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

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The phase behavior of a binary mixture consisting of a supercritical fluid and an imidazolium-based ionic liquid was studied experimentally. Carbon dioxide (CO_2) and 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]) were the selected supercritical fluid and ionic liquid (IL), respectively. A synthetic method was used to measure the phase behavior of the binary system CO_2 + [hmim][BF_4]. Bubble-point pressures of this binary mixture were reported for CO_2 concentrations ranging from (10.3 up to 70.3) mol % and within a temperature range of (293.18 to 368.16) K. The experimental results obtained in this work were compared with the available phase behavior data of the binary system CO_2 + 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]) to investigate the effect of the anion group on the phase behavior of this type of system. The three-phase liquid−liquid−vapor (LLV) equilibrium of this system was also measured. On the basis of the LLV measurements, the type of fluid phase behavior of this system most likely will be type III according to the classification of Scott and Van Konynenburg. The CO_2 + [hmim][BF_4] binary system has a two-phase liquid−vapor region extending up to very high pressures.

Introduction

Room-temperature ionic liquids (ILs) are organic salts, which, because of their unique characteristics, are the subject of much research nowadays as potential replacements for organic solvents. ILs have very good solvency power for both organic and inorganic materials, polar and nonpolar. In addition, ILs have insignificant vapor pressures and, therefore, eliminate environmental pollution and greatly reduce working exposure hazards in comparison with the conventional organic solvents currently being used in industry. Most ILs are in the liquid state at room temperature and will remain liquid up to very high temperatures, so processes such as heterogeneous reactions can instead be performed in a single liquid phase within a wide temperature range. ILs are thermally stable and nonflammable. On the basis of these outstanding characteristics, Brennecke and Maginn[1] gave an extensive perspective of potential industrial applications of ILs in catalytic reactions, gas separations, liquid−liquid extractions, and electrolyte/fuel cells and as lubricants and heat-transfer fluids.

Although the literature contains many articles on the synthesis of ILs[2−6] and the application of ILs as solvents in catalytic reactions,[7−11] studies on the phase behavior of ILs in the presence of supercritical fluids are scarce. Brennecke and co-workers presented some potential applications for the systems ILs + supercritical fluids. They showed that it is possible to extract a solute from an IL using supercritical CO_2 without any contamination of the extracted solute with the IL solvent.[12,13] They also investigated the use of supercritical CO_2 for separating ILs from organic solvents.[14] The application of supercritical CO_2 induces the formation of an additional liquid phase that is rich in IL, even when the original solution is quite dilute in IL. Later, they showed that the introduction of CO_2 may allow for the separation of both hydrophobic and hydrophilic imidazolium-based ILs from aqueous solutions.[15] For example, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) can be separated from an IL-saturated aqueous solution at 293 K and at a CO_2 pressure of 4.9 MPa.

To gain insight into the phase behavior of IL + supercritical fluid systems, Blanchard et al.,[16] Anthony et al.,[17] Liu et al.,[18] Perez-Salado Kamps et al.,[19] and Shariati and Peters[20−22] have presented the phase behavior of a number of such systems. This work is a continuation of our previous studies. In the underlying study, the phase behavior of the system CO_2 + [hmim][BF_4] was studied experimentally. Solubilities of CO_2 in [hmim][BF_4] were determined within temperature and pressure ranges of (293.18 to 368.16) K and (0.54 to 86.60) MPa, respectively. In addition, the LLV equilibrium of this system was also measured.

Experimental Section

High-pressure experiments were carried out in an autoclave for the higher concentrations of CO_2 ($x_{CO_2} > 0.498$). The Cailletet apparatus was used at lower concentrations of CO_2 ($x_{CO_2} \leq 0.498$), where equilibrium pressures were lower than 12.0 MPa(i.e., the pressure limit of the Cailletet apparatus). Both facilities operate according to the synthetic method. Details of the experimental facilities and procedures can be found elsewhere.[20]

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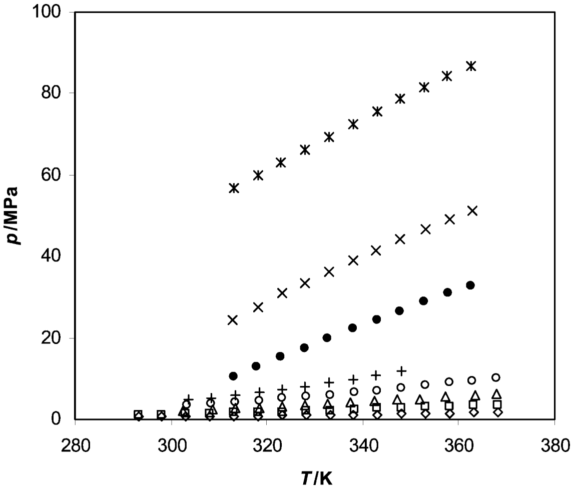

Figure 1. Experimentally determined isopleths for several concentrations of the system CO_2 (1) + [hmim][BF_4] (2). x_1: ◇, 0.103; □, 0.201; △, 0.299; ○, 0.404; +, 0.498; ●, 0.602; ×, 0.653; *, 0.703.

The CO_2 used for the measurements was supplied by Messer Griesheim and had an ultrahigh purity of 99.995%. Liquid [hmim][BF_4] with a purity of over 99.0% was provided by Professor Roger Sheldon from the Organic Chemistry Group of Delft University of Technology, The Netherlands. Prior to use, the [hmim][BF_4] was dried under vacuum conditions at room temperature for several days. The water content of the dried IL, determined by Karl Fischer analysis, was less than 0.025 mass %. Within the temperature range of the experiments, the samples did not show any decomposition or reaction with CO_2 during the measurements. This was indicated by the reproducibility of the data measured on different days.

The thermometer of the Cailletet apparatus has an accuracy of ±0.01 K for temperature measurements. The pressure in the Cailletet apparatus is kept constant and measured with a dead-weight gauge with an uncertainty of ±0.003 MPa.

The accuracy of the pressure measurements in the autoclave apparatus is better than ±0.04% of the pressure reading from (3.0 to 100.0) MPa. The uncertainty in the measured temperatures is ±0.051 K. The synthetic method is used to prepare each binary mixture of CO_2 + [hmim][BF_4], and the uncertainty in the mole fraction after drying [hmim][BF_4] is between 0.003 and 0.007.

Results and Discussion

The phase behavior of the binary system CO_2 + [hmim][BF_4] was determined by measuring its bubble-point pressures at different temperatures for several isopleths and also determining its LLV three-phase boundary. Table 1 summarizes the bubble-point pressures of this system, and Figure 1 shows the results graphically. This Figure shows that the equilibrium pressures of this system are low at lower concentrations of CO_2. For example, the bubble-point pressure of a mixture of $x_{CO_2} = 0.103$ was 0.90 MPa at 323.14 K. However, when the CO_2 concentration is further increased isothermally, the equilibrium pressures increased dramatically; for instance, the equilibrium pressure increased to an unusually high value of 63.12 MPa at 323.02 K for $x_{CO_2} = 0.703$. This can be understood from a $p-x$ diagram, obtained by isothermally interpolating the experimental data of Table 1. Figure 2 shows the phase behavior of CO_2 + [hmim][BF_4] on such a $p-x$ diagram at (330 and 340) K. As expected, the solubility of CO_2 in the IL-rich phase decreased with an isobaric increase in temperature. Figure 2 also illustrates that the temperature dependency of the CO_2 solubility in [hmim][BF_4] was not significant at lower concentrations of CO_2 but gradually increased at higher CO_2 concentrations.

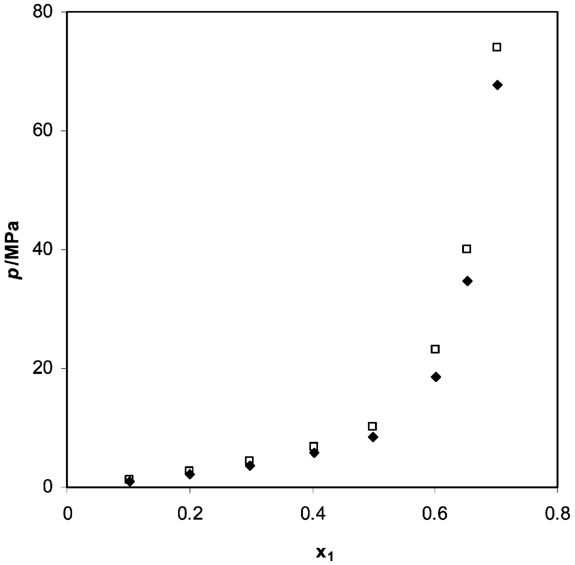

Figure 2. Isotherms at 330 K and 340 K of the system CO_2 (1) + [hmim][BF_4] (2): ◆, 330 K; □, 340 K.

Table 1. Bubble-Point Data for Various Concentrations of Carbon Dioxide in the CO_2 (1) + [hmim][BF_4] (2) System

x_1	T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
0.103	293.18	0.54	323.14	0.90	348.10	1.28
	298.18	0.57	328.13	0.97	353.13	1.37
	303.14	0.63	333.28	1.05	358.15	1.47
	308.14	0.69	338.10	1.11	363.19	1.57
	313.12	0.77	343.16	1.20	368.14	1.65
	318.17	0.83				
0.201	293.18	1.09	323.06	1.91	348.15	2.80
	298.14	1.19	328.14	2.08	353.13	2.99
	303.15	1.32	333.11	2.25	358.12	3.20
	308.17	1.45	338.15	2.43	363.13	3.40
	313.19	1.62	343.10	2.61	368.16	3.62
	318.13	1.76				
0.299	302.37	2.17	327.96	3.49	347.21	4.74
	308.66	2.46	328.04	3.52	351.75	5.05
	313.48	2.69	332.64	3.82	357.27	5.42
	318.40	2.96	337.39	4.09	363.33	5.84
	323.29	3.23	342.41	4.40	367.81	6.18
0.404	303.39	3.44	328.25	5.56	352.98	8.28
	308.37	3.81	333.25	6.06	358.23	8.92
	313.39	4.20	338.16	6.58	362.98	9.52
	318.33	4.63	343.13	7.12	367.82	10.16
	323.27	5.08	348.10	7.70		
0.498	303.63	4.81	323.07	7.31	337.87	9.77
	308.28	5.32	327.84	8.04	342.82	10.72
	313.39	5.96	332.91	8.89	348.15	11.77
	318.51	6.64				
0.602	313.07	10.46	332.80	19.82	352.87	28.78
	317.88	12.76	338.05	22.14	357.77	30.88
	322.98	15.22	342.88	24.34	362.68	32.92
	327.97	17.52	347.81	26.54		
0.653	312.95	24.52	332.97	36.28	352.94	46.56
	318.08	27.70	337.93	38.96	358.04	48.98
	323.07	30.84	342.80	41.58	362.94	51.32
	327.91	33.54	347.88	44.26		
0.703	313.03	56.74	333.04	69.40	352.92	81.68
	318.04	59.94	337.84	72.56	357.64	84.46
	323.02	63.12	342.93	75.52	362.58	86.60
	327.95	66.26	347.82	78.72		

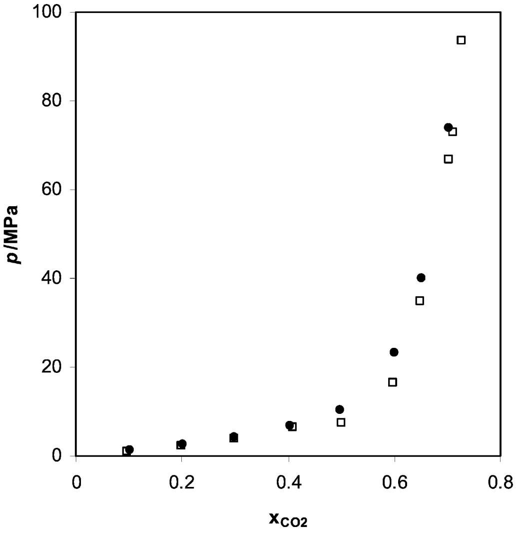

Figure 3. Comparison of the isotherms at 340 K of the binary systems of CO_2 + [hmim][BF_4] and CO_2 + [hmim][PF_6]: ●, [hmim][BF_4]; □, [hmim][PF_6].

Recently, Shariati and Peters[22] measured the phase behavior of the binary system CO_2 + 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]). Figure 3 compares the phase diagram of this binary system with the system CO_2 + [hmim][BF_4] at 340 K. Both systems show a two-phase region of an IL-rich liquid phase + supercritical fluid phase extending up to extremely high pressures. In both systems, CO_2 shows very high solubilities in the IL-rich phase at lower pressures, whereas the equilibrium pressures increase sharply at high concentrations of CO_2. Blanchard et al.[16] explained that this phase behavior is unusual because a system in which large amounts of CO_2 dissolve in the liquid phase at low pressures should generally have a simple two-phase envelope with a mixture critical point at moderate pressures. Figure 3 also illustrates that the solubility of CO_2 was higher in [hmim][PF_6] than in [hmim][BF_4]. Because the only structural difference between [hmim][BF_4] and [hmim][PF_6] is in their anions, this behavior can be related to the greater interaction between CO_2 and $[PF_6]^-$ than between CO_2 and $[BF_4]^-$, even though [hmim][PF_6] is slightly denser than [hmim][BF_4].

To be able to determine the type of fluid-phase behavior of the system CO_2 + [hmim][BF_4], the existence of a second liquid phase was also investigated in a temperature and pressure range close to the critical point of CO_2. For that purpose, a mixture of 97.5 mol % CO_2 and 2.5 mol % [hmim][BF_4] was prepared, and its phase behavior was studied experimentally. This system showed a three-phase LLV equilibrium at temperatures and pressures very close to the equilibrium temperatures and pressures of the pure CO_2. We assume that a point very close to the critical point of pure CO_2, the lighter liquid phase, which is almost pure CO_2 (L_1), and the vapor phase, which is also almost pure CO_2 vapor (V), is critical in the presence of the heavier liquid phase, which is the IL-rich phase (L_2). As a consequence, it is assumed that the system CO_2 + [hmim][BF_4] has an $L_1 = V + L_2$ type critical endpoint. According to the fluid-phase behavior classification of Scott and Van Konynenburg,[26] the system CO_2 + [hmim][BF_4] should have type III phase behavior. Although in principle type IV or type V could also be options for the fluid-phase behavior of the system CO_2 + [hmim][BF_4], the latter options are most unlikely because

- type IV binary systems occur very rarely; and
- type V binary systems with CO_2 are not known in the literature.

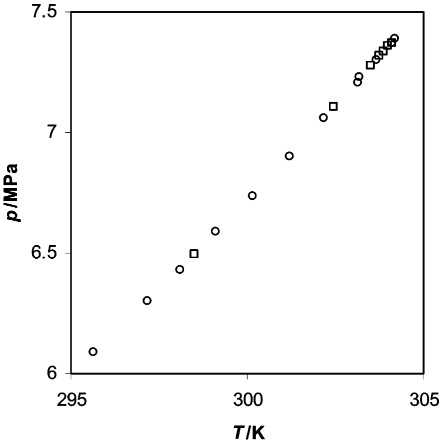

Figure 4. Comparison between the LLV three-phase equilibrium of the system CO_2 (1) + [hmim][BF_4] (2) and the LV boundary of pure CO_2 as reported by Shariati et al.:[25] ○, pure CO_2; □, CO_2 + [hmim]BF_4].

Table 2. LLV Data of the CO_2 (1) + [hmim][BF_4] (2) System

T/K	p/MPa
278.70	4.04
283.54	4.56
288.49	5.14
293.61	5.80
298.49	6.49
302.46	7.11
303.51	7.28
303.75	7.32
303.86	7.34
303.99	7.36
304.09	7.37

Table 2 summarizes the LLV data of the system CO_2 + [hmim][BF_4]. Figure 4 compares the LLV line of the system CO_2 + [hmim][BF_4] and the LV line of pure CO_2 graphically. The insignificant differences between the LLV line of the system CO_2 + [hmim][BF_4] and the LV line of pure CO_2 result from the fact that the solubility of [hmim][BF_4] in CO_2 is very small. Wu et al.[27] showed experimentally that the solubility of [bmim][PF_6] in pure CO_2 is extremely low. For example, the [bmim][PF_6] mole fraction in supercritical CO_2 determined by Wu et al.[27] at 313.15 K and 15.00 MPa is 3.2×10^{-7}.

Conclusions

The phase behavior of the binary mixture CO_2 + IL [hmim][BF_4] was studied experimentally. CO_2 has good solubility in [hmim][BF_4] at lower pressures, but instead of showing mixture critical points at moderate pressures, its two-phase boundary extends almost vertically to very high pressures.

There are similarities between the phase behavior of the binary systems CO_2 + [hmim][BF_4] and CO_2 + [hmim][PF_6]. CO_2 was found to be more soluble in [hmim][PF_6] than in [hmim][BF_4]. According to the classification of the binary fluid phase behavior of Scott and Van Konynenburg,[26] the system CO_2 + [hmim][BF_4] most likely will have type III fluid-phase behavior. The results obtained in this study emphasize the importance and necessity of obtaining accurate phase behavior data of ILs and components of interest for industrial process design.

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