LIQUID-LIQUID EQUILIBRIUM IN BINARY MIXTURES OF 1-ETHYL-3-METHYLIMIDAZOLIUM ETHYLSULFATE AND HYDROCARBONS

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Increasing attention has been paid to room-temperature ionic liquids over the past decade, because of their potential use as new, more efficient solvents. In addition, the number of ions that can be combined to create an ionic liquid being substantial, they can be "tailor-made" to various applications, this making them prospective designer solvents.

In this work, liquid-liquid equilibrium in binary systems 1-ethyl-3-methylimidazolium ethylsulfate (abbr. $[emim][C_2H_5SO_4]$) + n-heptane (methylcyclohexane, toluene) was investigated. The interest of this study was to compare qualitatively and quantitatively the liquid phase behaviour of mixtures of $[emim][C_2H_5SO_4]$ with aliphatic, cyclic and aromatic hydrocarbons.

To obtain experimental data, the volumetric method proposed by Řehák et al. was used, enabling us to obtain tie lines.

The author is not aware of literature data for these systems, apart from works by Meindersma et al. who studied the extraction of toluene from n-heptane by $[emim][C_2H_5SO_4]$.

KEYWORDS: liquid-liquid equilibrium, room-temperature ionic liquids, volumetric method

INTRODUCTION

There is growing interest in possible industrial use of room-temperature ionic liquids e.g. as non-volatile solvent alternative to harmful volatile organic compounds or entrainers in extractive distillation processes leading to an increasing demand for experimental data on their thermodynamic properties, particularly for solubility data.

Reliable data on liquid-liquid equilibrium in multicomponent systems of are of great importance in many industrial processes, namely in extraction design. Ionic liquids occur to be potentially utilisable in such processes, owing to their negligible vapour pressure that makes them readily recyclable for repeatable use or utilisable without any losses on material at low to vacuum pressures.

The present work is a part of a systematic study on 1-ethyl-3-methylimidazolium ethylsulfate (abbr. $[emim][C_2H_5SO_4]$), namely on its solubilities with different compounds at atmospheric pressure and at supercritical conditions. New data on liquid-liquid equilibrium in binary systems containing $[emim][C_2H_5SO_4]$ and hydrocarbons are presented. Experimental data were obtained by the volumetric method [1] in binary

systems of [emim][$C_2H_5SO_4$] with n-heptane, methylcyclohexane, and toluene. According to Meindersma et al. [3] who have studied selectivities and distribution coefficients in ternary system [emim][$C_2H_5SO_4$] + n-heptane + toluene, [emim][$C_2H_5SO_4$] is a suitable solvent for extraction of aromatics from naphtha cracker feeds. The selected hydrocarbons in this contribution are aliphatic, cyclic, and aromatic ones respectively, the aim of this work being to compare both qualitatively and quantitatively mutual solubilities with [emim][$C_2H_5SO_4$] in the series.

The volumetric apparatus following work of Řehák et al. [2] was previously used successfully in determining liquid-liquid equilibrium in binary mixtures of ionic liquids [1]; the acquired data showed satisfactory to good agreement with results obtained in our laboratory by the cloud-point method as well as with those presented by other authors. The principal advantage of this experimental method lies in its simplicity and in the fact that it helps economise the amount of the ionic liquid used in the measurements.

EXPERIMENTAL SECTION

The ionic liquid [emim][$C_2H_5SO_4$] (ECOENG^{TM} 212) was provided by Solvent Innovation GmbH. Prior to experiments, the ionic liquid was dried under vacuum (10^{-4} Pa) for at least 48 hrs. n-Heptane (anhydrous), methylcyclohexane (anhydrous), and toluene (anhydrous) were furnished by Sigma Aldrich and were used as delivered. Table 1 gives an overview of purities stated by the manufacturers as well as refractive indices measured for all the compounds in this work compared with literature values where these were available.

The volumetric method was used to obtain the equilibrium compositions in the investigated binary systems. It consists in measuring the volumes of the equilibrium phases and in subsequent calculation of the equilibrium compositions (tie lines) from the mass balance:

$$x_1^{(1)} = \frac{n_{1,I}V_{2,II} - n_{1,II}V_{2,I}}{V_{2,II}(n_{1,I} + n_{2,I}) - V_{2,I}(n_{1,II} + n_{2,II})} \tag{1}$$

$$x_1^{(2)} = \frac{n_{1,II}V_{1,I} - n_{1,I}V_{1,II}}{V_{1,I}(n_{1,II} + n_{2,II}) - V_{1,II}(n_{1,I} + n_{2,I})} \tag{2}$$

Table 1. Purity and refractive indices of the measured compounds

Compound	Assay (wt.%)[a]	n_D at 298.15 K	
		This work	Literature data
[emim][$C_2H_5SO_4$]	99%	1.4783	–
n-Heptane	99%	1.3850	1.38513 [5]
Methylcyclohexane	≥99%	1.4206	1.42058 [5]
Toluene	99.8	1.4940	1.49411 [5]

[a]Stated by the manufacturer.

where $x_i^{(k)}$ is the mole fraction of the i-th component in the k-th phase, $V_{k,I}$ and $V_{k,II}$ is the volume of the k-th phase in the first and second set of measurements respectively, and $n_{i,I}$ and $n_{i,II}$ is the chemical amount of the i-th component in the first set and second set of measurements respectively.

Two calibrated ampoules were filled with known amounts of the measured compounds. They were then placed in a thermostated jacket and brought to the required temperature. The apparatus was set on a shaker where the content of the ampoules was stirred for at least 8 hrs. The mixtures were then let stand for at least 12 hrs to equilibrate. In case that the interfacial tension between the two liquids was significant with droplets of one phase appearing in the other, the ampoules were placed prior to settling in a warm ultrasound bath for 5 minutes to avoid this occurrence.

To obtain the most precise volumes possible, it had to be accounted for the curvature of the phase interfaces; for this purpose, a graphical determination of the phase volumes was carried out. The phase interfaces were photographed and the exact volumes of the phases were then determined, approximating the meniscus with a rotational ellipsoid. Figure 1 represents a typical snapshot for a convex meniscus shape from which the exact phase volumes were acquired.

In the figure, $h = a_1 - a_2$ is the height of the meniscus, a_1 and a_2 being the read-outs on the volume scale for the upper and the lower meniscus edge respectively, D_{in} and D_{out} are the ampoule's inner and outer diameter respectively, and a and b are the horizontal semiaxes of the ellipsoid approximating the meniscus shape. The volume of the ellipsoid cap above the a_2 read-out is then

$$V_{cap} = \frac{\pi}{3}(3a - h)\left(\frac{bh}{a}\right)^2 \qquad (3)$$

Řehák et al. [2] gives a detailed study of the graphical determination of the liquid phase volumes on using the volumetric method.
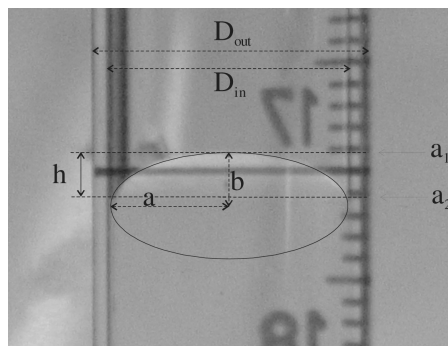

Figure 1. Evaluation of liquid phase volume

The experimental uncertainties for the volumetric method were determined from the standard deviations obtained from the error-propagation law. They were found to be ± 0.001 mole fraction units and ± 0.002 mole fraction units for the organic phase and the IL-rich phase respectively.

RESULTS AND DISCUSSION

Liquid-liquid equilibrium at various temperatures was acquired for systems [emim][C_2H_5 SO_4] + n-heptane, [emim][$C_2H_5SO_4$] + methylcyclohexane, and [emim][$C_2H_5SO_4$] + toluene by means of the volumetric method. The obtained results are summarized in Table 2 and represented in Figures 2 to 4. It is evident, that the solubility of the ionic liquid in all three compounds is very low, as well as the solubility of n-heptane in

Table 2. Equilibrium compositions in system [emim][$C_2H_5SO_4$] (1) + n-heptane (2), [emim][$C_2H_5SO_4$] (1) + methylcyclohexane (2), and [emim][$C_2H_5SO_4$] (1) + toluene (2)

| Organic phase x'_1	IL-rich phase x''_1	T [K]
[emim][$C_2H_5SO_4$] (1) + n-Heptane (2)		
0.0038	0.9968	293.15
0.0042	0.9961	303.15
0.0040	0.9954	313.15
0.0047	0.9929	323.15
0.0095	0.9942	333.15
[emim][$C_2H_5SO_4$] (1) + Methylcyclohexane (2)		
0.0145	0.9792	293.15
0.0095	0.9777	303.15
0.0094	0.9742	313.15
0.0071	0.9690	323.15
0.0063	0.9600	333.15
[emim][$C_2H_5SO_4$] (1) + Toluene (2)		
0.0061	0.7588	293.15
0.0046	0.7608	303.15
0.0058	0.7561	313.15
0.0046	0.7594	323.15
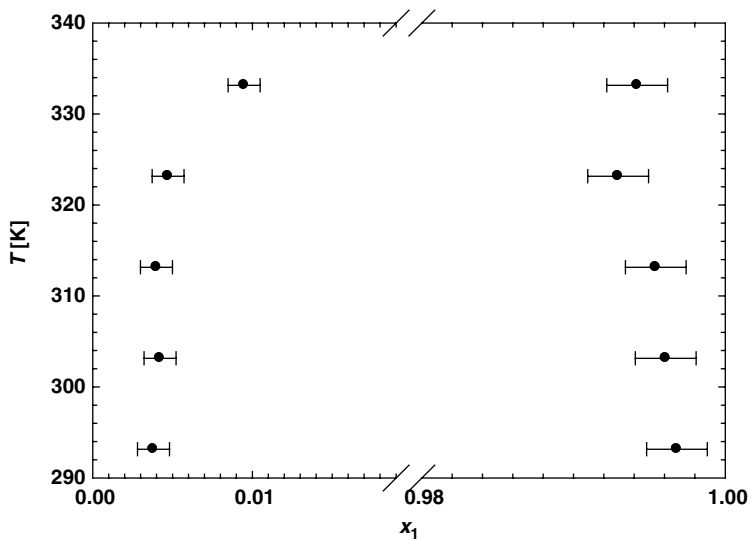
Figure 2. Liquid-liquid equilibrium in system [emim][$C_2H_5SO_4$] (1) + n-heptane (2)
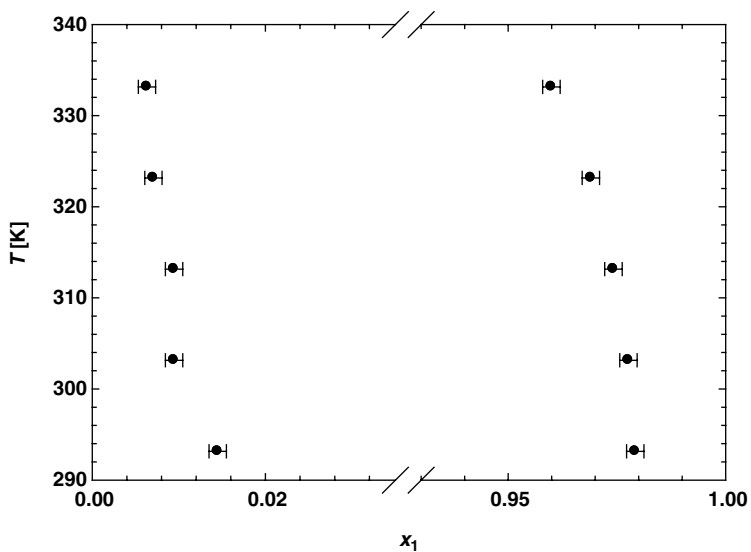

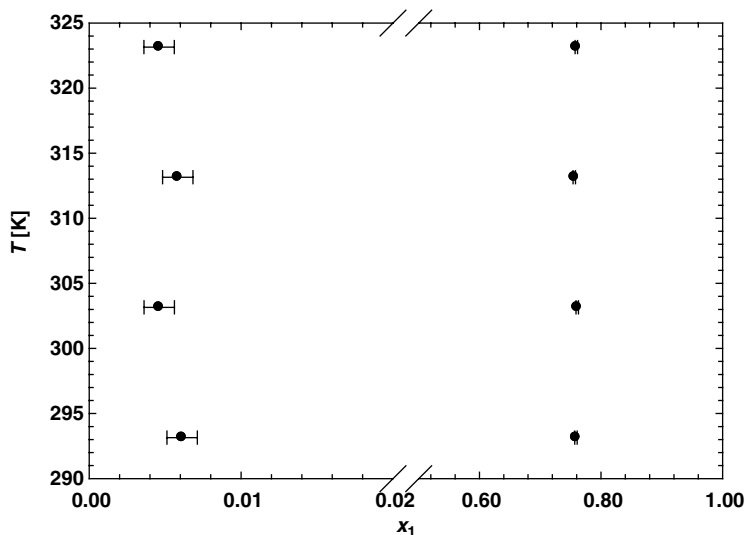**Figure 3.** Liquid-liquid equilibrium in system [emim][$C_2H_5SO_4$] (1) + methylcyclohexane (2)

Figure 4. Liquid-liquid equilibrium in system [emim][C$_2$H$_5$SO$_4$] (1) + toluene (2)

[emim][C$_2$H$_5$SO$_4$]; the order of magnitude of the solubility values is only of thousandths mole fraction units. These values correspond in order of magnitude to values of experimental uncertainties. The solubility of methylcyclohexane in [emim][C$_2$H$_5$SO$_4$] is higher than that of heptane, of hundredths, the highest values of solubility being observed in the system toluene + [emim][C$_2$H$_5$SO$_4$], of order of magnitude of tenths mole fraction units. This corresponds to the results obtained by Meindersma et al. [3, 4], giving high selectivity values S$_{tol/hept}$ for mixtures of n-heptane, toluene and [emim][C$_2$H$_5$SO$_4$].

It follows from the obtained results, that the volumetric method yields reliable data for systems showing mutual solubilities of at least hundredths mole fraction units. The acquired data are less reliable in systems with lower solubilities; however, the experimental method can be used in such systems as a simple tool for estimates of liquid-liquid equilibria prior to more precise measurements. Moreover, it was shown in previous work [1] that such estimates may be in satisfactory agreement with data obtained by other experimental methods. However, in this work all three systems present a very weak dependence of liquid-liquid equilibrium on temperature in the investigated temperature range. This, along with the fact that toluene and [emim][C$_2$H$_5$SO$_4$] form an isorefractive mixture, made impossible the verification of the acquired results by the cloud-point method. In the frames of this project, further measurements using a direct analytical method that is being presently developed in our laboratory are planned.

CONCLUSION
In the present paper, a study on liquid-liquid equilibrium at various temperatures in three binary systems [emim][$C_2H_5SO_4$] + n-heptane, [emim][$C_2H_5SO_4$] + methylcyclohexane, and [emim][$C_2H_5SO_4$] + toluene is presented. To obtain experimental tie-line data, volumetric method was used. It occurs that for the mutual solubility of [emim][$C_2H_5SO_4$] and heptane the experimental values correspond in the order of magnitude to the experimental uncertainty as estimated by the error-propagation law. Similarly low solubility was observed for the ionic liquid in the other two hydrocarbons. Methylcyclohexane and toluene present higher values of solubility in [emim][$C_2H_5SO_4$], toluene being more soluble in the ionic liquid than methylcyclohexane. The acquired results are in qualitative agreement with those published by Meindersma et al. [3, 4] who obtained high values of selectivity $S_{tol/hept}$ in mixtures [emim][$C_2H_5SO_4$], toluene and n-heptane. The volumetric method appears to be a simple and satisfactorily reliable tool for estimating low solubilities, presenting good accuracy for systems with mutual solubilities of units to tens mole fraction units. To verify the data acquired in the present work, experiments using another suitable experimental method are necessary, measurements using the cloud-point method having revealed itself impracticable in this particular case. Measurements on liquid-liquid equilibrium in the present binary systems are planned to continue using a suitable direct analytical method.

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