Bubble Pressures and Liquid Molar Volumes of the System Chlorotrifluoromethane–1,1,2-Trichlorotrifluoroethane

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A previously described static method, using the principle of a variable-volume cell, has been used for determining bubble pressures and liquid molar volumes of chlorotrifluoromethane ($CClF_3$)-trichlorotrifluoroethane (CCl_2FCClF_2) binary mixtures at five temperatures: 298.15, 303.15, 323.15, 348.15, and 373.15 K. Peng and Robinson's equation of state, using only one binary interaction parameter, represents well the vapor-liquid equilibrium data, but calculated liquid volumes show a mean deviation of 5%. The mixing volume contraction is described qualitatively, especially at lower temperatures.

Introduction

Chlorofluoroalkane mixtures are of interest as working fluids in heat pumps. Their thermodynamic properties, especially vapor-liquid equilibria, are necessary to select optimal compositions and the best components of the mixtures.

An apparatus described previously (*1*) is used to investigate several binary chlorofluoroalkane mixtures, and among them the system $CClF_3$-CCl_2FCClF_2 is described in this paper. For this system, we report the following data: P, T, x, $v_S{}^L$ to 373.15 K and 5 MPa. At a given temperature, the bubble pressure and the saturated molar volume of the liquid are directly and simultaneously measured for a mixture of given composition.

Determination of molar volumes at constant temperature and pressure as a function of composition makes possible calculation of partial molar volumes, which are useful to test the validity of mixing rules in equations of state for mixtures. These data also give an estimate of the pressure effect on nonideality in the liquid phase, the so-called Poynting correction.

Bubble pressures and saturated liquid molar volumes were also calculated by using the Peng and Robinson equation of state (*2*).

Experimental Section

Apparatus. A simplified flow diagram of the apparatus is shown in Figure 1. This apparatus (*1*) has been designed to allow simultaneous determination of bubble pressures and saturated liquid molar volumes. The equilibrium cell, EC, is placed into a pressurizing cell, PC, maintained at a constant temperature by means of a thermostated oil bath, LB. The internal volume of the equilibrium cell can be changed by moving a piston by displacement of a compressed hydraulic fluid, HF. A volumetric pump, HP, connected to the pressurizing cell, is used to introduce known quantities of the hydraulic fluid. Mixing inside the equilibrium cell is achieved by efficient stirring through a magnet, M, driven by a gas turbine, GT. A calibrated pressure transducer screwed into the piston gives a continuous reading of pressures within 0.01 MPa during compression of the mixture (see Table I). The curve P vs. V_T (where V_T is the total volume of the cell) exhibits a break point when the vapor phase disappears (see Figure 2). The coordinates of the break point are exactly the bubble pressure and the saturated liquid molar volume multiplied by the total number of moles of the mixture. At the bubble point, the liquid mole fractions are exactly equal to the total mole fractions, obtained by weighing, within 10^{-4} g, each component introduced into the equilibrium cell at the beginning of the experiment.

Table I. Pressure as a Function of Total Cell Volume for the Chlorotrifluoromethane (1)-Trichlorotrifluoroethane (2) Mixture at $z_1 = 0.4994$ and Different Temperatures

P, MPa	V_T, cm^3	P, MPa	V_T, cm^3
$T = 298.15$ K[a]			
1.65	49.4210	1.71	37.2569
1.66	48.2979	1.71	37.1592
1.67	46.3439	1.84	37.0870
1.68	44.3898	2.13	37.0103
1.69	41.4582	2.44	36.8503
1.70	39.5042	2.80	36.6936
1.71	37.5502	3.68	36.3025
$T = 303.15$ K[b]			
1.81	49.4210	1.87	38.0724
1.82	48.8802	1.88	37.7775
1.83	46.9151	1.88	37.6802
1.84	44.9500	2.05	37.5036
1.85	42.9848	2.41	37.3469
1.87	41.0196	3.58	36.7897
1.87	39.0555		
$T = 323.15$ K[c]			
2.46	49.4210	2.57	39.6795
2.47	49.3216	2.57	39.5790
2.47	49.0200	2.57	39.4785
2.50	47.0113	2.63	39.3857
2.52	45.0030	2.77	39.3007
2.54	42.9941	2.96	39.2212
2.56	40.9855	3.76	38.8024
2.57	39.9812	4.54	38.3943
$T = 348.15$ K[d]			
3.41	49.4210	3.55	42.3587
3.42	48.9571	3.55	42.3070
3.45	46.8950	3.55	42.2553
3.50	44.8330	3.59	42.2092
3.51	44.3175	3.65	41.1653
3.52	43.8019	3.90	41.9853
3.53	43.2865	4.14	41.8064
3.54	42.7710	4.36	41.6243
$T = 373.15$ K[e]			
4.49	49.4210	4.59	46.4610
4.50	49.2099	4.60	46.3560
4.51	48.6805	4.63	46.2532
4.53	48.1521	4.66	46.1504
4.55	47.6238	4.74	46.0532
4.57	47.0943	4.81	45.9560
4.59	46.5671	4.90	45.8598

[a] $P_b = 1.71$ MPa, $V_T = 37.1592$ cm^3, $v_S{}^L = 105.8$ cm^3 mol^{-1}.
[b] $P_b = 1.88$ MPa, $V_T = 37.6802$ cm^3, $v_S{}^L = 107.2$ cm^3 mol^{-1}.
[c] $P_b = 2.57$ MPa, $V_T = 39.4785$ cm^3, $v_S{}^L = 112.3$ cm^3 mol^{-1}.
[d] $P_b = 3.55$ MPa, $V_T = 42.2553$ cm^3, $v_S{}^L = 120.2$ cm^3 mol^{-1}.
[e] $P_b = 4.60$ MPa, $V_T = 46.3560$ cm^3, $v_S{}^L = 131.9$ cm^3 mol^{-1}.

The temperature is read within 0.1 K through calibrated iron-constantan thermocouples. The accuracy (*1*) on saturated liquid molar volumes is estimated to be 0.5%.

Chemicals. Chlorotrifluoromethane was supplied by Matheson with a guaranteed purity of not less than 99%. 1,1,2-Trichlorotrifluoroethane from Sepic has a certified minimum purity of 99.85%. These two components have been used without further purification, but trichlorotrifluoroethane was degassed before mixing.

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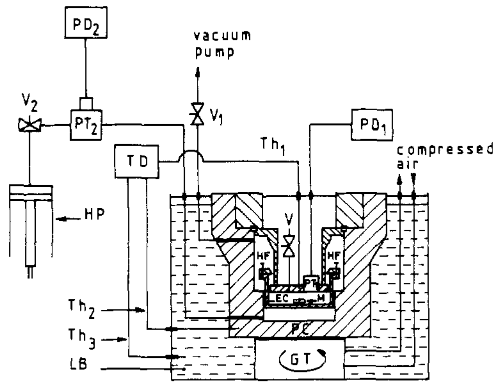

Figure 1. Simplified flow diagram of the apparatus: (EC) equilibrium cell; (GT) gas turbine; (HF) pressurizing liquid; (HP) hydraulic pump; (LB) liquid bath; (M) magnet; (PC) pressurizing cell; (PD_1, PD_2) pressure electronic displays; (PT_1, PT_2) pressure transducers; (TD) temperature display; (Th_1, Th_2, Th_3) thermocouples; (V, V_1, V_2) valves.

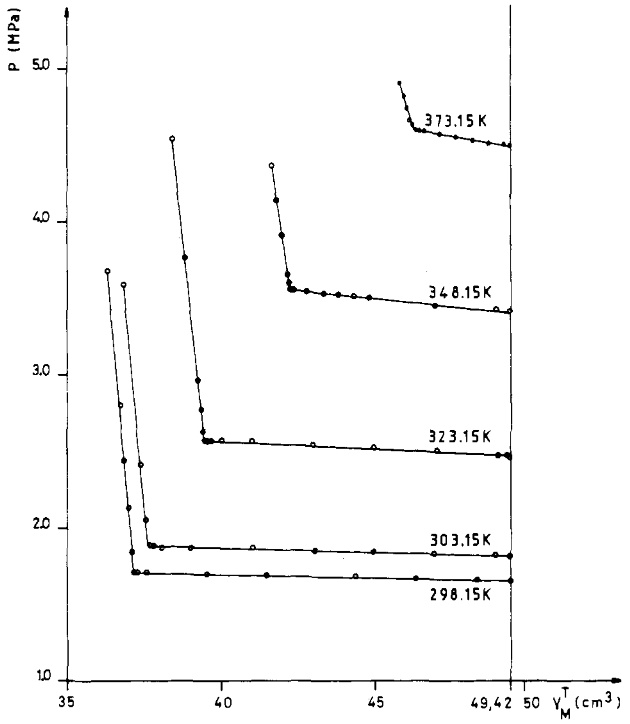

Figure 2. Pressure as a function of cell volume for a $CClF_3$ (1)–$C_2Cl_3F_3$ (2) mixture at X_1 = 0.4994 and different temperatures.

Table II. Vapor Pressure and Saturated Liquid Molar Volume of Chlorotrifluoromethane at 298.15 K

P_S, MPa				v_S^L, cm^3 mol^{-1}			
this work	ref *3*	ref *4*	ref *5*	this work	ref *3*	ref *4*	ref *5*
3.56	3.56	3.56	3.56	127.6	126.0	127.1	126.0

Results

The two pure components were studied in the same experimental equipment to compare our data to those of the literature.

Measurements have been performed for $CClF_3$ only at 298.15 K because its critical temperature is around 302 K. Results appear in Table II. Our bubble pressures are the same as those given in the "ASHRAE Handbook" (*3*), those of Vargaftik and Touloukian (*4*), and those of Oguchi et al. (*5*). Measured saturated liquid molar volumes are 0.4% higher than those of Vargaftik and Touloukian (*4*).

Measurements with CCl_2FCClF_2 were performed at three temperatures; below 323 K, pressures are too low to be accurately determined without changing the pressure transducer. Results appear in Table III. There is no difference between measured bubble pressures and those in the literature. There is very good agreement between measured saturated liquid molar volumes and those in the literature (mean deviation less than 0.3%).

Table III. Vapor Pressures and Saturated Liquid Molar Volumes of Trichlorotrifluoroethane at 323.15, 348.15, and 373.15 K

	P_S, MPa			v_S^L, cm^3 mol^{-1}		
T, K	this work	ref *3*	ref *4*	this work	ref *3*	ref *4*
323.15	0.11	0.11	0.109	124.9	124.6	124.6
348.15	0.23	0.235	0.231	130.4	130.2	130.0
373.15	0.44	0.445		137.1	136.7	

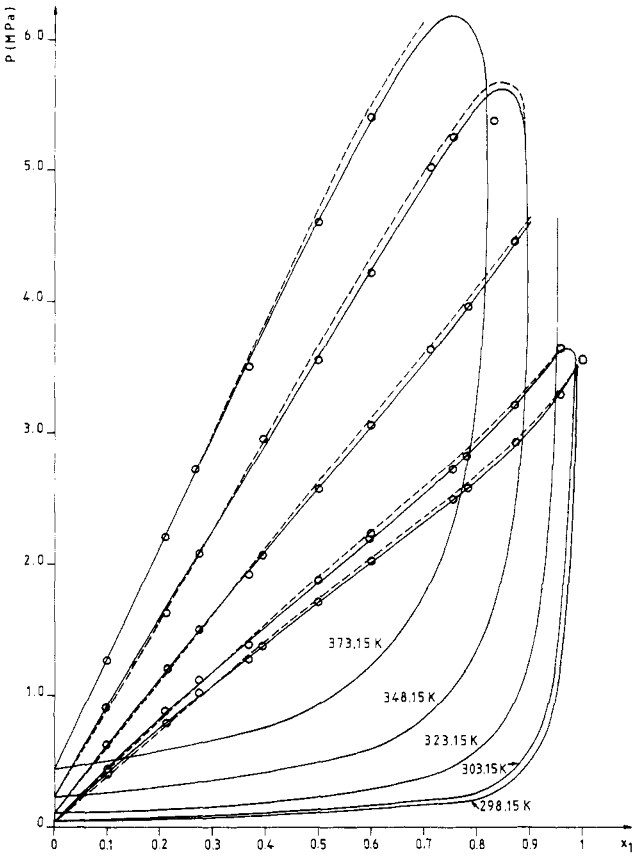

Figure 3. Pressure as a function of $CClF_3$ (1) mole fraction at different temperatures: (O) experimental; (- - -) calculated through Peng and Robinson equation (mixing rules 5–7); (—) calculated through Peng and Robinson equation (mixing rules 5, 6, 8, and 9).

Results for mixtures $CClF_3$–CCl_2FCClF_2 appear in Table IV. Columns 1–4 give respectively the liquid mole fraction of $CClF_3$, the bubble pressure, and the saturated liquid molar volume for each experimental determination.

The isotherms-bubble pressures vs. liquid mole fractions and the isoconcentrations-bubble pressures vs. temperatures are represented in Figures 3 and 4, respectively.

The isotherms-saturated liquid molar volume vs. liquid mole fraction and the isoconcentrations-saturated liquid molar volume vs. temperature are represented in Figures 5 and 6, respectively.

Representation of Experimental Results. The representation used in this work is based on the equation of state of Peng and Robinson (*2*). This equation was preferred to that of Soave (*6*) because it gives a better representation of volumetric data. The equation of state of Peng and Robinson is

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

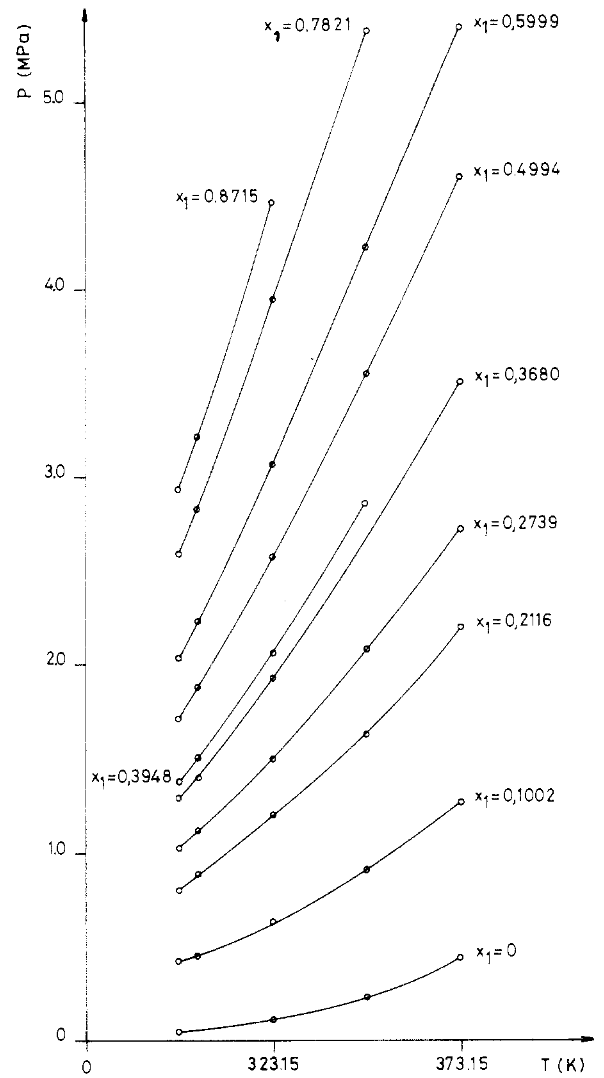

Figure 4. Pressure as a function of temperature at given $CClF_3$ (1) liquid mole fraction (experimental data).

At the critical temperature, pure-component parameters a and b are given by

$$a(T_c) = 0.45724R^2T_c^{\,2}/P_c \qquad (2)$$

$$b(T_c) = 0.07780RT_c/P_c \qquad (3)$$

Peng and Robinson set the temperature dependence of a as

$$a(T) = [1 + m(1 - (T_R)^{1/2}]^2 a(T_c) \qquad (4)$$

Pure-component vapor pressures in the whole temperature range of the study can be represented by the method of Asselineau et al. (7), using critical values P_c and T_c to obtain $a(T_c)$ and $b(T_c)$ from eq 2 and 3, and using one value of a pure-component vapor pressure remote from the critical point to obtain m. For chlorotrifluoromethane, m is found to be equal to 0.6399 from P_S(191.7 K) = 0.1013 MPa. For chlorotrifluoroethane, m is 0.7488 from P_S(323.15 K) = 0.11 MPa. Peng and Robinson suggest the following mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (5)$$

$$a_{ij} = (a_{ii}a_{jj})^{1/2}(1 - k_{ij}) \qquad (6)$$

$$b = \sum_i x_i b_{ii} \qquad (7)$$

k_{ij} is a binary interaction parameter, empirically determined, which characterizes the attractive forces between molecules i and j.

Table IV. Experimental Bubble Pressures and Saturated Liquid Molar Volumes along with Vapor Mole Fractions as a Function of Liquid Mole Fractions in the System Chlorotrifluoromethane (1)-Trichlorotrifluoroethane (2)

x_1	P, MPa	v_S^L, cm^3 mol^{-1}	y_1[a]
	T = 298.15 K		
0.1002	0.42	117.4	0.8816
0.2116	0.80	114.6	0.9383
0.2739	1.02	113.1	0.9508
0.3680	1.29	109.7	0.9620
0.3948	1.38_5	108.6	0.9642
0.4994	1.71	105.8	0.9709
0.5999	2.03	103.8	0.9754
0.7549	2.50	102.6	0.9810
0.7821	2.58_5	102.8	0.9820
0.8715	2.93	104.3	0.9857
0.9578	3.30	113.0	0.9919
	T = 303.15 K		
0.1002	0.45	118.5	0.8686
0.2116	0.89	115.8	0.9307
0.2739	1.12	114.0	0.9445
0.3680	1.40	110.3	0.9568
0.3948	1.51	109.5	0.9593
0.4994	1.88	107.2	0.9665
0.5996	2.20	105.4	0.9714
0.5999	2.23	105.6	0.9714
0.7549	2.73	104.5	0.9773
0.7821	2.83	105.1	0.9783
0.8715	3.21	108.8	0.9821
0.9578	3.54	120.5	0.9886
	T = 323.15 K		
0.1002	0.63	122.5	0.9091
0.2116	1.20	119.6	0.8940
0.2739	1.50	118.1	0.9133
0.3680	1.92	115.5	0.9304
0.3948	2.06_5	114.5	0.9338
0.4994	2.57	112.3	0.9434
0.5999	3.06	112.0	0.9491
0.7132	3.63	112.8	0.9529
0.7821	3.95_5	115.9	0.9542
0.8715	4.46	127.4	0.9533
	T = 348.15 K		
0.1002	0.91	128.2	0.7190
0.2116	1.63	125.3	0.8324
0.2739	2.08	124.0	0.8591
0.3948	2.86	121.6	0.8868
0.4994	3.55	120.2	0.8978
0.5996	4.22	122.3	0.9015
0.5999	4.22_5	122.2	0.9015
0.7132	5.02	133.4	0.8970
0.7549	5.26	138.8	0.8913
0.7821	5.38	143.0	0.8853
	T = 373.15 K		
0.1002	1.27	134.6	0.6156
0.2116	2.20	132.5	0.7520
0.2739	2.72	132.0	0.7855
0.3680	3.50	131.9	0.8136
0.4994	4.60	131.9	0.8273
0.5999	5.40	141.7	0.8218

[a] Calculated from Peng and Robinson's equation of state with mixing rules 5–7 (one parameter, k_{ij}).

To improve classical mixing rules, when computing volumetric properties, one can introduce a second binary interaction parameter, k'_{ij}

$$b = \sum x_i x_j b_{ij} \qquad (8)$$

with

$$b_{ij} = \frac{b_{ii} + b_{jj}}{2}(1 - k'_{ij}) \qquad (9)$$

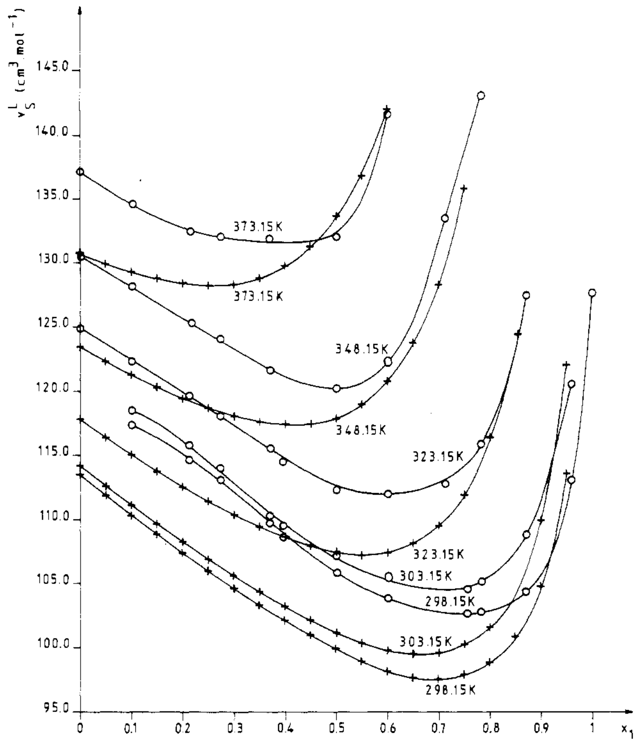

Figure 5. Experimental and calculated saturated liquid molar volumes as a function of CClF$_3$ (1) liquid mole fractions at different temperatures: (O) experimental; (+) calculated through Peng and Robinson equation of state, using mixing rules 5-7.

Mixing rules 5-7 or 5, 6, 8, and 9 are used to represent the present data, by equating vapor and liquid fugacities of each component, but it is useful to check the dispersion of data by using a more flexible mixing rule developed by Huron and Vidal (*8*). They derive new empirical mixing rules by relating the excess molar Gibbs energy to the fugacity coefficient ϕ of the mixture by

$$g^E = RT[\ln \phi(T,P,x_i) - \sum x_i \ln \phi(\text{pure } i,T,P)]$$

where ϕ is defined by

$$\ln \phi = \sum_i x_i \ln \phi_i \quad (10)$$

and calculated from eq 1 as

$$\ln \phi = \frac{Pv}{RT} - 1 - \ln\frac{P(v-b)}{RT} - \frac{a}{2\sqrt{2}bRT}\ln\frac{v+(1+\sqrt{2})b}{v+(1-\sqrt{2})b} \quad (11)$$

Equation 11 is also valid for the fugacity of a pure substance: ϕ(pure *i*, *T*, *P*). From eq 10 and 11 the following expression for g^E is found:

$$\frac{g^E}{RT} = \frac{Pv(x_i,T,P)}{RT} - \sum_i x_i\frac{Pv(\text{pure } i,P,T)}{RT} - \left\{\ln\frac{P[v(x_i,P,T)-b]}{RT} - \sum_i x_i \ln\frac{Pv(\text{pure } i,P,T)-b_i}{RT}\right\} - \frac{1}{2\sqrt{2}RT}\left[\frac{a}{b}\ln\frac{v(x_i,P,T)+(1+\sqrt{2})b}{v(x_i,P,T)+(1-\sqrt{2})b} - \sum_i x_i\frac{a_{ii}}{b_{ii}}\ln\frac{v(\text{pure } i,P,T)+(1+\sqrt{2})b_i}{v(\text{pure } i,P,T)+(1-\sqrt{2})b_i}\right] \quad (12)$$

The limit of g^E at infinite pressure has a finite value if mixing rule 7 is used for parameter *b*. The relation between g^E_∞ and the mixing rule for *a* is

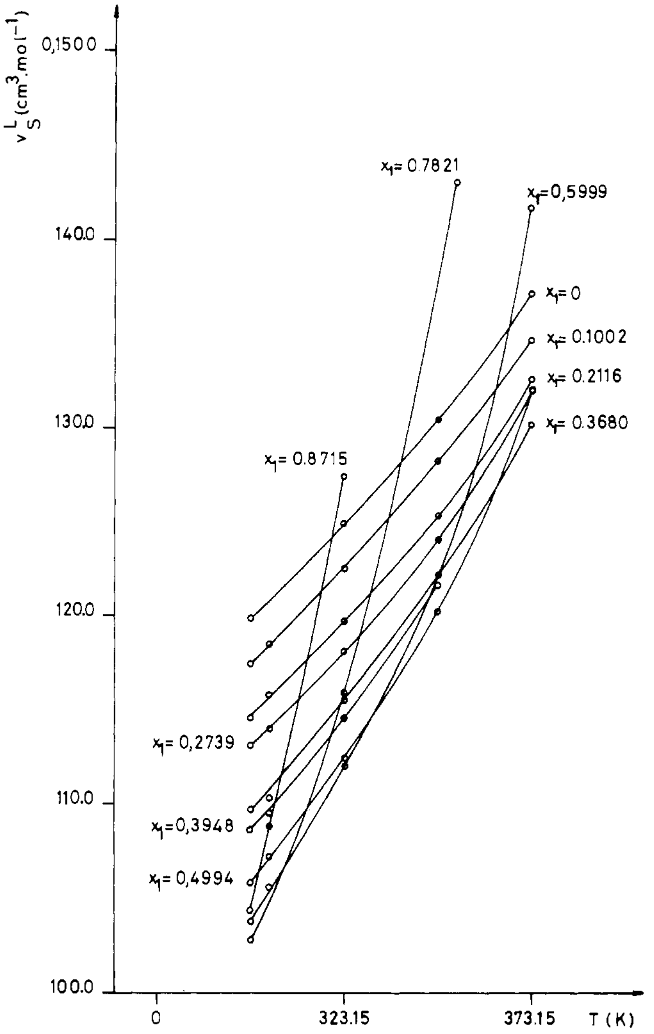

Figure 6. Saturated liquid molar volume as a function of temperature at given CClF$_3$ (1) mole fractions.

$$a(T) = b\left[\sum_i x_i\frac{a_{ii}(T)}{b_{ii}} + \frac{2\sqrt{2}}{\ln\dfrac{2-\sqrt{2}}{2+\sqrt{2}}}g^E_\infty\right] \quad (13)$$

To evaluate the dispersion of our experimental data, the polynomial expansion of Redlich and Kister (*9*) is chosen for g^E_∞ to obtain a flexible mixing rule for *a*:

$$g^E_\infty = RTx_1x_2\sum_{l=0}^{N_P} A_{l+1}(x_1 - x_2)^l \quad (14)$$

Parameters A_i are obtained by minimizing objective function *S*:

$$S = \sum_{N=1}^{N_T}(P_{i,\text{calcd}} - P_{i,\text{exptl}})^2/\sigma_P^2 \quad (15)$$

σ_P^2 is the resulting variance of pressure, *P*; it is obtained from experimental variances $\sigma_{\text{exptl},x}^2$, $\sigma_{\text{exptl},T}^2$, and $\sigma_{\text{exptl},P}^2$ assumed to be uncorrelated:

$$\sigma_P^2 = \sigma_{\text{exptl},P}^2 + (\partial P/\partial x)_T^2\sigma_{\text{exptl},x}^2 + (\partial P/\partial T)_x^2\sigma_{\text{exptl},T}^2 \quad (16)$$

where $\sigma_{\text{exptl},P} = 0.01$, $\sigma_{\text{exptl},x} = 0.0003$, and $\sigma_{\text{exptl},T} = 0.1$. Here, only the first term is significant in the left member of eq 16.

Under some conditions, when the normalized standard deviation $\sigma^N = [S/(N_T - N_P)]^{1/2}$ lies between 0.5 and 2.0, estimation of experimental errors can be considered valid (Peneloux

Table V. Parameters of Polynomial Mixing Rules Used in Peng and Robinson's Equation of State

T, K	no. of points	adjusted parameters A_1	A_2	σ^N	$\sigma_P{}^A$,[a] MPa
298.15	11	0.3741	0	2.2	0.02
		0.3485	0.0578	2.0	0.02
303.15	12	0.3288	0	1.5	0.015
		0.3341	−0.0120	1.5	0.015
323.15	10	0.2679	0	1.2	0.01
		0.2720	−0.0085	1.2	0.01
348.15	10	0.2107	0	2.7	0.03
		0.2171	−0.0104	2.8	0.03
373.15	6	0.1815	0	0.6	0.006
		0.1789	0.0072	0.4	0.004

[a] $\sigma_P{}^A = \sigma^N \sigma_{\text{exptl},P}$, absolute standard deviation in pressure.

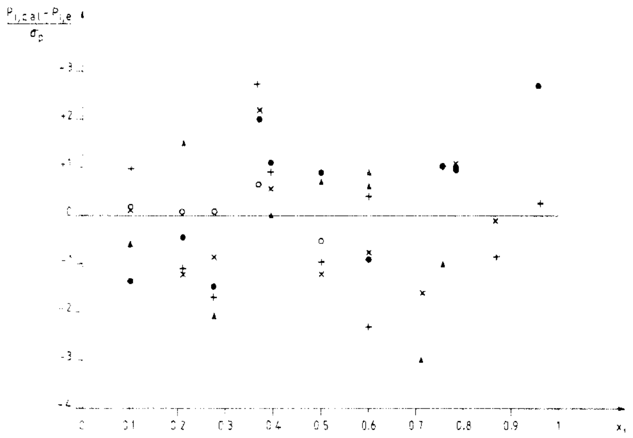

Figure 7. Normalized deviation in pressures for polynomial mixing rule with one or two parameters and given number of experimental points N_T and temperature T: (●) T = 298.15 K, N_T = 11, N_P = 2; (+) T = 303.15 K, N_T = 12, N_P = 2; (X) T = 323.15 K, N_T = 10, N_P = 1; (▲) T = 348.15 K, N_T = 10, N_P = 1; (O) T = 373.15 K, N_T = 6, N_P = 1.

Table VI. Representation of P, V, T, and x Data Through Peng and Robinson's Equation of State, Using Classical Mixing Rules

objective function[a]	mixing rules	k_{ij}	k'_{ij}	$\sigma'_P{}^A$,[b] MPa	$\sigma_P{}^R$,[c] %	$\sigma_v{}^R$,[d] %
	5-7	0		0.10	7.6	
$S_P{}^A$	5-7	0.0191		0.04		5.4
$S_P{}^R$	5-7	0.0259			2.0	5.4
$S_P{}^A$	5, 6, 8, 9	0.0099	−0.0182	0.02		4.7
$S_P{}^R$	5, 6, 8, 9	0.0088	−0.0215		1.0	4.6

[a] $S_P{}^A = \Sigma_{i=1}{}^{N_T}(P_{i,\text{calcd}} - P_{i,\text{exptl}})^2$. $S_P{}^R = \Sigma_{i=1}{}^{N_T}[(P_{i,\text{calcd}} - P_{i,\text{exptl}})^2/P_{i,\text{exptl}}{}^2]$. [b] $\sigma'_P{}^A = [S_P{}^A/(N_T - N_P]^{1/2}$. [c] $\sigma_P{}^R = [S_P{}^R/(N_T - N_P)]^{1/2}$. [d] $\sigma_v{}^R = [\Sigma_{i=1}{}^{N_T}(v^L{}_{i,\text{calcd}} - v^L{}_{i,\text{exptl}})/v^L{}_{i,\text{exptl}}]/(N_T - N_P)$.

et al. (*10*)). One and two parameters (A_{l+1}) were adjusted for each isothermal curve. Results are presented in Table V. σ^N is between 0.5 and 2.0, except for the isotherm at 348.15 K, as shown in Table V. Figure 7 represents $(P_{i,\text{calcd}} - P_{i,\text{exptl}})/\sigma_P$ as a function of mixture composition. The data points are randomly distributed. The experimental point corresponding to x_1 = 0.8715 at 348.15 K seems far off the curve. An explanation is that this point is close to the critical region. This explains also why σ^N for the isotherm at 348.15 K is higher than 2.0. At lower temperatures and higher concentrations (x_1 > 0.8), the dispersion of the points is more important because $(\partial P/\partial T)_x$ is larger and $\sigma_{\text{exptl},T}$ has more influence on σ_P (see Figure 4).

Moreover, the same data were represented by using the classical mixing rules 5-7 or 5, 6, 8, and 9 with zero, one, and two interaction parameters. The results are given in Table VI. Columns 4 and 5 give absolute and relative normalized standard deviations on pressures. It is not appropriate to assume k_{ij} = 0 for that mixture.

The one-parameter (k_{ij}) model gives a better representation which can still be improved by using the two-parameter (k_{ij}, k'_{ij}) model. It is found that the Peng-Robinson model with two parameters is equivalent to the Huron and Vidal model with one parameter, as can be seen by comparing results in $\sigma_P{}^A$ in Tables V and VI. It has the advantage of temperature-independent parameters.

Figure 5 shows saturated liquid molar volumes ($v_S{}^L$) vs. liquid mole fractions. Mean deviation between experimental and calculated values (see column 6 in Table VI), through the Peng and Robinson equation of state using mixing rules 5-7, is about 5%. For this mixture, the equation of state represents only qualitatively the volume contraction. No significant improvement has been observed by using mixing rules 5, 6, 8, and 9 or the mixing rules proposed by Huron and Vidal (*8*).

Acknowledgment

We are grateful to Professor J. Vidal for helpful discussions and the use of his computer programs.

Glossary

A_l	Redlich-Kister polynomial parameters
a, b	Peng-Robinson equation of state parameters
g	Gibbs free energy
k	interaction parameter associated with a
k'	interaction parameter associated with b
m	parameter in eq 4
n_T	total number of moles in the equilibrium cell
N_T	number of experimental points
N_P	number of parameters
P	pressure, MPa
P_b	bubble pressure, MPa
R	gas constant
S	objective function
T	temperature, K
v	molar volume, cm^3 mol^{-1}
V	volume of one phase (either vapor or liquid)
V_M	maximum volume of the cell
V_T	total volume offered to the compressed mixture, cm^3
x	liquid mole fraction
y	vapor mole fraction
z	total mole fraction

Superscripts

A	absolute value
E	excess value
L	liquid
R	relative value
N	normalized property

Subscripts

b	bubble property
c	critical property
exptl	experimental value
calcd	calculated value
i, j	component identification
l	index in Redlich-Kister expansion
r	reduced property
S	saturated property
∞	at infinite pressure

Greek Letters

ϕ	fugacity coefficient of the mixture
ϕ_i	fugacity coefficient of component i in the mixture
σ	standard deviation
ω	acentric factor

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Vapor–Liquid Equilibria of Methane–Benzene, Methane–Methylbenzene (Toluene), Methane–1,3-Dimethylbenzene (*m*-Xylene), and Methane–1,3,5-Trimethylbenzene (Mesitylene) at 313.2 K up to the Critical Point

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A static method, described in a previous article, has been used to perform high-pressure vapor–liquid equilibria up to the critical point on methane–aromatic hydrocarbon systems. Comparisons with literature data are presented. New data are given for the systems methane–*m*-xylene and methane–mesitylene.

Introduction

Methane solubility in hydrocarbons is a very important property for optimization of tertiary oil recovery processes by miscible gas drive. The data on many methane–hydrocarbon binary systems were already reported, but new measurements up to the critical point are needed to determine the influence of the chemical nature and degree of branching of the hydrocarbon upon vapor–liquid equilibria. Here the degree of substitution of methyl groups for hydrogen on the benzene ring is considered, and the data of several authors are compared to present data to establish a basis for choice of the most reliable experimental method and source of data.

Experimental Section

Apparatus. The experimental setup described in a previous paper (*1*) is based on a static method. The equilibrium cell with an internal capacity of 100 cm^3 is kept at constant temperature (±0.25 K) in an air thermostat. Pressure measurements inside the cell are obtained within 10^5 Pa through a pressure transducer (BLH type GPH 0–1380 × 10^5 Pa) calibrated at the equilibrium temperature against a dead-weight gauge (Budenberg type 280 H). The temperature is read through calibrated thermocouples within 0.2 K. The mixture is vigorously stirred by means of a small magnet rotating in a magnetic field induced by four solenoids located outside the cell.

Sampling of both phases is achieved by using two microcells the internal volumes of which are less than 15 μL. Analysis of the samples is performed by gas chromatography using an original injection port assembly. This original sampling method associated with gas-chromatography analysis is especially suitable for study of mixtures at equilibrium temperatures lower than the boiling point of one or several components. Mean accuracies have been estimated within 0.01 for liquid mole fractions and 0.005 for vapor mole fractions.

Table I. Density and Refractive Index of Liquid Components

	refractive index at 293.15 K		density at 293.15 K	
	this work	lit. values (*15*)	this work	lit. values (*15*)
benzene	1.5012_6	1.501 12	0.8791_7	0.8790
toluene	1.4969_1	1.496 93	0.8669_8	0.86696
m-xylene	1.4975_8	1.497 22	0.8643_4	0.86417
mesitylene	1.4995_2	1.499 37	0.8653_3	0.8653

Table II. Vapor-Liquid Equilibrium Data for the System Methane (1)-Benzene (2) at $T = 313.2$ K

$10^{-5}P$, Pa	x_1	y_1	K_1	K_2
36.6	0.0986	0.987[a]	10.01	0.014
36.6		0.987		
101.0	0.210	0.987[a]	4.70	0.016_5
101.0	0.212		4.66	
148.7	0.287	0.986	3.44	0.020
148.7	0.288		3.42	
199.8	0.369	0.984[a]	2.67	0.025
199.8	0.367		2.68	
250.3	0.442	0.977	2.21	0.041
250.3	0.439		2.23	
310.4	0.521	0.951	1.83	0.102
351.1	0.593	0.883	1.49	0.287
351.1	0.586		1.51	0.283
368.7	0.661	0.836	1.27	0.47
368.7		0.840		0.48
374.2	0.688	0.801	1.16	0.64
374.2		0.805	1.17	0.63

[a] Interpolated values.

Chemicals. Methane was supplied by Air-Gas with a specified minimum purity of 99.95 vol %. Benzene, toluene, and *m*-xylene were purchased from Merck with reported GLC purities of 99.7%, 99.5%, and 98.5%, respectively. The impurities contained in *m*-xylene were *o*-xylene (0.5%), *p*-xylene (0.5%), and ethylbenzene (0.5%). Mesitylene was obtained