Table II. Generalized Correlation Curve Parameters

acid	W_0, mol/kg	$(RT/E)^{2.1}$	affinity coeff[a]
oxalic	1.6278	0.04488	0.8625
malonic	2.4585	0.02711	1.1063
succinic	1.3848	0.02927	1.0000
glutaric	1.8347	0.01692	1.2750
adipic	1.2093	0.03349	0.9125
pimelic	1.4156	0.02735	0.9938

[a] $\beta = E/E_0$. Succinic acid was chosen as the standard substance, $E_{\text{succinic}} = E_0$.

a fit to the data as did the potential theory, they are not shown in this paper. The application of these equations to the adsorption of dicarboxylic acids was shown by Lee et al. (*2*) to be inferior to the potential theory.

Glossary

C	equilibrium solution concentration
C_s	solubility in water
E	characteristic energy
E_0	characteristic energy of a standard component
n	parameter of the Dubinin–Astakhov equation
R	gas constant
T	temperature
W	filled volume, $W = X/\rho$
W_0	parameter of the Dubinin–Astakhov equation (total pore volume)
X	weight of substance adsorbed
β	affinity coefficient
ϵ	adsorption potential
ρ	liquid density

Registry No. Carbon, 7440-44-0; glutaric acid, 110-94-1; adipic acid, 124-04-9; pimelic acid, 111-16-0.

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Bubble Pressures and Saturated Liquid Molar Volumes of Trifluorotrichloroethane–Fluorochlorohydrocarbon Mixtures. Experimental Data and Modelization

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An apparatus described elsewhere has been used to get bubble pressure and saturated liquid molar volume data at four temperatures for binary systems composed of trifluorotrichloroethane (Refrigerant R113) with trifluoromethane (Refrigerant R23) and difluoroethane (Refrigerant R152A), and a ternary system composed of trifluorotrichloroethane–difluoroethane–difluorodichloromethane (Refrigerant R12). Experimental bubble pressures of the two binary systems are represented within 2% by a one adjustable parameter cubic equation of state. Without use of an interaction parameter, the cubic equations of state are not able to reproduce accurately the experimental data (standard deviations as high as 20 and 25%). A volume translation, used in combination with the Peng–Robinson equation of state, makes it possible to simultaneously represent vapor–liquid equilibria and saturated liquid molar volumes within 2%.

Introduction

This work is a part of a project to extend the thermodynamic data base on refrigerant mixtures. A bibliographic study was cited in a paper by Meskel-Lesavre (*1*) along with new experimental results. Other new data on refrigerant systems are available in ref *2* and *3* along with details about the apparatuses used.

The static method with a variable volume cell which is very convenient for liquid-phase studies was used here. The corresponding apparatus is the same as that in ref *3*.

Experimental Section

Details about the experimental equipment are given in papers *3* and *4*. The accuracy of pressure, temperature, and composition measurements are given in the tables of results.

Chemicals. Difluoroethane was supplied by Matheson with a certified GPC minimum purity of 98%, trifluorotrichloroethane by Labosi with a certified GPC minimum purity of 99.9%, and trifluoromethane and difluorodichloromethane by Dehon with respective certified GPC minimum purities of 99 and 99.9%.

Results

Experimental results appear in Tables I–III. Experimental errors on mole fractions and saturated molar volumes reported in the tables come from expressions cited in paper 3.

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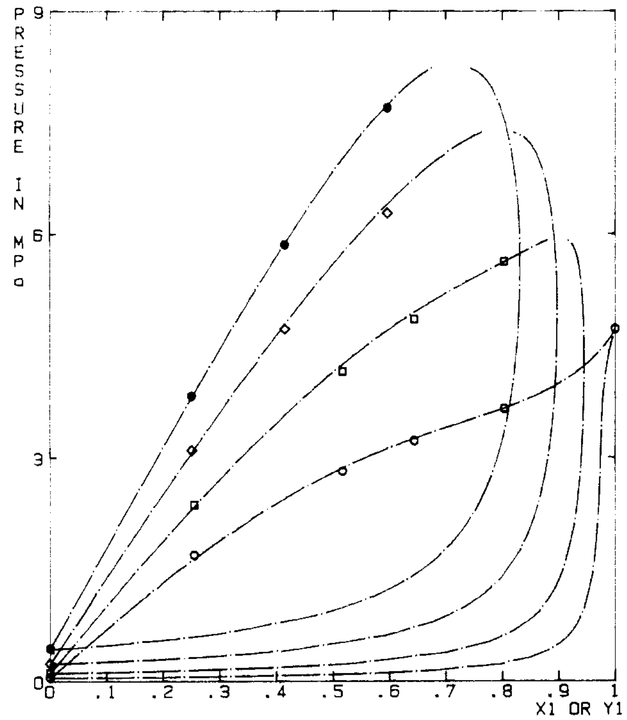

Figure 1. Pressure vs. composition equilibrium diagram for the trifluoromethane (1)–trifluorotrichloroethane (2) mixture at different temperatures. Experimental data: (○) at 298 K; (□) at 323 K; (◇) at 348 K; (●) at 373 K. Calculated results with the Peng–Robinson equation of state and $\delta_{ij} = 0.111$, •–•.

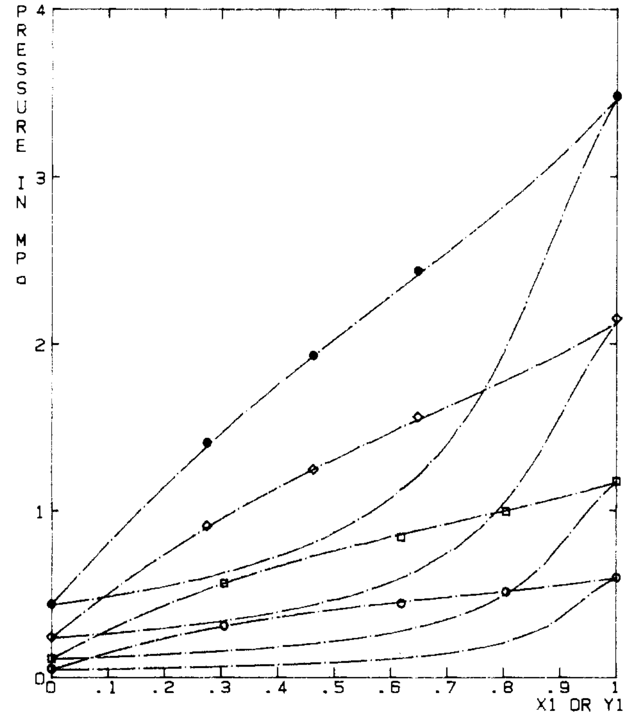

Figure 2. Pressure vs. composition equilibrium diagram for the difluoroethane (1)–trifluorotrichloroethane (2) mixture at different temperatures. Experimental data: (○) at 298 K; (□) at 323 K; (◇) at 348 K; (●) at 372 K. Calculated results with the Peng–Robinson equation of state and $\delta_{ij} = 0.084$, •–•.

Pressures and saturated molar volumes as a function of mole fractions are plotted respectively in Figures 1 and 2 and Figures 3 and 4.

Representation of Experimental Results. Three cubic equations of state were used here and quite similar results were obtained with each of them. The one binary parameter Peng–Robinson (*5*) equation of state is significantly the best to compute the saturated liquid molar volumes (standard deviation is about 5%, while for Soave (*6*) and Mathias (*7*) equations it is close to 18%). Only caculations with the Peng–Robinson

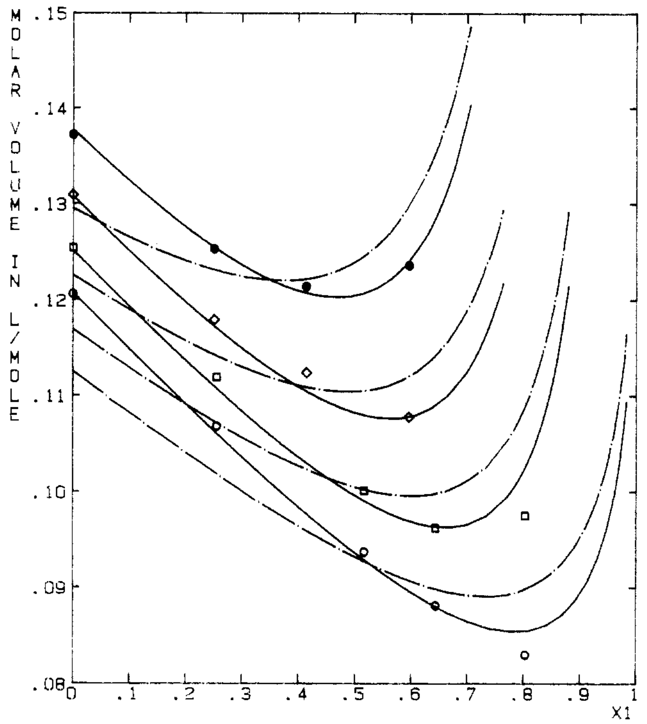

Figure 3. Saturated liquid molar volumes vs. composition diagram for the trifluoromethane (1)–trifluorotrichloroethane (2) mixture at various temperatures. Experimental data: (○) at 298 K; (□) at 323 K; (◇) at 348 K; (●) at 373 K. Calculated results with the Peng–Robinson equation of state and $\delta_{ij} = 0.111$, –•–•. Calculated results with the Peng–Robinson equation of state, $\delta_{ij} = 0.111$ and volume translation, —.

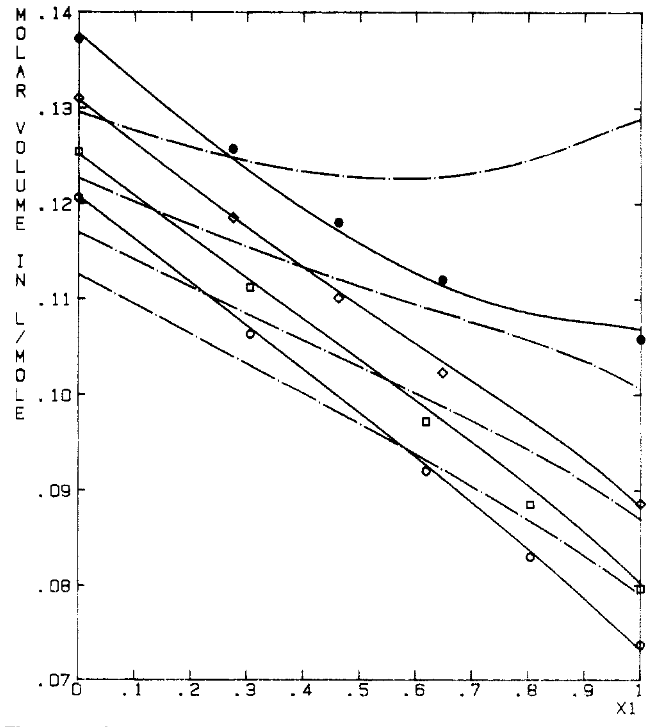

Figure 4. Saturated liquid molar volumes versus composition diagram for the difluoroethane (1)–trifluorotrichloroethane (2) mixture at various temperatures. Experimental data: (○) at 298 K; (□) at 323 K; (◇) at 348 K; (●) at 372 K. Calculated results with the Peng–Robinson equation of state and $\delta_{ij} = 0.084$, –•–•. Calculated results with the Peng–Robinson equation of state, $\delta_{ij} = 0.084$ and volume translation, —.

Table I. Experimental Bubble Pressures and Saturated Liquid Molar Volumes, and Calculated Bubble Pressures and Vapor Mole Fractions, y_1, corresponding to Liquid Mole Fraction, x_1, and Temperature, T, for the Trifluoromethane (1)-Trifluorotrichloroethane (2) Mixture[a]

T, K	P_{exptl},[b] MPa	$x_{1,\mathrm{exptl}}$	Δx ($\times 10^{-4}$)	v^{LS} ($\times 10^{-3}$) L·mol^{-1}	Δv^{LS} ($\times 10^{-4}$), L·mol^{-1}	P_{calcd}, MPa	$y_{1,\mathrm{calcd}}$
298.1	1.688 (2)	0.2551_4	0.3	106.8	1	1.639	0.963
298.0_5	2.815 (2)	0.5170_3	0.6	93.7	1	2.857	0.974
298.1_5	3.224 (3)	0.6444_5	1	88.1	1	3.260	0.976
298.0_5	3.654 (3)	0.8034_9	1	83.0	1	3.656	0.978
322.9_5	0.112 (1)	0		125.4	2	0.111	0
322.6	2.362 (2)	0.2551_4	0.3	111.9	1	2.328	0.933
322.8_5	4.151 (2)	0.5170_3	0.6	100.1	1	4.247	0.945
322.9_5	4.852 (3)	0.6444_5	1	96.2	1	4.949	0.943
322.8	5.627 (3)	0.8034_9	1	97.5	1	5.613	0.935
347.6_5	0.231 (1)	0		130.8	2	0.231	0
348.0_5	3.097 (2)	0.2508_9	0.4	117.9	2	3.058	0.883
348.2	4.720 (3)	0.4148_1	0.5	112.4	1	4.783	0.898
348.3	6.275 (3)	0.5966_3	1	107.8	1	6.399	0.884
372.3_5	0.435 (1)	0		137.2	2	0.433	0
371.9	3.821 (2)	0.2508_9	0.4	125.3	2	3.786	0.818
373.0_5	5.855 (3)	0.4148_1	0.5	121.4	1	5.892	0.830
372.9	7.685 (3)	0.5966_3	1	123.6	1	7.741	0.794

[a] $T = \pm 0.1$ K. [b] (1) $\Delta P = \pm 0.003$ MPa. (2) $\Delta P = \pm 0.005$ MPa. (3) $\Delta P = \pm 0.008$ MPa.

Table II. Experimental Bubble Pressures and Saturated Liquid Molar Volumes, and Calculated Bubble Pressures and Vapor Mole Fractions, y_1, corresponding to Liquid Mole Fraction, x_1, and Temperature, T, for the Difluoroethane (1)-Trifluorotrichloroethane (2) Mixture[a]

T, K	P_{exptl},[b] MPa	$x_{1,\mathrm{exptl}}$	Δx ($\times 10^{-4}$)	v^{LS} ($\times 10^{-3}$), L·mol^{-1}	Δv^{LS} ($\times 10^{-4}$), L·mol^{-1}	P_{calcd}, MPa	$y_{1,\mathrm{calcd}}$
298.2	0.307 (2)	0.3058_8	0.5	106.3	2	0.306	0.877
298.3	0.442 (2)	0.6188_4	1	92.0	2	0.453	0.938
298.4	0.513 (2)	0.8043_8	1	83.0	1	0.519	0.961
298.1	0.595 (2)	1		73.6	1	0.594	1
322.9_5	0.112 (2)	0		125.4	2	0.111	0
323.0	0.563 (2)	0.3058_8	0.5	111.2	2	0.564	0.832
323.0	0.841 (2)	0.6188_4	1	97.2	2	0.859	0.917
323.0_5	0.994 (2)	0.8043_8	1	88.5	1	1.002	0.951
323.0	1.177 (2)	1		79.7	1	1.173	1
347.6_5	0.231 (2)	0		130.8	2	0.231	0
348.3	0.908 (2)	0.2751_3	0.5	118.5	4	0.894	0.760
348.5	1.246 (1)	0.4623_5	0.8	110.1	2	1.247	0.845
348.6_5	1.560 (1)	0.6482_0	1	102.3	2	1.546	0.896
348.1	2.131 (3)	1		88.6	1	2.107	1
372.3_5	0.435 (2)	0		137.2	2	0.433	0
372.5_5	1.405 (2)	0.2751_3	0.5	125.7	2	1.384	0.696
372.5	1.929 (1)	0.4623_5	0.8	118.0	2	1.921	0.798
372.6	2.434 (1)	0.6482_0	1	112.0	2	2.413	0.861
372.3	3.462 (3)	1		105.8	1	3.449	1

[a] $T = \pm 0.1$ K. [b] (1) $\Delta P = \pm 0.005$ MPa. (2) $\Delta P = \pm 0.003$ MPa. (3) $\Delta P = \pm 0.008$ MPa.

Table III. Experimental Bubble Pressures and Saturated Liquid Molar Volumes for the Difluoroethane (1)-Difluorodichloromethane (2)-Trifluorotrichloroethane (3) Mixture at Different Temperatures[a]

T, K	P_{exptl},[b] MPa	$x_{1,\mathrm{exptl}}$	Δx_1 ($\times 10^{-4}$)	$x_{2,\mathrm{exptl}}$	Δx_2 ($\times 10^{-4}$)	$x_{3,\mathrm{exptl}}$	Δx_3 ($\times 10^{-4}$)	v^{LS} ($\times 10^{-3}$), L·mol^{-1}	Δv^{LS} ($\times 10^{-4}$), L·mol^{-1}
298.0_5	0.307 (2)	0.1482_7	1	0.1777_3	0.4	0.6740_0	1	108.4	1
298.2_5	0.425 (2)	0.1970_4	1	0.3034_7	0.9	0.4994_5	1	102.7	2
298.0_5	0.595 (2)	0.2982_0	0.5	0.4596_7	0.8	0.2421_3	0.4	93.6	1
322.9_5	0.112 (2)	0		0		1		125.4	2
323.0_5	0.556 (2)	0.1482_7	1	0.1777_3	0.4	0.6740_0	1	113.4	2
323.0	0.767 (2)	0.1970_4	1	0.3034_7	0.9	0.4994_5	1	107.9	2
322.9_5	1.087 (2)	0.2982_0	0.5	0.4596_7	0.8	0.2421_3	0.4	99.6	1
347.6_5	0.231 (2)	0		0		1		130.8	2
347.9_5	0.238 (2)	0		0		1		130.9	1
348.3_5	0.757 (2)	0.0978_0	1.5	0.1486_5	1	0.7535_5	2	122.4	5
348.1_5	1.256 (1)	0.1986_1	1	0.2929_9	1	0.5084_0	1.7	114.2	3
348.4_5	1.794 (1)	0.3083_3	1	0.4108_6	1.3	0.2808_2	0.9	108.1	2
372.3_5	0.435 (2)	0		0		1		137.2	2
373.1	1.182 (2)	0.0978_0	1.5	0.1486_5	1	0.7535_5	2	130.1	5
372.8_5	1.944 (1)	0.1986_1	1	0.2929_9	1	0.5084_0	1.7	122.8	3
372.8	2.743 (1)	0.3083_3	1	0.4108_6	1.3	0.2808_2	0.9	119.1	2

[a] $T = \pm 0.1$ K. [b] (1) $\Delta P = \pm 0.005$ MPa; (2) $\Delta P = \pm 0.003$ MPa.

equation of state are reported in this paper. To improve saturated density representation, we used a volume translation (*8*). This latter was performed directly on the saturated molar volume data computed through the Peng–Robinson equation of state obtained through the following equations:

$$v_{\mathrm{trans}} = v_{\mathrm{calcd}} - \sum_i c_i x_i \tag{1}$$

with

$$c_i = \sum_{J=1}^{3} c_{i,J} T^{J-1} \tag{2}$$

v_{trans} is the translated volume.

Critical parameters T_c and P_c and acentric factors used in calculations are reported in Table IV.

Parameter adjustments were carried out by minimizing the objective function Q, temperature and liquid composition being chosen as independent variables:

$$Q = \sum_{J=1}^{n} \left[\frac{P_{J,\mathrm{exptl}} - P_{J,\mathrm{calcd}}}{P_{J,\mathrm{exptl}}} \right]^2 \tag{3}$$

Data representation results appear in Table V. If the interaction parameter is not adjusted and has a null value, the resulting computed bubble pressures are very far from experimental data (deviation of 23% on the trifluoromethane–trifluorotrichloroethane system and 26% on the difluoroethane–trifluorotrichloroethane system). By adjusting one interaction parameter in the mixing rule for the energy parameter, a, the corresponding deviations are decreased to less than 2% (see Table V). Adjusting a second parameter on the mixing rule for the volume parameter, b, has no significant influence on the quality of representation.

Relative standard deviations given in Table V were calculated through eq 4

$$\sigma^{R}_{u} = 100 \left[\sum_{i=1}^{n} \left(\frac{u_{i,\mathrm{exptl}} - u_{i,\mathrm{calcd}}}{u_{i,\mathrm{exptl}}} \right)^2 \Big/ (n - m) \right]^{1/2} \tag{4}$$

where u is either P, v, or v_{trans} and, m is the number of parameters used ($m = 1$ for data reported in Table V).

For trifluorotrichloroethane and difluoroethane, the parameters $c_{i,J}$ were obtained by adjustment on pure-component densities at respectively three and four experimental temperatures. The $c_{i,J}$ parameters for trifluoromethane, which is supercritical at temperatures higher than 298.75 K, were adjusted on the trifluoromethane–trifluorotrichloroethane saturated density data. $c_{i,J}$ data appear in Table VI. The results of the representation are reported in Table V. We may note that $\sigma^{R}_{v_{\mathrm{trans}}}$ is in both cases lower than 2%. By examining figures 3 and 4, we may note the curves, obtained through volume translations, are in very good agreement with experimental data.

Glossary

a	energy parameter in the Peng–Robinson equation of state
b	volume parameter in the Peng–Robinson equation of state
c_i	pure-component parameter in eq 3, L·mol^{-1}
n	number of experimental points
P	pressure, MPa
Q	objective function in eq 3
T	temperature, K
v	molar volume, L·mol^{-1}
x	liquid mole fraction
w	acentric factor

Table IV. Critical Parameters and Acentric Factors Used in the Cubic Equations of State[a]

refrigerant	crit press., MPa	crit. temp., K	acentric factor
trifluorotrichloroethane (R113)	3.44 (1)	487.26 (1)	0.252 (1)
trifluoromethane (R23)	4.78 (2)	298.75 (2)	0.272 (2)
difluoroethane (R152A)	4.50 (1)	386.70 (1)	0.270 (1)

[a] (1) Data from ref *9*. (2) Data from ref *10*.

Table V. Representation of Vapor–Liquid Equilibria and Saturated Liquid Molar Volumes of Refrigerant Binary Mixtures Using the Peng–Robinson Equation of State

mixture	no. of binary data used for adjustment[a]	δ_{ij}	σ^{R}_{P}, %	σ^{R}_{V}, %	$\sigma_{V\mathrm{trans}}$, %
trifluoromethane–	14	0	23	3.7	
trifluorotrichloroethane		0.111	1.4	5.1	1.6
difluoroethane–	12	0	16	7.2	
trifluorotrichloroethane		0.084	1.1	7.7	0.8

[a] All experimental binary data are included in the data treatment.

Table VI. $C_{i,j}$ Parameter Values Used in the Volume Translation

refrigerant	C_{i1}, 10^{-3} L·mol^{-1}	C_{i2}, 10^{-3} L·mol^{-1}·K^{-1}	C_{i3}, 10^{-3} L·mol^{-1}·K^{-2}
trifluorotrichloroethane (R113)	−8.20	0	0
trifluoromethane (R23)	−24.0	0.105	0
difluoroethane (R152A)	357.6	−2.30	0.00375

Subscripts

c	critical property
calcd	calculated property
exptl	experimental property
i,j	components i and j
P	pressure
trans	translated property
V	volume

Superscripts

R	relative quantity

Greek Letters

δ	binary interaction parameter
Δ	uncertainty
σ	standard deviation

Registry No. R113, 76-13-1; R23, 75-46-7; R152A, 75-37-6; R12, 75-71-8.

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