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Phase Behavior of Methane with Carboxylic Acids

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Vapor–liquid equilibria for the binary mixtures methane + dodecanoic acid, methane + hexadecanoic acid, and methane + eicosanoic acid have been measured in a semiflow apparatus under the temperatures ranging from 373.2 to 473.2 K at pressures up to 5.07 MPa. A correlation is developed to describe the results and to calculate the gas solubilities of these systems. Henry's constants and the partial molar volumes at infinite dilution of methane are evaluated from gas solubilities.

Introduction

Studies on the solubility of methane in heavy compounds at high temperatures and pressures are limited. Chao and co-workers (*1–3*) have reported the solubilities of methane in *n*-eicosane, *n*-octacosane, and *n*-hexatriacontane under temperatures ranging from 373.2 to 573.2 K at pressures from 1.01 to 5.07 MPa. Schwarz and Prausnitz (*4*) have determined the solubilities of methane in heavy fossil-fuel fractions at temperatures to 573 K. Malone and Kobayashi (*5*) have measured P–T–x data of the methane + phenanthrene system at temperatures of 398–473 K and pressures to 24.2 MPa. The solubilities of methane in *n*-tetracosane and *n*-dotriacontane over the temperature range from 373.2 to 623.2 K at pressures up to 5.07 MPa have been measured (*6*). However, limited data are available on systems involving methane with heavy carboxylic acids which are solids at room temperature. In the present study, the solubilities of methane in dodecanoic acid (lauric acid), hexadecanoic acid (palmitic acid), and eicosanoic acid (arachidic acid) have been measured at temperatures ranging from 373.2 to 473.2 K at pressures from 1.01 to 5.07 MPa. The isothermal vapor–liquid equilibrium (VLE) data obtained are correlated by the modified Soave equation of state (*7*) with one binary interaction parameter. In addition, Henry's constants, the partial molar volumes of methane at infinite dilution, and the Margules parameters are obtained by fitting the solubility data to the Krichevsky–Ilinskaya equation (*8*).

Experimental Section

A semiflow vapor–liquid equilibrium apparatus has been used for the measurement of gas solubilities. The experimental equipment and sampling procedure have been described elsewhere (*9*). Briefly, methane is passed continuously from a high-pressure cylinder through two cells in series. The first cell was the presaturator and the second the equilibrium cell. The molten carboxylic acid was kept in these two cells, which were housed in a thermostated nitrogen bath. To promote mixing and equilibration, the cells were packed with raschig rings.

After sufficient time for equilibration was allowed, the liquid sample from the equilibrium cell was withdrawn, reduced in pressure, and collected in a trap which was immersed in an ice bath. The collected sample was weighed with an analytical balance, and the liberated gas from the solidified sample was determined volumetrically in a buret. The sampling procedure for the gas phase was similar to that of the liquid phase, except that a wet test meter was used in place of a buret to measure the gas volume. The temperature of the equilibrium cell was measured with a type J thermocouple inserted in the equilibrium cell to an accuracy of ±0.2 K. The pressure was measured with a Heise gauge to ±0.01 MPa.

Table I. VLE Data for Methane (2) + Dodecanoic Acid (1)

T/K	P/MPa	x_2	y_2	K_2
373.2	1.01	0.0264	1.0000	37.78
	2.03	0.0492	1.0000	20.31
	3.04	0.0738	1.0000	13.55
	4.05	0.0975	1.0000	10.26
	5.07	0.1175	1.0000	8.51
423.2	1.01	0.0257	0.9994	38.89
	2.03	0.0506	0.9997	19.76
	3.04	0.0757	1.0000	13.21
	4.05	0.0994	1.0000	10.06
	5.07	0.1256	1.0000	7.96
473.2	1.01	0.0222	0.9943	44.79
	2.03	0.0491	0.9965	20.30
	3.04	0.0733	0.9979	13.62
	4.05	0.0942	0.9987	10.60
	5.07	0.1179	0.9997	8.48

Table II. VLE Data for Methane (2) + Hexadecanoic Acid (1)

T/K	P/MPa	x_2	y_2	K_2
373.2	1.01	0.0297	1.0000	33.67
	2.03	0.0627	1.0000	15.95
	3.04	0.0926	1.0000	10.80
	4.05	0.1217	1.0000	8.22
	5.07	0.1531	1.0000	6.53
423.2	1.01	0.0303	0.9995	32.99
	2.03	0.0590	1.0000	16.95
	3.04	0.0867	1.0000	11.53
	4.05	0.1159	1.0000	8.63
	5.07	0.1422	1.0000	7.03
473.2	1.01	0.0283	0.9992	35.31
	2.03	0.0571	0.9995	17.50
	3.04	0.0860	0.9997	11.62
	4.05	0.1142	0.9998	8.75
	5.07	0.1414	1.0000	7.07

The methane was purchased from Air Products and Chemicals, Inc., with a stated purity of 99.99 mol %. The dodecanoic acid and hexadecanoic acid were from Merck, and the eicosanoic acid was from Tokyo Kasei Kogyo Co., Ltd., with minimum purities of 99, 98 and 99 mol %, respectively. The chemicals were used without further purification.

Results

Tables I–III present the experimental vapor–liquid equilibrium measurements for methane + dodecanoic acid, methane + hexadecanoic acid, and methane + eicosanoic acid, respectively. For each system, measurements were made at

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Table III. VLE Data for Methane (2) + Eicosanoic Acid (1)

T/K	P/MPa	x_2	y_2	K_2
373.2	1.01	0.0359	1.0000	27.86
	2.03	0.0679	1.0000	14.73
	3.04	0.1001	1.0000	9.99
	4.05	0.1335	1.0000	7.49
	5.07	0.1618	1.0000	6.18
423.2	1.01	0.0303	1.0000	33.00
	2.03	0.0612	1.0000	16.34
	3.04	0.0889	1.0000	11.25
	4.05	0.1235	1.0000	8.10
	5.07	0.1504	1.0000	6.65
473.2	1.01	0.0292	1.0000	34.25
	2.03	0.0564	1.0000	17.73
	3.04	0.0863	1.0000	11.59
	4.05	0.1176	1.0000	8.50
	5.07	0.1447	1.0000	6.91

Table IV. Critical Temperatures T_c, Critical Pressures P_c, and Acentric Factors ω of the Substances Used in This Work

substance	T_c/K	P_c/MPa	ω
methane	190.55	4.599	0.013
dodecanoic acid	734.75	1.934	1.021
hexadecanoic acid	780.00	1.510	1.175
eicosanoic acid	820.26	1.238	1.448

three temperatures: 373.2, 423.2, and 473.2 K. Along each isotherm, measurements were made at five pressures: 1.01, 2.03, 3.04, 4.05, and 5.07 MPa. Each reported datum is the average value of at least three replicate samples. The sample compositions were generally reproducible within ±2% in the mole fractions of methane for the liquid phase and ±0.05% for the vapor phase. The K_2 values of methane listed in Tables I–III were calculated from the average values of x_2 and y_2 according to the definition $K_2 = y_2/x_2$. The solubilities of these systems usually decrease with rising temperature and increase with pressure over the pressure and temperature ranges studied.

Correlation

We used the modified Soave equation of state (*7*) to correlate our results, as was the case for our previously measured solubilities of systems containing CO_2 (*10–12*) and methane in heavy *n*-paraffins (*6*). For the modified Soave equation, the specific relation is

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

where v is the molar volume

$$a = z_1^2 a_{11} + 2 z_1 z_2 a_{12} + z_2^2 a_{22} \tag{2}$$

$$b = z_1 b_1 + z_2 b_2 \tag{3}$$

$$a_{12} = (a_{11} a_{22})^{0.5} (1 - k_{12}) \tag{4}$$

$$a_{ii} = 0.42748 \alpha_i R^2 T_{c,i}^2 / P_{c,i} \qquad i = 1, 2 \tag{5}$$

$$b_i = 0.08664 R T_{c,i} / P_{c,i} \tag{6}$$

$$\alpha_i = [1 + m_i (1 - T_{r,i}^{0.5})]^2 \tag{7}$$

$$m_i = 0.48508 + 1.55171 \omega_i - 0.15613 \omega_i^2 \tag{8}$$

$T_{c,i}$, $P_{c,i}$, $T_{r,i}$ and ω_i are, respectively, the critical temperature, critical pressure, reduced temperature, and acentric factor of component i, and z_i represents the mole fraction of component i in the vapor or liquid phase.

In the fitting of the modified Soave equation of state to experimental results, the values for the optimum interaction parameters are dependent on the properties $T_{c,i}$, $P_{c,i}$, and ω_i used in the evaluation of the pure-component parameters (a and b) in the equations. Table IV presents the properties of each substance utilized in the present work. The critical data and acentric factor of methane were taken from Reid et al. (*13*). The critical properties and acentric factors of heavy carboxylic acids were estimated by Lydersen's method (*14*) and the Lee–Kesler correlations (*15*), respectively. The normal boiling points of dodecanoic acid and hexadecanoic acid needed in calculations for T_c were taken from the *CRC Handbook of Chemistry and Physics* (*16*), while the normal boiling point of eicosanoic acid was obtained by extrapolation of those of dodecanoic acid, hexadecanoic acid, and octadecanoic acid.

Table V. Correlation of VLE Data with the Modified Soave Equation for Five Data Points at Each Temperature

solvent	T/K	P range/ MPa	k_{12}	$100\Delta P/P^a$	$\Delta y_2^b/10^{-4}$
dodecanoic acid	373.2	1.01–5.07	−0.0019	1.50	0.12
	423.2	1.01–5.07	−0.0419	1.25	1.67
	473.2	1.01–5.07	−0.0086	3.41	6.95
hexadecanoic acid	373.2	1.01–5.07	−0.0451	2.82	0.02
	423.2	1.01–5.07	−0.0698	0.87	1.09
	473.2	1.01–5.07	−0.0784	2.23	1.32
eicosanoic acid	373.2	1.01–5.07	−0.0788	1.22	0.03
	423.2	1.01–5.07	−0.0858	3.03	0.04
	473.2	1.01–5.07	−0.0872	3.13	0.28

[a] $\Delta P/P = (1/n)\sum_{i=1}^{n}|(P_{\mathrm{calcd},i} - P_{\mathrm{exptl},i})/P_{\mathrm{exptl},i}|$. [b] $\Delta y_2 = (1/n)\sum_{i=1}^{n}|y_{2,\mathrm{calcd},i} - y_{2,\mathrm{exptl},i}|$, where n is the number of measurements.

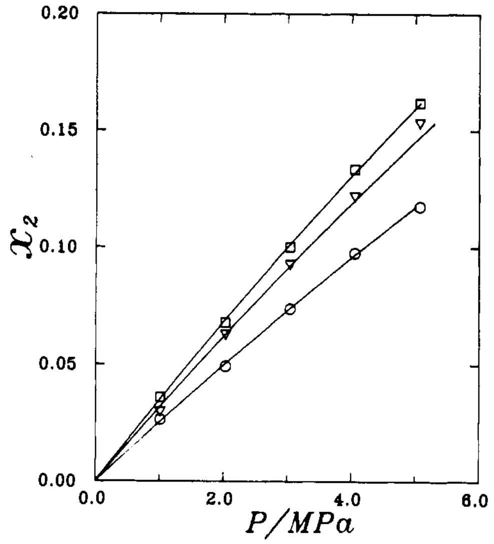

Figure 1. Comparison of the calculated mole fraction x_2 of methane in heavy carboxylic acids (lines) with experimental data (points) as a function of pressure P at 373.2 K: (○) dodecanoic acid, (▽) hexadecanoic acid, (□) eicosanoic acid.

The optimum values of k_{12} can be calculated from the VLE results by minimizing the bubble pressure variance. The calculated results with the optimum values of k_{12} for each isotherm are listed in Table V. For the majority of isotherms, the calculated bubble pressures agree with the experimental data within 3% on the average. Figures 1–3 show the calculated solubility in comparison with the results for methane in a series of heavy carboxylic acids at different temperatures and indicate that the modified Soave equation with one interaction parameter is adequate to correlate solubility.

Henry's constants H_2, the partial molar volumes of methane at infinite dilution $\bar{v}_2^{\infty}$, and the Margules parameters A were

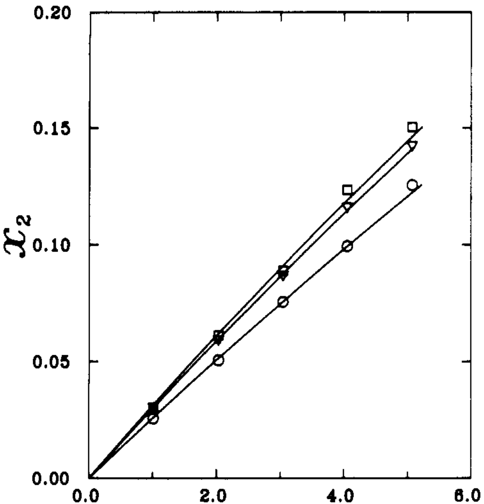

Figure 2. Comparison of the calculated mole fraction x_2 of methane in heavy carboxylic acids (lines) with experimental data (points) as a function of pressure P at 423.2 K: (○) dodecanoic acid, (▽) hexadecanoic acid, (□) eicosanoic acid.

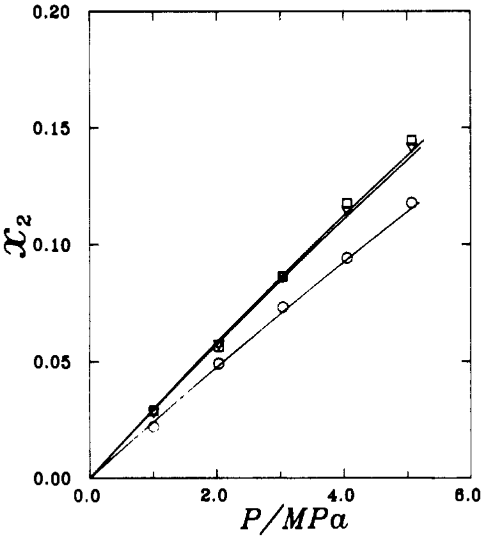

Figure 3. Comparison of the calculated mole fraction x_2 of methane in heavy carboxylic acids (lines) with experimental data (points) as a function of pressure P at 473.2 K: (○) dodecanoic acid, (▽) hexadecanoic acid, (□) eicosanoic acid.

determined by fitting the solubility data to the Krichevsky–Ilinskaya equation (*8*)

$$\ln (f_2/x_2) = \ln H_2 + A(x_1^2 - 1)/RT + \bar{v}_2^{\infty}(P - P_1^{s})/RT \quad (9)$$

where f_2 is the fugacity of the solute methane and P_1^{s} is the saturated vapor pressure of the solvent carboxylic acid in combination with the modified Soave equation using the optimum values of k_{12} of Table V by the Bender et al. approach (*17*). Table VI presents the calculated values of Henry's constants, the partial molar volumes of methane at infinite dilution, and the Margules parameters. The values of all the parameters increase with temperature except Henry's constant of the methane + dodecanoic acid system. Figure 4 shows the calculated results of Henry's constants as a function of temperature for each system. It can be seen that Henry's constants increase with increasing temperature except for the methane + dodecanoic acid system, and decreasing carbon numbers of carboxylic acid.

Table VI. Thermodynamic Parameters for Methane Solubilities: Henry's Constants H_2, Margules Constants A, and the Partial Molar Volumes of Methane at Infinite Dilution $\bar{v}_2^{\infty}$

solvent	T/K	H_2/MPa	A/(J·mol^{-1})	$\bar{v}_2^{\infty}$/(cm^3·mol^{-1})
dodecanoic acid	373.2	38.4	361.0	62.4
	423.2	38.0	433.9	74.8
	473.2	40.7	674.2	93.7
hexadecanoic acid	373.2	30.6	207.4	64.1
	423.2	32.5	282.8	76.7
	473.2	33.5	417.8	94.5
eicosanoic acid	373.2	28.0	129.6	63.4
	423.2	31.3	202.4	75.4
	473.2	33.0	309.1	91.7

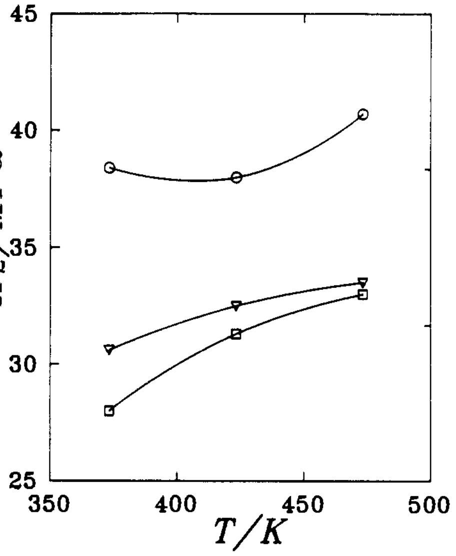

Figure 4. Henry's constants versus temperature for methane + carboxylic acid systems: (○) dodecanoic acid, (▽) hexadecanoic acid, (□) eicosanoic acid.

Glossary

A	Margules constant
a	parameter in the modified Soave equation
b	parameter in the modified Soave equation
f	fugacity
H	Henry's constant
K	vaporization equilibrium ratio, y/x
k	binary interaction parameter
m	parameter in the modified Soave equation
n	number of measurements
P	pressure
R	molar gas constant
T	temperature
v	molar volume
$\bar{v}$	partial molar volume
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
z	mole fraction (liquid or vapor phase)

Greek Letters

α	parameter in the modified Soave equation
ω	acentric factor

Superscripts

s	saturated property
∞	infinite dilution

Subscripts

1	component 1 (solvent, carboxylic acid)
2	component 2 (solute, methane)
c	critical property
i	component i
r	reduced property

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