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Solubility of Anthracene and Anthraquinone in Cyclohexanone + Carbon Dioxide

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The solubilities of anthracene and anthraquinone were measured in cyclohexanone + carbon dioxide as a function of the temperature and pressure of carbon dioxide at 291, 300, and 313 K and from 1.8−12.4 MPa. Average equilibrium solubilities and recoveries of both solids increased with increasing normalized concentration and pressure. The average separation factor of anthracene to anthraquinone, due to the effect of the mixed solvent, was 2.88 ± 1.91.

Introduction

In the processing of an anthracene oil fraction from coal tar, a mixture of anthracene and anthraquinone is required to be separated to obtain products of high purity. Difficulties involved in the separation have been reported by Cepeda et al. (*1*), Gurevich et al. (*2*), Lisicki et al. (*3*), Litvinenko et al. (*4*), and Rodriguez et al. (*5*). In the present study, we have measured the solubilities of anthracene and anthraquinone in cyclohexanone upon the addition of CO_2 under pressure. The objective is to define the pressure-dependent solubility relationship under equilibrium conditions.

Experimental Section

Apparatus. Figure 1 shows the schematic representation of equipment to investigate the solubilities of anthracene and anthraquinone in cyclohexanone + CO_2. A saturator capable of operating to 373 K and 15.0 MPa was equipped with a sight glass (Jerguson Gauge, 4-T-20) and was initially filled with a 50 cm^3 solution of anthracene and anthraquinone in cyclohexanone, which has individual mass fractions of w = 1.0, 0.9, 0.8, 0.7, 0.6, and 0.5, with respect to the saturated solubility of each solid in cyclohexanone at 0.1 MPa. The bottom of the saturator was packed first with three layers of hydrophobic polymer membrane (Millipore, 0.45 μm) supported by a 200 mesh grid stainless steel screen, and then with a magnetic minibar (o.d. 0.2 cm, length 0.5 cm) on the top of the membrane. This device provided an even distribution of CO_2 gas bubbles into the solution. Liquid CO_2 with a minimum purity of 99.5 mol % was delivered from a cylinder to a duplex piston pump (LDC, NSI-33R) and was pumped into a 1 L storage vessel (Whitey, 50DFB-316L) acting as the preheater and storage tank. The system pressure was controlled to within ±0.4 MPa using a feed-forward pressure regulator (Go, PR-56) between the saturator and the storage vessel, which was normally maintained at 17 MPa greater than the system pressure. CO_2 flowed through the storage vessel to reach thermal equilibrium with the solution inside the saturator within ±1.0 K as measured with a K-type thermocouple located at the top of the saturator. The system was equilibrated inside an air bath.

At a fixed injection rate, the gaseous CO_2 was injected into the saturator through an inlet valve (Swagelok, SS31RS4). Pressure and temperature were allowed to equilibrate within 1 h. During crystallization under pressure, solid particles of anthracene and anthraquinone could be seen on the surface of the sight glass. At the equilibrated pressure the mixture left the saturator through an outlet valve in the range of 2.3 ± 0.6 L/min (STP). The mixture containing CO_2, anthracene, anthraquinone, and cyclohexanone separated into gas and liquid phases inside a separating flask, which was immersed in an ice-water bath. The gas was then routed to a wet test meter (Shinagawa, W-NK-1A) to measure the total volume of CO_2 passed through the system.

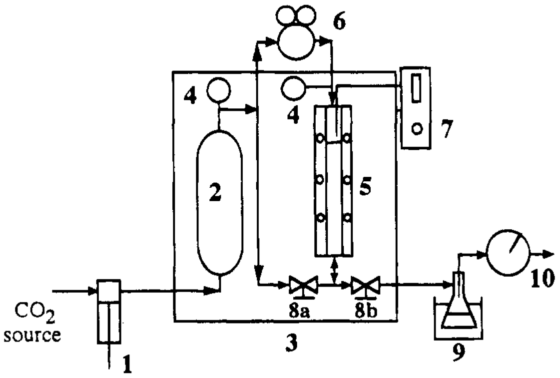

Figure 1. High-pressure equilibrium system: (1) duplex piston pump; (2) storage vessel; (3) air bath; (4) pressure gauges; (5) equilibrator; (6) pressure regulator; (7) temperature controller; (8a) inlet valve; (8b) outlet valve; (9) separation flask; (10) wet test meter.

Analysis. The liquid samples in the flask were collected and analyzed using HPLC. In the quantitative analysis of anthracene and anthraquinone in the liquid samples, we used a reference standard method. Anthracene (Merck, 96+%), anthraquinone (Merck, 98+%), carbazole (Merck, 98+%), and analytical-grade solvent such as methanol and cyclohexanone were used as received without further purification. For the analysis, 0.1 g of each liquid sample was weighed with a digital balance (Mettler, AJ100) and then 3.9 g of cyclohexanone was added to dilute it to a suitable concentration. One gram of 500 ppm carbazole standard solution in cyclohexanone was then added to the sample for HPLC analysis. The HPLC system consisted of a single-piston solvent delivery system. Two microliter samples were injected via a manual injection valve. The eluant was monitored at 254 nm, the wavelength maximum of anthracene and anthraquinone in the mobile phase, by using a UV/vis detector equipped with a deuterium lamp. The mobile phase was 82% (v/v) methanol and 18% (v/v) water at a flow rate of 1.2 mL/min. Anthracene and anthraquinone were separated from their internal standard and other impurities through a Nova-Pak C18 column (0.39 × 15 cm, Waters). The analog signal was recorded by an integrator that permitted adjustment of the chromatographic baseline before integration.

The solubilities of anthracene and anthraquinone in cyclohexanone at 0.1 MPa condition were measured quantitatively

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Table 1. Solubilities of Anthracene and Anthraquinone in Cyclohexanone at 0.1 MPa

	C_i^{sat}/(g/kg of CX)[a]			C_i^{sat}/(g/kg of CX)[a]	
T/K	anthracene	anthraquinone	T/K	anthracene	anthraquinone
291	30.64	4.48	300	36.91	6.92
295	33.56	5.49	313	45.93	10.20

[a] CX is cyclohexanone.

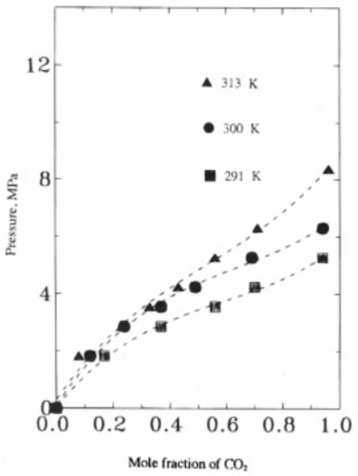

Figure 2. Phase behavior of CO_2 + cyclohexanone at 291, 300, and 313 K in the quaternary system of CO_2 + cyclohexanone + anthracene + anthraquinone.

Table 2. Average Equilibrium Solubility of the Solid as a Function of Solvent Composition in Anthracene + Anthraquinone + Cyclohexanone + CO_2 at 291, 300, 313 K[a]

T/K	P/MPa	$CO_2/(CO_2 + CX)$/(g/g)	$\overline{C_{AN}^{sat}(P)}$/(g/kg of CX)	CV/%	$\overline{C_{AQ}^{sat}(P)}$/(g/kg of CX)	CV/%
291	1.8	0.083	30.64		4.48	
291	2.8	0.211	29.57		4.43	
291	3.5	0.366	27.59	3.84	4.33	
291	4.2	0.516	25.08	2.56	3.98	3.74
291	5.2	0.620	21.81	2.24	3.60	5.46
291	6.2	0.669	18.91	3.48	3.09	8.67
291	8.3	0.674	15.95	5.93	2.98	8.70
291	10.3	0.676	13.30	3.42	2.71	11.93
291	12.4	0.677	11.06	3.33	2.50	10.14
300	1.8	0.059	36.91		6.92	
300	2.8	0.122	36.36		6.90	
300	3.5	0.205	35.58		6.82	
300	4.2	0.297	32.60	3.19	6.38	4.54
300	5.2	0.494	29.99	4.12	6.47	3.28
300	6.2	0.604	25.27	12.60	5.29	12.50
300	8.3	0.651	21.80	13.16	4.99	13.47
300	10.3	0.656	18.30	6.54	4.67	12.99
300	12.4	0.662	15.77	6.13	4.28	15.12
313	1.8	0.037	45.93		10.20	
313	2.8	0.117	45.93		10.20	
313	3.5	0.180	43.41		10.20	
313	4.2	0.257	41.53	2.62	9.91	
313	5.2	0.361	39.99	2.21	9.32	4.86
313	6.2	0.518	36.03	3.85	8.68	6.35
313	8.3	0.639	32.16	5.51	8.50	7.00
313	10.3	0.648	28.62	6.06	7.50	13.80
313	12.4	0.655	26.13	8.60	7.11	12.74

[a] CV = coefficient of variation, %.

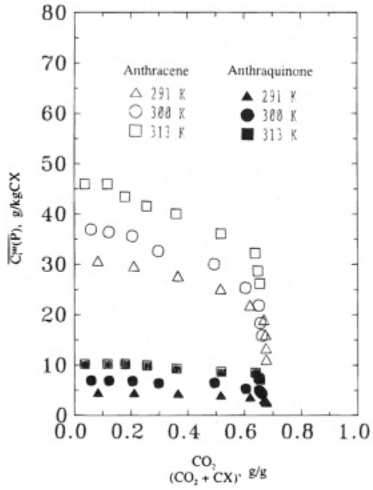

Figure 3. Average equilibrium solubilities of anthracene and anthraquinone in mixed CO_2 + cyclohexanone solvent at 291, 300, and 313 K.

by the same procedure. Equilibrium experiments at 0.1 MPa were carried out in a constant-temperature air bath (Firstec, S300R), which was controlled within ± 0.1 K and was continuously shaken for at least 12 h. Table 1 shows the solubilities of anthracene and anthraquinone resulting from these equilibrium experiments.

Results

Equilibrium Solubility in CO_2 + Cyclohexanone. In order to determine the maximum recovery of anthracene and anthraquinone, the solubilities of these two solids in the four-component high-pressure solutions should be determined. Upon the addition of CO_2, anthracene and anthraquinone were partially precipitated out according to the operating pressure and the mother liquor then saturated with anthracene and anthraquinone in the mixed solvent of CO_2 and cyclohexanone. The solubility data were measured to obtain the equilibrium solubilities of anthracene and anthraquinone in these four-component mixtures. The determination was made in the solvents under different pressures at 291, 300, and 313 K, for various CO_2 concentrations in cyclohexanone, and for the range of solvent compositions corresponding to equilibrated saturation with respect to anthracene and anthraquinone. Figure 2 shows the phase behavior of CO_2 + cyclohexanone at 291, 300, and 313 K, with the largest solubilities of CO_2 in cyclohexanone at 291 K as a result of the large expansion of solution at 291 K. Before the determination of the solid solubility, analyses were made to check the total cyclohexanone and total solid contents before and after depressurizations to find any mass loss by evaporation and by carrying over with CO_2 flow. The analyses showed that all the anthracene and anthraquinone in the vessel were accounted for without any loss in depressurization. The cyclohexanone loss in the depressurization process was also within 5%. The amounts of anthracene and anthraquinone dissolved in CO_2 were negligible. Therefore, the equilibrium solubilities of anthracene and anthraquinone in the mother liquor under pressures could be treated as the remaining concentrations of anthracene and anthraquinone in the solution expanded to 1 atm.

From the solubility data (Table 2) plotted in Figure 3, the y-coordinate is the solubility defined as the masses of anthracene and anthraquinone per unit mass of cyclohexanone as solid solutes being insoluble in CO_2 under pressure. The x-coordinate is the solvent composition defined as the mass fraction of CO_2 in the mixture. The pressure-dependent solubility data represent the mean values of six equilibrium solubilities measured under isobaric operations of six normalized concentrations equal to 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0, respectively. The aver-

Table 3. Recoveries and Minimum Equilibrium Concentrations of Anthracene in Anthracene + Anthraquinone + Cyclohexanone + CO_2 at 291, 300, and 313 K

		Y_{AN}/(g/g)						
T/K	*P*/MPa	$C_{AN}^* = 1.0$	$C_{AN}^* = 0.9$	$C_{AN}^* = 0.8$	$C_{AN}^* = 0.7$	$C_{AN}^* = 0.6$	$C_{AN}^* = 0.5$	$C_{AN}^{min}(P)$/(g/kg of CX)
291	12.3	0.632	0.609	0.555	0.460	0.389	0.309	7.73
291	10.3	0.552	0.516	0.451	0.367	0.381	0.188	9.67
291	8.3	0.489	0.409	0.315	0.224	0.125	0.073	11.76
291	6.2	0.391	0.301	0.200	0.109	0.026		16.02
291	5.2	0.277	0.194	0.115	0.013			20.65
291	4.2	0.160	0.092	0.002				24.49
291	3.5	0.075	0.027					27.07
291	2.8	0.035						29.00
291	1.8							30.64
300	12.3	0.524	0.497	0.471	0.386	0.313	0.225	11.44
300	10.3	0.498	0.421	0.362	0.270	0.169	0.137	13.21
300	8.3	0.320	0.264	0.238	0.168	0.106	0.053	17.64
300	6.2	0.207	0.173	0.151	0.102	0.036		20.74
300	5.2	0.163	0.082	0.032				28.12
300	4.2	0.097	0.041					30.45
300	3.5	0.036						34.14
300	2.8	0.015						36.02
300	1.8							36.91
313	12.3	0.378	0.318	0.278	0.183	0.106	0.017	22.37
313	10.3	0.328	0.290	0.211	0.145	0.043		25.31
313	8.3	0.255	0.210	0.135	0.068			28.57
313	6.2	0.192	0.117	0.062				33.12
313	5.2	0.116	0.048					38.26
313	4.2	0.079	0.014					40.46
313	3.5	0.055						43.54
313	2.8							45.93
313	1.8							45.93

Table 4. Recoveries and Minimum Equilibrium Concentrations of Anthraquinone in Anthracene + Anthraquinone + Cyclohexanone + CO_2 at 291, 300, and 313 K

		Y_{AQ}/(g/g)						
T/K	*P*/MPa	$C_{AQ}^* = 1.0$	$C_{AQ}^* = 0.9$	$C_{AQ}^* = 0.8$	$C_{AQ}^* = 0.7$	$C_{AQ}^* = 0.6$	$C_{AQ}^* = 0.5$	$C_{AQ}^{min}(P)$/(g/kg of CX)
219	12.3	0.385	0.329	0.267	0.207	0.134	0.066	1.91
291	10.3	0.314	0.261	0.207	0.142	0.085	0.010	2.18
291	8.3	0.274	0.213	0.159	0.087	0.033		2.40
291	6.2	0.256	0.187	0.118	0.046	0.005		2.84
291	5.2	0.155	0.100	0.053				3.15
291	4.2	0.088	0.041					3.71
291	3.5	0.034						4.18
291	2.8	0.012						4.36
291	1.8							4.48
300	12.3	0.267	0.229	0.187	0.132	0.105	0.026	3.13
300	10.3	0.214	0.189	0.163	0.105	0.066		3.54
300	8.3	0.156	0.129	0.107	0.043	0.010		4.08
300	6.2	0.130	0.106	0.082	0.014			4.70
300	5.2	0.087	0.044					5.52
300	4.2	0.048	0.007					6.18
300	3.5	0.014						6.75
300	2.8	0.003						6.85
300	1.8							6.92
313	12.3	0.194	0.156	0.135	0.083	0.026		5.64
313	10.3	0.142	0.112	0.074	0.027	0.005		6.40
313	8.3	0.109	0.073	0.032				7.37
313	6.2	0.097	0.050	0.006				8.08
313	5.2	0.055	0.019					8.75
313	4.2	0.028						9.76
313	3.5							10.20
313	2.8							10.20
313	1.8							10.20

age equilibrium solubility is calculated by

$$\overline{C_i^{sat}(P)} = (1/6)\{\Sigma C_i^{sat}(1 - Y_i)C_i^*\} \qquad (1)$$

where $\overline{C_i^{sat}(P)}$ = the average equilibrium solubility of the solid at *P*, g of solid/kg of cyclohexanone, C_i^{sat} = the solubility of the solid in cyclohexanone at 0.1 MPa, g of solid/kg of cyclohexanone, C_i^* = the normalized concentration of the solid at 0.1 MPa (0.5–1.0), *Yi* = the recovery of the solid, g of precipitated solid/g of solid in original solution, and *i* = anthracene or anthraquinone.

Minimum Equilibrium Concentration in CO_2 + Cyclohexanone. Tables 3 and 4 show a total of 86 experimental runs under the following conditions: temperature 291, 300, and 313 K; normalized concentration 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0; and pressure 1.8, 2.8, 3.5, 4.2, 5.2, 6.2, 8.3, 10.3, and 12.3 MPa. The recovery of anthracene and anthraquinone, Y_i, increased with increasing normalized concentration and pressure (i.e., the dilution ratio of CO_2 to the CO_2-free cyclohexanone). The values in the last column of Tables 3 and 4 are the extrapolations to zero recovery of those equilibrium solubilities. They can

Table 5. Separation Factors of Anthracene from Anthraquinone in Anthracene + Anthraquinone + Cyclohexanone + CO_2 at 291, 300, and 313 K

		α, β					
T/K	P/MPa	C_i^* = 1.0	C_i^* = 0.9	C_i^* = 0.8	C_i^* = 0.7	C_i^* = 0.6	C_i^* = 0.5
291	12.3	1.642, 2.743	1.851, 3.180	2.079, 3.426	2.222, 3.264	2.903, 4.110	4.682, 6.296
291	10.3	1.758, 2.690	1.977, 3.020	2.179, 3.146	2.584, 3.494	3.306, 4.204	
291	8.3	1.785, 2.538	1.921, 2.554	1.981, 2.434	2.575, 3.042	3.788, 4.206	
291	6.2	1.527, 1.866	1.610, 1.874	1.724, 1.908	2.370, 2.542		
291	5.2	1.787, 2.093	1.940, 2.171	2.170, 2.321			
300	12.3	1.962, 3.250	2.170, 3.326	2.519, 3.870	2.924, 4.138	2.981, 3.897	8.654, 10.740
300	10.3	2.327, 3.647	2.228, 3.120	2.221, 2.908	2.571, 3.162	2.561, 2.859	
300	8.3	2.051, 2.540	2.046, 2.426	2.224, 2.600	3.907, 4.489	10.600, 11.800	
300	6.2	1.592, 1.740	1.632, 1.771	1.841, 2.000	7.286, 8.143		
300	5.2	1.874, 2.053	1.864, 1.935				
313	12.3	1.948, 2.523	2.038, 2.519	2.060, 2.468	2.205, 2.489	4.077, 4.370	
313	10.3	2.310, 2.940	2.589, 3.238	2.851, 3.338	5.370, 6.071		
313	8.3	2.339, 2.803	2.877, 3.367	4.219, 4.727			
313	6.2	1.979, 2.224	2.340, 2.490	10.333, 11.000			
313	5.2	2.109, 2.259	2.526, 2.632				

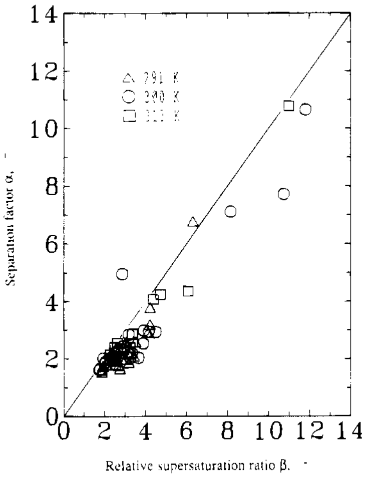

Figure 4. The relationship of α and β in the separation of anthracene and anthraquinone in mixed CO_2 + cyclohexanone solvent.

be considered as the minimum equilibrium concentration of the solid, $C_i^{min}(P)$.

Discussion

Effects of Temperature and Pressure on the Separation. Due to the effect of the mixed solvent (i.e., CO_2 + cyclohexanone), the separation of anthracene and anthraquinone from the solution has been achieved in this study. In order to compare the efficiency of separation, the separation factor is defined as the ratio of the composition in the precipitate to the composition in the original solution, i.e., [(% anthracene in precipitate/% anthraquinone in precipitate)/(% anthracene in original solution/% anthraquinone in original solution)]. In other words, the separation factor, α, is the ratio of recoveries, i.e.,

$$\alpha = Y_{AN}/Y_{AQ} \tag{2}$$

The effects of normalized concentration and other experimental conditions on the ability to separate anthracene from anthraquinone are listed in Table 5. In these experiments the original solutions contain equal saturations of anthracene and anthraquinone. The result indicated that the separation factor increased with a decrease of both saturations in the solution, when separation was carried out at the same pressure. When pressure and normalized concentration decreased below 5.2 MPa and 0.8 C_i^{sat}, respectively, there was practically no separation factor. In order to explain the influence of temperature and pressure on the separation factor, it is proposed that a driving force can be the relative ratio as a function of recoveries of anthracene and anthraquinone, i.e.,

$$\beta = \left\{\frac{Y_{AN}/(- Y_{AN})}{Y_{AQ}/(1 - Y_{AQ})}\right\} \tag{3}$$

According to the definition of β, the relative ratio decreases with the increase of normalized concentration at the same pressure and temperature. Even though a few data are not consistent due to experimental error in recoveries, statistically they are in decreasing order as the normalized concentration increases. In Figure 4 the separation factor is plotted against β for all temperatures and pressures; it shows clearly the increase in separation factor with β but not with temperature. The linear regression line was drawn through the data at constant temperature, although the slopes of the three lines are different but statistically significant.

Conclusions

The mixture of anthracene and anthraquinone was separated in cyclohexanone by the addition of high-pressure CO_2. The data obtained in this study supported the following conclusions for the CO_2 + cyclohexanone + anthracene + anthraquinone system.

Equilibrium solubilities of anthracene and anthraquinone in CO_2 + cyclohexanone solution are essentially the concentrations of these two solids in the solution expanded to 1 atm condition. Their average equilibrium solubilities and minimum equilibrium concentrations decreased with increasing normalized concentration and pressure; i.e., the recoveries of both solids increased with increasing normalized concentration and pressure. Therefore, pressure and normalized concentration are two major factors in this pressure-driven equilibrium.

The separation factor is essentially linear with respect to the relative ratio of recoveries and is independent of temperature. Over the temperature range 291−313 K and the pressure range 5.2−12.3 MPa, the separation factor decreased with increasing normalized concentration. In 62 experiments the average separation factor was 2.88 ± 1.91.

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