Solubility of CO_2 in a Choline Chloride + Urea Eutectic Mixture

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The solubility of CO_2 in choline chloride + urea eutectic mixtures was determined at 313.15 K, 323.15 K, and 333.15 K under pressures up to 13 MPa. The mole ratios of choline chloride to urea selected were 1:1.5, 1:2, and 1:2.5. The Henry's constants and enthalpy of solution of the gas were calculated from the solubility data. The solubility of CO_2 in the mixtures increased with increasing pressure, and the solubility is more sensitive to pressure in the low-pressure range. The solubility of CO_2 in the mixtures decreased with increasing temperature at all the pressures. The enthalpy of solution is negative at all conditions.

Introduction

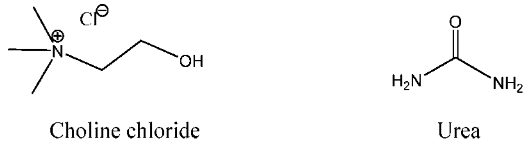
In recent years, utilization of green solvents, such as supercritical CO_2, ionic liquids (ILs), and poly(ethylene glycol) (PEG), has attracted much attention.[1–3] The eutectic mixtures based on choline chloride (Scheme 1) have high ion concentration, and they have unusual solvent properties compared with most molecular solvents, are more typical of the properties observed for ionic liquids, and are greener media.[4–6] The mixture of choline chloride with urea (Scheme 1) shows a large eutectic effect when the mole ratio of choline chloride to urea is 1:2; its melting point of 12 °C is much lower than those of choline chloride and urea.[4] As an environmentally more acceptable solvent, the choline chloride + urea eutectic mixture has been used in different areas, such as synthesis of microporous crystalline zeolites[7] and chemical reactions,[8] and has great potential for other processes.[4,6]

The combination of CO_2 and other green solvents is an interesting area.[9] In addition, some liquid green solvents also show potential for the separation of gas mixtures and/or absorption of gases. It is clear that a study on the phase behavior of CO_2 + liquid green solvent mixtures is of great importance to their effective applications. Many studies have been carried out to research the phase behaviors of CO_2 + IL[10–14] and CO_2 + PEG systems.[15,16] In this work, we determined the solubility of CO_2 in the choline chloride + urea mixtures at different temperatures and pressures. The enthalpy of solution was also calculated from the dependence of solubility on temperature. The data are important for some applications, such as absorption of CO_2 and conducting chemical reactions in biphasic mixtures consisting of CO_2 and the eutectic mixtures.

Experimental

Materials. CO_2 with a purity of 99.995 % was supplied by Beijing Analytical Instrument Factory. Choline chloride (> 99.5 %) was produced by Beijing Chemical Reagent Plant. Urea (> 99.7 %) was produced by Beijing Chemical Plant. The chemicals were used as received. The choline chloride and urea mixtures were obtained by melting them togather at suitable temperatures and were dried under a vacuum at 353 K for 48 h before use.

Scheme 1. Structures of Choline Chloride and Urea



Apparatus and Procedures. The apparatus and procedures used were similar to those reported previously.[17] The apparatus was composed mainly of a CO_2 cylinder, a computer-controlled metering syringe pump (DB-80), a constant-temperature water bath, a pressure gauge, a volume-variable view cell, a sample bomb, and a magnetic stirrer. The volume of the view cell could be changed in the range of (23 to 50) cm^3 by moving the piston. The temperature of the constant-temperature water bath was controlled by a Haake-D8 temperature controller. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT model 93) and an indicator. Its accuracy was ± 0.025 MPa in the pressure range of (0 to 20) MPa. The temperature was determined by accurate mercury thermometers with an uncertainty of less than ± 0.05 K.

In a typical experiment, the desired amount of eutectic mixture was loaded into the view cell, and the air in the system was replaced by CO_2. The cell was placed in the constant-temperature water bath, and then CO_2 was charged into the system using the high-pressure pump until a suitable pressure was reached. The valve connected to the view cell was closed, and the liquid phase was stirred. The system was considered to have reached equilibrium if the pressure of the system had been unchanged with time for 5 h. Then the pressure of the system was recorded. The valve of the sample bomb for sampling the liquid phase was opened slowly to collect some sample. At the same time, the volume of the view cell was adjusted to keep the pressure unchanged during the sampling process. The sampling valve was closed after enough liquid samples had been collected in the sample bomb. The sample bomb was then removed for composition analysis.

To determine the composition of the liquid phase, the mass of the sample bomb was first determined with an electronic balance (Mettler MP1200) with a resolution of 0.001 g. The mass of the sample in the sample bomb was known from the masses of the sample bomb before and after sampling. To

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Table 1. Solubility x_1 of CO_2 in the Choline Chloride (CH) + Urea Mixtures of Different Mole Ratios (n_{CH}:n_{urea})

	n_{CH}:n_{urea} = 1:1.5		n_{CH}:n_{urea} = 1:2		n_{CH}:n_{urea} = 1:2.5	
T/K	P/MPa	x_1	P/MPa	x_1	P/MPa	x_1
313.15	11.84	0.201	12.5	0.309	12.45	0.203
	9.86	0.195	10.46	0.283	10.57	0.188
	8.21	0.178	9.12	0.270	8.61	0.176
	6.09	0.159	7.96	0.253	6.67	0.155
	4.21	0.122	6.23	0.233	4.53	0.125
	2.52	0.096	4.37	0.191	2.67	0.088
	1.07	0.051	2.85	0.150	1.15	0.046
			1.13	0.077		
323.15	12.52	0.191	11.1	0.271	12.28	0.186
	10.55	0.183	9.29	0.252	10.53	0.170
	8.19	0.164	7.22	0.229	8.25	0.156
	6.13	0.144	6.51	0.216	7.13	0.147
	3.69	0.097	4.74	0.180	6.2	0.134
	2.33	0.079	3.17	0.132	4.12	0.107
	0.85	0.033	2.24	0.107	2.5	0.078
			1.01	0.060	1.06	0.039
333.15	12.5	0.172	12.73	0.270	12.55	0.168
	12.35	0.169	11.1	0.248	10.04	0.152
	10.52	0.164	9.51	0.233	8.04	0.139
	8.38	0.143	7.92	0.215	5.98	0.117
	6.55	0.122	6.31	0.198	4.03	0.090
	4.78	0.098	4.8	0.155	2.54	0.068
	2.59	0.069	2.36	0.099	1.08	0.032
	1.23	0.038	1.00	0.051		

determine the mass of CO_2 in the sample bomb, CO_2 in the sample was released slowly, and the CO_2 was further removed under vacuum until the mass of the sample remained constant with time. Advanced simulation experiments showed that all the CO_2 in the sample could be removed by this method. The solubility was known from the masses of the liquid and the CO_2 in the sample. Sampling at equilibrium conditions was crucial for determining the solubility. In this work, equilibrium was confirmed by the fact that the solubilities determined at different equilibration times were the same within the experimental error.

Results and Discussion

Solubility of CO_2 in Eutectic Mixtures. The solubility of CO_2 in eutectic mixtures was determined at 313.15 K, 323.15 K, and 333.15 K under pressures up to 13 MPa. The mole ratios of choline chloride to urea selected were 1:1.5, 1:2, and 1:2.5. Table 1 lists the solubility data at different conditions determined in this work. In the table, x_1 stands for the mole fraction of CO_2 in the liquid phase. It is estimated that the uncertainty of the x_1 values in the table is 1.0 %. Figures 1 to 3 demonstrate the dependence of the solubility on temperature and pressure. The solubility of CO_2 in the mixtures increased with increasing pressure, and the solubility is more sensitive to pressure in the low-pressure range. It can also be seen that the solubility of CO_2 in the mixtures decreased with increasing temperature at all the pressures.

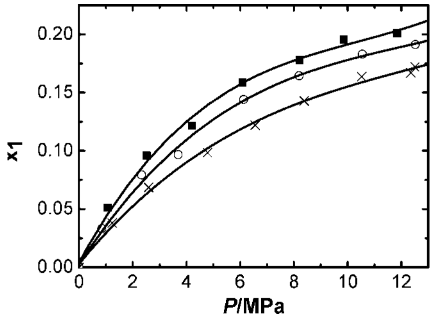

Figure 1. Solubility of CO_2 in the choline chloride (CH) + urea mixture of n_{CH}:n_{urea} = 1:1.5: ■, 313.15 K; ○, 323.15 K; ×, 333.15 K; —, correlation.

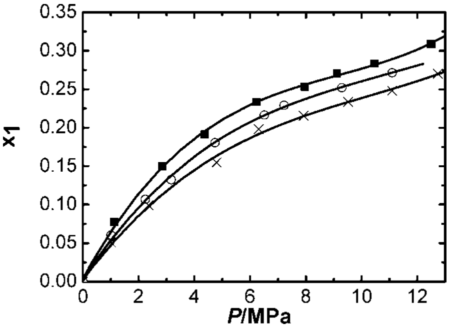

Figure 2. Solubility of CO_2 in the choline chloride (CH) + urea mixture of n_{CH}:n_{urea} = 1:2: ■, 313.15 K; ○, 323.15 K; ×, 333.15 K; —, correlation.

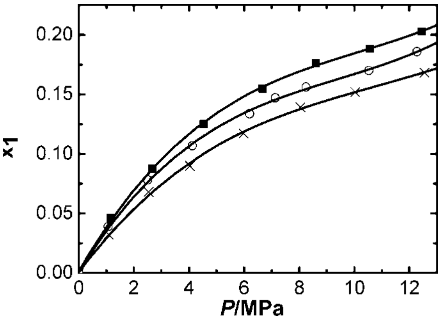

Figure 3. Solubility of CO_2 in the choline chloride (CH) + urea mixture of n_{CH}:n_{urea} = 1:2.5: ■, 313.15 K; ○, 323.15 K; ×, 333.15 K; —, correlation.

Table 2. Henry's Law Constants of CO_2 in the Choline Chloride (CH) + Urea Mixtures

	k_H/MPa		
T/K	n_{CH}:n_{urea} = 1:1.5	n_{CH}:n_{urea} = 1:2	n_{CH}:n_{urea} = 1:2.5
313.15	18.5	12.3	22.4
323.15	23.0	15.1	23.5
333.15	28.7	18.2	29.0

It can be known by comparing the data in Figures 1 to 3 that at the same temperature and pressure the solubility of CO_2 in a eutectic mixture is highest when the mole ratio of choline chloride to urea is 1:2. The solubilities were very similar as the mole ratios were 1:1.5 and 1:2.5. As the mole ratio of choline chloride to urea is 1:2, the melting point of the mixture is lowest, and special composition and molecular interaction favor the dissolution of the gas.

Henry's Constant. The gaseous phase can be assumed to be pure CO_2 due to the negligible vapor pressure of the liquid at the experimental temperature. Henry's law can be expressed as follows.[10]

$$k_H = \lim_{x_1 \to 0} \frac{f_1}{x_1} \approx \frac{P_1}{x_1} \tag{1}$$

where k_H is Henry's constant; x_1 stands for the mole fraction of gas in the liquid phase; and f_1 and P_1 are the fugacity and pressure of the CO_2, respectively. In this work, Henry's constant was obtained by extrapolation of f_1/x_1 vs pressure curves to zero pressure, and f_1 was calculated from the Peng–Robinson equation of state.[18] Henry's constants at different temperatures are listed in Table 2. The estimated uncertainty of Henry's constant is 2.0 %.

Table 3. Enthalpy of Solution of CO_2 in the Choline Chloride (CH) + Urea Mixtures (T = 313 K to 333 K)

$n_{CH}:n_{urea} = 1:1.5$		$n_{CH}:n_{urea} = 1:2$		$n_{CH}:n_{urea} = 1:2.5$	
x_1	$\frac{-\Delta_{sol}H}{kJ \cdot mol^{-1}}$	x_1	$\frac{-\Delta_{sol}H}{kJ \cdot mol^{-1}}$	x_1	$\frac{-\Delta_{sol}H}{kJ \cdot mol^{-1}}$
0.033	19.3	0.030	17.0	0.033	12.7
0.051	19.4	0.060	17.1	0.051	13.0
0.064	19.7	0.095	17.0	0.064	13.6
0.079	20.0	0.125	17.2	0.079	14.0
0.095	20.4	0.150	17.1	0.095	14.7
0.125	21.6	0.180	17.4	0.125	17.1

Enthalpy of Solution. The enthalpy of solution $\Delta_{sol}H$ is an important parameter of the system because it is related with strength of interaction between the liquid and the gas. $\Delta_{sol}H$ can be evaluated from the dependence of the solubility on temperature using the following well-known equation.

$$\frac{\Delta_{sol}H}{R} = \left(\frac{\partial \ln P_1}{\partial(1/T)}\right)_{x_1} \qquad (2)$$

where x_1 is the mole fraction of CO_2 in the liquid phase. The P_1 values at different temperatures and at fixed x_1 were obtained from the curves in Figures 1 to 3. The ln P_1 is a linear function of $1/T$ at fixed x_1. Therefore, the $\Delta_{sol}H$ is independent of temperature and can be calculated from the slopes of the curves. $\Delta_{sol}H$ values at different compositions are listed in Table 3. The estimated uncertainty of the enthalpy of solution is 3.0 %. At all the conditions, the enthalpy of solution is negative, i.e., the dissolution of the gas is exothermic.

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