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Mutual solubilities of ammonium-based ionic liquids with water and with water/methanol mixture

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Abstract

Over the last two decades, ionic liquids have gained importance as alternative solvents to conventional VOCs in the field of homogeneous catalysis. This success is not only due to their ability to dissolve a large amount of metal catalysts, but it is also due to their potential to enhance yields of enantiopure products. The art of preparation of a specific enantiomer is a highly desired one and searched for in pharmaceutical industry. This work presents a study on solubility in water and in water/methanol mixture of a set of ILs composed of the bis(trifluoromethylsulfonyl)imide anion and of the N-alkyl-triethyl-ammonium cation (abbrev. $[N_{R,222}][NTf_2]$) with the alkyl chain R ranging from 6 to 12 carbons. Mutual solubilities between ILs and water, as well as between ILs and methanol/water mixture were investigated in detail. These solubilities were measured using two well-known and accurate experimental techniques based on a volumetric and a cloud-point methods. Both methods enabled us to measure the Tx diagrams reflecting the mutual solubilities between water (or water/methanol) and selected ILs in the temperature range from 293.15 to 338.15 K. The data were fitted by using the modified Flory-Huggins equation proposed by de Sousa and Rebelo and compared also with the prediction carried out by the Cosmo-RS methodology.

Keywords: Ionic liquids; liquid-liquid equilibria; solubility; COSMO-RS; modified Flory-Huggins equation; gnostic regression

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1. Introduction

Room-temperature ionic liquids have undergone a considerable development since Walden's synthesis of ethylammonium nitrate in 1914 [1]. Practically non-volatile, with properties tunable to meet the needs of specific applications thanks to a large number of cation and anion combinations, ionic liquids have been focused upon for almost two last decades [2]. They are efficient solvents with considerable potential for chemical synthesis and separation processes, being successfully implemented into practical applications such as he BASF BASIL ™ processes [3, 4].

Noyori-type stereoselective hydrogenations catalyzed by Ru-BINAP complexes belong to the many applications that may benefit from the use of ionic liquids. Floriš *et al.* [5] have studied the use of N-alkyl-triethylammonium bis(trifluoromethylsulfonyl)imides in methanolic solution as reaction media and catalytic support in Ru-BINAP catalyzed enantioselective hydrogenations of β-ketoesters, observing a rise in enantioselectivity of up to 13 % as compared to reaction carried out in pure methanol. It appears that these ionic liquids immobilize the catalyst in the mixture for easier recycling and further re-use and protect it from air/oxygen. However, the reaction is carried out in a homogeneous mixture, the final separation of the product is therefore carried out by rinsing the solution with water, which may also wash out the ionic liquid with the catalyst. To prevent the potential loss of both catalyst and support, separation must be optimized based upon the previous knowledge of the solubility of the ionic liquid in water, as well as in methanol/water mixtures.

In this paper, we report on the mutual solubility (liquid-liquid equilibrium) of N-alkyl-triethylammonium bis(trifluoromethylsulfonyl)imides (abbrev. $[N_{R,222}][NTf_2]$, where R = 6 to 12) with water and solubility of this homologous ionic liquids' series in water/methanol mixtures (1:1 ratio in weight). For these systems, liquid phase behavior was evaluated and discussed in terms of the influence of the alkyl chain length, R, on the alkylammonium cation $[N_{R,222}]^+$ on the solubility and in view of the separation of the ionic liquids with catalysts from the reaction mixtures. Indeed, considering what has been said above, the knowledge of the hydrophobicity of the ionic liquids and of the way it changes on addition of a co-solvent is essential.

The correlation of the measured data by the modified Flory-Huggins equation was also carried out in this work by the methodology originally proposed by de Sousa and Rebelo [6]. A robust gnostic regression has been used to optimize the model parameters. Finally, liquid phase behavior of each studied system was calculated by the COSMO-RS methodology using the COSMOthermX software. These calculated values are compared with experimental data to evaluate the predictive capability of this method for involved systems [7].

2. Experimental section

2.1. Chemicals used

The $[N_{R,222}][NTf_2]$ ionic liquids used in this work were provided by the Department of Organic Technology, Institute of Chemical Technology Prague. The purity of each ionic liquid sample determined by NMR analysis is close to 99.5 wt. %. The ionic liquids were dried overnight at 353 K and under mild vacuum (approx. 0.1 Pa) before use. Afterwards, the water content in the studied ionic liquids was determined by means of Karl-Fischer titration and was typically found to range between 0.002 and 0.02 wt. %. Anhydrous methanol (purity 99.8 wt. %) was purchased from Sigma-Aldrich and used as delivered. Distilled water with conductivity 2.1 μS prepared in our laboratory was used in the experiments.

2.2. Experimental equipment and procedure

The water content of the ionic liquids was determined before the measurements by volumetric Karl-Fisher titration using a Schott TitroLine titrator. The determination of water contents was carried out with an uncertainty of ± 0.001 wt. %.

Liquid-liquid equilibria in binary systems ionic liquid + water were measured using the volumetric method; the solubility of the ionic liquids in the water/methanol mixture (1:1 ratio in weight) was measured using the cloud point method.

The volumetric method uses an apparatus built in-house in E. Hála Laboratory of Thermodynamics. It enabled us to determine compositions of the phases in equilibrium by measuring volumes of equilibrium phases of two mixtures of known compositions in calibrated ampoules. The compositions were then calculated from the experimentally obtained volumes using a mass balance (see [8] for the description of the apparatus and a more detailed description of the method).

The cloud-point method was used to measure solubility of ionic liquids in water/methanol mixtures (1:1 ratio in weight). Known amounts of the ionic liquid and water/methanol mixture were weighed into a thermostated equilibrium cell and brought to a temperature at which the mixture became homogeneous. Then, using a programmable thermostat, the temperature in the cell was decreased at a defined rate to find the narrowest possible interval in which the mixture became heterogeneous. The same procedure was repeated in the opposite direction, *i.e.* the solution was heated to find the temperature at which it cleared out. Both the cloud and the clearing points were determined optically, by measuring the intensity of a laser beam light scattered by the mixture [9]. Hysteresis in the cloud and clearing points temperatures of approx. 0.2 to 0.5 K was observed, hence the resulting solution temperature was found as an average of the cloud and clearing point temperatures.

For both methods, the uncertainty in weighing was found to be ± 0.00002 g, the overall uncertainty in the global composition ± 0.0002 in mole fraction units, and the temperature was kept constant within ± 0.02 K. Temperature was determined with an uncertainty of ± 0.03 K in the cloud point method. In the volumetric method phase volumes were determined with an uncertainty of ± 0.01 cm^3. The experimental uncertainty estimated for the system $[N_{6,222}][NTf_2]$ + water by means of the error propagation law was found to be ± 0.0001 and ± 0.01 in mole fraction for the aqueous phase and ionic liquid phase, respectively. In the systems $[N_{10,222}][NTf_2]$ + water and $[N_{12,222}][NTf_2]$ + water the uncertainties were estimated to be ± 0.00004 and ± 0.01 in mole fraction units, respectively.

3. Results and discussion

3.1. Liquid-liquid equilibrium in systems $[N_{R,222}][NTf_2]$ + water

It appears from experimental data for the studied ionic liquids + water binary systems, summarized in Table 1 and shown in Figure 1, that their mutual solubility decreases with the increasing alkyl chain length, *R*, on the ammonium cation $[N_{R,222}]^+$. All the studied systems appear to show upper critical solution temperature (UCST) behavior. The solubility of the ionic liquid in water is typically lower than 0.0003 mole fraction units, *i.e.* sufficiently low for the desired catalytic application. In the ionic liquid phase the solubility of water in the ionic liquid is fairly high, of approx. 0.25 to 0.35 in mole fraction units and does not change dramatically with the increasing alkyl chain length on the ammonium cation. On the other hand, the solubility of the ionic liquids in water drops by an order of magnitude in the aqueous phase with increasing of the alkyl chain length from *R* = 6 to 12 for each higher member of the homologous series.

Table 1. Liquid-liquid equilibrium in systems of $[N_{R,222}][NTf_2]$ (1) + water(2) binary mixture as the function of temperature measured by the volumetric method

T / K	$x_1{'}$ aqueous phase	$x_1{''}$ ionic liquid phase
	$[N_{6,222}][NTf_2]$	
303.15	0.0002	0.66(6)
308.15	0.0003	0.67(0)
313.15	0.0003	0.66(8)
318.15	0.0002	0.66(5)
323.15	0.0002	0.64(2)
328.15	0.0002	0.61(4)
333.15	0.0002	0.62(6)
338.15	0.0003	0.56(4)
343.15	0.0002	0.55(8)
	$[N_{10,222}][NTf_2]$	
298.15	0.00005	0.71(5)
303.15	0.00009	0.70(0)
308.15	0.00001	0.70(2)
313.15	0.00013	0.68(0)
318.15	0.00007	0.68(3)
323.15	0.00008	0.64(0)
328.15	0.00007	0.67(9)
333.15	0.00011	0.64(9)
338.15	0.00000(8)	0.69(2)
	$[N_{12,222}][NTf_2]$	
298.15	0.00006	0.75(1)
303.15	0.00004	0.73(3)
308.15	0.00004	0.74(3)
313.15	0.00011	0.78(3)
318.15	0.00013	0.74(2)
323.15	0.00008	0.73(6)
328.15	0.00007	0.69(7)
333.15	0.00007	0.67(8)
338.15	0.00010	0.66(0)

The liquid-liquid equilibrium data measured by the volumetric method were correlated by the modified Flory-Huggins equation proposed by de Sousa and Rebelo [6]. The dimensionless excess Gibbs energy according to this model is

$$G^E/RT = (rx_1 + x_2)\, \chi(T)\, \varphi_1 \varphi_2 \qquad (1)$$

where x_i are mole fractions, $\chi(T)$ is the segment-segment interaction parameter the temperature dependence of which is given by the relation

$$\chi(T) = d_0 + d_1/(T) - d_2 \ln(T), \qquad (2)$$

and φ_i are the segment fractions:

$$\varphi_1 = rx_1/(rx_1 + x_2) \qquad\qquad \varphi_2 = x_2/(rx_1 + x_2) \qquad (3)$$

where r is the number of segments occupied by component 1, subscripts 1 and 2 referring to the larger and smaller molecule respectively. The interaction parameter is considered to be pressure-independent in this work. The number of segments r does not differ greatly from the ratio of molar volumes of the components ($r \approx V_1/V_2$).
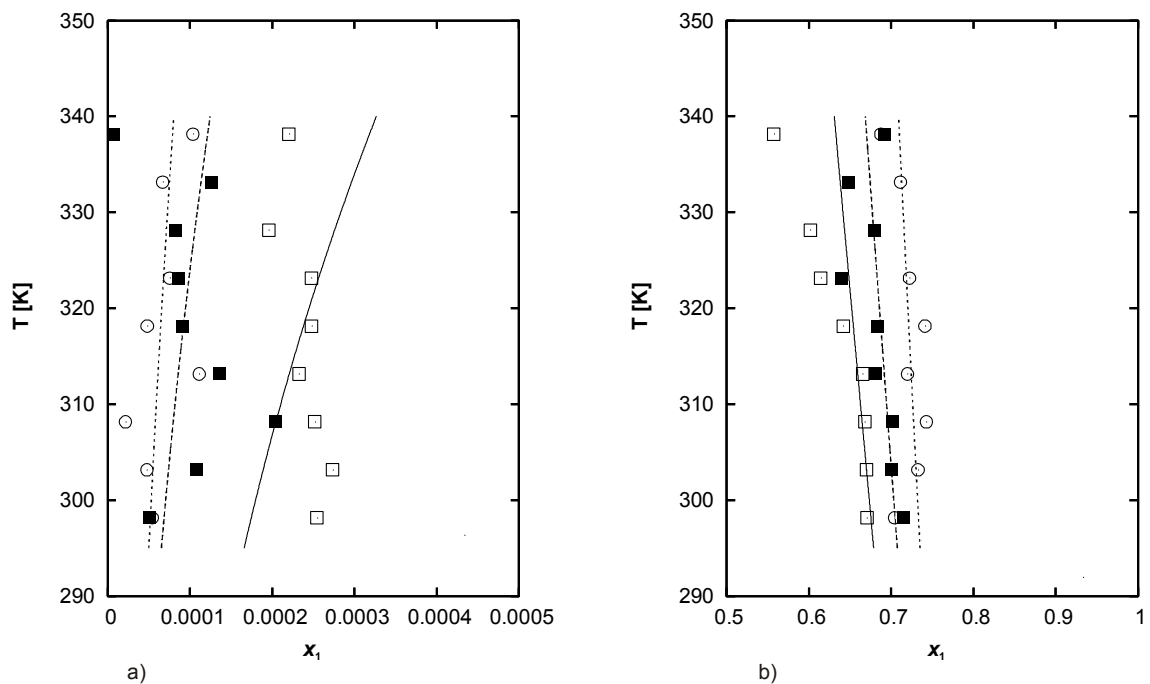

Fig. 1. Mutual solubility in binary systems [N_{R,222}][NTf_2] (1) + water (2) and correlation by the modified Flory-Huggins equation. (a) aqueous phase, (b) ionic liquid phase. □ [N_{6,222}][NTf_2]; ■ [N_{10,222}][NTf_2]; ○ [N_{12,222}][NTf_2]; full line, modified Flory-Huggins equation for system [N_{6,222}][NTf_2] + water; dash line, modified Flory-Huggins equation for system [N_{10,222}][NTf_2] + water; dotted line modified Flory-Huggins equation for system [N_{12,222}][NTf_2] + water

The parameters were obtained using a regression along a gnostic influence function using a procedure described in detail in previous work [8]. These are summarized in Table 2 and the correlation of the experimental liquid-liquid equilibrium data is shown in Figure 1. Residuals [9, 10] were analyzed in order to check for outliers using the following objective function:

$$S = \sum_{i=1}^{N} \left[w_{\text{aq},i} \left(\frac{x_{\text{aq},i}^{\text{exp}} - x_{\text{aq},i}^{\text{calc}}}{\sigma_{x,aq}} \right)^2 + w_{\text{IL},i} \left(\frac{x_{\text{IL},i}^{\text{exp}} - x_{\text{IL},i}^{\text{calc}}}{\sigma_{x,\text{IL}}} \right)^2 \right] \tag{5}$$

where i refers to points on the tie lines, x is the molar fraction, and subscripts *IL* and *aq* correspond to the ionic liquid and aqueous phases, respectively, N is the number of experimental tie lines. The values used in this work are: $\sigma_{x,1} = 0.02$, $\sigma_{x,2} = 0.0001$. Initially variables $w_{\text{aq},i}$ and $w_{\text{IL},i}$ are equal to one, these variables denote the robustifying weights determined iteratively by application of the gnostic influence function (more details and comments about the modified Flory-Huggins methodology used herein are provided in the [11]).

Correlation using the modified Flory-Huggins equation shows good agreement with the experimental data (see Figure 1) even in the aqueous phase where the differences between the experimental and calculated values are within the limits of the measurement uncertainty, no outliers have been detected.

Table 2. Parameters of the modified Flory-Huggins equation.

System	r	d_0	d_1	d_2
$[N_{6222}][NTf_2]$ + water	5.26802	7.64338	-0.00726	0.97804
$[N_{10222}][NTf_2]$ + water	5.51882	7.21009	0.92918	0.88194
$[N_{12222}][NTf_2]$ + water	5.39682	6.02658	0.08828	0.65803

3.2. Solubility of $[N_{R,222}][NTf_2]$ in water/methanol mixture (1:1 ratio in weight)
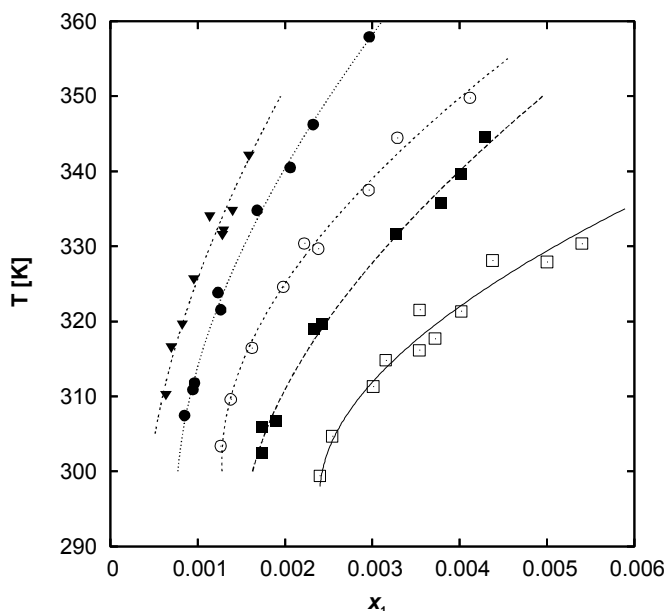

Fig. 2. Solubility of ionic liquids $[N_{R,222}][NTf_2]$ (1) in water/methanol mixture (1:1 ratio in weight) (2). □ $[N_{6,222}][NTf_2]$; ■ $[N_{7,222}][NTf_2]$; ○ $[N_{8,222}][NTf_2]$; ● $[N_{10,222}][NTf_2]$; ▼ $[N_{12,222}][NTf_2]$. The individual lines represent the description by Eq. 6 with parameters reported in the Table 4.

The experimentally obtained data of solubility of ionic liquids in water/methanol mixture (1:1 ratio in weight) are summarized in Table 3 and shown in Figure 2. The ratio of water to methanol was chosen based upon the amount of water used to extract the reaction products from methanolic solution after the finished stereoselective hydrogenation [12] A quick comparison between data in Tables 1 and 3 and Figures 1a and 2 shows the effect of the addition of methanol on the liquid-liquid equilibrium of selected ionic liquids and water. The solubility of ionic liquid in the molecular solvent phase increases approximately by one order of magnitude in mole fraction unit as compared with its solubility in pure water, similarly to binary systems with water, all pseudobinary systems show UCST behavior. From Figure 2, it is also apparent that similarly to binary systems with water the solubility of the ionic liquid decreases with increasing length of the alkyl on the ammonium cation. The temperature trend of solubility also changes slightly with the changing cation structure - solubility dependence on temperature is less pronounced in higher members of the homologous series.

Quite predictably it was observed in our previous work [13] that the $[N_{R,222}][NTf_2]$ ionic liquids tend to a more rigid and organized structure as the molecule gets bulkier, presenting larger viscosity and lower density as the cation alkyl chain length increases. Such structure effects corroborate the structural and temperature trends of the measured solubility data for all systems presented in this work.

Table 3. Solubility of ionic liquids [N$_{R,222}$][NTf$_2$] in mixture water/methanol (1:1 ratio in weight) as the function of temperature measured by the cloud point method

x_1	T/K	x_1	T/K
[N$_{6,222}$][NTf$_2$]		[N$_{8,222}$][NTf$_2$]	
0.0037	317.70	0.0016	316.45
0.0035	316.14	0.0014	309.60
0.0032	314.80	0.0013	303.38
0.0024	299.42	0.0041	349.78
0.0054	330.36	0.0024	329.68
0.0050	327.93	0.0033	344.46
0.0044	328.12	0.0030	337.49
0.0035	321.52	0.0022	330.38
0.0028	316.26	0.0020	324.59
0.0025	304.68	[N$_{10,222}$][NTf$_2$]	
0.0040	321.33	0.0030	357.91
0.0030	311.30	0.0013	321.53
0.0026	316.26	0.0010	310.88
[N$_{7,222}$][NTf$_2$]		0.0023	346.23
0.0024	319.66	0.0021	340.49
0.0019	306.77	0.0017	334.78
0.0017	302.44	0.0012	323.83
0.0017	305.96	0.0010	311.78
0.0023	318.95	0.0009	307.46
0.0033	331.59	[N$_{12,222}$][NTf$_2$]	
0.0038	335.79	0.0006	310.35
0.0040	339.57	0.0007	316.67
0.0043	344.55	0.0008	319.70
		0.0010	325.76
		0.0011	334.12
		0.0016	342.22
		0.0014	334.91
		0.0013	332.23
		0.0013	331.64

We have described the experimental data using a simple model derived from the empirical relationship for the temperature dependence of heats of solution [14]. In this model, the mole fractions of the ionic liquid in the solution water/methanol may be obtained from the following equation:

$$\ln x_i = A + \frac{B}{T} + C \ln T \tag{6}$$

where *A*, *B* and *C* are adjustable parameters. The parameters of the model obtained by non-linear regression are summed up in Table 4. As shown in Figure 3, the chosen equation describes the data with good accuracy.

Table 4. Parameters of Eq. 6. along with standard deviations in composition σ_x

system	*A*	*B*	*C*	σ_x
$[N_{6,222}][NTf_2]$ + water/methanol	-3.30210	146.50136	0.49374	0.00026
$[N_{7,222}][NTf_2]$ + water/methanol	-1.38072	60.10773	0.20723	0.00010
$[N_{8,222}][NTf_2]$ + water/methanol	-1.71318	76.98075	0.25559	0.00012
$[N_{10,222}][NTf_2]$ + water/methanol	-0.84146	37.12962	0.12596	0.00005
$[N_{12,222}][NTf_2]$ + water/methanol	-0.62338	27.12326	0.09352	0.00009

COSMO-RS methodology was examined to assess its predictive capability of the solubility in the studied systems. It had previously been found to predict liquid-liquid equilibria in a range of other systems involving ionic liquids by our groups [11] and by others [15 - 20]. Details of the COSMO files generation are described in detail in previous work, [11, 21]. The generated sigma profiles from the COSMO files are then used to predicted fluid phase behavior of studied systems by using the VLE/LLE calculations options in COSMOThermX software (version C21_0108). From Figure 4 where prediction by COSMO-RS is compared to the correlation of the experimental data by the modified Flory-Huggins equation, it appears that COSMOThermX is able to predict the correct UCST trends observed in the case of binary systems containing water + $[N_{R,222}][NTf_2]$ with *R* = 6, 10, and 12, as well as the very low solubility of each ionic liquid in the aqueous phase. Furthermore, as shown in Figure 4, COSMOThermX predicts a decrease of the mutual solubility of the ionic liquid and water with the increasing the of the ammonium cation alkyl chain length, as observed experimentally. From this study, it therefore appears that COSMO-RS is able to provide qualitative information on the studied binary systems, estimating the correct order of magnitude of the solubility of water in ionic liquids, as well as of the solubility of ionic liquids in water.
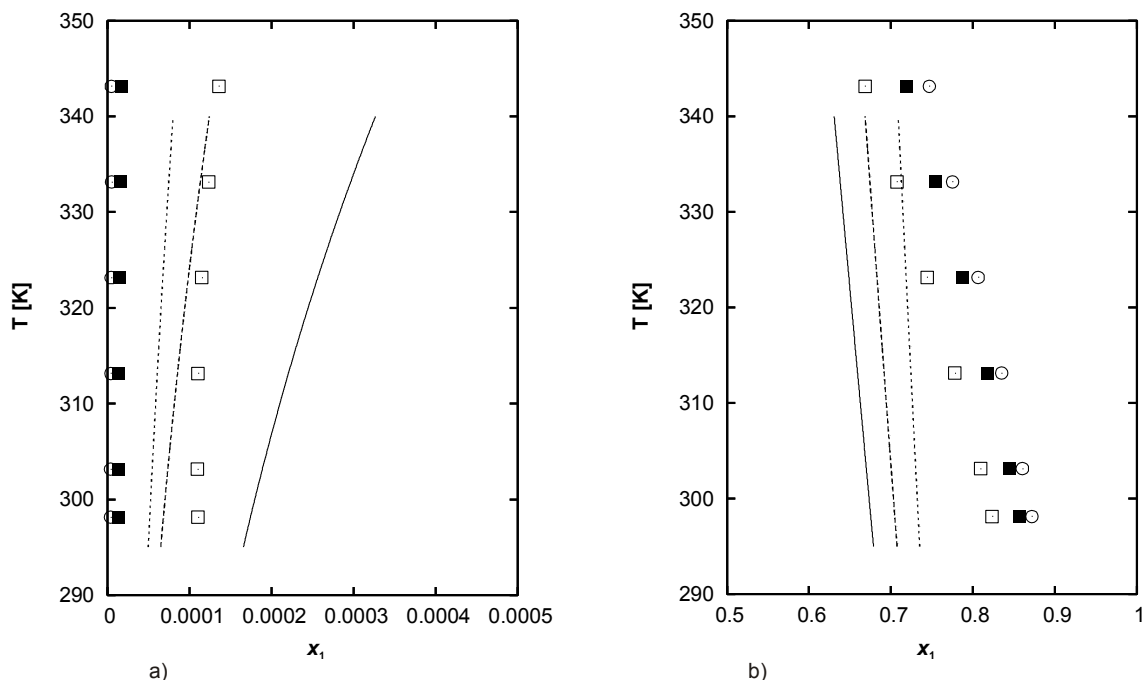
Fig. 4. Mutual solubility in binary systems [N$_{R,222}$][NTf$_2$] (1) + water (2). Comparison of the correlation by the modified Flory-Huggins equation with COSMO-RS prediction. (a) aqueous phase, (b) ionic liquid phase. Points – prediction by COSMO-RS, □ [N$_{6,222}$][NTf$_2$]; ■ [N$_{10,222}$][NTf$_2$] ; ○ [N$_{12,222}$][NTf$_2$] ; full line, modified Flory-Huggins equation for system [N$_{6,222}$][NTf$_2$] + water; dash line, modified Flory-Huggins equation for system [N$_{10,222}$][NTf$_2$] + water; dotted line modified Flory-Huggins equation for system [N$_{12,222}$][NTf$_2$] + water.

Prior to calculating systems involving the ionic liquids, water, and methanol, mutual miscibility of methanol with [N$_{R,222}$][NTf$_2$] (with R = 6, 7, 8, 10, or 12) was evaluated over the whole composition range and as function of temperature from 293 to 373 K within COSMOThermX. As appears from the prediction results and as expected from experimental observation, methanol is fully miscible with all studied ionic liquids. Additionally, to cover the same composition range studied experimentally for each ionic liquid + water/methanol pseudobinary system, a binary mixture "cosmo file" containing water and methanol at the 1:1 weight ratio was created by using the metafile editor option within COSMOThermX, which then provides the estimate of the pseudo binary liquid-liquid equilibria systems containing water/methanol (1:1 weight ratio) + [N$_{R,222}$][NTf$_2$] with R = 6, 7, 8, 10, or 12, as a function of temperature. In Figure 5 the prediction by COSMO-RS is compared to the description of the experimental data by Equation 6 with the parameters reported in Table 4. It is evident that COSMOThermX is able to predict the correct order of magnitude of the experimentally measured solubility of each ionic liquid in the binary mixture of water/methanol at the 1:1 weight ratio. COSMOThermX calculations predict in each case an UCST shape as a function of temperature. Furthermore, as shown in Figure 5, COSMOThermX predicts a decrease of the mutual solubility of the ionic liquid in the water/methanol mixture at 1:1 weight ratio with the increasing alkyl chain length of the ammonium cation which is in agreement with experiment. In other words, like in the previous case it appears that COSMOThermX is able to provide qualitative information on each studied pseudobinary system, providing the correct order of magnitude of the solubility of the studied ionic liquids in water/methanol mixture.
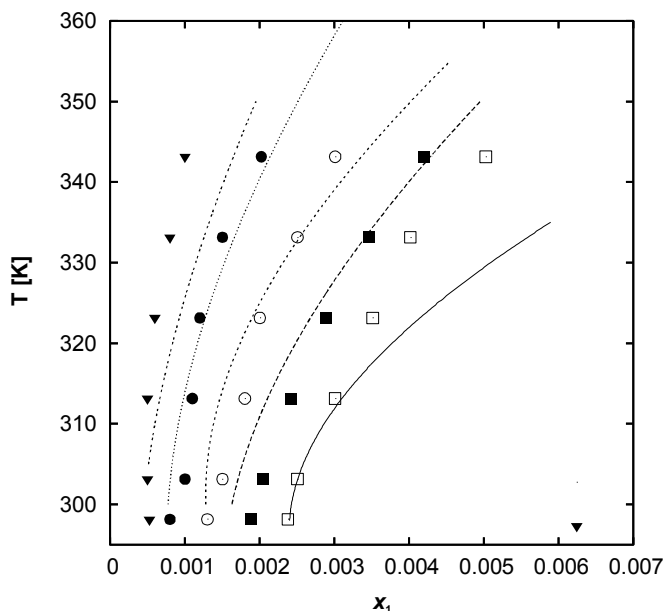
Fig. 5. Solubility of ionic liquids $[N_{R,222}][NTf_2]$ (1) in water/methanol mixture (1:1 ratio in weight) (2). Comparison of the description of experimental data using the Eq. 6 with COSMO-RS prediction.. □ $[N_{6,222}][NTf_2]$; ■ $[N_{7,222}][NTf_2]$; ○ $[N_{8,222}][NTf_2]$; ● $[N_{10,222}][NTf_2]$ ▼ $[N_{12,222}][NTf_2]$. The individual lines represent the description by Eq. 6 by using parameters reported in Table 4

4. Conclusion

Liquid-liquid equilibria (mutual solubility) in systems of ionic liquids $[N_{R,222}][NTf_2]$ with water have been measured by the volumetric method. The experimental data show that the solubility decreases on increasing of the alkyl chain length, *R*, on the ammonium cation, with the differences being more pronounced in the aqueous phase than in the ionic-liquid phase. Further, it appears from the obtained data that the solubility of the studied ionic liquids in water is equal to and lower than 2.10^{-4} mole fraction units, *i.e.* they show a very low solubility in water. To find the phase boundary in pseudobinary systems of $[N_{R,222}][NTf_2]$ ionic liquids with water/methanol mixture, a second set of measurements by the cloud-point method was carried-out. From which, the solubility of each selected ionic liquid in the water/methanol (1:1 ratio in weight) mixture was measured as the function of temperature. Similarly to the aqueous binary systems, the solubility of the ionic liquids decreases with the increasing alkyl chain length, however, the hydrophobicity of the ionic liquid is only slightly decreased by the added methanol. This degree of hydrophobicity makes them unlikely to be washed out by water from a reaction mixture. From this point of view they are suitable for use as reaction media and catalyst support in enantioselective hydrogenations.

The liquid-liquid equilibrium data were correlated by the modified Flory-Huggins equation proposed by de Sousa and Rebelo which occurs to describe the present data with good accuracy. Solubility of the studied ionic liquids in water/methanol mixtures was described successfully with a simple empirical model based on the temperature dependence of heats of solution. At the same time, the prediction of the solubility by the COSMO-RS methodology appears to qualitatively correspond with the experiments,

which confirms again the potential of this theoretical model to predict thermodynamic data with good reliability.

Acknowledgments

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