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Liquid−Liquid Equilibria of Hydrofluoroethers and Ionic Liquid 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide

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Binary liquid−liquid equilibria (LLE) in mixtures of five hydrofluoroethers and room-temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, have been measured for the first time using the volume−mass method. All five binary systems show large immiscibility gaps. The ionic liquid-rich side solutions become increasingly more soluble in HFE (hydrofluoroether) as the HFE normal boiling point decreases. Observed LLE are well correlated by use of the nonrandom two liquid (NRTL) solution model. The excess molar volumes of the HFE and ionic liquid rich side solutions are small and similar to ordinary binary mixtures which is opposite to what we have previously reported with hydrofluorocarbons (HFCs) in ionic liquids. Therefore, the insertion of an ether oxygen has changed the liquid structure of HFEs vs HFCs in ionic liquids.

Introduction

The present report is part of our continuing studies on the phase behavior of room-temperature ionic liquids (RTILs) with fluorinated compounds. Although we have conducted many solubility studies for various hydrofluorocarbons (HFCs) in RTILs,[1−11] this is the first study to report the solubility of hydrofluoroethers (HFEs) in RTILs. HFEs are an important new class of compounds that many researchers[12−16] and industrial companies such as 3M[17] are studying and producing as long-term alternatives to ozone-depleting compounds. The insertion of an ether oxygen atom into the HFC molecule was originally done to modify the thermophysical properties of the compounds for specific end uses such as solvents, cleaning, heat transfer, and other applications. However, one of the principal advantages of the HFE structure has been determined to be the significantly shorter atmospheric lifetimes when compared to many HFCs; thus HFEs reduce greatly the global warming impact due to the greenhouse effect. The wide range of structures and thermophysical properties makes this class of compounds interesting to study with mixtures of RTILs.

Therefore, to understand the solubility behavior of hydrofluoroethers in RTIL mixtures, we have studied liquid−liquid equilibria (LLE) of binary mixtures of five fluoroethers + RTIL (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide: [emim][Tf_2N]); see Figure 1 for the chemical structure. LLE experiments have been performed using the mass−volume method.[6,7,9−11] Solubility data and data correlation with the nonrandom two liquid (NRTL) solution model[18] are presented.

Experimental Procedures

Materials. HFE-7000 (Novec 7000 Engineered Fluid, I.D. No. 98-0212-2969-9, Lot No. 920013, 1-methoxyheptafluoropropane, $CF_3CF_2CF_2{-}O{-}CH_3$, HFOC-347sE$\gamma\delta$, CAS registry no. 375-03-1), HFE-7100 (Novec 7100 Engineered Fluid, I.D. No. 98-0211-8940-6, Lot No. 924322, consists of two inseparable isomers with essentially identical properties: 1-methoxynonafluoroisobutane $(CF_3)_2CFCF_2{-}O{-}CH_3$, HFOC-449mmzcE$\gamma\delta$, CAS registry no. 163702-08-7, and 1-methoxynonafluorobutane $CF_3CF_2CF_2CF_2{-}O{-}CH_3$, HFOC-449E$\delta\epsilon$, CAS registry no. 163702-07-6), HFE-7200 (Novec 7200 Engineered Fluid, I.D. No. 98-0211-9362-2, Lot No. 924175, consists of two inseparable isomers with essentially identical properties: 1-ethoxynonafluoroisobutane $(CF_3)_2CFCF_2{-}O{-}CH_2CH_3$, HFOC-569mmzcE$\gamma\delta$, CAS registry no. 163702-06-5, and 1-ethoxynonafluorobutane $CF_3CF_2CF_2CF_2{-}O{-}CH_2CH_3$, HFOC-569sfE$\delta\epsilon$, CAS registry no. 163702-05-4), HFE-7300 (Novec 7300 Engineered Fluid, 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)-pentane, $CF_3CF_2CF(OCH_3)CF(CF_3)_2$, HFOC-569sfE$\delta\epsilon$, CAS registry no. 132182-92-4), and HFE-7500 (Novec 7500 Engineered Fluid, I.D. No. 98-0212-2932-7, Lot No. 920038, 2-trifluoromethyl-3-ethoxydodecafluorohexane, $CF_3CF_2CF_2CF(OCH_2CH_3)CF(CF_3)_2$, HFOC-64-13mmzzsE$\delta\delta$’, CAS registry no. 297730-93-9) were obtained from 3M (St. Paul, MN).[17] The molecular weight, normal boiling points, global warming potential (GWP), and atmospheric lifetime (ALT) for the hydrofluoroethers are provided in Table 1. The purities of these five hydrofluoroethers were each $\geq$ 99.0 % and were determined using a gas chromatography mass spectrometry (GCMS) method (Agilent 6890N, Restek Rtx-200 column, 105 m × 0.25 mm). The ionic liquid [emim][Tf_2N] (EMIIm, electrochemical grade, assay $\geq$ 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).[19] Methyl alcohol (assay $\geq$ 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

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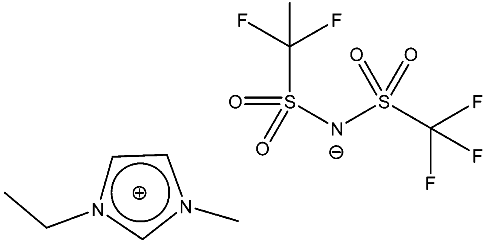
Chemical Name	Abbreviation	Structure	Molar Mass
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[emim][Tf_2N]		391.31

Figure 1. Chemical structure of ionic liquid [emim][Tf_2N].

Table 1. Hydrofluoroether Chemical Formula and Physical and Environmental Properties

HFE	chemical structure	MW g·mol^{-1}	NBP[c] K	GWP[d]	ALT[e] yrs
HFE-7000	$CF_3CF_2CF_2-O-CH_3$	200	307.2	370	4.9
HFE-7100	$CF_3CF_2CF_2CF_2-O-CH_3$[a]	250	334.2	320	4.1
HFE-7200	$CF_3CF_2CF_2CF_2-O-CH_2CH_3$[b]	264	349.2	55	0.77
HFE-7300	$CF_3CF_2CF(OCH_3)CF(CF_3)_2$	350	371.2	200	3.8
HFE-7500	$CF_3CF_2CF_2CF(OCH_2CH_3)CF(CF_3)_2$	414	401.2	210	2.5

[a] $(CF_3)_2CFCF_2-O-CH_3$ consists of two inseparable isomers with essentially identical properties. See text for details. [b] $(CF_3)_2CFCF_2-O-CH_2CH_3$ consists of two inseparable isomers with essentially identical properties. See text for details. [c] Normal boiling point ($P = 1$ atm) (ref 17). [d] Global warming potential (GWP), 100-year integrated time horizon (ITH); $CO_2 = 1$, ref 17, HFC-134a (CH_2FCF_3) GWP = 1600 provided for comparison, ref 21. [e] Atmospheric lifetime (ALT), ref 17, HFC-134a (CH_2FCF_3) ALT = 13.6 yrs provided for comparison, ref 21.

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·min^{-1}; sample loop, 100 μL). The fluorine, chlorine, and bromine ions were found to be below the detection limit (< 5 μg·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 and 480)·10^{-6}, with an average of (460 ± 20)·10^{-6}.

Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Inc. (Woodside, NY),[20] 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.[19]

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 4·10^{-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 again measured by Karl Fischer titration, and the dried sample contained 188·10^{-6}.

Experimental Method. A detailed description of the experimental equipment, procedure, and principle of the method is available in our previous reports.[6,7,9–11] Therefore, only the basic experimental technique and experimental uncertainties are given here.

Table 2. Hydrofluoroether Vapor Pressure and Liquid Density Correlations[a]

HFE	*A*	*B*	*C*	*D*
HFE-7000	22.978[b]	3548.6[b]	2.25930[b]	28.800[b]
HFE-7100	22.415[b]	3641.9[b]	2.29859[c]	26.410[c]
HFE-7200	22.289[b]	3752.1[b]	2.11006[b]	23.026[b]
HFE-7300	22.939[b]	4245.2[b]	2.37176[b]	24.000[b]
HFE-7500	22.517[b]	4409.2[b]	2.24048[c]	20.930[c]

[a] Vapor pressure: $\ln(P/\mathrm{Pa}) = A - B/(T/\mathrm{K})$. Liquid density: $\rho\ (\mathrm{g\cdot cm^{-3}}) = C - D\cdot 10^{-4}\ (T/\mathrm{K})$. [b] Ref 17. [c] This work.

Low-pressure sample containers were fabricated from borosilicate glass tubing with an outside diameter of 12.69 mm, an inside diameter of 7.94 mm, and an overall length of 15.5 cm. The glass tubing was sealed with a torch on one end and open on the other. The borosilicate glass tubes were cleaned in an ultrasonic bath filled with acetone for 2 h and dried overnight in a vacuum oven at 348.15 K. The volume of each liquid layer was obtained by measuring the liquid height from the bottom of the glass tubing, as described in our previous works[6,7,9–11] using an electronic caliper (Mitutoyo Corp., model no. CD-6” CS, code no. 500-196) with an accuracy of ± 0.01 mm. The volume, v, versus the height, h, was calibrated experimentally using methyl alcohol, and a linear relation was obtained. The uncertainty in the volume is estimated to be ± 0.25 %.

The sample containers were initially weighed to determine the tare mass. The samples were then prepared in a nitrogen purged drybox to minimize water contact with the hygroscopic [emim][Tf_2N] ionic liquid. A glass pipet was used to add the required amounts of [emim][Tf_2N] ionic liquid and hydrofluoroethers. Two samples containing mole fractions of about (30 and 90) % for each hydrofluoroether and [emim][Tf_2N] ionic liquid were prepared. The uncertainty in the mole fraction was estimated to be ± 0.01 % (i.e., 10^{-4}). A Swagelok stainless steel (SS316) cap and plug with Teflon ferrules was used to seal the open end of the glass tubing before removing from the drybox. Care is required when tightening the cap so that the ferrules seal against the glass tubing, but overtightening can crack the glass. The masses remained constant within the accuracy (± 0.0001 g) of the balance (Mettler Toledo, model AG204) even after several weeks.

Table 3. Hydrofluoroethers (1) + [emim][Tf_2N] (2) System[a]

T/K	$100x_1'$	$100x_1$	V'/$cm^3 \cdot mol^{-1}$	V/$cm^3 \cdot mol^{-1}$	$V^{E'}$/$cm^3 \cdot mol^{-1}$	V^E/$cm^3 \cdot mol^{-1}$
			HFE-7000 (1) + [emim][Tf_2N] (2)			
283.0 ± 0.2	17.3 ± 1.3	99.7 ± 0.3	233.7 ± 1.1	138.6 ± 0.6	−1.3 ± 1.1	−0.3 ± 0.6
294.9 ± 0.2	18.0 ± 0.9	99.9 ± 0.1	234.8 ± 1.1	141.5 ± 0.3	−1.8 ± 1.1	−0.4 ± 0.3
303.4 ± 0.2	18.3 ± 1.0	99.8 ± 0.2	236.2 ± 0.4	144.0 ± 0.6	−1.7 ± 0.4	−0.5 ± 0.6
313.7 ± 0.2	19.0 ± 0.7	99.7 ± 0.3	237.2 ± 0.5	146.8 ± 0.6	−1.9 ± 0.5	−1.1 ± 0.6
323.7 ± 0.2	19.1 ± 0.7	99.7 ± 0.3	238.9 ± 0.4	150.0 ± 0.6	−2.1 ± 0.4	−1.0 ± 0.6
333.0 ± 0.2	19.3 ± 0.6	99.7 ± 0.3	239.8 ± 0.6	153.0 ± 0.6	−3.0 ± 0.6	−1.1 ± 0.6
			HFE-7100 (1) + [emim][Tf_2N] (2)			
283.0 ± 0.2	10.4 ± 1.8	99.8 ± 0.2	244.2 ± 3.0	161.8 ± 2.0	−1.2 ± 3.0	0.3 ± 2.0
297.1 ± 0.2	10.4 ± 1.8	99.6 ± 0.4	246.7 ± 2.9	165.5 ± 1.7	−1.3 ± 2.9	0.0 ± 1.7
303.4 ± 0.2	10.8 ± 1.8	99.6 ± 0.4	247.0 ± 2.8	167.0 ± 1.7	−1.8 ± 2.8	−0.3 ± 1.7
313.7 ± 0.2	11.2 ± 1.2	99.5 ± 0.4	248.5 ± 2.8	169.8 ± 1.0	−1.9 ± 2.8	−0.5 ± 1.0
323.7 ± 0.2	11.5 ± 0.9	99.5 ± 0.4	250.2 ± 2.8	172.8 ± 1.0	−1.9 ± 2.8	−0.6 ± 1.0
333.1 ± 0.2	11.9 ± 0.9	99.6 ± 0.4	250.9 ± 2.2	176.2 ± 1.0	−2.2 ± 2.2	−0.4 ± 1.0
			HFE-7200 (1) + [emim][Tf_2N] (2)			
283.1 ± 0.2	6.9 ± 1.0	99.5 ± 0.5	247.6 ± 1.0	181.1 ± 0.8	−2.5 ± 1.0	−0.4 ± 0.8
297.2 ± 0.2	7.3 ± 0.9	100.0 − 0.3	250.3 ± 1.3	184.6 ± 0.9	−2.1 ± 1.3	−0.5 ± 0.9
303.4 ± 0.2	7.4 ± 0.9	99.6 ± 0.4	251.2 ± 1.1	186.7 ± 0.8	−2.2 ± 1.1	−0.6 ± 0.8
313.7 ± 0.2	7.5 ± 0.9	100.0 − 0.3	253.0 ± 1.0	189.6 ± 0.7	−2.3 ± 1.0	−0.5 ± 0.7
323.8 ± 0.2	8.0 ± 0.8	99.7 ± 0.3	254.4 ± 0.9	193.0 ± 0.7	−2.4 ± 0.9	−0.6 ± 0.7
333.1 ± 0.2	8.1 ± 0.8	100.0 − 0.3	256.0 ± 1.0	196.2 ± 0.7	−2.6 ± 1.0	−0.4 ± 0.7
			HFE-7300 (1) + [emim][Tf_2N] (2)			
283.1 ± 0.2	99.9 ± 0.1	2.8 ± 0.7	206.6 ± 1.0	254.0 ± 1.5	−0.2 ± 1.0	−1.0 ± 1.5
296.6 ± 0.2	100.0 − 0.2	2.9 ± 0.6	210.7 ± 1.2	255.1 ± 1.3	−0.1 ± 1.2	−1.1 ± 1.3
303.5 ± 0.2	100.0 − 0.2	2.9 ± 0.7	212.7 ± 1.1	257.1 ± 1.1	−0.2 ± 1.1	−0.8 ± 1.1
313.1 ± 0.2	99.9 ± 0.1	3.8 ± 0.8	215.5 ± 1.0	258.3 ± 0.9	−0.5 ± 1.0	−0.8 ± 0.9
322.8 ± 0.2	99.9 ± 0.1	4.8 ± 0.8	219.0 ± 1.0	258.5 ± 1.3	−0.1 ± 1.0	−1.6 ± 1.3
333.3 ± 0.2	99.9 ± 0.1	3.6 ± 0.7	222.0 ± 0.9	261.7 ± 1.1	−0.5 ± 0.9	−1.4 ± 1.1
			HFE-7500 (1) + [emim][Tf_2N] (2)			
283.3 ± 0.2	99.5 ± 0.5	1.3 ± 0.8	251.3 ± 2.2	255.1 ± 2.0	−0.1 ± 2.2	−0.2 ± 2.0
297.3 ± 0.2	99.5 ± 0.5	2.1 ± 1.0	255.4 ± 2.0	257.4 ± 2.0	−0.3 ± 2.0	−0.2 ± 2.0
303.5 ± 0.2	99.8 ± 0.2	1.9 ± 0.8	257.2 ± 1.6	258.9 ± 1.8	−0.6 ± 1.6	−0.4 ± 1.8
313.5 ± 0.2	99.7 ± 0.3	1.7 ± 1.1	260.6 ± 1.8	260.2 ± 1.8	−0.7 ± 1.8	−0.4 ± 1.8
323.8 ± 0.2	99.9 ± 0.1	1.4 ± 0.8	263.9 ± 1.7	262.2 ± 1.9	−0.8 ± 1.7	−0.2 ± 1.9
333.1 ± 0.2	99.5 ± 0.5	4.3 ± 0.7	267.3 ± 2.0	264.2 ± 1.3	−0.8 ± 2.0	−0.1 ± 1.3

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

Initially, the samples were mixed at room temperature (293.2 K) by vigorously shaking the sample containers. To establish thermodynamic equilibrium, sufficient time and mixing were required. A custom-made mixing apparatus, which can hold 14 sample containers, was designed for rocking the tubes back and forth inside a water-filled Plexiglas tank, and the temperature was controlled with an external temperature bath (PolyScience, model 1190S, Niles, IL) which circulated water through a copper coil inside the tank. The water bath was stirred with an agitator (Arrow Engineering Co., Inc., model 1750, Hillside, NJ), and the temperature was measured with a thermocouple (Fluke Corporation, model 52II thermometer, Everett, WA). The Fluke thermocouple 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 accuracy to ± 0.005 K. The water bath temperature uncertainties were ± 0.2 K.

The water bath temperature was initially set at about 283 K. Before height measurements were taken, the sample holder was positioned upright below the water level of the tank for (6 to 12) h. The volume of each liquid layer was obtained by measuring the liquid height from the bottom of the glass tube using the electronic caliper. The most difficult problem of the experiments was to establish the equilibrium state. The mixing and measurement procedure was repeated each day, and the heights were plotted as a function of time until no further change in the heights was detected. Using this procedure required 5 days to reach equilibrium at 283 K. These experiments were repeated at various temperatures up to about 333 K.

Results

Measurement Results and Uncertainty Estimation. To use the mass−volume method, the vapor phase was assumed to contain only HFE (negligible vapor pressure for [emim][Tf_2N] ionic liquid).[6,7,9−11] The HFE vapor density is also needed and was calculated assuming ideal gas behavior and using the Antoine equation ($\ln (P/\mathrm{Pa}) = A - B/(T/\mathrm{K})$) with coefficients provided in ref 17 and shown in Table 2. The uncertainty estimation for neglecting the moles of nitrogen in the vapor space during the filling process was calculated using an EOS program.[22] The vapor correction resulted in a negligible change in the liquid compositions ($x_1 = 0.03$ % and $x_1' = 0.0001$ % for the upper and lower liquid phases) and molar volumes ($\Delta V = 0.05\ \mathrm{cm^3 \cdot mol^{-1}}$ and $\Delta V' = 0.001\ \mathrm{cm^3 \cdot mol^{-1}}$ for the upper and lower liquid phases); therefore, our assumption to neglect the nitrogen in the sample container was justified.

The final equilibrium results for the molar compositions and volumes are provided in Table 3. 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 ($V^{E'}$ and

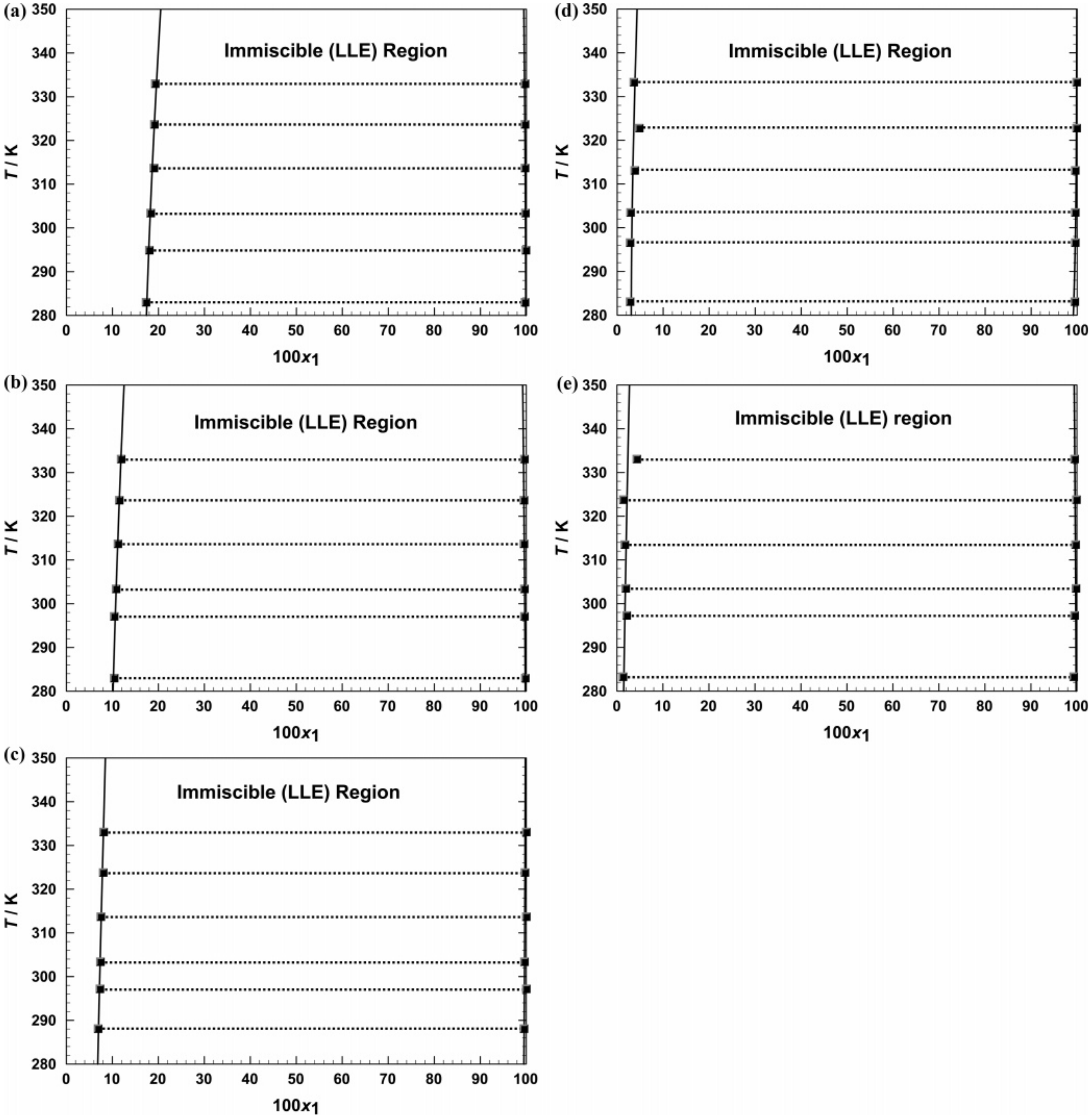


Figure 2. Temperature−composition LLE diagram of (a) HFE-7000 (1) + [emim][Tf_2N] (2), (b) HFE-7100 (1) + [emim][Tf_2N] (2), (c) HFE-7200 (1) + [emim][Tf_2N] (2), (d) HFE-7300 (1) + [emim][Tf_2N] (2), and (e) HFE-7500 (1) + [emim][Tf_2N] (2). Solid line: the NRTL model calculation. Broken lines: experimental LLE tie lines. Symbols: ■, experimental data by the volumetric method.

V^E) can be obtained, by use of the pure component molar volumes V_1^0 (HFE) and V_2^0 ([emim][Tf_2N]) using

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

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 HFE (1) and [emim][Tf_2N] (2) in phases L′ and L, respectively. Saturated liquid molar volumes for the HFEs were calculated using molecular weight and liquid density data. We checked the accuracy of the liquid density data provided in ref 17 using a 10 mL pycnometer and found that the data for HFE-7000, HFE-7200, and HFE-7300 were within 0.2 % of our measurements at 293 K, so we have used this data as given in Table 2. However, the liquid densities provided in ref 17 for HFE-7100 and HFE-7500 were not consistent with our measurements, so we have developed our own correlation ($\rho/\text{g}\cdot\text{cm}^{-3} = C - D\cdot 10^{-4}\ T/\text{K}$) which is provided in Table 2. The molar volume for [emim][Tf_2N] was calculated from known liquid density data.[23]

Total uncertainties in the final composition and molar volume determination are provided in Table 3. Total uncertainties ($\delta x_{TE} = \sqrt{\delta x_{RE}^2 + \delta x_{SE}^2}$) were estimated by calculating both the overall random (δx_{RE}) and systematic uncertainties (δx_{SE}). The overall random uncertainties were estimated using the following error propagation method

$$\delta x_{\mathrm{RE}} = \sqrt{\sum_{i=1}^{n}\left[\delta p_i\left(\frac{\partial x}{\partial p_i}\right)\right]^2} \qquad (2)$$

where δx_{RE} is the mole fraction or molar volume random uncertainty of the liquid composition; $\partial x/\partial p_i$ is the partial derivative of x with respect to the ith experimental parameter p_i, which is calculated from the sensitivity analysis of each parameter; and δp_i is the estimated uncertainty of the experimental parameter p_i. The following experimental parameters were considered to have an effect on the random uncertainty: sample container calibration constants, mass of HFE and [emim][Tf$_2$N], height of lower and upper phases. The heights had the largest overall effect. The systematic uncertainties (δx_{SE}) include properly correcting for the area expansion, meniscus, and vapor-phase moles. For additional details on estimation of total uncertainties, see refs 6 and 7.

Model Comparisons of LLE Results. Results with the mass−volume method are given in Table 3 with estimated uncertainties. LLE data measurements are shown in Figures 2(a−e) with the following model correlation. Observed LLE data have been modeled with the NRTL (nonrandom two liquid) solution model.[18] 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

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

$$\tau_{12} \equiv \frac{\Delta g_1}{RT} \text{ and } \tau_{21} \equiv \frac{\Delta g_2}{RT}:$$

(adjustable binary interaction parameters) (6)

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

x_i = mole fraction of the ith species

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

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

The binary LLE (L1 for liquid 1 and L2 for liquid 2) are mathematically described by the following equilibrium condition

$$\gamma_i^{\mathrm{L1}} x_i^{\mathrm{L1}} = \gamma_i^{\mathrm{L2}} x_i^{\mathrm{L2}} \; (i = 1, 2) \qquad (8)$$

Then, the two unknown adjustable parameters τ_{12} and τ_{21} at a given T can be determined from one set of LLE experimental (mass−volume method) data, using eq 8 (two nonlinearly coupled equations). We have several sets of such LLE data and can obtain τ_{12} and τ_{21} as a function of T. Thus, the empirical four parameters in eq 7 have been determined and are shown in Table 4. Lines in Figures 2(a−e) are calculated with the present NRTL model using these parameters.

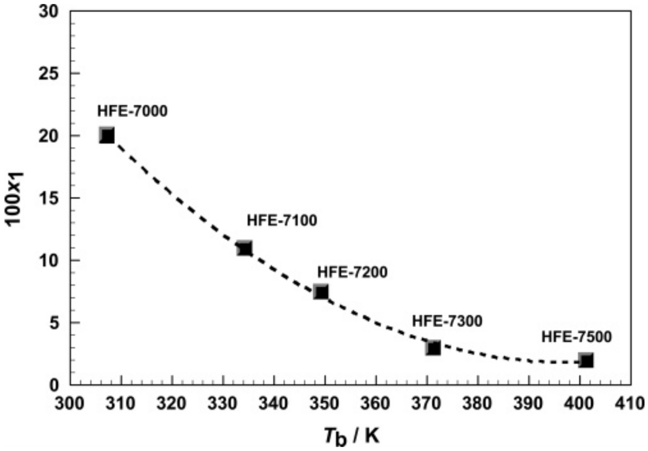


Figure 3. HFE solubility (x_1) vs HFE normal boiling point (T_b) correlation at about 300 K (the behavior at other temperatures is the same within a mole fraction of ± 1 %). Dashed line: a trend line. Symbols: ■, experimental data by the volumetric method.

Table 4. Binary Interaction Parameters in Equation 7

system (1)/(2)	$\tau_{12}^{(0)}$	$\tau_{12}^{(1)}$	$\tau_{21}^{(0)}$	$\tau_{21}^{(1)}$
HFE-7000/[emim][Tf$_2$N]	0.0	1794.73	−0.63869	245.46
HFE-7100/[emim][Tf$_2$N]	0.0	1535.22	0.0	209.87
HFE-7200/[emim][Tf$_2$N]	9.40745	−1399.81	0.0	320.46
HFE-7300/[emim][Tf$_2$N]	16.3152	−3561.72	0.0	547.25
HFE-7500/[emim][Tf$_2$N]	0.0	1355.92	0.0	707.90

Discussion

All binary systems of the present study have shown large immiscibilities. In the systems containing HFE-7000, HFE-7100, and HFE-7200, the upper liquid phase (V) was HFE-rich and the lower liquid phase (V') was [emim][Tf$_2$N]-rich. However, for the larger hydrofluoroethers (HFE-7300 and HFE-7500), the liquid densities (1.656 g·cm^{-3} and 1.616 g·cm^{-3} at 298.15 K, respectively) are larger than [emim][Tf$_2$N] (1.517 g·cm^{-3} at 298.15 K), and the opposite observation was found as shown in Table 2. LLE data have been well correlated with the nonelectrolyte NRTL solution model as shown in Figures 2(a−e). The solubility behavior for all HFEs at about 300 K (similar for other temperatures within a mole fraction of ± 1 %) was compared vs the normal boiling point temperature as shown in Figure 3. The behavior shows that as the normal boiling point decreases the solubility in [emim][Tf$_2$N] significantly increases. This phenomenon has led us to continue our study of HFEs with lower boiling points. Work is underway with lower-boiling HFEs (HFE-125, $CHF_2{-}O{-}CF_3$, T_b = 237 K at 1 atm, and HFE-143a, $CH_3{-}O{-}CF_3$, T_b = 249 K at 1 atm)[16] to examine this trend in increasing solubility vs lower boiling point and will be reported in the near future.

The present volumetric method for LLE also provides the information of the excess molar volume for each separated liquid. The excess molar volume for HFE + [emim][Tf$_2$N] is similar to other ordinary binary mixtures[24] where the excess molar volume is at most ± (2 to 3) cm^3·mol^{-1}. This is very different from what we have previously found with HFCs[6,7,9−11] and CO$_2$[25−26] which show very large negative (about (−10 to −25) cm^3·mol^{-1}) excess molar volumes for ionic liquid rich side solutions. It is interesting to see that the insertion of an ether oxygen atom into the HFC molecule significantly reduces the excess molar volume for HFEs + [emim][Tf$_2$N] and indicates liquid structures different from those in the HFCs with ionic liquids. This poses another unique and interesting challenge for theoretical modelers to explain the differences observed for HFEs and HFCs in ionic liquids.

Conclusions

Solubilities in five binary mixtures of hydrofluoroethers + RTIL ([emim][Tf_2N]) have been measured with the mass−volume method for the first time. All binary systems show large immiscibility gaps. The [emim][Tf_2N]-rich side solutions become more soluble in HFE as the HFE normal boiling point decreases (i.e., molecular size decreases). This behavior will be studied further in future work. LLE data are well correlated with the nonelectrolyte NRTL model, and excess molar volumes of the HFE and [emim][Tf_2N]-rich side solutions are similar to other ordinary binary mixtures where the excess molar volume is at most ± (2 to 3) $cm^3 \cdot mol^{-1}$. This is very different from what we have previously reported with HFCs in ionic liquids (large negative excess volumes) and indicates that the insertion of an ether oxygen has significantly changed the liquid structure with ionic liquids from that of HFC + RTIL solutions.

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Literature Cited

(1) Shiflett, M. B.; Yokozeki, A. Solubility and diffusivity of hydrofluorocarbons in room-temperature ionic liquids. *AIChE J.* **2006**, *52*, 1205−1219.

(2) Shiflett, M. B.; Junk, C. P.; Harmer, M. A.; Yokozeki, A. Solubility and diffusivity of difluormethane in room-temperature ionic liquids. *J. Chem. Eng. Data* **2006**, *51*, 483−495.

(3) Shiflett, M. B.; Junk, C. P.; Harmer, M. A.; Yokozeki, A. Solubility and diffusivity of 1,1,1,2-tetrafluoroethane in room-temperature ionic liquids. *Fluid Phase Equilib.* **2006**, *242*, 220−232.

(4) Shiflett, M. B.; Yokozeki, A. Separation of difluoromethane and pentafluoroethane by extractive distillation using ionic liquid. *Chem. Today* **2006**, *24*, 28−30.

(5) Shiflett, M. B.; Yokozeki, A. Gaseous absorption of fluoromethane, fluoroethane, and 1,1,2,2-tetrafluoroethane in 1-butyl-3-methylimidazolium hexafluorophosphate. *Ind. Chem. Eng. Res.* **2006**, *45*, 6375−6382.

(6) Shiflett, M. B.; Yokozeki, A. Vapor−liquid−liquid equilibria of pentafluoroethane and ionic liquid [bmim][PF_6] mixtures studied with the volumetric method. *J. Phys. Chem. B* **2006**, *110*, 14436−14443.

(7) Shiflett, M. B.; Yokozeki, A. Vapor−liquid−liquid equilibria of hydrofluorocarbons + 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Chem. Eng. Data* **2006**, *51*, 1931−1939.

(8) Yokozeki, A.; Shiflett, M. B. Global phase behaviors of trifluoromethane in room-temperature ionic liquid [bmim][PF_6]. *AIChE J.* **2006**, *52*, 3953−3957.

(9) Shiflett, M. B.; Yokozeki, A. Phase equilibria of hydrofluorocarbon-4310mee mixtures with ionic liquids: miscibility of *threo*- and *erythro*-diastereomers in ionic liquids. *Ind. Eng. Chem. Res*. **2007**, submitted.

(10) Shiflett, M. B.; Yokozeki, A. Hydrogen substitution effect on the solubility of perhalogenated compounds in ionic liquid [bmim][PF_6]. *Fluid Phase Equilib.* **2007**, 10.1016/j.fluid.2007.07.035.

(11) Shiflett, M. B.; Yokozeki, A. Solubility differences of halocarbon isomers in ionic liquid [emim][Tf_2N]. *J. Chem. Eng. Data* **2007**, *52*, 2007−2015.

(12) Tokuhashi, K.; Takahashi, A.; Kaise, M.; Kondo, S.; Sekiya, A.; Yamashita, S.; Haruaki, I. Rate constants for the reactions of OH radicals with $CH_3OCF_2CHF_2$, $CHF_2OCH_2CF_2CHF_2$, $CHF_2OCH_2CF_2$-CF_3, and $CF_3CH_2OCF_2CHF_2$ over the temperature range 250−430 K. *J. Phys. Chem. A* **2000**, *104*, 1165−1170.

(13) Murata, J.; Yamashita, S.; Akiyama, M. Vapor pressures of hydrofluoroethers. *J. Chem. Eng. Data* **2002**, *47*, 911−915.

(14) Yasumoto, M.; Yamada, Y.; Murata, J.; Urata, S.; Otake, K. Critical parameters and vapor pressure measurements of hydrofluoroethers at high temperatures. *J. Chem. Eng. Data* **2003**, *48*, 1368−1379.

(15) Defibaugh, D. R.; Gillis, K. A.; Moldover, M. R.; Morrison, G.; Schmidt, J. W. Thermodynamic properties of CHF_2-O-CHF_2 bis-(difluoromethyl) ether. *Fluid Phase Equilib.* **1992**, *81*, 285−305.

(16) Wang, B.-H.; Adcock, J. L.; Mathur, S. B.; Van Hook, W. A. Vapor pressures, liquid molar volumes, vapor non-idealities, and critical properties of some fluorinated ethers: $CF_3OCF_2OCF_3$, $CF_3OCF_2CF_2H$, *c*-$CF_2CF_2CF_2O$, CF_3OCF_2H, and CF_3OCH_3; and of CCl_3F and CF_2-ClH. *J. Chem. Thermodyn.* **1991**, *23*, 699−710.

(17) 3M, www.3m.com/electronics/chemicals, St. Paul, MN.

(18) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001, pp 8.12−8.17.

(19) Covalent Associates, Inc., www.covalentassociates.com, Woburn, MA.

(20) Schwarzkopf Microanalytical Laboratory, www.schwarzkopfmicrolab.com, Woodside, NY.

(21) WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion*; 1998, Global Ozone Research and Monitoring Project, Report No. 44, 1998.

(22) Lemmon, E. W.; McLinden, M. O.; Huber, M. L. *NIST reference fluid thermodynamic and transport properties - REFPROP*, version 7.0, users' guide; U. S. Department of Commerce, Technology Administration, National Institute of Standards and Technology, Standard Reference Data Program: Gaithersburg, MD 2002.

(23) Krummen, M.; Wasserscheid, P.; Gmehling, J. Measurement of activity coefficients at infinite dilution in ionic liquids using the dilutor technique. *J. Chem. Eng. Data* **2002**, *47*, 1411−1417.

(24) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*, 3rd ed.; Butterworth: London, 1982.

(25) Shiflett, M. B.; Yokozeki, A. Solubility of CO_2 in room-temperature ionic liquid [hmim][Tf_2N]. *J. Phys. Chem. B* **2007**, *111*, 2070−2074.

(26) Shiflett, M. B.; Kasprzak, D. J.; Junk, C. P.; Yokozeki, A. Phase behavior of carbon dioxide + [bmim][Ac] mixtures. *J. Chem. Thermodyn.* **2007**, doi:10.1016/j.jct.2007.06.003.

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