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An IUPAC Task Group Study: The Solubility of Carbon Monoxide in [hmim][Tf_2N] at High Pressures

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ABSTRACT: As part of an International Union of Pure and Applied Chemistry (IUPAC) investigation on the properties of a selected ionic liquid (IL), a synthetic technique was employed to experimentally determine the high-pressure phase behavior of the binary system carbon monoxide + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide in the form of bubble points. The pressure necessary to dissolve the last bubble of vapor was determined at different temperatures for binary mixtures of various concentrations. Solubility data were obtained within a temperature range of (300 to 440) K and a pressure range up to about 12 MPa. The results were compared with those from the laboratory of Maurer, also a collaborator in the IUPAC Task Force and using the same IL sample. The agreement between the two data sets was shown to be very good.

1. INTRODUCTION

The discrepancy observed in thermodynamic and thermophysical properties of various ionic liquids (ILs) and their mixtures with some gases resulted in the establishment of the International Union of Pure and Applied Chemistry (IUPAC) Task Force[1] aiming to systematically provide a data bank of reliable data for a typical IL and to determine the underlying cause of the prevailing differences in literature data.[1−13] The task group selected 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, also known as 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and commonly abbreviated to [hmim][Tf_2N] in literature as their reference fluid because it is stable, has low viscosity compared to the commonly investigated ILs based on hexafluorophosphate and tetrafluoroborate anions, has low water solubility, and is easily prepared and purified.[1] Within this larger IUPAC project (Project 2002-005-1-100: Thermodynamics of Ionic Liquids, Ionic Liquid Mixtures, and the Development of Standardized Systems), this study has the task to determine the high-pressure solubility of carbon monoxide in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide and compare the results with literature data to examine if there are significant disagreements between different laboratories on the gas solubility in the IL.

2. EXPERIMENTAL SECTION

The Cailletet equipment, which was used to carry out the solubility measurements, has been explained in detail elsewhere.[14,15] The equipment consists of a glass equilibrium cell, filled with fixed amounts of CO and the IL. The solubility is observed visually by the disappearance of the last bubble of vapor as the pressure is increased at fixed temperature. Temperatures can be increased up to 450 K and pressures up to 15 MPa, respectively. The uncertainties of measurements are within 0.02 K for temperature, 0.001 for mole fraction, and 0.03 % of the reading for pressure.

The IL [hmim][Tf_2N] was synthesized and purified by the IUPAC Task Force group members at the University of Notre Dame (Notre Dame, IN) and the National Institute of Standards and Technology (Boulder, CO) and delivered to us in sealed Schlenk tubes.[1,13] The sample had a water mass fraction in the order of $1 \cdot 10^{-5}$ and a minimum purity of 0.995 in mole fraction as indicated by ^{1}H and ^{19}F NMR spectroscopy. It was further dried with molecular sieves under vacuum. The carbon monoxide used had a purity of 99.997 %.

3. RESULTS

Data for the experimentally measured CO isopleths and the resulting interpolated isotherms are presented in Tables 1 and 2, respectively. Table 1 consists of solubility data in the form of bubble-point pressures required to dissolve carbon monoxide at four different concentrations up to pressures of about 12 MPa. These data are presented graphically in Figure 1.

The three curves at lower carbon monoxide concentrations show slightly positive-sloped $P-T$ curves. This indicates that, in contrast to some other gases, the solubility of carbon monoxide is not greatly affected by changes in temperature. However, the topmost curve corresponding to a carbon monoxide concentration of 12.53 %, which is further extended to higher temperatures,

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Table 1. Experimentally Measured Solubility Data (Bubble-Point Curves) for CO (1) in [hmim][Tf_2N] (2)

	T	P	T	P	T	P
x_1	K	MPa	K	MPa	K	MPa
0.0518	300.70	4.049	308.21	4.069	315.78	4.089
	315.80	4.099	323.25	4.119	323.25	4.099
	330.72	4.139	338.21	4.169	345.70	4.189
	353.26	4.199	360.77	4.199	368.22	4.209
0.0750	308.28	6.195	315.77	6.245	323.18	6.285
	330.70	6.315	338.29	6.355	345.71	6.375
	353.25	6.405	360.83	6.405	368.35	6.405
0.1001	300.87	8.597	308.38	8.647	315.93	8.707
	315.94	8.707	323.20	8.782	323.39	8.767
	330.86	8.817	338.42	8.837	345.87	8.867
	353.39	8.877	360.91	8.877	368.39	8.877
0.1253	310.15	11.452	321.24	11.532	332.81	11.592
	345.48	11.642	357.31	11.672	369.33	11.652
	381.36	11.612	393.51	11.542	400.92	11.492
	413.06	11.422	425.14	11.322	437.29	11.222

reveals a curve which is concave downward and has a maximum pressure. This indicates that solubility decreases with temperature up to a certain temperature, after which the temperature effect is switched to increased solubility upon temperature increase. The phase behavior of the same binary system has been previously measured by Kumelan et al.[5] in the form of solubility pressure versus gas molality. Although they also reported a very small temperature effect on solubility of carbon monoxide, which diminished upon temperature increase, they did not observe the switch because their measurements were limited to lower temperatures and pressures where solubility pressure still retained an increasing trend with temperature. The reason behind this shape is explained in detail elsewhere.[16]

The data of Table 2 are graphically presented in Figure 2, which highlights the extent of solubility better than Figure 1 because its coordinates are solubility pressure versus mole fraction of dissolved carbon monoxide. This figure indicates that in contrast to CO_2 solubilities which have been shown[2,7,8,17−20] to be quite high in [hmim][Tf_2N], for example exceeding 60 mole percent at 8 MPa and 300 K, the corresponding solubilities of carbon monoxide are limited to smaller amounts. For instance, at about 300 K, pressures higher than 8 MPa are required to dissolve only 10 mol % of carbon monoxide in [hmim][Tf_2N].

The data of this work are compared in Figure 3 with the solubility data of carbon monoxide in the same synthesized IUPAC IL sample, measured by our other IUPAC Task Force colleagues at the University of Kaiserslautern (Kaiserslautern, Germany).[5] As evident in this figure, there is a very good match between the phase behavior measured in the two laboratories. For example, at a temperature of 333.2 K, the error defined as the difference between the absolute pressure measured in the two laboratories divided by the pressure of the lab of Kumelan et al.[5] summed over all of the composition points measured by Kumelan et al. is only 2.1 %. This is yet another affirmation of the result we drew in a previous IUPAC study on the solubility of CO_2 in the reference IL, [hmim][Tf_2N], concerning the discrepancies on IL solubility data in literature.[11] In contrast to this study for which data from only two laboratories are available, the former study on CO_2 solubility was very rich with literature data from a total of seven different laboratories throughout the world, four using the IUPAC sample, and three using non-IUPAC samples of [hmim][Tf_2N]. In that study,[11] we concluded that the inconsistencies of CO_2 solubility data in literature are probably more the result of varying experimental techniques than from the impurities of the [hmim][Tf_2N] samples. In this work, considering that the data of Kumelan et al. are measured on the same IUPAC IL sample and their technique of solubility measurement, similar to our work, uses the synthetic method, the high degree of data agreement was to be expected. Similarly, we[12] obtained an almost perfect overlap of H_2 solubility in [hmim][Tf_2N] with the data of Kumelan et al.[4] So, one may point out, as a conclusion of the IUPAC Task Force study, that the major cause of thermodynamic data discrepancies in literature on gas solubility in [hmim][Tf_2N] is now understood. The perfect match between solubility data of CO_2, H_2, and now CO, between the laboratories of Delft University of Technology and the University of Kaiserslautern, for example, are witness to the fact that a "standardized" scientific data bank can be established for ILs. It remains to investigate the various experimental techniques available for phase behavior measurements and determine their accuracies and capabilities. It should be noted, however, that in general, the measurement of phase equilibria should cover a

Table 2. Interpolated Isothermal Solubility for CO (1) in [hmim][Tf_2N](2)

x_1	0.0518	0.0750	0.1001	0.1253
T/K	P/MPa	P/MPa	P/MPa	P/MPa
313.15	4.082	6.226	8.694	11.472
333.15	4.148	6.332	8.820	11.608
353.15	4.199	6.398	8.879	11.657
373.15				11.634
393.15				11.550
413.15				11.419
433.15				11.255

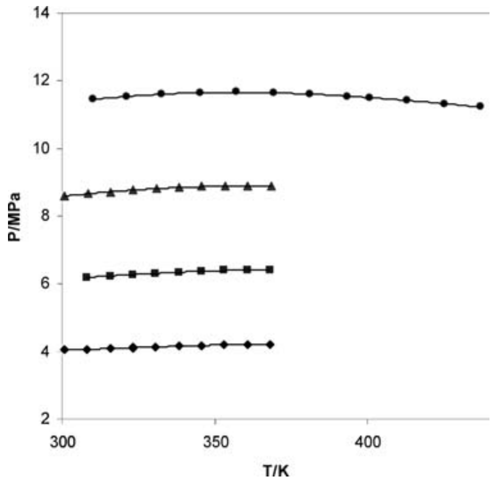

Figure 1. Experimentally measured bubble-point pressures of CO in [hmim][Tf_2N] as a function of temperature for four different molar concentrations of CO: ●, 0.1253; ▲, 0.1001; ■, 0.0750; ♦, 0.0518.

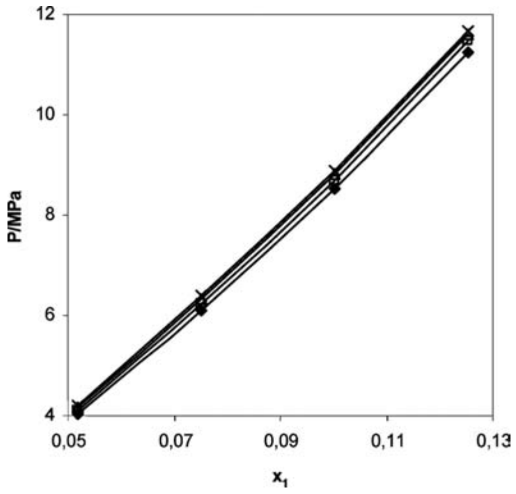

Figure 2. Bubble-point pressure versus molar concentration of CO in [hmim][Tf$_2$N] at four different temperatures: ♦, 293.15 K; □, 313.15 K; △, 333.15 K; ×, 353.15 K.

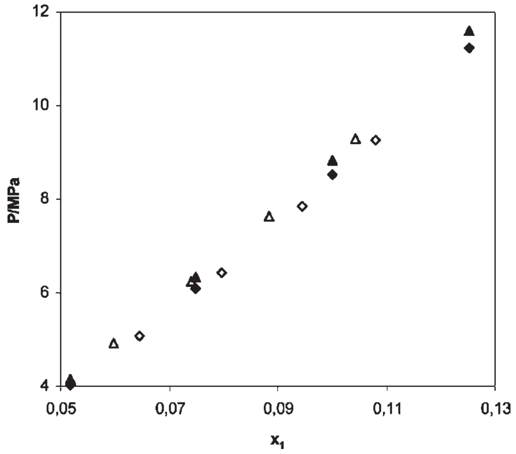

Figure 3. Comparison of CO solubility data in [hmim][Tf$_2$N] measured in this study to that in literature: ♦, this work at 293.15 K; ◇, Kumelan et al.[5] at 293.3; ▲, this work at 333.15 K; △, Kumelan et al.[5] at 333.2 K.

variety of techniques, since the data obtained by various methods can be complementary. For example, although the synthetic technique has proven to produce accurate data, it is incapable of providing compositional data from the various phases in equilibrium. To determine this, it is necessary to use methods that can take samples from the phases in equilibrium for further analysis.

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