Equations 5 and 6 were used to calculate the solubilities of 1-octadecanol and stearic acid in supercritical carbon dioxide. The values of β_{12}, together with the calculated fluid-phase compositions, are presented in Tables I and II. A comparison between these calculated compositions and the corresponding experimental measurements produced an overall average deviation of 24.0% (17 points) for 1-octadecanol and 5.14% (17 points) for stearic acid. These average deviations are comparable to those obtained from an earlier experimental study (*8*) for the 1-hexadecanol-carbon dioxide and palmitic acid-carbon dioxide systems in which the overall average deviations were 11.4% (18 points) and 20.2% (19 points), respectively.

It should be noted that the solutes investigated in the present study contain up to 5% impurities that may affect the measured solubilities in spite of the fact that the experimental procedure was designed to minimize these effects by discarding the initial samples of each experimental run. The fact that impurities exist makes the meltings point of the pure solutes uncertain, since their presence lowers these melting points and indirectly influences the proper value of the ratio, $f^\circ{}_2^{s}/f^\circ{}_2^{l}$, to be used with eq 2.

Conclusions. Solubility measurements for 1-octadecanol and stearic acid in supercritical carbon dioxide were made, and the results obtained have been modeled by using two different approaches. One approach utilizes the involvement of only density and two adjustable parameters while the other employs three-dimensional solubility parameters and a single adjustable interaction parameter. Both models predict the composition of the solute present in the supercritical fluid phase. Both systems exhibited an interesting experimental behavior for the 45 °C isotherm for which a maximum solubility is encountered at pressures around 280-300 bar.

Glossary

A, B	parameters, eq 1
f	fugacity, bar
ΔH	molar heat, kcal/mol
P	pressure, bar
R	gas constant, 1.9872 cal/(mol·K)
T	temperature, K
v	molar volume, cm^3/mol
y	mole fraction of solute in vapor phase

Greek Letters

β	interaction parameter
γ	activity coefficient
δ	solubility parameter, $(cal/cm^3)^{1/2}$
ρ	density, g/cm^3
τ	$(\delta_p{}^2 + \delta_h{}^2)^{1/2}$

Subscripts

1	solvent
2	solute
c	critical
d	dispersion
h	hydrogen bonding
l	liquid phase
m	melting point
P	polar
R	reduced
t	total

Superscripts

fus	fusion
l	liquid
o	pure component
s	solid
vap	vaporization
∞	infinite

Registry No. $CH_3(CH_2)_{16}CH_2OH$, 112-92-5; $CH_3(CH_2)_{16}COOH$, 57-11-4; CO_2, 124-38-9.

Literature Cited

(1) Peters, S.; et al. *Chem. Eng. Technol.* **1987**, *10*, 37.
(2) Coenen, H.; Hartwig, J.; Kriegel, E. Report presented at the 2nd World Congress on Chemical Engineering, Montreal, Canada, Oct 4-9, 1981.
(3) Kramer, A.; Thodos, G. *J. Chem. Eng. Data* **1988**, *33*, 230.
(4) Kennedy, Jr., J. T.; Thodos, G. *J. Chem. Eng. Data* **1960**, *5*, 293.
(5) Hansen, C. M. Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient Importance in Surface Coating Formulation. Doctoral Dissertation, Danish Technical Press: Copenhagen, 1967.
(6) Kramer, A.; Thodos, G. *Ind. Eng. Chem. Res.* **1988**, *27*, 1506.
(7) Giddings, J. C.; Myers, J. C.; McLaren, L.; Keller, R. A. *Science* **1968**, *162*, 67.
(8) Kramer, A. Dissertation, Northwestern University, Evanston, IL, 1988.
(9) Koenhen, D. M.; Smolders, C. A. *J. Appl. Polym. Sci.* **1975**, *19*, 1163.
(10) Smith, B. D. *Thermodynamic Data for Pure Compounds*; Physical Science Data 25; Elsevier: New York, 1986.
(11) Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1984.
(12) Mosselman, C.; Mourik, J.; Dekker, H. *J. Chem. Thermodyn.* **1974**, *6*, 477.
(13) Shaake, R. C. F.; van Mittenburg, J. C.; de Kruif, C. G. *J. Chem. Thermodyn.* **1982**, *14*, 771.

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Solubilities of Ethane in Heavy Normal Paraffins at Pressures to 7.8 MPa and Temperatures from 348 to 423 K

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Solubility data have been obtained for ethane in the heavy normal paraffin solvents *n*-eicosane, *n*-octacosane, *n*-hexatriacontane, and *n*-tetratetracontane. Measurements were made over the temperature range from 348 to 423 K (167-302 °F) at pressures up to 7.8 MPa (1127 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 per isotherm are used in the equation.

Introduction

This work is a continuation of our studies of binary vapor-liquid phase behavior for selected solute gases (e.g. CO_2, ethane) in a series of heavy hydrocarbon solvents of interest in the processing of petroleum products, production of coal liquids, and enhanced oil recovery operations. Previously, we have reported data on the solubility of CO_2 in a number of paraffinic (*1*), naphthenic (*2*), and aromatic (*3*, *4*) solvents. Correlations describing the behavior of the CO_2 + *n*-paraffin systems have also been presented (*5*).

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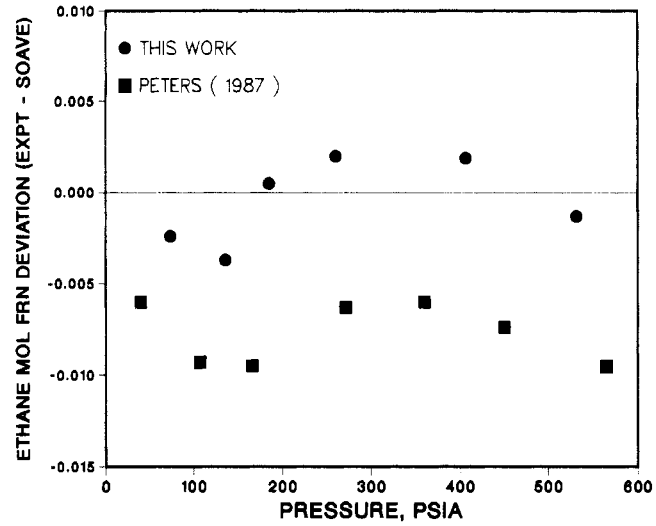

Figure 1. Comparison of ethane solubilities in n-eicosane at 323.2 K.

In the present study, solubilities were measured for ethane in the following members of the normal paraffin homologous series: n-eicosane (n-C$_{20}$), n-octacosane (n-C$_{28}$), n-hexatriacontane (n-C$_{36}$), and n-tetratetracontane (n-C$_{44}$). These data should provide a valuable complement to our previously reported solubility data for ethane in n-decane (*6*) and to the available literature data for ethane in lighter paraffins. The combined studies should facilitate the development and testing of correlations to describe the phase behavior of multicomponent systems involving ethane.

Experimental Method

The experimental apparatus and procedures used in this work were 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 (*7–9*). Results indicate expected uncertainties of 0.1 °C in temperature and less than 0.002 in mole fraction. The uncertainty in the bubble-point pressure depends on the steepness of the p–x relation and leads to average expected error of 6 psi for the systems reported here. The amounts of materials in the equilibrium cell were determined from volumetric injections; densities of the substances were taken from the literature for ethane (*10*) and the n-paraffins (*11*).

Materials

The ethane had a stated purity of 99.9+ mol % and was supplied by Matheson. The n-paraffins were from Alfa Products with reported purities of 99 mol %. No further purification of the chemicals was attempted.

Results

The complete experimental results appear in Table I. Differences in the lowest temperatures at which the systems were studied were dictated by the melting points of the n-paraffins, which are solids at room temperature. Comparisons of our measurements with those reported by various investigators appear in Figures 1–4. The comparisons are shown in terms of deviations of the solubilities from values predicted using the Soave–Redlich–Kwong equation of state. Interaction parameters employed in the equation-of-state predictions were obtained by fitting our data for each isotherm in each system.

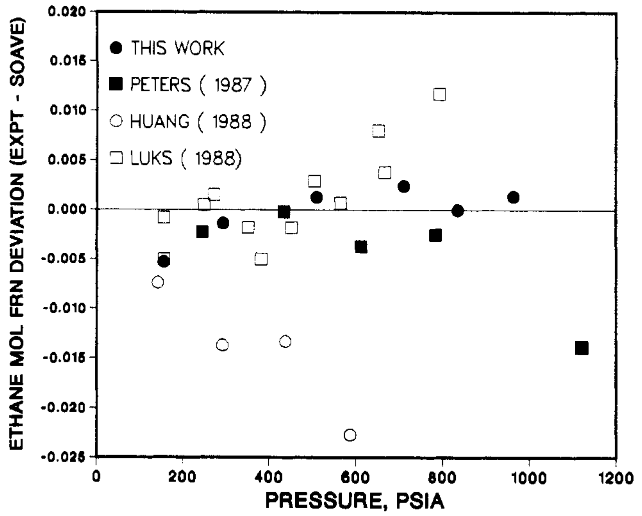

Figure 2. Comparison of ethane solubilities in n-eicosane at 373.2 K.

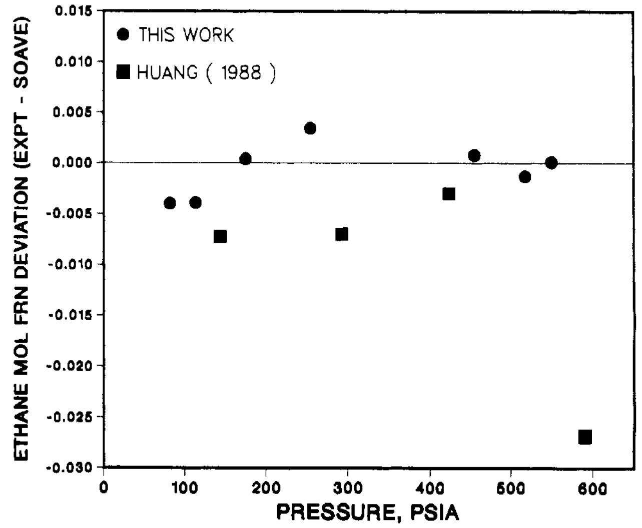

Figure 3. Comparison of ethane solubilities in n-octacosane at 373.2 K.

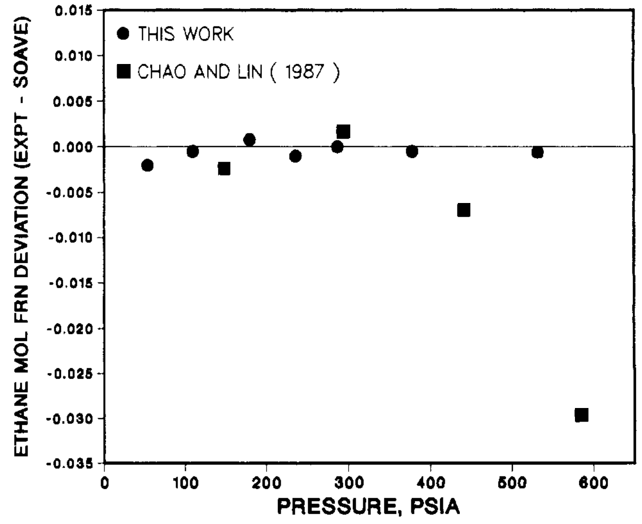

Figure 4. Comparison of ethane solubilities in n-hexatriacontane at 373.2 K.

Figures 1 and 2 show significant disagreement among the various investigators for the n-C$_{20}$ data at 50 and 100 °C. At 50 °C, Figure 1 indicates a systematic difference (0.005–0.008 in mole fraction) between our data and those reported by Peters

Table I. Solubility Data for Ethane in Heavy *n*-Paraffins

	pressure			pressure	
mole fraction of ethane	MPa	psia	mole fraction of ethane	MPa	psia
Ethane + *n*-Eicosane at 323.2 K (50 °C, 122 °F)					
0.149	0.505	73.2	0.411	1.793	260.1
0.249	0.938	136.1	0.553	2.801	406.3
0.320	1.274	184.8	0.649	3.666	531.7
Ethane + *n*-Eicosane at 373.2 K (100 °C, 212 °F)					
0.175	1.073	155.7	0.551	4.886	708.8
0.298	2.021	293.2	0.604	5.754	834.6
0.445	3.504	508.3	0.653	6.644	963.8
Ethane + *n*-Eicosane at 423.2 K (150 °C, 302 °F)					
0.118	0.931	135.1	0.466	5.298	768.5
0.257	2.338	339.1	0.525	6.411	930.0
0.324	3.138	455.2	0.582	7.687	1115.1
0.400	4.218	611.8			
Ethane + *n*-Octacosane at 348.2 K (75 °C, 167 °F)					
0.149	0.589	85.5	0.373	1.852	268.7
0.207	0.883	128.1	0.413	2.170	314.8
0.256	1.112	161.3	0.434	2.318	336.3
0.299	1.381	200.3	0.503	2.917	423.1
0.350	1.740	252.4	0.520	3.113	451.5
Ethane + *n*-Octacosane at 373.2 K (100 °C, 212 °F)					
0.111	0.563	81.6	0.450	3.134	454.6
0.150	0.784	113.7	0.487	3.561	516.5
0.221	1.204	174.7	0.508	3.788	549.5
0.300	1.755	254.5			
Ethane + *n*-Octacosane at 423.2 K (150 °C, 302 °F)					
0.102	0.691	100.3	0.366	3.215	466.4
0.179	1.293	187.6	0.451	4.394	637.3
0.253	1.972	286.1	0.500	5.182	751.6
0.300	2.437	353.5			
Ethane + *n*-Hexatriacontane at 373.2 K (100 °C, 212 °F)					
0.087	0.368	53.4	0.354	1.978	286.9
0.166	0.752	109.1	0.427	2.605	377.8
0.251	1.238	179.5	0.531	3.671	532.5
0.307	1.627	236.0			
Ethane + *n*-Hexatriacontane at 423.2 K (150 °C, 302 °F)					
0.153	0.965	140.0	0.408	3.393	492.1
0.207	1.357	196.8	0.468	4.256	617.4
0.315	2.315	335.3	0.500	4.760	690.4
Ethane + *n*-Tetratetracontane at 373.2 K (100 °C, 212 °F)					
0.110	0.387	56.1	0.361	1.762	255.5
0.167	0.620	89.9	0.448	2.476	359.1
0.245	0.994	144.2	0.501	3.004	435.7
0.304	1.373	199.1	0.516	3.107	450.7
0.360	1.724	250.1			
Ethane + *n*-Tetratetracontane at 423.2 K (150 °C, 302 °F)					
0.099	0.527	76.5	0.303	1.937	281.0
0.122	0.656	95.1	0.340	2.266	328.6
0.209	1.234	179.0	0.409	2.981	432.3

(*12*). Similar differences occur at 150 °C. In contrast, excellent agreement at 100 °C is shown in Figure 2 between our data and Peters', while the data of Huang et al. (*13*) show serious disagreement (up to 0.025 in mole fraction at his highest pressures); these variations are well beyond the combined uncertainties of the data sets.

To resolve the discrepancies in the reported data for n-C_{20} at 100 °C, Professor Kramer D. Luks (*14*) performed measurements of the solubility of ethane in n-eicosane at 100 °C. The comparisons presented in Figure 2 show our data to be in good agreement with both Peters' and Luks' at pressures up to 700 psi. At the highest pressure measured by Luks (800 psia), his data indicate a higher solubility, which is in the opposite direction to Huang's data.

Inspection of Figures 3 and 4 reveals reasonable agreement between our data and that of Huang et al. (*15*) for n-C_{28} and of Lin and Chao (*16*) for n-C_{36} at 100 °C, with the exception of the highest pressure points, where significantly lower solubility is indicated by Huang's data. For n-C_{44}, no previous studies are available for comparison.

Correlation

As was the case for our previously measured solubilities of CO_2 in a variety of hydrocarbon solvents (*1–5*), the present data for ethane systems may be represented adequately by the Soave (*17*) or Peng–Robinson (*18*) equations if two interaction parameters (C_{12}, D_{12}) are used for each binary system. For the Soave equation, the specific relations used are

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

where

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

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

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

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

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

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

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

$$m_i = 0.480 + 1.57\omega_i - 0.176\omega_i^{\ 2}$$

The optimum values of C_{ij} and D_{ij} for each binary mixture were determined by minimizing the sum of squares of differences between the calculated and experimental bubble-point pressures. Results are shown in Table II. Representations using one (C_{ij}) and two (C_{ij}, D_{ij}) interaction parameters are shown for cases where (a) the parameters were optimized for each isotherm separately and (b) all isotherms for a given binary system were treated simultaneously. The Peng–Robinson equation yields errors essentially identical with those of the Soave equation, with slightly different interaction parameters. As documented in Table II, the equations are capable of describing the data with root-mean-square (rms) errors no greater than 0.007 mole fraction when two binary interaction parameters are used for each binary pair (over the complete temperature range). When two parameters are fitted to each isotherm, rms errors are within 0.003; this result illustrates both the ability of the equations of state and the correctness of our estimates of the precision of the reported data.

As shown previously by our studies involving CO_2/hydrocarbon systems (*1–5*) and as indicated by the results in Table II using a single parameter, C_{ij} (rms = 0.03), the use of two interaction parameters provides significant improvement in the predictive ability of the equation of state. Figure 5 shows the variation in the Soave interaction parameters with the solvent carbon number for the ethane systems, based on the present data and data reported previously (*6*). Variations in the value of C_{ij} (and D_{ij}) are observed as a function of carbon number. However, the quality of fit is not significantly affected when constant values of C_{ij} (0.02) and D_{ij} (−0.01) are used for all these *n*-paraffin systems.

In fitting equations of state to experimental data, the values for the optimized interaction parameters are dependent on the properties (T_{c_i}, p_{c_i}, ω_i) used to evaluate the pure-component parameters (a, b) in the equations. Table III presents the properties used in the present work, where for the lighter *n*-paraffins up to *n*-C_{12} values for T_c, p_c, and ω were obtained from the literature (*19*). For the heavier *n*-paraffins, estimates for such properties were calculated by use of the asymptotic behavior correlation (ABC) of Gasem and Robinson (*5*) as determined by Ross (*9*).

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
ω	acentric factor
x	mole fraction in the liquid phase

Table II. Soave and Peng–Robinson Equation-of-State Representations of Ethane Solubility Data

	Soave param (P–R param)		error in ethane mole fraction	
temp, K (°F)	C_{12}	D_{12}	rms	max
	Ethane + *n*-Eicosane			
323.2 (122)	0.028 (0.025)	−0.023 (−0.023)	0.002	0.004
	0.001 (−0.003)		0.025	0.051
373.2 (212)	0.030 (0.025)	−0.025 (−0.026)	0.003	0.005
	0.006 (0.001)		0.020	0.031
423.2 (302)	0.039 (0.032)	−0.033 (−0.034)	0.002	0.002
	−0.004 (−0.010)		0.017	0.023
323.2, 373.2 423.2	0.033 (0.028)	−0.028 (−0.029)	0.005	0.012
	0.001 (−0.004)		0.021	0.032
	Ethane + *n*-Octacosane			
348.2 (167)	0.030 (0.021)	−0.020 (−0.021)	0.003	0.004
	−0.019 (−0.028)		0.018	0.027
373.2 (212)	0.030 (0.019)	−0.019 (−0.020)	0.003	0.004
	−0.014 (−0.024)		0.016	0.023
423.2 (302)	0.042 (0.030)	−0.025 (−0.027)	0.001	0.003
	−0.020 (−0.032)		0.015	0.019
348.2, 373.2 423.2	0.034 (0.024)	−0.022 (−0.023)	0.004	0.008
	−0.018 (−0.028)		0.017	0.027
	Ethane + *n*-Hexatriacontane			
373.2 (212)	0.043 (0.027)	−0.019 (−0.020)	0.001	0.002
	−0.018 (−0.034)		0.019	0.025
423.2 (302)	0.082 (0.065)	−0.026 (−0.028)	0.003	0.005
	−0.001 (−0.018)		0.019	0.026
373.2, 423.2	0.062 (0.046)	−0.022 (−0.024)	0.005	0.011
	−0.008 (−0.025)		0.021	0.031
	Ethane + *n*-Tetratetracontane			
373.2 (212)	0.069 (0.048)	−0.023 (−0.025)	0.002	0.003
	−0.028 (−0.050)		0.026	0.039
423.2 (302)	0.059 (0.038)	−0.016 (−0.018)	0.002	0.002
	−0.030 (−0.053)		0.010	0.013
373.2, 423.2	0.052 (0.031)	−0.018 (−0.020)	0.007	0.013
	−0.028 (−0.051)		0.021	0.039

Table III. Pure Fluid Properties Used in Equations of State

component	T_c, K	p_c, MPa	ω	ref
C_2	305.3	4.871	0.1004	*19*
n-C_{10}	617.6	2.097	0.4885	*19*
n-C_{12}	658.3	1.806	0.5708	*19*
n-C_{20}	766.6	1.069	0.8791	*9*
n-C_{28}	827.4	0.661	1.1617	*9*
n-C_{36}	864.0	0.428	1.4228	*9*
n-C_{44}	886.6	0.290	1.6664	*9*

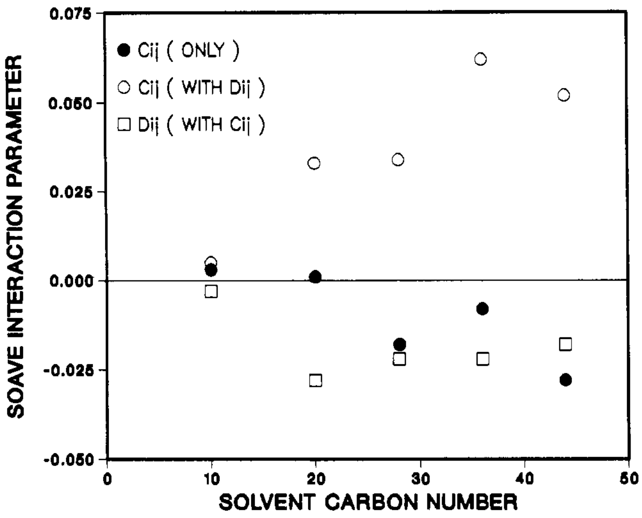

Figure 5. Soave interaction parameters, C_{ij} and D_{ij}, for ethane + heavy *n*-paraffins.

z mole fraction (liquid or vapor phase)

Registry No. n-C_{20}, 112-95-8; n-C_{28}, 630-02-4; n-C_{36}, 630-06-8; n-C_{44}, 7098-22-8; C_2H_6, 74-84-0.

Literature Cited

(1) Gasem, K. A. M.; Robinson, Jr., R. L. *J. Chem. Eng. Data* **1985**, *30*, 53-56.
(2) Anderson, J. M.; Barrick, M. W.; Robinson, Jr., R. L. *J. Chem. Eng. Data* **1986**, *31*, 172-175.
(3) Gupta, M. K.; Li, Y.-H.; Hulsey, B. J.; Robinson, Jr., R. L. *J. Chem. Eng. Data* **1982**, *27*, 55-57.
(4) Anderson, J. M.; Barrick, M. W.; Robinson, Jr., R. L. *J. Chem. Eng. Data* **1987**, *32*, 372-374.
(5) Gasem, K. A. M.; Robinson, Jr., R. L. Paper presented at the Spring National Meeting of the American Institute of Chemical Engineers, Houston, TX, March 24-28, 1985.
(6) Bufkin, B. A.; Robinson, Jr., R. L.; Estera, S. S.; Luks, K. D. *J. Chem. Eng. Data* **1986**, *31*, 421-423.
(7) Anderson, J. M. M.S. Thesis, Oklahoma State University, Stillwater, OK, May 1985.
(8) Barrick, M. W. M.S. Thesis, Oklahoma State University, Stillwater, OK, May 1985.
(9) Ross, C. H. M.S. Report, Oklahoma State University, Stillwater, OK, December 1987.
(10) Goodwin, R. D.; Roder, H. M.; Straty, G. C. *NBS Tech. Note* **1976**, *No. 684*.
(11) Doolittle, A. K.; Peterson, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2145.
(12) Peters, C. J.; Roo, J. L.; Lichtenthaler, R. N. *Fluid Phase Equilib.* **1987**, *34*, 287-308.
(13) Huang, S. H.; Lin, H. M.; Chao, K. C. *J. Chem. Eng. Data* **1986**, *33*, 145-147.
(14) Luks, K. Personal Communication, University of Tulsa, 1988.
(15) Huang, S. H.; Lin, H. M.; Chao, K. C. *J. Chem. Eng. Data* **1988**, *33*, 143-145.
(16) Chao, K. C.; Lin, H. M. *Synthesis Gas Solubility in Fischer-Tropsch Slurry*; DE-AC22-84PC70024, final report, Department of Energy; Government Printing Office: Washington, DC, July 1987.
(17) Soave, G. *Chem. Eng. Sci.* **1972**, *15*, 1197-1203.
(18) Peng, D.-Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59-64.
(19) Ely, J. F.; Hanley, J. M. *NBS Tech. Note* **1981**, *No. 1039*.

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Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for CO_2 + Hydrocarbon Systems. 5. CO_2 + *n*-Tetradecane

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Experimental vapor–liquid phase compositions, phase densities, and interfacial tensions are presented for CO_2 + *n*-tetradecane at 160 °F and pressures from 1000 psia to the critical point (interfacial tensions as low as 0.01 mN/m). These data, in combination with our previously reported results for CO_2 + *n*-butane and CO_2 + *n*-decane, provide useful information on the effects of molecular size on the behavior of CO_2 + *n*-paraffin systems.

Introduction

The work presented here is part of our continuing studies on phase behavior and interfacial tension (IFT) in mixtures of CO_2 (and ethane) with a series of hydrocarbon solvents, including pure and mixed hydrocarbons and reservoir oils. The present data on CO_2 + *n*-tetradecane complement our previous results for CO_2 + *n*-butane (*1*) and CO_2 + *n*-decane (*2*). The combined results now provide information on the behavior of CO_2 in 4-, 10- and 14-carbon *n*-paraffin solvents. These data provide a basis for developing/testing models for representation of such data and, more particularly, permit evaluation of model parameters (e.g., binary interaction parameters) which may be generalized to permit interpolation or extrapolation for describing the behavior of systems involving *n*-paraffins of different molecular sizes.

Experimental Method

The experimental facility and procedures have been described in detail previously (*1*–*3*). Several modifications have been made for the present work, as described below.

Initial measurements on the present mixtures produced vapor densities that appeared to be too high. After considerable investigation of the causes for this, a second Mettler/Parr vibrating U-tube densitometer was installed. The densitometer used for vapor-phase measurements was positioned slightly above the vapor–liquid interface in the windowed equilibrium cell, and the liquid densitometer was positioned below the interface. Each was mounted in a vertical position; the vapor densitometer was installed with the bend in the U-tube at the

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