Solubility of Methane in Heavy Normal Paraffins at Temperatures from 323 to 423 K and Pressures to 10.7 MPa

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Solubility data are presented for methane in four heavy normal paraffins at temperatures from 323 to 423 K and pressures up to 10.7 MPa. The paraffins studied are eicosane (n-C_{20}), octacosane (n-C_{28}), hexatriacontane (n-C_{36}), and tetratetracontane (n-C_{44}). The data obtained for the solubility of methane in n-C_{20}, n-C_{28}, and n-C_{36} are in good agreement with the earlier measurements of Chao and co-workers. The new data can be described with RMS errors of about 0.001 in mole fraction by the Soave–Redlich–Kwong (SRK) or Peng–Robinson (PR) equation of state when two interaction parameters per isotherm are used. Henry's constants and partial molar volumes at infinite dilution for methane have also been evaluated from the data.

Introduction

Multiple phases are present in essentially all stages of feed preparation, conversion reactions, and product separation in numerous industrial processes. In general, effective design, operation, and optimization of such processes require accurate knowledge of the phase behavior of the fluid mixtures encountered. Studies of the solubility of light gases in heavy hydrocarbons are of particular interest in the processing of coal and petroleum products, enhanced oil recovery, and supercritical fluid processes. Moreover, such studies are valuable in the development and evaluation of solution theories for mixtures.

Previously, we have reported and analyzed solubility data for carbon dioxide and ethane in a series of heavy hydrocarbons (*1–5*). We have recently completed an experimental study on the solubility of methane in a series of heavy hydrocarbons (paraffins, naphthenes, and aromatics). Solubility data for the binary mixtures of methane with eicosane, octacosane, hexatriacontane, and tetratetracontane are presented here and correlated using the Soave (*6*) and Peng–Robinson (*7*) equations of state. Solubilities were measured at temperatures from 323 to 423 K (from 122 to 302 °F) and pressures up to 10.7 MPa (1550 psia). These data should provide a valuable complement to the available literature data and should prove useful in the development and testing of correlations describing phase behavior in multicomponent systems containing methane.

Experimental Method

The experimental apparatus used in this study was a modified version of the apparatus used by Raff (*5*). Three major modifications were implemented.

(1) The stirred equilibrium cell was replaced by a rocking one. The cell, housing five steel balls, is designed to rock from 45° below to 45° above the horizontal level.

(2) To a large extent, the dead volume was eliminated from the cell, tubing, and connections. This was achieved by injecting solute, solvent, and mercury through a single line in the bottom of the equilibrium cell, while having no connections at the other end of the cell.

(3) In our previous cleaning procedure, heavy solvents (which are solid at room temperature) could be trapped in some of the lines outside the high-temperature bath, thus plugging the lines and causing unnecessary delays. This problem was alleviated by devising a different strategy for cleaning. A detailed description of the apparatus and experimental procedures is given elsewhere (*8*).

Estimated uncertainties in experimental measurements are ±0.1 K in temperature and less than ±0.002 in mole fraction. The uncertainty in the measured bubble point pressure depends on the steepness of the p–x relation and is on the order of ±0.04 MPa (*8*).

Materials

The methane used in this study had a stated purity of 99.97+ mol % and was supplied by Matheson. Eicosane, octacosane, and hexatriacontane were from Aldrich Chemical Co. with quoted purities of 99+ mol %. Tetratetracontane was supplied by Alfa Products with a stated purity of 96+ mol %. No further purification of the chemicals was attempted.

Results

The experimental data are presented in Tables I–IV. In general, the lowest temperature at which a system was studied was dictated by the melting point of the solvent. The effects of temperature and pressure on methane solubility (liquid-phase mole fraction of methane) are illustrated in Figure 1 for the octacosane measurements. Typical of all the n-paraffins considered, the solubility of methane in a n-paraffin decreases with increasing temperature at a fixed pressure. This behavior is similar to that observed earlier for carbon dioxide solubilities (*2*). Similarly, the effect of the solvent molecular weight (or, equivalently, the carbon number) on methane solubility is shown in Figure 2 for the four n-paraffins at 373.2 K; for a given pressure, the solubility of the solute gas increases with increasing solvent molecular weight.

Comparisons of our results with those reported by various researchers appear in Figures 3–5. The comparisons are shown in terms of deviations of the solubilities from values predicted using the Soave–Redlich–Kwong (SRK) (*6*) equation of state (discussed below). Interaction parameters employed in the equation-of-state predictions were obtained by fitting our data for each isotherm in each system.

In general, these comparisons reveal reasonable agreement between our data and those from the literature. For methane + eicosane (Figure 3), the equation-of-state parameters regressed from our data predict lower solubilities (higher bubble point pressures) at 473.2 K and higher solubilities at 373.2 K than those reported by Huang et al. (*10*). The two

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Table I. Solubility, x_1, of Methane (1) in Eicosane (2)

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
		323.2 K			
0.0512	0.95	0.1185	2.32	0.1773	3.68
0.0992	1.89	0.1503	3.02	0.2121	4.55
		373.2 K			
0.0747	1.58	0.1502	3.43	0.2510	6.42
0.1132	2.48	0.2003	4.82	0.2511	6.40
		423.2 K			
0.0737	1.68	0.2496	6.77	0.3006	8.63
0.1560	3.85	0.2510	6.79	0.3500	10.69
0.2002	5.16	0.2748	7.67		

Table II. Solubility, x_1, of Methane (1) in Octacosane (2)

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
		348.2 K			
0.0568	0.93	0.1493	2.61	0.2521	5.02
0.0840	1.36	0.1992	3.72		
0.1374	2.38	0.2369	4.63		
		373.2 K			
0.0736	1.26	0.1516	2.84	0.2766	6.17
0.1268	2.36	0.1751	3.43	0.3247	7.74
		423.2 K			
0.0737	1.41	0.1537	3.16	0.2505	5.67
0.1092	2.13	0.2016	4.33	0.2992	7.09

Table III. Solubility, x_1, of Methane (1) in Hexatriacontane (2)

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
		373.2 K			
0.0567	0.87	0.2316	4.21	0.3151	6.37
0.1380	2.27	0.2595	4.86		
0.1677	2.80	0.2655	4.95		
		423.2 K			
0.0511	0.84	0.1978	3.69	0.3506	7.93
0.1021	1.74	0.2478	4.89		
0.1515	2.67	0.3003	6.31		

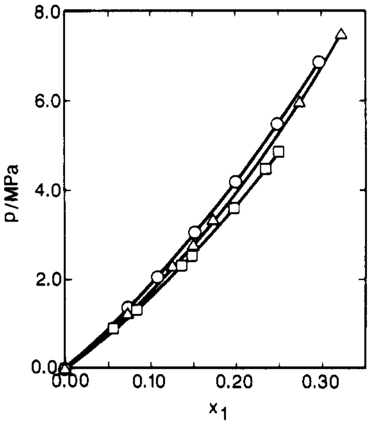

Figure 1. Solubility of methane in octacosane: □, 348.2 K; △, 373.2 K; ○, 423.2 K.

sets of solubilities agree within 0.003 mole fraction at 373.2 K and 0.004 at 473.2 K (extrapolating our data).

Comparisons for methane + n-C_{28} and methane + n-C_{36} are shown in Figures 4 and 5. The agreement in the mole fractions from this study and those of Huang et al. (*11*) for methane + n-C_{28} is within 0.005 at 373.2 K. For methane + n-C_{36}, the agreement between the mole fractions from this work and those of Tsai et al. (*12*) is within 0.004 at 373.2 K (Figure 5). For methane + n-C_{44}, no literature data are available for comparisons.

Equation-of-State Data Correlation

The experimental data have been correlated using the SRK (*6*) and Peng–Robinson (PR) (*7*) cubic equations of state.

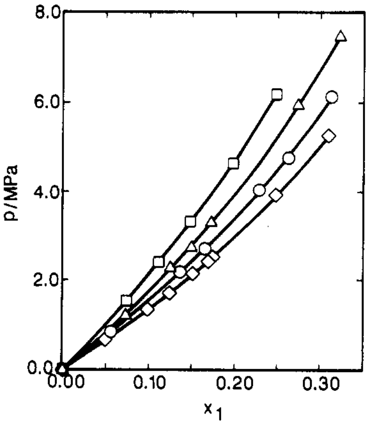

Figure 2. Solubility of methane in n-paraffins at 373.2 K: □, n-C_{20}; △, n-C_{28}; ○, n-C_{36}; ◇, n-C_{44}.

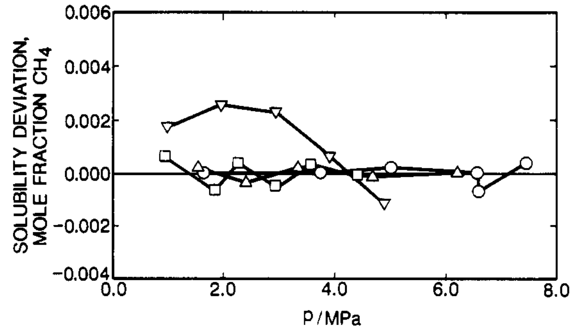

Figure 3. Comparison of methane solubilities in eicosane: (this work) □, 323.2 K; △, 373.2 K; ○, 423.2 K; (Huang (*10*)) ▽, 373.2 K.

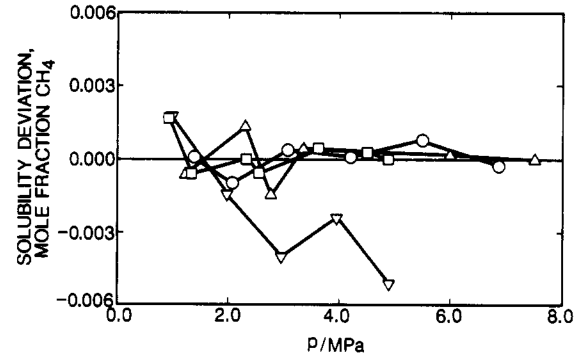

Figure 4. Comparison of methane solubilities in octacosane: (this work) □, 348.2 K; △, 373.2 K; ○, 423.2 K; (Huang (*11*)) ▽, 373.2 K.

The Soave equation is given by

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

where

$$a(T) = a_c\alpha(T) \tag{2}$$

$$b = 0.08664RT_c/P_c \tag{3}$$

and

$$a_c = 0.42748R^2T_c^2/P_c \tag{4}$$

$$\alpha(T) = [1 + k(1 - T_r^{1/2})]^2 \tag{5}$$

$$k = 0.480 + 1.574\omega - 0.176\omega^2 \tag{6}$$

To apply the SRK or PR equations of state to mixtures, the values of a and b were determined using the mixing rules (4)

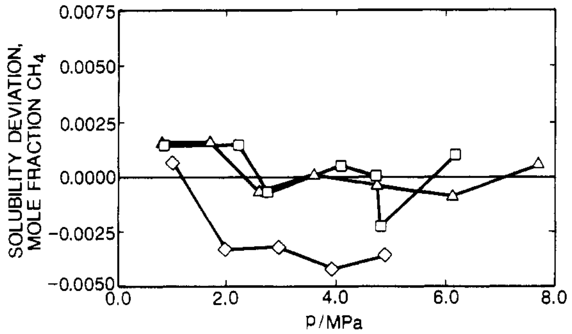

Figure 5. Comparison of methane solubilities in hexatriacontane: (this work) □, 373.2 K; △, 423.2 K; (Tsai (*12*)) ◇, 373.2 K.

Table IV. Solubility, x_1, of Methane (1) in Tetratetracontane (2)

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
		373.2 K			
0.0501	0.68	0.1521	2.21	0.2504	4.06
0.0996	1.38	0.1706	2.51	0.3112	5.46
0.1257	1.78	0.1766	2.62		
		423.2 K			
0.0861	1.25	0.2111	3.42	0.3042	5.57
0.1211	1.81	0.2535	4.37		
0.1568	2.42	0.2788	4.89		

Table V. Critical Pressure, P_c, Critical Temperature, T_c, and Acentric Factor, ω, for the n-Alkanes in the SRK and PR Equations of State

component	P_c/MPa	T_c/K	ω	ref
methane	4.660	190.5	0.0110	17
C_{10}	2.097	617.5	0.4885	18
C_{20}	1.069	766.6	0.8941	9
C_{28}	0.661	827.4	1.1617	9
C_{36}	0.428	864.0	1.4228	9
C_{44}	0.290	866.6	1.6664	9

$$a = \sum_i^N \sum_j^N z_i z_j (1 - C_{ij})(a_i a_j)^{1/2} \tag{7}$$

$$b = 0.5 \sum_i^N \sum_j^N z_i z_j (1 + D_{ij})(b_i + b_j) \tag{8}$$

In eqs 7 and 8 the summations are over all chemical species and C_{ij} and D_{ij} are empirical binary interaction parameters characterizing the binary interactions between components i and j. Values of these parameters were determined by fitting the experimental binary data to minimize the objective function, SS, which represents the sum of squared errors in predicted bubble point pressures:

$$\mathrm{SS} = \sum_i^n (P_{\mathrm{exptl}} - P_{\mathrm{calcd}})_i^2 \tag{9}$$

Further details of the data reduction techniques employed in this study are given by Gasem (*9*). The input parameters for the pure components (acentric factors, critical temperatures, and critical pressures) required by the SRK and PR equations of state, together with the literature sources, are presented in Table V.

Table VI. SRK and PR Equation-of-State Representations of the Solubility of Methane in Eicosane

	Soave params (PR params)		error in methane mole fraction[a]	
T/K	C_{12}	D_{12}	RMS	|max|
323.2	0.072 (0.069)	−0.008 (−0.007)	0.0005	0.0007
	0.029 (0.031)		0.0015	0.0024
373.2	0.096 (0.091)	−0.016 (−0.016)	0.0002	0.0003
	0.017 (0.016)		0.0032	0.0046
423.2	0.106 (0.101)	−0.020 (−0.022)	0.0005	0.0008
	0.021 (0.015)		0.0047	0.0067
323.2, 373.2, 423.2	0.058 (0.039)	−0.008 (−0.005)	0.0036	0.0070
	0.022 (0.019)		0.0039	0.0066

[a] Errors are essentially identical for the SRK and PR equations.

Table VII. SRK and PR Equation-of-State Representations of the Solubility of Methane in Octacosane

	Soave params (PR params)		error in methane mole fraction[a]	
T/K	C_{12}	D_{12}	RMS	|max|
348.2	0.136 (0.127)	−0.013 (−0.014)	0.0007	0.0016
	0.033 (0.029)		0.0039	0.0056
373.2	0.170 (0.158)	−0.017 (−0.018)	0.0009	0.0014
	0.041 (0.034)		0.0057	0.0069
423.2	0.122 (0.112)	−0.012 (−0.014)	0.0004	0.0007
	0.025 (0.012)		0.0025	0.0038
348.2, 373.2, 423.2	0.153 (0.140)	−0.015 (−0.016)	0.0014	0.0028
	0.034 (0.027)		0.0044	0.0098

[a] Errors are essentially identical for the SRK and PR equations.

Table VIII. SRK and PR Equation-of-State Representations of the Solubility of Methane in Hexatriacontane

	Soave params (PR params)		error in methane mole fraction[a]	
T/K	C_{12}	D_{12}	RMS	|max|
373.2	0.192 (0.179)	−0.010 (−0.012)	0.0013	0.0023
	0.091 (0.078)		0.0042	0.0065
423.2	0.223 (0.208)	−0.012 (−0.015)	0.0010	0.0016
	0.110 (0.092)		0.0050	0.0074
373.2, 423.2	0.220 (0.201)	−0.013 (−0.014)	0.0020	0.0040
	0.099 (0.084)		0.0053	0.0110

[a] Errors are essentially identical for the SRK and PR equations.

Table IX. SRK and PR Equation-of-State Representations of the Solubility of Methane in Tetratetracontane

	Soave params (PR params)		error in methane mole fraction[a]	
T/K	C_{12}	D_{12}	RMS	|max|
373.2	0.243 (0.229)	−0.008 (−0.009)	0.0009	0.0018
	0.138 (0.123)		0.0040	0.0059
423.2	0.263 (0.249)	−0.008 (−0.010)	0.0011	0.0017
	0.161 (0.139)		0.0029	0.0041
373.2, 423.2	0.258 (0.242)	−0.008 (−0.010)	0.0023	0.0040
	0.148 (0.130)		0.0045	0.0079

[a] Errors are essentially identical for the SRK and PR equations.

The equation-of-state representations of the solubilities for the systems under study are documented in Tables VI–IX. The equations are capable of describing the data with RMS errors within 0.002 in mole fraction when a single pair of interaction parameters, C_{ij} and D_{ij}, is used over the complete temperature range for any system studied (except for the methane + n-eicosane system which has an RMS error of 0.0036). When two parameters are fitted to each isotherm, RMS errors are less than 0.0015 for all systems; however, a certain degree of correlation between the C_{ij} and D_{ij} is revealed in their tabulated values. These results illustrate both the ability of the equations of state and the precision of our reported data.

Krichevsky–Kasarnovsky Analysis

In the range of methane mole fractions reported in this study, the binary solubilities of methane in n-C_{20}, n-C_{28}, n-C_{36},

Table X. Henry's Constant, H_1, and Infinite Dilution Partial Molar Volume, v_1^∞, for Methane (1) in *n*-Paraffins (2)

T/K	ref	H_1/bar	v_1^∞/(cm^3 mol^{-1})	RMS(x_1)
		Eicosane		
323.2	this work	178 ± 1[a]	1230 ± 80[a]	0.0005
373.2	this work	199 ± 1	1470 ± 25	0.0003
373.4	10	208 ± 1	1075 ± 45	0.0003
423.2	this work	217 ± 1	1520 ± 25	0.0007
473.5	10	226 ± 3	1490 ± 220	0.0009
		Octacosane		
348.2	this work	153 ± 1	1855 ± 110	0.0007
373.2	this work	162 ± 2	2080 ± 150	0.0013
373.4	11	165 ± 2	1720 ± 200	0.0014
423.2	this work	179 ± 1	1950 ± 75	0.0005
473.5	11	192 ± 3	1740 ± 230	0.0012
		Hexatriacontane		
373.2	this work	147 ± 1	2000 ± 50	0.0010
373.4	12	143 ± 2	2075 ± 155	0.0013
423.2	this work	157 ± 1	2195 ± 40	0.0006
473.5	12	159 ± 3	2420 ± 290	0.0019
		Tetratetracontane		
373.2	this work	128 ± 1	2270 ± 90	0.0009
423.2	this work	135 ± 1	2585 ± 60	0.0009

[a] These values are the standard deviations of the estimated parameters.

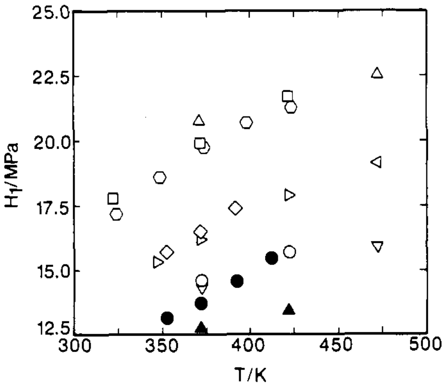

Figure 6. Comparison of Henry's constants of methane in paraffins: (this work) □, *n*-C_{20}; ▷, *n*-C_{28}; ○, *n*-C_{36}; ▲, *n*-C_{44}; (Chappelow (*15*)) ⬡, *n*-C_{20}; (Huang (*10*)) △, *n*-C_{20}; (Huang (*11*)) ◁, *n*-C_{28}; (Ping (*16*)) ◇, *n*-C_{28}; ●, *n*-C_{36}; (Tsai (*12*)) ▽, *n*-C_{36}.

and *n*-C_{44} are represented within 0.0015 by the Krichevsky–Kasarnovsky (KK) equation (*13*) (definitions of variables appear in the List of Symbols):

$$\ln (f_1/x_1) = \ln H_1 + (v_1^\infty/RT)(p - p_2) \qquad (10)$$

Values of the methane fugacity, f_1, required for the KK equation were obtained from Bender's equation of state for methane (*14*), since the vapor phase is essentially pure methane.

Solubility data for methane + *n*-paraffins of this work, as well as those found in the literature, were analyzed using eq 10 above. The resultant Henry's constants and the infinite-dilution partial molar volumes of methane are presented in Table X. Care should be taken in attributing physical significance to the values of infinite dilution partial molar volumes which are considered less accurate than the corresponding Henry's constants.

Comparisons of Henry's constants are shown in Figure 6. The Henry's constants of Chappelow (*15*) were obtained from equilibrium cell data, those of Ping (*16*) were obtained using gas chromatographic techniques, and the others (including the present work) were obtained, as described above, by regression of solubility data using eq 10. For methane + *n*-C_{20}, our Henry's constants agree within 0.5 MPa with those of Huang (*10*), and Chappelow (*15*). Similar agreement is observed between Henry's constants of this work and other researchers (*11*, *16*, *12*) for methane + *n*-C_{28} and methane + *n*-C_{36}.

Figure 6 also shows the effects of the solvent carbon number and temperature of Henry's constants. For a given temperature, Henry's constant decreases with increasing carbon number of the solvent, and for a given *n*-paraffinic solvent, increases with temperature, which is the expected behavior.

Conclusions

Data have been obtained on the solubility of methane in each of the *n*-paraffin solvents eicosane, octacosane, hexatriacontane, and tetratetracontane at temperatures from 323 to 423 K and pressures to 10.7 MPa. These data are well described by the Soave–Redlich–Kwong and Peng–Robinson equations of state and the Krichevsky–Kasarnovsky correlation. These results will be of value in establishing interaction parameters in other equations of state for light gases in heavy hydrocarbon solvents.

List of Symbols

$a(T)$,b	parameters in the SRK or PR equation of state
C_{ij},D_{ij}	binary interaction parameters in the SRK or PR equation of state
f_1	fugacity of methane in the liquid (or vapor) phase
H_1	Henry's constant of methane at the vapor pressure of the solvent
k	equation-of-state parameter defined in eq 6
n	number of data points
N	number of components in mixture
p	pressure
p_2	hydrocarbon solvent vapor pressure
R	universal gas constant
RMS	root mean square error
SS	objective function defined by eq 9
T	temperature
x_1	liquid mole fraction of methane (solubility)
V	molar volume
v_1^∞	infinite dilution partial molar volume of methane
z_i	mole fraction of component i in a mixture
Greek Letters	
ω	acentric factor
$\alpha(T)$	temperature-dependent parameter in eqs 1 and 2
Subscripts	
c	critical state
calcd	calculated
exptl	experimental
i	component i in a mixture
r	reduced property

Literature Cited

(1) Robinson, R. L., Jr.; Anderson, J. M.; Barrick, M. W.; Bufkin, B. A.; Ross, C. H. Phase behavior of Coal Fluids: Data for Correlation Development. Final Report DE-FG22-86PC90523; Department of Energy: Washington, DC, January 1987.
(2) Gasem, K. A. M.; Robinson, R. L., Jr. *J. Chem. Eng. Data* **1985**, *30*, 53.
(3) Anderson, J. M.; Barrick, M. W.; Robinson, R. L., Jr. *J. Chem. Eng. Data* **1986**, *31*, 172.
(4) Gasem, K. A. M.; Bufkin, B. A.; Raff, A. M.; Robinson, R. L., Jr. *J. Chem. Eng. Data* **1989**, *34*, 187.
(5) Raff, A. M. M.S. Thesis, Oklahoma State University, Stillwater, OK, 1989.
(6) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.

(7) Peng, Y. D.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.

(8) Darwish, N. A. Ph.D. Dissertation, Oklahoma State University, Stillwater, OK, 1990.

(9) Gasem, K. A. M. Ph.D. Dissertation, Oklahoma State University, Stillwater, OK, 1986.

(10) Huang, S. H.; Lin, H.-M.; Chao, K. C. *J. Chem. Eng. Data* **1988**, *33*, 145.

(11) Huang, S. H.; Lin, H.-M.; Chao, K. C. *J. Chem. Eng. Data* **1988**, *33*, 143.

(12) Tsai, F.-N.; Stanley, H. H.; Lin, H.-M.; Chao, K. C. *J. Chem. Eng. Data* **1987**, *32*, 467.

(13) Krichevsky, I. R.; Kasarnovsky, J. S. *J. Am. Chem. Soc.* **1935**, *57*, 2168.

(14) Sievers, U.; Schulz, S. *Fluid Phase Equilib.* **1980**, *5*, 35.

(15) Chappelow, C. C.; Prausnitz, J. M. *AIChE J.* **1974**, *20*, 1097.

(16) Ping, J. L.; Parcher, J. F. *J. Chromatogr. Sci.* **1982**, *20*, 33.

(17) Goodwin, R. D. Thermophysical Properties of Methane from 90 to 500 K at Pressures to 700 Bar. NBS Technical Note 653; National Bureau of Standards: Washington, DC, 1974.

(18) Ely, J. F.; Hanley, H. J. M. NBS Technical Note 1039; National Bureau of Standards: Washington, DC, 1981.

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