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over the entire mole fraction range. This fact suggests that there must be a lack of specific intermolecular forces in the mixture and pure components while strong dipole–dipole forces predominate. With regard to the pure components, the deviations from Trouton's constant (a value higher than 21), their high boiling points, and the weak temperature dependence of their g_k values (0.986 for PC and 1.26 for AN at 45 °C) seem to support the observation stated above.

Glossary

ϵ^E	excess dielectric constant
η^E	excess viscosity
V^E	excess molar volume
x	mole fraction
d	density
n	refractive index
G^{*E}	excess free energy of activation of the flow

Registry No. PC, 108-32-7; AN, 75-05-8.

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Received for review June 14, 1989. Revised February 15, 1990. Accepted June 26, 1990.

Vapor–Liquid Equilibria for the Systems Carbon Dioxide–Ethylbenzene and Carbon Dioxide–Styrene

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Vapor–liquid equilibrium data were measured for the systems CO_2–ethylbenzene and CO_2–styrene over a pressure range from 14 to 85 atm at 308, 318, and 328 K. Vapor–liquid equilibrium data were also measured over the same pressure and temperature ranges for the system CO_2–ethylbenzene–styrene, where the ratio of styrene to ethylbenzene in the liquid phase was kept at 1.86.

Introduction

Styrene is an important petrochemical raw material that is commonly produced by dehydrogenation of ethylbenzene (EB). Because of incomplete reaction, vacuum distillation is generally employed to separate these two compounds from the effluent stream, containing about 65% styrene and 35% EB. Due to the extensive energy required for vacuum distillation, use of liquid or supercritical CO_2 as a solvent to separate styrene and EB may be an alternative separation method. In order to determine if this is the case, phase equilibrium data for CO_2–styrene and CO_2–EB are needed. Although the equilibrium data for several CO_2–aromatic C_7 or C_8 systems have been reported in the literature (*1–4*), the data for these two systems do not appear to be available. In this work the vapor–liquid equilibrium data for these two systems and for the system CO_2–styrene–EB over the pressure range from 14 to 85 atm at 308, 318, and 328 K are reported.

Experimental Section

The experimental apparatus used in this work is illustrated in Figure 1. The entire apparatus was constructed with 0.63-cm-o.d. stainless steel 316 tubing, except the equilibrium cells. EB was purchased from Merck Co. with a minimum purity of 99.9%. Styrene was supplied by Taiwan Styrene Monomer Corp., with a claimed purity of 99+%, and contained 3 ppm of inhibitor 4-*tert*-butylcatechol, as received. Both chemicals were used without further purification. The first equilibrium cell, having a diameter of 2.54 cm, was filled with about 120 mL of styrene, EB, or styrene + EB. In order to prevent entrainment, several layers of glass beads supported by a perforated stainless steel disk were placed at the top of the cell. To assure saturation, a second equilibrium cell was also employed. However, the data indicated that a single cell was enough when the flow rate of the gas after expansion was less than 30 mL/min. This value was also observed to be the maximum flow rate allowed to obtain the equilibrium data. The equilibrium cells were immersed in a constant-temperature bath, which could be controlled to within ±0.5 K.

The experiment started with the compression of CO_2 (minimum purity of 99.8%) into a surge tank by a diaphragm compressor (Superpressure Inc.). In each experiment the pressure could be maintained to within ±10 psi of the desired value. A preheating coil was used to ensure that the carbon dioxide reached the temperature of the bath. The gas coming from the equilibrium cells was expanded across a metering valve, which was wrapped with heating tape. The condensed styrene, EB, or styrene + EB was collected in a cold trap, containing 400 mL of alcohol. The cold trap was surrounded by a mixture of salt and ice at about −10 °C. Samples of 4.8 μL were sent to a flame ionization detector gas chromatograph (Varian 3700) for composition analysis. To assure that all the hydrocarbons coming from the equilibrium cells can be collected, two cold traps in series were used in the preliminary runs. However, it was found that only one cold trap was needed since no hydrocarbons could be detected in the second cold trap and in the effluent gas stream. The total amount of CO_2 passed through the equilibrium cells was determined by measuring the volume of the expanded gas as it passed through a cold trap and a wet test meter. To eliminate possible measurement error, liquids in the cold trap and in the wet test meter were saturated with carbon dioxide first, which was done by passing the pure carbon dioxide through them before each experiment. The composition in the gas phase could be determined from the measured amounts of condensed solute and CO_2. At least ten

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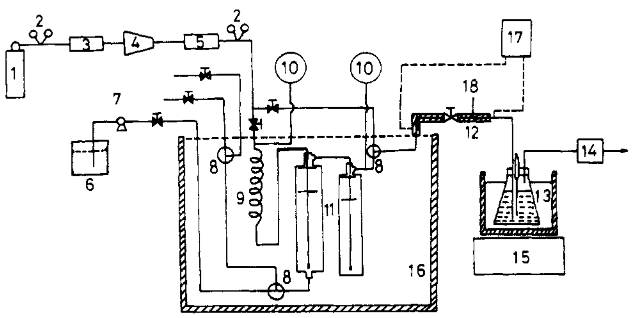

1	CO_2 Cylinder	7	Pump	13	Cold Trap
2	Regulator	8	Three-Way Valve	14	Wet Test Meter
3	Filter	9	Preheater	15	Magnetic Stirrer
4	Compressor	10	Pressure Indicator	16	Constant Temperature Bath
5	Surge Tank	11	Equilibrium Cell	17	Temperature Controller
6	Solvent	12	Heating Tape	18	Thermocouple

Figure 1. Schematic diagram of experimental apparatus.

Table I. Comparison of Vapor-Liquid Equilibrium Data for CO_2-Toluene at 311 K

	x_{CO_2}		y_{CO_2}	
P, atm	this study	Ng-Robinson[a]	this study	Ng-Robinson[a]
14.7	0.131	0.133	0.9931	0.993
40.1	0.418	0.406	0.9954	0.996
55.0	0.614	0.603	0.9944	0.994
68.4	0.866	0.869	0.9923	0.992

[a] From ref 2.

measurements at different times (approximately every 30 min) were conducted to see if the composition in the gas phase reached a stable value. It was observed that the deviation in compositions among these measurements was less than 2.0%.

The composition in the liquid phase was determined at the end of the experiment. The liquid in the equilibrium cell was collected in a place between the two three-way valves indicated in Figure 1. The volume of this collected part was 8.2 mL. After the expansion, the amount of CO_2 in this part could be determined by a wet test meter. Because of the condensation of the solute in this part, 900 mL of alcohol was used to wash this part. A portion of this liquid was sent to the GC for analysis. From the measured amount of CO_2 and solute, the compositions in the liquid phase could be determined.

Results and Discussion

In order to ensure that the present apparatus is applicable for vapor-liquid equilibrium measurement, the data for the system CO_2-toluene was first measured over the pressure range from 14 to 70 atm at 311 K. The results were found to agree well with those reported by Ng and Robinson (*2*), with a maximum deviation of less than 3.0% (Table I).

Vapor-liquid equilibrium data for the system CO_2-EB and CO_2-styrene are tabulated in Tables II and III and represented graphically in Figures 2 and 3, respectively, for three isotherms at 308, 318, and 328 K. The results indicate that CO_2 can extract more EB than styrene at the same extraction conditions.

The Peng-Robinson equation of state (*5*)

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{1}$$

where

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad a_{ij} = (1 - \delta_{ij})(a_i a_j)^{1/2} \tag{2}$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = (1 - \eta_{ij})\frac{b_i + b_j}{2} \tag{3}$$

Table II. Vapor-Liquid Equilibrium Data for CO_2-Ethylbenzene

P, atm	x_{CO_2}	y_{EB}	K_{CO_2}	K_{EB}
		T = 308 K		
13.6	0.117	0.0020	8.53	0.0023
27.2	0.254	0.0016	3.93	0.0021
41.2	0.408	0.0017	2.45	0.0029
53.4	0.585	0.0021	1.71	0.0051
71.1	0.921	0.0037	1.08	0.0468
		T = 318 K		
14.6	0.109	0.0033	9.14	0.0037
27.6	0.220	0.0024	4.53	0.0031
40.8	0.335	0.0025	2.98	0.0038
54.4	0.475	0.0030	2.10	0.0057
70.4	0.698	0.0041	1.43	0.0136
77.2	0.803	0.0047	1.24	0.0239
83.3	0.875	0.0065	1.14	0.0520
		T = 328 K		
15.3	0.107	0.0048	9.30	0.0054
28.6	0.214	0.0035	4.66	0.0045
40.8	0.310	0.0033	3.22	0.0048
54.4	0.418	0.0037	2.38	0.0064
67.7	0.549	0.0049	1.81	0.0109
81.6	0.687	0.0066	1.45	0.0211

Table III. Vapor-Liquid Equilibrium Data for CO_2-Styrene (st)

P, atm	x_{CO_2}	y_{st}	K_{CO_2}	K_{EB}
		T = 308 K		
15.0	0.122	0.0014	8.19	0.0016
21.0	0.164	0.0012	6.09	0.0014
28.2	0.238	0.0011	4.20	0.0014
40.1	0.369	0.0012	2.71	0.0019
55.5	0.543	0.0018	1.84	0.0039
67.1	0.803	0.0025	1.24	0.0127
		T = 318 K		
14.4	0.108	0.0020	9.24	0.0022
27.6	0.198	0.0014	5.04	0.0017
41.8	0.325	0.0015	3.07	0.0022
57.7	0.462	0.0023	2.16	0.0043
69.9	0.611	0.0035	1.63	0.0090
79.3	0.772	0.0051	1.29	0.0224
		T = 328 K		
14.2	0.082	0.0039	12.15	0.0042
27.5	0.174	0.0027	5.73	0.0033
41.8	0.264	0.0026	3.78	0.0035
55.1	0.354	0.0029	2.82	0.0045
68.8	0.477	0.0042	2.09	0.0080
82.0	0.614	0.0062	1.62	0.0161

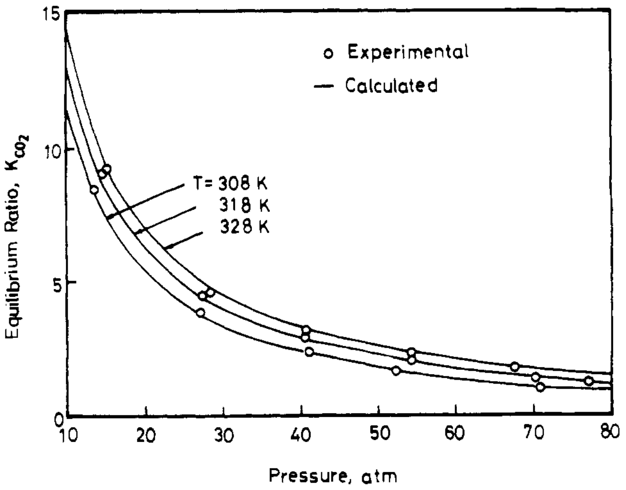

Figure 2. Equilibrium ratio for carbon dioxide in the carbon dioxide-ethylbenzene sytem.

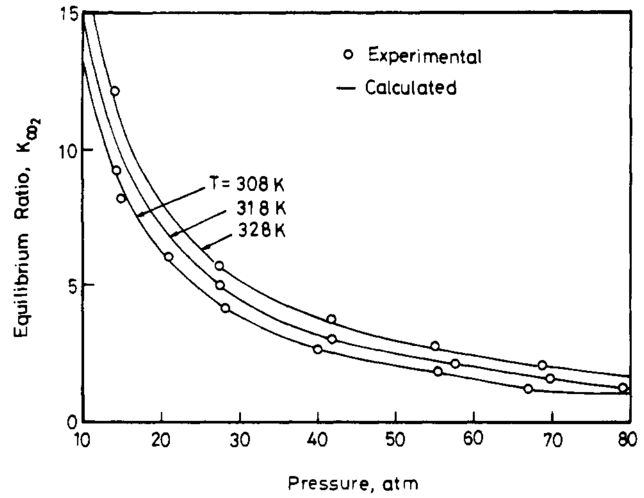

Figure 3. Equilibrium ratio for carbon dioxide in the carbon dioxide–styrene system.

Table IV. Vapor–Liquid Equilibrium Data for CO_2–EB–Styrene with x_{st}/x_{EB} = 1.86

P, atm	$y_{EB} \times 10^3$	$y_{st} \times 10^3$	y_{st}/y_{EB}
	T = 308 K		
15.2	0.71	0.87	1.23
25.9	0.58	0.71	1.22
43.5	0.62	0.83	1.34
54.2	0.74	0.99	1.34
66.0	1.07	1.60	1.50
	T = 318 K		
14.9	1.14	1.39	1.22
21.6	0.94	1.22	1.30
39.8	0.91	1.18	1.30
59.2	1.05	1.46	1.39
68.6	1.49	2.29	1.54
81.6	2.63	4.56	1.73
	T = 328 K		
14.6	1.91	2.41	1.26
23.4	1.33	1.70	1.28
36.0	1.17	1.57	1.34
47.1	1.21	1.58	1.31
62.5	1.50	2.16	1.44
83.5	2.92	4.73	1.62

was used to calculate the fugacity coefficients for both solutes and CO_2. The solid lines in Figures 2 and 3 are the calculated equilibrium ratios for CO_2 with δ_{ij} = 0.075 and η_{ij} = −0.0396 for CO_2–EB and δ_{ij} = 0.071 and η_{ij} = −0.0375 for CO_2–styrene. From these figures it can be found that the agreement is satisfactory with an average deviation about 2.2% and 2.8% for CO_2–EB and CO_2–styrene, respectively. The values of δ_{ij} and η_{ij} for the present two systems are close to those reported by Occhiogrosso et al. (*6*), who suggested that the values δ_{ij} = 0.066 and η_{ij} = −0.04 are applicable for all systems of CO_2–aromatic with alkyl groups. When the latter two values were used to calculate the equilibrium ratio, K_{CO_2}, a good agreement between the calculated and experimental values was also observed and the average deviations are about 2.6% and 5.0% for CO_2–EB and CO_2–styrene, respectively. This agreement strongly supports the suggestion given by Occhiogrosso et al.

Vapor–liquid equilibrium data for the ternary system CO_2–EB–styrene were also measured in this work. The liquid mixture consisted of 35% EB and 65% styrene at the beginning of the experiment. Since the amount of liquid charged to the equilibrium cell was quite large as compared with the amount extracted, the ratio of styrene to EB in the liquid phase (1.86) was observed not to change significantly after each experiment. Table IV indicates that this ratio in the gas phase increased with pressure when the temperature was fixed; however, it never exceeded 1.86 over the entire pressure and temperature range studied in this work. It was also found that the mole fractions of EB and styrene in the gas phase for the ternary system were much smaller than those for the binary systems.

Nomenclature

K, equilibrium ratio, y/x
x, mole fraction in the liquid phase
y, mole fraction in the gas phase
δ_{ij}, η_{ij}, interaction parameters in the Peng–Robinson equation of state

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Received for review August 7, 1989. Revised April 20, 1990. Accepted July 3, 1990. We express our thanks to the Taiwan Styrene Monomer Corp. for the financial support and the supply of styrene.