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Experimental Determination of the Solubility of Thiophene in Carbon Dioxide and in Carbon Dioxide + Ethanol

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The solubility of thiophene (1) in CO_2 (2) and in CO_2 (2) + ethanol (3) mixtures were measured from (313 to 363) K using a static-analytical method connected on-line to a gas chromatograph. The solubility of thiophene in CO_2 was obtained at (314.53, 334.12, and 363.55) K. Isothermal solubilities of thiophene in CO_2 + ethanol mixtures with mass fractions of ethanol (w_3) on a solute-free basis of 0.0245, 0.0548, and 0.0820 were obtained at (333 and 363) K. The solubility of thiophene was not greatly enhanced when ethanol was added to CO_2 at any composition. The experimental results were compared with those calculated values from Peng−Robinson equation of state using classical mixing rules.

Introduction

New efforts have been applied to obtain low-sulfur fuels.[1−5] Extraction of sulfur compounds using ionic liquids,[1−3] the use of zeolites as selective sorbents for the desulfurization of fuels,[4] and the formation of sulfur salts from the reaction of sulfur compounds[5] are some of the recent investigations conducted to reduce sulfur content in commercial fuels. The extraction of sulfur compounds using supercritical solvents is another possible process. Its development requires previous study of phase equilibria[6] and thermophysical properties. CO_2 is the most used and attractive supercritical fluid.[7] However, the solvent power of pure CO_2 is not sufficient to dissolve light and high polar compounds;[7] therefore, some liquid solvents have been added in small quantities to improve the capacity and selectivity of CO_2.[7,8] The success of a SFE strongly depends on choosing of the right cosolvent. On the other hand, thiophene is one of the principal sulfur compounds present in commercial fuels.[6] This compound can be used as model sulfur compound as in previous papers.[1−4] Information about phase equilibria involving sulfur compounds, CO_2 and liquid solvents reported in the literature are scarce. Triday[9] reported the vapor−liquid equilibria of thiophene + light alcohols binary systems at low pressures. Recently, we have reported the solubility of thiophene in CO_2 and CO_2 + 1-propanol.[6] The addition of 1-propanol did not improve significantly the solubility of thiophene. In this work, ethanol was used as cosolvent in order to investigate its influence on the solubility of thiophene. We chose ethanol at mass fractions up to 0.0820 due to the critical properties for the CO_2 + ethanol are lower than those for the CO_2 + 1-propanol and are near the critical point of the CO_2 as reported by Yeo et at.[10]

Experimental Section

Materials. Air Products-Infra, México, supplied CO_2 and helium with a minimum purity of 99.995 mol % and 99.998 mol %, respectively. Aldrich Chemical Co., USA, supplied thiophene with a minimum purity of 99+ %. Ethanol was obtained from Merck, México, with a stated purity of 99.8 %. These compounds were used without any further purification. Thiophene and ethanol were degassed and vigorously stirred under vacuum before they were used.

Apparatus and Procedure. The apparatus and experimental procedures have been described previously.[6,11] The apparatus is based on the static-analytical method. An equilibrium cell with a volume of about 100 cm^3 is the main component of this apparatus, and the temperature of the cell was regulated by air bath. Two platinum probes Pt100 (Specitec, France) immersed in two thermometric wells at the top and bottom of the cell body were used for temperature measurements. The Pt100 were calibrated against a 25-Ω reference probe (model 162CE, Rosemount) connected to a calibration system (model F300S, Automatic Systems Laboratories). A thermoregulated pressure transducer (model PDCR, Druck) recorded the pressure of the system. This sensor was calibrated against a dead weights gauge (model 5304 Class S2, Desgranges & Huot). Estimated uncertainties were within ± 0.03 K for temperature and within ± 0.04 % for pressure.

A movable capillary takes samples from the cell, and these are sent to a gas chromatograph (HP-5890 II) for composition analyses by means of a thermoregulated transferring circuit using helium as carrier gas. The gas chromatograph was equipped with a thermal conductivity detector (TCD). The carrier gas was set to 30 mL/min through a packed column (Porapak Q 80/100, Alltech) with a length of 1.2 m and an external diameter of 0.32 cm. The TCD was calibrated by introducing known amounts of each component through calibrated syringes in the injector of the analytical equipment. Experimental composition uncertainties were estimated to be within ± 1 %. The TCD calibration for thiophene is shown in Figure 1, and the uncertainty did not exceed ± 0.8 %, as is demonstrated in Figure 2. Similar results were obtained for CO_2 and ethanol.

After the calibrations of the TCD detector, temperature probes, and pressure transducer,[12] the measurements were carried out. Thiophene was fed into the equilibrium cell followed by degassing under vacuum and stirring. Then the solvent (CO_2 or CO_2 + ethanol) was introduced into

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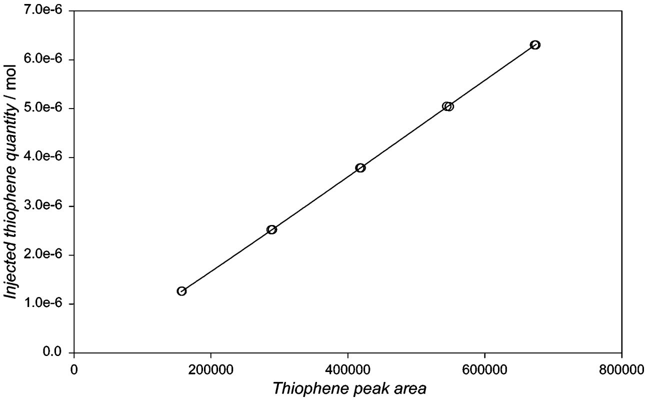

Figure 1. TCD calibration curve for thiophene.

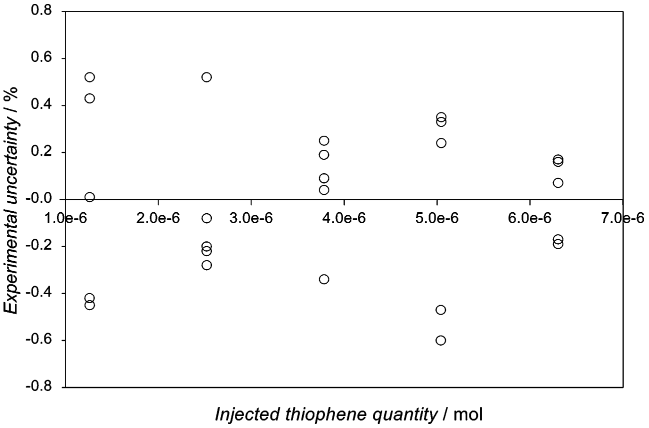

Figure 2. Uncertainty for the experimental mole number of thiophene.

the cell. CO_2 was introduced by means of a syringe pump (100DM, Isco). A volume variable cell (~80 cm^3) was used to feed the CO_2 + ethanol mixture to the equilibrium cell. The samples with the desired compositions were prepared by successive loadings of the pure compounds. The amounts of the compounds were determined by weighing carried out with an uncertainty of $\pm 10^{-7}$ kg with a comparator balance (CC1201, Sartorius), which was periodically calibrated with a standard mass of 1 kg of class E1. The resulting uncertainty for the mass fraction composition of the mixtures was lower than $\pm 10^{-4}$. Equilibrium measurements were performed when temperature and pressure were kept constant. At this point, five consecutive samples for each phase were taken to check for the reproducibility and perform mole fraction error analysis. Liquid and vapor were sampled within a volume of 1 μL from the equilibrium cell. Once liquid and vapor compositions were determined, at constant temperature, the next measurement was achieved by adding more solvent into the cell. Isothermal solubility curves were obtained by consecutive increments of pressure.

Results and Discussion

Experimental Data. The solubility of thiophene (1) in CO_2 (2) was determined at (314.53, 334.12, and 363.55) K. The obtained solubilities are reported in Table 1 and in Figure 3. The solubility values of this system were compared with those reported by Elizalde-Solis and Galicia-Luna[6] in order to check for the experimental consistency and methodology. It is important to point out that no more phase equilibrium data are reported in the literature for this system. These sets of data were in agreement, and the obtained deviations were within the experimental uncertainty.

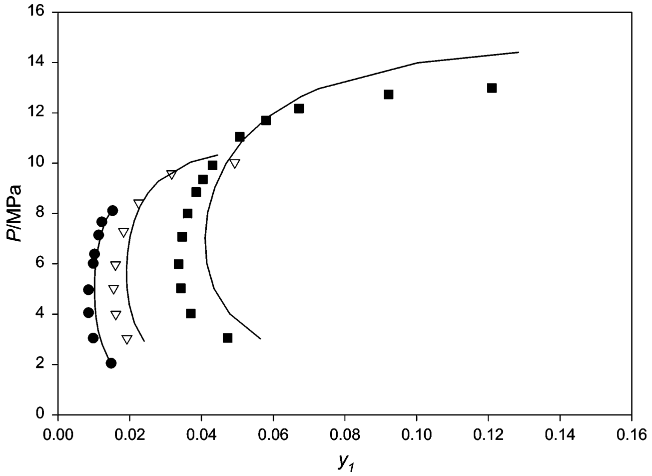

Figure 3. Mole fraction solubility of thiophene (1) in CO_2 (2) at ●, 314.53 K; ▽, 334.12 K; ■, 363.55 K; and —, P–R EoS.

Table 1. Mole Fraction Solubility of Thiophene (1) in CO_2 (2)

P/MPa	y_1	P/MPa	y_1	P/MPa	y_1
T = 314.53 K		T = 334.12 K		T = 363.55 K	
2.049	0.0148	3.033	0.0192	3.055	0.0473
3.047	0.0098	3.998	0.0161	4.024	0.0370
4.058	0.0085	5.027	0.0155	5.027	0.0343
4.969	0.0085	5.964	0.0160	5.993	0.0336
6.013	0.0098	7.289	0.0183	7.074	0.0346
6.387	0.0102	8.423	0.0225	7.996	0.0361
7.142	0.0113	9.584	0.0317	8.850	0.0385
7.662	0.0122	10.024	0.0493	9.357	0.0404
8.112	0.0152			9.915	0.0431
				11.050	0.0507
				11.696	0.0580
				12.173	0.0672
				12.732	0.0922
				12.990	0.1210

Table 2. Mole Fraction Solubility of Thiophene (1) in CO_2 (2) + Ethanol (3)

T/K	P/MPa	y_1	y_2	T/K	P/MPa	y_1	y_2
			w_3 = 0.0245				
333.90	2.527	0.0232	0.9714	363.29	2.034	0.0667	0.9328
	3.001	0.0205	0.9748		3.548	0.0473	0.9506
	3.899	0.0173	0.9789		5.131	0.0399	0.9590
	5.035	0.0164	0.9802		7.039	0.0372	0.9597
	6.048	0.0173	0.9794		8.027	0.0390	0.9575
	7.081	0.0191	0.9776		8.854	0.0408	0.9554
	7.744	0.0211	0.9763		9.764	0.0442	0.9515
	8.392	0.0234	0.9733		10.792	0.0508	0.9441

The solubility of thiophene (1) in CO_2 (2) + ethanol (3) mixtures was measured for three different loadings of the cosolvent on a solute-free basis of w_3 = 0.0245, 0.0580, and 0.0820. The solubility measurements for w_3 = 0.0245 were obtained at (333.90 and 363.29) K. These results are listed in Table 2. For w_3 = 0.0580, measurements were carried out at (333.84 and 363.17) K and for w_3 = 0.0820, measurements were made at (334.30 and 363.64) K. For these last loadings the vapor–liquid equilibrium is reported in Table 3. Ethanol was added as cosolvent to determine the influence of this polar component on the enhancement of the solubility of thiophene in supercritical CO_2. No more solubility data could be obtained at higher pressures than the studied range due to the restriction of the small volume of the loading cell where the solvent mixtures (CO_2 + ethanol) were prepared.

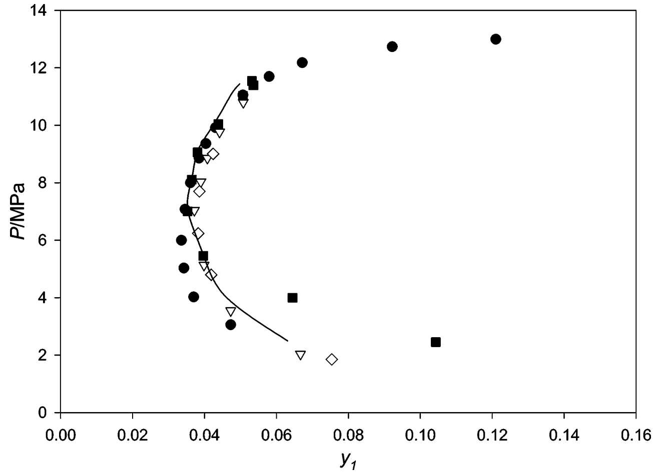

Figure 4. Mole fraction solubility of thiophene (1) in CO_2 (2) + ethanol (3) at ~363 K: ◇, $w_3 = 0.0820$; ■, $w_3 = 0.0580$; ▽, $w_3 = 0.0245$; ●, $w_3 = 0.0$ (pure CO_2); and —, P−R EoS for $w_3 = 0.0580$.

Table 3. Experimental VLE Data for Thiophene (1) + CO_2 (2) + Ethanol (3) Mixtures

T/K	P/MPa	x_1	x_2	y_1	y_2
		$w_3 = 0.0580$			
333.84	2.009	0.7432	0.1329	0.0307	0.9641
	3.172	0.6709	0.2153	0.0207	0.9712
	4.834	0.5500	0.3465	0.0175	0.9751
	6.090	0.4486	0.4645	0.0179	0.9750
	7.125	0.3591	0.5710	0.0194	0.9734
	8.147	0.2689	0.6785	0.0215	0.9712
363.17	2.450			0.1043	0.8900
	3.995			0.0645	0.9290
	5.455			0.0397	0.9531
	7.002			0.0353	0.9571
	8.105			0.0365	0.9551
	9.059			0.0381	0.9531
	10.038			0.0439	0.9458
	11.028			0.0507	0.9370
	11.385			0.0536	0.9333
		$w_3 = 0.0820$			
334.30	2.056	0.7208	0.1392	0.0249	0.9644
	3.024	0.6523	0.2162	0.0200	0.9718
	4.037	0.5840	0.2967	0.0181	0.9748
	5.002	0.5084	0.3843	0.0178	0.9756
	5.639	0.4976	0.4382	0.0182	0.9767
	6.347	0.3861	0.5279	0.0182	0.9758
	6.801	0.3605	0.5734	0.0191	0.9752
	7.410	0.2941	0.6382	0.0285	0.9639
363.64	1.852	0.8797	0.1092	0.0754	0.9206
	4.795	0.7363	0.2388	0.0419	0.9528
	6.238	0.6217	0.3458	0.0383	0.9559
	7.700	0.5090	0.4516	0.0386	0.9545
	9.003	0.3926	0.5530	0.0424	0.9474

In the studied range, the solubility of thiophene in CO_2, and CO_2 + ethanol mixtures depended on temperature and pressure changes, the solubilities increased as temperature was increased. At a given temperature and above the critical pressure of the CO_2, the solubility of thiophene increased greatly with increasing pressure. The solubility of thiophene in CO_2 + ethanol mixtures is plotted in Figure 4 at ~363 K. The mole fraction solubility of thiophene was improved about 6 % for $w_3 = 0.0245$. However, about the same solubility values for thiophene were obtained for the three loadings of cosolvent. Moreover, the experimental solubilities of thiophene (1) in CO_2 (2) + ethanol (3) at $w_3 = 0.0245$ are compared with those previously reported with the CO_2 (2) + 1-propanol (3) mixture at $w_3 = 0.0231$[6] in Figure 5. The addition of ethanol improved the solubility of thiophene in an order of about 5.7 % compares to that obtained with the addition of 1-propanol.

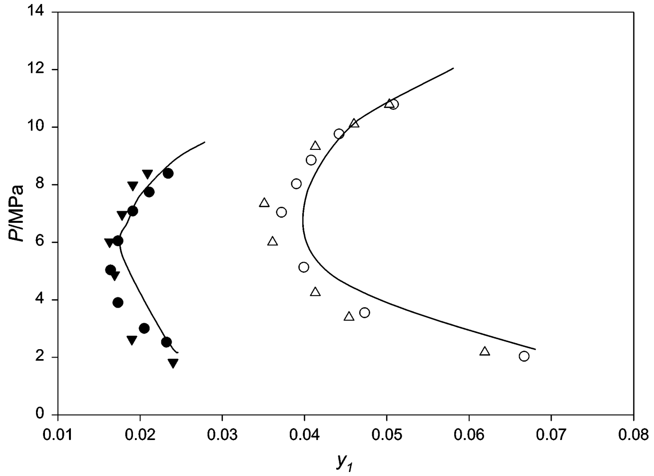

Figure 5. Mole fraction solubility of thiophene (1) in CO_2 (2) + ethanol (3) with $w_3 = 0.0245$ at ●, 333.90 K; and O, 363.29 K. Mole fraction solubility of thiophene (1) in CO_2 (2) + 1-propanol (3) from Elizalde-Solis et al.[6] with $w_3 = 0.0231$ at ▼, 333.89 K; △, 363.35 K; and —, P−R EoS.

Table 4. Properties of Pure Compounds[14,15]

component	MW	T_c/K	P_c/MPa	ω
CO_2	44.010	304.12	7.374	0.225
ethanol	46.069	513.92	6.148	0.649
thiophene	84.142	580.00	5.660	0.193

Modeling. The Peng−Robinson equation of state (P−R EoS)[13] with classical mixing rules was used to predict ternary systems. The explicit form of this EoS can be written as follows:

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

where P and T are the pressure and temperature, respectively; R is the gas constant; and v is the molar volume. The energy (a) and co-volume (b) parameters are related to

$$a(T) = 0.45724\frac{R^2 T_c^{\,2}}{P_c}\alpha(T_r) \tag{2}$$

and

$$b = 0.07780\frac{RT_c}{P_c} \tag{3}$$

The subscritpt "c" denotes the critical property for the constituent, and α is the temperature-dependent factor. The properties of pure compounds were taken from literature data[14,15] and are presented in Table 4. The a and b parameters for mixtures are defined by

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{4}$$

$$b_m = \sum_i x_i b_i \tag{5}$$

where a_{ij} is defined by

$$a_{ij} = (1 - k_{ij})\sqrt{a_{ii} a_{jj}} (i \neq j) \tag{6}$$

k_{ij} is the binary interaction parameter that is related to molecular interactions between each pair of components i

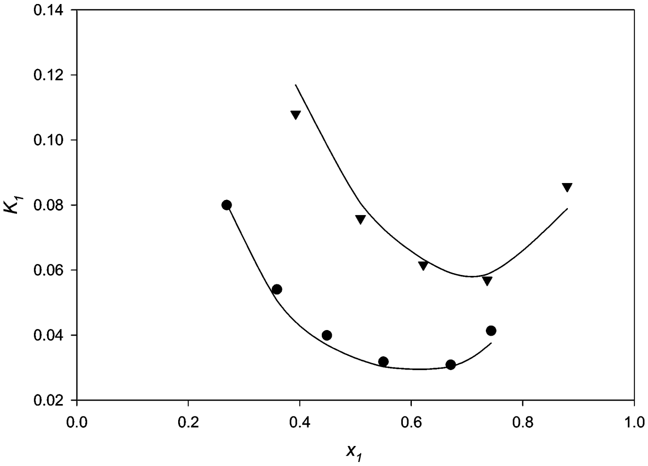

Figure 6. Distribution coefficients for the system thiophene (1) in CO_2 (2) + ethanol (3) at different loadings of the cosolvent: ●, $w_3 = 0.0580$ at 333.84 K; ▼, $w_3 = 0.0820$ at 363.64 K; and —, P−R EoS.

Table 5. k_{ij} Calculated from Binary Mixtures

mixtures	k_{ij}
thiophene (1) + CO_2 (2)	0.07508
CO_2 (2) + ethanol (3)	0.09589
thiophene (1) + ethanol (3)	0.08660

and j involved in the mixture. The k_{ij} values listed in Table 5 were obtained by correlating VLE data from binary mixtures reported in the literature.[6,9,12] Afterward, the k_{ij} parameters were used with the same model to predict experimental solubility of thiophene (1) in CO_2 (2) and in CO_2 (2) + ethanol (3) mixtures.

The absolute average deviation (AAD %) for y_1 and P were within 4 % for $w_3 = 0.0580$. For the case of $w_3 = 0.0820$, the AAD % was 6.5 % for y_1 and 12.3 % for P. These deviations were calculated as follows:

$$\text{AAD}\ \% = \frac{\sum_{i=1}^{N_\text{d}} |(y_\text{i}^\text{exptl} - y_\text{i}^\text{calcd})/y_\text{i}^\text{exptl}|}{N_\text{d}} \times 100 \qquad (7)$$

where N_d is the number of data points. The calculated equilibrium ratios (K_1) for thiophene had similar trends as compared with the experimental sets of data. This comparison is shown in Figure 6. It can be seen that the presence of thiophene in the vapor phase was higher when the mass fraction of ethanol was increased and with increasing temperature.

Conclusions

Experimental solubility data of thiophene in CO_2 measured in this work were compared with those values reported in the literature.[6] Deviations were found to be within the experimental uncertainty. An enhancement on the solubility values was not obtained when ethanol was added as cosolvent. Moreover, the solubility of thiophene had about the same values for the different loadings of CO_2 + ethanol mixtures. The solubility of thiophene in CO_2 + ethanol mixtures was compared with the only reported results for the solubility of thiophene in CO_2 + 1-propanol mixtures.[6] The small increase on the solubility of thiophene (1) in CO_2 (2) + ethanol (3) at $w_3 = 0.0245$ against 1-propanol (3) at $w_3 = 0.0231$ on a solute-free basis was caused due to the higher concentration of ethanol. However the solubility of thiophene in the supercritical solvent was not greatly increased with the addition of any of these two cosolvents. It means that they did not enhance substantially the solubility of thiophene in comparison with those obtained in pure CO_2.

Solubility data were calculated with the P−R EoS for the solvent mixtures at $w_3 = 0.0580$ and 0.0820. Although the deviations between calculated and experimental solubilities had higher AAD % values of about 4 % and 6 %, this simple model predicts with reasonable consistency the isothermal solubilities.

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