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Liquid−Liquid Equilibria in Binary Mixtures Containing Fluorinated Benzenes and Ionic Liquid 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide

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Binary liquid−liquid equilibria in mixtures of fluorinated benzenes and ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]), have been measured using the volumetric method over a temperature range from about (283 to 373) K. A general trend between the magnitude of the dipole moment (polarity) and the miscibility was found, although other intermolecular interactions (higher-order moments, π-electron effects, and hydrogen bonding) may also be playing a role for a more detailed trend. The fluorinated benzenes having the largest dipole moments (1,2-difluorobenzene, 1,2,3,4-tetrafluorobenzene, and 1,2,3-trifluorobenzene) were completely miscible in the [emim][Tf_2N]. The binary systems (1,4-difluorobenzene, 1,3,5-trifluorobenzene, and 1,2,4,5-tetrafluorobenzene) with zero dipole moments, and the binary systems (1,2,4-trifluorobenzene, fluorobenzene, 1,3-difluorobenzene, pentafluorobenzene, and 1,2,3,5-tetrafluorobenzene) with dipole moments of about 1.4 D were only partially miscible in [emim][Tf_2N] (immiscibility gaps from about (11 to 50) mol % in [emim][Tf_2N]). The binary system (1,2,4-trifluorobenzene + [emim][Tf_2N]) shows a lower critical solution temperature (LCST) of about 354 K. The excess molar volumes range from (−1 to −10) $cm^3 \cdot mol^{-1}$. Observed LLE are well correlated by use of the nonrandom two liquid (NRTL) solution model.

Introduction

Liquid−liquid equilibria (LLE) of various chemicals with room-temperature ionic liquids (RTILs) provide important information to evaluate potential new applications such as chemical separation and extraction.[1−4] This report is a continuation of our previous study[5] on the phase behavior of benzene and hexafluorobenzene in RTIL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]). The present work includes the LLE behavior of fluorinated benzenes (fluorobenzene, 1,2-difluorobenzene, 1,3-difluorobenzene, 1,4-difluorobenzene, 1,2,3-trifluorobenzene, 1,2,4-trifluorobenzene, 1,3,5-trifluorobenzene, 1,2,3,4-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4,5-tetrafluorobenzene, and pentafluorobenzene) in [emim][Tf_2N] over a temperature range from (283 to 373) K. We have previously studied the thermodynamic properties of RTILs with a variety of fluorinated hydrocarbons[6−15] and fluorinated ethers.[16,17] The present phase equilibrium study of fluorinated benzenes with [emim][Tf_2N] is part of our continuing investigations to understand the interactions (or phase behaviors) of fluorinated compounds with RTILs.

There are several solubility studies of RTIL mixtures with aromatic hydrocarbons and alkanes in the literature.[18−21] Blesic et al. recently reported phase equilibria for hexafluorobenzene and 1,3,5-trifluorobenzene in [emim][Tf_2N];[22] however, to the best of our knowledge, we are the first to report LLE for all the fluorinated benzene isomers in [emim][Tf_2N]. This report combines both our current work on the interactions of fluorinated benzenes ($C_6H_nF_{6-n}$: $n = 1,...,5$) along with comparisons of our original work on the differences between benzene (C_6H_6) and hexafluorobenzene (C_6F_6).

Experimental

Materials. Fluorobenzene (C_6H_5F, assay 99 %, Product and Batch no. F6001-100G-A 16006LH, CAS registry no. 462-06-6), 1,2-difluorobenzene (1,2-$C_6H_4F_2$, assay 98 %, Product and Batch no. 126152-10G 09903HC, CAS registry no. 367-11-3), 1,3-difluorobenzene (1,3-$C_6H_4F_2$, assay ≥ 99 %, Product and Batch no. D102008-10G 07528KI, CAS registry no. 372-18-9), 1,4-difluorobenzene (1,4-$C_6H_4F_2$, assay ≥ 99 %, Product and Batch no. D102202-25G 13105AO, CAS registry no. 540-36-3) 1,2,3-trifluorobenzene (1,2,3-$C_6H_3F_3$, assay 99 %, Product and Batch no. 324752-5G 14431AE, CAS registry no. 1489-53-8), 1,2,4-trifluorobenzene (1,2,4-$C_6H_3F_3$, assay 98 %, Product and Batch no. 196843-25G 16623ME, CAS registry no. 367-23-7), 1,3,5-trifluorobenzene (1,3,5-$C_6H_3F_3$, assay 97 %, Product and Batch no. 196851-5G 10815PH, CAS registry no. 372-38-3), 1,2,3,4-tetrafluorobenzene (1,2,3,4-$C_6H_2F_4$, assay 99 %, Product and Batch no. T11630-5G 08119EE, CAS registry no. 551-62-2), 1,2,3,5-tetrafluorobenzene (1,2,3,5-$C_6H_2F_4$, assay 95 %, Product and Batch no. 306029-5G 02317EH, CAS registry no. 2367-82-0), 1,2,4,5-tetrafluorobenzene (1,2,4,5-$C_6H_2F_4$, assay ≥ 99 %, Product and Batch no. T11657-25G 11809TC, CAS registry no. 327-54-8), and pentafluorobenzene (C_6HF_5, assay 99 %, Product and Batch no. P5301-25G 04329EH, CAS registry no. 363-72-4) were obtained from Sigma-Aldrich, Inc. (St. Louis, MO). The identities of fluorinated benzenes (1,3-difluorobenzene, 1,4-difluorobenzene, 1,2,3,5-tetrafluorobenzene, and 1,2,4,5-tetrafluorobenzene) were confirmed by ^1H NMR and ^{19}F NMR. The fluorinated benzenes were used without further purification.

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][Tf_2N] (electrochemical grade, assay ≥ 99.5 %, $C_8H_{11}F_6N_3O_4S_2$, Lot and Catalog no. 259095 IL-201-20-E, CAS registry no. 174899-82-2) was purchased from

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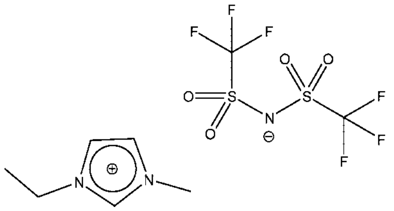
Chemical Name	Abbreviation	Structure
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[emim][Tf_2N]	

Figure 1. Schematic molecular structure and abbreviation of 1-ethyl-3-methylimdazolium bis(trifluoromethylsulfonyl)imide. Molar mass: 391.31.

Covalent Associates, Inc. (Woburn, MA). Figure 1 provides the chemical structure and molecular mass. Elemental analysis was used to check the purity of the [emim][Tf_2N] sample. The purity was ≥ 99.4 %, and a detailed description of the analysis can be found in our previous work.[7] The [emim][Tf_2N] was dried and degassed by filling a borosilicate glass tube with about 10 g of the ionic liquid and pulling a coarse vacuum with a diaphragm pump (Pfeiffer, model MVP055-3, Nashua, NH) followed by further evacuation using a turbopump (Pfeiffer, model TSH-071) to a pressure of about $4 \cdot 10^{-7}$ kPa while simultaneously heating and stirring the ionic liquid at a temperature of about 348 K for 5 days. The final mass fraction of water was measured by Karl Fischer titration, and the dried sample contained $188 \cdot 10^{-6}$ H_2O.

Experimental Method. A detailed description of the LLE experimental equipment and procedures is available in our previous reports.[11,12] Therefore, only the basic experimental techniques and measurement uncertainties are given here. LLE experiments were made with samples containing (89.9, 93.8, and 95.1) mole percent fluorobenzene + [emim][Tf_2N], (80.1, 85.2, 86.9, 90.1, and 94.9) mole percent 1,2-difluorobenzene + [emim][Tf_2N], (85.1 and 95.0) mole percent 1,3-difluorobenzene + [emim][Tf_2N], (84.8 and 95.0) mole percent 1,4-difluorobenzene + [emim][Tf_2N], (80.2 and 90.2) mole percent 1,2,3-trifluorobenzene + [emim][Tf_2N], (89.9 and 94.9) mole percent 1,2,4-trifluorobenzene + [emim][Tf_2N], (85.0 and 95.0) mole percent 1,3,5-trifluorobenzene + [emim][Tf_2N], (84.7 and 95.0) mole percent 1,2,3,4-tetrafluorobenzene + [emim][Tf_2N], (84.9 and 94.9) mole percent 1,2,3,5-tetrafluorobenzene + [emim][Tf_2N], (84.6 and 95.0) mole percent 1,2,4,5-tetrafluorobenzene + [emim][Tf_2N], and (85.0 and 95.1) mole percent pentafluorobenzene + [emim][Tf_2N]) at constant temperatures from about (283 to 373) K using the volumetric method.[11,12]

To measure LLE over a wider range of temperatures, the water-filled constant-temperature bath in our previous experiments[11,12] was replaced with a silicone oil-filled temperature bath (Tamson Instruments, TV4000LT, Zoetermeer, Netherlands). The uncertainty in temperature was ± 0.2 K and was determined using a standard platinum resistance thermometer (SPRT model 5699, Hart Scientific, American Fork, UT, range 73 to 933 K) and readout (Blackstack model 1560 with SPRT module 2560) with a NIST certified traceable accuracy to ± 0.005 K.

The liquid density of the fluorinated benzenes was measured at two temperatures, (296 to 297) K and (324 to 331) K, using a pycnometer method [(2, 5, and 10) cm^3 measuring bulbs].[23] The liquid density of benzene was also measured and compared with literature data[24] to determine the uncertainty in the method. The sample densities and uncertainties are provided in Table 1.

Results

Experimental Data. To use the mass−volume method,[11,12] the vapor phase was assumed to contain only fluorinated benzenes (negligible vapor pressure for [emim][Tf_2N] ionic liquid). The vapor density for certain fluorinated benzenes (fluorobenzene, 1,2,3,4-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4,5-tetrafluorobenzene, and pentafluorobenzene) was calculated assuming ideal gas behavior and known vapor pressure data.[25] The calculated vapor densities including benzene and hexafluorobenzene correlated nicely with the molecular mass (vapor density increases with increasing molecular mass). Therefore, the vapor densities for the unknown fluorinated benzenes were estimated by interpolating between the known vapor pressures using the molecular mass. The uncertainties for the estimated vapor densities were checked and resulted in a small change in the liquid compositions ($\Delta x_1 < 0.1$ mol % and $\Delta x_1' < 0.1$ mol %) and molar volumes ($\Delta V < 0.1\ cm^3 \cdot mol^{-1}$ and $\Delta V' < 0.4\ cm^3 \cdot mol^{-1}$). The total uncertainties were estimated by calculating both the overall random and systematic uncertainties. The following experimental parameters were considered to have an effect on the random uncertainty: sample container calibration constants, mass of fluorinated benzenes and ionic liquid, and the height of the lower and upper phases. The heights had the largest overall effect. The systematic uncertainties include properly correcting for the area expansion, meniscus, and vapor phase moles. Total uncertainties in the final composition and molar volume are provided in Table 2. For additional details on estimation of total uncertainties, see refs 11 and 12.

One of the most useful pieces of information in the present method is to be able to obtain the molar volume of each separated liquid simultaneously with the mole fraction of each liquid at any given isothermal condition. Then, the excess molar volume of each liquid solution ($V^{ex'}$ and V^{ex}) can be obtained, by use of the pure component molar volumes V_1^0 (fluorinated benzenes) and V_2^0 ([emim][Tf_2N]) using

$$V^{ex'} = V_m - x'_1 V_1^0 - x'_2 V_2^0 \quad \text{or} \quad V^{ex} = V_m - x_1 V_1^0 - x_2 V_2^0 \tag{1}$$

where V_m is the measured molar volume of the mixture ($V_m = V'$ for the lower phase L′ or $V_m = V$ for the upper phase L), and x'_1, x'_2 or x_1, x_2 are mole fractions of fluorinated benzenes (1) and ionic liquid (2) in phase L′ and L, respectively. Saturated liquid molar volumes for fluorinated benzenes were calculated using the measured liquid density data provided in Table 1 with a linear temperature correlation over the range of measured LLE temperatures [(283 to 373) K].

Cloud-point measurements have also been conducted to prove the existence of a LCST for the 1,2,4-trifluorobenzene + [emim][Tf_2N] binary system. Starting at room temperature (293 K), where only one liquid phase existed, the temperature was slowly increased ($5\ K \cdot h^{-1}$) until a second liquid phase began to appear.

Thermodynamic Model Analysis. Liquid−liquid equilibria for an *N*-component system at low pressures can be described by the following set of nonlinear equations with liquid mole fractions, x_i, and activity coefficients, γ_i:[28]

$$\gamma_i^{L1} x_i^{L1} = \gamma_i^{L2} x_i^{L2} \ (i = 1,...,N) \tag{2}$$

where $N = 2$ for a binary system; superscripts L1 and L2 indicate two liquid phases of LLE; and $i = 1$ designates species

Table 1. Chemical Name, Molecular Weight, Boiling Point, and Liquid Density

chemical name	MW $g \cdot mol^{-1}$	T_b (K)	ρ_L $(g \cdot cm^{-3})$ / T (K)
fluorobenzene	96.104	357.9[a]	1.022 ± 0.004 / 296.2 ± 0.2 0.985 ± 0.008 / 330.1 ± 0.2
1,2-difluorobenzene	114.094	366.2 ± 1.0[c]	1.156 ± 0.014 / 296.2 ± 0.2 1.117 ± 0.018 / 331.1 ± 0.2
1,3-difluorobenzene	114.094	355.2 ± 1.0[c]	1.139 ± 0.014 / 296.2 ± 0.2 1.094 ± 0.018 / 330.6 ± 0.2
1,4-difluorobenzene	114.094	362.0[a]	1.146 ± 0.014 / 296.1 ± 0.2 1.110 ± 0.018 / 327.2 ± 0.2
1,2,3-trifluorobenzene	132.086	367.7 ± 0.5[c]	1.292 ± 0.016 / 296.0 ± 0.2 1.240 ± 0.020 / 331.6 ± 0.2
1,2,4-trifluorobenzene	132.086	361.2[c]	1.280 ± 0.004 / 296.6 ± 0.2 1.247 ± 0.010 / 330.7 ± 0.2
1,3,5-trifluorobenzene	132.086	351.2[c]	1.268 ± 0.004 / 297.2 ± 0.2 1.225 ± 0.010 / 324.9 ± 0.2
1,2,3,4-tetrafluorobenzene	150.076	367.5[a]	1.408 ± 0.016 / 296.4 ± 0.2 1.360 ± 0.020 / 327.4 ± 0.2
1,2,3,5-tetrafluorobenzene	150.076	357.6[a]	1.403 ± 0.014 / 296.3 ± 0.2 1.352 ± 0.018 / 325.9 ± 0.2
1,2,4,5-tetrafluorobenzene	150.076	363.5[b]	1.421 ± 0.004 / 296.7 ± 0.2 1.370 ± 0.010 / 327.4 ± 0.2
pentafluorobenzene	168.066	358.9[b]	1.511 ± 0.004 / 296.9 ± 0.2 1.453 ± 0.010 / 327.6 ± 0.2

[a] Ref 25. [b] Ref 26. [c] Ref 27.

1 (fluorinated benzenes) while $i = 2$ corresponds to species 2, the ionic liquid [emim][Tf$_2$N]. For the activity coefficient, we use the NRTL (nonrandom two liquids) solution model[25] in the present study.

The binary activity coefficients of the NRTL are given by

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1 G_{12})^2}\right] \qquad (3)$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2 G_{21})^2}\right] \qquad (4)$$

where

$$G_{12} \equiv \exp(-\alpha\tau_{12}) \quad \text{and} \quad G_{21} \equiv \exp(-\alpha\tau_{21}) \qquad (5)$$

$$\tau_{12} \equiv \frac{\Delta g_1}{RT} \quad \text{and}$$

$$\tau_{21} \equiv \frac{\Delta g_2}{RT} \text{ (adjustable binary interaction parameters)} \qquad (6)$$

$\alpha = 0.2$ (assumed to be a constant of 0.2 in this work). x_i = mole fraction of the i-th species.

The temperature-dependent binary interaction parameter (τ_{ij}) is modeled here by a two-term empirical equation

$$\tau_{12} = \tau_{12}^{(0)} + \tau_{12}^{(1)}/T/\text{K} \quad \text{and} \quad \tau_{21} = \tau_{21}^{(0)} + \tau_{21}^{(1)}/T/\text{K} \qquad (7)$$

Then, the two unknown adjustable parameters τ_{12} and τ_{21} at a given T can be determined from *one* set of LLE experimental (the present volumetric method) data, using eq 2 (two nonlinearly coupled equations). We have six sets of such LLE data for each binary system, as shown in Table 2, and can obtain a set of τ_{12} and τ_{21} at a respective temperature. Thus, the four empirical parameters in eq 7 have been determined from the obtained τ_{ij} data and are given in Table 3.

Once the binary interaction parameters of the NRTL model have been determined as a function of temperature, we can calculate the Tx (temperature−composition) phase diagram at any temperature by solving eq 2. Numerical solutions of eq 2 have been obtained by use of a robust flash algorithm.[28] Calculated Tx diagrams for the present LLE systems were successfully constructed and compared well with the experimental solubility data as shown in Figures 2 to 6.

Discussion

The solubility behavior of a substance often gives us a clue to the intermolecular interactions between solute and solvent. Although no VLE measurements have been made in this work, we have measured the LLE behavior from (283 to 373) K for the binary systems of the fluorinated benzenes ($C_6H_nF_{6-n}$: n = 1,...,5) + [emim][Tf$_2$N] to provide some insight on these molecular interactions. Solubility theories often include three types of molecular interactions: dispersion forces, polar forces, and hydrogen bonding forces.[29,30] Dispersion forces are present to some degree in all molecules but are generally weak intermolecular attractions in nonpolar liquids created by induced dipole-induced dipole interactions. If the distribution of the electron cloud is uneven (thicker in one place and thinner in another), small local charge imbalances are created. The parts of the molecule with a larger electron density will be negatively charged, and the parts of the molecule with a smaller electron density will be positively charged. The molecule as a whole is neutral and thus will have properties with equal but oppositely charged poles, referred to as the molecular (electric) dipole

Table 2. LLE Composition and Molar Volume of the Systems

(a) Fluorobenzene (1) + [emim][$\mathrm{Tf_2N}$] (2) System

T/K	$100x_1'$	$100x_1$	$\frac{V'}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E'}}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E}}{\mathrm{cm^3\cdot mol^{-1}}}$
282.5 ± 0.2	87.5 ± 0.4	99.2 ± 0.8	112.5 ± 2.8	93.1 ± 1.0	−0.3 ± 2.8	−0.7 ± 1.0
297.9 ± 0.2	87.5 ± 0.3	99.1 ± 0.9	113.7 ± 2.0	94.5 ± 1.0	−0.9 ± 2.0	−1.1 ± 1.0
315.5 ± 0.2	87.4 ± 0.3	99.0 ± 1.0	115.0 ± 2.0	96.1 ± 1.0	−1.7 ± 2.0	−1.5 ± 1.0
333.2 ± 0.2	87.2 ± 0.3	98.9 ± 0.9	116.9 ± 2.6	98.4 ± 1.1	−2.2 ± 2.6	−1.3 ± 1.1
353.1 ± 0.2	86.9 ± 0.3	98.9 ± 0.8	119.7 ± 2.6	101.0 ± 1.2	−2.4 ± 2.6	−0.9 ± 1.2
373.0 ± 0.2	86.5 ± 0.3	98.9 ± 0.9	123.1 ± 2.8	103.5 ± 1.2	−2.2 ± 2.8	−0.8 ± 1.2

(b) 1,3-Difluorobenzene (1) + [emim][$\mathrm{Tf_2N}$] (2) System

T/K	$100x_1'$	$100x_1$	$\frac{V'}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E'}}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E}}{\mathrm{cm^3\cdot mol^{-1}}}$
283.3 ± 0.2	75.7 ± 0.4	100.0 − 0.3	134.0 ± 3.6	98.2 ± 3.3	−2.8 ± 3.6	−0.5 ± 3.3
294.4 ± 0.2	75.5 ± 0.4	100.0 − 0.3	136.3 ± 3.6	99.3 ± 3.4	−2.2 ± 3.6	−0.7 ± 3.4
316.1 ± 0.2	75.3 ± 0.4	100.0 − 0.3	140.4 ± 3.5	102.0 ± 3.4	−1.3 ± 3.5	−0.5 ± 3.4
333.3 ± 0.2	74.8 ± 0.3	100.0 − 0.3	142.9 ± 3.4	104.0 ± 3.5	−1.9 ± 3.4	−0.6 ± 3.5
353.1 ± 0.2	74.2 ± 0.3	100.0 − 0.3	146.0 ± 3.3	106.5 ± 3.5	−2.6 ± 3.3	−0.7 ± 3.5
373.0 ± 0.2	73.6 ± 0.3	100.0 − 0.3	149.2 ± 3.3	109.0 ± 3.8	−3.3 ± 3.3	−0.9 ± 3.8

(c) 1,4-Difluorobenzene (1) + [emim][$\mathrm{Tf_2N}$] (2) System

T/K	$100x_1'$	$100x_1$	$\frac{V'}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E'}}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E}}{\mathrm{cm^3\cdot mol^{-1}}}$
283.4 ± 0.2	81.6 ± 0.5	100.0 − 0.2	123.9 ± 2.6	97.6 ± 3.2	−3.3 ± 2.6	−0.7 ± 3.2
294.4 ± 0.2	81.4 ± 0.5	100.0 − 0.2	125.5 ± 3.0	98.8 ± 3.2	−3.2 ± 3.0	−0.6 ± 3.2
316.2 ± 0.2	81.0 ± 0.4	100.0 − 0.2	128.8 ± 3.6	101.0 ± 3.2	−3.1 ± 3.6	−0.6 ± 3.2
343.2 ± 0.2	80.7 ± 0.4	99.9 ± 0.1	133.7 ± 3.6	103.8 ± 3.0	−2.0 ± 3.6	−0.9 ± 3.0
353.1 ± 0.2	80.4 ± 0.4	99.9 ± 0.1	135.4 ± 3.6	105.0 ± 3.0	−2.0 ± 3.6	−0.8 ± 3.0
373.0 ± 0.2	79.9 ± 0.4	99.9 ± 0.1	138.7 ± 3.6	106.9 ± 3.0	−2.1 ± 3.6	−1.2 ± 3.0

(d) 1,2,4-Trifluorobenzene (1) + [emim][$\mathrm{Tf_2N}$] (2) System

T/K	$100x_1'$	$100x_1$	$\frac{V'}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E'}}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E}}{\mathrm{cm^3\cdot mol^{-1}}}$
362.4 ± 0.2	89.3 ± 0.8	97.7 ± 1.0	124.2 ± 2.6	113.5 ± 3.0	−3.5 ± 2.6	−0.8 ± 3.0
367.4 ± 0.2	89.2 ± 0.8	97.7 ± 1.0	124.7 ± 2.8	114.0 ± 3.1	−3.6 ± 2.8	−0.8 ± 3.1
372.4 ± 0.2	89.1 ± 0.7	97.7 ± 0.9	125.2 ± 2.9	114.5 ± 3.1	−3.8 ± 2.9	−0.7 ± 3.1

(e) 1,3,5-Trifluorobenzene (1) + [emim][$\mathrm{Tf_2N}$] (2) System

T/K	$100x_1'$	$100x_1$	$\frac{V'}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E'}}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E}}{\mathrm{cm^3\cdot mol^{-1}}}$
283.5 ± 0.2	49.7 ± 2.3	100.0 − 0.8	175.4 ± 6.0	101.3 ± 1.5	−3.9 ± 6.0	−1.2 ± 1.5
298.2 ± 0.2	49.8 ± 2.2	100.0 − 0.7	176.2 ± 6.5	103.5 ± 1.5	−4.9 ± 6.5	−0.8 ± 1.5
316.6 ± 0.2	48.7 ± 2.3	100.0 − 0.6	179.0 ± 6.6	105.7 ± 1.6	−6.9 ± 6.6	−1.0 ± 1.6
333.2 ± 0.2	48.2 ± 2.3	100.0 − 0.7	181.5 ± 6.5	108.0 ± 1.8	−8.8 ± 6.5	−1.0 ± 1.8
353.1 ± 0.2	47.8 ± 2.3	100.0 − 0.8	183.0 ± 6.1	110.8 ± 1.8	−10.2 ± 6.1	−1.0 ± 1.8
373.0 ± 0.2	48.2 ± 2.2	100.0 − 0.8	184.6 ± 6.0	114.4 ± 1.8	−11.4 ± 6.0	−0.4 ± 1.8

(f) 1,2,3,5-Tetrafluorobenzene (1) + [emim][$\mathrm{Tf_2N}$] (2) System

T/K	$100x_1'$	$100x_1$	$\frac{V'}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E'}}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E}}{\mathrm{cm^3\cdot mol^{-1}}}$
283.5 ± 0.2	65.9 ± 0.5	100.0 − 0.3	152.3 ± 4.8	105.3 ± 1.5	−4.2 ± 4.8	0.0 ± 1.5
298.3 ± 0.2	65.2 ± 0.7	100.0 − 0.3	156.2 ± 5.1	106.9 ± 1.7	−3.5 ± 5.1	−0.3 ± 1.7
316.7 ± 0.2	64.7 ± 0.6	100.0 − 0.3	157.9 ± 5.1	109.6 ± 1.8	−5.3 ± 5.1	−0.1 ± 1.8
333.2 ± 0.2	63.8 ± 0.7	100.0 − 0.3	160.5 ± 5.1	111.9 ± 2.0	−6.6 ± 5.1	−0.2 ± 2.0
353.1 ± 0.2	63.1 ± 0.7	100.0 − 0.3	164.0 ± 5.4	114.9 ± 2.5	−7.4 ± 5.4	−0.1 ± 2.5
373.0 ± 0.2	62.3 ± 0.7	100.0 − 0.3	168.8 ± 5.4	118.0 ± 2.5	−7.2 ± 5.4	−0.1 ± 2.5

(g) 1,2,4,5-Tetrafluorobenzene (1) + [emim][$\mathrm{Tf_2N}$] (2) System

T/K	$100x_1'$	$100x_1$	$\frac{V'}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E'}}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E}}{\mathrm{cm^3\cdot mol^{-1}}}$
283.3 ± 0.2	73.6 ± 0.5	99.9 ± 0.1	142.2 ± 1.5	103.0 ± 1.0	−1.8 ± 1.5	−1.2 ± 1.0
298.2 ± 0.2	73.1 ± 0.5	99.9 ± 0.1	144.9 ± 1.7	104.7 ± 1.1	−1.8 ± 1.7	−1.3 ± 1.0
315.5 ± 0.2	72.5 ± 0.6	100.0 − 0.2	147.3 ± 2.7	107.4 ± 1.0	−2.7 ± 2.7	−0.6 ± 1.0
333.2 ± 0.2	71.8 ± 0.6	100.0 − 0.2	150.8 ± 2.6	109.5 ± 1.3	−2.9 ± 2.6	−0.9 ± 1.3
353.1 ± 0.2	71.0 ± 0.6	100.0 − 0.2	155.1 ± 2.5	112.4 ± 1.4	−2.9 ± 2.5	−0.7 ± 1.4
373.0 ± 0.2	70.2 ± 0.6	100.0 − 0.2	159.5 ± 2.4	115.7 ± 1.5	−2.8 ± 2.4	−0.3 ± 1.5

(h) Pentafluorobenzene (1) + [emim][$\mathrm{Tf_2N}$] (2) System

T/K	$100x_1'$	$100x_1$	$\frac{V'}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E'}}{\mathrm{cm^3\cdot mol^{-1}}}$	$\frac{V^{E}}{\mathrm{cm^3\cdot mol^{-1}}}$
283.4 ± 0.2	71.5 ± 0.8	99.7 ± 0.3	148.4 ± 2.8	109.3 ± 2.0	−2.6 ± 2.8	−0.5 ± 2.0
298.2 ± 0.2	70.4 ± 0.6	99.8 ± 0.2	152.3 ± 2.9	110.9 ± 2.1	−2.5 ± 2.9	−0.8 ± 2.1
316.6 ± 0.2	69.6 ± 0.4	99.7 ± 0.3	155.2 ± 2.9	113.9 ± 2.1	−3.7 ± 2.9	−0.6 ± 2.1
333.2 ± 0.2	68.1 ± 0.5	100.0 − 0.4	160.5 ± 3.0	115.5 ± 2.2	−3.1 ± 3.0	−1.1 ± 2.2
353.1 ± 0.2	66.9 ± 0.5	100.0 − 0.4	165.2 ± 3.0	118.7 ± 2.3	−3.5 ± 3.0	−1.0 ± 2.3
373.0 ± 0.2	65.7 ± 0.6	100.0 − 0.4	169.2 ± 3.1	122.8 ± 2.4	−4.7 ± 3.1	−0.2 ± 2.4

Table 3. NRTL Binary Interaction Parameters in Equation 7

compound (**1**) in [emim][Tf$_2$N] (**2**)	$\tau_{12}^{(0)}$	$\tau_{12}^{(1)}$/K	$\tau_{21}^{(0)}$	$\tau_{21}^{(1)}$/K
benzene	9.3428	136.38	−2.6571	−113.78
fluorobenzene	6.6107	662.50	−2.7247	−260.84
1,3-difluorobenzene	8.2176	223.03	−2.19708	−185.92
1,4-difluorobenzene	9.4868	236.59	−2.78928	−191.75
1,2-difluorobenzene	---	---	---	---
1,3,5-trifluorobenzene	6.0396	109.66	−0.88669	−105.56
1,2,4-trifluorobenzene	7.8682	14.00	−0.24121	−1150.0
1,2,3-trifluorobenzene	---	---	---	---
1,2,3,5-tetrafluorobenzene	7.2386	273.91	−1.30318	−245.68
1,2,4,5-tetrafluorobenzene	7.6334	332.63	−1.6912	−282.76
1,2,3,4-tetrafluorobenzene	---	---	---	---
pentafluorobenzene	6.8282	509.38	−0.97305	−442.94
hexafluorobenzene	7.5042	394.38	−0.98914	−358.91

moment. Molecules that have permanent (electric) dipole moments are said to be polar *in general*, while molecules with no dipole moment are said to be nonpolar. For example, benzene, hexafluorobenzene, 1,3,5-trifluorobenzene, etc., have zero dipole moment, due to their molecular symmetries. Thus, these molecules are said to be nonpolar. However, a more rigorous definition for the molecular polarity must include multipole charge distributions in a molecule. In the multipole charge expansion, the term next to the dipole is the electric quadruple moment. The importance of the benzene-ring quadrapole moments (ion−quadrupole interactions) will be discussed later in this section.

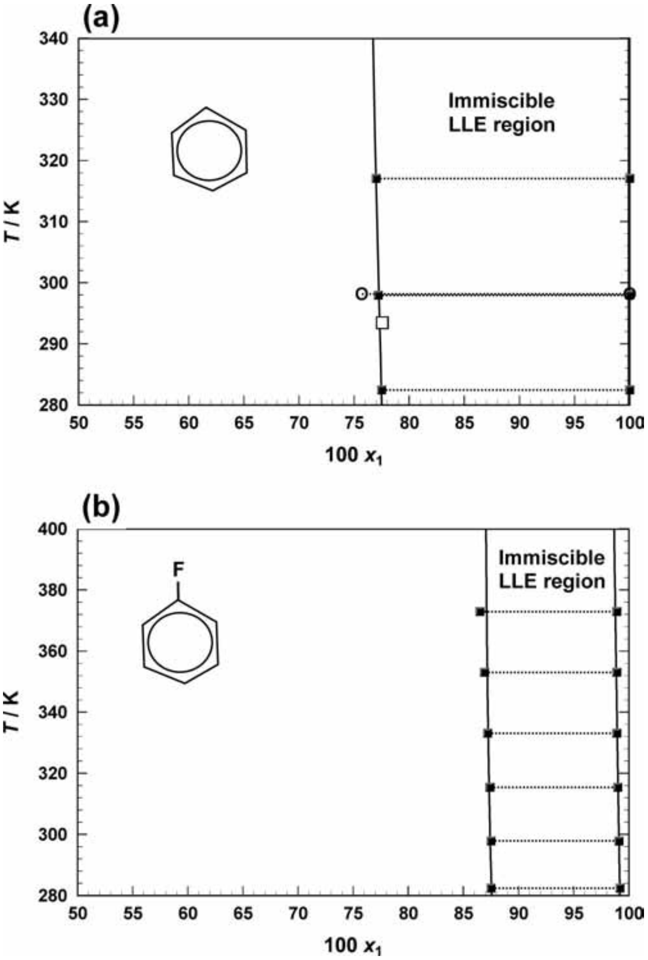


Figure 2. *Tx* phase diagrams for LLE of (a) benzene (1) + [emim][Tf$_2$N] (2) and (b) fluorobenzene (1) + [emim][Tf$_2$N] (2). Solid line: the NRTL model calculation. Broken lines: experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method; ○, experimental data in ref 20; □, experimental data in ref 22.

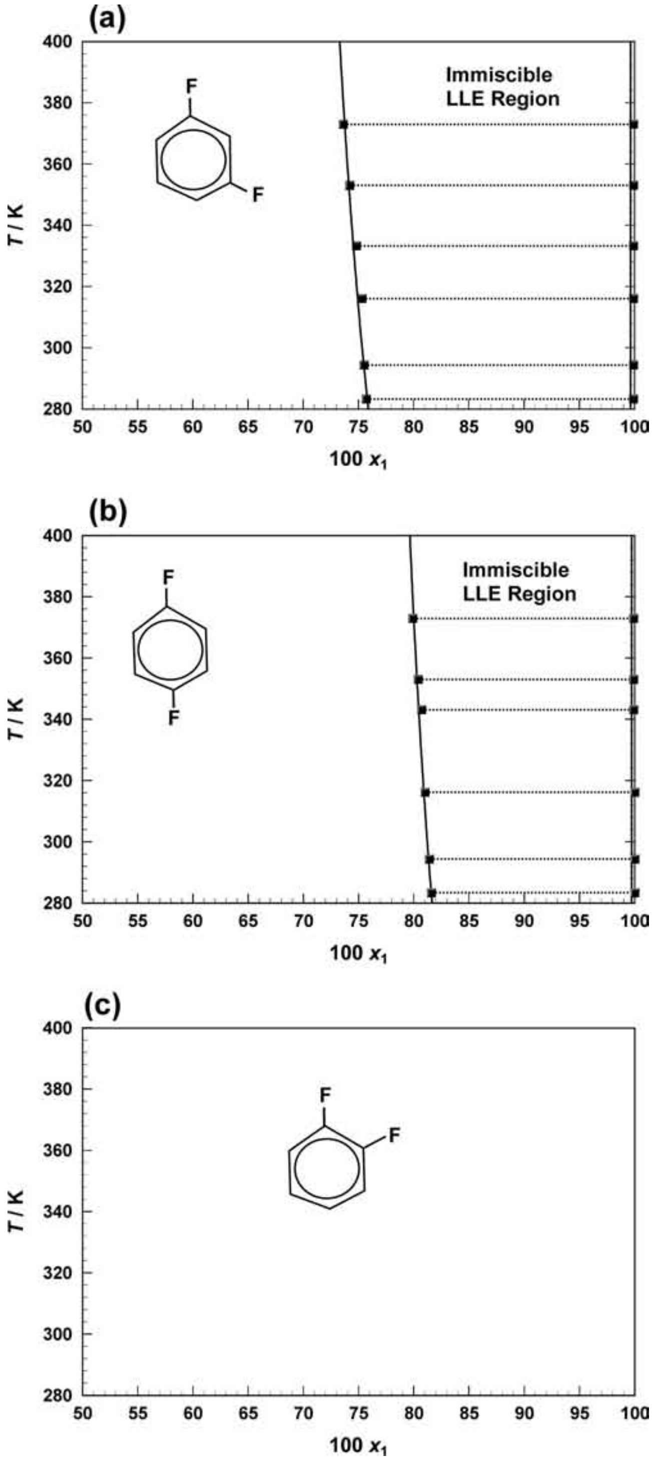


Figure 3. *Tx* phase diagrams for LLE of (a) 1,3-difluorobenzene (1) + [emim][Tf$_2$N] (2), (b) 1,4-difluorobenzene (1) + [emim][Tf$_2$N] (2), and (c) 1,2-difluorobenzene (1) + [emim][Tf$_2$N] (2) which is completely miscible in the presently studied temperature range (283 to 373) K. Solid line: the NRTL model calculation. Broken lines: experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method.

Fluorobenzene is known to have a dipole moment of 1.4 D (1 D = $3.33564 \cdot 10^{-30}$ C·m),[25] while those in other fluorinated benzenes are not reported in the literature. Here, using the well-known vector-sum method of bond-dipole moments, the molecular dipole moments for the other fluorinated benzenes were calculated. In the case of 1,3-difluorobenzene, 1,2,4-trifluorobenzene, 1,2,3,5-tetrafluorobenzene, and pentafluorobenzene, the molecules have a dipole moment of about 1.4 D. Further-

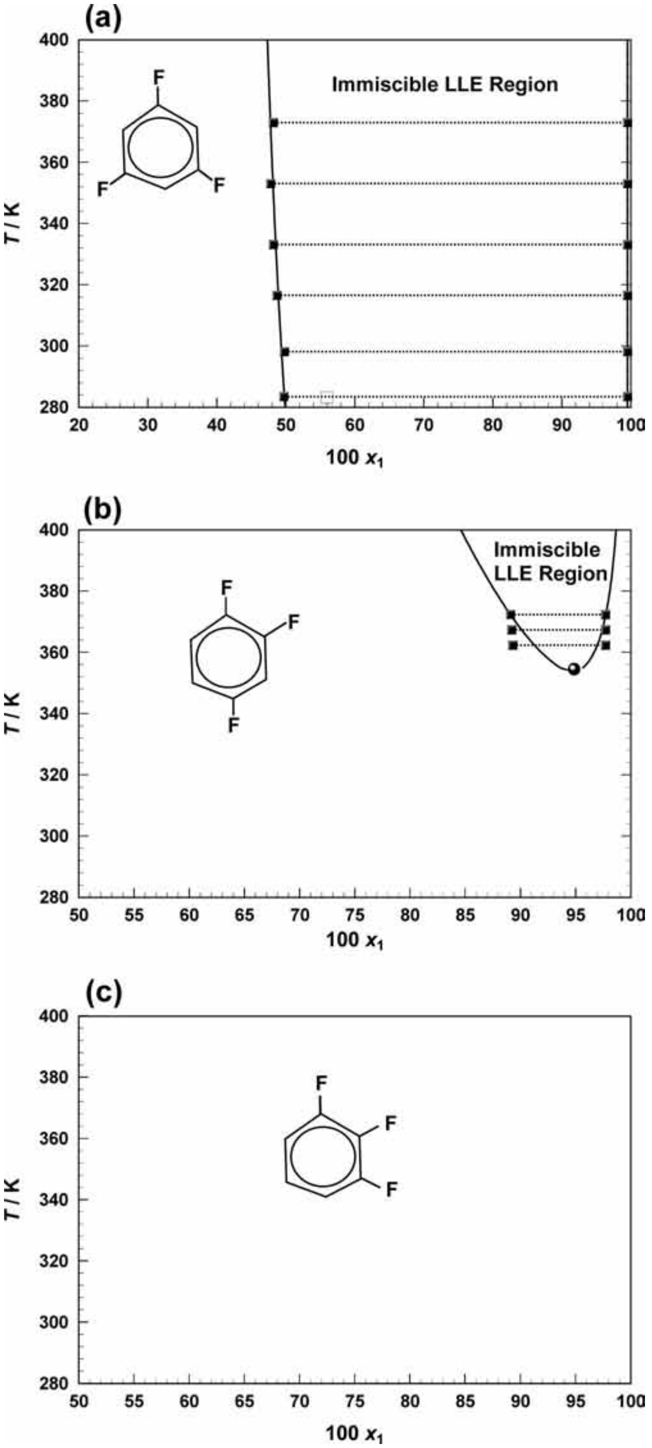


Figure 4. *Tx* phase diagrams for LLE of (a) 1,3,5-trifluorobenzene (1) + [emim][Tf_2N] (2), (b) 1,2,4-trifluorobenzene (1) + [emim][Tf_2N] (2), and (c) 1,2,3-trifluorobenzene (1) + [emim][Tf_2N] (2) which is completely miscible in the presently studied temperature range (283 to 373) K. Solid line: the NRTL model calculation. Broken lines: experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method; ●, experimental data by the cloud point method; □, experimental data in ref 22.

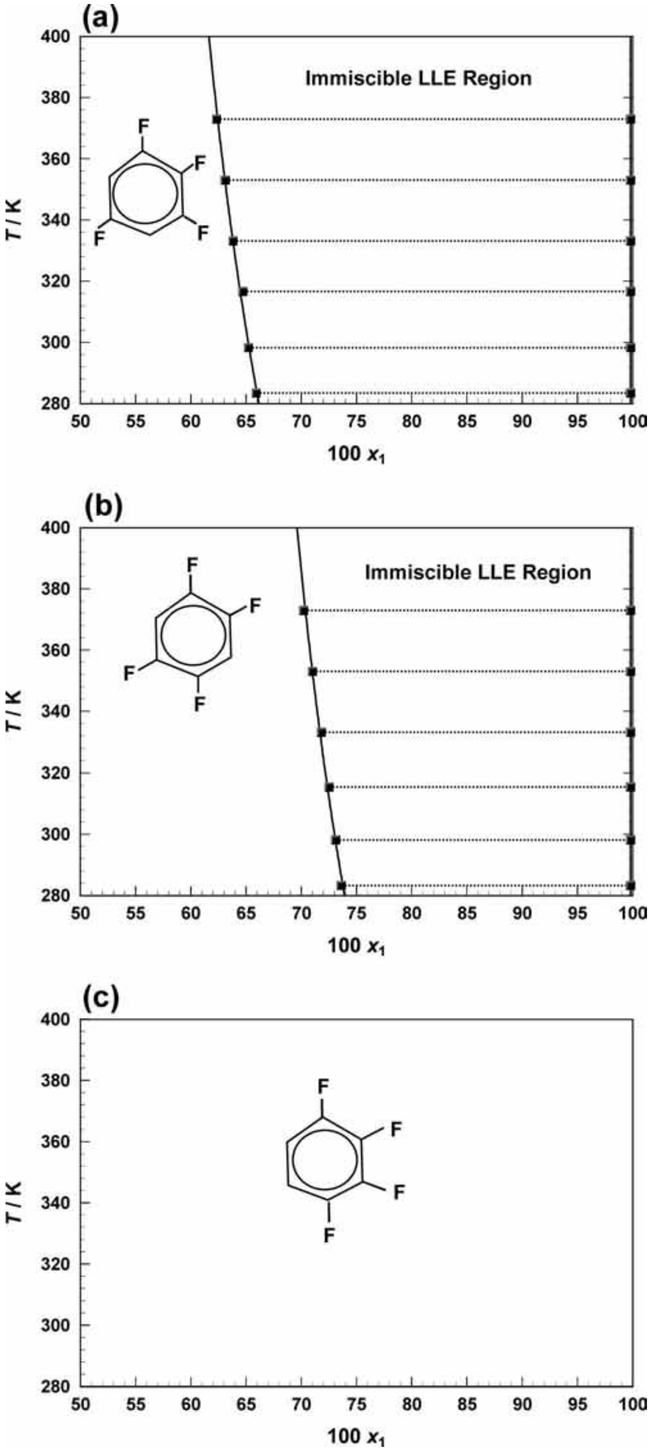


Figure 5. *Tx* phase diagrams for LLE of (a) 1,2,3,5-tetrafluorobenzene (1) + [emim][Tf_2N] (2), (b) 1,2,4,5-tetrafluorobenzene (1) + [emim][Tf_2N] (2), and (c) 1,2,3,4-tetrafluorobenzene (1) + [emim][Tf_2N] (2) which is completely miscible in the presently studied temperature range (283 to 373) K. Solid line: the NRTL model calculation. Broken lines: experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method.

more, 1,2-difluorobenzene and 1,2,3,4-tetrafluorobenzene have a dipole moment of about 2.4 D, and 1,2,3-trifluorobenzene has the largest dipole moment of about 2.8 D.

The polarity of RTILs is an area of current research interest. Both solvatochromic and fluoresecent dyes have been utilized to determine the polarity of these molten salts, and different combinations of cations and anions lead to solvents with different polarities.[31−37] In the case of the [emim][Tf_2N], both the cation and the anion have a dipole moment, and the molecule is considered to be polar. This leads the novice to the typical association rule of "like dissolves like" and suggests that the fluorinated benzenes with the large dipole moments (polar) should be more miscible in [emim][Tf_2N] than the fluorinated benzenes with small (or zero) dipole moments (nonpolar).

In general, this trend (magnitude of the dipole moment of the solutes with the immiscibility gap) does correlate with the

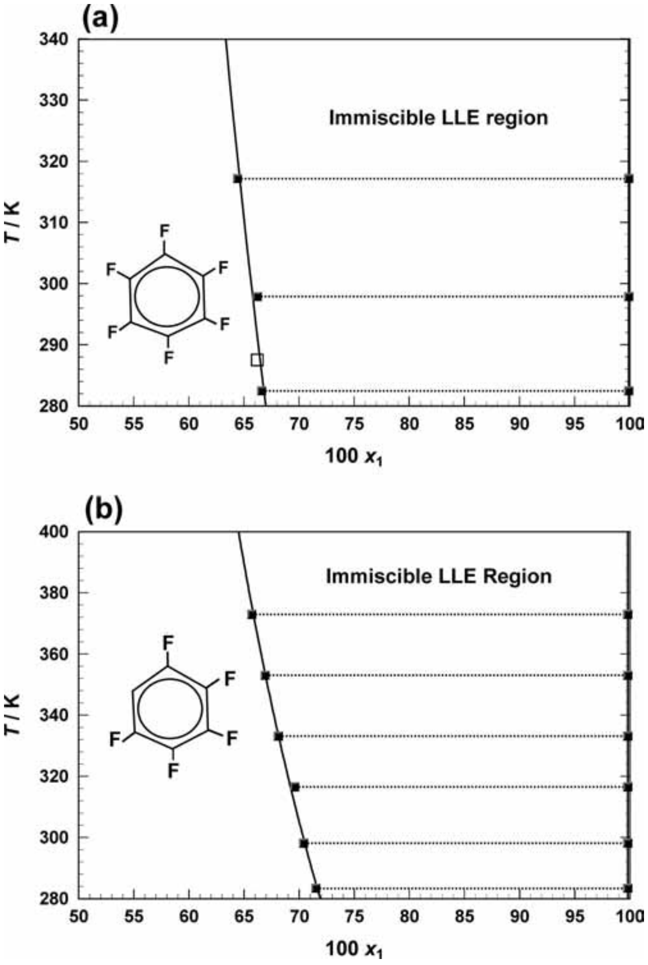


Figure 6. *Tx* phase diagrams for LLE of (a) hexafluorobenzene (1) + [emim][Tf_2N] (2) and (b) pentafluoroethane (1) + [emim][Tf_2N] (2). Solid line: the NRTL model calculation. Broken lines: experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method; □, experimental data in ref 22.

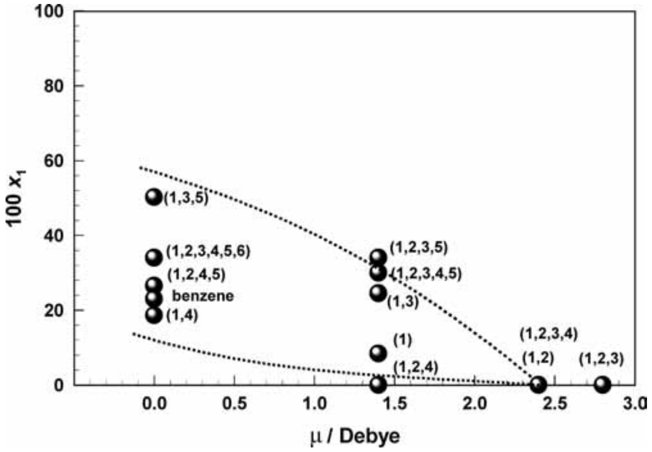


Figure 7. Correlation of immiscibility gap (100x_1) in [emim][Tf_2N] with dipole moments (μ) of fluorinated benzene (including benzene) solutes at 298 K. Parentheses define chemical compound (e.g. (1,3,5) is 1,3,5-trifluorobenzene). (1 D = $3.33564 \cdot 10^{-30}$ C·m).

experimental results. For example, the binary systems with the largest dipole moments (1,2-difluorobenzene and 1,2,3,4-tetrafluorobenzene with a dipole moment of 2.4 D and 1,2,3-trifluorobenzene with a dipole moment of 2.8 D) were completely miscible in [emim][Tf_2N] over the temperature range investigated from (283 to 413) K. In the case of the other fluorinated benzenes with dipole moments of (1.4 and 0) D, the solutes were only partially miscible in the [emim][Tf_2N]. Here, it is worth mentioning that the present solubility trend between fluorinated benzenes and ionic liquid is quite different from that observed between fluorinated aliphatic hydrocarbons (HFCs) and RTILs.[6] In the case of the HFC + RTIL mixtures, the molecular polarity (HFC's dipole moments) has absolutely no correlation with the solubility behavior.[6] Then, it has been suggested that the hydrogen-bonding interaction between HFC and RTIL molecules is a dominant factor to the solubility behavior.

Figures 2 to 6 provide the phase diagram (*Tx*) for all the binary fluorinated benzene + [emim][Tf_2N] systems and also include our previous work[5] with benzene and hexafluorobenzene for comparison. The binary systems (1,4-difluorobenzene, benzene, 1,2,4,5-tetrafluorobenzene, hexafluorobenzene, and 1,3,5-trifluorobenzene) with a zero dipole moment show immiscibility gaps of about (x_2 = 18, 23, 27, 34, and 50) mole percent, respectively, at 298 K. The binary systems (fluorobenzene, 1,3-difluorobenzene, pentafluorobenzene, and 1,2,3,5-tetrafluorobenzene) with a dipole moment of about 1.4 D show immiscibility gaps of about (x_2 = 13, 25, 30, and 35) mole percent, respectively, at 298 K. The trend of the immiscibility gap with a dipole moment is shown for all binary systems at 298 K in Figure 7.

Although a general trend between the dipole moment and the solubility exists as shown in Figure 7, there are a few exceptions. In the case of the difluorobenzene isomers as shown in Figure 3, the order of increasing dipole moments [1,4-difluorobenzene (0 D) < 1,3-difluorobenzene (1.4 D) < 1,2-difluorobenzene (2.4 D)] does not correlate with the measured immiscibility gaps [1,3-difluorobenzene (x_2 = 25 mol %) > 1,4-difluorobenzene (x_2 = 19 mol %) > 1,2 difluorobenzene (completely miscible, x_2 = 0 mol %)]. The 1,3- and 1,4-difluorobenzene isomers are out of order. The same is true in the case of the tetrafluorobenzene isomers as shown in Figure 5. The order of increasing dipole moments [1,2,4,5-tetrafluorobenzene (0 D) < 1,2,3,5-tetrafluorobenzene (1.4 D) < 1,2,3,4-tetrafluorobenzene (2.4 D)] does not correlate with the measured immiscibility gaps [1,2,3,5-tetrafluorobenzene (x_2 = 35 mol %) > 1,2,4,5-tetrafluorobenzene (x_2 = 27 mol %) > 1,2,3,4-tetrafluorobenzene (completely miscible, x_2 = 0 mol %)]. The 1,2,3,5- and 1,2,4,5-tetrafluorobenzene isomers are out of order. Only in the case of the trifluorobenzene isomers as shown in Figure 4 does the order of increasing dipole moments [1,3,5-trifluorobenzene (0 D) < 1,2,4-trifluorobenzene (1.4 D) < 1,2,3-trifluorobenzene (2.8 D)] correlate with the measured immiscibility gaps [(1,3,5-trifluorobenzene (x_2 = 50 mol %) > 1,2,4-trifluorobenzene (x_2 = 11 mol %) > 1,2,3-trifluorobenzene (completely miscible, x_2 = 0 mol %)] over the presently studied temperature range [(283 to 373) K].

For an explanation of the immiscibility gaps in the cases of the difluorobenzene and tetrafluorobenzene isomers, we have to consider additional intermolecular interactions. For example, we have discussed in our previous work[7,15] the unique H-bonding capability (H−F−H) between fluorinated compounds and ionic liquids. Additional interactions such as higher-order moments (quadrupole, octupole)[37−39] and π-electron (π-cation and π-anion) effects[37,40−42] may also have a role to play in determining the immiscibility gaps. Here, when the ion−dipole attraction is missing or small, it is no doubt that the electrostatic interactions are thought to be dominated by the attraction between the positive charge and quadrupole moment of the aromatic ring as well as induction and dispersion forces.[41,42]

This poses a unique and interesting challenge for theoretical modelers to explain these measurements.

As shown in Figure 4b, the 1,2,4-trifluorobenzene + [emim][Tf_2N] binary system was found to have a lower critical solution temperature (LCST). The observed cloud point for 1,2,4-trifluorobenzene (1) and [emim][Tf_2N] (2) was $x_1 = 94.9$ % at (354.4 ± 1) K. In this study, the LCST behavior was observed only in the 1,2,4-trifluorobenzene case. However, many other systems (Figures 2 to 6) suggest the LCST behavior at much lower temperatures, based on the observed curvatures of the immiscibility gap, although at such low temperatures the system may be interfered by the solid−liquid equilibrium lines.[21,22] It is interesting to note that in our previous work with fluoroalkanes (HFCs) and RTILs we found several examples of the LCST behavior.[11−14]

Finally, LLE data have been well correlated with the nonelectrolyte NRTL solution model, and the LLE behavior is similar to certain fluoroalkane[7,14,15] ($CFCl_3$, $CHCl_3$, $CFCl_2-CF_2Cl$, $CHCl_2-CF_3$, $CF_3CHFCHFCF_2CF_3$) and fluoroether[16] ($CF_3CF_2CF_2-O-CH_3$, $CF_3CF_2CF_2CF_2-O-CH_3$, $CF_3CF_2CF_2$-$CF_2-O-CH_2CH_3$, $CF_3CF_2CF(OCH_3)CF(CF_3)_2$, $CF_3CF_2CF_2CF$-$(OCH_2CH_3)CF(CF_3)_2$) + ionic liquid mixtures. The present volumetric method for LLE also provides information for the excess molar volume for each separated liquid. In ordinary binary mixtures,[43] the excess molar volume is at most ± (2 to 3) $cm^3 \cdot mol^{-1}$, but we have found for the cases with the largest immiscibility gaps [1,3,5-trifluorobenzene ($x_2 = 50$ mol %), 1,2,3,5-tetrafluorobenzene ($x_2 = 35$ mol %), and pentafluorobenzene ($x_2 = 30$ mol %)] as shown in Table 2 that large negative (about (−4 to −10) $cm^3 \cdot mol^{-1}$) excess molar volumes do exist for these systems. Similar large negative excess molar volumes have been observed in various HFC mixtures with RTILs.[11−13] Such information provides new insight on the physical structures in the liquid solutions containing RTILs.

Conclusions

Liquid−liquid equilibria in binary mixtures of fluorinated benzenes and RTIL [emim][Tf_2N] have been measured with the volumetric and cloud-point methods. The fluorinated benzenes having the largest dipole moments (1,2-difluorobenzene 2.4 D, 1,2,3,4-tetrafluorobenzene 2.4 D, and 1,2,3-trifluorobenzene 2.8 D) were completely miscible over the temperature range studied [(283 to 413) K], while the other fluorinated benzenes with a dipole moment of 1.4 D (1,2,4-trifluorobenzene, fluorobenzene, 1,3-difluorobenzene, pentafluorobenzene, and 1,2,3,5-tetrafluorobenzene) and 0 D (1,4-difluorobenzene, benzene, 1,2,4,5-tetrafluorobenzene, hexafluorobenzene, and 1,3,5-trifluorobenzene) were only partially miscible in [emim][Tf_2N]. Although a trend between the dipole moment and the miscibility was discovered, other intermolecular interactions (higher-order moments (particularly well-known large quadrupole moments of the aromatic ring), π-electron effects, and hydrogen bonding) may also play a role in controlling the degree of miscibility in these mixtures. LLE data are well correlated with the nonelectrolyte NRTL model, and the binary mixtures with the largest immiscibility gaps (1,3,5-trifluorobenzene, 1,2,3,5-tetrafluorobenzene, and pentafluorobenzene) show the largest negative excess molar volumes (about (−4 to −10) $cm^3 \cdot mol^{-1}$).

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