

COMPLEX MOLECULAR STRUCTURES IN BINARY MIXTURES OF SOME [NR₁R₂R₃R₄]⁺[Tf₂N]⁻ IONIC LIQUIDS IN ETHANOL

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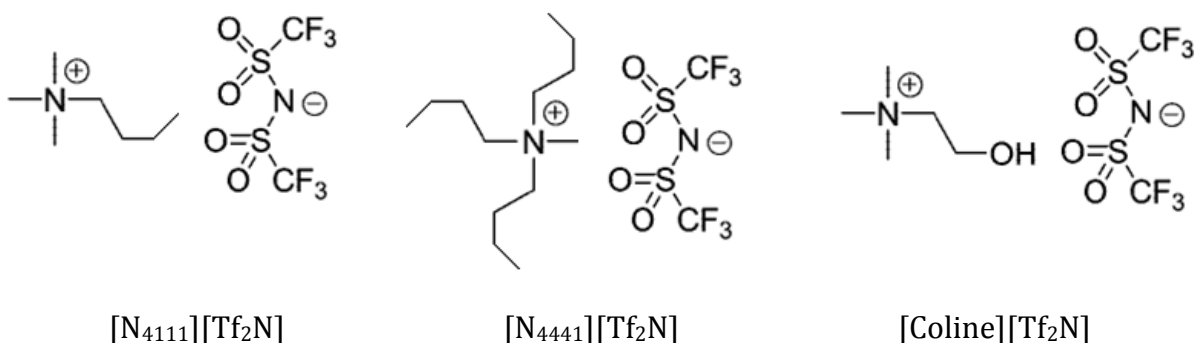
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Introduction: Ionic liquids (ILs) have a set of unique physical and chemical properties that make them alternative solvents for common organic solvents (VOC). Depending on desired applications there is the possibility of designing ionic liquids in accordance with the predominance of some key properties such as, thermal stability, electrical conductivity, width of electrochemical window and characteristics as solvent [1]. The characterization of ILs and their mixtures with molecular organic solvents, such as aliphatic alcohols, is very important since most of their large-scale applications occur in mixtures, where those organic compounds are used as co-solvents [2]. This work is devoted to the macro and micro characterization of three [NR₁R₂R₃R₄]⁺[Tf₂N]⁻ ILs and their mixtures with ethanol.



The choice of these ILs has been done according with criteria as follow: low melting point, low viscosity, possibility of cation chain size effect evaluation and consequences of increasing the hydrophilic nature of the cation, as for instances the introduction of a -OH group. The common anion Tf₂N⁻ was preferred because it usually contributes to lower melting point and viscosity values and to an increase of thermal stability and electrical and electrochemical conductivities. Density and ultrasound speed as a function of composition and temperature, $T = 293$ to 308 K, and solvatochromic parameters as a function of composition at $T = 298$ K were obtained. Changes of derived thermodynamic

properties, such as partial molar volumes and isentropic compression with composition and temperature, jointly with preferential solvation information obtained from changes in solvatochromic parameters with composition, were interpreted in terms of aggregative species formation.

Experimental: Densities and ultrasound speeds were measured with an Anton Paar vibrating tube densimeter and sound analyser, Model DSA 5000M, at temperatures in the range $T = (293.15 \text{ to } 308.15) \text{ K}$. The instrument was calibrated for density in accordance with a procedure previously described [3]. Calibration for ultrasound speed measurements has been made using ultra pure water at $T = 293.15 \text{ K}$, as recommended by the manufacturer. All solutions were prepared by weight. Buoyancy corrections were applied. Five dyes were used to determine solvatochromic parameters. UV-Vis spectroscopic measurements were performed with a double beam Nicolet Evolution 300 spectrometer (VISION prosoftware).

Results and discussion: Curve profiles of some measurements are shown in Figure 1 as examples.

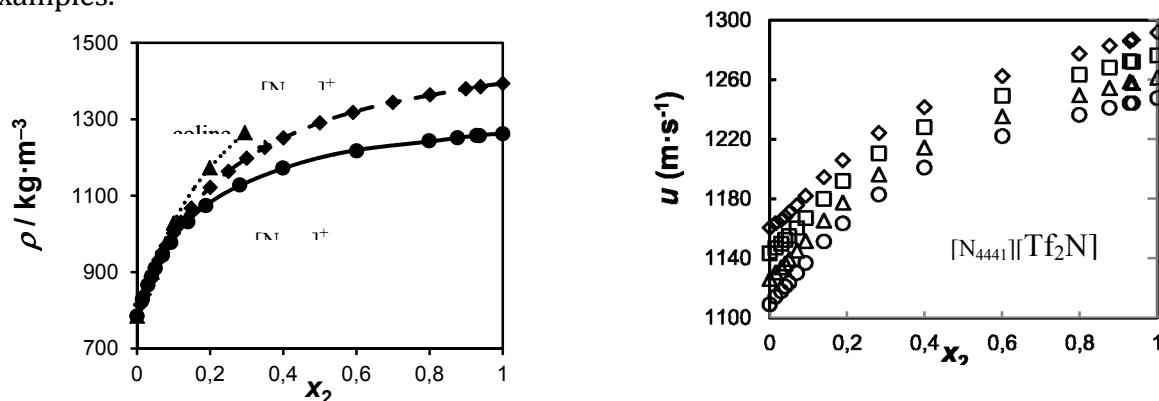


Figure 1. Density, ρ , for the three ethanol (1) + $[\text{NR}_1\text{R}_2\text{R}_3\text{R}_4][\text{Tf}_2\text{N}]$ (2) systems, at 298 K. Ultrasound speed, u , for temperatures ranging from ($T = 293, \diamond$; 298, Δ ; 303, \square ; and 308, \circ) K for $[\text{N}_{4441}][\text{Tf}_2\text{N}]$.

Examples of some derived thermodynamic properties are shown in Figures 2 and 3.

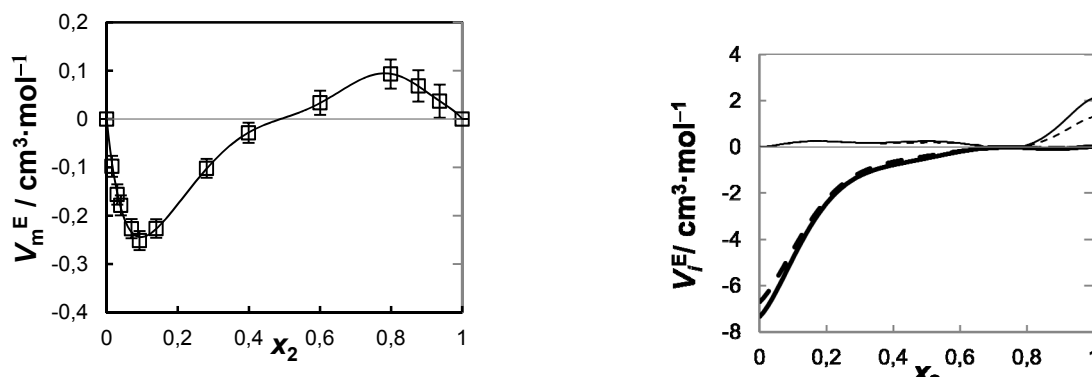


Figure 2. Excess molar volumes, V_m^E , at 298 K and excess partial molar volumes, V_i^E at 293 and 308 K in the system ethanol (1) + $[\text{N}_{4441}][\text{Tf}_2\text{N}]$ (2). Full lines in V_i^E curves stand for the 308 K isotherm. Thicker lines correspond to V_2^E .

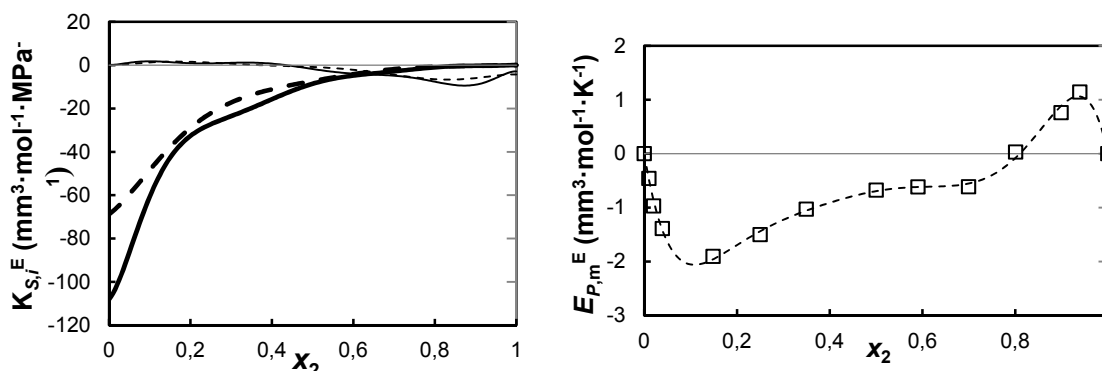


Figure 3. Excess partial molar isentropic compression, $K_{S,i}^E$, for the mixture ethanol (1) + $[N_{4111}][Tf_2N]$ (2), as a function of composition. (---), $K_{S,1}^E$ at 293 K; (—), $K_{S,1}^E$ at 308 K; (---), $K_{S,2}^E$ at 293 K and (—), $K_{S,2}^E$ at 308 K. Excess molar isobaric expansion for the mixture ethanol (1) + $[N_{4111}][Tf_2N]$ (2), as a function of composition at 298 K.

The preferential solvation of the betaine probe, in two of the mixtures studied, is depicted in Figure 4, using the polarity parameter E_T^N [4].

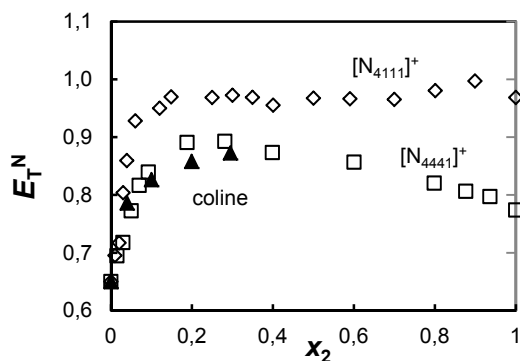


Figure 4. Solvatochromic parameter E_T^N , as a function of composition, at 298 K for the three ethanol (1) + $[NR_1R_2R_3R_4][Tf_2N]$ (2) systems.

Summary: Synergistic behaviour, mainly observed in the ethanol + $[N_{4441}][Tf_2N]$ system (Figure 4) and temperature dependence of some derived thermodynamic properties, lead us to suspect the formation of stable complex entities in definite composition ranges.

References:

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