# Phase Equilibria of (1-Ethyl-3-methylimidazolium Ethylsulfate + Hydrocarbon, + Ketone, and + Ether) Binary Systems

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The mutual solubilities of [EMIM][EtSO$_4$], namely, 1-ethyl-3-methylimidazolium ethylsulfate, with *n*-alkanes (hexane or octane), aromatic hydrocarbons (benzene, toluene, or ethylbenzene), ketones (pentan-2-one, pentan-3-one, hexan-2-one, or heptan-4-one), ethers (dibutyl ether, *tert*-butyl-methyl ether, *tert*-butyl-ethyl ether, or tetrahydrofuran), and with dimethylsulfoxide, DMSO, have been measured at ambient pressure by a dynamic method from (250 to 420) K. The upper critical solution temperatures (UCSTs) were not observed for these systems, because they were at a temperature $>$420 K. The solubilities of [EMIM][EtSO$_4$] in *n*-alkanes and aromatic hydrocarbons decrease with an increase of the molecular weight of the solvent. The experimental results have been correlated using the NRTL equation. The average root-mean square deviation of the equilibrium mole fraction for all the liquid−liquid equilibrium (LLE) data was 0.0033.

## Introduction

Room temperature ionic liquids (ILs) show interesting thermophysical properties and solution thermodynamic behavior.[1–4] To design any process involving ionic liquids on an industrial scale, it is necessary to know a range of physical properties including not only viscosity and density but also heat capacity and other thermodynamic properties including phase equilibria.[2–7] A major point for IL research is the possibility of using them as substitutes for classical industrial solvents, most of which are volatile organic compounds (VOCs).

The solid–liquid phase equilibria (SLE) and liquid–liquid phase equilibria (LLE) measurements of IL systems based on *N*,*N*′-dialkyl-substituted imidazolium cations, ammonium cations, or phosphonium cations are attracting increasing attention for applications in liquid–liquid extraction.[8–10]

Many factors that control the phase behavior of ionic liquids with molecular liquids, especially with aromatic hydrocarbons, ketones, or ethers, may be described from the phase equilibria measurements. For a better understanding of the IL behavior and with a view to applications in chemical engineering or the development of thermodynamic models, reliable experimental data are required.

The SLE diagrams with immiscibility in the liquid phase with the upper critical solution temperature (UCST) were observed in mixtures of {[EMIM][PF$_6$] + benzene, toluene, or ethylbenzene}.[11] The liquidus curves exhibited similar shapes for different solvents. The evident differences were observed in the liquid phase for aromatic hydrocarbons—the mutual solubility of [EMIM][PF$_6$] in benzene and its alkyl derivatives decreases with an increase of the alkyl substituent at the benzene ring.

Solid at room temperature, an IL presents usually a much lower immiscibility gap in benzene than in alkanes. Ionic liquids based on the 1-alkyl-3-methylimidazolium cation, [C$_n$MIM]$^-$ or tetraalkylammonium cation, [Alk$_4$N]$^-$, are among the most popular and commonly studied, or used in technological improvements. As for the anions, bis{(trifluoromethyl)sulfonyl}imide [Tf$_2$N]$^-$ and methyl-, ethyl-, or octylsulfate [C$_n$SO$_4$]$^-$ are much superior compared to the more commonly investigated anions as hexafluorophosphate, [PF$_6$]$^-$, and tetrafluoroborate, [BF$_4$]$^-$. They are less viscous and more hydrolytically stable. Two other imidazolium-based ILs, namely, 1,3-dimethylimidazolium methylsulfate, [MMIM][CH$_3$SO$_4$], and 1-butyl-3-methylimidazolium methylsulfate, [BMIM][CH$_3$SO$_4$], have shown immiscibility in *n*-alkanes in the whole IL mole fraction range from $x_{\mathrm{IL}} = 10^{-4}$ to 0.98.[5] The 1-butyl-3-methylimidazolium octylsulfate, [BMIM][OcSO$_4$] has a higher solubility in *n*-alkanes—the immiscibility gap for heptane, for example, was observed in the IL mole fraction range from $x_{\mathrm{IL}} = 10^{-4}$ to 0.5 at room temperature.[12] The phase diagrams of ILs with benzene and benzene derivatives differ from those for the aliphatic hydrocarbons. The solubility of ILs is much higher in aromatic hydrocarbons than in aliphatic hydrocarbons, what is the result of interaction with the benzene ring. The interaction can be as $n-\pi$ and $\pi-\pi$ or even forming well-organized phases as clathrate-type structures in the liquid phase.[13] In a very recent work, it was found that in the system ([EMIM][Tf$_2$N] + benzene), an equimolar congruently melting inclusion compound, [EMIM][Tf$_2$N]·C$_6$H$_6$, exists.[13]

**Table 1. Thermophysical Constants of Pure Ionic Liquid: Temperature of Glass Transition, $T_{\mathrm{tr,1(g)}}$, $\Delta C_{\mathrm{p(g)}}$ at the Glass Transition, and Temperature of the Decomposition, $T_{\mathrm{dec}}$**

| IL | $T_{\mathrm{tr,1(g)}}$/K | $\Delta C_{\mathrm{p\,(g)}}$/J·K$^{-1}$·mol$^{-1}$ | $T_{\mathrm{dec}}$/K |
|---|---|---|---|
| [EMIM][EtSO$_4$][a] | 187.7 | 107.5 | 637.8[b] |

[a] Reference 16. [b] The step of the decomposition, 46.9 % mass loss.

The interaction of IL with ketones and ethers is slightly less than that with aromatic hydrocarbons.[14,15] Usually, the immiscibility in the liquid phase is observed with the UCST.

This article is concerned with the investigation of phase equilibria of mixtures containing the [EMIM][EtSO$_4$] with *n*-alkanes (hexane or octane), aromatic hydrocarbons (benzene, toluene, or ethylbenzene), ketones (pentan-2-one, pentan-3-one, hexan-2-one, or heptan-4-one), ethers (dibutyl ether, *tert*-butyl-methyl ether, *tert*-butyl-ethyl ether, or tetrahydrofuran), and with dimethylsulfoxide (DMSO).

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The data presented here will be useful from the technological perspective, because they show partial immiscibility at room temperature.

## Experimental Section

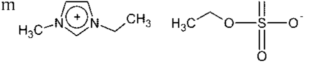
***Materials.*** The origins of the chemicals (in parentheses are the Chemical Abstracts registry numbers, the manufactures reported, and mass percent purities) were as follows: [EMIM][$EtSO_4$] (99420-1, Solvent Innovation GmbH, >98 %); hexane (110-54-3, Merck, 99 %); octane (111-65-9, Sigma-Aldrich, 99 %); benzene (71-43-2, Sigma-Aldrich, 99.97+ %); toluene (108-88-3, Fluka, > 99.7 %); ethylbenzene (100-41-4, Sigma-Aldrich, 99 %); pentan-2-one (107-87-9, Aldrich, 0.998 %); pentan-3-one (96-22-0, Aldrich, 0.999 %); hexan-2-one (591-78-6, Aldrich, 0.99+ %); heptan-4-one (110-43-0, Aldrich, 0.99+ %); dibutyl ether, (142-96-1, Aldrich, 0.99+ %); *tert*-butyl-methyl ether (MTBE) (1634, Reachim, 0.99 %), *tert*-butyl-ethyl ether (ETBE) (637-92-3, Aldrich, 0.99+ %); tetrahydrofuran (109-99-9, Sigma-Aldrich, 0.99+ %); dimethylsulphoxide (DMSO) (67-68-5, Aldrich, 0.998 %). The IL was dried for 24 h at 300 K in a vacuum before use. All solvents were fractionally distilled over different drying reagents to a mass fraction purity better than 99.8 % and were stored over freshly activated molecular sieves of type 4A (Union Carbide). All compounds were checked by GLC analysis, and no significant impurities were found. Analysis, using the Karl Fischer technique, showed that the water mass fraction in the IL and solvents was less than $1.8 \cdot 10^{-4}$. The physico-chemical characterization of the IL is presented in Table 1.

***Phase Equilibria Measurements.*** Solubilities have been determined using a dynamic method that has been described in detail previously.[6,11,15] Appropriate mixtures of the IL and solvent placed under the nitrogen in a drybox into a Pyrex glass cell were heated very slowly (less than $2\ K \cdot h^{-1}$ near the equilibrium temperature) with continuous stirring inside a cell. The sample was placed in a glass thermostat filled with silicone oil, water, or acetone with dry ice. The temperature of the liquid bath was varied slowly until one phase was obtained. The two phase disappearance temperatures in the liquid phase were detected visually during an increasing temperature regime. The temperature was measured with an electronic thermometer P 550 (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostatting liquid. The thermometer was calibrated on the basis of ITS-90. Mixtures were prepared by mass, and the uncertainty was estimated to be better than ± 0.0002 and ± 0.05 K in the mole fraction and temperature, respectively. The results of the LLE measurements for the binary systems of {[EMIM][$EtSO_4$] (1) + hydrocarbons (2)} are presented in Table 2, those of {[EMIM][$EtSO_4$] (1) + ketones (2)} are in Table 3, and those of {[EMIM][$EtSO_4$] (1) + ethers (2)} are in Table 4. The results of the SLE measurements for the binary system of {[EMIM][$EtSO_4$] (1) + DMSO (2)} are listed in Table 5. The tables include the direct experimental results of the LLE and SLE temperatures, $T$ versus $x_1$, the mole fraction of the IL at the equilibrium temperatures for the investigated systems.

## Results and Discussion

The formula of the ionic liquid and the abbreviation are as follows:

1-ethyl-3-methylimidazolium ethylsulfate



[EMIM][$EtSO_4$]

**Table 2. Liquid–Liquid Phase Equilibria of the Binary System {[EMIM][$EtSO_4$] (1) + Hexane, Octane, Benzene, Toluene, or Ethylbenzene (2)}**

| $x_1$ | $T^{LLE\,a}$/K | $x_1$ | $T^{LLE\,a}$/K |
|---|---|---|---|
| hexane | | | |
| 0.8552 | 301.24 | 0.7262 | 324.55 |
| 0.7678 | 313.09 | 0.6772 | 339.18 |
| 0.7325 | 321.82 | | |
| octane | | | |
| 0.9871 | 317.15 | 0.9253 | 346.65 |
| 0.9770 | 326.15 | 0.9184 | 351.45 |
| 0.9684 | 331.15 | 0.8986 | 358.15 |
| 0.9633 | 334.75 | 0.8842 | 360.68 |
| 0.9463 | 340.23 | 0.8546 | 365.04 |
| 0.9352 | 345.10 | 0.8184 | 368.97 |
| benzene | | | |
| 0.4883 | 288.00 | 0.3576 | 314.12 |
| 0.4418 | 294.60 | 0.3277 | 319.64 |
| 0.4205 | 302.56 | 0.2893 | 328.22 |
| 0.4048 | 309.09 | 0.2648 | 336.51 |
| 0.3915 | 311.11 | 0.2445 | 346.31 |
| toluene | | | |
| 0.7246 | 311.75 | 0.7012 | 325.78 |
| 0.7153 | 319.55 | 0.6823 | 333.44 |
| 0.7080 | 324.78 | 0.6351 | 359.15 |
| ethylbenzene | | | |
| 0.8890 | 297.12 | 0.8487 | 334.14 |
| 0.8806 | 304.87 | 0.8411 | 336.66 |
| 0.8697 | 313.20 | 0.8318 | 340.52 |
| 0.8666 | 322.60 | 0.8206 | 342.75 |
| 0.8598 | 324.87 | 0.7500 | 375.15 |

[a] The results are for example (311.75 ± 0.05) K.

The ethylsulfate anion is less viscous, more hydrolytically stable, and more environmental friendly than other popular anions such as bis{(trifluoromethyl)sulfonyl}imide, $[Tf_2N]^-$, hexafluorophosphate, $[PF_6]^-$, or tetrafluoroborate, $[BF_4]^-$. Unfortunately, the sulfate based anions are known to be thermally less stable. The IL investigated in this work has revealed a first decomposition temperature at 600 K with mass loss of 10 %. The compound has been decomposed in one step. The decomposition temperature for the mass loss close to the 50 % is higher than 630 K (see Table 1).

The experimental data of LLE of the measured binary systems of [EMIM][$EtSO_4$] are presented in Figures 1 to 4. The upper critical solution temperatures (UCSTs) of the curves were not observed because the boiling temperatures of solvents were much lower. For the investigated mixtures, it was impossible to detect, by the visual method, the mutual solubility of the IL in the solvent-rich phase. It was possible to predict such a data with the COSMO-RS model for two similar ILs, [MMIM][$CH_3SO_4$] and [BMIM][$CH_3SO_4$], and the solubility was in a range of $x_1 = 1 \cdot 10^{-4}$.[5,14] It was assumed in this work that the solubility is in the range of $x_1 = 1 \cdot 10^{-4}$ in *n*-alkanes and $x_1 = 1 \cdot 10^{-3}$ in other solvents. It was confirmed by two experimental points in dibutyl ether. The same results were found by the experimental infrared spectroscopy for [BMIM][$PF_6$].[3]

For the shorter chains of *n*-alkanes and the alkyl substituent at the benzene ring, the area of the immiscibility was lower. As a matter of fact, this is typical solution behavior observed for every IL measured by us.[5,11,14,15]

Figure 2 shows the experimental equilibrium curves for the three binary systems studied with aromatic hydrocarbons as a function of temperature, for different compositions. As it can be observed, the solubility decreases as the alkyl chain at the benzene ring increases. To the eye, the change in solubility

**Table 3. Liquid–Liquid Phase Equilibria of the Binary System {[EMIM][EtSO$_4$] (1) + Pentan-2-one, Pentan-3-one, Hexan-2-one, or Heptan-4-one (2)}**

| $x_1$ | $T^{\mathrm{LLE}\,a}$/K | $x_1$ | $T^{\mathrm{LLE}\,a}$/K |
|---|---|---|---|
| | pentan-2-one | | |
| 0.6122 | 281.90 | 0.5751 | 321.66 |
| 0.6064 | 293.59 | 0.5549 | 332.57 |
| 0.6012 | 297.78 | 0.5441 | 338.48 |
| 0.5977 | 302.91 | 0.5277 | 349.27 |
| 0.5881 | 311.26 | 0.5089 | 358.95 |
| 0.5819 | 316.97 | | |
| | pentan-3-one | | |
| 0.6305 | 288.15 | 0.5760 | 331.37 |
| 0.6244 | 299.00 | 0.5599 | 340.66 |
| 0.6180 | 307.60 | 0.5528 | 343.08 |
| 0.6107 | 314.89 | 0.5351 | 350.50 |
| 0.6054 | 319.05 | 0.5256 | 354.01 |
| 0.5679 | 336.15 | 0.5024 | 360.23 |
| 0.5836 | 327.65 | 0.4858 | 365.15 |
| | hexan-2-one | | |
| 0.7818 | 273.62 | 0.7032 | 354.77 |
| 0.7666 | 306.66 | 0.6957 | 360.55 |
| 0.7627 | 314.63 | 0.6874 | 363.41 |
| 0.7545 | 320.05 | 0.6773 | 367.68 |
| 0.7492 | 323.11 | 0.6646 | 371.97 |
| 0.7430 | 328.02 | 0.6487 | 379.93 |
| 0.7347 | 334.08 | 0.6273 | 383.71 |
| 0.7212 | 342.30 | 0.5988 | 393.45 |
| 0.7141 | 349.05 | 0.5653 | 399.55 |
| | heptan-4-one | | |
| 0.9783 | 302.15 | 0.9082 | 361.47 |
| 0.9674 | 306.70 | 0.8960 | 367.71 |
| 0.9605 | 312.75 | 0.8731 | 375.15 |
| 0.9508 | 325.36 | 0.8500 | 383.15 |
| 0.9471 | 331.20 | 0.8234 | 392.78 |
| 0.9423 | 341.65 | 0.7961 | 399.49 |
| 0.9327 | 347.20 | 0.7491 | 407.38 |
| 0.9201 | 353.10 | | |

[a] The results are for example (325.36 ± 0.05) K.

**Table 4. Liquid–Liquid Phase Equilibria of the Binary System {[EMIM][EtSO$_4$] (1) + Dibutyl Ether, *tert*-Butyl-methyl Ether, *tert*-Butyl-ethyl Ether, or Tetrahydrofuran (2)}**

| $x_1$ | $T^{\mathrm{LLE}\,a}$/K | $x_1$ | $T^{\mathrm{LLE}\,a}$/K |
|---|---|---|---|
| | dibutyl ether | | |
| 0.9931 | 316.10 | 0.9427 | 371.90 |
| 0.9865 | 321.13 | 0.9300 | 385.58 |
| 0.9824 | 322.77 | 0.9199 | 398.66 |
| 0.9740 | 327.10 | 0.9067 | 408.95 |
| 0.9660 | 334.32 | 0.0040 | 338.97 |
| 0.9556 | 344.12 | 0.0029 | 336.24 |
| 0.9480 | 353.09 | | |
| | *tert*-butyl-methyl ether | | |
| 0.8966 | 308.15 | 0.8566 | 335.33 |
| 0.8795 | 320.15 | 0.8352 | 345.08 |
| 0.8740 | 325.47 | 0.7930 | 368.06 |
| | *tert*-butyl-ethyl ether | | |
| 0.9701 | 305.69 | 0.8916 | 342.06 |
| 0.9451 | 316.01 | 0.8731 | 349.34 |
| 0.9341 | 324.01 | 0.8485 | 357.78 |
| 0.9109 | 331.86 | 0.8095 | 371.85 |
| | tetrahydrofuran | | |
| 0.5730 | 313.75 | 0.5278 | 347.50 |
| 0.5679 | 317.78 | 0.4953 | 358.00 |
| 0.5626 | 330.53 | 0.4562 | 385.56 |
| 0.5587 | 335.04 | 0.4211 | 406.23 |
| 0.5548 | 338.40 | 0.3905 | 419.29 |
| 0.5498 | 341.60 | 0.0014 | >433.15 |
| 0.5403 | 346.00 | | |

[a] The results are for example (313.75 ± 0.05) K.

**Table 5. Solid–Liquid Phase Equilibria of the Binary System {[EMIM][EtSO$_4$] (1) + DMSO (2)}**

| $x_1$ | $T^{\mathrm{SLE}\,a}$/K | $x_1$ | $T^{\mathrm{SLE}\,a}$/K |
|---|---|---|---|
| 0.4596 | 250.52 | 0.1931 | 275.87 |
| 0.4481 | 252.20 | 0.1680 | 277.93 |
| 0.4283 | 254.30 | 0.1447 | 279.96 |
| 0.4077 | 255.85 | 0.1188 | 281.89 |
| 0.3821 | 258.95 | 0.0940 | 283.84 |
| 0.3589 | 261.49 | 0.0771 | 285.06 |
| 0.3477 | 262.92 | 0.0570 | 286.89 |
| 0.3298 | 264.86 | 0.0384 | 288.14 |
| 0.3057 | 266.57 | 0.0225 | 289.48 |
| 0.2689 | 269.98 | 0.0107 | 290.57 |
| 0.2428 | 271.95 | 0.0025 | 291.40 |
| 0.2220 | 273.50 | 0.0000 | 291.66 |

[a] The results are for example (273.50 ± 0.05) K.

between the benzene and toluene is double that for toluene and ethylbenzene. The same results were presented by us earlier for [EMIM][PF$_6$] in aromatic hydrocarbons.[11] As can be seen from Figure 2, the solubility of [EMIM][PF$_6$] is much lower than that of [EMIM][EtSO$_4$] in benzene and similar or minimally lower in toluene and ethylbenzene. The interaction of the ethylsulfate anion with an aromatic ring is much higher than that of the hexafluorophosphate anion.

Experimental phase diagrams with ketones, investigated in this work, are characterized by the following order in solubility: pentan-2-one > pentan-3-one > hexan-2-one > heptan-4-one. The difference in solubility is mainly dictated by the number of carbon atoms in the ketone chains; much less by the position of the carbonyl group (see pentan-2-one and pentan-3-one solubility curves in Figure 3; solubility in pentan-3-one is slightly lower in comparison with pentan-2-one). The better solubility in pentan-2-one is connected with specific interactions such as the carbonyl group of one molecule with the imidazolium ring and/or with the anion of another molecule. It was observed that in ketone with shorter carbon chains the solubility is higher.

The observed solubilities of the IL in ethers increases in the following order: dibutyl ether < *tert*-butyl-methyl ether < *tert*-butyl-ethyl ether < tetrahydrofuran. The second time we observe higher solubility of the IL in *tert*-butyl-methyl ether than in dibutyl ether.[13] The best solubility was observed in THF probably due to the similarity of molecules of the IL (five carbon atom rings) and the solvent (five atom rings). The shape of the liquidus curve of DMSO in [EMIM][EtSO$_4$] suggests that the eutectic point is at very low temperature and is shifted to the IL high mole fraction (see Figure 5). Unfortunately, using the visual method of the phase equilibria measurements, it was not possible to work below 250 K, thus the eutectic point was not detected and it was impossible to study SLE up to the IL-rich compositions.

Packing effects or conformational changes of the investigated molecules in the mixtures are difficult to categorize, especially in comparison with possible hydrogen bonding. All these interactions have an influence on liquid–liquid equilibria.

***Liquid−Liquid Equilibria and Solid–Liquid Equilibria Correlation.*** For LLE and SLE, one method is used to correlate the solute activity coefficients, $\gamma_1$, based on the NRTL model describing the excess Gibbs energy.[17] The experimental data were correlated using the same equations, described by us earlier.[6,11,15] The NRTL α parameter was set to a value of $\alpha = 0.2$ or 0.3.

The temperature dependent model adjustable parameters ($g_{12} - g_{22} = a_{12} + b_{12}T$) and ($g_{21} - g_{11} = a_{21} + b_{21}T$) were found

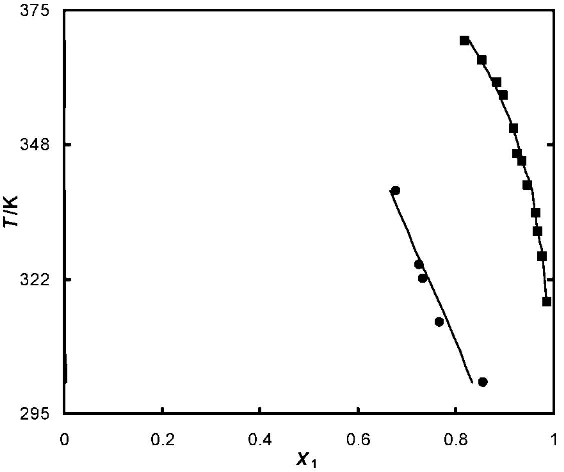


**Figure 1.** Liquid–liquid phase equilibria diagrams for binary systems: {[EMIM][EtSO$_4$] (1) + *n*-alkane (2)}: ●, hexane; ■, octane; solid line, NRTL equation.

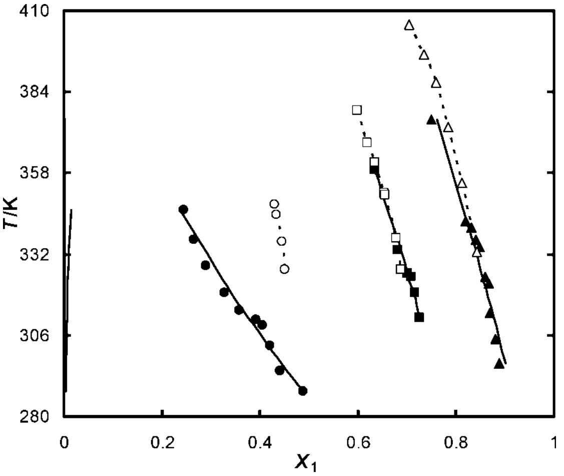


**Figure 2.** Liquid–liquid phase equilibria diagrams for binary systems: {[EMIM][EtSO$_4$] (1) + an aromatic hydrocarbon (2)}: ●, benzene; ■, toluene; ▲, ethylbenzene; solid line, NRTL equation. Comparison with the systems [EMIM][PF$_6$] (1) in the same solvents: ○, benzene; □, toluene; Δ, ethylbenzene; dotted line, NRTL equation.[11]

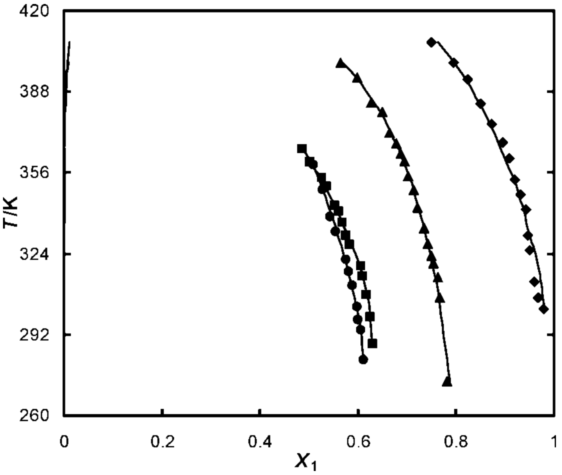


**Figure 3.** Liquid–liquid phase equilibria diagrams for binary systems: {[EMIM][EtSO$_4$] (1) + ketone (2)}: ●, pentan-2-one; ■, pentan-3-one; ▲, hexan-2-one; ◆, heptan-4-one; solid line, NRTL equation.

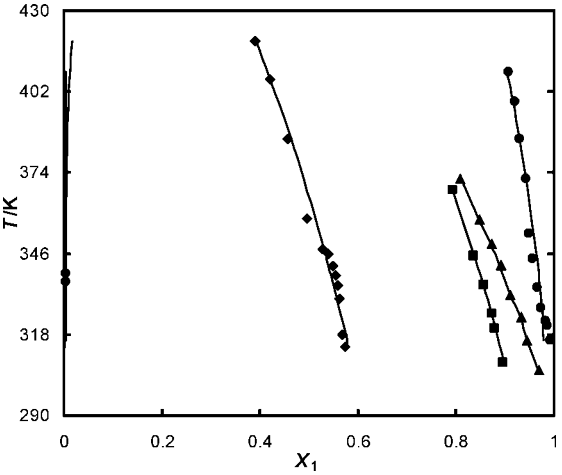


**Figure 4.** Liquid–liquid phase equilibria diagrams for binary systems: {[EMIM][EtSO$_4$] (1) + ether (2)}: ●, dibutyl ether; ■, *tert*-butyl-methyl ether; ▲, *tert*-butyl-ethyl ether; ◆, tetrahydrofuran; solid line, NRTL equation.

by minimization of the objective function OF:

$$\mathrm{OF} = \sum_{i=1}^{n} \left[(\Delta x_1)_i^2 + (\Delta x_1^*)_i^2\right] \tag{1}$$

where $n$ is the number of experimental points and $\Delta x$ is defined as

$$\Delta x = x_{\mathrm{calc}} - x_{\mathrm{exp}} \tag{2}$$

The root-mean-square deviation of mole fraction for the LLE calculations was defined as follows:

$$\sigma_x = \left(\frac{\sum_{i=1}^{n} (\Delta x_1)_i^2 + \sum_{i=1}^{n} (\Delta x_1^*)_i^2}{2n - 2}\right)^{1/2} \tag{3}$$

The root-mean-square deviation of temperature for the SLE calculations was defined as follows:

$$\sigma_T = \left(\sum_{i=1}^{n} \frac{(T_i^{\mathrm{exp}} - T_i^{\mathrm{cal}})^2}{n-2}\right)^{1/2} \tag{4}$$

It was assumed that the solubility at the dilute IL region is in the range of $x_1 = 1 \cdot 10^{-4}$ for *n*-alkanes and $x_1 = 1 \cdot 10^{-3}$ for other solvents. The results of the correlations—values of model parameters and the corresponding standard deviations—are given in Table 6. For the systems presented in this work, the average root-mean-square deviation, $\sigma_x$, equals 0.0033. The results of the correlations are presented in Figures 1−5. Positive deviations from ideality were found. The values of activity coefficients of the IL in the saturated solution, coming from the correlation data were higher than one ($\gamma_1 > 1$).

## Conclusion

The LLE for 13 and SLE for 1 new binary ionic liquid−organic solvent systems were determined. The experimental data of LLE in binary systems of [EMIM][EtSO$_4$] with aliphatic and aromatic hydrocarbons demonstrates typical behavior: the immiscibility in the liquid phase increases with an increase of the chain length of the solvent, as was observed for every mixture with the IL.

The existence of the liquid–liquid equilibria is the evidence that the interaction between the IL and the solvent is not significant.

Knowledge of the impact of different factors on the liquid phase behavior of the IL with other liquids is useful for developing ILs as designer solvents. The presented results may give new possibilities in extraction processes.

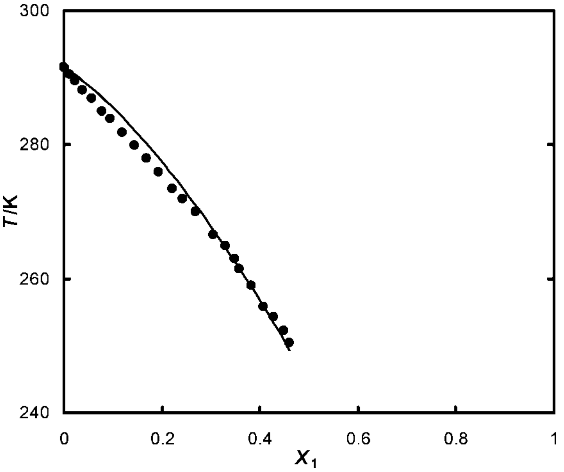


**Figure 5.** Solid–liquid phase equilibria diagram of binary sytem: {[EMIM]-[$EtSO_4$] (1) + DMSO (2)}: ●, experimental points; solid line, NRTL equation.

**Table 6. Correlation of the LLE and SLE Data by Means of the NRTL Equation: Parameters ($g_{12} - g_{22} = a_{12} + b_{12}T$), ($g_{21} - g_{11} = a_{21} + b_{21}T$), the Nonrandom Parameter, $\alpha_{12}$, and the Mole Fraction Deviations, $\sigma_x$**

| | NRTL parameters | | | | | | |
|---|---|---|---|---|---|---|---|
| | J·mol$^{-1}$ | | | | | | |
| | $g_{12} - g_{22}$ | | $g_{21} - g_{11}$ | | | | |
| solvent | $a_{12}$ | $b_{12}$ | $a_{21}$ | $b_{12}$ | $\alpha_{12}$ | $\sigma_x$ | $\sigma_T$/K |
| hexane | 18578 | −59.51 | −32281 | 153.2 | 0.2 | 0.0082 | |
| octane | 46176 | −123.3 | 38496 | −57.14 | 0.2 | 0.0030 | |
| benzene | 14931 | −63.02 | −1676 | 61.81 | 0.2 | 0.0074 | |
| toluene | 9354 | −31.99 | 18177 | 3.29 | 0.2 | 0.0019 | |
| ethylbenzene | 10816 | −29.91 | −16.95 | 48.92 | 0.2 | 0.0045 | |
| pentan-2-one | 8384 | −33.97 | 32748 | −34.17 | 0.2 | 0.0014 | |
| pentan-3-one | 20522 | −58.21 | 35586 | −50.12 | 0.3 | 0.0010 | |
| hexan-2-one | 15435 | −46.21 | 56349 | −94.37 | 0.2 | 0.0024 | |
| heptan-4-one | 29211 | −64.82 | 52405 | −95.58 | 0.3 | 0.0032 | |
| dibutyl ether | 16689 | −34.09 | −6086 | 56.26 | 0.2 | 0.0042 | |
| MTBE | 13171 | −35.52 | 19371 | −2.15 | 0.2 | 0.0010 | |
| ETBE | 33761 | −80.70 | 71115 | −146.7 | 0.3 | 0.0010 | |
| tetrahydrofuran | 16689 | −34.09 | −6086 | 56.26 | 0.2 | 0.0042 | |
| DMSO[a] | −3427 | 0 | 2457 | 0 | 0.3 | | 1.43 |

[a] SLE data.

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