



# Excess molar volumes and excess molar enthalpies in binary systems N-alkyl-triethylammonium bis(trifluoromethylsulfonyl)imide + methanol



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## ABSTRACT

In the present paper, a study on the influence of the alkyl chain length in N-alkyl-triethylammonium bis(trifluoromethylsulfonyl)imide ionic liquids,  $[N_{R,222}][Tf_2N]$  ( $R = 6, 8$  or  $12$ ), on the excess molar enthalpy at 303.15 K and excess molar volume within the temperature interval (283.15–338.15 K) of ionic liquid + methanol mixtures is carried out. Small excess molar volumes with highly asymmetric curves (i.e. S-shape) as a function of mole fraction composition were obtained, with negative values showing in the methanol-rich regions. The excess molar volumes increase with the increase of the alkyl-chain length of the ammonium cation of the ionic liquid and decrease with temperature. The excess enthalpies of selected binary mixtures are positive over the whole composition range and increase slightly with the length of the alkyl side-chain of the cation on the ionic liquid. Both excess properties were subsequently correlated using a Redlich–Kister-type equation, as well as by using the ERAS model. From this semipredictive model the studied excess quantities could be obtained from its chemical and physical contribution. Finally, the COSMOTermX software has been used to evaluate its prediction capability on the excess enthalpy for investigated mixtures at 303.15 K and 0.1 MPa. From this work, it appears that COSMOTermX method predicts this property with good accuracy of approx. 10%, providing at the same time the correct order of magnitude of the partial molar excess enthalpies at infinite dilution for the studied ILs,  $\bar{H}_1^{E,\infty}$ , and methanol,  $\bar{H}_2^{E,\infty}$ .

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## 1. Introduction

In general, the term ionic liquids (ILs) indicates a group of substances composed of organic/inorganic ions with melting points lower than 100 °C. Their unique properties such as a practically negligible vapor pressure, good thermal stability, and a wide liquid range have led to extensive studies of their properties, both pure and in mixtures. Versatile solvents bound to replace volatile organic compounds, ILs occur to be useful in many other fields and applications, e.g. electrochemistry [1], catalysis [2], synthesis [3] or separation processes such as extraction, distillation or membrane separation processes [4]. Physical properties of ILs may be tuned to required applications thanks to a large number of combinations of cations and anions, ILs are therefore a continuous source of new inspiration. In the present paper,

the thermodynamic properties of ILs based on hydrophobic ions like the bis(trifluoromethylsulfonyl)imide anion and the N-alkyl-triethylammonium cation series with alkyl chain length,  $R$ , of 6, 8 and 12 carbons (abbrev.  $[N_{6,222}][Tf_2N]$ ,  $[N_{8,222}][Tf_2N]$ , and  $[N_{12,222}][Tf_2N]$ ), were studied in mixture with methanol. Floris et al. [5] have investigated their use in homogeneous catalysis as solvents and catalyst support. At the same time, it appears that these ( $[N_{R,222}][Tf_2N]$  + methanol) binary mixtures act as a protection of the catalyst against air humidity. Moreover, small amounts of selected ILs based on the N-alkyl-triethylammonium bis(trifluoromethylsulfonyl)imide added to methanol in enantioselective hydrogenation of  $\beta$ -keto esters catalyzed by the chiral complex (R)-Ru-BINAP helped to enhance enantioselectivity towards methyl 3-(R)-hydroxy butyrate [6]. These efficient enantioselective reactions are of key importance to pharmaceutical industry as drugs with less side effects may be produced from enantiopure compounds (pharmacodynamics). Also, from the economic point of view, stereoselective reactions are less tedious and costly than separating enantiomers from the racemic mixture.

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Therefore, hydrophobic ILs have a great potential as pharmaceutical co-solvents, [7] and possible drug reservoirs for controlled release [8]. In the catalytic setup proposed by Floris et al. [5] the reactants, the selected IL, and the chiral catalyst form a one-phase system. When the reaction is finished, the mixture is washed with pure water. Products are dissolved in the water phase while the catalyst remains in the IL-phase. To better understand the structural behavior of the above-mentioned ILs in methanolic solution, as well as their interaction in solutions, excess molar volume as a function of the temperature from 283.15 K to 338.15 K and excess enthalpy at 303.15 K of binary systems  $[N_{R,222}][Tf_2N] + \text{methanol}$  ( $R = 6, 8$  or  $12$ ) at 0.1 MPa were studied in the present paper.

## 2. Experimental

### 2.1. Chemicals used

The ionic liquids studied in this work were synthesized at the Department of Organic Technology, Institute of Chemical Technology Prague. Each IL was dried overnight at 323 K under high vacuum (1 Pa) prior to use. Anhydrous methanol with a purity close to 99.8% was supplied by Sigma–Aldrich and was used as received. The properties of the selected pure compounds at 293.15 K and at 298.15 K, as well as the water contents in the samples are summarized in Table 1. Water contents were measured by using a volumetric Schott TitroLine Karl–Fischer titrator. To measure refractive indices of pure ILs at 298.15 K, a Bellingham and Stanley Ltd. Abbe refractometer 60/ED with an uncertainty of  $\pm 0.00002$  was used. Refractive index of methanol was checked using a Mettler Toledo RE50 refractometer.

### 2.2. Experimental equipment and technique

Measurements of excess volumes and enthalpies were carried out at the Laboratory of Applied Physics, Universidade de Vigo. The densities of pure compounds and their mixtures were measured using an Anton Paar DMA-5000 vibrating-tube densitometer with a sensitivity close to  $10^{-5} \text{ g cm}^{-3}$ . Calibration was carried out using dry air and Milli-Q water with declared term of resistivity  $18.2 \text{ M}\Omega \text{ cm}$  at 298.15 K. The measured densities were automatically corrected for highly viscous liquids by the apparatus according to a procedure described previously in a critical review of the instrument used in this work [9]. Uncertainty in density measurements was estimated by the error-propagation law to be  $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$ . All the mixtures were prepared by weighing, using a Mettler AE-240 balance with weighing uncertainty  $\pm 0.00001 \text{ g}$ , the uncertainty in composition was then  $\pm 0.0001 \text{ mol fraction units}$ .

To be able to predict the studied properties using the ERAS model (see Section 3.1) knowledge of isobaric thermal expansivity,  $\alpha_p$ , and isothermal compressibility,  $\kappa_T$ , is necessary. These properties enabled us to determine pure-product parameters, needed for the model fit. They were determined from their definition:

$$\alpha_p = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p \quad (1)$$

$$\kappa_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial p} \right)_T \quad (2)$$

Isobaric thermal expansivity,  $\alpha_p$ , was thus obtained with an uncertainty of  $\pm 0.005 \text{ kK}^{-1}$  from the temperature dependence of density at atmospheric pressure of pure ILs and methanol. These density data measured in this work are listed in Table S1 of the supporting information. However,  $\kappa_T$  cannot be determined from density at atmospheric pressure. In order to determine  $\kappa_T$ , density at 298.15 K and in the pressure interval (0.1–5 MPa) was estimated

**Table 1**  
Properties of pure ILs compared with literature.

Compound	Purity (wt.%)	$\rho$ ( $\text{g cm}^{-3}$ ) at 293.15 K	$\rho_{\text{IL}}$ ( $\text{g cm}^{-3}$ ) at 293.15 K	$n_D^{298\text{K}}$	$n_D^{298\text{K,IL}}$	w(H <sub>2</sub> O) (wt.%)	$\alpha_p$ ( $\text{kK}^{-1}$ ) at 298.15 K	$\kappa_T$ ( $\text{T Pa}^{-1}$ ) at 298.15 K
$[N_{6,222}][Tf_2N]$	99.5 [5]	1.29291	1.29332 [11]	1.42567	1.42599 [11]	0.00186	0.651	523
$[N_{8,222}][Tf_2N]$	99.5 [5]	1.25339	1.25380 [11]	1.42903	1.42871 [11]	0.00228	0.658	529
$[N_{12,222}][Tf_2N]$	99.5 [5]	1.19169	1.19221 [11]	1.43454	1.43414 [11]	0.01658	0.673	545
Methanol	99.8 <sup>a</sup>	0.79152	0.79104 [12]	1.3264	1.32652 [12]	0.03220	1.189 [13]	1248 [13]

Experimental uncertainties:  $u(\rho) = \pm 0.00002$ ;  $u(\rho) = \pm 0.00001 \text{ g cm}^{-3}$ ;  $u(w(\text{H}_2\text{O})) = \pm 0.00001$  weight fraction units;  $u(\alpha_p) = \pm 0.005 \text{ kK}^{-1}$ ;  $u(\kappa_T) = \pm 5\%$ .  
The ILs were treated by vacuum at 323.15 K before each measurement.

<sup>a</sup> Stated by the manufacturer.

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