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Solubility of CO_2, N_2, and $CO_2 + N_2$ Gas Mixtures in Isooctane

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The solubility of CO_2 in isooctane at 270.8 K, 275.0 K, and 282.5 K and at pressures from (1.46 to 3.64) MPa and the solubility of N_2 in isooctane at 269.9 K, 274.5 K, and 282.3 K and at pressures from (2.70 to 9.45) MPa were measured. The solubility of CO_2 in isooctane is one order of magnitude greater than that in water at the same conditions. Temperature has no significant effect on the solubility of N_2 in isooctane. The equilibrium compositions of CO_2 and N_2 binary mixtures in isooctane at 273.8 K and at a CO_2 mole fraction range of (0.079 to 0.675) in the gas phase were also determined. The selectivity of CO_2 over N_2 in isooctane ranges from (7.2 to 14.6) at 273.8 K.

Introduction

It is believed that global climate change is due to the increased concentration of greenhouse gases (GHGs) in the atmosphere. By far, CO_2 is the most important of the GHGs, being responsible for about 60 % of the greenhouse effect. The concentration of CO_2 in the atmosphere has risen from the preindustry level of 280 ppm to 350 ppm today as a result of anthropogenic CO_2 emission.[1] Refining current options and developing new technologies for CO_2 capture from emitting sources including power plants, oil and gas refining, hydrogen and ammonia processing, iron and steel manufacturing, and cement production are necessary to continuously use fossil fuels, which is unavoidable at present and in the near future. The most likely options identifiable for CO_2 capture are physical adsorption, chemical/physical absorption, low-temperature distillation, and gas separation membranes. Currently, one or more of these methods are used to reduce CO_2 emission.[2–6]

As a new way of industrial practice, the formation and dissociation of gas hydrates can be used to capture CO_2 from many different sources. It is well-known that CO_2 forms hydrates at much milder conditions than N_2.[7–10] Hence, high selectivity can be expected for CO_2 capture from flue gas streams. Kang and Lee[9] proposed a hydrate-based CO_2 capture approach that can recover more than 99 % CO_2 from a power plant effluent stream. The hydrate-based CO_2 capture technology has several advantages:[11,12] mild operating conditions, process simplicity, high CO_2 selectivity, solid CO_2 hydrates for economic transport and/or direct discharge into the ocean, and few pollution problems due to only water and a small amount of additive being used. At present, the largest challenge to the industrial application of hydrate-based CO_2 capture is the slow hydrate formation rate. Irvin et al.[13] reported that direct injection of water into isooctane saturated with ethylene leads to rapid hydrate formation. This concept can be used in hydrate-based CO_2 capture technology. At present, no reports can be found on the solubility of N_2 and CO_2 in isooctane, which could be important information for the further development of hydrate-aided CO_2 separation. In this work, the solubility of N_2, CO_2, and CO_2 (1) + N_2 (2) gas mixtures in isooctane will be measured at a wide range of pressures and CO_2 composition in the gas phase.

Table 1. Critical Properties and Acentric Factors of CO_2 and N_2[15]

component	T_c/K	P_c/MPa	ω
CO_2	304.2	7.38	0.225
N_2	126.2	3.39	0.040

Table 2. Summary of Solubility of CO_2 and N_2, x, in Isooctane at Three Temperatures

	CO_2 solubility			N_2 solubility	
	P/MPa	$100x$		P/MPa	$100x$
270.8 K	1.46	36.18 ± 1.42	269.9 K	2.70	4.65 ± 0.30
	2.10	49.05 ± 1.29		5.41	8.88 ± 0.61
	2.24	56.31 ± 1.07		6.52	11.58 ± 0.73
	2.44	62.28 ± 1.50		7.90	14.67 ± 1.04
	2.78	78.66 ± 1.16		8.97	16.31 ± 1.18
275.0 K	1.59	33.08 ± 1.60	274.5 K	2.75	4.58 ± 0.30
	2.27	48.58 ± 1.32		5.53	8.30 ± 0.61
	2.44	54.25 ± 1.19		6.67	10.96 ± 0.75
	2.68	61.09 ± 1.61		8.03	15.37 ± 1.02
	3.09	77.31 ± 1.33		9.16	16.36 ± 1.20
282.5 K	1.75	29.65 ± 1.80	282.3 K	2.82	5.04 ± 0.30
	2.59	47.67 ± 1.37		5.68	9.73 ± 0.59
	2.77	50.64 ± 1.43		6.86	12.20 ± 0.72
	3.06	59.15 ± 1.81		8.24	16.34 ± 1.00
	3.64	74.56 ± 1.73		9.45	17.14 ± 1.20

Experimental Section

Materials. Isooctane (2,2,4-trimethylpentane) with a certified purity of > 99 mol % was purchased from Sigma-Aldrich, Inc. N_2 was supplied by Labelmaster with a purity of 99 mol %, and CO_2 was obtained from T. W. Smith with a minimum purity of 99 mol %. All chemicals were used as received without further purification. Deionized water was produced in our laboratory with a resistivity of 17 $m\Omega \cdot cm^{-1}$.

Apparatus. Figure 1 shows the schematic diagram of the experimental setup for measuring the solubility of N_2, CO_2, and CO_2 (1) + N_2 (2) gas mixtures in isooctane. The stainless steel reactor equipped with two view windows manufactured by Parr Instrument can be operated at temperatures between (253 and 623) K and at pressures up to 18 MPa, and the volume of the reactor

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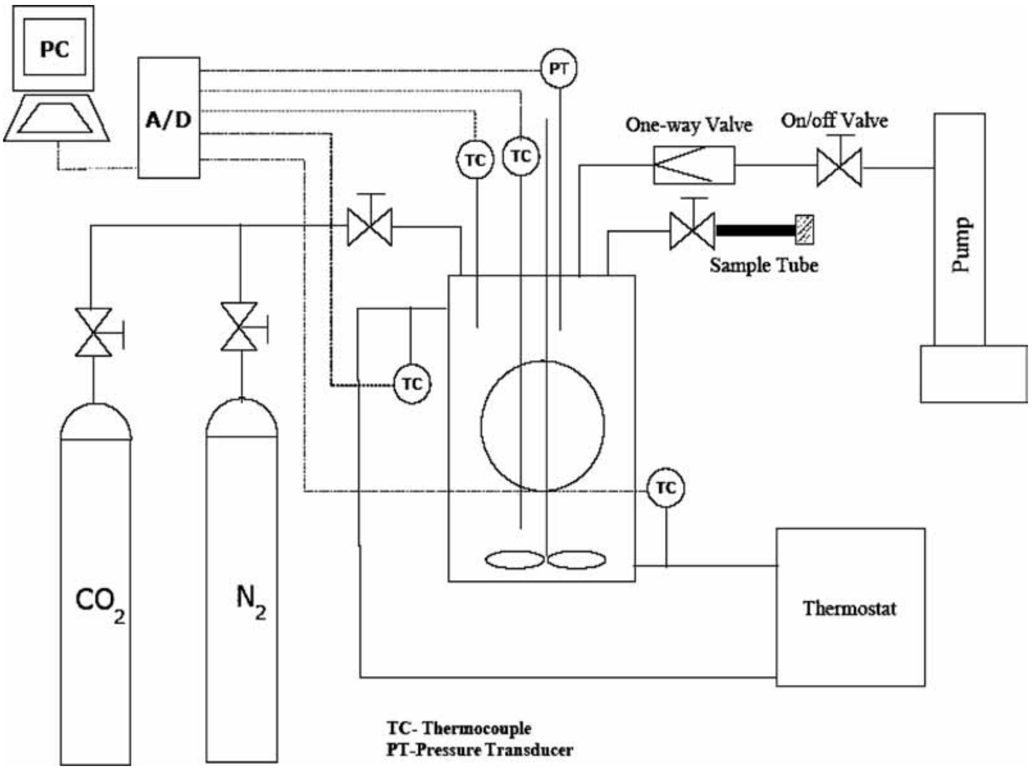

Figure 1. Schematic diagram of the experimental setup.

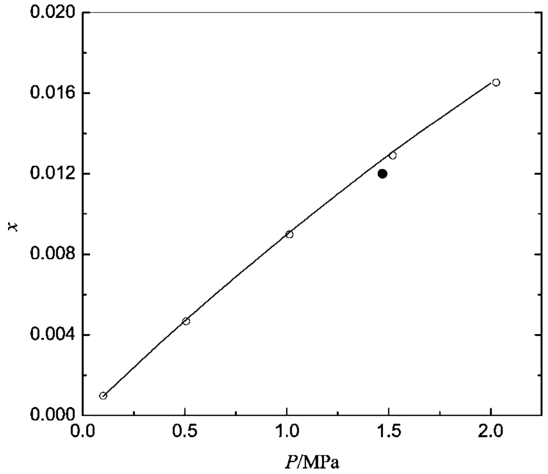

Figure 2. Experimental and reported solubilities of CO_2, x, in water at 283.1 K: ○, Bartholomé and Friz;[16] ●, this work; −, prediction by CO2SOL.[17]

including the void space of fitting is 474 cm^3. The volume of the sample tube is 0.3 cm^3. The temperature of the reactor is controlled by circulating the coolant from an Isotemp 3006P thermostat (Fisher Scientific) with a stability of ± 0.01 K inside the jacket around the cell. The temperature of the reactor was monitored with two type T thermocouples (Omega Engineering): one is immersed in the liquid, and the other is placed in the headspace. The uncertainty of temperature measurement is ± 0.2 K. The pressure of the reactor is measured by using a 9001PDM pressure transducer (Ashcroft, (0 to 34.47) MPa) with the uncertainty of ± 0.05 MPa. Temperatures of the liquid and gas phases as well as the pressure are sampled every 20 s by the Labview interface. Isooctane is injected to the reactor through an ISCO 260-D pump (Teledyne Isco) with the uncertainty of ± 0.01 cm^3.

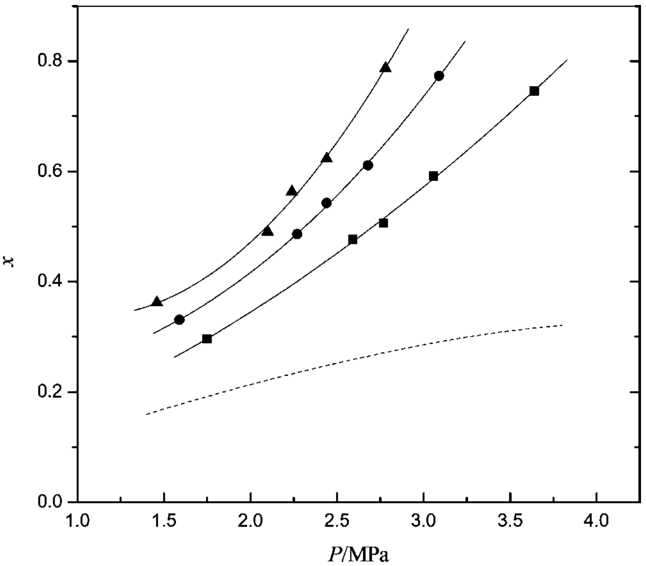

Figure 3. Solubility of CO_2, x, in isooctane at three temperatures and in water at 275.0 K: ■, 282.5 K; ●, 275.0 K; ▲, 270.8 K; −, polynomial fit. The dashed line is the solubility, $10x$, in water predicted by CO2SOL.[17]

Procedures. We set the temperature of the thermostat bath and then switched on the coolant circulation system. After the temperature of the reactor reaches the target point, the reactor is purged with N_2 or CO_2 twice at 0.7 MPa and then the reactor is charged with N_2 or CO_2 to the desired pressure. When measuring the solubility of the CO_2 (1) + N_2 (2) gas mixture, CO_2 is charged first followed by N_2 and then agitated at a speed of 300 rpm for 2 h. After thermal equilibrium is reached, isooctane is injected into the reactor, and the liquid phase is continuously stirred at a speed of 300 rpm. Absorption equilibrium is reached in about 2 h. The composition of the gas phase before and after isooctane injection is analyzed by using a Hawlett-Packard gas chromatograph (HP5890 Series II Plus)

Table 3. Fitting Parameters of the Second-Order Polynomial and Linear Equation

	CO$_2$ solubility				N$_2$ solubility			
	$x = a + b \cdot P + c \cdot P^{2a}$				$x = a + b \cdot P^{a}$			
T/K	a	b	c	r^2	T/K	a	b	r^2
270.8	0.506	−0.321	0.152	0.997	269.9	−0.007	0.019	0.990
275.0	0.252	−0.076	0.079	0.999	274.5	−0.014	0.019	0.966
282.5	0.056	0.089	0.028	0.999	282.3	−0.082	0.019	0.980

[a] P in MPa.

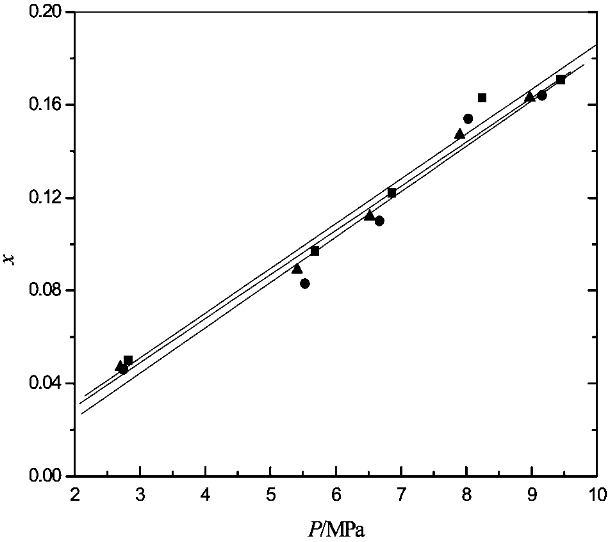

Figure 4. Solubility of N$_2$, x, in isooctane at three temperatures: ■, 282.3 K; ●, 274.5 K; ▲, 269.9 K; −, linear fit.

Table 4. Solubility of CO$_2$ (1) + N$_2$ (2), x, Gas Mixture in Isooctane at 273.8 K.

	gas-phase mole fraction		liquid-phase mole fraction		selectivity
P/MPa	$100y_1 \pm 0.2$	$100y_2 \pm 0.2$	$100x_1$	$100x_2$	K^a
3.70	7.85	92.15	5.03 ± 0.24	8.19 ± 0.31	7.2
3.84	13.87	86.13	10.97 ± 0.49	7.40 ± 0.29	9.2
3.99	21.28	78.72	14.82 ± 0.63	5.42 ± 0.32	10.1
3.92	38.39	61.61	26.84 ± 1.02	4.17 ± 0.26	10.3
3.72	67.53	32.47	54.73 ± 1.29	1.81 ± 0.13	14.6

[a] $K = (x_1/x_2)/(y_1/y_2)$.

at least three times with a GS-GasPro column in a helium carrier. Three gas samples were consecutively withdrawn from the sampling tube (Figure 1) by using a syringe. The time delay between sampling was less than 10 min, and the analysis was completed in 30 min. The average values were taken as the equilibrium concentrations. The uncertainty of composition of the gas phase (mole fraction) is ± 0.002. The content of isooctane in the gas phase is neglected. The amount of gas dissolved in isooctane is calculated by using the Peng–Robinson equation of state without considering the compressibility of isooctane. The classical mixing rule is used to determine the mole number of CO$_2$ (1) + N$_2$ (2) gas mixtures (binary interaction parameter, $k_{ij} = -0.017^{14}$). Then, the solubility is determined by taking the difference in the mole number of the gas phase before the charge of isooctane and after reaching the equilibrium. Table 1 gives the critical properties and acentric factors of CO$_2$ and N$_2$ used in this work.

Results and Discussions

Test Run. To check the validity of the method used in this work, the solubility of CO$_2$ in water is determined at 283.1 K and 1.46 MPa in our high-pressure reactor. The result is given in Figure 2. The solubility of CO$_2$ in water under this condition is (1.20 ± 0.09) %, very close to the value of 1.27 predicted by CO2SOL, which confirms the validity of our method.

Solubility of CO$_2$ and N$_2$ in Isooctane. The solubility of CO$_2$ and N$_2$ in isooctane at three temperatures is summarized in Table 2, and the experimental data are also plotted in Figures 2 and 3. The solubility of CO$_2$ in isooctane at 275.0 K is one order higher than that in water at a pressure range of (1.5 to 4.0) MPa. The mole fraction of CO$_2$ in water is 0.017 at 275.0 K and 1.54 MPa (CO2SOL[17]), which is 20 times lower than that in isooctane at the same temperature and pressure.

The lines in Figure 3 are the second-order polynomial fitting of the solubility data of CO$_2$ in isooctane, and the values of parameters of polynomial regression are listed in Table 3. The correlation coefficient ranges from 0.997 to 0.999, indicating that the second-order polynomial fits the solubility well.

Figure 4 shows that the solubility of N$_2$ in isooctane is independent of temperature at a pressure range of (2.7 to 9.5) MPa, suggesting that the dissolution heat of N$_2$ in isooctane is relatively small. At temperatures between (269.9 and 282.3) K, the solubility of N$_2$ linearly increases with the pressure. The linear fitting results are given in Table 3.

Solubility of CO$_2$ (1) + N$_2$ (2) Gas Mixtures in Isooctane. The solubility of CO$_2$ (1) + N$_2$ (2) gas mixtures in isooctane at 273.8 K and pressures from (3.70 to 3.99) MPa is listed in Table 4. The selectivity of CO$_2$ over N$_2$ in isooctane is around 7 to 15 at 273.8 K with respect to the gas phase compositions. At y_1 = 0.384, the CO$_2$ (1) + N$_2$ (2) binary hydrate formation pressure is 3.6 MPa (CSMHYD[7]) at 273.8 K, and the water-free mole fraction of CO$_2$ in the binary hydrate phase is 0.895. The selectivity of CO$_2$ over N$_2$ in hydrates is 14 under this condition. Although the selectivity of CO$_2$ in binary hydrates is a little higher than that (10.3 in Table 4) in isooctane, solid hydrates may reduce the transport and/or discharge cost.

Conclusions

The solubility of N$_2$, CO$_2$, and CO$_2$ + N$_2$ gas mixtures in isooctane was measured. At a temperature range of (270.8 to 282.5) K, the mole fraction of CO$_2$ in isooctane is well fitted by a second-order polynomial. The solubility of CO$_2$ in isooctane is one order of magnitude higher than that in water at 275.0 K at the same CO$_2$ pressure. The solubility of N$_2$ in isooctane linearly increases with the pressure at temperatures between (269.9 and 282.3) K, and temperature has an insignificant effect on N$_2$ solubility at pressures from (2.7 to 9.5) MPa. At 273.8 K, the selectivity of CO$_2$ over N$_2$ in isooctane is around 7 to 15.

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