J. Chem. Eng. Data **2006,** *51,* 645−647

Solubilities of Gases in 1,1,3,3-Tetramethylguanidium Lactate at Elevated Pressures

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Solubilities of O_2, N_2, H_2, and CH_4 in 1,1,3,3-tetramethylguanidium lactate (TMGL) at the temperatures ranging from (308 to 327) K and the pressures ranging from (0 to 11) MPa were measured. The solublilities were correlated using the Krichevisky−Kasarnovsky equation, from which Henry's constants and partial molar volumes of these four gases were obtained. It was found that the solubilities increase with increasing pressure and decrease with increasing temperature. The solubilities of these four gases in TMGL follow the sequence $x_{CH_4} > x_{O_2} > x_{N_2} > x_{H_2}$ (i.e., $H_{CH_4} < H_{O_2} < H_{N_2} < H_{H_2}$). Comparing the solubility data of these four gases with that of CO_2 in TMGL, it is observed that the solubilities of these four gases in TMGL are much lower than that of CO_2. This means that TMGL may be used as a potential solvent for capturing CO_2 from mixed gases.

Introduction

In recent years, ionic liquids (ILs)[1] have attracted extensive attention of various fields[2−4] due to their unique properties[1] such as negligible vapor pressure and high ionic conductivity. With favorable properties of negligible vapor pressure and nontoxicity, ILs have also been studied to absorb and separate gases,[5−8] of which the solubilities of gases in ILs are of most importance. Due to pollution of CO_2 to the environment and the advantages of ionic liquids (ILs) as benign solvents, we have investigated the solubilities of CO_2 in ionic liquid 1,1,3,3-tetramethylguanidium lactate (TMGL) at elevated pressures,[6] which showed that TMGL is a good solvent to absorb CO_2 as compared to other[9−14] ILs such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-octyl-3-methylimidazolium tetrafluoroborate ([C_8mim][BF_4]), 1-butyl-3-methyl imidazolium nitrate ([bmim][NO_3]), 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8mim][PF_6]), *N*-butylpyridinium tetrafluoroborate ([Nbupy][BF_4]), and 1-ethyl-3-methylimidazolium ethyl sulfate ([emim][$EtSO_4$]). Besides, TMGL was investigated to absorb and fix SO_2[15] and as a recyclable catalyst[16] for Henry reactions to produce 2-nitro alcohols. In nature or industry, CO_2 practically exists in mixed gases including CH_4, N_2, O_2, H_2, etc. Therefore, it is of critical importance to separate CO_2 from the mixed gases. For achieving such a goal, the solubility of these gases in TMGL are indispensable.

In this work, as a part of a series of our work, the solubilities of O_2, N_2, H_2, and CH_4 in TMGL at temperatures ranging from (308 to 328) K and pressures ranging from (0 to 11) MPa were determined. The solubilities were correlated using the Krichevisky−Kasarnovsky equation,[17] from which Henry's constants and partial molar volumes of these four gases were obtained. Also, we compared the solubility data of these four gases with that of CO_2 in TMGL so as to provide the fundamental basis for separation of CO_2 from mixed gases using TMGL.

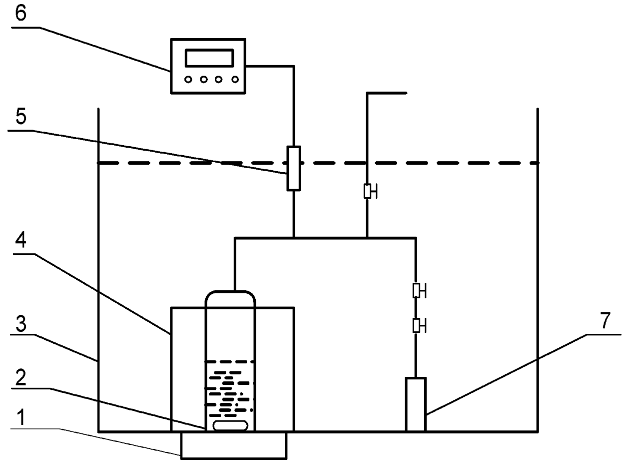

Figure 1. Experimental apparatus for solubility measurement: 1, magnetic rotator; 2, magnetic stirrer; 3, water bath; 4, high pressre cell; 5, pressure sensor; 6, pressure display; 7, storage tank.

Experimental Section

Chemicals. 1,1,3,3-Tetramethylguanidium lactate (TMGL) was synthesized according to the literature.[16] The materials such as 1,1,3,3-tetramethylguanidine (> 99 %, Fluka) were used as received from the provider, and DL-lactic acid (95 %, Acros) was distilled over KOH under vacuum before use. The synthesized TMGL samples were dried under vacuum at 373 K for 24 h before use. The water content of ILs after drying was less than 200 ppm measured by 787 KF Titrino (a titrator for water determination according to Karl Fisher method). O_2, N_2, CH_4, and H_2 were purchased from Beijing Analytical Instrument Factory with purity of (99.95, 99.95, 99.90, and 99.90) % respectively.

The synthesized TMGL was characterized by ^{1}H NMR spectrum measured on a Bruker AM 400 MHz spectrometer, using D_2O and $CDCl_3$ as solvent with TMS as internal standard. FTIR spectrums was taken by a Perkin-Elmer IR spectrometer, using a NaCl disk. The results are as follows: ^{1}H NMR (400

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10.1021/je050437s CCC: $33.50

Table 1. Solubilities of O_2, N_2, H_2, and CH_4 in TMGL at Different Pressures and Temperatures

$T = 308$ K		$T = 318$ K		$T = 328$ K	
P/MPa	x	P/MPa	x	P/MPa	x
O_2					
1.18	0.0037	1.25	0.0035	1.33	0.0030
1.50	0.0049	1.57	0.0043	1.65	0.0034
1.98	0.0067	2.07	0.0058	2.17	0.0054
2.87	0.0106	3.01	0.0093	3.14	0.0084
3.27	0.0147	3.42	0.0118	3.59	0.0107
3.91	0.0176	4.09	0.0147	4.30	0.0131
5.76	0.0282	6.03	0.0228	6.33	0.0204
6.70	0.0323	7.02	0.0279	7.37	0.0233
7.99	0.0363	8.37	0.0318	8.78	0.0275
8.85	0.0405	9.27	0.0335	9.72	0.0306
N_2					
2.16	0.0036	2.27	0.0032	2.40	0.0027
3.23	0.0054	3.35	0.0049	3.41	0.0038
3.49	0.0059	3.66	0.0052	3.80	0.0042
3.60	0.0060	3.89	0.0055	4.00	0.0046
4.30	0.0072	4.52	0.0062	4.75	0.0052
5.04	0.0084	5.27	0.0072	5.47	0.0057
6.19	0.0105	6.46	0.0089	6.75	0.0068
6.80	0.0112	7.16	0.0095	7.45	0.0073
8.05	0.0129	8.37	0.0103	8.74	0.0083
H_2					
1.26	0.0014	1.30	0.0013	1.35	0.0012
1.91	0.0021	1.96	0.0018	2.01	0.0015
3.51	0.0037	3.60	0.0031	3.74	0.0025
4.29	0.0043	4.43	0.0036	4.57	0.0029
4.95	0.0049	5.11	0.0040	5.25	0.0033
5.37	0.0051	5.54	0.0043	5.72	0.0034
6.93	0.0062	7.16	0.0054	7.38	0.0044
7.22	0.0065	7.41	0.0056	7.65	0.0045
8.51	0.0075	8.79	0.0064	9.05	0.0051
9.33	0.0079	9.60	0.0069	9.91	0.0055
CH_4					
1.04	0.0025	1.07	0.0016	1.11	0.0009
1.42	0.0042	1.47	0.0036	1.56	0.0028
2.56	0.0121	2.65	0.0091	2.73	0.0071
3.41	0.0171	3.51	0.0129	3.69	0.0104
4.29	0.0221	4.43	0.0173	4.57	0.0135
5.73	0.0291	5.97	0.0227	6.14	0.0184
6.51	0.0329	6.69	0.0272	6.93	0.0222
7.73	0.0386	7.97	0.0323	8.23	0.0255
8.61	0.0418	8.91	0.0355	9.19	0.0281
9.66	0.0431	9.99	0.0386	10.34	0.0305

MHz, D_2O) 1.30 (d, 3H), 2.95 (s, 12H), 4.17 (q, 1H). IR (3203, 2970, 1606, 1571, 1410) cm^{-1}. Comparing the data of ^1H NMR of our sample with those reported by Wu et al.[8] and Gao et al.,[18] respectively, it is found that the agreement is good. The purity of TMGL is 98.2 %.

Solubility Measurement. The experimental equipment and procedure are similar to the previous work[6] for CO_2 solubility determination in ILs. The apparatus sketch is given in Figure 1. The apparatus used for solubility determination mainly consists of a high-pressure cell, storage tank, and pressure sensor. The water bath is transparent, and there is a volume scale in the high-pressure cell so that the volume of TMGL could be read through it.

Predetermined amounts of TMGL were loaded in the high-pressure cell and degassed for 12 h. The gas was pressed into the storage tank using a high-pressure pump. Through weighing the mass of gas-storaged tank and gas-off tank, the accurate amount of gas can be known. Then the storage tank was linked with the high-pressure cell using the pipelines. The water bath was controlled at the desired temperature with a temperature uncertainty of ± 0.1 K. The pressure of the gas in pipelines can be read in pressure display through pressure sensor transmitting. When the gas was entered into the cell and absorbed by TMGL, the pressure decreased gradually. When the pressure was stable, the equilibrium could be considered to be reached. Then the pressure of gas was recorded, and the volume of TMGL was read.

The volume of the high-pressure cell and the storage tank adding the pipelines were measured using nitrogen at a certain

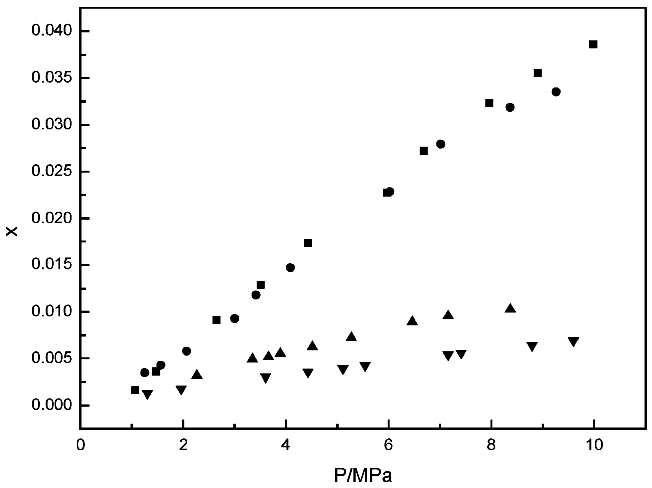

Figure 2. Comparison of the mole fraction solubilities x of these four gases in TMGL at 318 K: ■, CH_4; ●, O_2; ▲, N_2; ▼, H_2.

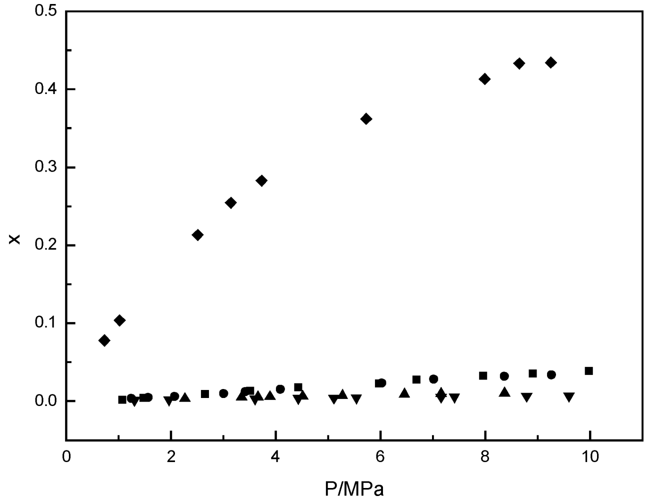

Figure 3. Comparison of the mole fraction solubility x of these four gases in TMGL with that of CO_2 at 318 K: □, CO_2; ■, CH_4; ●, O_2; ▲, N_2; ▼, H_2.

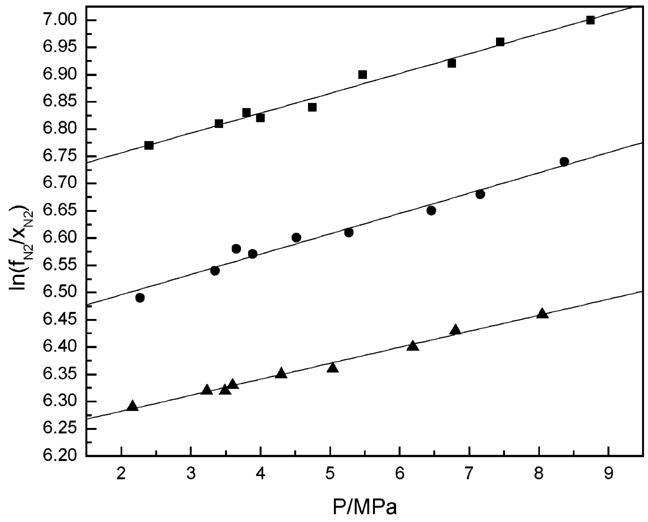

Figure 4. *K*−*K* equation analysis of the solubilities of N_2 in TMGL: ■, 328 K; ●, 318 K; ▲, 308 K.

Table 2. Henry's Constants and Partial Volumes of O_2, N_2, H_2, and CH_4

	$T = 308$ K		$T = 318$ K		$T = 328$ K	
	H	$\bar{V}^\infty$	H	$\bar{V}^\infty$	H	$\bar{V}^\infty$
	MPa	$cm^3 \cdot mol^{-1}$	MPa	$cm^3 \cdot mol^{-1}$	MPa	$cm^3 \cdot mol^{-1}$
O_2	169.54	83.223	208.97	81.959	242.26	92.445
N_2	503.91	75.285	614.31	98.616	798.55	99.263
H_2	834.72	121.890	981.03	132.193	1238.06	126.805
CH_4	141.40	109.855	177.63	126.112	239.91	142.349

temperature, and the densities of all these gases at certain temperature and pressure were determined before the experiment. At the equilibrium, the volume of TMGL was read, and then the volume of the gas phase was gotten. Using all these parameters, we can get the mass of the gas in the gas phase. Then the mass of gas dissolved in TMGL can be gotten through mass subtracting.

Masses of the gases and TMGL were obtained using an electronic balance with uncertainty of ± 0.0001 g. Uncertainty of the gas pressure was ± 0.25 %. Calculated by the error transferring method, the estimated uncertainty of the solubility measurement is ± 0.8 %.

Krichevsky−Kasarnovsky Equation

The Krichevsky−Kasarnovsky equation[17] has been increasing been used for expressing the solubility of sparingly soluble gases up to very high pressures. The equation is presented in the following, in which subscript 1 and 2 represent solvent and gas solute, respectively:

$$\ln\frac{f_2}{x_2} = \ln H_2^{P,s} + \frac{\bar{V}_2^\infty (P - P_1^s)}{RT} \qquad (1)$$

In eq 1, f_2 is the fugacity of gas solute 2 in the gas phase, P_1^s is the saturated vapor pressure of solvent 1, and H_2 is Henry's constant of gas solute 2 in solvent 1. In case that the vapor pressure of ILs is negligible, f_2 can be substituted by the fugacity of pure gas and the saturated vapor pressure, and P_1^s can be considered as zero. Equation 1 then can be turned to eq 2:

$$\ln\frac{f_2}{x_2} = \ln H_2 + \frac{\bar{V}_2^\infty}{RT}P \qquad (2)$$

Results and Discussions

The solubility data of O_2, N_2, H_2, and CH_4 in TMGL measured up to a pressure of 10.34 MPa at three temperatures from (308 to 328) K are presented in Table 1. It can be seen from Table 1 that the solubilities of these four gases in TMGL increase with increasing pressure and decrease with increasing temperature. For comparison, the solubilities of these four gases in TMGL at 318 K are presented in Figure 2. It can be seen that the difference of solubilities of these four gases in TMGL is distinct and the solubilities of CH_4 and O_2 in TMGL are much larger than those of N_2 and H_2. The solubilities of these four gases in TMGL are compared with that of CO_2 in TMGL[6] at temperature of 318 K in Figure 3. It can be seen that the solubilities of CO_2 in TMGL are much larger than those of these four gases. The above results indicated that TMGL may be used as a potential solvent for capturing CO_2 from the industrial gas containing CH_4, H_2, N_2, and O_2 effectively.

In Figure 4, the logarithm of the ratio of fugacity to the solubility of N_2 was plotted versus the vapor pressure, from which Henry's constants and partial volumes of N_2 in TMGL were obtained. The same approach can be applied to the other three gases. Henry's constants and partial volumes of these four gases in TMGL are listed in Table 2. The sequence of Henry's constants of these four gases is $H_{CH_4} < H_{O_2} < H_{N_2} < H_{H_2}$, and Henry's constants increase with increasing temperature. Therefore, the solubility follows the sequence of $x_{CH_4} > x_{O_2} > x_{N_2} > x_{H_2}$ and decrease with increasing temperature. From Table 2, we can see that the values of the partial molar volume ($\bar{V}^\infty$) of N_2 and CH_4 increase with increasing temperature, while for O_2 gas, $\bar{V}^\infty$ goes down and then up with temperature, and for H_2 gas it goes up and down with temperature. The reason for this is not clear at this stage; a related study will be carried in the future.

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Received for review October 20, 2005. Accepted January 12, 2006. We are grateful to the Natural Science Foundation of China (20436050) and the National High Tech Research and Development Program of China (863 Program (2004AA649030)) for the financial support.

JE050437S