Solubility of Carbon Dioxide in the Ionic Liquid 1-Ethyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide

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Solubility of carbon dioxide in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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Abstract

In this work, the phase behaviour of the binary system of carbon dioxide and the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]) has been studied experimentally. The equipment used for the experiments is the Cailletet set-up, based on visual observations of phase transitions of systems with constant overall composition. Results are reported for carbon dioxide concentrations ranging from 12.3 to 59.3 mol%, and within temperature and pressure ranges of 310–450 K and 0–15 MPa, respectively. The data reveal an extremely high capacity of the selected ionic liquid for dissolving CO_2 gas, for example, reaching up to about 60 mol% within the above-mentioned pressure and temperature range. Also, the solubility of CO_2 in the ionic liquid [emim][Tf_2N] is compared to the solubility of CO_2 in the ionic liquid [emim][PF_6], an ionic liquid that shares the same cation.

Keywords: Green solvents; Ionic liquids; Phase behaviour; Gas separation

1. Introduction

Ionic liquids are defined as salts that exist in the molten state at ambient conditions. They often consist of large heterocyclic organic cations and anions. However, they are liquid at ambient temperatures, mainly as a result of the low lattice energy due to the asymmetric cations and weak coulombic forces [1,2]. Due to some unique characteristics, ionic liquids are the subjects of extensive research. In general, they have a very good solvency power for both organic and inorganic materials. Also, ionic liquids have a negligible vapour pressure, thereby reducing environmental pollution and working exposure hazards in comparison with conventional organic solvents. Besides that, the phase behaviour of ionic liquids is significantly different in comparison to normal organic liquids. Ionic liquids show, in general, very high solubilities of water and carbon dioxide and a very low solubility of hydrogen compared to conventional organic solvents [3,4]. Therefore, besides their use as potential new green solvents or reaction media, ionic liquids also show potential for the separation of gases such as carbon dioxide and hydrogen. The very low vapour pressures of ionic liquids make them even further attractive for gas separations as they show almost no solubility in the gaseous phase.

Although literature contains a number of articles on the solubility of CO_2 in ionic liquids, most of the data available are at atmospheric conditions. Such low-pressure data, in the form of Henry's constants, have led us to select 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]) as an ionic liquid with potentially high capacities to dissolve CO_2 at high temperatures and low pressures. To prove this hypothesis, high-pressure phase behaviour data of the binary system CO_2 + [emim][Tf_2N] have been measured in this work. This has been done by measuring bubble point pressures at a number of temperatures for eight different isopleths ranging from 12.3 up to 59.3 mol% CO_2. Fig. 1 shows the chemical structure of [emim][Tf_2N].

2. Experimental

The equipment used to study the phase behaviour of the binary system of the ionic liquid and carbon dioxide was the

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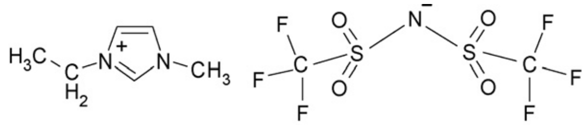

Fig. 1. Chemical structure of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]).

Cailletet set-up. This equipment is based on visual observation of phase transitions of systems with constant composition. A sample having the desired overall composition is brought into the Cailletet tube. This is a glass tube, prepared of thick-walled Pyrex glass, so that it is resistant to high temperatures and elevated pressures. The sample is confined in the closed top of the tube. The bottom of the tube is open and sealed by a mercury column. The bottom end is placed in an autoclave, where the mercury reservoir is connected to a hydraulic oil system. Therefore, the mercury column is used both for sealing the sample and for transferring pressure to the system. The temperature can be set and kept constant by using a thermostatic bath that circulates silicon oil around the tube. To measure the temperature of the sample, a platinum resistance thermometer with an accuracy of 0.02 K is placed close to the sample. The pressure can be varied by means of a screw-type hand pump. A dead-weight pressure gauge is used to measure the pressure inside the autoclave with an accuracy of 0.03% of the reading. The smallest weight that is used is 0.05 bar. A small stainless steel ball that is placed inside the Cailletet tube stirs the mixture. The metal ball moves up and down by using two magnets that are placed at both sides of the tube. The speed of the magnets can be varied according to the viscosity of the liquid. A light source is placed behind the system as to provide better visibility and a microscope helps to improve the visual clarity.

An apparatus called the gas rack is used to fill the Cailletet tube with the preferred gas. It is very important that the amount of gas in the tube is known accurately and that there are no impurities present, including air. Therefore, the procedure for filling the tube by use of the gas rack involves careful degassing of the liquid, vacuuming, injection of a known amount of desired gas, as well as sealing the sample with mercury. For further details on the experimental facility and the experimental procedures, one is referred to elsewhere [5].

The ionic liquid [emim][Tf_2N] was purchased from Sigma-Aldrich Chemie BV and had a purity of more than 97%. Prior to use, the ionic liquid was dried under vacuum conditions at room temperature for a few days.

3. Results and discussion

The solubility of carbon dioxide in [emim][Tf_2N] was determined by measuring the bubble point pressures of binary systems of carbon dioxide and [emim][Tf_2N] for a number of isopleths at different temperatures. The results are presented numerically and graphically in Table 1 and Fig. 2, respectively. It can be observed that the equilibrium pressures increase with increasing temperatures. A P–x diagram can be obtained by interpolation of the P–T data of Table 1. The interpolated bubble point pressures for various isotherms are presented in Table 2 and the resulting P–x graph is shown in Fig. 3. It can be observed that with increasing concentrations of CO_2 the equilibrium pressures increase gradually at first, but more rapidly at higher CO_2 concentrations. This figure also exhibits the very large capacity of

Table 1
Measured bubble point data for various molar concentrations of carbon dioxide in the binary system carbon dioxide and [emim][Tf_2N]

x_{co_2}	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
0.123	312.17	0.626	361.51	1.273	410.91	2.103
0.123	322.00	0.742	371.39	1.428	420.81	2.247
0.123	331.87	0.852	381.26	1.583	430.71	2.412
0.123	341.79	1.002	391.12	1.748	440.59	2.572
0.123	351.66	1.137	401.02	1.923	450.49	2.743
0.212	312.10	1.212	361.51	2.493	410.89	4.053
0.212	321.95	1.442	371.35	2.793	420.80	4.383
0.212	331.84	1.697	381.24	3.088	430.71	4.723
0.212	341.74	1.933	391.11	3.423	440.63	5.078
0.212	351.64	2.198	401.00	3.733	450.48	5.418
0.303	312.14	1.902	361.54	3.952	410.85	6.538
0.303	322.00	2.267	371.36	4.437	420.80	7.078
0.303	331.85	2.622	381.25	4.937	430.69	7.588
0.303	341.76	3.052	391.09	5.463	440.58	8.123
0.303	351.64	3.497	400.97	6.008	450.49	8.648
0.392	312.14	2.738	361.55	5.908	410.85	9.863
0.392	322.00	3.278	371.43	6.653	420.76	10.683
0.392	331.88	3.848	381.22	7.418	430.68	11.523
0.392	341.77	4.518	391.08	8.208	440.55	12.338
0.392	351.65	5.188	400.96	9.028	450.46	13.153
0.479	312.13	3.786	351.69	7.321	391.11	11.852
0.479	322.00	4.541	361.55	8.386	401.00	13.062
0.479	331.89	5.401	371.40	9.501	410.90	14.307
0.479	341.77	6.321	381.26	10.681		
0.519	312.11	4.399	341.74	7.474	371.34	11.409
0.519	321.98	5.309	351.65	8.715	381.23	12.854
0.519	331.86	6.334	361.52	10.035	391.11	14.329
0.570	312.16	5.244	341.78	9.180	370.40	14.180
0.570	322.00	6.394	351.67	10.790		
0.570	331.89	7.699	361.52	12.550		
0.593	312.14	5.789	331.88	8.634		
0.593	317.04	6.418	336.88	9.480	351.63	12.305
0.593	322.01	7.103	341.76	10.375	356.57	13.340
0.593	326.93	7.839	346.69	11.320	361.51	14.402

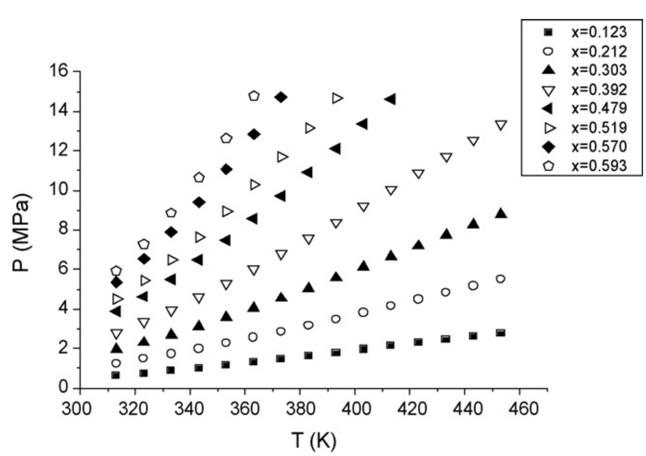

Fig. 2. Pressure–temperature diagram for [emim][Tf_2N] and carbon dioxide, showing the measured bubble points at various concentrations of carbon dioxide.

Table 2
Interpolated bubble point pressures for the binary system carbon dioxide and [emim][Tf_2N] at various temperatures

Temperature (K)	Pressure (MPa)							
	0.123[a]	0.212[a]	0.303[a]	0.392[a]	0.479[a]	0.519[a]	0.570[a]	0.593[a]
313.15	0.639	1.239	1.944	2.790	3.861	4.490	5.354	5.916
323.15	0.752	1.469	2.295	3.340	4.637	5.421	6.529	7.268
333.15	0.876	1.716	2.684	3.944	5.506	6.478	7.883	8.848
343.15	1.010	1.978	3.107	4.597	6.457	7.647	9.397	10.637
353.15	1.153	2.254	3.558	5.292	7.482	8.911	11.053	12.617
363.15	1.303	2.543	4.036	6.023	8.569	10.258	12.832	14.770
373.15	1.460	2.842	4.534	6.787	9.708	11.671	14.714	
383.15	1.621	3.153	5.049	7.577	10.890	13.136		
393.15	1.787	3.472	5.577	8.387	12.103	14.639		
403.15	1.954	3.799	6.113	9.212	13.338			
413.15	2.122	4.132	6.654	10.047	14.584			
423.15	2.291	4.471	7.195	10.886				
433.15	2.457	4.815	7.733	11.724				
443.15	2.621	5.161	8.263	12.555				
453.15	2.780	5.509	8.780	13.374				

[a] Mole fraction CO_2.

[emim][Tf_2N] to dissolve carbon dioxide, for example, reaching as high as 60 mol% at pressures as low as 6 MPa. In Fig. 4, the solubility of CO_2 in [emim][Tf_2N] is compared to another ionic liquid sharing the same cation, but having a different anion, namely [emim][PF_6] [6]. It can be seen that at $T = 333.15$ K CO_2 is more soluble in the ionic liquid with the [Tf_2N] anion, especially at higher CO_2 concentrations. This is probably due to the presence of fluoroalkyl groups in [Tf_2N] which are known to be CO_2-philic. It is even known from literature [7] that carbon dioxide solubility increases with increasing number of fluoroalkyl groups in the anion. This may be the result of the favourable interaction between the negative fluorine atoms of these anions and the positive charge on the carbon of carbon dioxide [7].

For ionic liquids with the [Tf_2N] anion and other cations, no experimental data have been published in the temperature and pressure range of our work. Therefore, no further comparisons could be made.

Measurements were done up to a temperature of 450 K. Since the data were reproducible within a sample, even after being kept at such high temperatures for hours or even days, it can be concluded that the ionic liquid [emim][Tf_2N] is thermally stable up to 450 K in the presence of CO_2 but the absence of air.

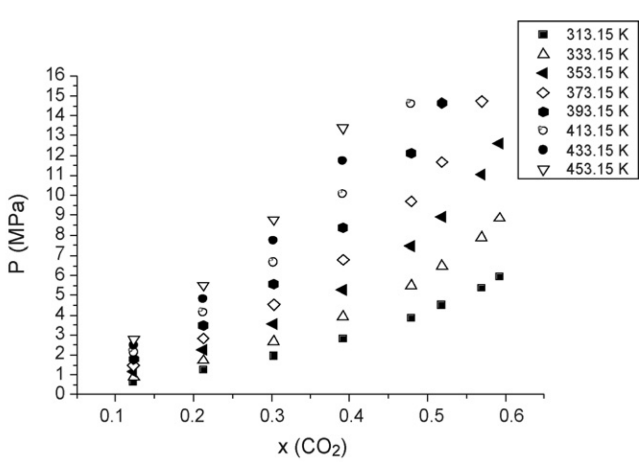

Fig. 3. Pressure–composition diagram for [emim][Tf_2N] and carbon dioxide at various temperatures.

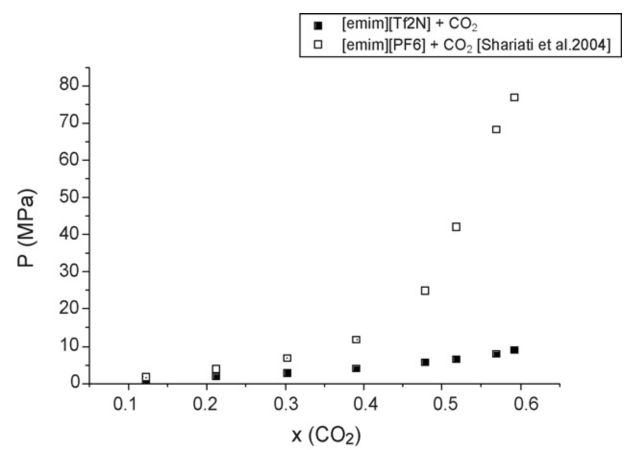

Fig. 4. Pressure–composition diagram of CO_2 and two ionic liquids with different anions, but sharing the [emim] cation at $T = 333.15$ K.

4. Conclusions

In order to show the solubility of CO_2 in the ionic liquid [emim][Tf_2N], the phase behaviour of the binary system of CO_2 and [emim][Tf_2N] was studied experimentally by measuring its bubble point pressures at different temperatures for a number of isopleths. The results showed that the solubility of CO_2 in [emim][Tf_2N] increases with increasing pressure and decreasing temperature. The CO_2 solubility is very high in the ionic liquid [emim][Tf_2N] in comparison to the ionic liquid [emim][PF_6]. This difference becomes even larger at higher CO_2 concentrations. Due to unavailability of literature data, no comparison could be made with other systems with the same anion but a different cation. The results obtained in this work show that the ionic liquid [emim][Tf_2N] has an excellent potential to be used for processes which require a solvent with high CO_2 solubilities, for example, in reactions or in gas separations.

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References

[1] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2003) 156–164.
[2] P. Scovazzo, D. Camper, J. Kieft, J. Poshusta, C. Koval, J. Noble, Ind. Eng. Chem. Res. 43 (2004) 6855–6860.
[3] J.L. Anthony, A.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 106 (2002) 7315–7320.
[4] P.J. Dysen, G. Laurenczy, C.A. Ohlin, J. Vallance, T. Welton, Chem. Commun. 19 (2003) 2418–2419.
[5] S. Raeissi, C.J. Peters, J. Supercrit. Fluids 20 (2001) 221–228.
[6] A. Shariati, C.J. Peters, J. Supercrit. Fluids 29 (2004) 43–48.
[7] S.N.V.K. Aki, B.R. Mellein, E.M. Saurer, J.F. Brennecke, J. Phys. Chem. B 108 (2004) 20355–20365.