Phase Behavior of Carbon Dioxide in Ionic Liquids: [emim][Acetate], [emim][Trifluoroacetate], and [emim][Acetate] + [emim][Trifluoroacetate] Mixtures

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The solubility (vapor−liquid equilibria) of carbon dioxide (CO_2) has been measured in ionic liquids, 1-ethyl-3-methylimidazolium acetate ([emim][Ac]), 1-ethyl-3-methylimidazolium trifluoroacetate ([emim][TFA]), and a mixture containing a fixed mole ratio of 49.98 ([emim][Ac])/50.02 ([emim][TFA]) using a gravimetric microbalance at three temperatures (298.1, 323.1, and 348.1) K and pressures up to about 2 MPa. The [emim][Ac] strongly (chemically) absorbed CO_2 with hardly any vapor pressure above the mixture up to about 20 % mole fraction of CO_2 at 298.1 K. The [emim][TFA] did not show the same behavior and physically absorbed CO_2. The ionic liquid mixture containing equimolar amounts of [emim][Ac] and [emim][TFA] showed a combination of both chemical and physical effects, and the CO_2 solubility was well predicted at a fixed pressure using either a molar average of the pure component solubilities or a model based on linear isobaric lines in the ternary phase diagram. The binary pressure−temperature (*PTx*) data at 298.1 K have also been analyzed by use of an equation-of-state (EOS) model, and predictions at higher temperatures and of the ternary system are reasonable.

Introduction

The present report is a continuation of our previous studies on the solubility of carbon dioxide (CO_2) in room-temperature ionic liquids (RTILs).[1−5] RTILs are molten salts at room temperature, and various applications have been proposed for this new class of compounds during the past several years.[6,7] Among the many potential applications, a promising application may be the capture of gases such as CO_2, H_2S, and SO_2 from fossil fuel burning, electric power plant emissions using the unique absorption characteristics, and low volatility of RTILs.[8] Although there are commercially available organic solvents to capture these flue gases (e.g., monoethanolamine), the energy penalty associated with such processes is still uneconomical.[9] Therefore, new solvents are required, and RTILs may provide a more energy efficient and environmentally friendly alternative.

To efficiently capture acid or sour gases from flue gas streams requires a solvent with strong absorption because of the relatively small partial pressures (e.g., in the case of CO_2, volume fractions of (5 to 15) % CO_2 at atmospheric pressure) of the gases in these streams. We define strong absorption to mean "chemical" absorption (or reversible chemical complex formation) versus simple "physical" absorption (or no chemical reactions). It is well-known that CO_2 possesses relatively high solubility in RTILs; however, most of the literature provides only examples of physical absorption.[1,2,5,6,10−19] In our previous work,[3,4] we show RTILs that contain the acetate anion [CH_3−COO^-] and exhibit a strong absorption for CO_2, and to the best of our knowledge, only a few examples have been reported.[8,20] We have also shown that the strong absorption can be analyzed using an ideal association model and that two types of complex formation are possible.[4]

The purpose of the present study is to compare the CO_2 solubility of the chemically absorbing ionic liquid, 1-ethyl-3-methylimidazolium acetate ([emim][Ac]), with the physically absorbing ionic liquid, 1-ethyl-3-methylimidazolium trifluoroacetate ([emim][TFA]), as a function of temperature at (298 to 348) K, and this is an extension of our previous work[4] at a single temperature of 298 K. In addition, the CO_2 solubility for a binary mixture containing equimolar amounts of both ionic liquids (a fixed mole ratio of 49.98 ([emim][Ac])/50.02 ([emim][TFA])) was measured over the same temperature range to determine whether the gas solubility for the pure ionic liquids can be used to predict the gas solubility for the mixed ionic liquid system. Methods based on the molar averages of the binary CO_2 solubility and pressure data as well as predictions using an equation of state (EOS) model will be discussed.

Experimental

Materials. Carbon dioxide (purity > 99.99 %, CAS no. 124-38-9) was purchased from MG Industries (Philadelphia, PA). The [emim][Ac] (assay ≥ 95 %, $C_8H_{14}N_2O_2$, CAS no. 143314-17-4, Lot and Filling code S25819 14804B38) was obtained from Fluka/Aldrich (Buchs, Switzerland). The [emim][TFA] (assay ≥ 95 %, $C_8H_{11}F_3N_2O_2$, CAS no. 174899-65-1, Lot and Filling code S4934747 814) was obtained from EMD Chemicals, Inc. (Gibbstown, New Jersey). Figure 1 provides the chemical structures for the [emim][Ac] and [emim][TFA]. The [emim][Ac] and [emim][TFA] samples were 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 ionic liquids were completely evacuated using a turbopump (Pfeiffer, model TSH-071) to a pressure of about $4 \cdot 10^{-7}$ kPa

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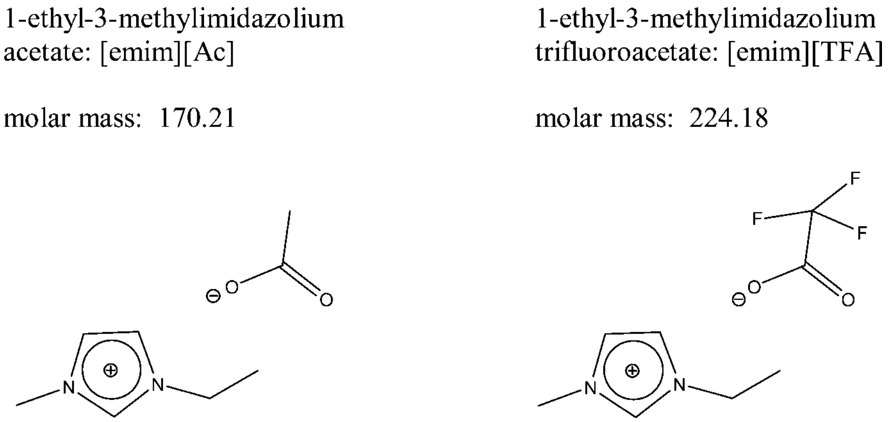

Figure 1. Chemical structures and molar mass of [emim][Ac] and [emim][TFA].

while simultaneously heating and stirring the ionic liquid at a temperature of about 348 K for 5 days. The final mass fraction of water was measured by Karl Fischer titration (Aqua-Star C3000, solutions AquaStar Coulomat C and A), and the dried [emim][Ac] and [emim][TFA] samples contained mass fractions of (1276 and 1339)$\cdot 10^{-6}$ H_2O, respectively. Three mixtures containing [emim][Ac] and [emim][TFA] were prepared in a nitrogen purged glovebox from the dried samples. The mixtures contained mole fractions of (24.64, 50.02, and 74.68) % [emim][TFA].

Experimental Method. Detailed descriptions of experimental equipment and procedures for the gas solubility (vapor−liquid equilibria) measurements are given in our previous reports;[1,21] therefore, only the basic experimental techniques and measurement uncertainties are presented here.

The gas solubility measurements were made using a gravimetric microbalance (Hiden Isochema Ltd., IGA 003, Warrington, United Kingdom).[1] A molecular sieve trap was installed to remove trace amounts of impurities from the CO_2. Initially, about 70 mg of ionic liquid 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 and/or other volatile impurities. The final mass fraction loss after drying for the [emim][TFA] and [emim][Ac] was (2.4 and 5.8) %, respectively. Similar to our findings with 1-butyl-3-methylimidazolium acetate [bmim][Ac],[3] we believe that a portion of the mass loss for the [emim][Ac] was due to the initial water content (as received, water mass fraction was $5\cdot 10^{-3}$), and the remaining mass loss was due to the non-negligible vapor pressure.

The IGA003 apparatus can operate in both dynamic (continuous gas flow) and static (intermittent gas flow) modes. Absorption and desorption measurements were performed in static mode in this study. The sample temperature was measured with a type K thermocouple with an uncertainty of ± 0.1 K. The 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 uncertainty to ± 0.005 K. Three isotherms of about (298.1, 323.1, and 348.1) K were measured beginning with 298.1 K for both the [emim][Ac] and [emim]TFA] ionic liquids. Pressures from (10^{-2} to 2.0) 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 also a NIST certified secondary pressure standard with a traceable uncertainty of 0.008 % of full scale. The upper pressure limit of the microbalance reactor was 2.0 MPa, and solubilities at several isobars up to 2.0 MPa [(0.01, 0.05, 0.1, 0.4, 0.7, 1.0, 1.3, 1.5, and 2.0) MPa] were measured in the present study. In our previous reports,[1,2,5,21] to ensure sufficient time for VLE, each T,P condition was maintained for a minimum of 3 h with a maximum time of 8 h. In this work, a maximum of 10 h was set for isotherms measured at (323 and 348) K and 20 h for the 298 K isotherm. In addition to the isotherms measured for the pure ionic liquids ([emim][Ac] and [emim][TFA]), the CO_2 solubility for a RTIL mixture containing a fixed mole ratio of 49.98 ([emim][Ac])/50.02 ([emim][TFA]) was measured over the same temperature range, (298.1, 323.1, and 348.1) K.

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 solubility data due to both random and systematic uncertainties have been estimated to be less than 0.006 mole fraction at given T and P except for low temperature and pressure (298 K, < 1 MPa) cases where hysteresis between absorption and desorption can significantly increase the estimated uncertainties.[3] Another large source of uncertainty in the present solubility experiments is due to the buoyancy correction in the data analysis.[1,21] Analysis of the buoyancy effects requires an accurate measurement of the ionic liquid density and CO_2 gas density.[22] Liquid density data for [emim][Ac], [emim][TFA], and mixed ionic liquids prepared containing mole fractions of (24.64, 50.02, and 74.68) % [emim][TFA] were measured using a 1.0 mL pycnometer (1.053 ± 0.001) cm^3 at 298.15 K. The liquid density data are provided in Table 1, and the uncertainty in the measurement was ± 0.003 g$\cdot$cm^{-3}. The data were well correlated using linear regression as a function of temperature, as shown in Figure 2 for the pure ionic liquids: [emim][Ac] $\rho/\mathrm{g\cdot cm^{-3}} = 1.2684 - 5.620\cdot 10^{-4}\, T/\mathrm{K}$; [emim][TFA] $\rho/\mathrm{g\cdot cm^{-3}} = 1.5076 - 6.948\cdot 10^{-4}\, T/\mathrm{K}$. The mixture results shown in Figure 2 were modeled using the following relationship

$$\rho_{\mathrm{mix}} = 1/\left(\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}\right) \tag{1}$$

where subscripts 1 and 2 are for [emim][Ac] and [emim][TFA], respectively; w_i is a mass fraction of the ith species; and eq 1 is derived from an assumption of the ideal molar volume of mixtures (i.e., zero excess molar volume).

A detailed description of the buoyancy correction is given in our previous reports.[1,21] The corrected solubility (PTx) data for the binary systems (CO_2 + [emim][Ac] and CO_2 + [emim][T-

Table 1. Experimental Density Data for [emim][TFA] (1) + [emim][Ac] (2)

T/K	$100x_1$	ρ/g·cm^{-3}
298.1	0.00	1.102
298.1	24.64	1.152
298.1	50.02	1.204
298.1	74.68	1.252
298.1	100.00	1.301
323.1	0.00	1.086
323.1	24.64	1.136
323.1	50.02	1.189
323.1	74.68	1.235
323.1	100.00	1.283
348.1	0.00	1.073
348.1	24.64	1.121
348.1	50.02	1.172
348.1	74.68	1.217
348.1	100.00	1.264
373.1	0.00	1.059
373.1	24.64	1.107
373.1	50.02	1.157
373.1	74.68	1.202
373.1	100.00	1.250

FA]) and ternary system (CO_2 + [emim][Ac] + [emim][TFA]) are provided in Tables 2 and 3, respectively. Solubility data at 298.1 K (Table 2) are previously reported in ref 4 and are reproduced here for comparison with the higher temperature data (323.1 and 348.1) K.

Discussion

Similar to our previous work[3] of the CO_2 solubility in 1-butyl-3-methylimidazolium acetate [bmim][Ac], we have found that CO_2 strongly (chemically) absorbs in the ionic liquid [emim][Ac].[4] Figure 3a shows this highly unusual (nonideal) phase behavior, and at low CO_2 concentrations [$100x_1$ < 15 mole fraction at (298, 323, and 348) K], the binary mixtures have hardly any vapor pressures, reflecting a strong attractive (or complex formation) interaction between the CO_2 and [emim][Ac]. A separate absorption−desorption experiment was conducted at 298.1 K (Figure 3b) to show that the complex is reversible (i.e., desorption measurements are within the experimental uncertainty of the absorption measurements). This behavior is similar to what we have previously described for the CO_2 and [bmim][Ac] system,[3] where a highly asymmetric phase behavior with respect to concentration was reported. Such a phase behavior is extremely rare,[23] and one of the few known examples is a binary system of HCl and water.[23,24] Furthermore, reversible complex formation of AB_2 (A = CO_2 and B = [bmim][[Ac]) was reported for the strong absorption.[4] In the

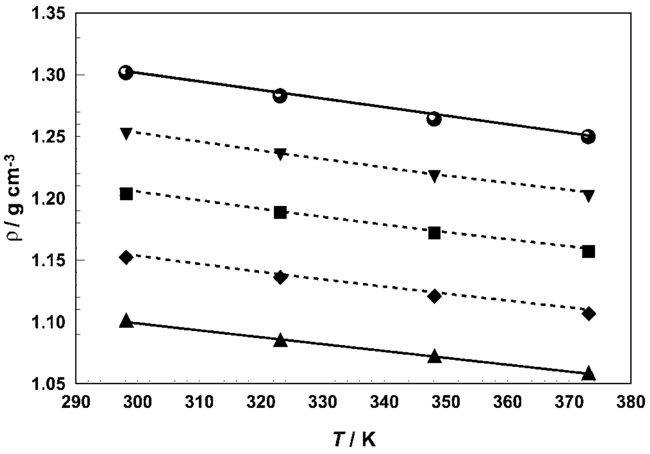

Figure 2. Liquid density measurements for [emim][Ac], [emim][TFA], and binary mixtures ([emim][Ac] + [emim][TFA]) from (298.15 to 373.15) K. Symbols: experimental data, ●, pure [emim][TFA]; ▼, mixture containing mole fractions of 25.32 % [emim][Ac] + 74.68 % [emim][TFA]; ■, mixture containing mole fractions of 49.98 % [emim][Ac] + 50.02 % [emim][TFA]; ♦, mixture containing mole fractions of 75.36 % [emim][Ac] + 24.64 % [emim][TFA]; and ▲, pure [emim][Ac]. Solid lines: linear T correlations; dashed lines are calculated using weight fraction average (eq 1). See text for details.

Table 2. Experimental Solublity (*PTx*) Data for CO_2 + [emim][Ac] and CO_2 + [emim][TFA][a]

CO_2 (1) + [emim][Ac] (2)			CO_2 (1) + [emim][TFA] (2)		
T/K	P/MPa	$100x_1$	T/K	P/MPa	$100x_1$
298.1	0.0100	18.9	298.1	0.0100	0.1
298.1	0.0499	24.6	298.1	0.0498	0.9
298.1	0.1000	26.7	298.1	0.0998	1.8
298.1	0.3996	31.3	298.1	0.3999	6.8
298.1	0.6995	34.0	298.1	0.6997	11.5
298.1	0.9996	36.2	298.1	0.9999	16.0
298.1	1.2998	38.4	298.1	1.2997	20.1
298.1	1.4997	39.8	298.1	1.4998	22.6
298.1	1.9998	42.8	298.1	1.9996	28.2
323.1	0.0100	13.8	323.1	0.0100	0.4
323.1	0.0499	20.3	323.1	0.0499	0.9
323.1	0.1000	23.0	323.1	0.1000	1.5
323.1	0.4000	28.5	323.1	0.4000	4.4
323.1	0.7000	31.4	323.1	0.7000	7.2
323.1	1.0001	33.6	323.1	1.0001	10.4
323.1	1.2997	35.0	323.1	1.2997	13.4
323.1	1.4998	36.1	323.1	1.4998	15.6
323.1	1.9996	39.0	323.1	1.9996	20.0
348.1	0.0101	9.4	348.1	0.0101	0.6
348.1	0.0501	15.7	348.1	0.0501	1.0
348.1	0.1002	18.6	348.1	0.1002	1.3
348.1	0.3997	24.1	348.1	0.3997	3.2
348.2	0.6996	26.4	348.2	0.6996	5.0
348.1	0.9998	28.0	348.1	0.9998	7.0
348.1	1.2996	29.4	348.1	1.2996	9.5
348.2	1.4997	29.8	348.1	1.4997	10.8
348.2	1.9996	32.1	348.2	1.9996	14.4

[a] Data at T = 298.1 K were taken from ref 4.

Table 3. Experimental Solubility (*PTx*) Data for CO_2 (1) + [emim][Ac] (2) + [emim][TFA] (3)[a]

T/K	P/MPa	$100x_1$
298.1	0.0101	10.6
298.1	0.0501	14.6
298.1	0.1001	16.4
298.1	0.3997	21.5
298.2	0.6996	25.0
298.1	0.9997	28.2
298.1	1.2996	31.0
298.1	1.4995	32.7
298.1	1.9995	37.1
323.1	0.0100	6.3
323.1	0.0500	10.5
323.1	0.1001	12.4
323.1	0.4000	17.1
323.1	0.6996	19.9
323.1	0.9996	22.3
323.1	1.2998	24.6
323.1	1.4998	25.8
323.1	1.9996	29.1
348.1	0.0102	4.5
348.1	0.0501	8.1
348.1	0.1002	9.9
348.1	0.4000	14.1
348.1	0.7000	16.0
348.2	0.9998	17.6
348.0	1.2997	18.9
348.1	1.4998	19.6
348.1	1.9995	22.3

[a] Ionic liquid mixture with a fixed mole ratio of 49.98 ([emim][Ac])/ 50.02 ([emim][TFA]).

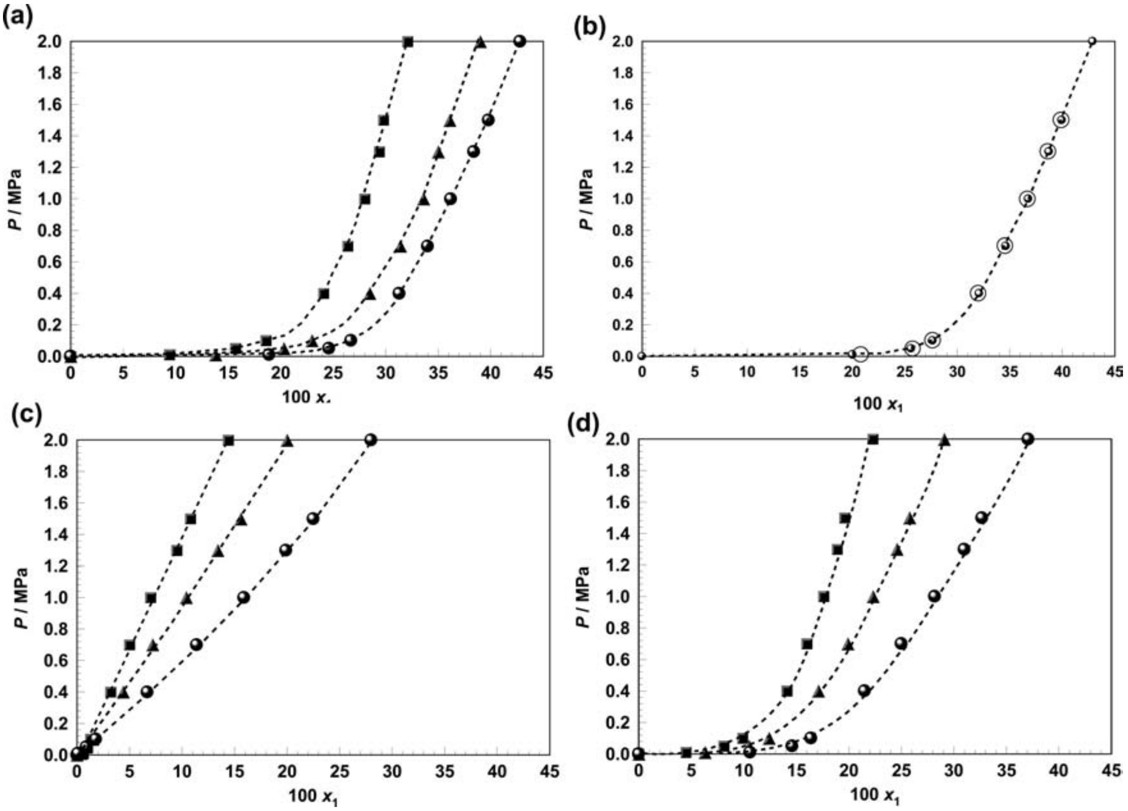

Figure 3. *PTx* phase diagrams of (a) CO_2 (1) + [emim][Ac] (2), (b) CO_2 (1) + [emim][Ac] (2) (absorption and desorption data), (c) CO_2 (1) + [emim][TFA] (2), (d) CO_2 (1) + [emim][Ac] (2) + [emim][TFA] (3) ionic liquid mixture with a constant mole ratio of [emim][Ac]/[emim][TFA] = 49.98/50.02. Symbols, experimental data: ●, absorption at 298.1 K; ○, desorption at 298.1 K; ▲, absorption at 323.1 K; and ■, absorption at 348.1 K using gravimetric measurement; dashed lines, trend lines.

present case, the CO_2 (A) and [emim][Ac] (B) are also forming a complex (AB_2)[4] which may be due to a Lewis acid base reaction.

The strong attraction is dramatically reduced when the acetate anion (X-COO^-) methyl group (X = CH_3) is replaced with the fluorinated methyl group (X = CF_3) as shown in Figure 3c. The isotherms for CO_2 and [emim][TFA] are essentially linear, indicating physical absorption.[4] It is known that the CF_3 group withdraws electron density from the COO^- moiety and will reduce the Lewis basicity of the anion.[25] If CO_2 is functioning as a Lewis acid, then this could explain the reduction in solubility (i.e., complex formation) and ideal phase behavior with [emim][TFA].

The excess molar volumes for the binary ionic liquid mixture ([emim][Ac] + [emim][TFA]) were calculated using the liquid density data provided in Table 1. The excess molar volumes were very small, (0.2 to 0.4) $cm^3 \cdot mol^{-1}$, relative to the total molar volumes for the mixture, (154 to 179) $cm^3 \cdot mol^{-1}$. Thus, the mixture′s molar volumes are very close to the molar average of the two ionic liquids, and the ([emim][Ac] + [emim][TFA]) binary system may be treated as an "ideal" mixture, which is consistent with eq 1 (see Figure 2).

Solubility isotherms were measured for a ternary mixture (CO_2 + [emim][Ac] + [emim][TFA]) with a fixed mole ratio of 49.98/50.02 for [emim][Ac]/[emim][TFA] as shown in Figure 3d, to determine whether the solubility of CO_2 can be predicted using only the measured binary data. Three methods to correlate the solubility data for CO_2 + [emim][Ac] + [emim][TFA] were examined. In method 1, we take the mole fraction average of the compositions assuming a 1:1 molar ratio for [emim][Ac]:[emim][TFA]; x_{1c} (CO_2 mole fraction in the ternary system) = $(x_{1a} + x_{1b})/2$ at constant *T* and *P*, where x_{1a} (CO_2 mole fraction in [emim][TFA]) and x_{1b} (CO_2 mole fraction in [emim][Ac]). In method 2, we assume that the VLE isobaric lines are linear and a 1:1 mole ratio for [emim][Ac]: [emim][TFA]. To visualize method 2, we provide Figure 4 with the following conditions:

(1) At a given *T* and *P*, CO_2 solubilities in both pure ionic liquids are known: Points A and B in Figure 4; CO_2 solubilities in [emim][TFA] and [emim][Ac] are x_{1a} and x_{1b}, respectively.

(2) The mixed ionic liquid solution has a constant mixing ratio (*r*): [emim][Ac]:[emim][TFA] = *r*:1.

(3) At a given constant *T*, a VLE isobaric curve is, however, unknown, except for the two points A and B. Since both CO_2 + [emim][TFA] and [emim][TFA] + [emim][Ac] binary

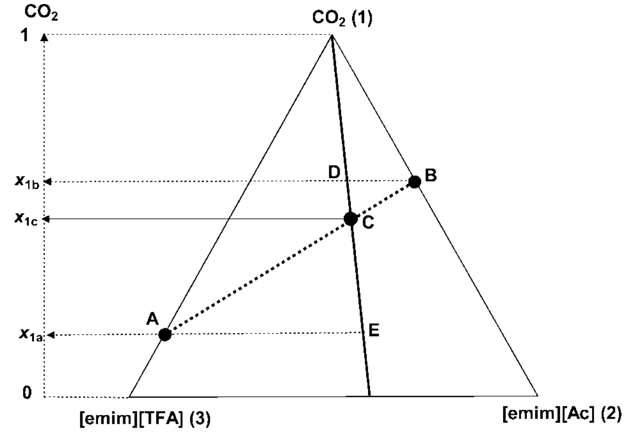

Figure 4. Schematic ternary *PTx* diagram (geometrical relationships) for CO_2 (1) + [emim][Ac] (2) + [emim][TFA] (3) at constant *T* and *P*. Thick solid line: ionic liquid mixture with a constant mole ratio of [emim][Ac]/[emim][TFA] = *r* = 1. Thick broken line (AB): isobaric VLE (bubble) points at a given *T*.

systems may be considered to be nearly ideal solutions, we assume that the VLE isobaric curve connecting points A and B is a straight line (AB).

Then, we have to find out the CO_2 composition (solubility: x_{1c}) at point C. From geometrical relations in Figure 4, the following proportionality holds:

$$\frac{\overrightarrow{\mathrm{DB}}}{\overrightarrow{\mathrm{AE}}} = \frac{\overrightarrow{\mathrm{CB}}}{\overrightarrow{\mathrm{CA}}} = \frac{x_{1b} - x_{1c}}{x_{1c} - x_{1a}} \tag{2}$$

$\overrightarrow{\mathrm{DB}}$ and $\overrightarrow{\mathrm{AE}}$ are given by elementary geometrical algebra

$$\overrightarrow{\mathrm{DB}} = \frac{2(1 - x_{1b})}{\sqrt{3}} \frac{1}{1 + r} \tag{3}$$

$$\overrightarrow{\mathrm{AE}} = \frac{2(1 - x_{1a})}{\sqrt{3}} \frac{r}{1 + r} \tag{4}$$

Using eqs 2 to 4, we obtain

$$\frac{1 - x_{1b}}{r(1 - x_{1a})} = \frac{x_{1c} - x_{1b}}{x_{1a} - x_{1c}} \tag{5}$$

Solving x_{1c} for eq 5

$$x_{1c} = \frac{x_{1a}(1 - x_{1b}) + r x_{1b}(1 - x_{1a})}{r(1 - x_{1a}) + 1 - x_{1b}} \tag{6}$$

This is the answer for a general r value. When $r = 1$ (equal mole ratio), eq 6 becomes

$$x_{1c} = \frac{x_{1a} + x_{1b} - 2x_{1a}x_{1b}}{2 - x_{1a} - x_{1b}} \tag{7}$$

In method 3, we fix the molar composition and take the mole fraction average of the pressure assuming a 1:1 molar ratio for [emim][Ac]:[emim][TFA]; $P = (P_1 + P_2)/2$, where P_1 (CO_2 + [emim][Ac]) and P_2 (CO_2 + [emim][TFA]) are at a given temperature and composition (see Appendix for details).

Figure 5 compares the calculated results using methods 1 and 2 with the measured binary and ternary systems at (298.1, 323.1, and 348.1) K. The relative AAD (relative absolute average deviation, $(\sum_1^n |1 - (x_{1,\mathrm{obs}}/x_{1,\mathrm{cal}})|/n)$ using method 1 was 0.62 at 298.1 K, 0.16 at 323.1 K, and 0.51 at 348.1 K. The relative AAD using method 2 was 0.29 at 298.1 K, 0.69 at 323.1 K, and 1.04 at 348.1 K. Both methods provide good predictions for the experimentally measured ternary system using only binary composition data at a fixed pressure. However, method 3 badly failed to correlate the experimental measurements, and a few calculated points are shown in Figure 5. The condition when method 3 is valid is shown in the Appendix.

Experimental solubility (VLE) data have also been analyzed using a generic RK (Redlich−Kwong) type of cubic equation of state (EOS), which is written in the following form

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \tag{8}$$

Detailed descriptions of how to model VLE for binary systems (i.e., CO_2 + [emim][Ac] and CO_2 + [emim][TFA]) have been described in our previous works;[1−4,26,27] therefore, only basic information is provided here. In this work, EOS parameters for

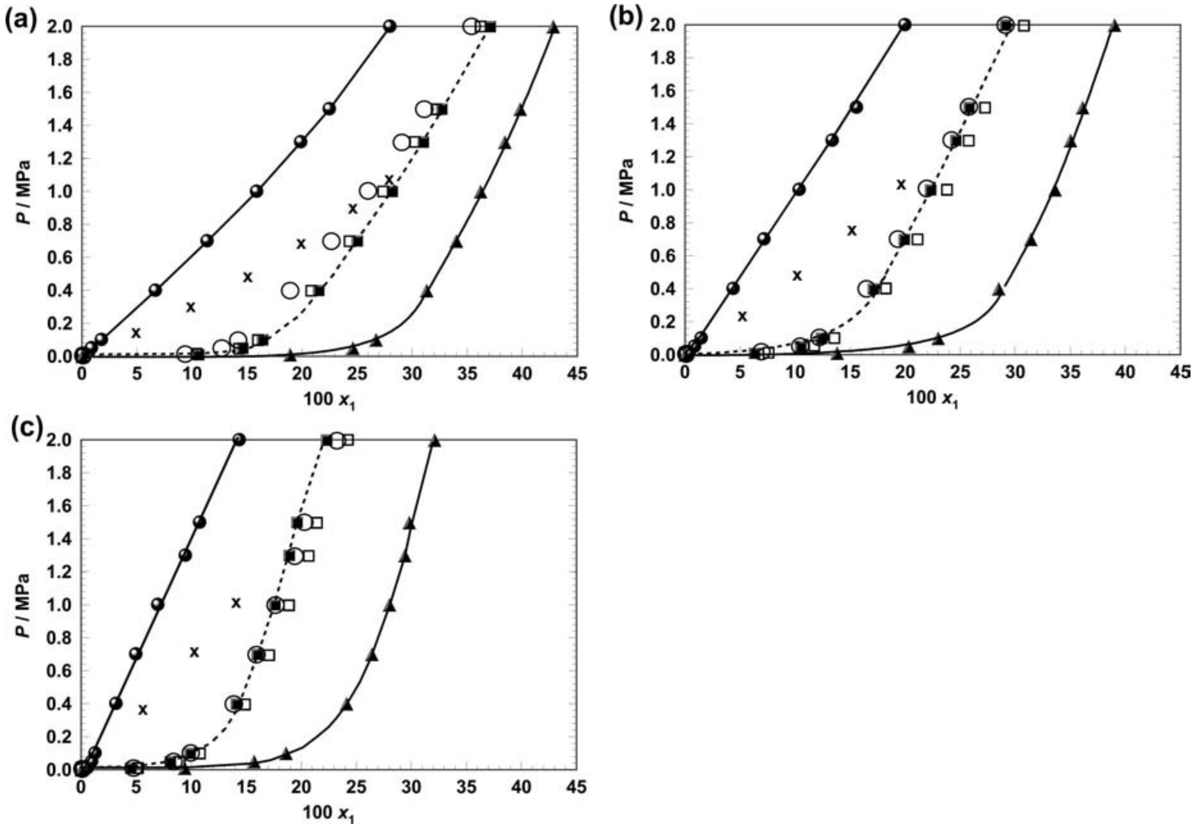

Figure 5. *PTx* phase diagrams of a CO_2 (1) + [emim][Ac] (2), CO_2 (1) + [emim][TFA] (2), and CO_2 (1) + [emim][Ac] (2) + [emim][TFA] (3) ionic liquid mixture with a constant mole ratio of 49.98 ([emim][Ac])/50.02 ([emim][TFA]) at (a) 298.1 K, (b) 323.1 K, and (c) 348.1 K. Filled symbols, experimental data: ●, [emim][TFA]; ■, [emim][Ac] + [emim][TFA]; and ▲, [emim][Ac] using gravimetric measurement. Open symbols, calculations: ○, method 1 based on mole fraction average ($x_{1c} = (x_{1a} + x_{1b})/2$) at constant T and P; □, method 2 based on linear isobaric lines (eq 7: $x_{1c} = (x_{1a} + x_{1b} - 2x_{1a}x_{1b})/(2 - x_{1a} - x_{1b})$ at constant T and P; ×, method 3 based on (eq A1: $P_C = (P_A + P_B)/2$); dashed and solid lines, trend lines; see text for details.

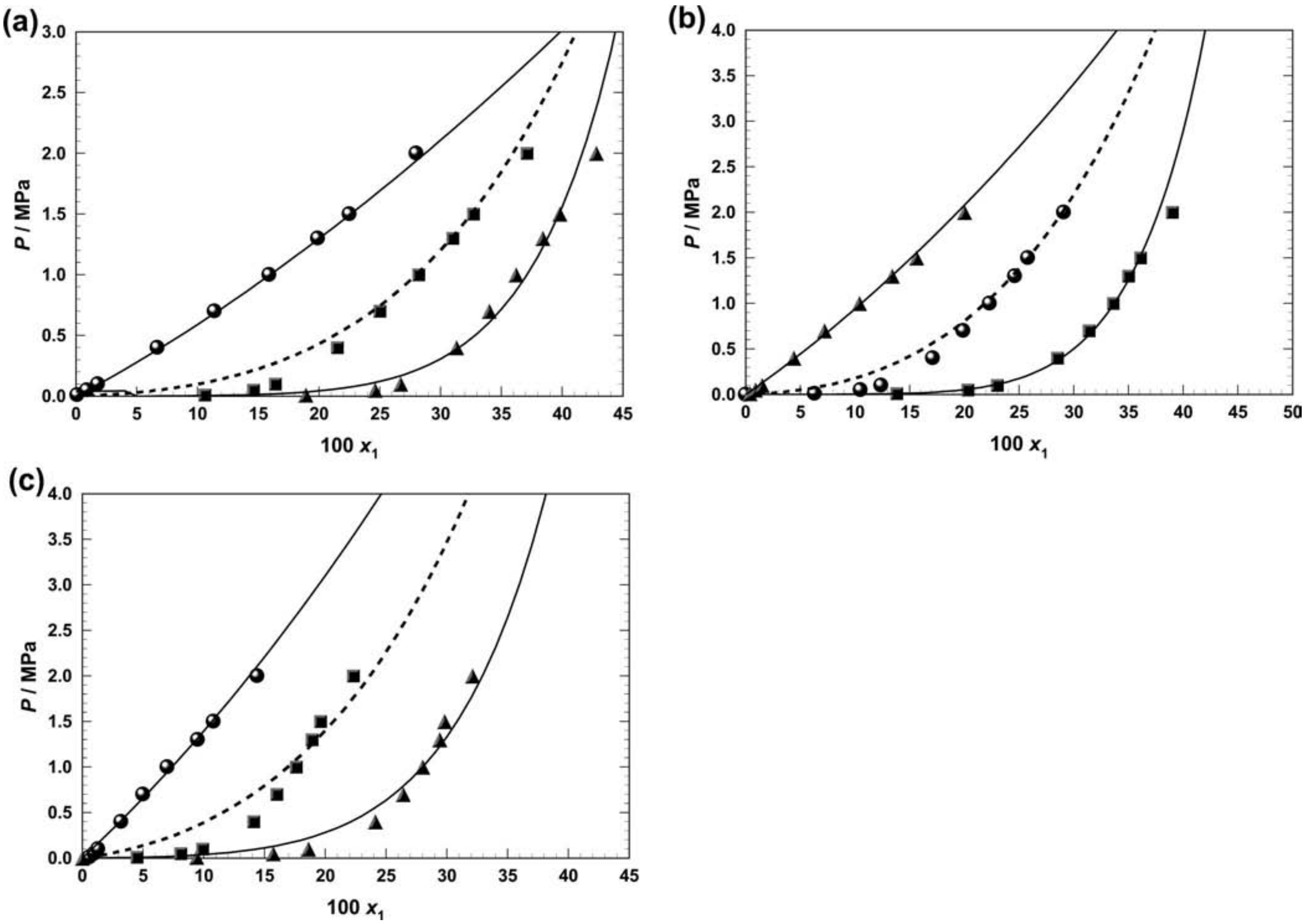

Figure 6. *PTx* phase diagrams of CO_2 (1) + [emim][Ac] (2), CO_2 (1) + [emim][TFA] (2), and CO_2 (1) + [emim][Ac] (2) + [emim][TFA] (3) ionic liquid mixture with a constant mole ratio of [emim][Ac]/[emim][TFA] = 49.98/50.02 at (a) 298.1 K, (b) 323.1 K, and (c) 348.1 K. Symbols, experimental data: ●, [emim][TFA]; ■, [emim][Ac] + [emim][TFA]; and ▲, [emim][Ac] using gravimetric measurement; dashed and solid lines, EOS calculations; see text for details.

these binary systems were taken from our previous report[4] at 298.1 K and applied here at the present temperatures, (298.1, 323.1, and 348.1) K, to make predictions of VLE. Interactions between the two ionic liquids can be considered nearly ideal (i.e., $k_{ij} = 0$, $m_{ij} = 0$, and $\tau_{ij} = 0$).[4,26,27] Figure 6 compares the EOS results with the measured binary and ternary systems over a range of temperatures, (298.1, 323.1, and 348.1) K. Predictions of the binary VLE (CO_2 + [emim][Ac] and CO_2 + [emim][TFA]) at higher temperatures of (323.1 and 348.1) K are quite good considering the EOS parameters were developed at 298.1 K. The predictions of the ternary system at low temperatures, (298.1 and 323.1) K, are reasonable, and relatively large deviations at 348.1 K (particularly at low CO_2 concentrations) may be due to the use of EOS parameters for 298.1 K.

Conclusions

The solubility of CO_2 has been measured over a range of temperatures, (298.1, 323.1, and 348.1) K, and pressures up to about 2 MPa for [emim][Ac], [emim][TFA], and a RTIL mixture containing a fixed mole ratio of 49.98 ([emim][Ac])/50.02 ([emim][TFA]). The [emim][Ac] exhibits strong chemical absorption for CO_2, which is reversible and similar to our previous measurements with [bmim][Ac].[3,4] The phase behavior belongs to an extremely rare case where the CO_2 solubility is highly asymmetric with respect to CO_2 concentration; refer to ref 3. The high solubility measured between CO_2 and the [emim][Ac] is dramatically reduced when the acetate anion methyl group (CH_3-COO^-) is replaced with a fluorinated methyl group (CF_3-COO^-). The CF_3 group withdraws electron density reducing the Lewis basicity of the anion and thus reducing the chemical complex formation and CO_2 solubility. The CO_2 solubility for the ternary mixture is reasonably well predicted using either a mole fraction average of the measured binary pair compositions or a model assuming that the VLE isobaric lines are linear at constant *T* and *P*. This fact indicates that the actual VLE isobaric (bubble) point curve in the ternary phase diagram is nearly a straight line at a given temperature studied here. Predictions for the ternary system (CO_2 + [emim][Ac] + [emim][TFA]), based on the equation-of-state model developed in our previous work at 298.1 K,[4] are also reasonable.

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Appendix

"Method 3" to Predict a Ternary Phase Diagram Based on Binary Systems.

Suppose we have VLE data for two binary systems, [C1] + [C2] and [C1] + [C3], at a given *T*. At a given mole fraction x([C1]), $P_A = P$([C1] + [C2]) and $P_B = P$([C1] + [C3]). Then, a ternary system, where [C1] is mixed with [C2] + [C3]

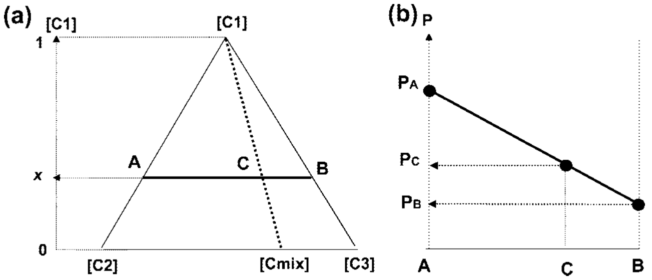

Figure A1. (a) Schematic ternary composition diagram at a given *T*. (b) Cross-section of ACB in (a) projected on the *Px* plane.

mixtures (a constant mole ratio of [C2]:[C3] = 1:1, a vapor pressure, P_C, at this *T*), and *x*([C1]) may be given under a certain condition by

$$P_C = \frac{P_A + P_B}{2} \qquad \text{(A1)}$$

Here, a question is what condition satisfies eq A1. To solve this problem, Figure A1 is prepared. Figure A1a is a ternary phase diagram at a given *T*, and *x* is a mole fraction of [C1]. Figure A1b presents a cross-section of ACB in Figure A1a, which is projected on a *Px* plane. P_A and P_B are known here (or given), but a pressure curve connecting A and B (inside the ternary region) is unknown and can be any form. Let's consider the simplest case: a linear line with respect to a variable ratio (*r* : 1) of [C2] and [C3].

Then, the following relation (proportionality) holds, having AC/BC = *r*

$$\frac{P_A - P_C}{P_A - P_B} = \frac{r}{1 + r} \qquad \text{(A2)}$$

By solving P_C for eq A2, we obtain

$$P_C = \frac{P_A}{1 + r} + \frac{rP_B}{1 + r} \qquad \text{(A3)}$$

With $r = 1$ (mixtures with equal mole ratio of [C2] and [C3]), eq A3 becomes eq A1. It should be noted that eq A3 holds for any binary pressure curves of P_A and P_B; e.g., both are linear w.r.t. *x*([C1]), one is linear and the other is quadratic, or both are quadratic, etc.

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