, 308.15, 318.15) K and at atmospheric. These data were used to calculate the corresponding derived properties such as excess molar volumes and excess molar isentropic compressions, which were fitted with the Redlich-Kister equation.

For the studied systems, the excess molar volume values show a sinusoidal behaviour with a minimum at high concentrations of alcohol due to changes from negative to positive values when the alcohol´s alkyl chain length increases. The excess molar isentropic compression values are negative over the whole composition range and presenting also a minimum at high concentrations of alcohol. It is possible observed that an increase of the temperature causes that the negative excess molar volume and excess molar isentropic compression values for the alcoholic mixtures deviate more from ideality.

INTRODUCTION

The need to replace the volatile organic compounds has led to an increase the study of alternative solvents, such as ionic liquids, and of their properties which make them a versatility compounds to use on many different process like organic synthesis, chemical processing, liquid-liquid separations.

Because of their importance and interest, detailed knowledge of the thermodynamic behavior of the mixtures of ionic liquids with organic solvents, is very important for using them in different processes [1].

The density and speed of sound data can be used to calculating the excess molar volumes and excess molar isentropic compressions, which are useful for the understanding of intermolecular interactions in the systems.

In this work, density and speed of sound were measured for the binary mixtures (ionic liquid + alcohol) for 1-Propyl-4-MethylpyridiniumBis(trifluoromethylsulfonil)imide [$^1P^4Mpy$][NTf_2] and 1-Propyl-3-Methylpyridinium Bis(trifluoromethylsulfonil)imide [$^1P^3Mpy$][NTf_2] with ethanol and 1-propanol.at T=(298.15, 308.15, 318.15) K. from these experimental results, excess molar volumes and excess molar isentropic compressions were calculated and fitted to a Redlich-Kister type equation.

EXPERIMENTAL

Ethanol and 1-propanol were purchased from Sigma–Aldrich with mass fraction purity higher than 0.999. They were degassed ultrasonically and dried over molecular sieves type 4.10^{-8} cm, supplied by Aldrich, and kept in bottles under inert atmosphere. The ionic liquid used in this work was acquired at IoLiTec with mass fraction purity higher than 0.99. This compound was dried under vacuum (p = 0.2 Pa) with stirring at moderate temperature (T = 343 K) for at least 48 h, to reduce the water content and volatile compounds to negligible values. All chemicals were always manipulated inside a glove box under an argon atmosphere to avoid water absorption. The purity of the solvents was checked by comparing the experimental density and refractive indices obtained with the data found in the literature [2-4] (Table 1).

All binary mixtures were prepared by weighing using a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3\ 10^{-4}$ g. Special care was taken to avoid variations in composition due to evaporation of solvent or pickup of water by the ionic liquid. For this, all samples were prepared immediately prior to measurements into stoppered bottles inside a glove box, which is under argon atmosphere.

APPARATUS AND PROCEDURE

Densities and speeds of sound of the pure ionic liquid were measured using an Anton Paar DSA-5000 digital vibrating-tube densimeter. The repeatability and uncertainty in experimental measurements have been found to be lower than $\pm(2 . 10^{-6}$ and $3 .10^{-5})$ g cm^{-3} for the density and ±(0.01 and 0.3) m s^{-1} for the speed of sound, respectively. This equipment has a temperature controller that keeps the samples at working temperature with an uncertainty of ±0.01 K. Moreover, the equipment automatically detects the presence of bubbles in the cell. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air according to the manual instructions. The calibration was checked with known density and speed of sound of pure organic compounds.

RESULTS AND DISCUSSION

The experimental density, ρ, speed of sound, u, were measured and excess molar volume, V^E , isentropic compressibility, k_s, and excess molar isentropic compressions, $K^E_{S;m}$ were determined for the binary systems {ethanol, or 1-propanol + [^{1}P^{4}Mpy][NTf$_2$] or [^{1}P^{4}Mpy][NTf$_2$] } at T = (298.15, 308.15 and 318.15) K and atmospheric pressure. The excess molar volume, V^E, and excess molar isentropic compression, $K^E_{S;m}$, vs x_1, for all the binary mixtures, at the three studied temperatures, are also plotted in figures 1 to 8. In general, these physical properties decrease with increasing concentration of alcohol, x_1, and with temperature for all the studied systems. The excess molar volumes were calculated using the following expression:

$$V^E = V_m - \sum_i x_i V_i^* \text{ [5]}$$

where V_m is the molar volume of the mixture, and x_i and V_i^* represent the mole fraction and the molar volume of component i, respectively. The speed of sound, u, is related to the isentropic compressibility, k_s, by Laplace equation:

$$k_s = -V_m^{-1}(\partial V_m/\partial \rho)_s = \rho^{-1}u^{-2} = V_m/(M_m u^2) \text{ [6]}$$

where, V_m is the molar volume, and M_m is the molar mass of the mixture and the pure components.

To achieve agreement with the other thermodynamic quantities, it is appropriate to shift from the volume-intensive k_s to the mole-intensive quantity $k_{S,m}$.

$$K_{S,m} = -(\partial V_m/\partial \rho)_S = V_m k_S = V_m^2/(M_m u^2) \text{ [7]}$$

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

The excess molar isentropic compression, $K^E_{S,m}$ is calculated by the following equation:

$$K^E_{S,m} = K_{S,m} - K^{id}_{S,m} \text{ [8]}$$

Where $K^{id}_{S,m}$ is defined by the approach developed by Benson and Kiyohara [42]:

$$K^{id}_{S,m} = \sum_i X_i \left[K^*_{S,i} + T\frac{\left(E^*_{p,i}\right)^2}{C^*_{p,i}}\right] - T\left[\frac{\left(\sum_i X_i E^*_{p,i}\right)^2}{\sum_i X_i C^*_{p,i}}\right] \text{ [9]}$$

where $K^*_{S,i}$ is the product of the molar volume, V_i^*, and the isentropic compressibility, $k^*_{S,i}$, 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 $\alpha^*_{p,i}\left(\alpha^*_{p,i} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p\right)$ and $C^*_{p,i}$ is the molar isobaric heat capacity of the pure component *i*. The values of $\alpha^*_{p,i}$ and $C^*_{p,i}$ for the alcohols studied have been experimentally calculated.

The excess properties were fitted to a Redlich-Kister type equation:

$$\Delta Q_{12} = x_1 x_2 \sum_{p=0}^{M} B_p\,(x_1 - x_2)^p \text{ [10]}$$

where ΔQ_{12} is the excess property, x_1 and x_2 are the mole fraction of component 1 and 2 respectively, B_P is the fitting parameter, and *M* is the degree of the polynomial expansion, which was optimized using the *F*-test [11]. These fiting parameters and standard relative deviations, σ, for the binary mixture {alcohol + [^{1}P^{4}Mpy][NTf$_2$]} in Table 2 and for{alcohol + [^{1}P^{3}Mpy][NTf$_2$]} in Table 3.

From these data, it is possible to observe that V^E shows sinusoidal behavior, with a small maximum at low concentration of alcohol, and a minimum between 0.6 < x1 < 0.8, for all studied systems. The $K^E_{S,m}$ show negative values over the whole composition range with a minimum between 0.6 < x1 < 0.8, showing asymmetrical curves, which are quite common in mixtures containing two components with a large molar volume difference. The minimum of the excess molar isentropic compression is shifted towards lower concentration of alcohol when alkyl chain length of alcohol increases. (Figure 5-8)

The excess molar volume depends mainly on the intermolecular forces between the components of the mixtures, and on the packing due to the differences in size and shape for the excess molar volume. So that the negative excess volumes can be attributed to strong interactions between the studied alcohols and these ionic liquid

Figures 1 to 8 show the temperature dependence of the excess molar volume and excess molar isentropic compressions. These quantities become more negative when the temperature increases

CONCLUSIONS

In this work, the excess molar volume and the excess molar isentropic compression for the binary systems have been studied. In general, these properties decrease with increasing alcohol concentration and temperature for all the studied systems. The V^E shows sinusoidal behaviour while$K^E_{S,m}$ values are negative over the whole composition range. According to Doctor Eliseo Amado, the excess volume becomes less negative with increasing chain length of the alcohol, which is explained by the molecular dipole-dipole interactions between the alcohol and the ionic liquid [12]. The minimum value of $K^E_{S,m}$ is shifted towards lower concentration of alcohol when alkyl chain length of alcohol increases. The above mentioned excess properties were satisfactorily fitted to Redlich-Kister equation.

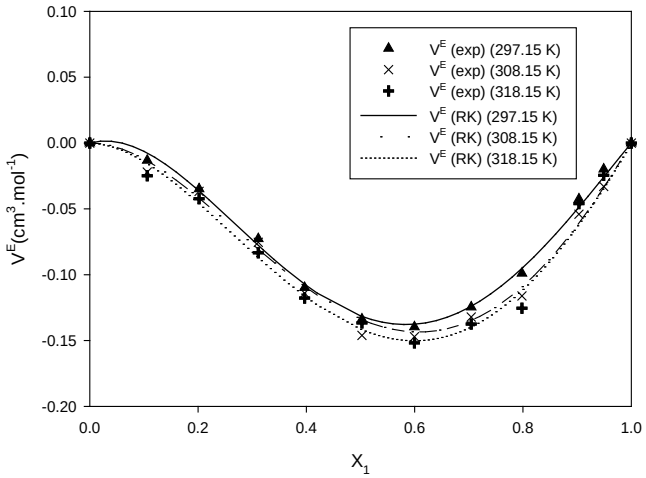

Figure 1 Excess molar volume (V^E) for the binary mixture Ethanol + [$^1P^4$Mpy][NTf_2] at different temperatures**,** the experimental data (exp) and the Redlich-Kister (RK) adjustment data.

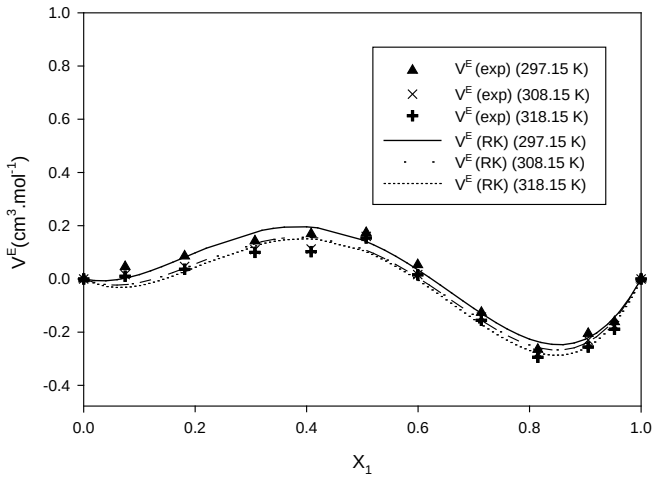

Figure 2 Excess molar volume (V^E) for the binary mixture 1-Propanol + [$^1P^4$Mpy][NTf_2] at different temperatures**,** the experimental data (exp) and the Redlich-Kister (RK) adjustment data.

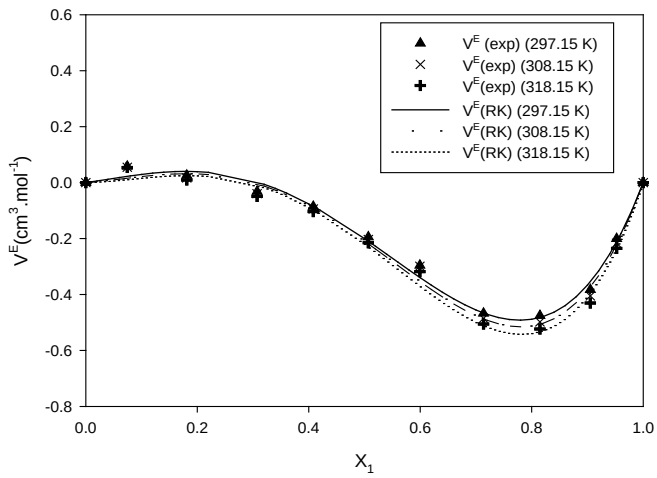

Figure 3 Excess molar volume (V^E) for the binary mixture Ethanol + [$^1P^3$Mpy][NTf_2] at different temperatures, the experimental data (exp) and the Redlich-Kister (RK) adjustment data.

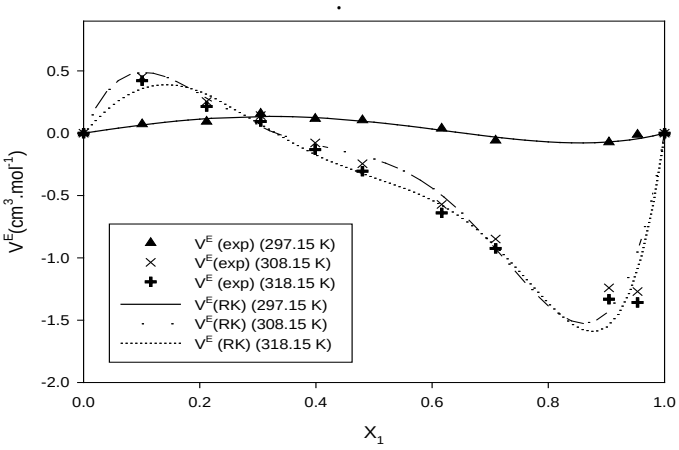

Figure 4 Excess molar volume (V^E) for the binary mixture 1-Propanol + [$^1P^3$Mpy][NTf_2] at different temperatures, the experimental data (exp) and the Redlich-Kister (RK) adjustment data.

Component	**Supplier**	**Purity, in mass fraction**	**ρ/(g.cm^{-3})**		**n_D**	
			Exp.	Lit.	Exp.	Lit.
Ethanol	**Sigma-Aldrich**	**> 0.999**	0.79106	0.78493	1.35967	1.35941
1-Propanol	**Sigma-Aldrich**	**> 0.999**	0.80088	0.7996	1.38276	1.3837
[$^1P^4$Mpy][NTf_2]	**Iolitec**	**> 0.990**	1.45104	n.a	1.44601	n.a.
[$^1P^3$Mpy][NTf_2]	**Iolitec**	**> 0.990**	1.44788	1.4475	1.44457	n.a.

Table 1. Supplier, density (ρ) and refractive indices (n_D) of purity components at T=298.15 K. (n.a.: not available)

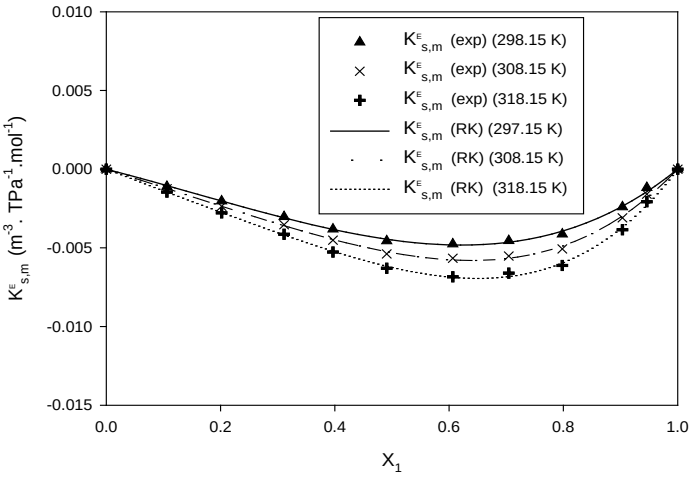

Figure 5 Excess molar volume isentropic compression $(K^E_{S,m})$ for the binary mixture Ethanol + $[^1P^4Mpy][NTf_2]$ at different temperatures, the experimental data (exp) and the Redlich-Kister (RK) adjustment data

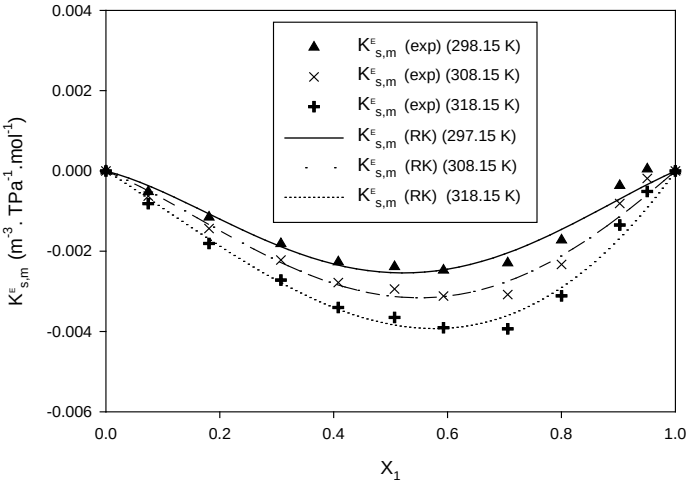

Figure 6 Excess molar volume isentropic compression $(K^E_{S,m})$ for the binary mixture 1-Propanol + $[^1P^4Mpy][NTf_2]$ at different temperatures, the experimental data (exp) and the Redlich-Kister (RK) adjustment data

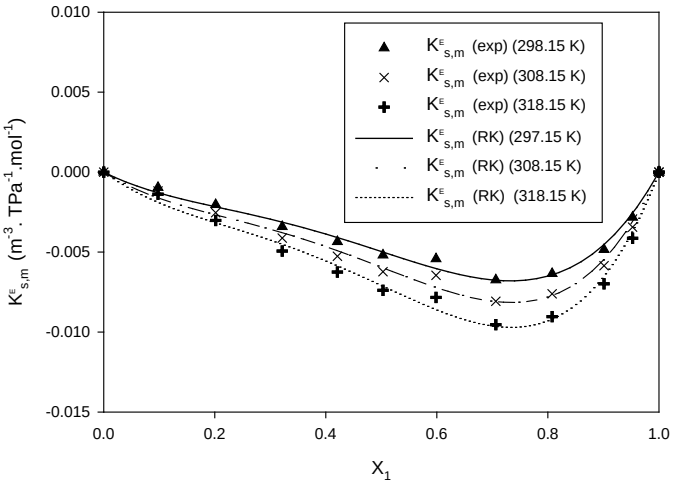

Figure 7 Excess molar volume isentropic compression $(K^E_{S,m})$ for the binary mixture Ethanol + $[^1P^3Mpy][NTf_2]$ at different temperatures, the experimental data (exp) and the Redlich-Kister (RK) adjustment data

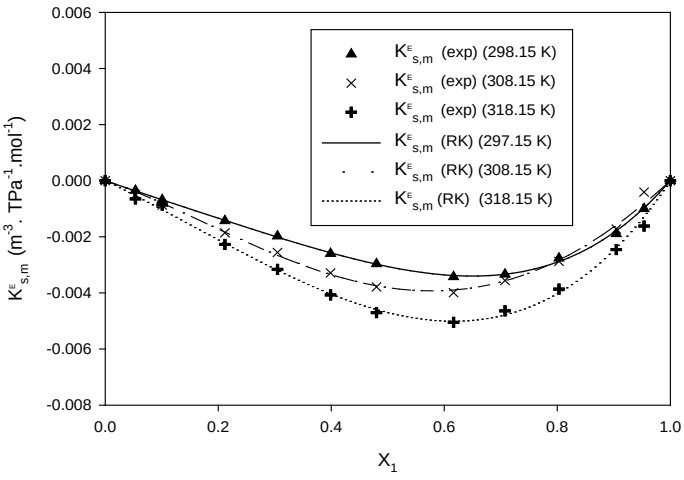

Figure 8 Excess molar volume isentropic compression $(K^E_{S,m})$ for the binary mixture 1-Propanol + $[^1P^3Mpy][NTf_2]$ at different temperatures, the experimental data (exp) and the Redlich-Kister (RK) adjustment data

Table 2	Alcohol	Excess property	B_0	B_1	B_2	B_3	σ
	Ethanol	T = 298.15 K					
		$V^E/cm^3.mol^{-1}$	-0.8	-2.748	-1.678		0.015
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.023	-0.024			0.001
		T = 308.15 K					
		$V^E/cm^3.mol^{-1}$	-0.837	-2.831	-1.857		0.016
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.027	-0.028			0.001
		T = 318.15 K					
		$V^E/cm^3.mol^{-1}$	-0.883	-2.937	-2.023		0.017
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.032	-0.033			0.001
	1-Propanol	T = 298.15 K					
		$V^E/cm^3.mol^{-1}$	0.355	-0.953	-0.605		0.017
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.13	-0.008			9.10^{-5}
		T = 308.15 K					
		$V^E/cm^3.mol^{-1}$	-0.832	-2.963	-6.992	-16.329	0.121
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.015	-0.006			2.10^{-4}
		T = 318.15 K					
		$V^E/cm^3.mol^{-1}$	-1.039	-2.996	-7.735	-17.168	0.13
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.019	-0.01			1.10^{-4}

Table 3	Alcohol	Excess property	B_0	B_1	B_2	σ
	Ethanol	T = 298.15 K				
		$V^E/cm^3.mol^{-1}$	-0.525	-0.306	0.329	0.003
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.018	-0.010		1.10^{-4}
		T = 308.15 K				
		$V^E/cm^3.mol^{-1}$	-0.535	-0.350	0.185	0.005
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.022	-0.013		2.10^{-4}
		T = 318.15 K				
		$V^E/cm^3.mol^{-1}$	-0.566	-0.341	0.210	0.007
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.026	-0.017		2.10^{-4}
	1-Propanol	T = 298.15 K				
		$V^E/cm^3.mol^{-1}$	0.588	-1.688	-02.743	0.023
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.009	-0.001		2.10^{-4}
		T = 308.15 K				
		$V^E/cm^3.mol^{-1}$	0.452	-1.590	-2.933	0.026
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.012	-0.003		2.10^{-4}
		T = 318.15 K				
		$V^E/cm^3.mol^{-1}$	0.428	-1.631	-3.144	0.027
		$K^E_{S,m}/m^3.TPa^{-1}.mol^{-1}$	-0.015	-0.005		2.10^{-4}

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