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Global Phase Behavior of Imidazolium Ionic Liquids and Compressed 1,1,1,2-Tetrafluoroethane (R-134a)

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*Novel processes involving ionic liquids with refrigerant gases have recently been developed. Here, the complete global phase behavior has been measured for the refrigerant gas, 1,1,1,2-tetrafluoroethane (R-134a) and 1-*n*-alkyl-3-methyl-imidazolium ionic liquids with the anions hexafluorophosphate [PF_6], tetrafluoroborate [BF_4] and bis(trifluoromethylsulfonyl)imide [Tf_2N] from ~0°C to 105°C and to 33 MPa. All of the systems studied were Type V from the classification scheme of Scott-van Konynenburg with regions of vapor-liquid equilibrium, miscible/critical regions, vapor-liquid-liquid equilibrium, and upper and lower critical endpoints (UCEP and LCEP). The effect of the alkyl chain length has been investigated, for ethyl-([EMIm]),* n*-butyl-([BMIm]), and* n*-hexyl-([HMIm]). With increasing chain length, the temperature of the lower critical end points increases and pressure at the mixture critical points decrease. With a common cation, the temperature of the LCEP increased and the mixture critical point pressures decreased in the order of [BF_4], [PF_6], and [Tf_2N].* © 2008 American Institute of Chemical Engineers *AIChE J,* 55: 486–493, 2009

Keywords: imidazolium ionic liquids, R-134a, global phase behavior, high-pressure, mixture critical points

Introduction

The solubility and separation of refrigerant gases are important problems for several industries. Many refrigerants and their intermediates have very similar physical and chemical properties which can often render their separation costly by traditional distillation. The separation of the common azeotropes encountered among refrigerant mixtures usually requires additional components in extractive distillation. Ionic liquids (ILs) have been shown to provide efficient solutions to these problems.[1] Absorption refrigeration with refrigerant gases uses a low-volatility solvent to first absorb the gas at low temperatures and then uses heat to liberate a high-pressure gas for the refrigeration cycle. However, widespread application of absorption refrigeration has been impeded by the often bulky equipment that is needed to purify the high-pressure gas from the generator; the presence of any absorption liquid significantly decreases the efficiency. Non-volatile ILs in these systems with refrigerants may help solve these problems.[2]

The high-pressure phase behavior and equilibria are the most important data needed to utilize any of the novel applications with ILs and refrigerant gases. The phase behavior indicates the conditions (temperature and pressure) of the different equilibria and transitions, whether vapor-liquid, liquid-liquid, etc. For instance, regions in which the IL and refrigerant are miscible would not be conducive to separations or absorption refrigeration. This study will investigate the phase behavior of a series of 1-*n*-alkyl-3-methyl imidazolium ILs with various alkyl groups and anions (see Figure 1.) with the

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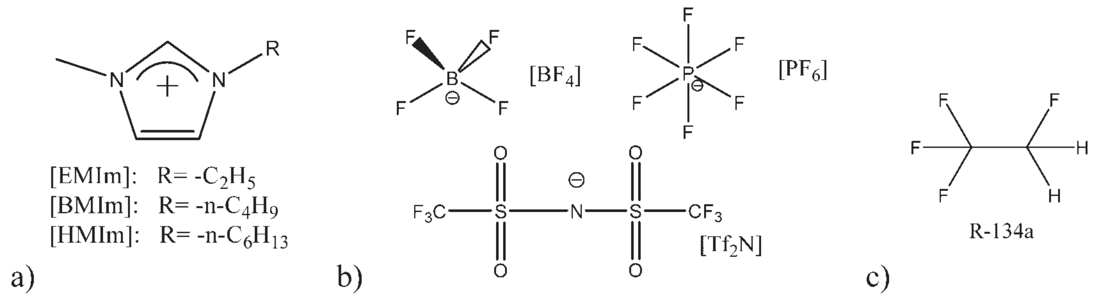

Figure 1. Ionic liquid cations and anions and refrigerant used in this study.

(a) Cation structures; (b) anion structures; (c) refrigerant gas: 1,1,1,2-tetrafluoroethane (R-134a).

common refrigerant 1,1,1,2-tetrafluoroethane from ~0°C to 105°C and to 330 bar.

Background

Ionic liquids

ILs are organic salts that are liquid at or near room temperature ($T_m < 100°C$). There are a myriad of cation/anion combinations that can yield an organic salt. The most common classes of IL cations are quaternary ammonium, imidazolium, pyridinium, and phosphonium. ILs can be molecularly engineered for specific physico-chemical properties through various "R-"groups and cation/anion selection, e.g., viscosity, solubility properties, density, acidity/basicity, etc. It has been estimated that ~10^{14} unique cation/anion combinations are possible.[3] Most ILs have immeasurably low vapor pressure which virtually eliminates their release into the environment through the air. These properties have lead researchers to claim ILs as potential "green" solvents. However, their toxicity and environmental impact must also be known before the "green" moniker can be applied. In addition, non-volatility may facilitate more efficient absorption refrigeration processes as discussed in the earlier section.

Ionic liquids/refrigerants

Combining ILs and refrigerants has a number of advantages. Most refrigerant gases have a high solubility in ILs.[4] One of the challenges of ILs is their viscosity which is often higher than conventional solvents[5] and leads to slower mass transport rates. In concurrent studies in our laboratory (Ahosseini et al., in Preparation), the viscosity of the IL, [HMIm][Tf$_2$N], has been measured and found to decrease approximately 80+% with up to 6 bar of R-134a at 25°C. This decrease in the mixture viscosity has been used to predict the diffusivity in the IL with approximately a five-fold improvement over the same pressure range. This dramatic increase in the mass transport properties will lead to processes with less capital intensity as smaller equipment (e.g., heat exchangers, contactors, etc.) can be used.

Only a few groups in the literature report phase equilibria data for ILs and refrigerant gases. Shiflett et al.,[6–9] have reported the majority of known data. They have measured the low-pressure (<10 bar) vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) data of a large series of refrigerants and ILs; see Shiflett and Yokozeki[9] and Ren et al.[10] for complete references. Shariati and Peters compared the high-pressure phase behavior between CO$_2$ and trifluoromethane (CHF$_3$) in [EMIm][PF$_6$] and [BMIm][PF$_6$].[11,12] Kim et al.[13] have studied the refractive index, heat capacity, and vapor pressure of mixtures of [BMIm][BF$_4$] and [BMIm][Br] with 2,2,2-trifloroethanol (TFE) and water.[14]

Global phase behavior

For the process design of any system with a compressed gas, the global phase behavior must be characterized. The Gibbs phase rule indicates that even for binary systems, up to four phases may coexist in equilibrium. Thus, one, two and three phase regions are likely to exist at various temperatures, pressures and compositions. van Konynenburg and Scott[15] were one of the first to provide a uniform classification scheme for binary phase behavior of liquids and gases, which are composed of six common types of behavior, labeled I through VI. Each type has a similar number of transitions and behavior for VLE; VLLE, liquid-liquid equilibrium (LLE), upper and lower critical endpoints (UCEP and LCEP), and mixture critical points (of either LLE or VLE). More recently, Bolz et al.[16] have proposed a new system for the International Union of Pure and Applied Chemistry (IUPAC) in which a more descriptive nomenclature is presented. The new designation conveys the topology and connectivity of critical curves.

As will be discussed below, refrigerant gases and ILs are believed to be mostly of Type V behavior as shown qualitatively with exaggerated features (for clarity) in Figure 2. Type V behavior of the Scott-van Konynenburg scheme is characterized by VLE at low temperatures, followed by a LCEP where another liquid phase forms (thus, VLLE), followed by an UCEP at higher temperatures in which the liquid phases merge. The mixture critical point extends from the LCEP to the pure component critical point of the less volatile component.

The qualitative pressure-composition behavior of a Type V system at three different isotherms is illustrated in Figure 3. Figure 3a illustrates the VLE for an isotherm at temperatures below the LCEP (T_a). Here, liquid 2 (L_2) is primarily composed of the less-volatile (liquid) component, whereas component 1 is the more volatile component (gas). At pressures above the vapor pressure of pure component 1 (pure liquid of component 1), the two liquids are completely miscible. At a temperature above the LCEP and below the pure component 1 critical temperature designated T_b, several different

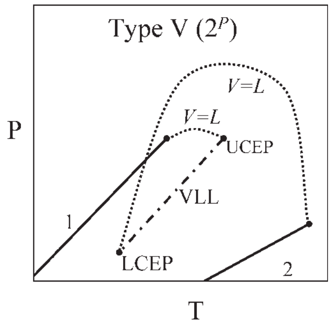

Figure 2. Global phase diagram of a Type V system according to Scott and van Konynenburg[15] and Bolz et al.[16]

equilibria are possible depending on the pressure and loading (ratio) of the components as shown in Figure 3b. At lower pressures, VLE exists until the pressure of transition to VLLE which has compositions symbolized by the solid squares in the figure. These compositions as exaggerated for clarity and the L_1 and V compositions occur more often at higher concentrations of the compressed gas. The newly formed liquid 1 phase is rich in, or mostly composed of, component 1. Beyond the VLLE pressure, two different equilibria are possible depending on the overall mole fraction composition. If an overall composition exists between the L_1 and V compositions of the VLLE (x^{L1} and x^{V} in the figure), then an increase in pressure will create VLE of the vapor and the L_1 phase. At pressures above the vapor pressure of component 1, then the L_1 phase and the pure liquid of component 1 are completely miscible. However, if the overall composition is between the L_2 and L_1 compositions of the VLLE (x^{L1} and x^{L2} in the figure), then increase in pressure produces LLE of the L_1 and L_2 phases. At higher pressures, the mixture critical point is obtained and the two phases become critical to one another (completely miscible). At a temperature above the UCEP (T_c in Figure 3c), then VLE exists to the mixture critical pressure, where the vapor becomes critical with L_2. Type IV is similar to Type V, except that a low temperature region of LLE, VLLE and a second UCEP exists (see Figure 2).

Yokozeki and Shiflett[17] predicted that the system of trifluoromethane and [BMIm][PF_6] is a Type V system using an modified Redlich-Kwong equation of state; however, complete experimental characterization of the global phase behavior is currently absent for all IL/refrigerant systems. Shiflett and Yokozeki[9] measured and modeled the low-pressure (<3.5 bar) VLE of R-134a and [EMIm][Tf_2N] with a modified cubic equation of state (EoS). From the parameters regressed from the data, they predict that the R-134a and [EMIm][Tf_2N] is a Type V system. Recently, we have experimentally measured the complete global phase behavior for the [EMIm][Tf_2N]/R-134a system and have confirmed that the system is indeed Type V.[10] In addition, the equation of state method with parameters from only low pressure VLE data was able to quantitatively predict the experimental higher pressure (3.5–160 bar) VLE, VLLE, LCEP, UCEP, and lower temperature mixture critical points ($L_1 = L_2$).

Overview

Here, the global phase behavior is experimentally measured for 1-*n*-alkyl-3-methyl-imidazolium ILs and the refrigerant, 1,1,1,2-tetrafluoroethane (R-134a). The effect of the alkyl chain length is investigated for ethyl-([EMIm]), *n*-butyl-([BMIm]), and *n*-hexyl-([HMIm]) cations. The anion effect with tetrafluoroborate ([BF_4]), hexafluorophosphate ([PF_6]), and bis(trifluoromethylsulfonyl)imide ([Tf_2N]) is also investigated.

Experimental

Phase behavior and equilibrium

The phase behavior and the temperature and pressure of the transitions were observed in a windowed high-pressure autoclave similar to a design by Koch and Leitner[18] and

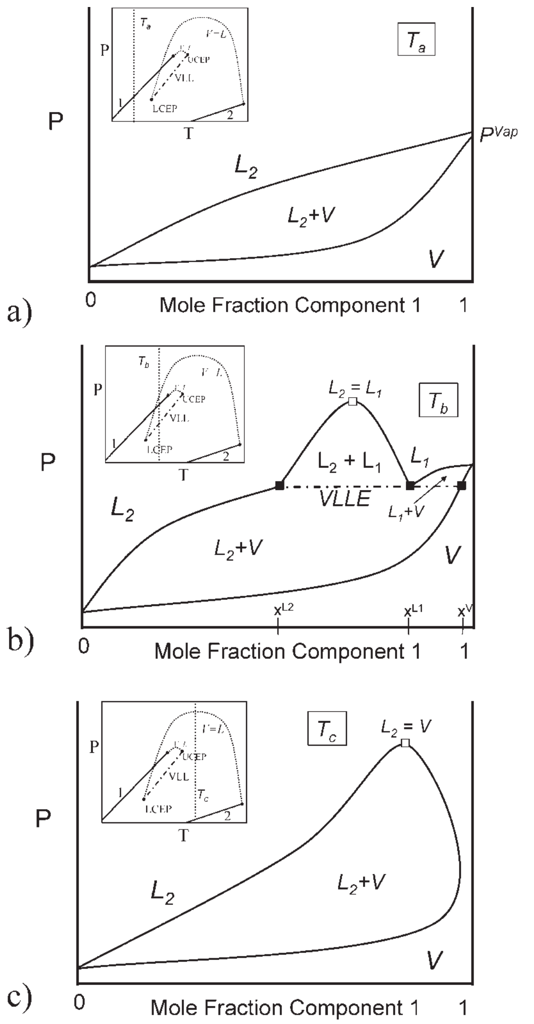

Figure 3. Qualitative pressure-composition diagrams of isotherms from Type V systems as shown in the inset.

(a) An isotherm below the LCEP; (b) an isotherm between the LCEP and critical temperature of component 1; (c) an isotherm above the UCEP.

modified in our group; for further details see Schleicher.[19] The ~10 mL viewcell has a temperature limit of 150°C and a pressure limit of 400 bar. Agitation is performed with a stirbar within the vessel. The temperature was maintained by a heating plate (Ika Werke, GmbH, PN: RET Basic C) with electronic temperature control (Ika Werke, GmbH, PN: IKATRON ETS-d4-fuzzy) using a Pt-1000 RTD placed through the wall of the autoclave; the temperature precision is ±0.1°C. Pressures were measured with a high precision digital pressure gauge, Omega DPG-7000-3K with an error band of 0.05% of full scale (FS = 3000 psi) for pressures less than 207 bar and an Omega DPG5000 with an error band of 0.25% of full scale (FS = 5000 psi) for pressures greater than 207 bar. Three different types of phase behavior transitions were observed: VLE to VLLE; VLLE to LLE; and VLE, VLLE or LLE to critical transitions including UCEP and LCEP. Approximately 1.5 mL (see below) IL was loaded into the cell and heated to the desired temperature. The refrigerant was slowly introduced by a high-pressure syringe pump (Teledyne-Isco, Inc. model 100 DM) and vented to remove any argon or air. R-134a was slowly added to the vessel to the desired pressure, stirred and allowed to reach equilibrium (~30 min). The pressure was slowly raised, stirred, and raised again until the first sign of the phase transition. The vessel was partially vented to a pressure just below the transition, and allowed to re-equilibrate. The process was repeated until the transition was reproduced within ±0.5 bar. In addition, the temperature of the system was changed at constant pressure. These temperatures were reproducible to approximately ±0.5°C. The amount of initial IL is also important as the liquid phase will expand significantly with increases pressure/solubility of the R-134a. Too much initial sample may result in the transition occurring above the window of the vessel. This is especially important for the mixture critical points. The amount of IL was varied so as to render the transition approximately at a height of 70% of the total window height.

Synthesis of ionic liquids

1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([HMIm][Tf$_2$N]). This was synthesized by anion exchange from 1-hexyl-3-methyl-imidazolium bromide ([HMIm][Br]).[20] [HMIm][Br] was synthesized by a quaternization reaction of 1-methyl-imidazole and bromohexane in acetonitrile at 40°C (Caution: this reaction is highly exothermic and adequate amounts of solvent or cooling should be used). The solvent was removed on a rotary evaporator under reduced pressure and 40°C. An anion exchange of [HMIm][Br] with lithium bis(trifluoromethylsulfonyl)imide (Li[Tf$_2$N]) was performed in deionized water.[21,22] The denser hydrophobic IL phase was decanted and washed with twice the amount of water for eight times. The IL was then dried under high-vacuum for at least 48 h and stored in Schlenk tubes under dry argon. Elemental analysis was performed by Desert Analytics Transwest Geochem. ^{1}H NMR spectra were recorded on a Bruker 400 NMR Spectrometer. The water content was determined by a Mettler Toledo DL32 Karl Fisher Coulometer and the Br content was measured by a Cole Parmer Bromide Electrode (27502-05) read with an Oakton Ion 510 series meter. ^{1}H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz: δ = 8.65 (s, 1H), 7.39 (d, 2H, J = 4.19), 4.17 (q, 2H, J = 7.4), 3.93 (s, 3H), 1.87 (m, 4H), 1.32 (6H, m) 0.87 (t, 3H, J = 6.53). Analysis calculated for C12H19N3F6S2O4: C, 32.21; H, 4.28; N, 9.39; S, 14.33. Found: C, 32.21; H, 4.27; N, 9.25; S, 14.19. The purity was estimated from elemental analysis and NMR to be 99+%. The water content was less than 100 ppm and the bromide content was 23 ppm.

1-Hexyl-3-methylimidazolium hexafluorophosphate ([HMIm][PF$_6$]). [HMIm][PF$_6$] was prepared in a similar manner as [HMIm][Tf$_2$N], but from the anion exchange of [HMIm][Br] with ammonium hexafluorophosphate in deionized water.[23,24] ^{1}H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz: δ = 8.43 (s, 1H), 7.33 (brs, 2H), 4.12 (t, 2H, J = 7.22), 3.87 (s, 3H), 1.85 (m, 4H), 1.28 (6H, m), 0.84 (t, 3H, J = 6.96). Analysis calculated for C10H19N2PF6: C, 38.47; H, 6.13; N, 8.97; P, 9.92. Found: C, 38.64; H, 6.01; N, 9.01; P, 9.62. The purity was estimated from elemental analysis and NMR to be 99+%. The water content was 62 ppm and the bromide content was <8 ppm.

1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF$_6$]). [BMIm][PF$_6$] was prepared in a similar manner as [HMIm][PF$_6$], but from the anion exchange of [BMIm][Br] with ammonium hexafluorophosphate in deionized water. ^{1}H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz: δ = 8.35 (s, 1H), 7.31(brs, 1H), 7.28 (brs, 1H), 4.09 (t, 2H, J = 7.4), 3.83 (s, 3H), 1.79 (quint, 2H, J = 7.4), 1.29 (hex, 2H, J = 7.4), 0.85 (t, 3H, J = 7.4). Analysis calculated for $C_8H_{15}N_2PF_6$: C, 33.81; H, 5.32; N, 9.86; P, 10.90; F, 40.11. Found: C, 33.69; H, 5.21; N, 9.63; P, 10.40; F, 41.70. The purity was estimated from elemental analysis and NMR to be 99+%. The water content was 62 ppm and the bromide content was <8 ppm.

1-Hexyl-3-methylimidazolium tetrafluoroborate ([HMIm][BF4]). [HMIm][BF$_4$] was prepared from the anion exchange of [HMIm][Br] with ammonium tetrafluoroborate in deionized water. H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz: δ = 8.72 (s, 1H), 7.52 (d, 2H, J = 3.6), 4.22 (t, 2H, J = 7.23), 3.96 (s, 3H), 1.89 (m, 4H), 1.32 (6H, m) 0.86 (t, 3H, J = 6.54). Analysis calculated for C10H19N2BF4: C, 47.27; H, 7.54; N, 11.02; B, 4.25. Found: C, 46.99; H, 7.21; N, 10.88; B, 4.39. The purity was estimated from elemental analysis and NMR to be 99+%. The water content was less than 64 ppm and the bromide content was 123 ppm.

Materials

1,1,1,2-Tetrafluoroethane (R-134a, 99.99%) was purchased from Linweld, Inc and used as received. 1-Methylimidazole, (CAS 616-47-7) 99+%, lithium bis(trifluoromethylsulfonyl)imide (CAS 90076-65-6) 99.95%, acetonitrile, ≥99.9%; ammonium hexafluorophosphate(CAS 16941-11-0) 99.99%, ammonium tetrafluoroborate (CAS 13826-83-0) 99.99%, were purchased from Sigma-Aldrich. 1-Bromoethane (CAS 74-96-4) 99+%, bromobutane (CAS 109-65-9) 99%, bromohexane (CAS 111-25-1) 99+%, was obtained from Acros. Compressed argon (CAS 7440-37-1) (Ultra High Purity grade) was obtained from Airgas, Inc. 1-Methylimidazole, 1-bromoethane, 1-bromobutane, and 1-bromo-hexane were distilled immediately before the synthesis.

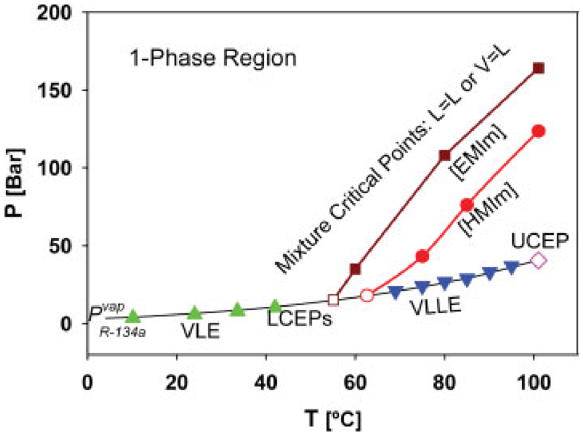

Figure 4. Experimental global phase behavior for [R-MIm][Tf_2N] and R-134a for R = ethyl ([EMIm]), and *n*-hexyl ([HMIm]).

Critical points and LCEP, respectively, of R-134a with [HMIm][Tf_2N] (●, ○) and [EMIm][Tf_2N] (■, □); ◇, upper critical endpoint (UCEP) with [HMIm][Tf_2N] (also R-134a critical point); ▲, VLE with confirmed miscibility at the vapor pressure of R-134a; ▼, vapor-liquid-liquid equilibrium (VLLE) for [HMIm][Tf_2N]; Solid line of mixture critical points are smoothed data. Solid line through VLE, VLLE, and UCEP is the vapor pressure of pure R-134a from Ref. 25. Data of [EMIm][Tf_2N]/R-134a from Ref. 10. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Results and Discussion

The global phase behavior of binary mixture between R-134a and [HMIm][Tf_2N], [HMIm][PF_6], [HMIm][BF_4], and [BMIm][PF_6] were studied between ~0°C to 105°C and pressures to 330 bar. These data represent some of the first complete global phase diagrams for compressed gases and ILs. The global phase behavior for [HMIm][Tf_2N] and R-134a was measured and is presented in Figure 4 and Table 1 illustrating the regions of 1-, 2-, and 3-phases. At lower temperatures below the LCEP, VLE exists with complete liquid miscibility above the vapor pressure of R-134a similar to Figure 3a. This point of miscibility at the vapor pressure has been confirmed experimentally for several temperatures and shown in Figures 4–6. This is different than the behavior of most gases with ILs (CO_2, ethane, etc.) which have liquid-liquid immiscibility above the vapor pressure as will be discussed below. The results from a previous study[10] with [EMIm][Tf_2N] and R-134a are shown for comparison. VLLE equilibrium exists between the LCEP and UCEP. The pressure-temperature profile of the VLLE data is equal, within experimental accuracy, to the pure component vapor pressure of R-134a as calculated from the REFPROP database version 8.0.[25] This often indicates that the second liquid phase is mostly R-134a ($x_{R\text{-}134a} < 0.01$), as confirmed experimentally by Shiflett and Yokozeki[9,26] for systems with refrigerant gases and [EMIm][Tf_2N], [HMIm][Tf_2N], [BMIm][PF_6], [HMIm][PF_6] and [HMIm][BF_4]. The LCEP is the start of both the VLLE line and the mixture critical points. At temperatures above the LCEP, but below the UCEP, four different equilibria are possible depending on the pressure. VLE exists at the lowest pressures and VLLE exists near or at the pure R-134a vapor pressure. At pressures above VLLE, LLE equilibrium exists until the mixture critical point, beyond which the system becomes critical/miscible. At very high loadings of R-134a, VLE would exist above the VLLE pressure; see Figure 3b. Although not explored experimentally, the region is estimated to be between a mole fraction of R-134a of 0.99–1.00. Above the UCEP, VLE exists and terminates at the mixture critical point (see Figure 3c). For [HMIm][Tf_2N]/R-134a, the LCEP was measured at 62.6°C

Table 1. Global Phase Behavior Data for ILs Studied and R-134a

	Mixture Critical Points		LCEP		UCEP		VLE*		VLLE	
Transitions	*T* (°C)	*P* (bar)	*T* (°C)	*P* (bar)	*T* (°C)	*P* (bar)	*T* (°C)	*P* (bar)	*T* (°C)	*P* (bar)
ILs										
[EMIm][Tf_2N]†	60.0	35.0	55.0	15.0	101	40.8	32.2	8.2	60.0	16.6
	75.0	92.3					38.2	9.7	82.0	27.4
	80.0	108.0					44.2	11.3	92.0	33.0
	101	164.0					48.2	12.6		
[HMIm][Tf_2N]	75.0	43.2	62.6	19.0	101	40.5	24.0	5.9	80.0	26.8
	85.0	76.1					33.6	7.9	90.1	33.2
	101	123.5					42.0	10.2	100	40.2
[HMIm][BF_4]	50.0	46.4	37.9	10.0	101	40.5	21.9	5.7	40.7	10.6
	75.0	143.3					23.0	6.7	60.5	17.8
	90.0	204.3					33.7	8.4	79.6	27.3
	105	254.7					35.6	8.7	94.1	37.2
[HMIm][PF_6]	50.0	27.7	48.3	12.5	101	40.5	5.0	3.4	50.0	13.0
	60.0	69.8					15.0	4.7	54.0	14.4
	75.0	128.8					25.1	6.3	60.0	16.7
	90.0	175.9					30.0	6.9	75.0	24.0
	105	225.2					40.0	9.9	90.0	32.6
[BMIm][PF_6]	50.0	111.9	27.8	7.3	101	40.5	10.0	4.2	40.0	9.8
	75.0	215.4					15.0	4.9	60.0	15.8
	90.0	277.7					20.0	5.7	80.2	26.1
	105	327.6					24.0	6.4	95.0	35.9

†Ren et al.[10]
*Confirmed points of VLE miscibility at the vapor pressure of R-134a.

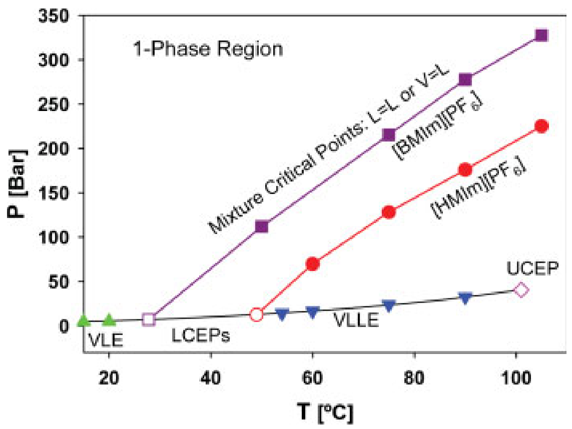

Figure 5. Experimental global phase behavior for [BMIm] and [HMIm][PF$_6$] and R-134a.

Mixture critical points and LCEP of [HMIm][PF$_6$] (●, ○) respectively) and [BMIm][PF$_6$] (■, □). See caption of Figure 4 for further details. [Color figure can be viewed in the online issue, which is available at www. interscience. wiley.com.]

and 19 bar. Mixture critical points technically extend from the LCEP to the critical point of the less-volatile component (see Figure 2, Type V). However, no known critical points of ILs are known to exist, due to decomposition.

From a recent study,[10] the LCEP and mixture critical points for [1-ethyl-3-methyl-imidazolium][Tf$_2$N] ([EMIm][Tf$_2$N]) are also displayed in Figure 4. As shown, the LCEP is lower and the slope of the mixture critical line is steeper for [EMIm][Tf$_2$N] than [HMIm][Tf$_2$N]. For instance at 80°C, the mixture critical pressure of the [EMIm][Tf$_2$N]/R-134a system is 108 bar, whereas that for [HMIm][Tf$_2$N] is 65.4 bar. Thus, an increase in the alkyl chain length of the cation increases the area (T and P) in which R-134a is 1-phase (miscible/critical) with imidazolium ILs. Thus, with longer alkyl-groups the LCEP temperature (and pressure) increases. This is the same trend for the solubility of refrigerant gases in ILs, viz. longer alkyl-groups result in higher solubility at a given temperature and pressure.[6] The added dispersion forces of the longer alkyl group and induced dipole forces with the polar compressed or liquefied gas provide more favorable interactions, and, thus, miscibility (or increased solubility) at lower temperatures and pressures. If a process requires no miscibility of the IL in the compressed gas phase, then shorter alkyl-chains are needed as the LCEP is lower in temperature and the critical points are higher but at the expense of slightly lower gas solubility.

The UCEP of the [HMIm][Tf$_2$N]/R-134a was measured at 101°C and 40.5 bar. As the R-134a-rich liquid phase is nearly pure, its UCEP is nearly indistinguishable (within experimental accuracy) with the pure component critical point of 101°C and 40.6 bar. Below the LCEP temperature, the system is in VLE until the pressure is raised to the vapor pressure of the pure R-134a, at which point the two liquids become miscible. These points of miscibility at the R-134a vapor pressure have been confirmed experimentally and are shown in Figure 4.

The presence of a single miscible phase or critical regions is unique to most hydrofluorocarbon refrigerant gases and ILs, as the majority of the high-pressure equilibria data for ILs and various compressed gases have no reported miscibility.[27–29] For ILs with CO$_2$, only VLE and then LLE are possible for temperatures below the pure CO$_2$ critical point. Brennecke and coworkers[30] report that [BMIm][PF$_6$] and CO$_2$ represent a two-phase system even beyond 3.1 kbar. This may indicate that most gases investigated with ILs form a Type III system with a critical locus that approaches hyperbaric to infinite pressure. Shariati and Peters[11,12] are the only other group to report a vapor-liquid mixture critical pressure and composition for [EMIm][PF$_6$] and high-pressure CHF$_3$.

The effect of the alkyl group was also investigated with the [PF$_6$] anion and the 1-butyl- and 1-hexyl-3-methylimidazolium cations ([BMIm] and [HMIm], respectively). Table 1 and Figure 5 illustrate the LCEP and mixture critical points of [BMIm][PF$_6$] and [HMIm][PF$_6$]. As the majority of the VLLE data and the UCEPs are nearly equal to the pure R-134a vapor pressure and critical point, respectively, most of the individual systems data have been omitted from the plot for clarity, but are found in Table 1. As shown, the addition of the two methylene (—CH$_2$—) groups changes the LCEP by 20°C. The mixture critical points for [HMIm] are less than that for [BMIm]. Again, the added length of the alkyl chain increases the area where the two components are miscible.

To determine the effect of the anion, three ILs were compared based on the cation 1-hexyl-3-metyl-imidazolium ([HMIm]) with the fluorinated anions [BF$_4$], [PF$_6$], and the aforementioned [Tf$_2$N] as shown in Figure 6. In contrast to the results with the [Tf$_2$N] anion, the pressures at which the mixture becomes critical for [PF$_6$] and [BF$_4$] dramatically increases. For instance at 75°C, the mixture critical pressure for [HMIm][BF$_4$] is 143.3 bar and 128.8 bar for [HMIm] [PF$_6$]; the critical point for [HMIm][Tf$_2$N] is nearly a hundred bar less at 43.2 bar. Thus, the anion has a very dramatic impact on the ultimate global phase behavior. The LCEP of

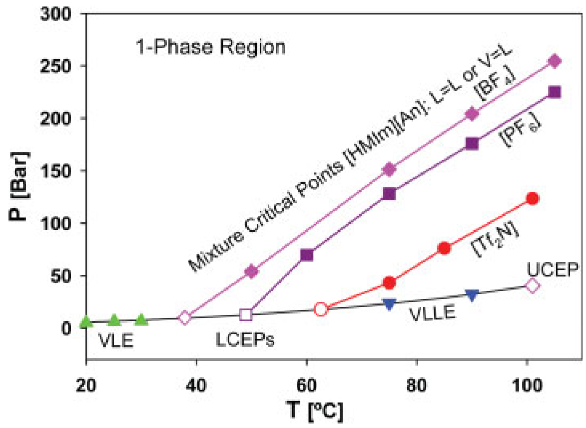

Figure 6. Experimental global phase behavior for [HMIm][An] for [An] = [BF$_4$] (◆), [PF$_6$] (■), and [Tf$_2$N] (●) with R-134a.

See caption of Figure 4 for more details. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

these three ILs decreases in the order of [HMIm][Tf_2N] at 62.6°C, [HMIm][PF_6] at 48.3°C and [HMIm][BF_4] at 37.9°C. This is the same trend for the solubility of refrigerant gases in ILs, viz. solubility at a given temperature and pressure in the order [Tf_2N]>[PF_6]>[BF_4].[4,9] This trend scales with the diameter of the anion or charge density as larger anions can have more disperse negative charge. Ions with more disperse charge can be more readily solvated by the polar compressed hydrofluorocarbon, and thus become miscible at lower temperatures. Therefore, as the temperature of the LCEP increases, the regions of temperature and pressure of miscibility increase. For certain processes, the anion can be designed to suit the needed property.

From the experimental data, the systems of 1-*n*-alkyl-3-methyl-imidazolium ILs and R-134a are believed to be classified as a Type V system (see Figure 2). The Type IV system is similar, but exhibits another lower temperature region of liquid-liquid immiscibility and VLLE ending at another UCEP. Phenyloctane and R-134a are a Type IV system and the difference between the lower-branch of the UCEP and the LCEP is 29°C.[31] The VLE region for the ILs and R-134a was confirmed experimentally to 0°C with no occurrence of liquid immiscibility; this is about 38–60°C below the LCEP of all ILs tested. Although cryogenic temperatures are beyond the capabilities of the experimental equipment, the current data and equation of state predictions for similar systems[10] indicate solely Type V behavior.

Conclusion

The global phase behavior and equilibria of [HMIm][Tf_2N], [HMIm][PF_6], [HMIm][BF_4], and [BMIm][PF_6] with the refrigerant gas, R-134a were measured. Regions of multiphase equilibria exist, viz. VLE, LLE, and VLLE. This phase behavior indicates that this is a Type V system according to the classification of Scott and van Konynenburg. The LCEP temperature increases and the mixture critical pressures decrease with increasing the alkyl-group on the cation. The anion has a more pronounced effect: the LCEP temperature increases and the mixture critical pressures decrease in the order of [BF_4], [PF_6], and [Tf_2N]. These data will allow the proper design of various processes that utilize ILs with refrigerant gases, such as absorption refrigeration.

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