High-Pressure Phase Behavior of Systems with Ionic Liquids: Part V. The Binary System Carbon Dioxide + 1-Butyl-3-methylimidazolium Tetrafluoroborate

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The phase behavior of the binary system consisting of the supercritical fluid carbon dioxide (CO_2) and the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) was studied experimentally. A synthetic method was used to measure its phase behavior. Bubble-point pressures of the system CO_2 + [bmim][BF_4] are reported for carbon dioxide concentrations ranging from (10.22 to 60.17) mole % and within a temperature range of (278.47 to 368.22) K. The CO_2 + [bmim][BF_4] binary system has a two-phase liquid−vapor region extending up to very high pressures. Most likely, the type of fluid-phase behavior is type III according to the classification of Scott and Van Konynenburg. The experimental results obtained were compared with the available phase behavior data of the binary system CO_2 + 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]) to investigate the effect of the length of the alkyl group on the phase behavior of this type of system. A larger alkyl group leads to lower bubble-point pressures and, therefore, to higher solubilities of carbon dioxide in the imidazolium-based ionic liquid.

Introduction

Ionic liquids have been described as novel environmentally benign solvents because of their remarkable characteristics.[1] Ambient-temperature ionic liquids are molten salts that are liquid at room temperature. The key property is that the vapor pressure of ionic liquids is negligibly small. As a result, ionic liquids do not evaporate even when exposed to vacuum, they do not combust, and they are odorless. The fact that ionic liquids are nonvolatile and nonflammable makes them a safer and more environmentally benign solvent for reactions and separations than the traditional volatile organic solvents. The ionic liquid can be recycled and reused, without leading to solvent emissions into the atmosphere. Moreover, ionic liquids do not cause solvent contamination when the product is separated via the vapor phase because they cannot evaporate. Other advantages that distinguish ionic liquids from traditional solvents are inherent to salts in the liquid state and include the wide temperature range allowing tremendous kinetic control in reactions, the good thermal stability, the high ionic conductivity, and the wide electrochemical window representing the high electrochemical stability of ionic liquids against oxidation or reduction reactions. Furthermore, ionic liquids have very good solvency power for both organic and inorganic materials, polar and nonpolar, which makes them suitable for catalysis. It is possible to tune the physical and chemical properties of ionic liquids by varying the nature of the anions and cations. In this way, ionic liquids can be made task-specific for a certain application. Applications include the use of ionic liquids as electrolytes in electrochemical devices, as solvents in chemical synthesis and catalysis and separation technology, and as lubricants or heat-transfer fluids.[2,3]

The number of articles about ionic liquids is steadily growing. Many articles on the synthesis of ionic liquids,[4−6] the physical and chemical properties of ionic liquids,[7−11] and the application of ionic liquids as reaction media in catalytic reactions[12−16] have been written. However, studies on the phase behavior of ionic liquids in the presence of supercritical fluids are scarce. Brennecke and co-workers showed the first results on the phase behavior of ionic liquids in the presence of supercritical carbon dioxide.[17−19] They showed that it was possible to extract a solute from an ionic liquid using supercritical carbon dioxide without any contamination by the ionic liquid. The reason is that carbon dioxide is not able to dissolve any ionic liquid. Later on, they also described a new method to separate ionic liquids from organic solvents[20] or water[21,22] using carbon dioxide as a separation switch. When carbon dioxide is pressed into the mixture, an additional liquid phase is formed that is rich in ionic liquid, even when the original solution is quite dilute in ionic liquid. Further pressurization leads to the disappearance of the vapor phase at the point, where the organic-rich phase merges with the vapor phase. At this moment, the last traces of ionic liquid that remained in the organic-rich liquid phase are expelled, and the resulting supercritical carbon dioxide/organic phase contains no detectable ionic liquid.

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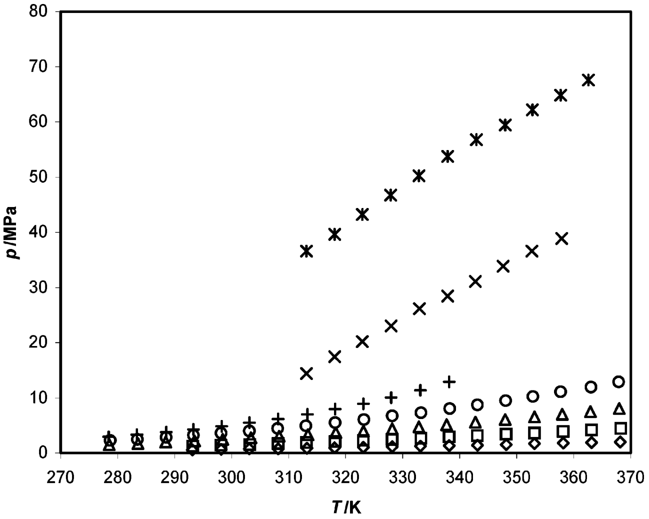

Figure 1. Experimentally determined isopleths for several compositions of carbon dioxide (mole %) in the system CO_2 + [bmim][BF_4]: ◇, 10.22% CO_2; □, 19.98% CO_2; △, 30.35% CO_2; ○, 40.05% CO_2; +, 48.25% CO_2; ×, 55.07% CO_2; *, 60.17% CO_2.

Further insight into the phase behavior of systems of supercritical fluids + ionic liquids is given by Blanchard et al.,[23] Husson-Borg et al.,[24] Perez-Salado Kamps et al.,[25] Liu et al.,[26] Camper et al.,[27] Shariati and Peters,[28−30] Constantini et al.,[31] and Shariati et al.[32] They presented the phase behavior of a number of such systems. In this study, the phase behavior of the system CO_2 + 1-butyl-3-methylimidazolium tetrafluoroborate is determined within temperature and pressure ranges of (278.47 to 368.22) K and (0.58 to 67.62) MPa, respectively. The experimental results obtained were compared to the available phase behavior data of the binary system CO_2 + 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]) to investigate the effect of the length of the alkyl group on the phase behavior of this type of system.[31]

Experimental Section

Measurements of the solubilities of CO_2 in the ionic liquid [bmim][BF_4] involve bubble-point pressures at different temperatures and compositions. The solubility of CO_2 in [bmim][BF_4] at the lower end of the concentration scale ($x_{CO_2} \leq 0.4825$) was determined using the Cailletet apparatus. This equipment allows measurements of phase equilibria within a pressure range of (0.1 to 15) MPa and temperatures from (255 to 470) K depending on the heat-transferring fluid used. The solubility of CO_2 in [bmim][BF_4] at the higher end of the concentration scale ($x_{CO_2} > 0.4825$) was determined in an autoclave facility because of the higher equilibrium pressures (higher than the 15 MPa pressure limit of the Cailletet apparatus). Both facilities operate according to the synthetic method.[28]

The temperature measurements in the Cailletet apparatus have an uncertainty of 0.01 K, which is the error in the reading of the thermometer. The temperature measurements in the autoclave apparatus have an uncertainty of ±0.05 K due to the temperature fluctuations in the water bath. The uncertainty of the pressure measurements is ±0.0025 MPa for the Cailletet apparatus and ±0.04% for the autoclave apparatus. The uncertainty in the compositions of the samples is ±0.005 mole fraction.

The carbon dioxide used for the measurements was supplied by Air Products and had a purity of 99.95%. The ionic liquid [bmim][BF_4] was prepared with a purity of >99.0% as previously described.[33] The purity was measured using boron analysis (ICP-AES) and NMR analysis. ^1H NMR (300.2 MHz, $CDCl_3$, TMS): δ 0.93 (t, 3H), 1.34 (m, 2H), 1.86 (m, 2H), 3.95 (s, 3H), 4.20 (t, 2H), 7.47 (s, 2H), 8.71 (s, 1H). Prior to use, the [bmim][BF_4] was dried under vacuum conditions at room temperature for several days. The water content of the dried ionic liquid was measured using Karl Fischer moisture analysis and was <0.03 mass %. Within the temperature range of the experiments, the ionic liquid did not show any decomposition or reaction with carbon dioxide.

Table 1. Bubble-Point Data for Various Compositions of Carbon Dioxide in the CO_2 + [bmim][BF_4] System

x_{CO_2}	T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
0.1022	293.13	0.587	323.11	1.044	348.12	1.539
	298.14	0.659	328.14	1.143	353.16	1.664
	303.15	0.740	333.16	1.239	358.17	1.769
	308.15	0.803	338.16	1.344	363.16	1.875
	313.19	0.885	343.14	1.438	368.14	1.989
	318.11	0.968				
0.1998	293.17	1.243	323.15	2.269	348.15	3.378
	298.17	1.388	328.12	2.466	353.16	3.629
	303.19	1.542	333.18	2.686	358.16	3.884
	308.19	1.710	338.12	2.909	363.16	4.150
	313.15	1.886	343.13	3.137	368.22	4.418
	318.12	2.074				
0.3035	278.53	1.547	313.39	3.332	342.73	5.577
	283.61	1.742	318.28	3.667	347.95	6.027
	288.47	1.957	323.16	4.002	353.11	6.512
	293.50	2.192	328.12	4.367	357.96	7.012
	298.47	2.447	332.82	4.757	362.91	7.522
	303.40	2.722	337.75	5.157	367.96	8.047
	308.36	3.012				
0.4005	278.68	2.233	313.00	4.953	343.12	8.748
	283.52	2.508	318.13	5.513	348.08	9.473
	288.51	2.838	323.22	6.098	352.82	10.233
	293.33	3.198	328.12	6.703	357.69	11.063
	298.15	3.573	333.19	7.343	363.02	11.968
	303.11	3.993	338.28	8.053	367.92	12.888
	308.10	4.458				
0.4825	278.47	2.926	303.16	5.496	323.10	8.921
	283.39	3.346	308.16	6.206	327.99	10.071
	288.55	3.801	313.27	7.046	333.10	11.406
	293.32	4.301	318.16	7.931	338.17	12.856
	298.28	4.861				
0.5507	313.12	14.44	332.94	26.12	347.66	33.82
	318.07	17.46	337.86	28.46	352.69	36.58
	322.95	20.22	342.78	31.12	357.90	38.86
	327.96	23.06				
0.6017	313.12	36.58	332.85	50.24	352.77	62.16
	318.08	39.66	337.85	53.70	357.71	64.82
	322.94	43.24	342.94	56.74	362.58	67.62
	327.91	46.72	347.98	59.46		

Results and Discussion

The solubility of carbon dioxide in 1-butyl-3-methylimidazolium tetrafluoroborate was measured using the Cailletet apparatus and the autoclave. This solubility is dependent on temperature and pressure. For systems with a fixed overall composition of carbon dioxide and ionic liquid, bubble-point pressures were measured as a function of temperature. The results are summarized in Table 1, and Figure 1 shows the results graphically.

From Figure 1, it is clear that bubble-point pressures increase when higher temperatures are used at fixed compositions. This means that the solubility of carbon dioxide in the ionic liquid decreases at higher temperatures. This is mostly the common trend for the solubility of gases in liquids.

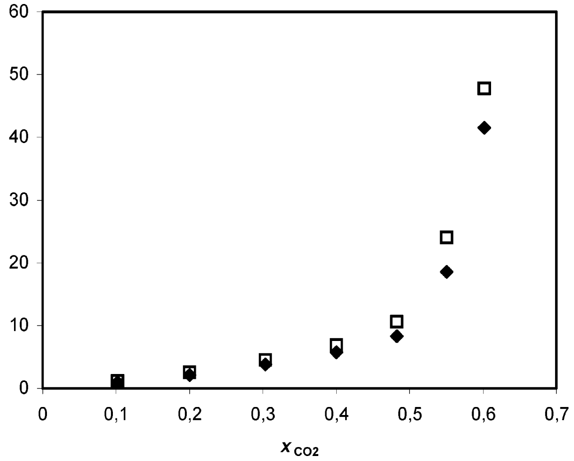

Figure 2. Isotherms at 320 K and 330 K for the system CO_2 + [bmim][BF_4]: ◆, 320 K; □, 330 K.

When the mole fraction of carbon dioxide is increased isothermally, the bubble-point pressures increase significantly. This can be more easily seen from a $p-x$ diagram in which the bubble-point pressure is plotted against the mole fraction of carbon dioxide at fixed temperature. Figure 2 shows the phase behavior of the CO_2 + [bmim][BF_4] system at 320 K and 330 K. From this Figure, it can also be noticed that the solubility of carbon dioxide in the ionic liquid decreases with an isobaric increase in temperature and the effect of temperature on carbon dioxide solubility is larger at higher mole fractions of carbon dioxide.

The phase behavior of the system CO_2 + [bmim][BF_4] is unusual: carbon dioxide dissolves well in 1-butyl-3-methylimidazolium tetrafluoroborate at lower pressures, and the bubble-point pressures sharply increase at higher mole fractions of carbon dioxide. A system in which large amounts of carbon dioxide dissolve in the liquid phase at low pressures, in general, has a simple two-phase envelope with a mixture critical point at moderate pressures.[23] However, instead of having such a critical point at moderate pressures, its two-phase boundary extends almost vertically to very high pressures. This remarkable behavior has been noticed more often for CO_2 + ionic liquid systems.[28−32] As has been discussed and explained in our previous work,[32] this behavior is common for this type of system. Therefore, the system CO_2 + [bmim][BF_4] also will most likely show type III fluid-phase behavior according to the classification of Scott and Van Konynenburg.[34]

The phase behavior of the binary system CO_2 + [bmim][BF_4] was compared to the recently measured phase behavior of the binary system CO_2 + [hmim][BF_4][31] in order to investigate the effect of the length of the alkyl group on the phase behavior of this type of system. Figure 3 compares the $p-x$ diagrams at 330 K and illustrates that the solubility of carbon dioxide is higher in [hmim][BF_4] than in [bmim][BF_4]. A larger alkyl group leads to lower bubble-point pressures and, therefore, to higher solubilities of carbon dioxide in the imidazolium-based ionic liquid.

Conclusions

The phase behavior of the binary mixture consisting of the supercritical fluid CO_2 and the ionic liquid [bmim][BF_4] was studied experimentally. CO_2 has a high solubility at lower pressures, but the solubility decreases dramatically at higher pressures. The two-phase boundary extends almost vertically up to very high pressures. This type of phase behavior indicates that most likely we are dealing with type III fluid-phase behavior according to the classification of Scott and Van Konynenburg.

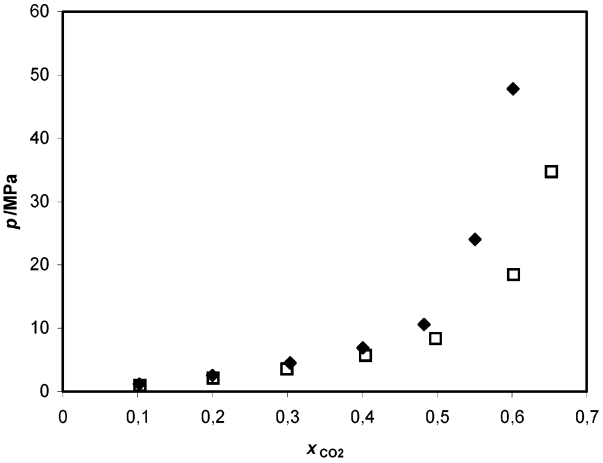

Figure 3. Comparison of the isotherms at 330 K for the binary systems CO_2 + [bmim][BF_4] and CO_2 + [hmim][BF_4]: ◆, [bmim][BF_4] + CO_2; □, [hmim][BF_4] + CO_2[29].

The phase behavior of the system CO_2 + [bmim][BF_4] shows similarities to the phase behavior of the system CO_2 + [hmim][BF_4], but carbon dioxide is more soluble in [hmim][BF_4] than in [bmim][BF_4]. Therefore, the larger alkyl group on the methylimidazolium cation leads to higher CO_2 solubility. The results emphasize the tunability of ionic liquids by the right choice of the cation (length of the alkyl groups) and anion and the necessity of phase behavior data for industrial process design.

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