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Solubilities of Carbon Dioxide in Naphthalene, Phenanthrene, and Pyrene at Pressures to 10.6 MPa and Temperatures from 373 to 433 K

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Solubilities have been measured for carbon dioxide in the aromatic solvents naphthalene, phenanthrene, and pyrene. Measurements cover the temperature range from 373 to 433 K (212–320 °F) at pressures up to 10.6 MPa (1540 psia). The data can be described with average deviations of less than 0.003 mole fraction by the Soave–Redlich–Kwong or Peng–Robinson equation when two interaction parameters are used in the equation.

Introduction

This work is a continuation of our studies on the phase behavior of CO_2 with hydrocarbon solvents that are of interest in the processing of petroleum products, production of coal liquids, and enhanced oil recovery operations. Previously reported data include the solubility of CO_2 in n-paraffins from n-C_{20} through n-C_{44} (*1*) and in the cycloparaffins cyclohexane and *trans*-Decalin (*2*). Correlations for describing the behavior of the CO_2 + n-paraffins have also been presented (*3*). In the present study, solubilities were measured for CO_2 in two-ring through four-ring aromatic solvents. These combined studies should provide a valuable data base for testing/developing correlations to describe the behavior of CO_2 in multicomponent mixtures containing various hydrocarbon molecular types. Work is currently in progress on the measurement of the solubilities of ethane in these same solvents.

Experimental Method

The experimental apparatus and procedures used in this work are identical with those described previously (*2*). Testing of the apparatus to demonstrate its applicability to the systems of interest is described in that work, and a detailed analysis of experimental errors is given elsewhere (*4*, *5*). Results indicate expected uncertainties of 0.1 °F in temperature and less than 0.001 in mole fraction. The uncertainty in the bubble point pressure depends on the steepness of the p–x relation and leads to maximum expected errors of 1 psi for CO_2 + benzene (data reported in ref *2*), 6 psi for naphthalene, 8 psi for phenanthrene, and 10 psi for pyrene. The amounts of materials in the equilibrium cell were determined from volumetric injections; densities of the substances were taken from the literature for CO_2 (*6*), benzene (*7*), naphthalene (*8*), phenanthrene (*8*), and pyrene (*9*).

Materials

The carbon dioxide had a stated purity of 99.99 mol % and was supplied by Linde Specialty Gases. The other chemicals were from Aldrich Chemical Co. with reported purities of 99+ mol %. No further purification of the chemicals was attempted.

Table I. Solubility Data for CO_2

CO_2 mole fraction	pressure		CO_2 mole fraction	pressure	
	MPa	psia		MPa	psia
CO_2 + Naphthalene at 373.2 K (100 °C, 212 °F)					
0.047	1.385	200.9	0.202	6.091	883.4
0.107	3.196	463.5	0.248	7.586	1100.2
0.133	3.978	577.0	0.336	10.451	1515.8
0.162	4.852	703.7			
CO_2 + Naphthalene at 423.2 K (150 °C, 302 °F)					
0.051	1.925	279.2	0.201	7.879	1142.8
0.107	4.129	598.9	0.224	8.845	1282.9
0.110	4.229	613.4	0.252	9.965	1445.2
0.515	5.873	851.8			
CO_2 + Phenanthrene at 383.2 K (110 °C, 230 °F)					
0.047	1.877	272.3	0.127	5.414	785.3
0.069	2.810	407.5	0.164	7.197	1043.8
0.086	3.606	523.0	0.229	10.615	1539.6
0.108	4.575	663.5			
CO_2 + Phenanthrene at 423.2 K (150 °C, 302 °F)					
0.058	2.761	400.5	0.149	7.526	1091.5
0.087	4.182	606.6	0.178	9.151	1327.3
0.102	4.957	719.0	0.195	10.208	1480.5
0.140	6.991	1014.0			
CO_2 + Pyrene at 433.2 K (160 °C, 320 °F)					
0.014	0.734	106.4	0.159	9.662	1401.4
0.058	3.135	454.7	0.163	9.843	1427.6
0.071	3.898	565.4	0.172	10.572	1533.4
0.101	5.817	843.7			

Results

The complete experimental results appear in Table I. Differences in the temperatures at which the three systems were studied were necessitated by the melting points of phenanthrene (ca. 373 K) and pyrene (ca. 433 K). For CO_2 + pyrene, no previous data exist; for CO_2 + naphthalene, Orlov et al. (*10*) have reported measurements, but we have yet to obtain these data.

Measurements for CO_2 + phenanthrene were conducted at 383.2 and 423.2 K. DeVaney et al. (*11*) have previously studied this system at temperatures from 378 to 700 K at pressures to 11.0 MPa. Their data were not taken at temperatures identical with those of the present work. However, comparisons made by interpolation (using a suitable equation of state) reveal that their data yield CO_2 mole fractions which are systematically lower than those of the present work. Differences range from 0.002 at the lowest pressures to 0.007 at 1500 psia.

Correlation

As was the case for our previously measured solubilities of CO_2 in paraffinic (1) and naphthenic (2) solvents, the present data may be represented adequately by the Soave (*12*) or Peng–Robinson (*13*) equations if two interaction parameters (C_{12}, D_{12}) are used for each binary system. For the Soave

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equation, the specific relations used are

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b)}$$

where

$$a = \sum_i \sum_j z_i z_j a_{ij}$$

$$b = \sum_i \sum_j z_i z_j b_{ij}$$

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - C_{ij})$$

$$b_{ij} = \tfrac{1}{2}(b_{ii} + b_{jj})(1 + D_{ij})$$

$$a_{ii} = 0.42747 \alpha_i R^2 T_{ci}^{\,2} / p_{ci}$$

$$b_{ii} = 0.08664 R T_{ci} / p_{ci}$$

$$\alpha_i = 1 + m_i (1 - T_{r_i}^{\,0.5})^2$$

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^{\,2}$$

The optimum values of C_{12}, D_{12} were determined by minimizing the sum of squares of differences between the calculated and experimental bubble point pressures.

Results are shown for the Soave equation in Table II. Representations using one (C_{12}) and two (C_{12}, D_{12}) interaction parameters are shown for cases where (a) the parameters were optimized for each isotherm separately, and (b) multiple isotherms were treated simultaneously. The Peng–Robinson equation yields equivalent errors with essentially identical interaction parameters. When parameters were determined for each isotherm, the quality of fit to the data (rms errors < 0.001) illustrates both (a) the ability of the equations and (b) the correctness of our assessment regarding the precision of the solubility data.

In fitting equations of state to experimental data, the values for the optimized interaction parameters are dependent on the properties (T_{ci}, p_{ci}, ω_i) used in the evaluation of the pure-component parameters (a, b) in the equations. Table III presents the properties utilized in the present work. Figure 1 shows the dependence of the interaction parameters (from Table II) on the number of rings in the aromatic solvent for the case where two interaction parameters are employed. For CO_2 + benzene, the interaction parameters ($C_{12} = 0.066$, $D_{12} = 0.043$) are taken from our earlier work (*18*). As Table II shows, use of two interaction parameters improves the fit (relative to use of C_{12} only), but the improvement is not as dramatic as was the case of CO_2 in long-chain paraffin solvents (*3*).

Table II. Soave Correlation of Solubility Data

	optimum parameters		errors, mole fraction	
temp, K	C_{12}	D_{12}	rms	max
	CO_2 + Naphthalene			
373.2	0.079	0.027	<0.001	<0.001
	0.118		0.007	0.009
423.2	0.068	0.031	<0.001	<0.001
	0.119		0.004	0.005
373.2 and 423.2	0.082	0.024	0.002	0.004
	0.119		0.006	0.010
	CO_2 + Phenanthrene			
383.2	0.100	0.021	<0.001	<0.001
	0.153		0.004	0.005
423.2	0.103	0.016	<0.001	<0.001
	0.147		0.002	0.003
383.2 and 423.2	0.113	0.014	0.003	0.005
	0.150		0.004	0.006
	CO_2 + Pyrene			
433.2	0.234	0.014	<0.001	0.001
	0.281		0.002	0.003

Table III. Critical Properties Used in Equations of State

solvent	press., MPa	temp, K	acentric factor	ref
benzene	4.898	561.7	0.225	*14*
naphthalene	4.114	748.4	0.315	*15*
phenanthrene	3.30	873.2	0.540	*16*
pyrene	2.60	938.2	0.344	*17*

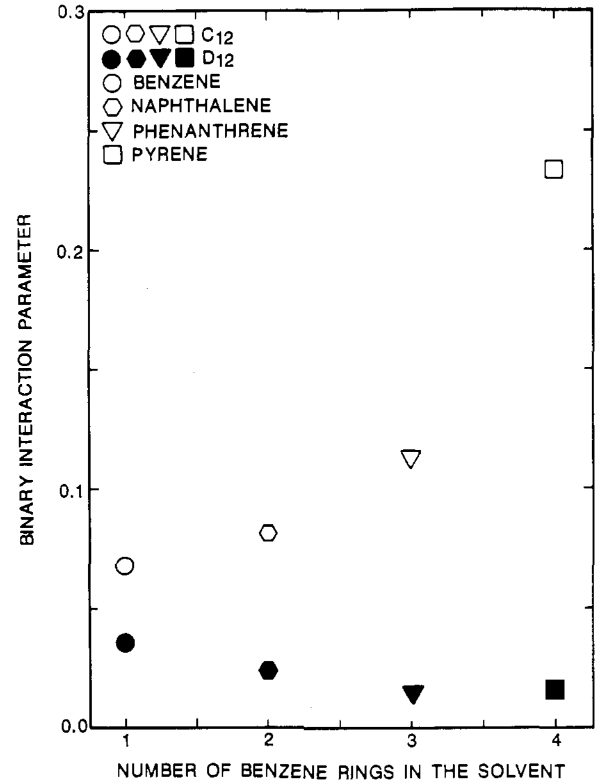

Figure 1. Soave interaction parameters for CO_2 + aromatic hydrocarbons.

Glossary

a, b	parameters in Soave equation of state
C_{ij}, D_{ij}	interaction parameters between components i and j in mixing rules for equation of state
p	pressure
p_c, T_c	critical pressure and temperature
R	universal gas constant
T	temperature
T_r	reduced temperature, T/T_c
v	specific volume
x	mole fraction in the liquid phase
z	mole fraction (liquid or vapor phase)
ω	acentric factor

Registry No. CO_2, 124-38-9; naphthalene, 91-20-3; phenanthrene, 85-01-8; pyrene, 129-00-0.

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Vapor–Liquid Equilibria of the System Ethane + 2-Aminopropane

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Bubble and dew point pressures have been measured as a function of temperature for 19 mixtures of the binary system ethane + 2-aminopropane in the temperature range 278.15–368.15 K. It is shown that the data can be represented by using the Peng–Robinson equation of state.

Introduction

One of the main disadvantages of the production of sodium chloride by solution mining is the rather high energy demand per ton of salt produced as a result of the evaporization of water from the brine in multiple effect crystallizing evaporators.

Alternatively sodium chloride can be produced from brine by solventing out through the addition of a miscible organic solvent to the brine. The organic solvent should then be removed from the mother liquor by supercritical extraction with, for instance, ethane. One of the promising aspects of this route is the prospect of reduced energy consumption. 2-Aminopropane appears to be a very good solventing-out chemical.

In this context knowledge of vapor–liquid equilibria of the ternary system ethane + water + 2-aminopropane and its binary subsystems is required. Here we present experimentally determined vapor–liquid equilibrium data on the binary subsystem ethane + 2-aminopropane in the temperature range of interest. The Peng–Robinson equation of state (*1*) is used to describe the data.

Experimental Section

The measurements were carried out in a glass tube apparatus for use with pressures up to 20 MPa and temperatures up to 473 K described earlier by de Loos et al. (*2*). With this so-called Cailletet apparatus dew points and bubble points of mixtures of known composition can be determined visually. A sample of the binary mixture with known composition is present in a narrow glass tube, surrounded by a thermostat with circulating water, guaranteeing a constant temperature within 0.02 K. The temperature is measured with a Pt-100 resistance thermometer, calibrated against a standard thermometer. The uncertainty in the measured temperature is approximately 0.02 K. Mercury is used as a pressure intermediate between the sample and the oil in the pressure generating system. The pressure is measured with a dead-weight pressure gauge (Büdenberg) with an accuracy within 1 kPa.

Variation of the pressure at constant temperature, for a mixture with known composition in the apparatus, allows determination of the pressure where a gas bubble is about to (dis)appear, the so-called bubble point, and the pressure at which a liquid droplet is about to (dis)appear, the so-called dew point. The reproducibility of measured bubble and dew point pressures proved to be 10 kPa. The preparation of the mixtures is described elsewhere (*3*).

The mole fraction purity of the ethane used was greater than 0.9999 and that of the 2-aminopropane greater than 0.998. The ethane was a research grade gas supplied by Matheson Gas Products; 2-aminopropane was supplied by Merck.

Results

The p,T behavior of the 19 binary ethane + 2-aminopropane mixtures investigated is given in Table I. From plots of these p,T isopleths isothermal p,x sections can be obtained by interpolation. When at lower temperatures no dew point pressures can be measured because the volume of the gas phase is too large, approximate dew point pressures can be obtained by means of linear extrapolation of $\ln p$ against $1/T$. Although this procedure is only sound thermodynamically for pure substances at low reduced temperature, we found that in many cases it can be applied to binary mixtures too. The p,x sections at 298.15, 328.15, and 358.15 K are given in Figures 1–3. The vapor pressure of pure 2-aminopropane is taken from Boublik et al. (*4*) and the vapor pressure of pure ethane from Douslin and Harrison (*5*). The purity of the ethane used was

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