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Liquid−Liquid Equilibria in Binary Mixtures Containing Chlorobenzene, Bromobenzene, and Iodobenzene with Ionic Liquid 1-Ethyl-3-methylimidazolim Bis(trifluoromethylsulfonyl)imide

Mark B. Shiflett,[*,†] **Anne Marie S. Niehaus,**[†] **and A. Yokozeki**[‡]

DuPont Central Research and Development, Experimental Station 304, Wilmington, Delaware 19880, and DuPont Fluoroproducts Laboratory, Chestnut Run Plaza 711, Wilmington, Delaware 19880

Liquid−liquid equilibria in binary mixtures of halogenated benzene (chlorobenzene, bromobenzene, and iodobenzene) with ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim]-[Tf_2N]), have been measured using a volumetric method over a temperature range from about (293 to 373) K. A general trend between the molecular size of the solute (monohalogenated benzene) and the immiscibility gap was discovered; the larger the size, the wider the gap. No correlation with the dipole moment exists, although other intermolecular interactions (higher-order moments, π-electron effects, and hydrogen bonding) may also play a role. The excess molar volumes range from (−1 to −5) $cm^3 \cdot mol^{-1}$; the magnitudes are larger than those of ordinary liquid solutions. Observed LLE are well correlated by use of the nonrandom two liquid (NRTL) solution model.

Introduction

Liquid−liquid equilibria (LLE) of halogenated benzenes in room-temperature ionic liquids (RTILs) are extremely important for evaluating RTILs as new solvents for chemical separation and extraction applications.[1−4] This article is a continuation of our previous studies[5,6] on the phase behavior of benzene and fluorobenzene isomers in RTIL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]). The present work includes the LLE behavior of chlorobenzene, bromobenzene, and iodobenzene in [emim][Tf_2N] over a temperature range from (293 to 373) K. We have also studied the thermodynamic properties of RTILs with a variety of halogenated hydrocarbons[7−16] and fluorinated ethers.[17,18] The present phase equilibrium study of chlorobenzene, bromobenzene, and iodobenzene with [emim][Tf_2N] is part of our continuing investigations to understand the interactions (or phase behaviors) of halogenated compounds with RTILs.

There are several solubility studies of RTIL mixtures with aromatic hydrocarbons and alkanes in the literature;[19−23] however, to the best of our knowledge, we are the first to report LLE for monohalogenated benzene isomers (fluoro-, chloro-, bromo-, iodobenzene) in [emim][Tf_2N]. This article combines both our current work on the interactions of monohalogenated benzenes (C_6H_5X: X = Cl, Br, and I) along with comparisons with our original work on fluorobenzene (C_6H_5F) in [emim][Tf_2N].[6]

Experimental Section

Materials. Chlorobenzene (C_6H_5Cl, assay 99.9 %, product and batch no. 270644-100 ML 02947BH, CAS registry no. 108-90-7) and iodobenzene (C_6H_5I, assay 98 %, product and batch no. I7632-100G-A 1395926 42608021, CAS registry no. 591-50-4) were obtained from Sigma-Aldrich (St. Louis, MO).[24] Bromobenzene (C_6H_5Br, assay 99.5 %, lot and filling code 1333487 20908268, CAS registry no. 108-86-1) was obtained from Aldrich/Fluka (Buchs, Switzerland). The halogenated 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 Covalent Associates (Corvallis, OR).[25] 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.[8] We dried and degassed the [emim][Tf_2N] 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 water mass fraction was measured by Karl Fischer titration (AquaStar C3000, solution AquaStar Coulomat C and A), 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.[12,13] Therefore, only the basic experimental techniques and measurement uncertainties are given here. LLE measurements were made with samples containing mole fractions of (90.0 and 97.0) % chlorobenzene + [emim][Tf_2N], mole fractions of (74.0 and 97.0) % bromobenzene + [emim][Tf_2N], and mole fractions of (63.1 and 97.0) % iodobenzene + [emim][Tf_2N] at constant temperatures from about (293 to 373) K using the volumetric method.[12,13]

To measure LLE over a wide range of temperatures, we utilized two thermostat baths. A water-filled thermostat bath, which was used in our previous experiments,[12,13] was used for measurements between temperatures of (293 and 333) K. Higher

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[*] Corresponding author. E-mail: mark.b.shiflett@usa.dupont.com.

[†] DuPont Central Research and Development.

[‡] DuPont Fluoroproducts Laboratory.

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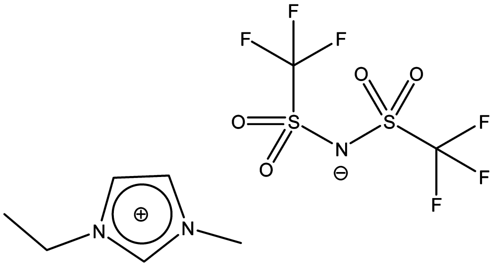
Chemical Name	Abbreviation	Structure
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[emim][Tf$_2$N]	

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

Table 1. Chlorobenzene (1) + [emim][Tf$_2$N] (2) System

T / K	$100x_1'$	$100x_1$	V' / cm^3·mol^{-1}	V / cm^3·mol^{-1}	$V^{E'}$ / cm^3·mol^{-1}	V^E / cm^3·mol^{-1}
			Chlorobenzene (1) + [emim][Tf$_2$N] (2) System			
293.3 ± 0.2	70.6 ± 0.3	99.7 ± 0.3	145.6 ± 1.4	102.1 ± 0.3	−1.7 ± 1.4	−0.2 ± 0.3
313.2 ± 0.2	71.1 ± 0.3	99.7 ± 0.3	147.3 ± 1.7	103.7 ± 0.4	−1.7 ± 1.7	−0.4 ± 0.4
332.7 ± 0.2	71.8 ± 0.4	99.7 ± 0.3	148.3 ± 1.9	105.9 ± 0.4	−2.0 ± 1.9	−0.4 ± 0.4
353.1 ± 0.2	72.9 ± 0.4	99.7 ± 0.3	146.9 ± 1.8	108.9 ± 0.6	−4.3 ± 1.8	−0.1 ± 0.6
372.9 ± 0.2	73.6 ± 0.6	99.6 ± 0.3	147.5 ± 2.2	111.4 ± 0.9	−5.3 ± 2.2	−0.1 ± 0.9
			Bromobenzene (1) + [emim][Tf$_2$N] (2) System			
293.0 ± 0.2	59.4 ± 0.6	100.0 − 0.2	164.5 ± 0.7	104.7 ± 0.4	−2.1 ± 0.7	−0.3 ± 0.4
313.2 ± 0.2	60.7 ± 0.4	100.0 − 0.2	164.9 ± 0.7	106.7 ± 0.4	−2.2 ± 0.7	−0.2 ± 0.4
332.3 ± 0.2	62.1 ± 0.6	100.0 − 0.2	165.4 ± 0.9	108.6 ± 0.3	−2.0 ± 0.9	−0.2 ± 0.3
353.1 ± 0.2	63.4 ± 0.6	100.0 − 0.2	166.0 ± 0.8	110.5 ± 0.6	−2.2 ± 0.8	−0.4 ± 0.6
372.9 ± 0.2	64.7 ± 0.3	100.0 − 0.2	166.4 ± 1.0	112.3 ± 0.6	−3.4 ± 1.0	−0.8 ± 0.6
			Iodobenzene (1) + [emim][Tf$_2$N] (2) System			
293.0 ± 0.2	99.8 ± 0.2	33.8 ± 0.4	111.2 ± 0.3	206.9 ± 1.0	−0.4 ± 0.3	−0.6 ± 1.0
313.2 ± 0.2	99.9 ± 0.1	36.1 ± 0.4	113.1 ± 0.3	205.6 ± 1.0	−0.1 ± 0.3	−1.5 ± 1.0
332.3 ± 0.2	100.0 − 0.2	38.7 ± 0.4	115.1 ± 0.3	203.8 ± 1.0	0 ± 0.3	−2.2 ± 1.0
353.1 ± 0.2	99.8 ± 0.2	41.5 ± 0.3	116.1 ± 0.5	202.8 ± 2.0	−0.9 ± 0.5	−2.0 ± 2.0
372.9 ± 0.2	99.9 ± 0.1	44.3 ± 0.4	118.2 ± 0.3	199.9 ± 1.0	−0.8 ± 0.3	−3.6 ± 1.0

temperature measurements at (353 to 373) K were performed using a silicone oil-filled thermostat bath (Tamson Instruments, TV4000LT, Zoetermeer, Netherlands). The uncertainty in temperature for both thermostat baths 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.

Results

Experimental Data. To use the mass−volume method,[12,13] we assumed that the vapor phase contained only monohalogenated benzenes (negligible vapor pressure for [emim][Tf$_2$N] ionic liquid). We calculated the vapor density for chlorobenzene, bromobenzene, and iodobenzene assuming ideal gas behavior and known vapor pressure data.[26] We estimated the total uncertainties 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 volume calibration, mass of monohalogenated benzenes and ionic liquid, and heights 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 1. For additional details of estimation of total uncertainties, see refs 12 and 13.

One of the advantages of using the present method is the ability to obtain the molar volume of each separated liquid simultaneously with the mole fraction of each liquid under any given isothermal condition. Then, the excess molar volume of each liquid solution ($V^{E\prime}$ and V^E) can be obtained by use of the pure component molar volumes V_1^0 (monohalogenated benzenes) and V_2^0 ([emim][Tf$_2$N]) using

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

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 monohalogenated benzenes (1) and ionic liquid (2) in phase L′ and L, respectively. Saturated liquid molar volumes for monohalogenated benzenes were calculated using the modified Rackett technique and measured liquid density data was provided in ref 26. Saturated liquid molar volumes for [emim][Tf$_2$N] were calculated using liquid density data measured by Krummen et al.[27]

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 2. NRTL Binary Interaction Parameters in Equation *7*

compound (1) in [emim][Tf_2N] (2)	$\tau_{12}^{(0)}$	$\tau_{12}^{(1)}/K$	$\tau_{21}^{(0)}$	$\tau_{21}^{(1)}/K$
chlorobenzene	9.3168 ± 0.1173	-347.88 ± 38.64	-3.3973 ± 0.0974	292.13 ± 32.10
bromobenzene	9.9579 ± 0.0673	-453.34 ± 22.16	-3.2499 ± 0.0589	422.74 ± 19.40
iodobenzene	9.2397 ± 0.1332	-596.78 ± 43.86	-2.7909 ± 0.1330	654.49 ± 43.78

1 (monohalogenated benzenes), whereas $i = 2$ corresponds to species 2, the ionic liquid [emim][Tf_2N]. For the activity coefficient, we used the NRTL (nonrandom two liquid) solution model[26] in the present study.

The binary activity coefficients of the NRTL model are given by

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \tag{3}$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] \tag{4}$$

where

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

$$\tau_{12} \equiv \frac{\Delta g_1}{RT} \quad \text{and} \quad \tau_{21} \equiv \frac{\Delta g_2}{RT} \quad \text{(adjustable binary interaction parameters)}$$

$$\alpha = 0.2 \quad \text{(assumed to be a constant of 0.2 in this work)}$$

$$x_i = \text{mole fraction of the } i\text{th species} \tag{6}$$

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

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

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 five sets of such LLE data for each binary system, as shown in Table 1, and can obtain a set of τ_{12} and τ_{21} at a respective temperature. Therefore, the four empirical parameters in eq 7 have been determined from the obtained τ_{ij} data and are given in Table 2.

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 the 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 Figure 2.

Discussion

We have continued our evaluation of the LLE behavior of monohalogenated benzenes (C_6H_5X: X = Cl, Br, I) with RTIL, [emim][Tf_2N], to provide some insight into these molecular interactions compared with our original work using fluorobenzene (C_6H_5F) and [emim][Tf_2N].[6] The solubility behavior of a substance often gives us a clue to the intermolecular interactions between solute (monohalogenated benzene) and solvent (RTIL). Monohalogenated benzenes have permanent (electric) dipole moments and are considered to be polar molecules. The dipole moments for fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene are (1.4, 1.6, 1.5, and 1.4) D ($1\ \mathrm{D} = 3.33564 \cdot 10^{-30}\ \mathrm{C \cdot m}$).[26]

The polarity of RTILs is an area of current research interest. Both solvatochromic and fluorescent 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.[29−35] In the case of [emim][Tf_2N], both the cation and 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 monohalogenated benzenes that all have similar dipole moments ((1.4 to 1.6) D) should have a similar miscibility range in [emim][Tf_2N]. Figure 2 provides the phase diagrams (*Tx*) for the binary systems chlorobenzene, bromobenzene, and iodobenzene + [emim][Tf_2N]. The binary pair of fluorobenzene + [emim][Tf_2N] from our previous work[6] has also been included for comparison. The mole fraction immiscibility gap ($\Delta 100 x_1$) at 293 K for fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene in [emim][Tf_2N] is about (11, 29, 41, and 66) %, respectively. The measured immiscibility gap does not correlate with the solute dipole moment.

For an explanation of the immiscibility gaps, we can compare the molecular size of the solutes. Figure 3 shows that a correlation exists between the immiscibility gap and the molecular size (collision diameter of benzene + halogen) of the solute.[36] One explanation using molecular dynamic calculations by Huang et al.[37] for the binary system (CO_2 + [bmim][PF_6]) indicates that small angular rearrangements of the anion can occur, which create localized cavities for molecules to fit above and below the imidazolium ring. In this case, angular rearrangements of the [Tf_2N] anion must create cavities for the halogenated benzenes to fit around the [emim] cation. The size of the solute determines the amount of halogenated benzene that can fit into these cavities and exist in the ionic liquid-rich phase. As the solute molecular size increases (fluorobenzene < chlorobenzene < bromobenzene < iodobenzene), less solute can fill these cavities, which results in the increase in the immiscibility gap. If we include benzene in our analysis from our previous work,[5] which has a collision diameter of 0.5349 nm,[36] the immiscibility gap no longer decreases but actually increases (23 mol percent). As discussed in our previous work,[5] benzene does not have a dipole moment (0 D), and the polarity does play a role in controlling the miscibility. However, in the present case where the solutes (monohalogenated benzenes) have similar polarities, other factors such as molecular size become important.

We must also consider additional intermolecular interactions that may be playing a role. For example, we have discussed in our previous work[8,16] the unique hydrogen-bonding capability (H−F−H) between fluorinated compounds and ionic liquids. Previous attempts to model the immiscibility gaps for fluorinated benzene isomers and [emim][Tf_2N] using COSMOtherm[38] were not successful and suggest that the hydrogen-bonding force, which is a directional force, is important to consider.[39] Additional interactions such as higher-order moments (quadrupole, octupole)[40−42] and π-electron (π-cation and π-anion) effects[40,43−45] may also be important. However, in this case, the size effect may be the most dominant effect. The unique interactions of halogenated molecules in ionic liquids continue to pose a unique

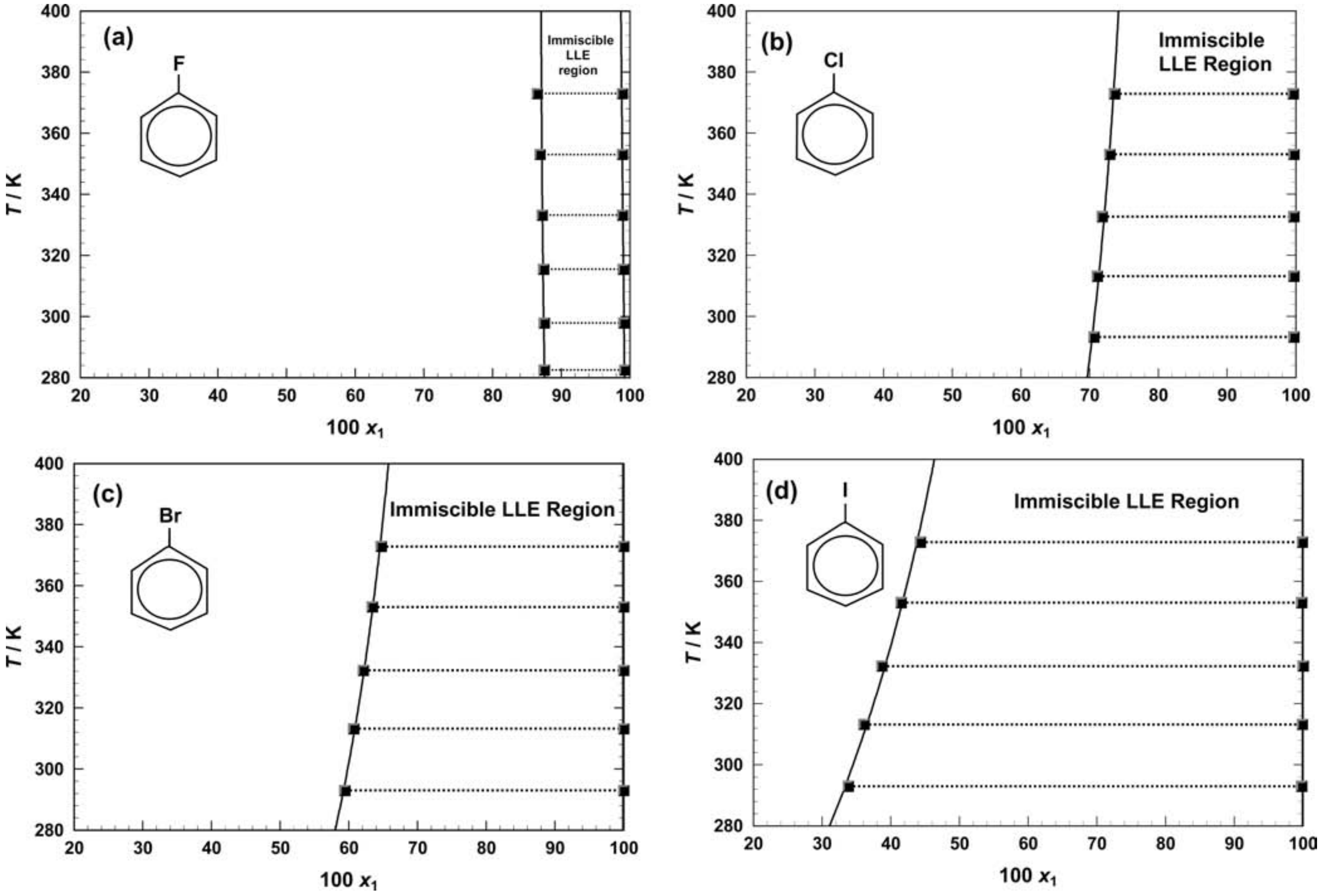


Figure 2. *Tx* phase diagrams for LLE of (a) fluorobenzene (1) + [emim][Tf$_2$N] (2), taken from ref 6; (b) chlorobenzene (1) + [emim][Tf$_2$N] (2); (c) bromobenzene (1) + [emim][Tf$_2$N] (2); (d) iodobenzene (1) + [emim][Tf$_2$N] (2). Solid line: the NRTL model calculation. Broken lines: experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method.

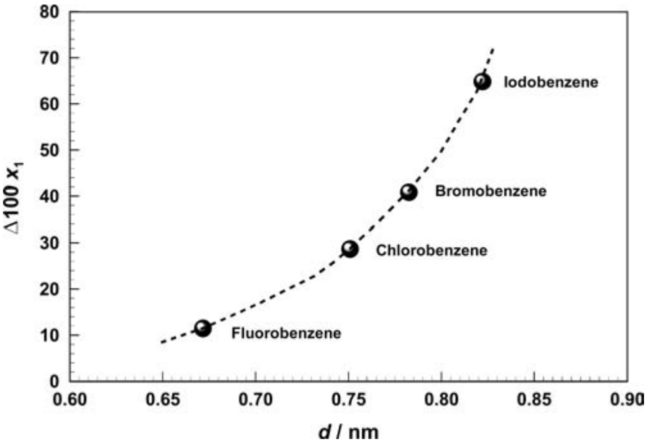


Figure 3. Correlation of immiscibility gap ($\Delta 100 x_1$) in [emim][Tf$_2$N] with molecular diameter (d) of solute at 293 K.

and interesting challenge for theoretical modelers to explain these measurements.

The present LLE data have been well correlated with the nonelectrolyte NRTL solution model; however, the LLE behavior is slightly different than fluorinated benzenes (including fluorobenzene)[6] in [emim][Tf$_2$N]. In the present case, as the temperature increases, the immiscibility gap decreases, as shown in Figure 2; however, for the fluorinated benzene isomers, the immiscibility gap increases with increasing temperature.[6] This is also apparent if one compares the temperature-dependent constants of eq 7 ($\tau_{12}^{(1)}$ $\tau_{21}^{(1)}$) in Table 2 with those from ref 6, which have opposite signs. Another interesting observation is that the monohalogenated benzene-rich phase contains a small amount of [emim][Tf$_2$N] (e.g., about 1 mol percent in fluorobenzene), which decreases as the molecular size of the solute increases, as shown in Figure 2. In most cases, the monohalogenated benzene-rich liquid (fluorobenzene, chlorobenzene, bromobenzene) is the upper phase (L); however, iodobenzene has a larger density (1.823 $\text{g}\cdot\text{cm}^{-3}$ at 293 K) than [emim][Tf$_2$N] (1.524 $\text{g}\cdot\text{cm}^{-3}$ at 293 K); therefore, the iodobenzene-rich liquid is the lower phase (L′).

The present volumetric method for LLE also provides information for the excess molar volume for each separated liquid. In this case, the halogenated benzene-rich phase (chlorobenzene, bromobenzene, iodobenzene) contains a mole fraction of (99.6 to 100) % monohalogenated benzene with an excess molar volume from (−0.1 to −0.9) $\text{cm}^3\cdot\text{mol}^{-1}$, which is within the uncertainty of the volumetric method. The [emim][Tf$_2$N]-rich phase for all three halogenated benzenes has an excess molar volume from (−1 to −5) $\text{cm}^3\cdot\text{mol}^{-1}$. In ordinary binary mixtures,[46] the excess molar volume is at most ± (1 to 2) $\text{cm}^3\cdot\text{mol}^{-1}$; therefore, like various HFC mixtures with RTILs,[12−14] these mixtures do not behave ideally. Such information provides new insight into the physical structures in the liquid solutions containing RTILs.

Conclusions

Liquid−liquid equilibria in binary mixtures of chlorobenzene, bromobenzene, and iodobenzene with RTIL [emim][Tf$_2$N] have been measured with the volumetric method. A general trend between the immiscibility gap and the molecular size of the solute was found. The smallest solute, fluorobenzene, has the smallest immiscibility gap in [emim][Tf_2N]. The smaller size allows more of the solute to exist in localized cavities above and below the imidazolium ring. As the solute molecular size increases (fluorobenzene < chlorobenzene < bromobenzene < iodobenzene), less of the solute can exist in these cavities, resulting in a larger immiscibility region. Although no trend between the dipole moment and the miscibility was discovered, other intermolecular interactions (higher-order moments, in particular, 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 negative excess molar volumes range from about (−1 to −5) $cm^3 \cdot mol^{-1}$.

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