v_i	liquid molar volume
x_i	liquid-phase mole fraction

Subscripts

1	solute
2	solvent

Registry No. CCl_4, 56-23-5; CS_2, 75-15-0; butanone, 78-93-3; chloroform, 67-66-3; 1,4-dioxane, 123-91-1; ethanol, 64-17-5; hexane, 110-54-3; nitromethane, 75-52-5; octane, 111-65-9; toluene, 108-88-3; cyclohexane, 110-82-7; acetone, 67-64-1; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 2-propanol, 67-63-0; methanol, 67-56-1; heptane, 142-82-5; methylcyclohexane, 108-87-2; ethyl acetate, 141-78-6; methyl iodide, 74-88-4.

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Bubble Pressures and Saturated Liquid Molar Volumes of Binary and Ternary Refrigerant Mixtures

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All measurements have been performed with a static apparatus using a variable volume cell described previously. The results are given at two temperatures for the dichlorotetrafluoroethane (1)-perfluoro-2-butyltetrahydrofuran (2) system [R114-FC75] and four temperatures for the three systems trifluoromethane (1)-trichlorofluoromethane (2) [R23-R11], trifluoromethane (1)-chlorodifluoromethane (2)-trichlorofluoromethane (3) [R23-R22-R11], and trifluoromethane (1)-chlorodifluoromethane (2)-dichlorotetrafluoroethane (3) [R23-R22-R114]. Experimental data of binaries are well represented by the one adjustable parameter Peng-Robinson equation of state involving a volume translation (simultaneous representation of vapor-liquid equilibria and saturated liquid molar volumes within 2%).

Introduction

This work is a continuing part of the development of a thermodynamic data base on refrigerant mixtures. Several systems have already been studied in the same laboratory (*1-4*).

The static method with a variable volume cell, which is very convenient for liquid-phase studies, was used here. Liquid composition is determined through accurate weighing on an analytical balance of 10^{-7}-kg sensitivity. The static cell used in this work is that described in Valtz et al. (*3*).

Experimental Section

Apparatus. Details about the equipment are given in Valtz et al. (*3*) and Fontalba et al. (*5*). The equipment was used as described in Valtz et al. (*3*).

Table I. Origin and Purity of Chemicals

component	origin	purity, % GLC
trichlorofluoromethane	Dehon	>99.9
chlorodifluoromethane	Prestogaz	>98
trifluoromethane	Dehon	>99
dichlorotetrafluoroethane	Dehon	>99.8
perfluoro-2-butyltetrahydrofuran	3M France	>95

Materials. The origin and purity of the chemicals are given in Table I. They were used without any further purification except for a careful degassing of the liquids.

Results

Two binary systems have been studied; results are reported in Tables II and III and displayed in Figures 1-4. The accuracies on data determination are either given inside the tables or in their legends. Figures 1 and 2 represent diphasic envelopes $P = f(x_1$ or $y_1)$, respectively, for trifluoromethane (1)-trichlorofluoromethane (2) at four temperatures and dichlorotetrafluoroethane-perfluoro-2-butyltetrahydrofuran at two temperatures. Figures 3 and 4 represent saturated liquid molar volumes as a function of mole fractions for the same two binary systems. The results on the two ternary systems are given in Tables IV and V.

Data simulation was performed with use of Soave (*6*) and Peng-Robinson (P-R) (*7*) equations of state (see Appendix). Quite similar results are obtained for bubble curve modeling with each of these equations. However, saturated liquid molar volumes are best represented by the Peng-Robinson equation of state when a volume translation is used. Only our calculations with the Peng-Robinson equation of state are reported here.

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Table II. Bubble Pressures and Saturated Liquid Molar Volumes as a Function of Temperature and Composition for the System Trifluoromethane (1)–Trichlorofluoromethane (2) [R23–R11]

T^a/K	P^b/MPa	x_1	$\sigma_{x_1}/10^{-4}$	$y_{1cal}{}^c$	$P_{cal}{}^c$/MPa	v^{LS}/(dm^3/mol)	$\sigma_{v^{LS}}/(10^{-4}$ dm^3/mol)
298.2_5	0.099 (1)	0				0.0931	1
298.1_5	2.028 (2)	0.2520_2	0.6	0.9315	1.994	0.0872	2
298.1_5	2.981 (2)	0.4999	1	0.9480	3.050	0.0821	2
298.3	3.590 (2)	0.7488	1	0.9545	3.592	0.0799	1
322.7_5	2.852 (2)	0.2520_2	0.6	0.8847	2.846	0.0919	2
322.9	4.424 (2)	0.4999	1	0.9029	4.567	0.0891	2
348.1_5	0.461 (1)	0				0.1019	1
348.0	3.212 (2)	0.2003_2	0.3	0.7980	3.177	0.0987	1
347.9_5	5.230 (2)	0.3997_6	0.8	0.8327	5.358	0.0975	1
348.2	6.335 (2)	0.5440	1	0.8182	6.516	0.0999	1
373.2_5	0.817 (1)	0				0.1084	1
372.9_5	4.053 (2)	0.2003_2	0.3	0.7039	4.018	0.1060	1
372.6	6.522 (2)	0.3997_6	0.8	0.7369	6.607	0.1079	1
372.3	7.727 (2)	0.5440	1	0.6949	7.860	0.1187	2

[a] Standard deviation: 0.1 K. [b] Numbers in parentheses correspond to the following deviations: (1) 0.005; (2) 0.008 MPa. [c] Calculated with the one-parameter Peng–Robinson equation of state. $\delta_{ij} = 0.129$.

Table III. Bubble Pressures and Saturated Liquid Molar Volumes as a Function of Temperature and Composition for the System Dichlorotetrafluoroethane (1)–Perfluoro-2-butyltetrahydrofuran (2) [R114–FC75]

T^a/K	P^b/MPa	x_1	$\sigma_{x_1}/10^{-4}$	$y_{1cal}{}^c$	$P_{cal}{}^c$/MPa	v^{LS}/(dm^3/mol)	$\sigma_{v^{LS}}/(10^{-4}$ dm^3/mol)
398.0_5	0.188	0				0.2819	2
398.0	0.609	0.2471_2	0.9	0.7000	0.612	0.2523	3
398.2_5	1.112	0.5147_3	1	0.8576	1.114	0.2224	2
398.1_5	1.604	0.7457_5	1	0.9280	1.602	0.1941	2
397.5_5	2.261	1				0.1678	2
423.4_5	0.355	0				0.3010	2
422.9_5	0.918	0.2471_2	0.9	0.6101	0.915	0.2720	3
423.2	1.622	0.5147_3	1	0.7935	1.607	0.2462	2
423.2	2.351	0.7457_5	1	0.8821	2.318	0.2230	2
418.8_5	3.270	1				0.2407	2

[a] Standard deviation: 0.1 K. [b] Standard deviation: 0.005 MPa. [c] Calculated with the one-parameter Peng–Robinson equation of state. $\delta_{ij} = 0.019$.

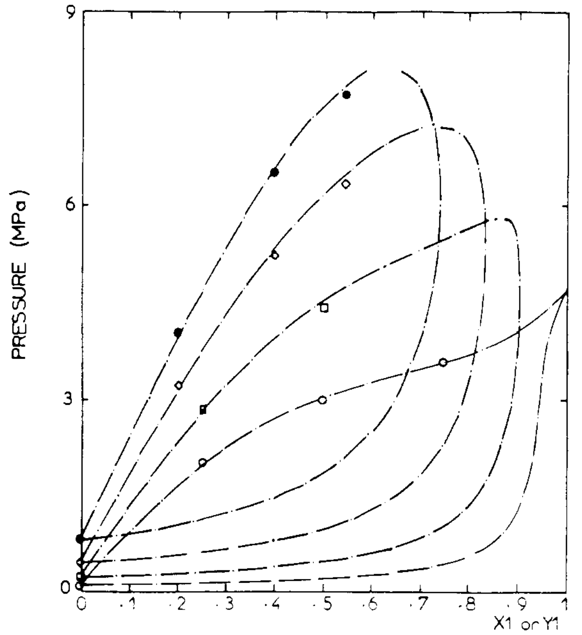

Figure 1. Pressure vs composition equilibrium diagram for the trifluoromethane (1)-trichlorofluoromethane (2) [R23-R11] mixture at different temperatures. Key: experimental data, (○) at 298 K, (□) at 323 K, (◇) at 348 K, (●) at 373 K; (–•–) calculated results with the Peng-Robinson equation of state and $\delta_{ij} = 0.129$.

Calculated pressure and vapor mole fractions are given in Tables II and III, along with the experimental results. The simulation of data is summarized in Table VI, with values of the binary interaction parameter adjusted by minimizing the objective function, Q, with the temperature and liquid composition being chosen as independent variables.

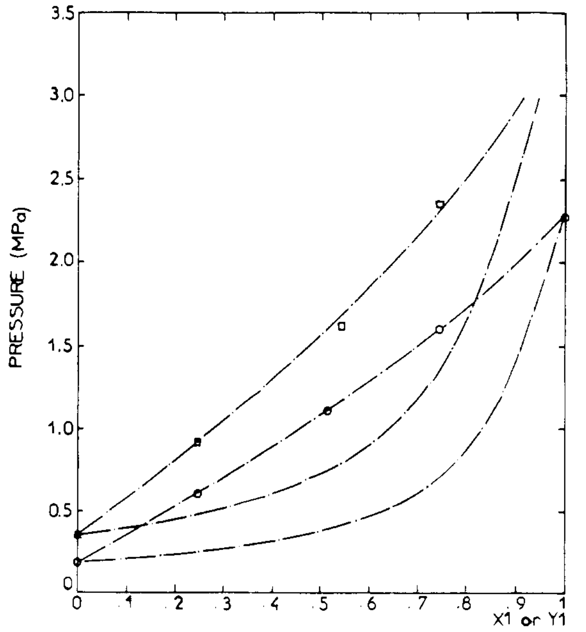

Figure 2. Pressure vs composition equilibrium diagram for the dichlorotetrafluoroethane (1)-perfluoro-2-butyltetrahydrofuran (2) [R114-FC75] mixture at different temperatures. Key: experimental data, (○) at 398 K, (□) at 423 K; (–•–) calculated results with the Peng-Robinson equation of state and $\delta_{ij} = 0.019$.

$$Q = \sum_{j=1}^{n} \left[\frac{P_{j,\mathrm{exp}} - P_{j,\mathrm{cal}}}{P_{j,\mathrm{exp}}} \right]^2 \tag{1}$$

Table IV. Bubble Pressures and Saturatd Liquid Molar Volumes as a Function of Temperature and Composition for the System Trifluoromethane (1)–Chlorodifluoromethane (2)–Trichlorofluoromethane (3) [R23–R22–R11]

T^a/K	P^b/MPa	x_1	$\sigma_{x_1}/10^{-4}$	x_2	$\sigma_{x_2}/10^{-4}$	x_3	$\sigma_{x_3}/10^{-4}$	v^{LS}/ (dm^3/mol)	$\sigma_{v^{LS}}$/ (10^{-4} dm^3/mol)
298.4_5	1.149 (1)	0.0811_8	1	0.7173	2	0.2015_5	1	0.0767	2
298.2_5	1.272 (2)	0.0800_3	0.5	0.8205	2	0.0994_7	1	0.0749	2
298.2	1.324 (1)	0.1070_3	1	0.7068_4	1	0.1861	1	0.0766_5	1
298.5	1.702 (1)	0.1570_4	1	0.7546	2	0.0883_4	1	0.0733	2
323.4	2.215 (1)	0.0811_8	1	0.7173	2	0.2015_5	1	0.0832	2
322.9	2.202 (2)	0.0800_3	0.5	0.8205	2	0.0994_7	1	0.0819	2
323.0	2.234 (1)	0.1070_3	1	0.7068_4	1	0.1861	1	0.0833_5	1
323.9_5	2.695 (1)	0.1570_4	1	0.7546	2	0.0883_4	1	0.0795	2
348.1_5	3.277 (1)	0.0793	1	0.7206	3	0.2000_5	1	0.0937	3
348.1_5	3.587 (2)	0.0796_8	0.6	0.8254_2	1	0.0949_0	0.4	0.0940	1
348.2_5	3.555 (1)	0.1189_3	1	0.6811	3	0.1999_3	1	0.0944	2
348.3_5	3.885 (1)	0.1210_1	1	0.7845	2	0.0944_8	1	0.0955	2
363.3_5	4.496 (1)	0.1189_3	1	0.6811	3	0.1999_3	1	0.1049	3
373.0	4.835 (1)	0.0793_5	1	0.7206	3	0.2000_5	1	0.1139	3

[a] Standard deviations: 0.1 K. [b] Numbers in parentheses correspond to the following deviations: (1) 0.005; (2) 0.008 MPa.

Table V. Bubble Pressures and Saturated Liquid Molar Volumes as a Function of Temperature and Composition for the System Trifluoromethane (1)–Chlorodifluoromethane (2)–Dichlorotetrafluoroethane (3) [R23–R22–R114]

T^a/K	P^b/MPa	x_1	$\sigma_{x_1}/10^{-4}$	x_2	$\sigma_{x_2}/10^{-4}$	x_3	$\sigma_{x_3}/10^{-4}$	v^{LS}/ (dm^3/mol)	$\sigma_{v^{LS}}$/ (10^{-4} dm^3/mol)
298.2	0.644 (1)	0.0500	1	0.1637	1	0.7863	2	0.1083	3
298.3	0.980 (1)	0.0683_2	1	0.4880_6	1	0.4436	2	0.0934	2
298.2_5	0.858 (1)	0.1025	1	0.0996_1	1	0.7979	2	0.1087	3
298.2_5	1.086 (2)	0.0898	1	0.4737	2	0.4365	2	0.0933	3
298.2_5	1.121 (2)	0.0996_9	0.9	0.4739	1	0.4264	1	0.0928	2
323.1_5	1.089 (1)	0.0500	1	0.1637	1	0.7863	2	0.1155	3
322.9	1.672 (1)	0.0683_2	1	0.4880_6	1	0.4436	2	0.1008	2
323.0_5	1.359 (1)	0.1025	1	0.0996_1	1	0.7979	2	0.1159	3
322.9	1.800 (2)	0.0898	1	0.4737	2	0.4365	2	0.1008	3
322.6_5	1.856 (2)	0.0996_9	0.9	0.4739	1	0.4264	1	0.1003	2
348.1_5	1.683 (1)	0.0501_1	1	0.1500_3	1	0.7999	2	0.1263	4
348.0_5	2.532 (2)	0.0500_8	1	0.5010_6	1	0.4489	5	0.1125	3
348.0	2.012 (2)	0.0995_8	1	0.0994_2	1	0.8010	2	0.1266	3
348.2	2.895 (2)	0.1030_7	0.8	0.4533	1	0.4436_0	0.9	0.1131	2
373.4_5	2.518 (1)	0.0501_1	1	0.1500_3	1	0.7999	2	0.1413	4
373.0_5	3.783 (2)	0.0500_8	1	0.5010_6	1	0.4489	5	0.1336	3
372.5_5	2.846 (2)	0.0995_8	1	0.0994_2	1	0.8010	2	0.1412	4
372.5_5	4.146 (2)	0.1030_7	0.8	0.4533	1	0.4436_1	0.9	0.1361	2

[a] Standard deviation: 0.1 K. [b] Numbers in parentheses correspond to the following deviations: (1) 0.005; (2) 0.008 MPa.

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

mixture	no. of binary data used for adjustment[a]	δ_{ij}[b]	standard deviation		
			$100\sigma_P^{Rc}$	$100\sigma_v^{Rd}$	$100\sigma_{v,\mathrm{trans}}^R$
trifluoromethane (1)–trichlorofluoromethane (2) [R23–R11]	11	0.129	2.0	3.5	1.9
dichlorotetrafluoroethane (1)–perfluoro-2-butyltetrahydrofuran (2) [R114–FC75]	6	0.019	0.8	6.5	1.5

[a] All experimental data are used. [b] Interaction parameter. [c] $\sigma_P^R = [[\sum_{i=1}^n[(P_{i,\mathrm{exp}} - P_{i,\mathrm{cal}})/P_{i,\mathrm{exp}}]^2]/(n-1)]^{1/2}$. [d] $\sigma_v^R = [[\sum_{i=1}^n[(v_{i,\mathrm{exp}} - v_{i,\mathrm{cal}})/v_{i,\mathrm{exp}}]^2](n-1)]^{1/2}$.

Table VII. Critical Parameters and Acentric Factors Used in the Cubic Equations of State

component	critical press/MPa	critical temp/K	acentric factor
trifluoromethane (R23)[a]	4.78	298.75	0.272
trichlorofluoromethane (R11)[b]	4.37	471.15	0.188
dichlorotetrafluoroethane (R114)[a]	3.26	418.85	0.244
perfluoro-2-butyltetrahydrofuran (FC75)[c]	1.60	500.15	0.567

[a] *ASHRAE Handbook Fundamentals*; American Society of Heating, Refrigerating and Air Conditioning Engineers: New York, 1977. [b] Reid, R. C.; Prausnitz, J. M.; Sherwood, T. R. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1977. [c] Fluorinert Electronic Liquids, General Properties. 3M Company, Information letter dated 28-08-1978.

When the P–R equation is used with a null δ_{ij}, computed bubble pressures are very far from experimental data (deviation of 32% for the trifluoromethane–trichlorofluoromethane system and 45% for the dichlorotetrafluoromethane–perfluoro-2-butyltetrahydrofuran system). When one interaction parameter in the mixing rule for the energy parameter, a, is adjusted, the corresponding deviations are decreased to 2% and 0.8%, respectively.

To improve the saturated liquid mole fractions, we used a volume translation (*8*) (see Appendix).

For trichlorofluoromethane, dichlorotetrafluoroethane, and perfluoro-2-butyltetrahydrofuran, the parameters $C_{i,j}$ were obtained by adjustment on pure-component densities. For trifluoromethane, which is supercritical at temperatures higher than 298.75 K, $C_{i,j}$ parameters were adjusted on the trifluoromethane–trichlorofluoroethane saturated density data (*4*). $C_{i,j}$ data are given in Table VII. Using a volume translation allows a better representation of saturated molar volumes (within 1.9% for the trifluoromethane (1)-trichlorofluoromethane (2) mixture and 1.5% for the dichlorotetrafluoroethane (1)-perfluoro-2-butyltetrahydrofuran (2) mixture, see Table VI).

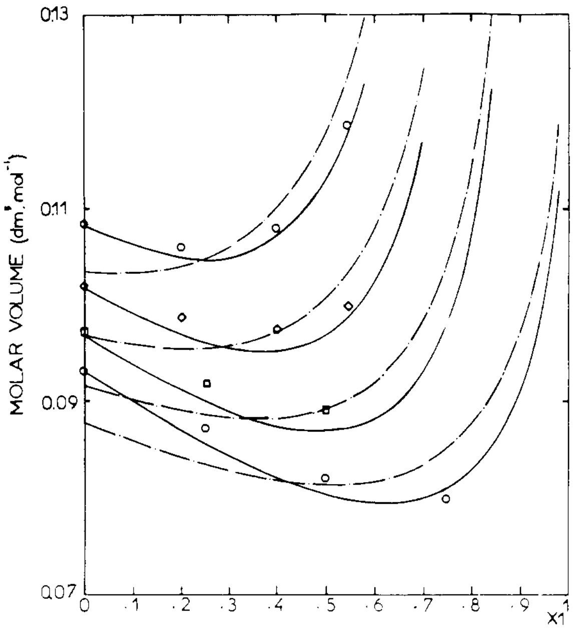

Figure 3. Saturated liquid molar volume vs composition diagram for the trifluoromethane (1)–trichlorofluoromethane (2) [R23–R11] mixture at various temperatures. Key: experimental data, (○) at 298 K, (□) at 323 K, (◇) at 348 K, (●) at 373 K; (–··–) calculated results with the Peng–Robinson equation of state and δ_{ij} = 0.129; (—) calculated results with the Peng–Robinson equation of state, δ_{ij} = 0.129, with volume translation.

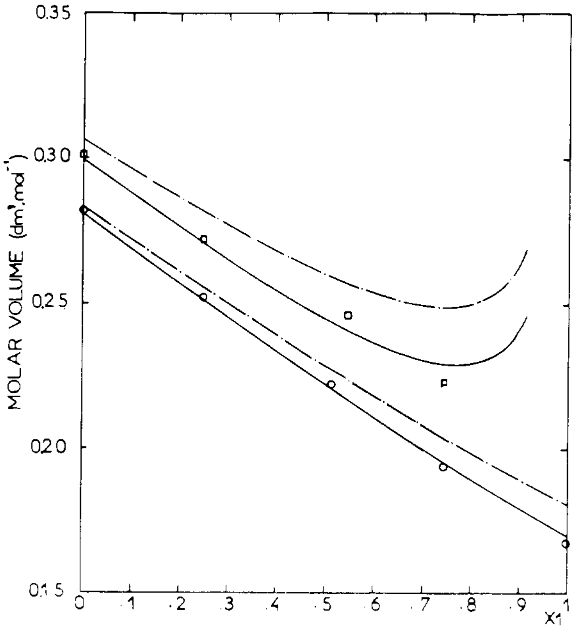

Figure 4. Saturated liquid molar volume vs composition diagram for the dichlorotetrafluoroethane (1)–perfluoro-2-butyltetrahydrofuran (2) [R114–FC75] mixture at various temperatures. Key: experimental data, (○) at 398 K, (□) at 423 K; (–··–) calculated results with the Peng–Robinson equation of state and δ_{ij} = 0.019; (—) calculated results with the Peng–Robinson equation of state, δ_{ij} = 0.019, with volume translation.

Appendix

Peng-Robinson Equation of State. The Peng–Robinson equation of state is

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

At the critical temperature, pure-component parameters a and b are given by $a(T_c) = 0.45724R^2T_c^{\,2}/P_c$ and $b(T_c) = 0.07780RT_c/P_c$. Peng and Robinson set the temperature dependence of a as

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

with $m = 0.37464 + 1.54226\omega - 0.26992\omega^2$. The mixing rules used here are those proposed by Peng and Robinson:

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

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

$$b = \sum_i x_i b_i$$

The volume translation consists of substituting in the P–R equation for the molar volume v with $v + \sum_{i=1}^{n} C_i x_i$ and covolume b with $b + \sum_{i=1}^{n} C_i x_i$ with $C_i = \sum_{j=1}^{3} C_{i,j} T^{j-1}$.

Glossary

a	energy parameter in the Peng–Robinson equation of state
b	covolume term in the Peng–Robinson equation of state
C	pure-component parameter in the equation for volume translation (see Appendix)
n	number of experimental points
P	pressure, MPa
Q	objective function for interaction parameter adjustment (see eq 1)
T	temperature, K
v	molar volume, dm³ mol⁻¹
x	liquid mole fraction
y	vapor mole fraction

Subscripts

cal	calculated property
exp	experimental property
i,j	components i and j
P	error in pressure
trans	translated property
v	error in molar volume
c	critical
R	reduced

Superscripts

LS	liquid, saturated
R	relative

Greek Letters

δ	binary interaction parameter in the Peng–Robinson equation of state
Δ	uncertainty
σ	standard deviation
ω	acentric factor

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