Solubility of Maleic Acid in Supercritical Carbon Dioxide

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The solubility of maleic acid in supercritical carbon dioxide has been measured at (318.15, 333.15, and 348.15) K over a pressure range of (7 to 30) MPa. Measurements were carried out using a static apparatus. The solubility ranged from a maleic acid mole fraction of $1.30 \cdot 10^{-5}$ at 318.15 K and 7 MPa to $59.17 \cdot 10^{-5}$ at 348.15 K and 30 MPa. The Chrastil and Méndez-Santiago and Teja (density-based) models were used to correlate the experimental data.

Introduction

Supercritical fluids, especially supercritical carbon dioxide ($scCO_2$), have been widely used in industrial, environmental, pharmaceutical, and fundamental studies.[1−4] The $scCO_2$ is widely used because its critical temperature and pressure are lower than the other supercritical fluids.[5] The solubility of compounds in $scCO_2$ is one of the important thermophysical parameters to measure. Generally, the solubility depends on the solute vapor pressure that is related to the intermolecular interactions, polarity, molecular weight, and the solution temperature and pressure.[6,7] In this work, the solubility of maleic acid have been measured in $scCO_2$ at different pressures and temperatures. To the best of our knowledge, no solubility data for maleic acid in any supercritical fluids have been reported in the literature so far.

Maleic acid is used in the organic synthesis of malic, succinic, aspartic, tartaric, propionic, lactic, malonic, and acrylic acids. It is also used in dyeing and finishing of cotton, wool, and silk, as a preservative for oils and fats, and in the manufacturing of artificial resins. It is used to prepare maleate salts of antihistamines and similar drugs such as ergometrine and methylergometrine injection. This acid is moderately toxic by ingestion and skin contact. Furthermore, maleic acid has been considered as an intermediate during the photocatalytic degradation of organic molecules such as phenol, catechol, and hydroquinone.[8−10] Barillaro et al. showed that maleic acid is able to modify the formation of the stable complexes between miconazole and cyclodextrins in $scCO_2$.[11] Furtheremore, it was shown that ion-pair formation in the $scCO_2$ saturated with trioctylamine can strongly increase the solubility and the extraction yield of maleic acid and phthalic acid from their mixtures[12] in the petrochemical wastes.

Experimental Section

Materials. Carbon dioxide with a mass purity of 99.95 % was purchased from Ardestan Co. Ltd. (Isfahan, Iran). Maleic acid, naphthalene, and ethanol with a mass purity of 99 % was purchased from Merck Chemical Co.

Experimental Procedure. The solubility measurements were carried out using a static apparatus shown in Figure 1.[13,14] In each experiment 750 mg of maleic acid mixed with glass beads (mesh size of 50 to 70) and was placed in the equilibrium cell with an inner diameter of 4 mm and a length of 50 mm. The glass beads was used to increase the contact surface of the acid molecules and the $scCO_2$ molecules to reach equilibrium and saturation condition. The liquid CO_2 was passed over a molecular sieve 5A filter to eliminate the possible water and hydrocarbon impurities. Then the liquid CO_2 was passed through a cooling coil and into a reciprocating LC pump (model Shimadzu LC-6A). The accuracy of the set liquid CO_2 pressure was within ± 10 kPa. The back-pressure regulator (model Jasco BP1580-81) was used to control the pressure of the equilibrium cell. The oven (model Jasco 6410 Plus) temperature was maintained within ± 0.1 K. The liquid CO_2 was pressurized through a preheated stainless steel coil (a tube with 0.8 mm inner diameter and 2 m length) and enabled CO_2 to reach oven temperature before entering the equilibrium cell. The stainless steel filters with 2 μm pores were used at the end of the cell to prevent physical transfer of solid materials to the sampling loop (with 100 μL volume) connected to the six-port, two-position switching valve. At the beginning of each experiment the system was maintained at the desired temperature and pressure for 60 min. The time was obtained experimentally by measuring solubility with different equilibration times, and we found that 60 min is enough for the system to reach equilibrium. Finally, with changing the position of switching valve the dissolved sample in $scCO_2$ was transferred and trapped into the sampling loop; then it was transferred to the collection vessel, and the loop was washed with ethanol. The amount of collected solutes were determined using a UV−vis spectrophotometer (model

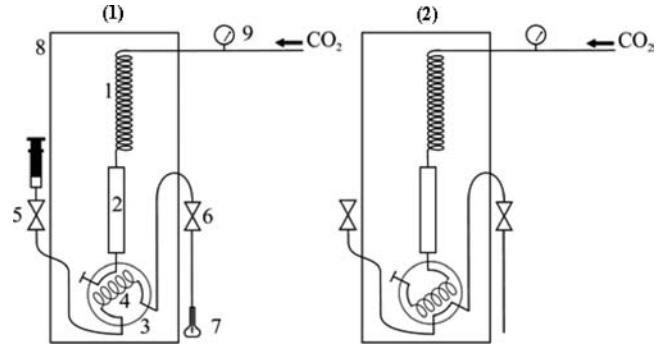

Figure 1. Schematic diagram of the static system for solubility measurements. 1, helical preheater; 2, equilibrium cell; 3, six-port two-position switching valve; 4, sampling loop; 5, 6, needle valves; 7, collection vessel; 8, oven; 9, pressure gauge.

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10.1021/je9008393
Published on Web 04/01/2010

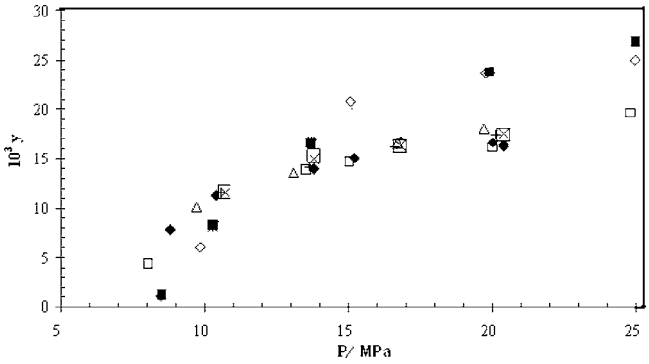

Figure 2. Mole fraction binary solubilities (y) of naphthalene along with the previously reported results. ◆, this work at 308.15 K; ■, this work at 318.15 K; △, ref 3 at 308.15 K; □, ref 12 at 308.15 K; +, ref 13 at 308.15 K; ◇, ref 14 at 318.15 K; ×, ref 15 at 308.15 K.

Jasco V-730). Five maleic acid standard solutions [(2 to 20) mg·L^{-1}] were prepared by appropriate dilution of a stock solution (500 mg·L^{-1}) and the external standard calibration curve obtained with a regression coefficient better than 0.9998. This curve was used to determine the concentration of the acid in the collection vial. The solubility was defined as the mole fraction of the solute in the $scCO_2$.

Results and Discussion

The accuracy of the static solubility measurements was verified by measuring the binary solubility of naphthalene at (308.15 and 318.15) K. Our results along with the reported results[3,13−16] are given in Figure 2 and Table 1. The solubility of maleic acid in $scCO_2$ along with its standard deviation of at least three measurments is given in Table 2. The trend of its solubilities versus pressure at different temperatures have been shown in Figure 3. The solubility of maleic acid increases with pressure due to a higher density of $scCO_2$ at higher pressures as a result of higher molecular interactions between the solute and the $scCO_2$ molecules. Moreover, the Poynting effect (effect of pressure on solid fugacity) might be significant in many systems. The solubility of maleic acid in $scCO_2$ increases with temperature according to the high volatility of solute at high temperatures.

Semiempirical Methods. Modeling is often used to correlate solubility data. Two approaches are generally found in the literature, namely, as the equation-of-state methods and the so-called semiempirical methods, many of which derived from the one originally proposed by Chrastil.[17]

On the basis of the Chrastil model, the molecules of solute associate with the molecules of the $scCO_2$ forming a solvation complex, AB_k, which is in equilibrium with the fluid. A, B, and k are respectively the solute molecule, solvent molecule, and the number of associated solvent molecules, that is, an association number. Isotherms at (318.15, 333.15, and 348.15) K for maleic acid have been fitted with the model eq 1:

$$\ln S = k \ln \rho + a/T + b \qquad (1)$$

in which S is the solubility in g·L^{-1}, $a = \Delta H/R$, and $b = \ln(M_A + kM_B) + q - k \ln M_B$ (Figure 4). a depends on $\Delta_{solv}H + \Delta_{vap}H$, b is a function of k, the molecular weight of solute and of the fluid are M_A and M_B, and q is a constant. k, a, b, and the correlation coefficient (R^2) of data used in the Chrastil model are given in Table 3.

Table 2. Mole Fraction Solubility (y) of Maleic Acid in the $SCCO_2$

T K	P MPa	ρ^a g·L^{-1}	10^5 y	AARD %
318.15	7	183.20	1.30 ± 0.10	6.60
	8	241.05	1.31 ± 0.14	
	10	498.25	1.84 ± 0.12	
	15	741.97	2.08 ± 0.16	
	20	812.69	2.22 ± 0.14	
	25	857.14	2.33 ± 0.18	
	30	890.33	2.41 ± 0.22	
333.15	7	155.53	3.13 ± 0.24	2.16
	8	191.62	3.49 ± 0.29	
	10	289.95	4.50 ± 0.30	
	15	604.09	7.32 ± 0.45	
	20	723.68	8.07 ± 0.58	
	25	786.55	8.65 ± 0.64	
	30	829.71	8.88 ± 0.75	
348.15	7	138.52	24.81 ± 1.94	8.35
	8	166.54	26.37 ± 2.10	
	10	233.43	31.90 ± 2.54	
	15	463.33	49.43 ± 2.45	
	20	626.23	58.23 ± 3.02	
	25	711.61	55.85 ± 4.54	
	30	766.83	59.17 ± 4.86	

[a] This is the pure CO_2 density computed using ref 22.

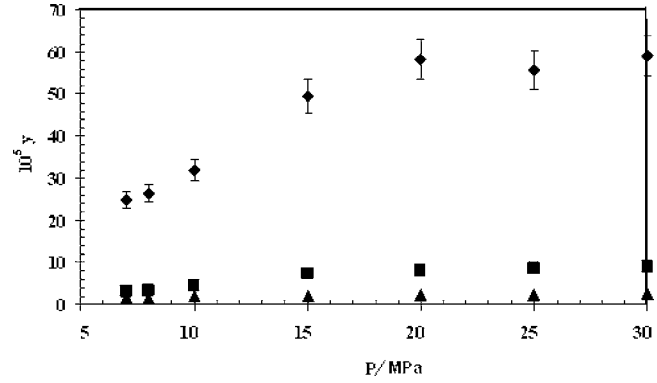

Figure 3. Mole fraction solubilities (y) of maleic acid in $scCO_2$. ▲, 318.15 K; ■, 333.15 K; ◆, 348.15 K.

Table 1. Mole Fraction Solubilities (y) of Naphthalene along with the Reported Results

temperature	this work		ref 14		ref 15		ref 3	
K	P/MPa	10^3 y	P/MPa	10^3 y	P/MPa	10^3 y	P/MPa	10^3 y
308.15	8.80	7.8 ± 0.4	8.05	4.4	10.70	11.6	9.70	10.1
	10.40	11.2 ± 0.6	13.52	13.9	13.80	15.0	13.10	13.6
	13.80	13.9 ± 0.5	15.05	14.7	16.80	16.3	16.70	16.6
	15.20	15.3 ± 0.7	20.03	16.1	20.40	17.5	19.70	18.0
	16.80	16.7 ± 0.6	24.82	19.6			25.20	17.8
	20.00	16.6 ± 0.8	29.92	17.5				
	20.40	16.4 ± 1.0						
318.15	8.50	1.1 ± 0.3	8.49	1.1				
	10.30	8.2 ± 0.5	9.83	6.0				
	13.70	16.5 ± 1.0	15.06	20.8				
	19.90	23.8 ± 1.4	19.77	23.7				
	25.00	25.8 ± 1.2	24.98	25.0				

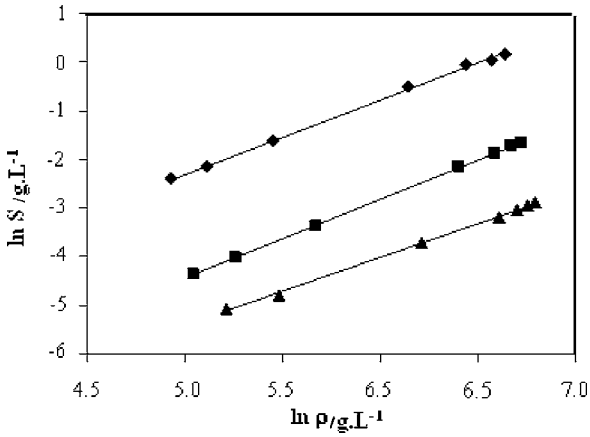

Figure 4. Chrastil plot of maleic acid solubility in $scCO_2$. ▲, 318.15 K; ■, 333.15 K; ◆, 348.15 K.

Table 3. Chrastil Parameters for Maleic Acid

temperature/K	k^a	a^a	b^a	R^{2b}
318.15	1.39	−11103.00	−1.97	0.9985
333.15	1.63	−11103.00	−2.82	0.9999
348.15	1.53	−11103.00	−2.47	0.9984

[a] k is the association number, $b = \ln(M_A + kM_B) + q - k \ln M_B$, and $a = \Delta H/R$. [b] R^2 is the correlation coefficient of data used in the Chrastil model at 313.15 K.

A method has also been proposed by Méndez-Santiago and Teja.[18,19] They proposed to plot the so-called enhancement factor as a function of the density of the solvent in the form of eq 2:

$$T \ln E = T \ln(y_2 P/P_2^{sub}) = A + B\rho_1 \qquad (2)$$

where T is the absolute temperature; E is the enhancement factor; y is the solute mole fraction; P is the total pressure; P_2^{sub} is the sublimation pressure of the solute; ρ is the density of the supercritical fluid; and A and B are regression constants. This equation is based on a rigorous theory of dilute solutions near the critical point of solvent which gives a straight line. The enhancement factor represents the ratio of the actual solubility to the ideal solubility, that is, calculated according to the ideal-gas law (P_2^{sub}/P). The main advantage of this model is that the solubility data at different temperatures can be represented by a single straight line. For this study, the Clausius−Clapeyron type equation, as an approximation, has been used to obtain the vapor pressure.[20] The data of the enthalpy of sublimation have been taken from ref 21. The values of A and B are equal to −2694.1 K and 1.23 $L \cdot g^{-1}$, respectively. For the regression analysis, P, ρ, and T were expressed in MPa, $g \cdot L^{-1}$, and K, respectively. Densities of carbon dioxide are computed from Span−Wagner equation of state.[22] Figure 5 shows that the data points for three isotherms follow the same trend, indicating good consistency of the data over the range of temperatures tested.

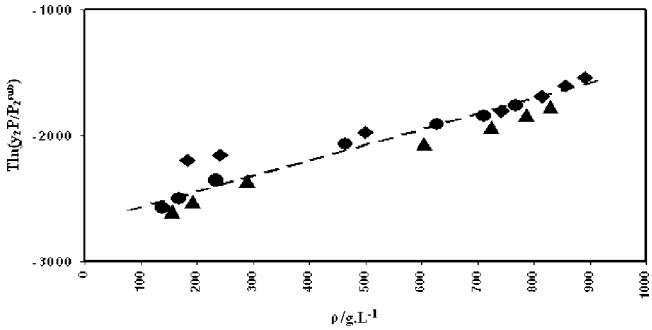

Figure 5. Méndez-Santiago and Teja plot resulting from multilinear regression. ◆, 318.15 K; ▲, 333.15 K; ●, 348.15 K; ---, model prediction.

Conclusions

The solubility of maleic acid in $scCO_2$ ranged from a mole fraction of $1.30 \cdot 10^{-5}$ at 318.15 K and 7 MPa to $59.17 \cdot 10^{-5}$ at 348.15 K and 30 MPa. The Chrastil and the Méndez-Santiago and Teja (density-based) models were good enough to correlate the experimental data.

Acknowledgment

The discussion with Dr. E. Keshavarzi on applying the Méndez-Santiago and Teja equation of state is gratefully acknowledged.

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Received for review October 16, 2009. Accepted March 19, 2010.

JE9008393