264 *J. Chem. Eng. Data* **1995,** *40,* 264−266

Solubilities of Methylbenzoic Acid Isomers in Supercritical Carbon Dioxide

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The solubilities of methylbenzoic acid isomers in supercritical carbon dioxide were measured by using a phase equilibrium apparatus over the temperature range from 313.2 to 333.2 K at pressures up to 24.6 MPa. The measured solubilities were correlated using the model proposed by Chrastil. The calculated results show good agreement with the experimental data.

Introduction

Extractions with supercritical fluids as solvent have received wide attention recently for potential applications in the special chemicals, food processing, pharmaceutical chemistry, and petroleum industries (*1*). Carbon dioxide is a preferred supercritical solvent for practical applications since it is nontoxic, nonflammable, and relatively inexpensive, and has a high solvent power for many low-volatile solutes (*2*).

The phase behavior of low-volatile components in a supercritical fluid is of great interest for the isolation and purification of pharmaceuticals. Although supercritical fluid phase equilibria have been reported by many researchers, literature data of solubilities of the isomers in supercritical carbon dioxide are limited. Krukonis and Kurnik (*3*) have measured the solubilities of hydroxybenzoic acid and dihydroxybenzene isomers in supercritical carbon dioxide. Chang and Morrell (*4*) have reported the solubilities of methoxy-1-tetralone and methyl nitrobenzoate isomers in supercritical carbon dioxide. The solubilities of 2,3-, 2,6-, and 2,7-dimethylnaphthalenes in supercritical carbon dioxide (*5, 6*) and the solubilities of 2,5-, 2,6-, and 3,4-xylenols in supercritical carbon dioxide (*7, 8*) were measured. Foster et al. (*9*) have measured the solubilities of ethyl linolenate isomers in supercritical carbon dioxide. Tan and Weng (*10*) have reported the solubilities of naphthol isomers in supercritical carbon dioxide.

In this work the solubilities of 2-, 3-, and 4-methylbenzoic acid in supercritical carbon dioxide were measured in the temperature range from 313.2 to 333.2 K and for pressures between 11.0 and 24.6 MPa. From these measurements, crossover pressures were observed. The resultant solubility data were correlated using the model proposed by Chrastil (*11*).

Experimental Section

A phase equilibrium apparatus was used to measure the solubilities of methylbenzoic acid in supercritical carbon dioxide. A detailed description of the equipment and sampling procedure was reported previously (*12*). Carbon dioxide supplied from a gas cylinder was liquefied through a cooling unit and compressed by a positive-displacement liquid pump (Laboratory Data Control minipump, model constaMetric 3200 P/F) into a preheating coil immersed in a large constant-temperature stirred water bath. The temperature of the water bath was measured with a mercury-in-glass thermometer having 0.1 K divisions. A back-pressure regulator (Tescom Model 26-1723-24) was used to maintain a constant pressure within the system. The equilibrium pressure was measured with a Bourdon gauge (Heise Model CMM; 0−276 bar) to an accuracy of ±0.3 bar. The uncertainty in the system pressure was about ±0.5 bar. Two equilibrium cells (30 cm in length with a 1.93 cm internal diameter stainless steel pipe, with reducer−adapter couplings at each end) connected in series were used.

Approximately 40 g of methylbenzoic acid was introduced into each equilibrium cell in three sections separated by 0.2 cm diameter stainless steel balls. The cells were attached to a preheating coil and immersed in a water bath controlled within ±0.1 K. After the flow had passed the equilibrium cells for about 1 h, the carbon dioxide saturated with solute was allowed to flow through a thermostated line and micrometering valve (Hoke 1335G2Y). At the micrometering valve the saturated carbon dioxide was expanded to atmospheric pressure, thereby precipitating the dissolved solute. The temperature of the line and valve was measured by a type J thermocouple, and adjusted by a heating tape (Omegalux STH 051-040) wrapped around the line and valve body to a temperature between 150 and 200 K above the water bath temperature, in order to avoid precipitation of the solute on the line (*13*).

Approximately 0.03−0.44 g of solute was collected after the expansion valve by two cold traps in series, which were partially packed with glass wool to promote entrainment of small particles of the solute in the expanded gas stream. These traps were immersed in an ice bath maintained at about 273.2 K. The solute collected in the tubes was weighed by an analytical balance (Shimadzu AEG-120; accuracy ±0.1 mg). The gas liberated from the traps was allowed to flow through a rotameter (Aalborg P23/1-082-03G), U-tube, and wet test meter (American Meter Model AL 17-1) having an accuracy of ±0.1% to measure the total volume of solvent used in each run.

The carbon dioxide supplied by San Fu Chemical Co., Taiwan, had a minimum purity of 99.8 mol %. The 2-methylbenzoic acid and 3-methylbenzoic acid with minimum purities of 99.5 and 99 mol %, respectively, were from Fluka. The 4-methylbenzoic acid was from Merck with a minimum purity of 99 mol %. The chemicals were used without further purification.

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0021-9568/95/1740-0264$09.00/0

Table 1. Solubilities of Methylbenzoic Acid Isomers in Supercritical Carbon Dioxide

		2-methylbenzoic acid		3-methylbenzoic acid		4-methylbenzoic acid		
T/K	P/MPa	10^4y_2	s/(g·L^{-1})	10^4y_2	s/(g·L^{-1})	10^4y_2	s/(g·L^{-1})	ϱ/(g·L^{-1})
313.2	11.0	9.02	1.93	9.10	1.95	1.48	0.31	691
	13.7	13.8	3.33	14.6	3.47	2.12	0.50	767
	16.4	18.2	4.55	18.8	4.70	2.67	0.66	807
	19.2	21.3	5.55	22.1	5.76	3.06	0.80	840
	21.9	23.8	6.36	24.0	6.42	3.44	0.92	862
	24.6	25.4	6.92	26.5	7.25	3.71	1.01	882
323.2	11.0	5.10	0.79	4.70	0.73	0.801	0.12	501
	13.7	15.1	3.14	13.7	2.85	2.09	0.43	671
	16.4	22.3	5.12	21.4	4.87	3.16	0.72	734
	19.2	28.8	6.99	28.6	6.94	3.97	0.96	782
	21.9	34.2	8.60	33.9	8.35	4.62	1.16	810
	24.6	38.2	9.93	38.7	9.96	5.13	1.33	837
333.2	11.0	2.40	0.27	1.84	0.21	0.430	0.05	369
	13.7	12.8	2.21	11.6	1.99	1.81	0.31	554
	16.4	25.7	5.25	22.9	4.66	3.47	0.70	656
	19.2	37.5	8.43	33.9	7.58	4.87	1.09	720
	21.9	48.1	11.31	46.5	10.93	6.00	1.40	756
	24.6	57.0	14.00	53.4	13.11	7.02	1.72	789

Table 2. Correlation of Solubility Data with Eq 1

solute	T/K	P range/MPa	k	a	b	$10^2\Delta y_2/y_2$
2-methylbenzoic acid	313.2	11.0–24.6	5.09	−6439.6	−12.05	3.33
	323.2	11.0–24.6	5.09	−6439.6	−12.05	3.14
	333.2	11.0–24.6	5.09	−6439.6	−12.05	3.05
						overall: 3.17
3-methylbenzoic acid	313.2	11.0–24.6	5.34	−6011.9	−15.04	1.51
	323.2	11.0–24.6	5.34	−6011.9	−15.04	3.86
	333.2	11.0–24.6	5.34	−6011.9	−15.04	3.82
						overall: 3.06
4-methylbenzoic acid	313.2	11.0–24.6	4.68	−5441.2	−14.37	1.56
	323.2	11.0–24.6	4.68	−5441.2	−14.37	2.58
	333.2	11.0–24.6	4.68	−5441.2	−14.37	1.88
						overall: 2.01

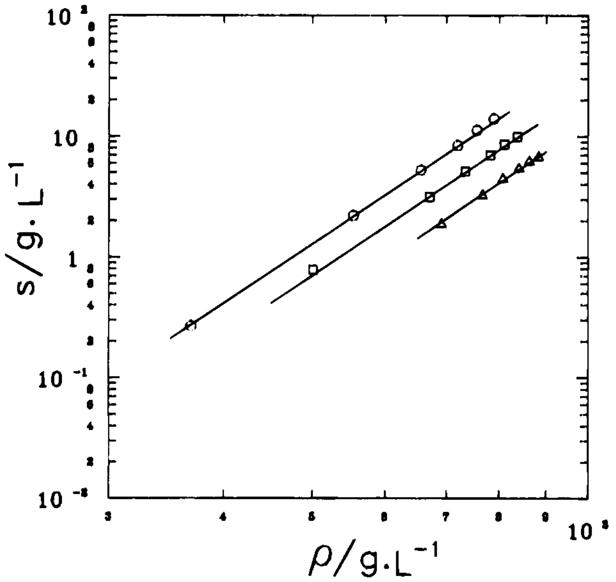

Figure 1. 2-Methylbenzoic acid solubility s in supercritical carbon dioxide against the carbon dioxide density ϱ: (△) 313.2 K; (□) 323.2 K; (○) 333.2 K; (—) calculated with eq 1.

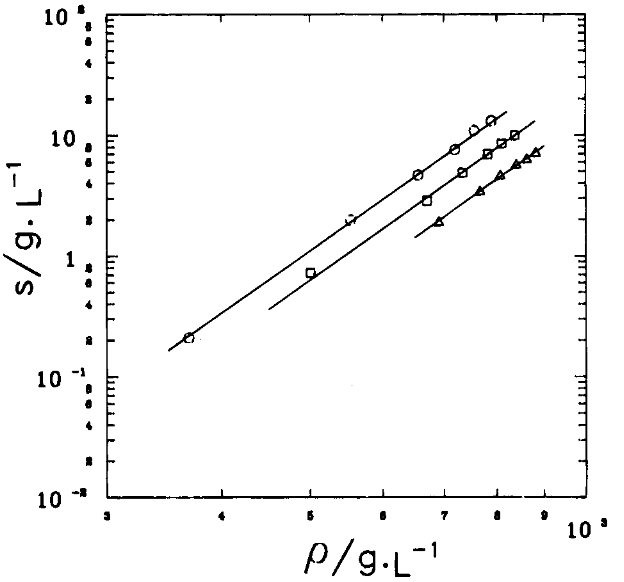

Figure 2. 3-Methylbenzoic acid solubility s in supercritical carbon dioxide against the carbon dioxide density ϱ: (△) 313.2 K; (□) 323.2 K; (○) 333.2 K; (—) calculated with eq 1.

Results

The measurements were carried out for several flow rates of carbon dioxide (0.2–0.6 normal L min^{-1}) at the same temperature and pressure. The solubilities obtained were independent of the flow rate of carbon dioxide. Each reported solubility is the average value of three replicate samples at the same flow rate. The mole fractions of the solute were generally reproducible within ±2%. Table 1 presents the solubilities of methylbenzoic acid isomers in carbon dioxide over the temperature range from 313.2 to 333.2 K at pressures from 11.0 to 24.6 MPa. The solubilities of the solutes increase with pressure. From the effect of temperature on the solubilities we find that the retrograde solubility (crossover pressure effect) behavior of these solutes (*14–16*) exists in the supercritical state.

The results were correlated using the model proposed by Chrastil (*11*). This model is based on the hypothesis that one molecule of a solute A associates with k molecules of a gas B to form one molecule of a solvato complex AB_k in equilibrium with the system. The model indicates a

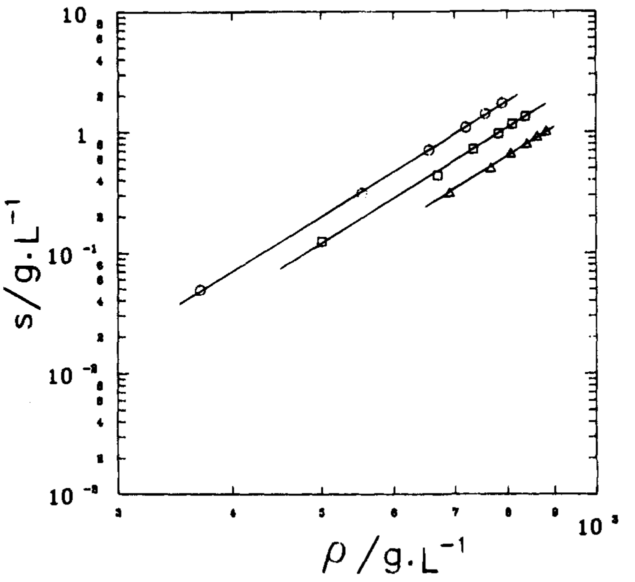

Figure 3. 4-Methylbenzoic acid solubility s in supercritical carbon dioxide against the carbon dioxide density ϱ: (△) 313.2 K; (□) 323.2 K; (○) 333.2 K; (—) calculated with eq 1.

linear relationship between the logarithm of the solubility s and the logarithm of the density of the pure solvent ϱ. The relationship is expressed as

$$\ln(s/(\text{g}{\cdot}\text{L}^{-1})) = k \ln(\varrho/(\text{g}{\cdot}\text{L}^{-1})) + \frac{a}{T/\text{K}} + b \qquad (1)$$

were T is the temperature, k is an association number, a is dependent on the heat of solvation and heat of vaporization of the solute, and b is dependent on the molecular weights of the solute and the solvent.

The densities of carbon dioxide, ϱ, at the operating conditions were obtained from Kennedy and Thodos (*17*). The solubility of the solute in carbon dioxide s (g·L^{-1}) is calculated from

$$s = \frac{\varrho M_2 y_2}{M_1(1 - y_2)} \qquad (2)$$

where M_1 and M_2 are the molecular weights of the solvent and the solute, respectively. The values of ϱ and s are also listed in Table 1.

The optimum values of k, a, and b for each solute are listed in Table 2. The average absolute deviations in y_2 are 3.17%, 3.06%, and 2.01% for carbon dioxide + 2-methylbenzoic acid, + 3-methylbenzoic acid, and + 4-methylbenzoic acid, respectively. These calculated results, as shown in Figures 1−3, indicate good agreement with the experimental data.

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Received for review June 28, 1994. Revised September 19, 1994. Accepted September 28, 1994.[⊗] Acknowledgment is made to the National Science Council of the Republic of China (Grant NSC 83-0402-E006-024) for financial support of this work.

JE940121C

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1994.