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SOLUBILITY OF CO_2 IN A MIXED SOLVENT OF *n*-OCTANE AND i-OCTANE AT ELEVATED PRESSURES *

HAN BUXING, YAN HAIKE ** and HU RIHENG

Institute of Chemistry, Academia Sinica, Beijing (P.R. China)

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ABSTRACT

The solubility of CO_2 in binary mixtures of *n*-octane and i-octane have been measured at 30.0, 45.0, 60.0, and 73.2° C and at pressures up to 70 atm. Some thermodynamic properties have been calaulated using the experimental results.

INTRODUCTION

Solubility data of gases in liquids are very important in both pure and applied sciences. The study of gas solubility in mixed solvents is of special importance. However, this kind of work is very limited. This study was conducted to determine the solubility of CO_2 in a mixed solvent of *n*-octane and i-octane, which has not been reported in the literature.

EXPERIMENTAL

Apparatus

The experimental equipment, consisting of a high-pressure gas–liquid equilibrium unit and a sample analyser, was the same as that described previously [1]. The high-pressure gas–liquid equilibrium unit is shown in Fig. 1. The equilibrium cell (with a volume of 1.2 l), circulation line, sample cell (10–20 ml), stirrer, circulating pump, valves, and fittings were made of stainless steel and all of them were housed in a constant-temperature air bath which was controlled to ±0.2° C. The temperature drift in the cell was less than ±0.1° C. The temperature in the air bath and the cell were

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** To whom correspondence should be addressed.

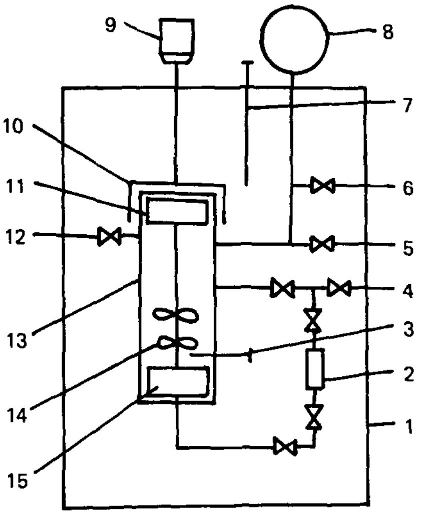

Fig. 1. Schematic diagram of the high-pressure equilibrium unit. 1, Constant-temperature air bath; 2, sample cell; 3,7, thermometer probes; 4,5, to vacuum system; 6, to high-pressure cylinder; 8, pressure gauge; 9, motor; 10, outer rotor; 11, inner rotor; 12, gas sampling tube; 13, equilibrium cell; 14, stirrer; 15, circulating pump.

determined by a digital thermometer with a resolution of 0.1° C. A 16 in. Heise pressure gauge was used to measure the pressure in the cell. The sample analyser, shown in Fig. 2, consisted of a flash chamber, ABCDEFGH, a thermostat which was regulated at 20.00 ± 0.02° C, a precision digital

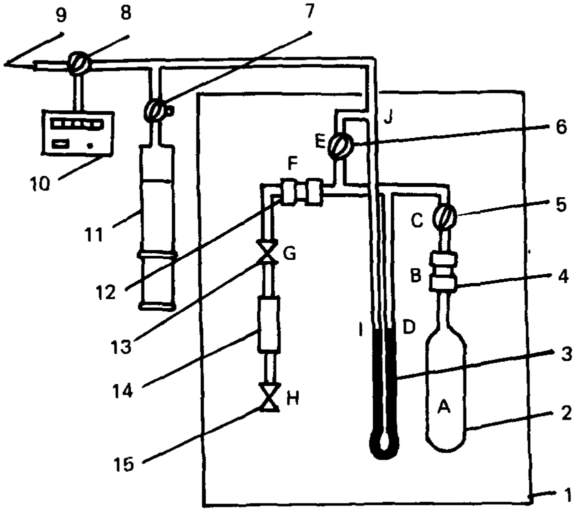

Fig. 2. Schematic diagram of the sample analyser. 1, Thermostat; 2, flask; 3, U-tube containing mercury; 4, 12, fittings; 5, stopcock II; 6, stopcock I; 7, three-way stopcock II; 8, three-way stopcock I; 9, to vacuum system; 10, digital Heise pressure gauge; 11, pressure-adjusting device; 13, valve I; 14, sample cell; 15, valve II.

Heise pressure gauge with a resolution of 0.01 psi, a pressure-adjusting device, and a vacuum system. A detailed description of the equipment was given in the literature [1].

Reagents

The CO_2 was of 99.99 mol.% purity and was supplied by the Beijing Instrument Factory. *n*-Octane and i-octane were analytical grade reagents produced by the Beijing Chemicals Co. Before use, the two solvents were purified by means of distillation in our laboratory. Chromatographic analysis showed that the purities of the purified solvents were better than 99.4%.

Procedure

The equilibrium cell was charged with the solvent to be studied. Being stirred and circulated, the solvent was degassed under vacuum. The equilibrium cell was then pressurized with CO_2. The entire system was allowed to reach equilibrium at the desired condition. After equilibrium was reached (about 5 h was required), the sample cell was isolated, removed from the circulation system and, after weighing, was connected to the sample analyser as shown in Fig. 2. The analyser was evacuated and stopcock I was closed. The three-way stopcock I was positioned to connect the pressure gauge to the left side of the mercury column. Valve I was slowly opened and the section EIJ was charged with air using three-way stopcock II and the pressure-adjusting device. The pressure in the chamber increased as the gas in the sample began to be evolved. If the two levels of mercury in the U-tube were at the same height, the readings of the pressure gauge showed the pressure of the chamber. When the pressure did not change with time, it was assumed that gas–liquid equilibrium had been established in the chamber. With a knowledge of the sample weight, the volume and pressure of the chamber, and the vapour pressure and density of the solvent at 20 ° C, the solubility of the gas in the solvent was readily calculated.

RESULTS AND DISCUSSION

The solubility of CO_2 in the mixed solvent of *n*-octane and i-octane was measured at 30.0, 45.0, 60.0, and 73.2 ° C and at pressures up to 70 atm. The results are given in Table 1. The precision of the measurements was better than ±0.2%.

The results in Table 1 show that the solubility of CO_2 in the mixed solvent decreases with temperature and the *n*-octane content of the solvent. The relation between the solubility of CO_2 and composition of the solvent

TABLE 1

Solubilities of CO_2 in mixed solvent of *n*-octane and i-octane

Y_n [a]	30.0 °C		45.0 °C		60.0 °C		73.2 °C	
	P_{CO_2} [b] /atm	X_m [b]	P_{CO_2} [b] /atm	X_m [b]	P_{CO_2} [b] /atm	X_m [b]	P_{CO_2} [b] /atm	X_m [b]
0.00	13.87	0.1854	14.98	0.1713	15.15	0.1506	25.92	0.2255
	18.84	0.2531	20.43	0.2325	26.36	0.2570	32.50	0.2801
	25.19	0.3398	26.70	0.3016	34.65	0.3341	41.90	0.3558
	30.90	0.4192	32.87	0.3691	42.67	0.4055	48.63	0.4077
	36.18	0.4966	33.65	0.3778	42.94	0.4082	54.49	0.4530
	40.00	0.5528	34.03	0.3821	43.41	0.4125	60.68	0.5014
			34.18	0.3844	44.15	0.4196		
			40.09	0.4488	48.67	0.4593		
			48.24	0.5392	54.88	0.5154		
0.20	11.86	0.1535	13.42	0.1480	16.55	0.1585	17.92	0.1539
	18.62	0.2415	19.46	0.2144	23.35	0.2216	24.61	0.2092
	27.04	0.3545	24.93	0.2724	28.02	0.2653	27.87	0.2362
	32.52	0.4293	33.20	0.3611	32.22	0.3019	34.15	0.2858
	37.12	0.4921	40.51	0.4407	39.66	0.3679	45.24	0.3721
	40.00	0.5330	46.37	0.5047	46.09	0.4252	55.34	0.4486
			51.18	0.5575	50.32	0.4614	62.92	0.5022
					55.58	0.5047		
0.50	12.37	0.1533	21.34	0.2234	15.78	0.1451	25.34	0.2070
	19.23	0.2393	27.06	0.2828	27.18	0.2463	30.56	0.2475
	25.92	0.3233	32.35	0.3374	37.63	0.3375	40.51	0.3243
	32.39	0.4090	36.55	0.3816	47.83	0.4254	47.16	0.3724
	38.76	0.4954	40.63	0.4237	50.00	0.4441	59.37	0.4630
	39.99	0.5127	47.98	0.5032	53.08	0.4706	63.60	0.4931
0.80	14.62	0.1720	14.28	0.1442	14.99	0.1327	18.76	0.1482
	19.45	0.2290	20.01	0.2008	21.66	0.1903	26.87	0.2097
	27.60	0.3276	30.00	0.2997	29.81	0.2587	35.97	0.2779
	33.17	0.3997	42.20	0.4227	40.76	0.3504	43.53	0.3327
	38.28	0.4682	46.06	0.4621	44.82	0.3840	50.72	0.3841
	40.00	0.4926			55.72	0.4751	59.58	0.4470
							67.43	0.5023
1.00	12.19	0.1381	14.89	0.1451	18.03	0.1531	19.45	0.1491
	14.23	0.1617	19.73	0.1921	24.22	0.2049	27.18	0.2068
	17.78	0.2020	30.00	0.2910	33.66	0.2823	34.10	0.2570
	26.83	0.3080	35.16	0.3411	44.50	0.3698	48.34	0.3594
	33.30	0.3870	47.88	0.4690	49.14	0.4075	53.45	0.3943
	36.96	0.4347	49.24	0.4822	56.83	0.4698	53.57	0.3966
	40.00	0.4745					55.74	0.4111
							67.55	0.4944

[a] Y_n is the mole fraction of *n*-octane in the mixed solvent.

[b] P_{CO_2} and X_m are the partial pressure of CO_2 and the solubility of CO_2 in the solvent, respectively.

TABLE 2

Henry's law constants and enthalpies of solution of CO_2 in mixed solvent of *n*-octane and i-octane

Y_n	H (atm)				$-\Delta H^\circ$ (kJ mol^{-1})			
	30.0 °C	45.0 °C	60.0 °C	73.2 °C	30.0 °C	45.0 °C	60.0 °C	73.2 °C
1.00	87.4	101.0	115.6	127.0	8.15	7.73	7.35	7.06
0.80	83.3	97.1	110.1	123.2	7.98	7.88	7.79	7.70
0.50	80.3	93.3	106.4	117.5	8.30	8.02	7.48	7.14
0.20	77.5	89.1	101.9	113.7	7.33	7.63	7.92	8.16
0.00	74.6	85.5	97.7	109.7	6.94	7.58	8.17	8.65

can be expressed approximately by

$$X_m = Y_n X_n + (1 - Y_n) X_i \tag{1}$$

where Y_n is the mole fraction of *n*-octane in the mixed solvent and X_m, X_n, and X_i are the solubilities (mole fractions) of CO_2 in the mixed solvent, pure *n*-octane, and pure i-octane, respectively. Why the solubility obeys eqn. (1) needs to be studied.

The Henry's law constants were evaluated by extrapolation of the plots of P_{CO_2}/X_m vs. P_{CO_2} and the results are listed in Table 2. It can be seen that the Henry's law constants increase with temperature and the *n*-octane content of the mixed solvent.

The enthalpy change (ΔH°) for the transfer of 1 mole of CO_2 at 1 atm partial pressure to the (hypothetical) solution phase of unit mole fraction can be calculated using the equation [2]

$$\frac{\mathrm{d} \ln H}{\mathrm{d}(1/T)} = \frac{\Delta H^\circ}{R} \tag{2}$$

where H, T, and R are the Henry's law constant, the absolute temperature, and the universal gas constant, respectively. The plots of ln H against $1/T$ are not linear. For each solvent composition, the temperature dependence of H was fitted to an expression of the form

$$\ln H = a + b\left(\frac{1}{T}\right) + c\left(\frac{1}{T}\right)^2 + d \ln\left(\frac{1}{T}\right) \tag{3}$$

where a, b, c, and d are constants. The values of ΔH° were calculated from eqn. (3) and are given in Table 2.

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