

Liquid–Vapor Equilibrium of the Systems Butylmethylimidazolium Nitrate–CO₂ and Hydroxypropylmethylimidazolium Nitrate–CO₂ at High Pressure: Influence of Water on the Phase Behavior

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Ionic liquids (IL) are receiving increasing attention due to their potential as “green” solvents, especially when used in combination with SC-CO₂. In this work liquid–vapor equilibria of binary mixtures of CO₂ with two imidazolium-based ionic liquids (IL) with a nitrate anion have been experimentally determined: butylmethylimidazolium nitrate (BMImNO₃) and hydroxypropylmethylimidazolium nitrate (HOPMImNO₃), using a Caillietet apparatus that operates according to the synthetic method. CO₂ concentrations from 5 up to 30 mol % were investigated. It was found that CO₂ is substantially less soluble in HOPMImNO₃ than in BMImNO₃. Since these ILs are very hygroscopic, water easily can be a major contaminant, causing changes in the phase behavior. In case these ILs are to be used in practical applications, for instance, together with CO₂ as a medium in supercritical enzymatic reactions, it is very important to have quantitative information on how the water content will affect the phase behavior. This work presents the first systematic study on the influence of water on the solubility of carbon dioxide in hygroscopic ILs. It was observed that the presence of water reduces the absolute solubility of CO₂. However, at fixed ratios of CO₂/IL, the bubble point pressure remains almost unchanged with increasing water content. In order to explain the experimental results, the densities of aqueous mixtures of both ILs were determined experimentally and the excess molar volumes calculated.

Introduction

Ionic liquids (ILs), sometimes also called molten salts, are liquids that are composed entirely of ions. They are in the liquid state at ambient or close-to-ambient temperature, which is in contrast to the high-temperature inorganic molten salts.¹ Their melting points are well below 100 °C, as they have a high degree of asymmetry, which prevents them for arrangements in a crystal lattice and, consequently, crystallization will not occur.²

A potential application of ionic liquids are as solvents in reactions.¹ This interest stems from their potential as “green” solvents. Their nonvolatile character, high thermal and chemical stability, and recoverability make them potentially attractive alternatives over environmentally unattractive organic solvents, in particular compared to chlorinated hydrocarbons.³ They are good solvents for a wide range of both inorganic and organic materials. Moreover, their properties can be tuned by appropriate modification of the cation, anion, or both.

Depending on their structure, ILs can be miscible or immiscible with water.³ This miscibility is mainly caused by the anion of the ionic liquid. The water content has a much stronger effect on the physical properties of the hydrophilic ILs than on the hydrophobic ones.³ Even the partially water-immiscible ILs are hygroscopic and are able to absorb up to 1 wt % of water from the environment.^{4,5} Cammarata et al.⁶ showed that for some ILs, including those with BF₄ and PF₆ anions, the water is associated with the anion of the ILs via H-bonding rather than of being self-associated. In those cases, the concentrations of the dissolved water are typically in the range of 0.2 ± 0.04 mol/L. Water molecules can also form self-associated liquidlike structures in ILs when anions with a strong basicity such as NO₃ are present. When these ILs are exposed to air, water concentrations easily may exceed 1.0 mol/L.

Despite all the advantages related to the ILs, their successful commercialization may be handicapped by difficulties in separating them from the reactants, products, or catalyst as these species all may occur in chemical reactions. A very convenient option could be the separation using supercritical CO₂ which, in principle, can be considered as an environmentally benign solvent, both as a solvent for extraction and as an antisolvent for precipitating the other components.^{7,8} Blanchard et al.^{9,10} proved that SC-CO₂ can be used to extract relatively nonvolatile compounds from ILs without any contamination of the ILs

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themselves. As an additional feature, CO₂ is able to force two or more immiscible phases to form one homogeneous phase upon pressure increase^{11–13} and, in reverse, to split a homogeneous fluid phase in two or three phases upon pressure decrease. These phenomena hold for both mixtures of ILs with organic solvents or aqueous solutions. This phenomenon is called miscibility switch^{14,15} and can be applied in combined reaction/separation systems for performing monophasic or biphasic reactions.¹⁶

Because of the advantages of using CO₂ in reactions and phase separations, an increasing interest in knowledge of the phase behavior of systems of CO₂–IL has been developed in the past couple of years. In general, ILs with cations based on the imidazolium group and anions based on the hexafluorophosphate (PF₆),^{17–23} tetraborofluorate (BF₄),^{22–25} and bis(trifluoromethylsulfonyl)imide (Tf₂N)^{21–23,26} groups are receiving a great deal of attention. Besides these ILs, also the CO₂ solubility of some other types of ILs has been determined.^{22,23} It has been observed that the phase behavior of IL–CO₂ systems have some features in common. For instance, large quantities of CO₂ dissolve in the IL-rich phase, but no measurable amount of the ILs, among them also BMImPF₆, dissolves in the CO₂-rich phase.¹⁰ Experiments performed at very high pressures in our group has proved that instead of reaching a critical point in an isothermal pressure–composition diagram, the phase envelope does not close, even at pressures as high as 100 MPa and CO₂ concentrations up to 70 mol %. This phenomenon was experimentally determined in various imidazolium-based ILs with PF₆ and BF₄ as the anions.^{17–20,24,25} McHugh^{23,27} also found similar behavior for the system BMImPF₆–CO₂ at pressures as high as 310.2 MPa and at a concentration of 3.1 mol % IL. Blanchard et al.²³ did ascribe this behavior to the fact that no volume expansion is observed even when CO₂ is dissolved into the IL phase up to high concentrations. Increasing the pressure will cause the CO₂ phase to increase in density, but since the liquid phase does not expand the two phases will never become identical; i.e., a mixture critical point will never be reached. Shariati et al.²⁰ simply did explain this behavior based on the shape of the critical locus in IL–CO₂ systems.

Some authors have found that there is a strong relationship between the solubility of CO₂ in an IL and the molar volume,^{23,26,28} indicating that a free volume contribution plays an important role in the CO₂ solubility in ILs. Using ATR-IR spectroscopy, Kazarian et al.²⁹ demonstrated that CO₂ forms weak Lewis acid–base complexes with the PF₆ and BF₄ anions. In addition, they argued that these interactions cannot be solely responsible for the solubility of CO₂ in ILs. Other authors also found an important influence of the anion on the solubility of CO₂ caused by the influence of the acidic hydrogen atom at position 2 in the imidazolium ring.³⁰ The length of the alkyl chain at position 3 of the imidazolium ring²² is considered to be of less importance.

The observation of Blanchard et al.²³ that a minor amount of water dissolved in BMImPF₆ can reduce the solubility of CO₂ by 77% made researchers aware of the crucial importance to dry ILs carefully in order to avoid large deviations in the solubility of CO₂. On the other hand, Fu et al.³¹ studied systematically the influence of water on the CO₂ solubility in BMImPF₆, resulting in less significant deviations, i.e., deviations less than 15%. In additional studies, it was discovered that the PF₆ anion is highly unstable in the presence of water,^{22,32,33} making all previous experimental observations with the PF₆ anion highly questionable. Also, some data on the influence of the water content on the solubility of CO₂ in ILs with the highly

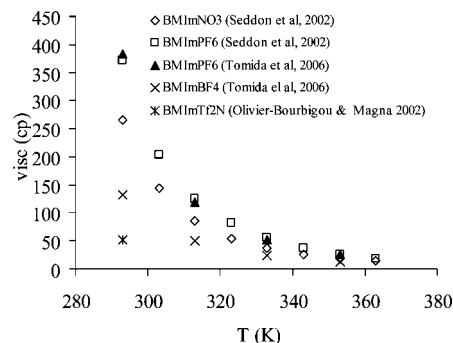


Figure 1. Comparison of the viscosities of BMImNO₃³⁴ with some of the most frequently studied ILs like, for instance, BMImPF₆,^{34,36} BMImBF₄,³⁶ and BMImTf₂N.^{37,38}

TABLE 1: Comparison of the Melting Points and Molecular Weights of Several ILs with the EMIm Cation

	<i>T_m</i> (°C)	MW	reference
(EMIm)(NO ₃)	38	173	Wilkes and Zaworotko, 1992 (35)
(EMIm)(PF ₆)	58–60	256	Wilkes and Zaworotko, 1992 (35)
(EMIm)(Tf ₂ N)	4	391	Bonhote et al., 1996 (37)
(EMIm)(BF ₄)	15	198	Wilkes and Zaworotko, 1992 (35)

hydrophobic Tf₂N anion has been reported.^{21,22,26} These studies mainly compare the solubility of CO₂ in the “dry” and the water-saturated ILs. Only a minor effect of the water content was observed.

Although imidazolium-type ionic liquids with a nitrate anion have been scarcely studied, a few characteristic features are known about them. Their density³⁴ is lower and their viscosity³⁴ and melting point³⁵ are higher than other ILs with the same cation and also compared to other frequently used anions. This can be seen in Figure 1 and Table 1. In a comparison of the viscosities of the BMImNO₃ with BMImBF₄, BMImPF₆, and BMImTf₂N,^{34,36–38} three of the most widely studied ILs, the viscosity of BMImNO₃ is much higher than that of BMImBF₄ and BMImTf₂N and slightly lower than that of BMImPF₆.

In Table 1 the melting points of several ILs with the EMIm cation^{35,37} and different anions are compared with EMImNO₃. The melting point of the IL with the nitrate anion is above ambient temperature, i.e., much higher than that of the ILs with BF₄ and Tf₂N anions.

Nitrate-based ILs are completely miscible with water, much more hygroscopic,^{5,6} and dissolve less CO₂ than other imidazolium-based ILs with different anions.²² The nitrate-based ILs also seem to be less resistant to high temperature than other ILs since the nitrate group serves as a strong oxidizer and reacts strongly with the alkyl groups at elevated temperatures, producing common combustion products.³⁹

Holbrey et al.⁴⁰ reported that incorporation of a secondary hydroxyl functionality in the cation of an imidazolium-based IL causes some interesting modifications in its behavior compared to the properties of ILs with an alkyl group instead. Their hydrophilicity and hygroscopicity increased, and their viscosity decreased more rapidly when heated above room temperature. The hydrophilicity caused by the hydroxyl group may be advantageous for stabilizing enzymatic catalyst systems in nonaqueous IL environments and may also provide new applications in metal complexation.

In this work the solubility of CO₂ in two imidazolium-based ionic liquids (ILs) with a nitrate anion, i.e., butylmethylimidazolium nitrate (BMImNO₃) and hydroxypropylmethylimidazolium nitrate (HOPMImNO₃), has been experimentally determined. The chemical structures of both ILs are shown in Figure 2.

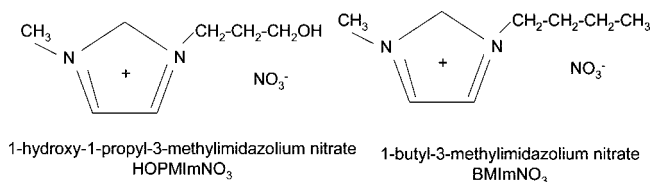


Figure 2. Ionic liquids studied in this work.

As both ILs are very hygroscopic, it is very likely that in possible industrial applications they will be contaminated with water. Consequently, it is very important to see how the water content may influence their phase behavior. For that purpose, fluid phase equilibria in the ternary systems CO₂ + H₂O + BMImNO₃ and CO₂ + H₂O + HOPMImNO₃ have been determined experimentally. In order to have a better understanding of the effect of water, the density of the ILs and their mixtures with water has been also experimentally determined and, in addition, the excess molar volumes of the solutions have been calculated as well. Of the selected ILs, BMImNO₃ has been studied scarcely, while on HOPMImNO₃ no phase equilibrium studies are reported in literature at all. The physical properties of the latter IL suggest that it might be a potential candidate solvent to stabilize enzymes; i.e., in combination with water and CO₂ this IL may be used in enzymatic reactions.

Experimental Section

Phase Equilibrium Measurements. For all phase equilibrium measurements a Cailletet apparatus was used. It operates according to the synthetic method; i.e., a sample of known overall composition was used. A schematic representation of the Cailletet apparatus is given in Figure 3. Essentially, a Cailletet tube consists of a thick-walled Pyrex glass tube, of which one end is closed and the other end is open, allowing the tube to be mounted into a stainless steel autoclave. The sample is confined at the closed top of the tube, while mercury is used as a sealing and pressure transmitting fluid. Inside the autoclave, the open end of the tube is always immersed in mercury. A mercury/oil separator prevents mercury to enter the hydraulic system of the facility and, on the other hand, preventing the hydraulic oil to be in contact with the sample. A small stainless steel ball inside the top of the tube allows stirring of the sample magnetically. A pressure balance (Budenberg) in combination with a hand screw type pump was used to measure pressures and, if applicable, to maintain a constant pressure in the system. The pressure balance has been designed to cover a range of 0.35–14 MPa, with a maximum accuracy of 0.005 MPa. The Cailletet tube is jacketed and water is used as a thermostatic fluid. The range of working temperature is from 283 up to 368 K. The thermometer used is a Pt-100 with an accuracy of 0.01 K. In this work, the measurements obtained from the Cailletet facility comprise the determination of bubble points. In order to perform such measurements, first the temperature is set at a fixed value and the pressure is brought to a value where two phases, liquid and vapor, coexist. Then the pressure is gradually increased until the vapor phase just disappears. It is crucial that after each change in pressure equilibrium between the coexisting phases is established. At the pressure where the vapor phase just disappears a homogeneous liquid phase is obtained, and consequently, the composition of this liquid is the same as the original overall composition. A point of the two-phase boundary is obtained when a small change in pressure results in formation of a vapor phase or elimination of the existing vapor phase. To prepare the sample,

the top of the Cailletet tube is filled with a weighted amount of the ionic liquid or with the mixture IL + water, weighed with an accuracy of 0.0001 g. In case of the pure IL, it is heated with hot water under high-vacuum conditions in order to degasify and to eliminate traces of water. However, in case of the aqueous solution, the sample is degasified by freezing with liquid nitrogen, melting again, and removal of the released gases under high-vacuum conditions. This procedure is repeated several times. The next step is adding a known quantity of CO₂ into the top of the Cailletet tube. For that purpose, a known volume of 67.43 cm³ is filled with a quantity of CO₂ whose temperature and pressure are measured. At highest, this procedure may cause a maximum dosing error of 0.01 cmHg in the pressure and a temperature reading error of 0.1 K. Finally, the Cailletet tube is removed from the gas-dosing system and then mounted into the stainless steel autoclave. Then the autoclave is closed, and by means of a hydraulic system pressure is applied. Further details of the experimental facility and procedures can be found elsewhere.⁴¹

The composition of the samples in the ternary systems has been calculated in two different ways: absolute molar composition (x_i) and relative water-free compositions (X_i) defined in eqs 1 and 2, respectively:

$$x_i = \frac{n_i}{n_{\text{H}_2\text{O}} + n_{\text{IL}} + n_{\text{CO}_2}} \times 100 \quad (1)$$

$$X_i = \frac{n_i}{n_i + n_{\text{IL}}} \times 100 \quad (2)$$

In these equations n_i is the number of moles of $i = \text{H}_2\text{O}$ or CO₂.

For the experiments double-distilled water was used. CO₂ (99.995 vol %) was purchased from Hoek-Loos. The ILs were synthesized in the Laboratory of Biocatalysis and Organic Chemistry of the Delft University of Technology, The Netherlands.

Synthesis of the ILs. The used materials *N*-methylimidazole, 1-chlorobutane, 1-chloro-3-propanol, and Dowex 1 × 8–200 anion-exchange resin were obtained from Acros Organics.

1-Butyl-3-methylimidazolium Nitrate (BMImNO₃): 1-Methylimidazole was reacted with 1-chlorobutane at 80 °C under a nitrogen atmosphere for 5 days. The excess of 1-chlorobutane was removed by rotary evaporation, yielding the slightly yellow viscous ionic liquid 1-butyl-3-methylimidazolium chloride (BMImCl). A column was packed with 250 g of Dowex 1 × 8–200 anion-exchange resin and flushed thoroughly with a 1 M NaNO₃ solution (1 L) and then with Milli-Q water (1 L). BMImCl was dissolved in Milli-Q water (1 M, 400 mL), and the resulting solution was slowly run over and eluted with Milli-Q water (1 L). The eluted liquid was collected and concentrated under reduced pressure in a rotavap. The residue was dried extensively under vacuum over phosphorus pentoxide. BMImNO₃ was obtained in near-quantitative yield as a colorless liquid that contained <30 ppm of Cl[−] according to the silver chromate test. The complete procedure is described in ref 42.

1-(1-Hydroxypropyl)-3-methylimidazolium Nitrate (HOPMImNO₃): 1-Methylimidazole was reacted with an excess (2:3) of 1-chloro-3-propanol at 60 °C under a nitrogen atmosphere for 4 days. The excess of 1-chloro-3-propanol was removed by extracting 3 times with ethyl acetate, yielding 1-(1-hydroxypropyl)-3-methylimidazolium chloride (HOPMImCl). A column

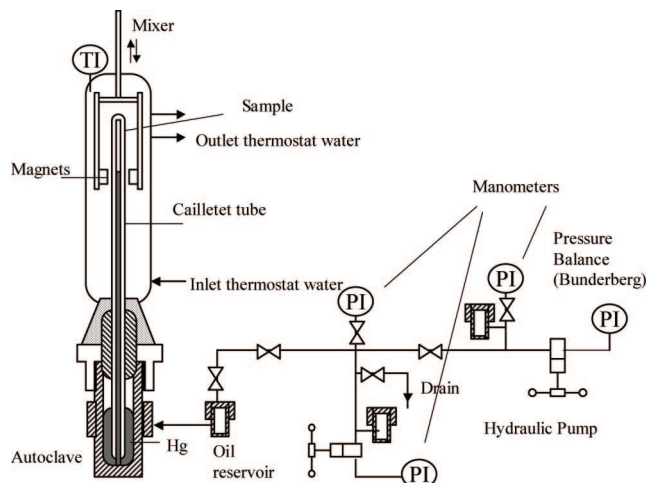


Figure 3. Schematic representation of a Cailliet apparatus.

TABLE 2: Densities of the ILs HOPMImNO₃ and BMImNO₃ and Its Aqueous Solutions

T (K)	$\rho_{\text{BMImNO}_3} \text{ (g/cm}^3\text{)}$			
	$x_{\text{H}_2\text{O}}$			
	0.00%	13.05%	19.46%	27.75%
292	1.1573	1.1547	1.1529	1.1500
302	1.1508	1.1481	1.1462	1.1432
312	1.1445	1.1417	1.1399	1.1369
322	1.1382	1.1354	1.1335	1.1305
332	1.1320	1.1292	1.1274	1.1244
342	1.1260	1.1231	1.1212	1.1181

T (K)	$\rho_{\text{HOPMImNO}_3} \text{ (g/cm}^3\text{)}$				
	$x_{\text{H}_2\text{O}}$				
	0.00%	10.08%	14.62%	21.21%	29.31%
292	1.2734	1.2703	1.2683	1.2648	1.2600
302	1.2668	1.2637	1.2616	1.2581	1.2533
312	1.2604	1.2572	1.2553	1.2516	1.2469
322	1.2544	1.2511	1.2490	1.2455	1.2408
332	1.2486	1.2450	1.2428	1.2394	1.2348
342	1.2427	1.2391	1.2369	1.2334	1.2287

was packed with 250 g of Dowex 1 \times 8–200 anion-exchange resin and flushed thoroughly with a 1 M NaNO₃ solution (1 L)

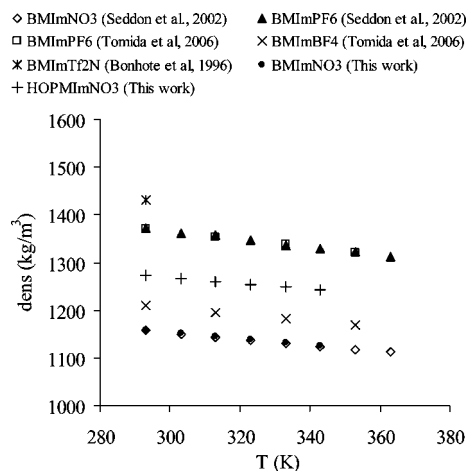
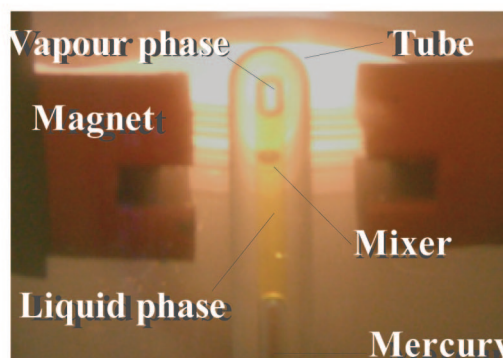


Figure 4. Comparison of the experimentally determined densities of BMImNO₃ and HOPMImNO₃ in this work with literature values of densities of BMImNO₃,³⁴ and with densities of some frequently studied ILs like BMImPF₆,^{34,36} BMImBF₄,³⁶ and BMImTF₂N.^{37,38}



and then with Milli-Q water (1 L). HOPMImCl was dissolved in Milli-Q water (1 M, 400 mL), and the resulting solution was slowly run over and eluted with Milli-Q water (1 L). The eluted liquid was collected and concentrated under reduced pressure in a rotavap. The residue was dried extensively under vacuum over phosphorus pentoxide. HOPMImNO₃ was obtained in near-quantitative yield as a colorless liquid that also contained <30 ppm of Cl[−] according to the silver chromate test.

Characterization of the ILs. Before using the ILs for the phase equilibrium measurements, they were dried further in an oven at 90 °C under vacuum. The water content of the IL is checked periodically by Karl Fischer moisture analysis (Mettler DL35 Karl Fischer titrator). The HOPMImNO₃ resulted to be highly hygroscopic, so its water content evolution was checked gravimetrically to assess that the IL was completely dry at the moment of the preparation of the samples. When working with aqueous solutions of ILs, no control of the absorption of water is possible from the moment that the solution is injected into the Cailliet tube until the tube is placed under vacuum again. Nevertheless, this absorbed moisture is expected to be negligible due to the short time used (between 10 and 15 min) and to the little surface area of the solution inside the tube that is exposed to the environment.

It was suspected that this IL might decompose upon heating at 90 °C in the oven at vacuum. However, NMR and IR spectroscopy analysis discarded this supposition. The molecular spectroscopy analysis was carried out in the FT-IR spectrometer Spectrum One of Perkin-Elmer. A droplet of the ionic liquid is placed between two pellets of potassium bromide (KBr), which were prepared with the KBr press.

The ILs were analyzed with ¹H NMR and ¹³C NMR using a frequency of 300.2 MHz. Deuterated chloroform as a solvent and tetramethylsilane (TMS) as a reference in the case of BMImNO₃ and heavy water as a solvent and *tert*-butyl alcohol (*t*-BuOH) as a reference were used in the Unity Inova 300 s of Varian. The obtained spectra are the following: BMImNO₃ (first batch) ¹³C NMR δ (ppm) 13.24; 19.26; 31.94; 36.10; 49.61; 122.30; 123.74; 137.30; ¹H NMR δ (ppm) 9.53 s1H (N=CH=N); 7.44; 7.40 d2H (CH=CH); 4.14; 4.12; 4.09 t 2H (N-CH₂-CH₂); 3.88 ppm s3H (N-CH₃); 1.76; 1.74; 1.73; 1.71; 1.69 m2H (CH₃-CH₂-); 1.26; 1.23; 1.21; 1.18 m2H (N-CH₂-CH₂-CH₂-CH₃); 0.83; 0.80; 0.78 t3H (CH₃-CH₂-). BMImNO₃ (second batch) ¹³C NMR δ (ppm) 13.44; 19.47; 32.16; 36.28; 49.81; 122.56; 123.96; 137.52; ¹H NMR δ (ppm) 9.71 ppm s2H (N=CH=N); 7.60; 7.56 ppm d 2H (CH=CH); 4.28; 4.26; 4.23 t

TABLE 3: Experimentally Determined Liquid–Vapor Equilibrium Data of the Binary System CO₂ + HOPMImNO₃^a

$x_{\text{CO}_2} = 5.28\%$		$x_{\text{CO}_2} = 10.04\%$		$x_{\text{CO}_2} = 14.33\%$		$x_{\text{CO}_2} = 20.74\%$		$x_{\text{CO}_2} = 24.84\%$		$x_{\text{CO}_2} = 30.81\%$	
<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)
0.851	303.36	1.784	303.93	2.595	303.51	3.921	303.63	5.545	303.39	5.976	293.47
1.021	313.36	2.140	314.59	3.165	313.43	4.884	313.37	6.975	313.11	8.101	298.57
1.206	323.24	2.564	325.73	3.815	323.56	6.110	323.43	7.915	318.42	9.925	300.86
1.416	333.60	3.184	338.60	4.485	333.27	6.702	328.20	8.790	323.10		
1.650	343.33	4.114	355.95	5.280	342.82	7.415	333.43	10.015	328.42		
1.920	353.34	4.609	363.55	6.205	353.38	9.076	344.17	11.305	333.15		
				7.205	363.33	10.647	353.42				
						11.621	358.63				

^a *P*: absolute pressure; $x_{\text{CO}_2} = n_{\text{CO}_2}/(n_{\text{CO}_2} + n_{\text{IL}})$; *n*: number of moles.

TABLE 4: Experimentally Determined Liquid–Vapor Equilibrium Data of the Binary System CO₂ + BMImNO₃^a

$x_{\text{CO}_2} = 3.82\%$		$x_{\text{CO}_2} = 9.99$		$x_{\text{CO}_2} = 14.91\%$		$x_{\text{CO}_2} = 20.00\%$		$x_{\text{CO}_2} = 0.2491$		$x_{\text{CO}_2} = 29.97\%$	
<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)
0.368	293.20	0.938	293.16	1.285	293.13	1.911	293.2	2.535	293.17	3.162	293.18
0.413	300.63	1.048	300.71	1.515	300.64	2.251	300.71	2.995	300.64	3.757	300.68
0.463	308.22	1.203	308.21	1.770	308.44	2.616	308.13	3.515	308.17	4.417	308.15
0.523	315.68	1.373	315.72	2.035	315.72	3.036	315.66	4.074	315.68	5.202	315.68
0.587	323.17	1.558	323.19	2.324	323.11	3.486	323.18	4.700	323.14	6.047	323.17
0.662	330.68	1.758	330.66	2.625	330.69	3.970	330.7	5.390	330.72	6.982	330.68
0.742	338.14	1.973	338.21	2.955	338.12	4.471	338.21	6.105	338.22	8.017	338.14
0.822	345.72	2.198	345.64	3.305	345.68	5.020	345.71	6.875	345.69	9.112	345.64
0.902	353.17	2.433	353.22	3.675	353.17	5.580	353.18	7.690	353.18	10.297	353.18
0.992	360.69	2.678	360.69	4.055	360.72	6.175	360.69	8.534	360.73	11.542	360.74
1.077	368.21	2.928	368.18	4.445	368.24	6.790	368.22	9.419	368.18	12.832	368.19

^a *P*: absolute pressure; $x_{\text{CO}_2} = n_{\text{CO}_2}/(n_{\text{CO}_2} + n_{\text{IL}})$; *n*: number of moles.

2H (N–CH₂–CH₂); 4.02 s3H (N–CH₃); 1.93; 1.90; 1.878; 1.85; 1.8 m2H (CH₃–CH₂–); 1.40; 1.37; 1.35; 1.32; 1.29 m2H (N–CH₂–CH₂–CH₂–CH₃); 0.96; 0.94; 0.91 t3H (CH₃–CH₂–). HOPMImNO₃ ¹³C NMR δ (ppm) 32.06; 35.95; 46.80; 58.25; 122.58; 123.92; 136.47; ¹H NMR δ (ppm) 8.75 s1H (N–CH=N); 7.52; 7.46 d2H (CH=CH); 4.67 s1H (D₂O; OH); 4.33; 4.31; 4.29 t2H (CH₂–CH₂OH); 3.91 s3H (CH₃–N); 3.65; 3.63; 3.61 t2H (N–CH₂–CH₂–CH₂OH); 2.15; 2.13; 2.11; 2.09; 2.07 m2H (–CH₂–CH₂–CH₂OH).

For the density measurements, a vibrating tube DMA 60 PAAR has been used.

Experimental Results

Densities of the Ionic Liquids HOPMImNO₃ and BMImNO₃ and Its Aqueous Solutions. The experimentally determined densities of the ILs HOPMImNO₃ and BMImNO₃ and their aqueous solutions at several temperatures in the range of 292–342 K are presented in Table 2. It is observed that the densities of BMImNO₃ are higher than those of HOPMImNO₃. Furthermore, the densities are lower when temperature and the concentration of water increase.

In Figure 4, the density of several ILs with a BMIm cation and different anions are depicted together with the densities of the ILs studied in this work. It can be observed that the densities determined for dry BMImNO₃ are consistent with those reported in literature³⁴ with a deviation lower than 0.2%. In general, the density of BMImNO₃ is lower than that of other BMIm ILs with other anions. Even when the molecular formula of both ILs is very similar, the density of HOPMImNO₃ is much higher and thus the molar volume is lower. This means that the packing of the HOPMImNO₃ is more compact, i.e., less free space is present, apparently due to the hydrogen bonds caused by the hydroxyl groups.

Bubble Points of the Binary Systems CO₂ + HOPMImNO₃ and CO₂ + BMImNO₃. Bubble points for the binary systems CO₂ + HOPMImNO₃ and CO₂ + BMImNO₃ have been

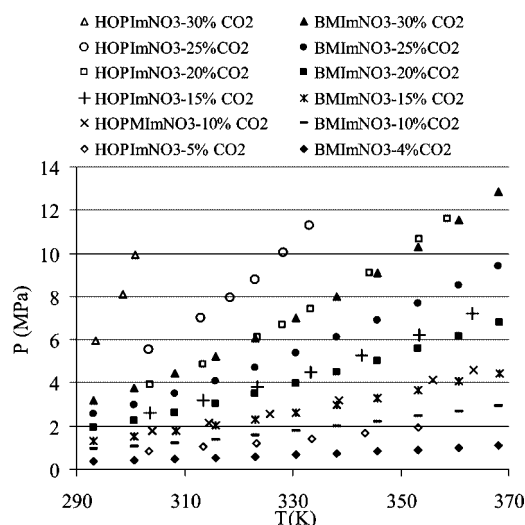


Figure 5. Comparison of the experimentally determined isopleths of the systems CO₂ + BMImNO₃ and CO₂ + HOPMImNO₃.

determined for several CO₂ concentrations ranging from 5 up to 30 mol % in a temperature region from 20 up to 95 °C and pressures up to 12 MPa. The obtained experimental data of the systems are summarized in Tables 3 and 4, respectively. For the system CO₂ + HOPMImNO₃ evidence of some degradation of the sample was found when kept at temperatures of 70–90 °C for several hours. Therefore, all samples were first measured at 40 and 60 °C, followed by measurements at the temperatures 30, 50, and 70 °C. If consistent data were obtained, measurements at an intermediate temperature like 45 °C were performed as well. In case no degradation was observed and if still consistency is obtained, measurements at as high as 80 °C were determined; otherwise, the sample is discarded. Surprisingly, no evidence of degradation was found when the IL was heated without CO₂ or even when the IL is kept in the presence of

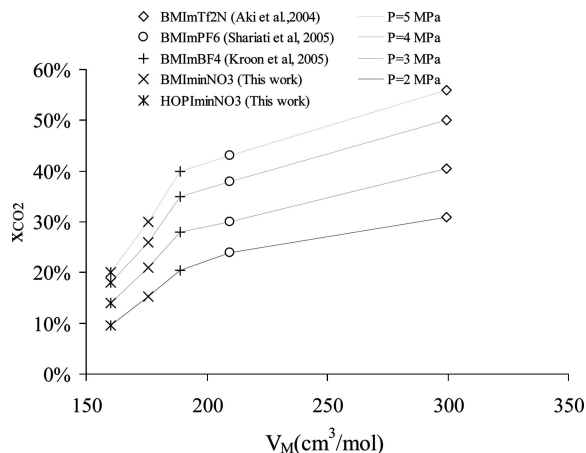


Figure 6. Solubility of CO₂ in several ILs at 313 K versus its molar volume at different pressures. Experimental phase equilibrium data taken from BMImTf₂N,²² BMImPF₆,¹⁹ and BMImBF₄.²⁴ In this figure x_{CO_2} represents the molar fraction and V_M the molar volume.

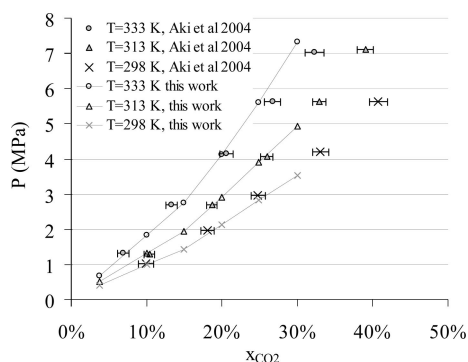


Figure 7. Comparison of some isotherms of the system CO₂ + BMImNO₃ presented in this work and those measured by Aki et al.²²

CO₂ for 2 weeks at room temperature. For the system CO₂ + BMImNO₃ no evidence of degradation was found, not even at temperatures as high as 95 °C.

The isopleths of both binary systems are plotted in Figure 5. As can be seen in this figure, the equilibrium pressures of the system increase with temperature and with CO₂ concentration as well. This means that, for a fixed concentration of carbon dioxide, the solubility of the carbon dioxide in the ionic liquid decreases toward higher temperatures. This effect is much more pronounced at higher CO₂ concentrations, while at lower CO₂ concentrations the effect is less significant. For the system CO₂ + HOPMImNO₃ at concentrations of CO₂ higher than 25% the pressure needed to dissolve the CO₂ increases substantially (see Figure 5). Therefore, for these concentrations bubble points could not be determined in the whole temperature range as the equilibrium pressures are exceeding the safety specifications of the facility. For the system CO₂ + BMImNO₃ bubble points could be determined in the whole range of CO₂ concentrations, i.e. up to 30% CO₂. Our observations agree with the common solubility behavior of CO₂ in ionic liquids,^{17–20} be it that in the case of BMImNO₃ the solubility of CO₂ is much lower than for other ILs, as previously reported by Aki et al.²² It can be concluded from our experimental work that in the case of BMImNO₃ the pressure needed for dissolving a fixed amount of CO₂ is considerably lower than the pressure needed for dissolving the same amount of CO₂ in HOPMImNO₃ (see Figure 5). This behavior is expected as the molar volume of BMImNO₃ is higher than that of HOPMImNO₃ ($V_{M,\text{BMImNO}_3} = 171 \text{ cm}^3/\text{mol} > V_{M,\text{HOPMImNO}_3} = 160 \text{ cm}^3/\text{mol}$, at 292 K); i.e., there is

more free volume in BMImNO₃ to dissolve CO₂. The solubility of the CO₂ in our ILs and in other ILs with a BMIm cation and different anion is plotted against the molar volume in Figure 6. Other authors^{23,26,28} have pointed out before that there exists a strong dependence of the CO₂ solubility with the molar volume.

In the literature there are two other series of data of the system CO₂ + BMImNO₃ available: those of Blanchard et al.²³ and those of Aki et al.²² The latter author remarks that the data of Blanchard et al. are not reliable due to the presence of impurities in the IL. Consequently, for comparison with our data only, the data of Aki et al. were considered. Interpolation of our experimental data is compared with the data of Aki et al.²² in Figure 7. Both series of data show good agreement.

Ternary Systems CO₂ + H₂O + HOPMImNO₃ and CO₂ + H₂O + BMImNO₃. Bubble points for the ternary system CO₂ + H₂O + HOPMImNO₃ have been determined for three water concentrations (3.3, 13.3, and 35.8 mol % H₂O) and several CO₂ concentrations varying from 5 to 22 mol % in a temperature range from 30 to 80 °C and pressures up to 12 MPa. The data are summarized Tables 5–7.

Bubble points for the ternary system CO₂ + H₂O + BMImNO₃ have been determined for three water concentrations (2, 9, and 21 mol % H₂O) at two CO₂ concentrations (10 and 25 mol % CO₂), in a temperature region from 10 up to 95 °C and pressures up to 12 MPa. The data are summarized in Table 8. Again evidence of some degradation was found in the case of HOPMImNO₃ but not in the case of BMImNO₃. For both systems, the equilibrium pressure of the system is increasing with temperature and with the CO₂ concentration.

Discussion

From this study, it became apparent that the presence of water in the IL affects the solubility of CO₂ in the solution. Following the assumptions of Perez,⁴³ we can analyze, at least qualitatively, the effect of adding water to the IL. Insight will be obtained how the bubble point pressure of the ternary mixture CO₂ + H₂O + HOPMImNO₃ and the solubility of CO₂ will be affected by the presence of water in the system.

Addition of water to the binary system IL + CO₂ will cause that in the resulting aqueous solution a part of the weak Lewis acid complexes²⁹ CO₂–IL will disintegrate, while at the same time new weak interactions water–CO₂ will occur. In addition, hydrogen bonding between water and the anions of the IL is expected to occur.⁶ As CO₂ has a relatively high solubility in ILs and a very low solubility in water, it seems obvious that the overall resulting effect will be that for the same amount of CO₂ in the ternary mixture CO₂ + H₂O + IL higher bubble point pressures will occur, as was observed in our experiments. In Figure 8, the equilibrium pressure is plotted versus the relative water concentration for a fixed absolute CO₂ concentration (x_{CO_2}) for the system CO₂ + H₂O + HOPMImNO₃. As not all the data have exactly the same CO₂ composition, some data with a slightly different concentration of CO₂ have been interpolated. These points are represented by open symbols. It can be seen that in general the equilibrium pressure increases dramatically with the CO₂ concentration, which means that the solubility of CO₂ in the liquid phase decreases with increasing water concentration.

Another way to consider the experimental results is on a water-free basis, i.e., when the ratio CO₂/IL remains constant and the IL has to dissolve the same amount of CO₂. In that case, the equilibrium pressures must remain constant if other effects are absent. In Figure 9, the equilibrium pressure is plotted versus the relative water concentration for a fixed relative water-

TABLE 5: Liquid–Vapor Data of the System CO₂ + H₂O + HOPMImNO₃ for 3.3 mol % H₂O and Various CO₂ Concentrations^a

$X_{\text{H}_2\text{O}} = 0.77\%, X_{\text{CO}_2} = 5.43\%,$ $x_{\text{H}_2\text{O}} = 0.73\%, x_{\text{CO}_2} = 5.39\%$		$X_{\text{H}_2\text{O}} = 4.11\%, X_{\text{CO}_2} = 9.90\%,$ $x_{\text{H}_2\text{O}} = 3.72\%, x_{\text{CO}_2} = 9.53\%$		$X_{\text{H}_2\text{O}} = 5.54\%, X_{\text{CO}_2} = 14.71\%,$ $x_{\text{H}_2\text{O}} = 4.76\%, x_{\text{CO}_2} = 14.01\%$		$X_{\text{H}_2\text{O}} = 3.99\%, X_{\text{CO}_2} = 19.32\%,$ $x_{\text{H}_2\text{O}} = 3.25\%, x_{\text{CO}_2} = 18.69\%$	
P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)
0.842	303.50	1.786	303.37	2.626	303.50	3.685	303.21
1.023	313.46	2.131	313.48	3.241	313.52	4.616	313.13
1.233	323.50	2.331	318.45	3.633	318.34	5.151	318.17
1.423	333.55	2.531	323.46	3.946	323.45	5.681	323.17
1.668	343.55	2.951	333.49	4.731	333.51	6.981	333.20
1.950	353.54	3.421	343.54	5.632	343.35	8.361	343.13
		3.926	353.52	6.633	353.43		

^a P : absolute pressure; $x_i = n_i/(n_{\text{CO}_2} + n_{\text{H}_2\text{O}} + n_{\text{IL}})$; $X_i = n_i/(n_i + n_{\text{IL}})$; $i = \text{CO}_2, \text{H}_2\text{O}$; n = number of moles.

TABLE 6: Liquid–Vapor Data of the System CO₂ + H₂O + HOPMImNO₃ for 13.3 mol % H₂O and Various CO₂ Concentrations^a

$X_{\text{H}_2\text{O}} = 13.37\%, X_{\text{CO}_2} = 6.02\%,$ $x_{\text{H}_2\text{O}} = 12.66\%, x_{\text{CO}_2} = 5.26\%$		$X_{\text{H}_2\text{O}} = 12.91\%, X_{\text{CO}_2} = 11.47\%,$ $x_{\text{H}_2\text{O}} = 11.47\%, x_{\text{CO}_2} = 10.14\%$		$X_{\text{H}_2\text{O}} = 15.10\%, X_{\text{CO}_2} = 17.74\%,$ $x_{\text{H}_2\text{O}} = 12.76\%, x_{\text{CO}_2} = 15.47\%$		$X_{\text{H}_2\text{O}} = 11.15\%, X_{\text{CO}_2} = 21.30\%,$ $x_{\text{H}_2\text{O}} = 8.99\%, x_{\text{CO}_2} = 19.38\%$	
P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)
0.953	303.18	2.152	303.42	3.516	303.49	4.557	303.40
1.159	313.31	2.542	313.43	4.206	313.27	5.697	313.33
1.388	323.08	3.027	323.44	5.206	323.40	6.406	318.40
1.526	328.24	3.552	333.37	6.151	333.38	7.052	323.49
1.644	333.34	4.187	343.43	7.371	343.37	8.676	333.50
1.926	343.11	4.811	352.97	8.496	352.92	9.536	338.43
2.250	352.85	5.536	363.34	10.072	362.89		

^a P : absolute pressure; $x_i = n_i/(n_{\text{CO}_2} + n_{\text{H}_2\text{O}} + n_{\text{IL}})$; $X_i = n_i/(n_i + n_{\text{IL}})$; $i = \text{CO}_2, \text{H}_2\text{O}$; n : number of moles.

TABLE 7: Liquid–Vapor Data of the System CO₂ + H₂O + HOPMImNO₃ for 35.8 mol % H₂O and Various CO₂ Concentrations^a

$X_{\text{H}_2\text{O}} = 34.11\%, X_{\text{CO}_2} = 7.33\%,$ $x_{\text{H}_2\text{O}} = 32.42\%, x_{\text{CO}_2} = 4.95\%$		$X_{\text{H}_2\text{O}} = 39.80\%, X_{\text{CO}_2} = 13.79\%,$ $x_{\text{H}_2\text{O}} = 36.30\%, x_{\text{CO}_2} = 8.78\%$		$X_{\text{H}_2\text{O}} = 34.84\%, X_{\text{CO}_2} = 18.28\%,$ $x_{\text{H}_2\text{O}} = 30.41\%, x_{\text{CO}_2} = 12.72\%$		$X_{\text{H}_2\text{O}} = 33.96\%, X_{\text{CO}_2} = 22.17\%,$ $x_{\text{H}_2\text{O}} = 28.59\%, x_{\text{CO}_2} = 15.83\%$	
P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)
1.237	303.28	2.476	303.15	3.596	303.34	5.153	303.23
1.481	313.28	2.986	313.35	4.382	313.30	6.293	313.18
1.655	318.38	3.280	318.20	4.914	318.20	7.878	323.29
1.768	323.39	3.571	323.16	5.346	323.24	9.606	333.22
2.071	333.37	3.900	328.29	6.427	333.26	11.338	341.35
2.403	343.34	4.307	333.32	7.552	342.92		
2.776	353.35	4.924	343.24				
		5.774	353.22				

^a P : absolute pressure; $x_i = n_i/(n_{\text{CO}_2} + n_{\text{H}_2\text{O}} + n_{\text{IL}})$; $X_i = n_i/(n_i + n_{\text{IL}})$; $i = \text{CO}_2, \text{H}_2\text{O}$; n : number of moles.

free CO₂ molar fraction (X_{CO_2}) for the system CO₂ + H₂O + HOPMImNO₃. As not all data have exactly the same CO₂ composition, some data with a different concentration of CO₂ have been obtained by interpolation. These points are represented by open symbols. It can be observed that in this case the equilibrium pressures remain almost unchanged with the water concentration. Of course, the equilibrium lines are shifted toward higher pressures with increasing CO₂ concentration as shown in Figure 9.

In Figure 10, the equilibrium pressure versus the relative water concentration for a fixed relative water-free CO₂ molar fraction (X_{CO_2}) is depicted for the system CO₂ + H₂O + BMImNO₃. Again, we can observe that in this case the equilibrium pressure remains almost unchanged with the water concentration. However, the equilibrium pressure for 10 mol % CO₂ (Figure 10a) is showing a minimum at lower water concentrations. After passing the minimum, the equilibrium pressure is increasing again but always remains lower than the pressure of the water-free system. In the case of 25 mol % CO₂ (Figure 10b), first the equilibrium pressure decreases, going through a minimum, and then increases

again with increasing water concentration. In fact, this observation means that at lower water concentrations an enhancement of the CO₂ solubility occurs.

A rationale for this behavior could be based on considering the excess molar volume (V^E) of the system. Addition of different molecules to the IL may cause a positive or negative value of V^E for the resulting mixture; i.e., these molecules will cause a more compact or lesser compact structure of the liquid phase, which is indicated by the value of V^E . If the resulting structure is less compact ($V^E > 0$), then there will be more free volume or void space for the CO₂ molecules available, and consequently, the pressure for dissolving the same amount of CO₂ will be lower. In the literature, both positive and negative values of V^E of mixtures of water–ILs have been reported, although negative V^E values are more common.^{44,45} From our measured densities V^E of the aqueous solutions of the considered ILs were calculated and plotted in Figure 11. For both ILs considered in this study, the excess molar volumes turned out to be positive in the major range of water concentrations. For BMImNO₃ slightly higher values have been observed for V^E . Consequently, the enhanced

TABLE 8: Liquid–Vapor Data of the System CO₂ + H₂O + BMImNO₃^a

$X_{\text{H}_2\text{O}} = 1.99\%$, $X_{\text{CO}_2} = 10.00\%$, $x_{\text{H}_2\text{O}} = 1.76\%$, $x_{\text{CO}_2} = 8.93\%$	$X_{\text{H}_2\text{O}} = 9.18\%$, $X_{\text{CO}_2} = 10.00\%$, $x_{\text{H}_2\text{O}} = 7.60\%$, $x_{\text{CO}_2} = 8.33\%$	$X_{\text{H}_2\text{O}} = 21.26\%$, $X_{\text{CO}_2} = 10.00\%$, $x_{\text{H}_2\text{O}} = 16.06\%$, $x_{\text{CO}_2} = 7.30\%$	$X_{\text{H}_2\text{O}} = 1.99\%$, $X_{\text{CO}_2} = 25.00\%$, $x_{\text{H}_2\text{O}} = 1.47\%$, $x_{\text{CO}_2} = 19.68\%$	$X_{\text{H}_2\text{O}} = 9.18\%$, $X_{\text{CO}_2} = 25.00\%$, $x_{\text{H}_2\text{O}} = 6.44\%$, $x_{\text{CO}_2} = 18.50\%$	$X_{\text{H}_2\text{O}} = 21.26\%$, $X_{\text{CO}_2} = 25.00\%$, $x_{\text{H}_2\text{O}} = 13.75\%$, $x_{\text{CO}_2} = 16.45\%$
P (MPa) T (K)	P (MPa) T (K)	P (MPa) T (K)	P (MPa) T (K)	P (MPa) T (K)	P (MPa) T (K)
0.894 293.13	0.853 293.15	0.930 293.21	2.418 293.16	2.534 293.18	2.671 293.18
1.029 300.66	0.998 300.67	1.070 300.66	2.858 300.65	2.994 300.66	3.136 300.69
1.179 308.13	1.151 308.13	1.175 308.14	3.328 308.25	3.514 308.34	3.646 308.15
1.349 315.66	1.321 315.62	1.345 315.69	3.857 315.66	4.054 315.66	4.226 315.66
1.529 323.21	1.508 323.17	1.525 323.21	4.428 323.17	4.658 323.18	4.846 323.20
1.714 330.64	1.708 330.66	1.720 330.73	5.037 330.71	5.308 330.70	5.541 330.69
1.914 338.16	1.913 338.20	1.925 338.21	5.707 338.17	5.998 338.20	6.251 338.17
2.124 345.65	2.118 345.69	2.135 345.72	6.437 345.71	6.723 345.66	6.991 345.65
2.349 353.16	2.338 353.21	2.355 353.20	7.212 353.18	7.503 353.20	7.791 353.17
2.579 360.68	2.563 360.65	2.585 360.68	8.022 360.68	8.313 360.65	8.616 360.67
2.824 368.20	2.803 368.18	2.830 368.20	8.887 368.22	9.183 368.21	9.471 368.20

^a P : absolute pressure; $x_i = n_i/(n_{\text{CO}_2} + n_{\text{H}_2\text{O}} + n_{\text{IL}})$; $X_i = n_i/(n_i + n_{\text{IL}})$; $i = \text{CO}_2, \text{H}_2\text{O}$; n : number of moles.

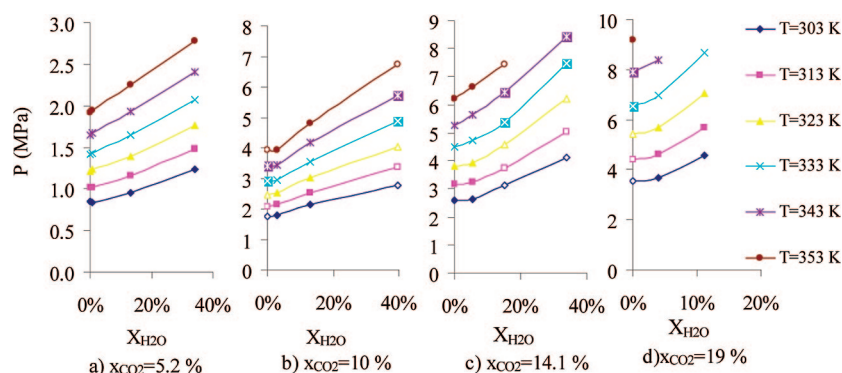


Figure 8. Influence of the water concentration on the bubble point pressure in the ternary system CO₂ + H₂O + HOPMImNO₃ for a fixed absolute CO₂ molar fraction. P : absolute pressure; $x_i = n_i/(n_{\text{CO}_2} + n_{\text{H}_2\text{O}} + n_{\text{IL}})$; $X_i = n_i/(n_i + n_{\text{IL}})$; $i = \text{CO}_2, \text{H}_2\text{O}$; n : number of moles; the open symbols are obtained by interpolation.

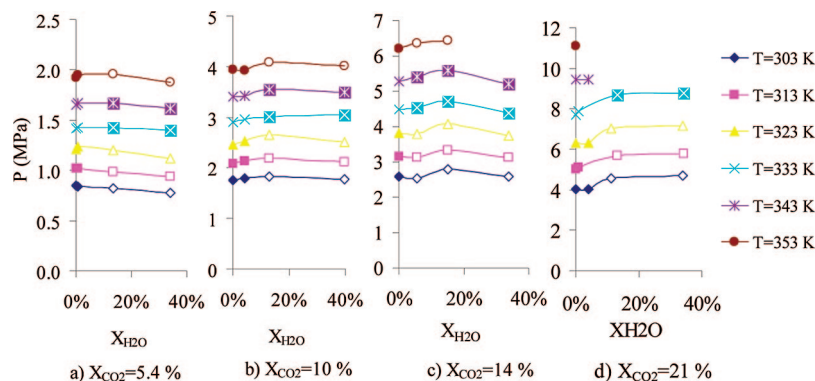


Figure 9. Influence of the water concentration on the bubble-point pressures in the ternary system CO₂ + H₂O + HOPMImNO₃ for fixed relative water-free CO₂ compositions. P : absolute pressure; $X_i = n_i/(n_i + n_{\text{IL}})$; $i = \text{CO}_2, \text{H}_2\text{O}$; n : number of moles; the open symbols are obtained by interpolation.

solubility of CO₂ in the ILs at lower water contents can be ascribed to the experimentally observed V^E behavior of both ILs. In particular, this holds for BMImNO₃.

Another effect to be considered is that when water molecules are added to the IL, the Coulombic forces associated with the ionic nature of the IL will decrease and lead to a small volume expansion. This effect also will contribute to an enhanced solubility of CO₂. In summary, the following four effects may contribute to the experimentally observed behavior of both ternary systems studied here: (1) In an aqueous solution of an IL, a part of the bonds

CO₂–IL will disappear. (2) New bonds water–CO₂ will be formed. (3) The excess molar volumes of both systems are positive. (4) The presence of water molecules affects the strengths of the Coulombic interactions. The first two effects apparently are dominant as the solubility of CO₂ in the studied ILs is decreasing in the mixtures with increasing water concentration. On the other hand, these effects are partially compensated by effects 3 and 4, leaving the solubility of CO₂ in the IL unchanged when the ratio CO₂/IL remains constant. Effects 3 and 4 also account for the observed behavior at lower water concentrations as shown in Figures

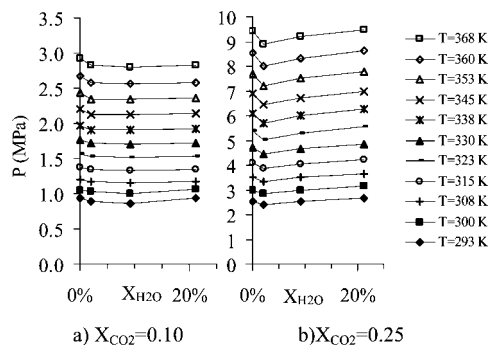


Figure 10. Influence of the concentration of water on the bubble-point pressures of the system $\text{CO}_2 + \text{H}_2\text{O} + \text{BMImNO}_3$ for a fixed relative water-free CO_2 composition. P : absolute pressure; $X_i = n_i/(n_i + n_{\text{IL}})$; $i = \text{CO}_2, \text{H}_2\text{O}$; n : number of moles.

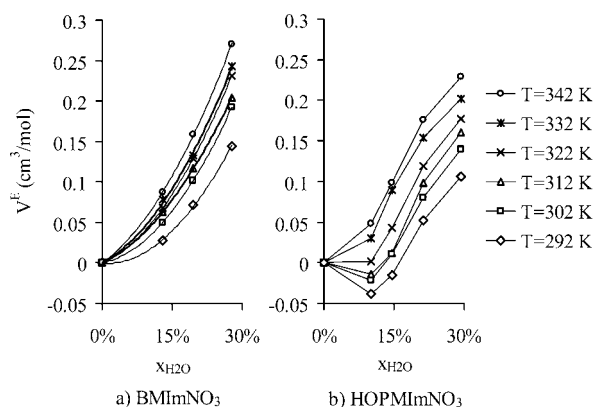


Figure 11. Excess molar volumes of the IL + water solutions. $x_i = n_{\text{H}_2\text{O}}/(n_{\text{H}_2\text{O}} + n_{\text{IL}})$, n : number of moles.

10 and 11; i.e., the occurrence of even a minimum in the equilibrium pressure in the case of BMImNO_3 can be explained.

Conclusions

In this study the solubility of CO_2 in two imidazolium-based ionic liquids with both nitrate as the anion: BMImNO_3 and HOPMImNO_3 . In addition, the density of the pure ILs and its mixtures with water as well were determined experimentally. The data for the BMImNO_3 are consistent with literature data. As was established before, the solubility of CO_2 in BMImNO_3 is lower than in other ILs with the same cation and other anions such as PF_6 or BF_4 . The solubility of CO_2 in HOPMImNO_3 is significantly lower than in BMImNO_3 , which is not surprising due to the lower molar volume of HOPMImNO_3 .

It was found that the $\text{HOPMImNO}_3\text{--CO}_2$ mixtures degrade at temperatures higher than 70–80 °C upon keeping them for several hours at these temperatures. No degradation was found at room temperature, even not by storage for 2 weeks time or when the IL was heated in absence of CO_2 . The system $\text{CO}_2 + \text{BMImNO}_3$ did not show any evidence of degradation in the temperature region of our measurements.

The influence of water concentrations on the solubility of CO_2 was extensively studied. It was found that when the ratio CO_2/IL is kept constant, this effect on the solubility of CO_2 is relatively small. However, when the solubility of CO_2 in the bulk solution is ascribed to the water concentration, it leads to lower CO_2 solubilities. It was also found that at low water concentrations the CO_2 solubility is slightly higher than compared with the water-free BMImNO_3 . This effect is

explained mainly by the positive excess molar volumes of the aqueous solutions at the working conditions in this study.

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