J. Chem. Eng. Data **1993**, *38*, 257-259

Effect of Pressure on Solid–Liquid Equilibrium for Decane + Octacosane, Decane + *p*-Xylene + Octacosane, and Decane + *p*-Xylene + Phenanthrene Mixtures

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Saturation conditions were measured for decane + octacosane, decane + *p*-xylene + octacosane, and decane + *p*-xylene + phenanthrene mixtures for approximately 10 mol % solid content and pressures up to 20 MPa. The solubility of octacosane in decane decreased by 43% at 312.4 K as the pressure increased from atmospheric to 20 MPa. The effect of pressure on phenanthrene solubility was much less.

Introduction

The solubility of heavy hydrocarbon solids in lighter hydrocarbon liquids has been studied extensively, but mostly for aromatics and their derivatives. In oil production, the solubilities of alkanes as well as other materials such as aromatics and naphthenes are important. The literature relating solubility for solid alkanes is very limited (*1–7*). The studies deal with solubility mostly at atmospheric pressure. In the production of crude oil, the pressure is generally elevated and precipitation of solids can be a troublesome problem. In this research, the effect of pressure on the solubility of hydrocarbon solids in hydrocarbon liquids was examined experimentally. For this purpose, the nC_{10} + nC_{28} binary paraffin mixture and nC_{10} + xylene + nC_{28} and nC_{10} + xylene + phenanthrene ternary mixtures were selected. In the ternary systems, the ratio of nC_{10} to xylene was fixed at 2.0, corresponding to the average ratio of paraffins to aromatics in residual oils.

Experimental Section

The experimental apparatus consisted of a Ruska pressure–volume–temperature (PVT) cell, two Ruska pumps, and reservoirs. A schematic diagram of this equipment is shown in Figure 1. The Ruska PVT setup housed two viewable 191 cm^3 equilibrium cells in a temperature-controlled air bath. The cells were manifolded with two Ruska pumps, and the cells and the pumps were manifolded with reservoirs. A temperature controller (Omega) for the air bath, a multipoint temperature indicator (Omega), and temperature elements (platinum RTD) were installed on the PVT cell, and pressure gauges (Heise Bourdon gauge) were installed on the pumps. A cathetometer was available for phase volume measurement. The maximum working pressure of the PVT cell was 27.6 MPa.

Mercury was used to pressurize the sample mixtures. The PVT cell in its housing could be turned upside down and could be rocked in a horizontal position for better mixing of the samples. The mercury in the cell also enhanced mixing during rocking of the cell. The presence of the solid could be observed visually through the sight glass of the cell and window of the housing or by the telescope installed with the cathetometer.

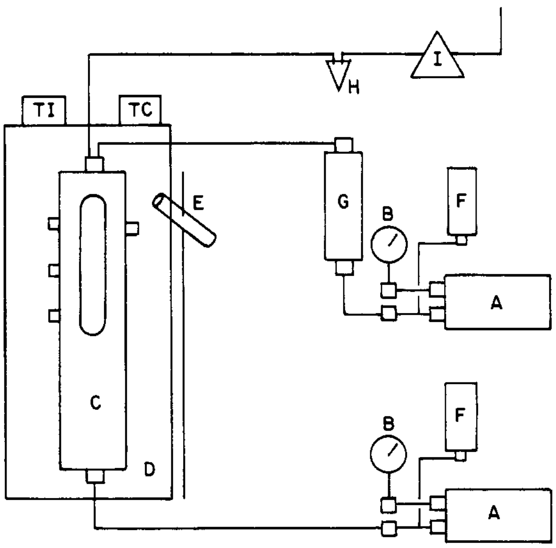

Figure 1. Pressure–volume–temperature (PVT) cell.

Table I. Saturation Conditions for the (1 − *x*) Decane + *x* Octacosane System

x = 0.060 13		*x* = 0.081 98		*x* = 0.1074	
T/K	*P*/MPa	*T*/K	*P*/MPa	*T*/K	*P*/MPa
307.2	0.1	310.0[a]	0.1	312.5	0.2
308.0	4.5	310.3	1.8	312.7	1.1
308.9	7.7	311.0	4.6	313.5	4.5
309.7	11.0	312.2	9.7	314.4	8.9
310.4	14.3	313.4	15.5	315.3	12.6
311.6	18.9	314.4	19.5	316.3	16.9
312.5	22.4	314.7	21.2	317.4	21.6

[a] Extrapolated value.

The materials used in this experiment were nC_{10}, decane, Aldrich, 99+%; nC_{28}, octacosane, Aldrich, 99+%; *p*-xylene, Aldrich, 99+%; and phenanthrene, Aldrich, 99+% (purified by the method described in ref 8). Known masses of liquid solvent and solid solute were put into the cell directly through a plug hole. Air inside the cell was removed by pumping mercury into the cell. The temperature was increased slowly until all the solid dissolved. When all the solid had dissolved, the temperature was allowed to stabilize. At this stabilized temperature, the pressure was increased slowly until the solid began to precipitate. When some solid had precipitated, the pressure was decreased little by little, rocking the cell for more than 5 min between pressure changes and observing if all the solid had dissolved. When all the solid had dissolved,

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0021-9568/93/1738-0257$04.00/0

Table II. Saturation Conditions for the Decane (1) + *p*-Xylene (2) + Phenanthrene (3) System with x_1/x_2 = 2.0

x_3 = 0.1484		x_3 = 0.098 03	
T/K	*P*/MPa	*T*/K	*P*/MPa
316.2	0.2	310.5	0.1
316.4	4.4	311.0	2.3
316.9	6.9	311.6	4.5
317.4	11.5	312.3	8.3
318.0	16.0	313.3	12.6
318.6	20.8	314.6	19.4
		315.3	21.8

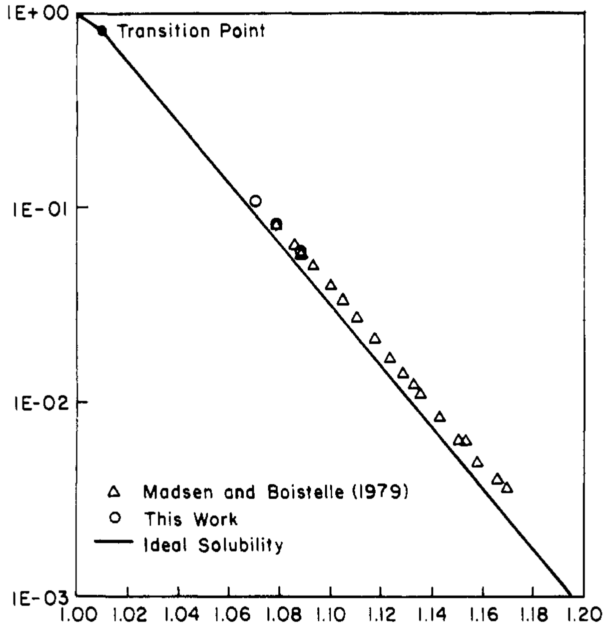

Figure 2. Solubility, *x*, of octacosane in decane.

the pressure was read as the saturation pressure. This procedure was repeated, changing the temperature, for the pressure range of atmospheric to above 20 MPa. The reproducibility of the temperature measurement by the Omega indicator and RTD was ±0.1 K, and the accuracy including the possible systematic errors is expected to be better than 0.2 K. Pressure could be read within 0.03 MPa by the Bourdon gage. The reproducibility of the pressure measurement was ±0.3 MPa. The maximum error in pressure was estimated to be 0.7 MPa. The mass of the sample was read within 0.01 g, and the maximum error in composition was estimated to be less than 1.0%.

Results

Experimental results are shown in Tables I and II. The low-pressure results for the nC_{10} + nC_{28} mixture are compared with literature values (*5*) in Figure 2. Agreement is good, and the solubility is higher than the ideal solubility. The pressure effect on the solubility of nC_{28} in nC_{10} can be seen clearly in Figure 3. For example, at 312.4 K, the solubility of nC_{28} in nC_{10} decreases about 43%, as the pressure increases from atmospheric to about 20 MPa. The slope of the saturation lines reflects the pressure effect on the solubility. The pressure effect in the nC_{10} + xylene + nC_{28} system is a little less, but almost the same as for the nC_{10} + nC_{28} system, and that in the nC_{10} + xylene + phenanthrene system is much less.

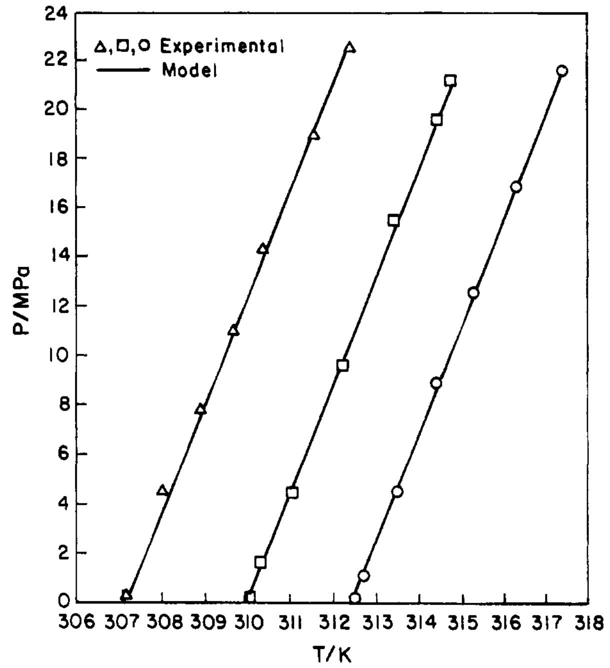

Figure 3. Saturation conditions in the *x* octacosane + (1 − *x*) decane system: △, *x* = 0.060 13; □, *x* = 0.081 98; ○, *x* = 0.1074.

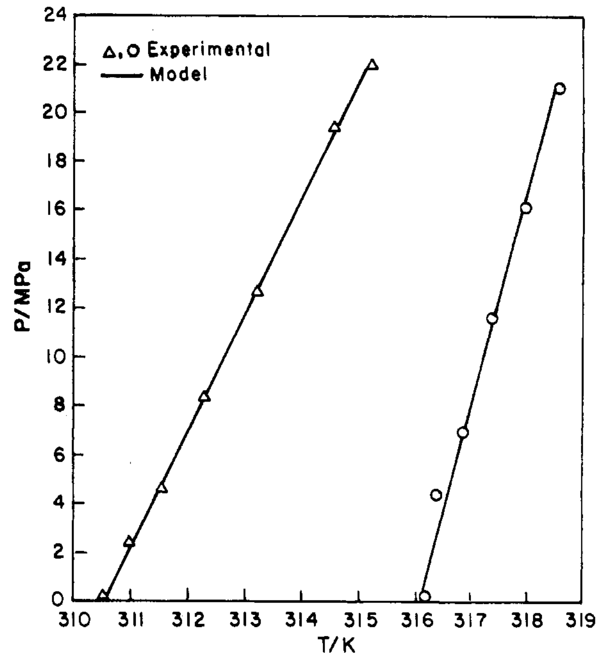

Figure 4. Saturation conditions in △, decane (1) + *p*-xylene (2) + octacosane (3) (x_1/x_2 = 2.0, x_3 = 0.098); and □, decane (1) + *p*-xylene (2) + phenanthrene (3) (x_1/x_2 = 2.0, x_3 = 0.1468).

Correlation

The solubility of the solid in the liquid was calculated using the ideal solubility and activity coefficient:

$$x_2 = x_{2,\mathrm{ideal}}/\gamma_2 \qquad (1)$$

An equation for the ideal solubility at low pressure was available from the literature (*9*). Neglecting the heat capacity terms, and adding terms for the heat of transition in the solid phase and the terms for the Poynting pressure corrections of both the solid and subcooled liquid, the ideal solubility

Table III. Constants of the Model Equations 3 and 4 and Deviations in Solubility

mixture	a_0	a_1	A	AAD[a]/%
nC_{10} + nC_{28}	−21.302	24.827	−11.531	0.7
nC_{10} + xylene + nC_{28}	1.8920		−8.5842	0.6
nC_{10} + xylene + phenanthrene	20.778		−5.0224	0.2

[a] Average absolute deviation: |correlation − experiment/experiment| × 100.

Table IV. Pure Component Properties Used in the Calculations

Molar Volume (cm^3/mol) and Temperature (K)

nC_{10}	$V^{L\,a} = 149.52 + 0.11803T + 0.8270E{-}04T^2 + 0.14445E{-}06T^3$
xylene	$V^{L\,b} = 0.1238T + 87.016$
nC_{28}	$V^{L\,c} = 0.42203T + 365.588$
	$V^{S\,d} = 0.11828T + 381.623$
phenanthrene	$V^{L\,e} = 0.09969T + 131.281$
	$V^{S\,f} = 151$

Phase Change

nC_{28}	$T_m{}^g$	334.35 K	$\Delta H_m{}^g$	64643 J/mol
	$T_t{}^g$	331.15 K	$\Delta H_t{}^g$	35438 J/mol
phenanthrene	$T_m{}^h$	372.80 K	$\Delta H_m{}^h$	16474 J/mol

[a] Modified using the density equation given in ref 10; valid at 0–50 °C. [b] Linear equation derived from 20 and 25 °C density data from ref 11. [c] Linear equation derived by regression of data from refs 12 and 13. [d] Estimated from the data of Templin (*13*). [e] Linear equation derived using data at 305 °C from ref 14 and 99.8 °C from ref 11. [f] Data from ref 15. [g] Data from ref 16. [h] Data from ref 17.

equation became

$$\ln x_{2,\mathrm{ideal}} = -\frac{\Delta H_\mathrm{m}}{RT_\mathrm{m}}\left(\frac{T_\mathrm{m}}{T} - 1\right) - \int_{P_2{}^\mathrm{S}}^{P} \frac{\Delta V_2}{RT}\,\mathrm{d}P \qquad (2)$$

The Flory–Huggins plus regular solution equation, including a pressure correction term, was used for correlating the activity coefficient of the mixture of hydrocarbon liquid and solid:

$$\ln \gamma_2 = \ln \frac{\phi_2}{x_2} + 1 - \frac{\phi_2}{x_2} + \frac{V_2{}^\mathrm{L}}{RT} D_{12}\phi_1{}^2 + \frac{AP}{RT} \qquad (3)$$

D_{12} may be calculated from solubility parameters, but for accurate correlations, it was calculated as a temperature-dependent parameter as follows:

$$D_{12} = a_0 + a_1 T/T_\mathrm{m} \qquad (4)$$

For the ternary systems, the solvent mixture nC_{10} + xylene was treated as one component using the average molar volume as follows:

$$V_1{}^\mathrm{L} = \sum_{\mathrm{solvent}} x_{\mathrm{s}i} V_i{}^\mathrm{L} \qquad (5)$$

Excellent agreement was obtained with this correlation, and the results are shown in Figures 3 and 4. The parameter values and the average deviation in the solubility are given in Table III. The thermodynamic properties used in the calculation are tabulated in Table IV.

Glossary

A	parameter for pressure correction of activity coefficient
D_{ij}	parameter for Flory–Huggins plus regular solution equation
H	enthalpy
ΔH_m	heat of melting of the solid
ΔH_t	heat of transition at the solid phase
P	pressure
R	gas constant (8.314 41 J/(mol·K))
T	temperature
V	molar volume
$\bar{V}$	partial molar volume
ΔV	volume change of the solute during the course of the phase change
x	mole fraction in the liquid mixture

Greek Letters

ϕ	volume fraction in a liquid mixture
γ	activity coefficient in system temperature and pressure

Subscripts

1	solvent component or solvent mixture
2	solute
m	melting
o	reference for Taylor series expansion
s	mixed solvent
t	transition

Superscripts

E	excess
L	liquid
S	solid

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Received for review June 19, 1992. Revised October 30, 1992. Accepted November 8, 1992. This work was supported by member companies of the Louisiana State University CO_2 Flooding Consortium including ARCO Oil and Gas, Chevron Oilfield Research, Greenhill Petroleum, and Texaco.