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Binary Vapor–Liquid and Vapor–Liquid–Liquid Equilibria of Hydrofluorocarbons (HFC-125 and HFC-143a) and Hydrofluoroethers (HFE-125 and HFE-143a) with Ionic Liquid [emim][Tf_2N]

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Solubility behaviors of binary HFC-125 (CF_3-CF_2H), HFE-125 (CF_3-O-CF_2H), HFC-143a (CF_3-CH_3), and HFE-143a (CF_3-O-CH_3) systems with room-temperature ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]) have been studied using a gravimetric microbalance method from (283 to 348) K and/or volumetric and cloud-point methods. Vapor–liquid equilibrium (VLE) data for HFC-125 + [emim][Tf_2N] and HFE-125 + [emim][Tf_2N] systems have been well correlated with our equation-of-state (EOS) model, which predicted vapor–liquid–liquid equilibria (VLLE) for both of these binary systems, and the VLLE have been experimentally proved. As for the binary systems of HFC-143a + [emim][Tf_2N] and HFE-143a + [emim][Tf_2N], only VLLE experiments have been made, and partial miscibility (temperature and composition: VLLE−*Tx*) data are well correlated with the NRTL (nonrandom two-liquids) activity model. While the immiscibility gap of the HFC-125 binary system is smaller than that of the HFE-125 system, the immiscibility behaviors for the HFC-143a and HFE-143a systems are opposite; the HFE-143a system is more soluble.

Introduction

This year is the 20th anniversary of the Montreal Protocol signed in 1987 on "Substances That Deplete the Ozone Layer".[1] Chlorofluorocarbons (CFCs) are some of the most useful compounds ever synthesized by human beings which have been used as refrigerants (air conditioning, heat pump, and refrigeration applications), solvents, cleaning agents, blowing agents, etc. However, it has been found that they were linked to the destruction of the important stratospheric ozone layer, which protects life on Earth from harmful UV light. Thus, the phase out schedule of the CFCs was set. Hydrochlorofluorocarbons (HCFCs) have been used as interim replacements of CFCs, but soon these compounds were also listed to be phased out due to small but nonzero ozone depletion potentials (ODP). Therefore, hydrofluorocarbons (HFCs) have been used as acceptable alternatives to HCFCs, because of their zero ODP.

However, at the United Nations Framework Convention on Climate Change in Kyoto in December 1997, HFCs were considered as greenhouse gases since some HFCs have relatively large GWPs (global warming potentials).[2] So, third-generation CFC alternatives are being considered such as the fluorinated ether series.[3–12] These species (hydrofluoroethers, HFEs) are analogous to HFCs with the addition of the ether linkage which reduces the atmospheric lifetimes and leads to lower GWP for these compounds compared to those of the HFCs, although there are some exceptions as mentioned below.

Therefore, HFEs are important compounds to be studied. Chemical and thermophysical properties of various HFEs have been widely investigated.[3–12] Recently, we have reported the solubility study of five HFEs in room-temperature ionic liquid (RTIL) for the first time.[13] This is part of our continuing work on the phase behavior of RTIL with fluorinated compounds.[14–20] In the present paper, we report on phase behaviors (VLE and VLLE) of binary HFC-125 (CF_3-CF_2H), HFE-125 (CF_3-O-CF_2H), HFC-143a (CF_3-CH_3), and HFE-143a (CF_3-O-CH_3) systems with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]). The schematic chemical structure of [emim][Tf_2N] is shown in Figure 1.

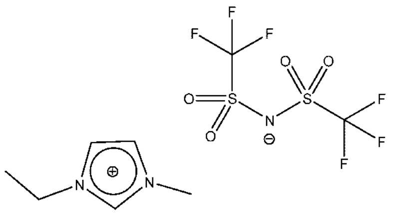
Chemical Name	Abbreviation	Structure	T_m	T_g
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[emim][Tf_2N]		(257-259) K	(178–186) K

Figure 1. Chemical structure of ionic liquid [emim][Tf_2N]. Molar mass (Mw) = 391.31. A melting point (T_m) is in the range of (257 to 259) K, and a glass transition temperature (T_g) is in the range of (178 to 186) K.[33,34]

It may be worth mentioning the GWPs of these HFCs and HFEs. As stated above (i.e., lower GWP for HFEs), the GWP of HFE-143a is indeed significantly lower than that of HFC-143a: 750 vs. 4300.[2] However, on the contrary, the GWP of HFE-125 is very large (14900), compared with that of HFC-125 (3400).[2] The GWP is nearly proportional to the atmospheric lifetime of a compound, and the atmospheric OH radical reaction is responsible for the lifetime (the compound destruction). Although the reaction kinetics are not directly related to the

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thermodynamic phase behavior (e.g., mixture solubility), it is interesting to see if such differences as observed in GWPs for the above HFCs and HFEs exist also in the solubility differences of these chemicals in RTIL.

Experimental

Materials. The hydrofluorocarbons (pentafluoroethane, HFC-125, CAS registry no. 354-33-6, and 1,1,1-trifluoroethane, HFC-143a, CAS registry no. 420-46-2) and hydrofluoroethers (difluoromethoxy trifluoromethane, HFE-125 or E125, CAS registry no. 3822-68-2, and trifluoromethoxy methane, HFE-143a or E143a, CAS registry no. 421-14-7) were obtained from DuPont Fluoroproducts (Wilmington, DE). The purity of the hydrofluorocarbons and hydrofluoroethers was measured using a gas chromatography–mass spectrometry (GCMS) method (Agilent 6890N, Restek Rtx-200 column, 105 m × 0.25 mm). The purities of the HFC-125, HFC-143a, and HFE-125 were each ≥ 99 %. The purity of the HFE-143a was ≥ 98 % (major impurity $C_2F_6S_2$). A limited amount of HFE-143a was available; therefore, only VLLE experiments were made. The ionic liquid [emim][Tf_2N] (EMIIm, 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 Inc. (Woburn, MA).[21] Methyl alcohol (assay ≥ 99.9 %, Product and Batch no. 646377-1L 05441CE, CAS registry no. 67-56-1) was obtained from Sigma-Aldrich, Inc. (St. Louis, MO), and was used as a reference fluid for volumetric calibration of the experimental LLE apparatus.

The [emim][Tf_2N] sample was analyzed to verify the stated purity. The initial as-received mass fraction of water was measured by Karl Fischer titration (Aqua-Star C3000, solutions AquaStar Coulomat C and A). The sample contained a water mass fraction of about $413 \cdot 10^{-6}$. A 20 mL sample of water was used to extract fluorine, chlorine, and bromine from 0.2 g of [emim][Tf_2N] at ambient temperature for 24 h. The extractable ions were measured by ion chromatography (column: DIONEX AS17; eluent: (0.4 to 50) mM NaOH; flow: 1.0 $mL \cdot min^{-1}$; sample loop: 100 μL). The fluorine, chlorine, and bromine ions were found to be below the detection limit (< 5 $\mu g \cdot mL^{-1}$). A 0.1886 g sample of [emim][Tf_2N] was combusted in a Wickbold torch, and the combustion gases were collected in water (99.86 mL) and analyzed by ion chromatography for total chlorine content. Two separate samples were analyzed and found to contain a chlorine mass fraction of $(440 \text{ and } 480) \cdot 10^{-6}$, average of $(460 \pm 20) \cdot 10^{-6}$.

Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Inc. (Woodside, NY),[22] for carbon (24.60 %), hydrogen (3.02 %), fluorine (29.70 %), nitrogen (10.75 %), and sulfur (17.05 %) content. Combining the results from each of the techniques described, we conclude that the [emim][Tf_2N] sample purity was ≥ 99.4 % which compares closely with the stated purity (≥ 99.5 %) by the manufacturer.[21]

The [emim][Tf_2N] was dried and degassed by first 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) for about 3 h. Next, the [emim][Tf_2N] was completely evacuated using a turbopump (Pfeiffer, model TSH-071) to a pressure of about $4 \cdot 10^{-4}$ Pa 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 again measured by Karl Fischer titration, and the dried sample contained $188 \cdot 10^{-6}$.

Experimental Method: VLE Experiments. A detailed description of the vapor–liquid equilibria (VLE) equipment and procedures is available in our previous report.[23] Therefore, only the basic experimental techniques and measurement uncertainties are given here. The gas solubility (VLE) measurements were made using a gravimetric microbalance (Hiden Isochema Ltd., IGA 003, Warrington, United Kingdom).[24] A molecular sieve trap was installed to remove trace amounts of water from HFC-125 and HFE-125. Initially, about (60 to 70) mg of [emim][Tf_2N] was loaded into the sample container and heated to 348.15 K under a vacuum of about 10^{-3} Pa for 10 h to remove any trace amounts of water or other volatile impurities. No measurable mass loss was detected during drying which is consistent with the initial low water mass fraction ($188 \cdot 10^{-6}$).

The IGA003 apparatus can operate in both dynamic (continuous gas flow) and static (intermittent gas flow) modes. In this study, absorption measurements were performed in static mode. The sample temperature was measured with a platinum resistance thermometer (PRT) within an uncertainty of ± 0.1 K. The PRT was calibrated 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). The Blackstack instrument and SPRT are a certified secondary temperature standard with a NIST traceable uncertainty of ± 0.005 K. Pressures from (10^{-2} to 1.0) MPa were measured using a piezo-resistive strain gauge (Druck, model PDCR4010) with an uncertainty of ± 0.8 kPa. The Druck pressure transducer was calibrated against a Paroscientific model 760-6K (Redmond, WA) pressure transducer (range (0 to 41.5) MPa, serial no. 62724). This instrument is a certified secondary pressure standard with a NIST traceable uncertainty of 0.008 % of full scale.

Four isotherms were measured at about (283, 298, 323, and 348) K over a pressure range from about (0.01 to 1.0) MPa for HFC-125 and from about (0.01 to 0.6) MPa for HFE-125. The upper pressure limit of the microbalance reactor was 2.0 MPa; however, the upper pressure limit for HFC-125 and HFE-125 was dependent on the saturation pressure (1.24 MPa, HFC-125, and 0.79 MPa, HFE-125) in the sample container at ambient temperature (294.15 K). To ensure sufficient time for gas–liquid equilibrium, the ionic liquid samples were maintained at each pressure set point for a minimum of 3 h and a maximum of 10 h.

The instrumental uncertainties in T and P are within ± 0.1 K and ± 0.8 kPa, respectively. These uncertainties do not cause any significant effects in the gas solubility measurement. The total uncertainties in the mole fraction solubility due to both random and systematic errors have been estimated to be less than 0.006 at given T and P. Another large source of uncertainty in the present solubility experiments is due to the buoyancy correction in the data analysis. Analysis of the buoyancy effects requires an accurate measurement of the [emim][Tf_2N] liquid density and the gas density for HFC-125 and HFE-125. Liquid density data for [emim][Tf_2N] were measured by Krummen et al.[25] We checked their density data at 298 K and found it to be in close agreement (less than 0.1 %) with our own measurement, so we used their data in our analysis. The liquid density data were correlated as $d/g \cdot cm^{-3} = 1.81638 – 9.97143 \cdot 10^{-4}\ T/K$ from (293 to 353) K. The NIST REFPROP[26] EOS computer program was used to calculate the gas density for HFC-125 and HFE-125. A detailed description of the buoyancy correction is provided in our previous report.[23] The corrected solubility (PTx) data are shown in Table 1 and Figures 2 and 3.

Experimental Method: VLLE Experiments. A detailed description of the vapor–liquid–liquid equilibria (VLLE) equipment and procedures is also available in our previous reports.[17,18]

Table 1. Experimental Solubility (*PTx*) Data for HFC-125 and HFE-125 + [emim][Tf_2N]

HFC-125 (1)/[emim][Tf_2N] (2)			HFE-125 (1)/[emim][Tf_2N] (2)		
T/K	P/MPa	$100x_1$	T/K	P/MPa	$100x_1$
283.1	0.0100	0.8	283.1	0.0101	1.0
283.1	0.1000	8.5	283.1	0.0498	4.7
283.1	0.1997	16.8	283.1	0.1001	9.5
283.1	0.2977	25.0	283.1	0.1997	19.4
283.1	0.3997	33.1	283.1	0.2997	30.1
283.1	0.4999	41.3	283.1	0.4002	42.3
283.1	0.5997	49.6	283.1	0.4997	56.5
283.1	0.6999	58.3			
283.1	0.7996	68.1			
298.1	0.0102	0.6	298.1	0.0103	0.6
298.1	0.0998	5.5	298.1	0.0500	3.0
298.1	0.1997	10.9	298.1	0.0998	6.0
298.1	0.2997	16.1	298.1	0.1997	12.1
298.2	0.3996	21.3	298.1	0.3000	18.5
298.2	0.4999	26.7	298.1	0.3997	24.7
298.2	0.5997	31.7	298.1	0.4999	31.4
298.1	0.8001	42.2	298.1	0.6000	38.3
298.1	0.9998	52.1			
323.1	0.0102	0.4	323.1	0.0102	0.4
323.1	0.0998	3.0	323.1	0.0497	1.6
323.1	0.2000	5.9	323.1	0.0999	3.1
323.1	0.2998	8.8	323.1	0.2000	6.5
323.1	0.3996	11.7	323.1	0.2999	9.1
323.1	0.5002	15.2	323.1	0.3997	12.5
323.1	0.5997	17.6	323.1	0.4999	15.7
323.1	0.7999	22.8	323.1	0.5998	18.7
323.1	1.0001	28.5			
348.1	0.0102	0.4	348.1	0.0102	0.2
348.1	0.1000	1.8	348.1	0.0500	0.9
348.1	0.1997	3.4	348.2	0.1002	1.7
348.1	0.2998	5.0	348.1	0.2001	4.0
348.1	0.3998	7.4	348.2	0.3001	6.0
348.1	0.5001	9.7	348.1	0.4000	7.4
348.1	0.5996	10.5			
348.2	0.7998	14.0			
348.1	0.9997	17.1			

Therefore, only the basic experimental techniques and measurement uncertainties are given here. High-pressure sample containers[17] were filled with dried [emim][Tf_2N] and hydrofluorocarbons (HFC-125 and HFC-143a) and hydrofluroethers (HFE-125 and HFE-143a) following the procedures outlined in our previous publications.[17,18] VLLE experiments have been made with these samples at constant temperatures from about (283 to 313) K with a corresponding pressure of about (0.4 to 2.0) MPa using the volumetric method. Detailed error analyses are also given in refs 17 and 18. The bath temperature was calibrated with the NIST traceable SPRT mentioned previously, and the uncertainty in temperature was ± 0.2 K. Special attention must be given to ensure that no leaks occur from the sample containers after being filled with the high-pressure HFC and HFE. The mass of the sample containers was checked several times before starting and after completing the VLLE experiments to ensure that no HFC or HFE had escaped from the sample container. To establish thermodynamic equilibrium, sufficient time and mixing were required and can take as long as (3 to 5) days. It is also important to mention that the vapor phase density which contains HFC or HFE with a negligible contribution of [emim][Tf_2N] must be calculated using the REFPROP EOS computer program[26] and properly accounted for in the mass balance equations described in refs 17 and 18. Observed liquid phase compositions and molar volumes are shown in Table 2 and Figures 2 to 4.

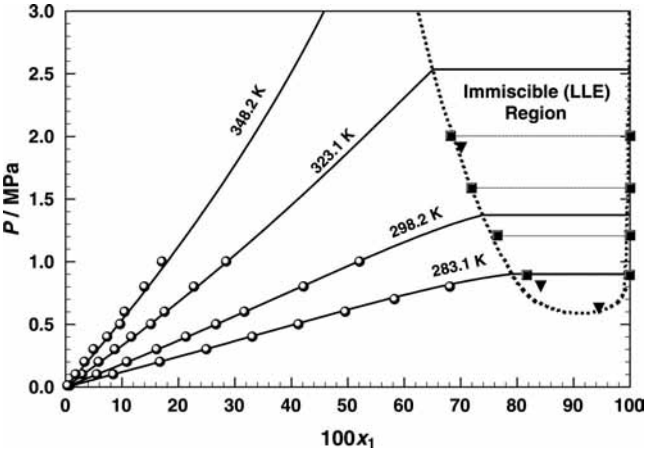

Figure 2. *PTx* (pressure−temperature−composition) phase diagram for HFC-125 (1) + [emim][Tf_2N] (2). x_1 = a mole fraction of HFC-125. Solid and broken lines, present EOS calculations. Symbols, experimental data; circles, VLE data; squares, VLLE data; triangles, cloud-point data. Dotted horizontal lines, experimental LLE tie lines.

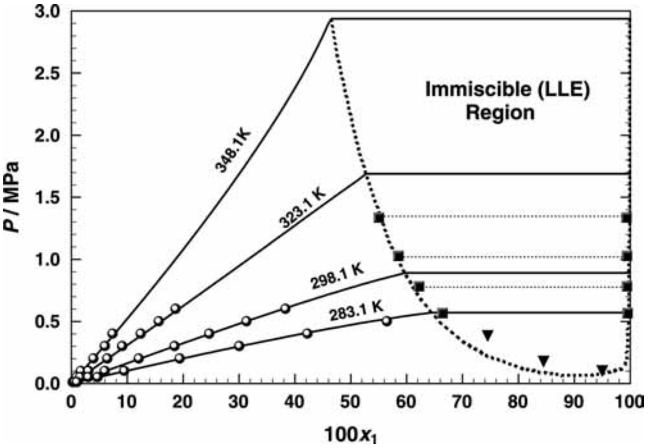

Figure 3. *PTx* (pressure−temperature−composition) phase diagram for HFE-125 (1) + [emim][Tf_2N] (2). x_1 = a mole fraction of HFE-125. Solid and broken lines, present EOS calculations. Symbols, experimental data; circles, VLE data; squares, VLLE data; triangles, cloud-point data. Dotted horizontal lines, experimental LLE tie lines.

To prove the existence of a lower critical solution temperature (LCST) of the LLE curve, cloud-point measurements were made with binary mixtures prepared using HFC-125 + [emim][Tf_2N] and HFE-125 + [emim][Tf_2N]. Three samples of HFC-125 + [emim][Tf_2N] and three samples of HFE-125 + [emim][Tf_2N] were prepared in high-pressure sample containers[17] containing mole fractions from (70 to 95) % HFC-125 and (75 to 95) % HFE-125, respectively. Starting at ambient temperature of about 293 K, where two liquid phases existed, the temperature was lowered (20 K·h^{-1}) with manual mixing in a constant temperature bath (Tamson Instruments, TV4000LT, Zoetermeer, Netherlands) until only a single phase existed for all the prepared mixtures. The bath temperature was calibrated with the NIST traceable SPRT mentioned previously, and the uncertainty in the bath temperature was ± 0.2 K. Once all the prepared samples were single phase, the temperature was slowly raised (5 K·h^{-1}) until a cloud layer became visible inside the glass sample tube. The temperature was recorded for each sample when the cloud layer formed. The liquid level in each tube at the cloud-point temperature must also be measured to calculate the vapor phase volume. The vapor is assumed to contain only HFC-125 or HFE-125, and using the EOS program,[26] the saturated vapor density was calculated at the cloud-point temperature to correct the amount of HFC-125 or HFE-125 in the liquid phase (reported cloud-point composition). Cloud points were measured for HFC-

Table 2. VLLE Data for the Binary HFC-125, HFE-125, HFC-143a, and HFE-143a Systems with Ionic Liquid [emim][Tf$_2$N][a]

T			V'	V	$V^{E\prime}$	V^E
K	$100x_1'$	$100x_1$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$
HFC-125 (1) + [emim][Tf$_2$N] (2) System						
282.7 ± 0.2	81.7 ± 1.0	99.9 ± 0.1	118.2 ± 1.6	94.2 ± 1.6	−5.4 ± 1.6	−0.1 ± 1.6
293.4 ± 0.2	76.5 ± 0.8	100.0 − 0.2	128.9 ± 1.4	98.6 ± 1.5	−7.0 ± 1.4	0.1 ± 1.5
303.7 ± 0.2	71.9 ± 0.6	100.0 − 0.2	139.5 ± 1.4	103.9 ± 1.5	−7.9 ± 1.4	0.0 ± 1.5
313.1 ± 0.2	68.2 ± 0.7	100.0 − 0.2	147.5 ± 1.3	110.3 ± 1.4	−10.6 ± 1.3	0.1 ± 1.4
HFE-125 (1) + [emim][Tf$_2$N] (2) System						
282.9 ± 0.2	66.4 ± 1.5	99.5 ± 0.5	150.9 ± 5.6	101.6 ± 1.5	−2.0 ± 5.6	−0.3 ± 1.5
293.6 ± 0.2	62.2 ± 1.6	99.4 ± 0.5	159.8 ± 5.7	105.3 ± 1.8	−2.7 ± 5.7	−0.6 ± 1.8
303.4 ± 0.2	58.5 ± 1.7	99.4 ± 0.5	168.8 ± 6.0	109.4 ± 1.8	−2.4 ± 6.0	−0.6 ± 1.8
313.5 ± 0.2	55.0 ± 1.8	99.3 ± 0.5	176.5 ± 6.3	114.4 ± 1.9	−3.5 ± 6.3	−0.8 ± 1.9
HFC-143a (1) + [emim][Tf$_2$N] (2) System						
293.0 ± 0.2	51.9 ± 2.4	100 − 0.4	164.5 ± 7.0	88.0 ± 3.0	−4.9 ± 7.0	−0.5 ± 3.0
303.3 ± 0.2	50.9 ± 2.1	100 − 0.4	167.8 ± 6.0	92.5 ± 2.6	−6.2 ± 6.0	−0.1 ± 2.6
313.2 ± 0.2	50.2 ± 2.0	99.7 ± 0.3	171.1 ± 5.5	97.9 ± 2.5	−7.7 ± 5.5	−0.3 ± 2.5
HFE-143a (1) + [emim][Tf$_2$N] (2) System						
283.2 ± 0.2	59.2 ± 1.5	99.9 ± 0.1	147.8 ± 7.0	87.6 ± 5.0	−8.4 ± 7.0	−0.4 ± 5.0
293.4 ± 0.2	57.6 ± 1.1	99.9 ± 0.1	152.5 ± 6.0	90.3 ± 4.5	−7.0 ± 6.0	−0.5 ± 4.5
303.6 ± 0.2	56.7 ± 1.0	99.9 ± 0.1	158.8 ± 5.0	92.9 ± 4.0	−6.1 ± 5.0	−0.3 ± 4.0
313.7 ± 0.2	56.1 ± 1.0	99.9 ± 0.1	162.5 ± 5.0	96.1 ± 3.0	−6.0 ± 5.0	−0.3 ± 3.0

[a] V', observed molar volume lower phase; V, observed molar volume upper phase; $V^{E\prime}$, excess molar volume lower phase; V^E, excess molar volume upper phase.

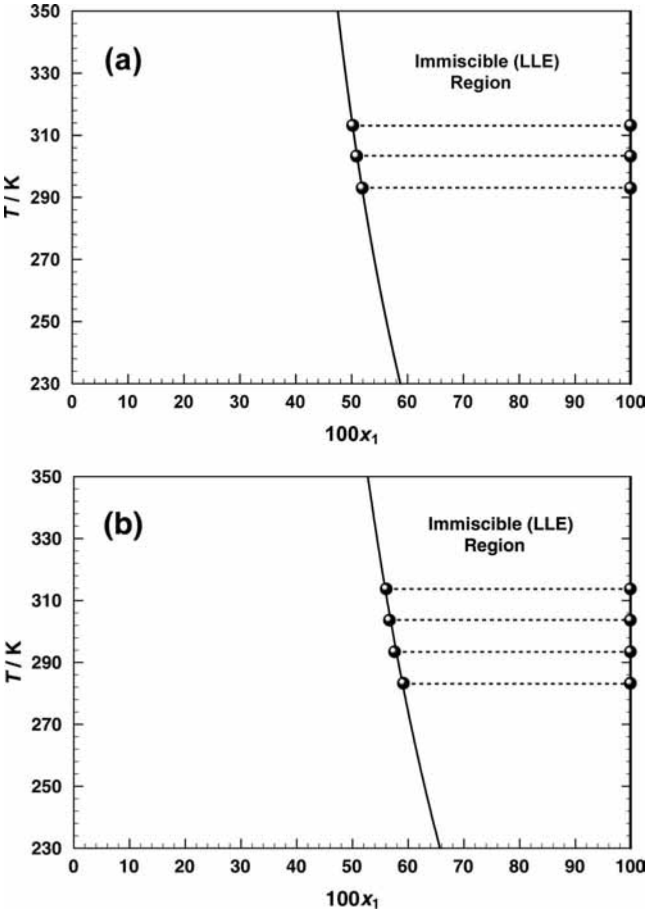

Figure 4. *Tx* (temperature−composition) phase diagrams for LLE (liquid–liquid demixing). x_1 = a mole fraction of HFC-143a or HFE-143a. Solid lines, NRTL model calculations; circles, experimental data; broken horizontal lines, experimental LLE tie lines. (a) HFC-143a (1) + [emim][Tf$_2$N] (2) system. (b) HFE-143a (1) + [emim][Tf$_2$N] (2) system.

125 + [emim][Tf$_2$N] containing mole fractions of (70.1, 84.2, and 94.5) % HFC-125 at (311 ± 2) K, (279 ± 2) K, and (271 ± 2) K, respectively. Cloud points were measured for mixtures of HFE-125 + [emim][Tf$_2$N] containing mole fractions of (74.5, 84.5, and 95.0) % HFE-125 at (271 ± 2) K, (251 ± 2) K, and (239 ± 2) K, respectively.

To determine if a LCST existed for HFC-143a + [emim][Tf$_2$N] and HFE-143a + [emim][Tf$_2$N], a second temperature bath was constructed, which could achieve even lower temperatures, using a 5 L glass tank filled with methanol and dry ice. Two samples of HFC-143a + [emim][Tf$_2$N] and two samples of HFE-143a + [emim][Tf$_2$N] were prepared in high-pressure sample containers containing mole fractions of (64 and 95) % HFC-143a and (65 and 95) % HFE-143a, respectively. The samples were manually mixed in the bath as dry ice was slowly added to lower the temperature. The temperature of the methanol−dry ice bath was measured using the SPRT/Blackstack instrument. All four samples remained two phases until a temperature of about (231 ± 5) K, when the lower liquid phase solidified. The samples were allowed to slowly warm until the lower phase melted. The cooling process was repeated again, and the same observation was recorded, which verified that the solid–liquid boundary for both HFC-143a + [emim][Tf$_2$N] and HFE-143a + [emim][Tf$_2$N] had been reached and no LCST existed.

Results

Data Correlation and Prediction. To analyze the present VLE and VLLE data, we have employed a generic RK (Redlich−Kwong) type of cubic equation of state (EOS), which has been used in our previous studies[17–19,27,28]

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \qquad (1)$$

Besides the above references, a detailed model description is also provided in the Supporting Information (SI) of this article. EOS parameters of pure compounds are given in Table S1 (SI). The empirical binary interaction parameters for the mixture EOS have been determined using only VLE data and are shown in Table S2 (SI). Average absolute (relative) deviations (AAD) in the pressure fit are 2.2 % and 3.2 % for HFC-125 and HFE-125 binary systems, respectively.

Using the present EOS parameters determined from the VLE data alone, we have predicted VLLE phase behaviors for the

HFC-125 and HFE-125 binary systems with [emim][Tf_2N]. The present EOS (VLE) correlation and (VLLE) prediction are shown in Figures 2 and 3 for these binary systems, compared with the present experimental VLE and VLLE data. Lower critical solution temperatures (LCSTs) in the VLLE are about (270 and 238) K for the HFC-125 (at $x_1 \approx 93$ %) and HFE-125 (at $x_1 \approx 93$ %) systems, respectively.

As mentioned earlier, due to the limited amount of HFE-143a available, we have only made VLLE experiments for HFE-143a (and HFC-143a) binary systems with [emim][Tf_2N], for the purpose of comparison. The vapor phase consists practically of pure HFE-143a or HFC-143a, and since the pressure effect on the solubility at the present temperature condition is negligible, the experimental VLLE data for these binary systems have been analyzed using the NRTL (nonrandom two-liquids) activity solution model,[29] which is shown in the SI as the thermodynamic model 2. The determined binary interaction parameters for the NRTL model are given in Table S3 (SI). The present NRTL model correlations are compared with the experimental data in Figure 4a and b.

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 ($V^{E\prime}$ and V^E) can be obtained, by use of the pure component molar volumes V_1^0 (HFC or HFE) and V_2^0 ([emim][Tf_2N]) using

$$V^{E'} = V'_m - x'_1 V_1^0 - x'_2 V_2^0 \qquad (2)$$

or

$$V^E = V_m - x_1 V_1^0 - x_2 V_2^0$$

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 HFC or HFE (1) and [emim][Tf_2N] (2) in phase L′ and L, respectively. Saturated liquid molar volumes for HFC-125, HFC-143a, and HFE-125[30] were calculated using the REFPROP computer program.[26] The molar volume for HFE-143a was calculated using the liquid density provided in ref 12. The liquid density correlation provided in ref 12 (eq 11 and/or Table 5) was incorrect since it cannot reproduce the experimental data. So, we have developed our own correlation, which is given in the SI. We have checked the accuracy of our correlation with the experimental data provided in ref 12, and the error in the fit is less than 0.02 %. Total uncertainties in the final composition and molar volume determination are provided in Table 2. Total uncertainties were estimated by calculating both the overall random and systematic uncertainties, and details are provided in refs 17 and 18.

Discussion

VLE (*PTx*) data for both binary systems of HFC-125 + [emim][Tf_2N] and HFE-125 + [emim][Tf_2N] have been well correlated using our simple EOS model.[17–19,27,28] VLLE phase behaviors for both binary systems predicted by the present EOS model have been experimentally validated by the volumetric and cloud-point methods. The liquid–liquid equilibria (LLE) in VLLE show LCSTs, and the EOS model predicts the phase behavior of the type V mixture for these binary systems.[31,32] The immiscibility gap of the HFC-125 system is much smaller than that of the HFE-125 system, as can be seen in Figures 2 and 3.

Liquid–liquid demixing (VLLE) experimental data for the binary systems of HFC-143a + [emim][Tf_2N] and HFE-143a + [emim][Tf_2N] have been well correlated using the NRTL activity model,[29] as shown in Figures 4a and b. The immiscibility gap of the HFC-143a system is larger than that of the HFE-143a system. This solubility behavior is opposite to the case of the HFC-125 and HFE-125 systems. It is interesting to observe such an opposite effect in these HFC vs HFE systems, in connection with the GWP (or atmospheric lifetime: OH radical reaction rates) differences as mentioned in the Introduction. However, needless to say, the thermodynamic phase behavior has no direct correlation with the gas phase reaction kinetics. To see whether LCSTs exist for both the 143a systems, the cloud-point experiments were conducted down to about 230 K; however, the systems were still two phases, and ionic liquid-rich side solutions became solid phases. Thus, the phase behavior of these systems will likely belong to the type III mixture,[32] which is similar to the case of the HFC-143a + ionic liquid [bmim][PF_6] (1-butyl-3-methylimidazolium hexafluorophosphate) system.[18]

Our previous solubility studies for HFC-125 + [bmim][PF_6] and HFC-143a + [bmim][PF_6] systems[17,18] can be compared with those of the present [emim][Tf_2N] binary systems. The present ionic liquid [emim][Tf_2N] is more soluble in these HFCs than [bmim][PF_6].

Finally, brief comments should be made on the excess molar volumes obtained from the present volumetric method. Ionic liquid-rich side solutions of all the present systems show rather large negative values, compared with those of ordinary organic solvents (typically within ± (1 to 2) $cm^3 \cdot mol^{-1}$).[32] Although some of the present experimental uncertainties are large, large negative excess molar volumes have been observed similarly for many HFC + ionic liquid systems.[16–19]

Conclusions

The present VLE and VLLE experiments show that the binary systems of HFC-125, HFE-125, HFC-143a, and HFE-143a with ionic liquid [emim][Tf_2N] exhibit partial miscibility (liquid–liquid demixing) behaviors. The immiscibility gap of the HFC-125 binary system is smaller than that of HFE-125 system, while that of the HFC-143a binary system is larger than that of the HFE-143a system.

Both HFC-125 and HFE-125 binary systems possess LCSTs (lower critical solution temperatures) in the liquid–liquid demixing, and the phase behaviors have been successfully modeled with our EOS.[17–19,27,28] These systems belong to the type V mixture. This behavior is similar to the case of the HFC-125 + ionic liquid [bmim][PF_6] system in our earlier work,[17] although the present ionic liquid [emim][Tf_2N] is more soluble in HFC-125 than in the case of [bmim][PF_6].

LCSTs of both HFC-143a and HFE-143a binary systems could not be detected even at about 230 K, where one of the two liquid phases became solid. The phase behavior of the present HFC-143a + [emim][Tf_2N] system is similar to the case of the HFC-143a + ionic liquid [bmim][PF_6] system in our earlier work,[18] although the present ionic liquid [emim][Tf_2N] is more soluble in HFC-143a than [bmim][PF_6].

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Supporting Information Available:

Materials and Tables S1 to S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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