Bubble Curves and Saturated Liquid Molar Volumes for Chlorofluorohydrocarbon-Hydrocarbon Mixtures. Experimental Data and Modeling

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Vapor-liquid equilibria and liquid densities were obtained using a static apparatus fitted with a variable-volume cell which was described in detail by Valtz et al. (*1*). Results are given at four temperatures for the binary systems butane-1,1,2-trichlorotrifluoroethane, pentane-1,2-dichloro-1,1,2,2-tetrafluoroethane, hexane-1,2-dichloro-1,1,2,2-tetrafluoroethane, heptane-1,1,2-trichloro-1,2,2-trifluoroethane, heptane-1,2-dichloro-1,1,2,2-tetrafluoroethane, and benzene-1,2-dichloro-1,1,2,2-tetrafluoroethane and the ternary system 1,2-dichloro-1,1,2,2-tetrafluoroethane-1,1,2-trichloro-1,2,2-trifluoroethane-heptane. The best simultaneous representation of pressures and saturated liquid molar volumes at a given temperature and liquid composition for these mixtures is obtained using either the Patel-Teja or Trebble-Bishnoi-Salim equation of state (TBS EOS) in either their standard or generalized form (maximum deviation 0.7% in pressure and 3.1% in saturated liquid molar volume with the TBS EOS).

Introduction

This work is a continuing part of the development of a thermodynamic database for mixtures containing chlorofluorocarbons (CFC). Several systems have already been studied in this laboratory (*1-7*).

The static method with a variable-volume cell, which is very convenient for liquid-phase studies, was used here. Liquid-phase compositions were determined accurately by mass on an analytical balance of 10^{-7}-kg sensitivity.

Experimental Section

Apparatus. Details about the equipment are given by Valtz et al. (*1*) and Fontalba et al. (*8*). The procedure was as described by Valtz et al. (*1*).

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

Results for six binary systems are reported in Tables II-VII and Figures 1-4. The accuracies corresponding to the experimental data are given either inside the tables or in the table footnotes. Uncertainties δx_2 on liquid mole fractions x_2 are given by

$$\delta x_1 = \delta x_2 = \frac{(m_1 + m_2)}{M_1 M_2} \frac{\delta m}{(m_1/M_1 + m_2/M_2)^2} \quad (1)$$

where m_i is the mass of component i, M_i is its molar mass, and $\delta m = 2 \times 10^{-3}$ g.

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Table I. Origin and Purity of Chemicals

component	origin	purity (GLC %)
butane	Matheson	>99.9
pentane	Fluka	>99.5
hexane	Fluka	>99.5
heptane	Aldrich	>99.9
benzene	Merck	>99.7
1,2-dichloro-1,1,2,2-tetrafluoroethane	Labosi	>99.8
1,1,2-trichloro-1,2,2-trifluoroethane	Dehon	>99.9

Uncertainties δv^{LS} on saturated molar volumes v^{LS} are given by

$$\delta v^{LS} = v^{LS}\left[\frac{\delta V^M + \delta S h^P + S \delta h^P}{V^M - S h^P} + \frac{\delta m}{(m_1/M_1 + m_2/M_2)(M_1 + M_2)}\right] \quad (2)$$

where h^P is the displacement of the piston, S is the internal section, V^M is the maximum internal volume, $\delta h^P = 2 \times 10^{-5}$ m, $\delta S = 3 \times 10^{-7}$ m^2, and $\delta V^M = 2 \times 10^{-8}$ m^3.

Figures 1 and 2 represent the isothermal P-x-y two-phase envelopes. Dew curves are obtained from the Trebble-Bishnoi-Salim equation of state (TBS EOS) (*10*) which is an improved version of that described in ref 9 with binary interaction parameters δ_{ij} adjusted on bubble curve data, using the following objective function:

$$Q = \sum_{j=1}^{n}\left(\frac{P_{j,exp} - P_{j,cal}}{P_{j,exp}}\right)^2 \quad (3)$$

For this adjustment, temperature and composition were chosen as independent variables and n is the number of experimental determinations. Saturated liquid molar volumes as a function of mole fraction are shown in Figures 3 and 4.

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Table II. Experimental P_{exp} and Calculated P_{cal} Bubble Pressures, Experimental $x_{1,exp}$ Liquid Mole Fraction, Calculated $y_{1,cal}$ Vapor Mole Fraction, and Saturated Liquid Molar Volumes v^{LS} for the Butane (1)–1,1,2-Trichloro-1,2,2-trifluoroethane (2) Mixture[a]

T/K	P_{exp}/MPa	$x_{1,exp}$	δx/10^{-4}	v^{LS}/(dm³·mol⁻¹)	δv^{LS}/(10^{-3} dm³·mol⁻¹)	P_{cal}[b]/MPa	$y_{1,cal}$[b]
363.0_5	0.589	0.2528	1	0.1310	2	0.588	0.5247
363.2_0	0.835	0.5263	2	0.1272	1	0.834	0.7581
363.0_5	1.025	0.7523	3	0.1244	2	1.025	0.8827
383.1_5	0.887	0.2528	1	0.1374	2	0.887	0.4850
383.2_5	1.231	0.5263	2	0.1345	1	1.237	0.7279
383.1_0	1.512	0.7523	3	0.1326	2	1.517	0.8655
403.2_5	1.290	0.2528	1	0.1454	2	1.288	0.4458
403.2_0	1.765	0.5263	2	0.1441	1	1.762	0.6947
403.1_5	2.165	0.7523	3	0.1444	2	2.162	0.8446
423.2_0	1.800	0.2528	1	0.1560	2	1.802	0.4060
423.2_5	2.435	0.5263	2	0.1583	1	2.434	0.6556
423.1_0	2.973	0.7523	3	0.1645	2	2.976	0.8162

[a] $\delta T = \pm 0.1$ K. $\delta P = \pm 0.005$ MPa. [b] Calculated values with the TBS EOS and $\delta_{ij} = 0.024$.

Table III. Experimental P_{exp} and Calculated P_{cal} Bubble Pressures, Experimental $x_{1,exp}$ Liquid Mole Fraction, Calculated $y_{1,cal}$ Vapor Mole Fraction and Saturated Liquid Molar Volumes v^{LS} for the 1,2-Dichloro-1,1,2,2-tetrafluoroethane (1)–Pentane (2) Mixture[a]

T/K	P_{exp}/MPa	$x_{1,exp}$	δx/10^{-4}	v^{LS}/(dm³·mol⁻¹)	δv^{LS}/(10^{-3} dm³·mol⁻¹)	P_{cal}[b]/MPa	$y_{1,cal}$[b]
363.1_0	0.720	0.2550_8	0.8	0.1351	2	0.719	0.4604
363.2_5	0.899	0.5037	2	0.1384	2	0.897	0.6693
363.1_5	1.041	0.7533	1	0.1399	1	1.035	0.8309
383.0_5	1.078	0.2550_8	0.8	0.1429	2	1.081	0.4275
383.1_0	1.339	0.5037	2	0.1478	2	1.339	0.6435
383.1_5	1.549	0.7533	1	0.1512	1	1.551	0.8177
403.3_0	1.569	0.2550_8	0.8	0.1534	2	1.571	0.3933
403.2_0	1.931	0.5037	2	0.1613	2	1.931	0.6137
403.2_5	2.229	0.7473	1	0.1689	2	2.235	0.7965
423.2_0	2.190	0.2550_8	0.8	0.1689	2	2.197	0.3564
423.1_5	2.675	0.5037	2	0.1856	2	2.689	0.5747
423.1_5	3.190	0.7473	1	0.2052	2	2.903	0.7473

[a] $\delta T = \pm 0.1$ K. $\delta P = \pm 0.005$ MPa. [b] Calculated values with the TBS EOS and $\delta_{ij} = 0.048$.

Table IV. Experimental P_{exp} and Calculated P_{cal} Bubble Pressures, Experimental $x_{1,exp}$ Liquid Mole Fraction, Calculated $y_{1,cal}$ Vapor Mole Fraction, and Saturated Liquid Molar Volumes v^{LS} for the 1,2-Dichloro-1,1,2,2-tetrafluoroethane (1)–Hexane (2) Mixture[a]

T/K	P_{exp}/MPa	$x_{1,exp}$	δx/10^{-4}	v^{LS}/(dm³·mol⁻¹)	δv^{LS}/(10^{-3} dm³·mol⁻¹)	P_{cal}[b]/MPa	$y_{1,cal}$[b]
363.1_5	0.540	0.3026_2	0.8	0.1448	2	0.541	0.7095
363.1_5	0.762	0.5530	1	0.1440	1	0.766	0.8397
363.1_5	0.921	0.7427	1	0.1434	2	0.921	0.9063
383.2_0	0.800	0.3026_2	0.8	0.1516	2	0.803	0.6621
383.2_0	1.129	0.5530	1	0.1524	1	1.133	0.8086
383.2_5	1.368	0.7427	1	0.1531	2	1.371	0.8869
403.1_5	1.152	0.3026_2	0.8	0.1599	2	1.143	0.6124
403.1_5	1.607	0.5530	1	0.1632	1	1.607	0.7721
403.2_5	1.962	0.7427	1	0.1672	2	1.956	0.8621
423.2_5	1.588	0.3026_2	0.8	0.1708	2	1.580	0.5585
423.2_5	2.206	0.5530	1	0.1791	2	2.205	0.7263
423.1_0	2.686	0.7427	1	0.1917	2	2.686	0.8256

[a] $\delta T = \pm 0.1$ K. $\delta P = \pm 0.005$ MPa. [b] Calculated values with the TBS EOS and $\delta_{ij} = 0.049$.

The experimental results for the ternary mixture 1,2-dichloro-1,1,2,2-tetrafluoroethane–1,1,2-trichloro-1,2,2-trifluoroethane–heptane are reported in Table VIII and shown in Figure 5.

Data modeling was performed with several equations of state: the Redlich–Kwong–Soave equation of state (RKS EOS) (*11*), Peng–Robinson equation of state (PR EOS) (*12*),

Table V. Experimental P_{exp} and Calculated P_{cal} Bubble Pressures, Experimental $x_{1,exp}$ Liquid Mole Fraction, Calculated $y_{1,cal}$ Vapor Mole Fraction, and Saturated Liquid Molar Volumes v^{LS} for the 1,2-Dichloro-1,1,2,2-tetrafluoroethane (1)–Heptane (2) Mixture[a]

T/K	P_{exp}/MPa	$x_{1,exp}$	δx/10^{-4}	v^{LS}/(dm³·mol⁻¹)	δv^{LS}/(10^{-3} dm³·mol⁻¹)	P_{cal}[b]/MPa	$y_{1,cal}$[b]
362.9_0	0.408	0.2556_0	0.7	0.1556	2	0.410	0.8291
363.1_0	0.664	0.5016_4	1	0.1503	2	0.663	0.9111
363.1_5	0.904	0.7626_6	1	0.1456	2	0.897	0.9558
378.5_5	0.548	0.2556_0	0.7	0.1601	2	0.550	0.7929
378.2_0	0.882	0.5016_4	1	0.1555	2	0.882	0.8904
378.0_0	1.207	0.7626_6	1	0.1521	2	1.201	0.9449
393.3_0	0.714	0.2556_0	0.7	0.1649	2	0.711	0.7558
393.0_0	1.139	0.5016_4	1	0.1613	2	1.140	0.8668
393.0_5	1.580	0.7626_6	1	0.1603	2	1.574	0.9310
408.2_0	0.909	0.2556_0	0.7	0.1704	2	0.905	0.7153
408.2_0	1.452	0.5016_4	1	0.1685	2	1.452	0.8384
408.2_0	2.027	0.7626_6	1	0.1711	2	2.022	0.9128

[a] $\delta T = \pm 0.1$ K. $\delta P = \pm 0.005$ MPa. [b] Calculated values with the TBS EOS and $\delta_{ij} = 0.051$.

Table VI. Experimental P_{exp} and Calculated P_{cal} Bubble Pressures, Experimental $x_{1,exp}$ Liquid Mole Fraction, Calculated $y_{1,cal}$ Vapor Mole Fraction, and Saturated Liquid Molar Volumes v^{LS} for the 1,1,2-Trichloro-1,2,2-trifluoroethane (1)–Heptane (2) Mixture[a]

T/K	P_{exp}/MPa	$x_{1,exp}$	δx/10^{-4}	v^{LS}/(dm³·mol⁻¹)	δv^{LS}/(10^{-3} dm³·mol⁻¹)	P_{cal}[b]/MPa	$y_{1,cal}$[b]
363.0_5	0.157	0.2482_6	0.6	0.1553	1	0.157	0.6027
363.3_0	0.225	0.4929_3	0.9	0.1489_5	1	0.223	0.7938
363.2_5	0.285	0.7428_2	1	0.1420	1	0.282	0.9056
363.2_0	0.340	1		0.1341_5	1	0.342	1
378.0_0	0.227	0.2482_6	0.6	0.1592_5	1	0.228	0.5729
378.1_5	0.320	0.4929_3	0.9	0.1530	1	0.320	0.7743
378.0_5	0.404	0.7428_2	1	0.1461_5	1	0.402	0.8962
378.2_0	0.490	1		0.1385	1	0.488	1
393.0_5	0.323	0.2482_6	0.6	0.1635_5	1	0.324	0.5440
393.3_5	0.448	0.4929_3	0.9	0.1570_5	1	0.449	0.7540
393.1_5	0.562	0.7428_2	1	0.1509	1	0.561	0.8862
392.8_0	0.675	1		0.1432_5	1	0.673	1
408.0_5	0.447	0.2482_6	0.6	0.1684_5	1	0.446	0.5161
408.1_0	0.605	0.4929_3	0.9	0.1626_5	1	0.608	0.7338
408.1_5	0.762	0.7428_2	1	0.1563	1	0.762	0.8757
408.0_0	0.916	1		0.1489	1	0.916	1

[a] $\delta T = \pm 0.1$ K. $\delta P = \pm 0.005$ MPa. [b] Calculated values with the TBS EOS and $\delta_{ij} = 0.025$.

Table VII. Experimental P_{exp} and Calculated P_{cal} Bubble Pressures, Experimental $x_{1,exp}$ Liquid Mole Fraction, Calculated $y_{1,cal}$ Vapor Mole Fraction, and Saturated Liquid Molar Volumes v^{LS} for the 1,2-Dichloro-1,1,2,2-tetrafluoroethane (1)–Benzene (2) Mixture[a]

T/K	P_{exp}/MPa	$x_{1,exp}$	δx/10^{-4}	v^{LS}/(dm³·mol⁻¹)	δv^{LS}/(10^{-3} dm³·mol⁻¹)	P_{cal}[b]/MPa	$y_{1,cal}$[b]
363.1_0	0.600	0.2951_5	0.7	0.1089	1	0.599	0.7978
363.1_5	0.758	0.4978_7	0.9	0.1171	1	0.757	0.8583
363.1_5	0.934	0.7397	1	0.1280	1	0.924	0.9161
383.0_5	0.866	0.2951_5	0.7	0.1130	1	0.870	0.7546
383.3_0	1.113	0.4978_7	0.9	0.1227	1	1.114	0.8278
383.1_5	1.383	0.7397	1	0.1359	2	1.372	0.8984
403.2_5	1.224	0.2951_5	0.7	0.1179	1	1.225	0.7077
403.3_5	1.577	0.4978_7	0.9	0.1295	1	1.574	0.7933
403.3_0	1.979	0.7397	1	0.1468	2	1.962	0.8762
423.0_5	1.645	0.2951_5	0.7	0.1241	1	1.660	0.6584
423.2_0	2.140	0.4978_7	0.9	0.1382	1	2.145	0.7534
423.2_0	2.708	0.7397	1	0.1638	2	2.698	0.8462

[a] $\delta T = \pm 0.1$ K. $\delta P = \pm 0.005$ MPa. [b] Calculated values with the TBS EOS and $\delta_{ij} = 0.049$.

Patel–Teja equation of state and its generalized form (PT EOS and PTg EOS) (*13*), and Trebble–Bishnoi–Salim equation of state and its generalized form (TBS EOS and TBSg

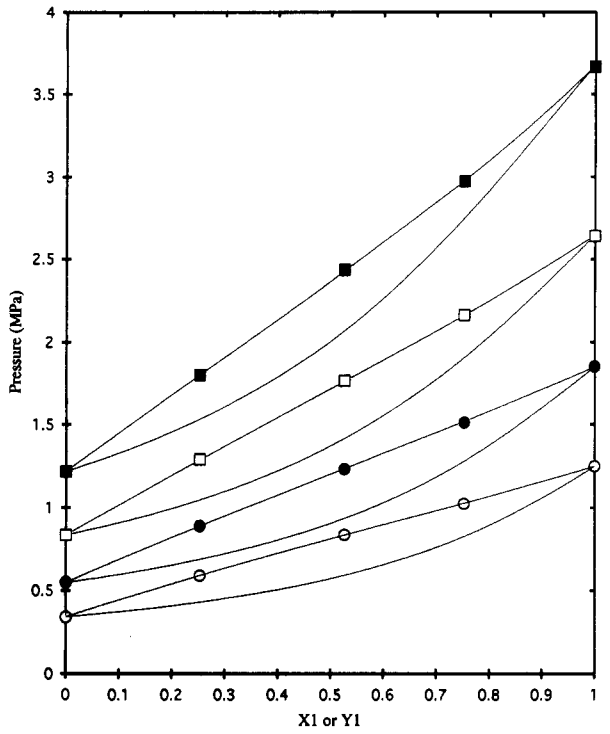

Figure 1. Pressure versus composition equilibrium diagram for the butane (1)–1,1,2-trichloro-1,2,2-trifluoroethane (2) binary system at different temperatures: 363 K (○); 383 K (●); 403 K (□); 423 K (■); (—) calculated results with the TBS EOS and binary parameters given in Table XII.

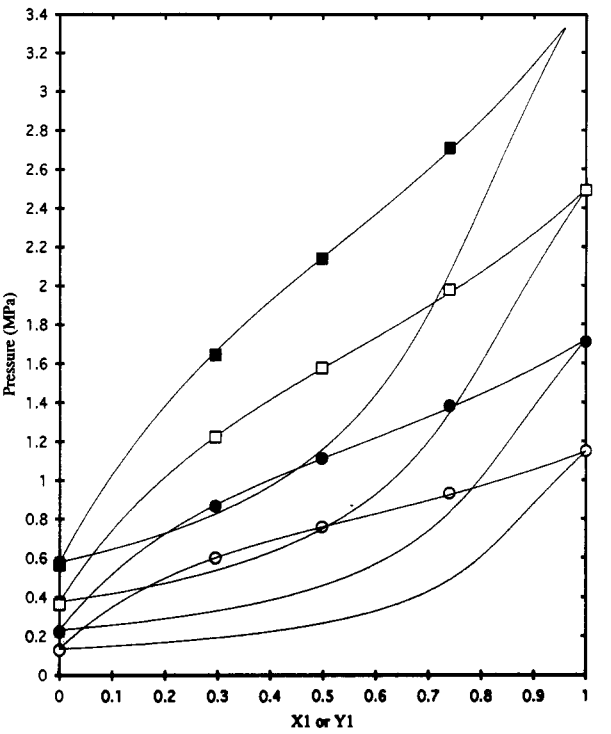

Figure 2. Pressure versus composition equilibrium diagram for the 1,2-dichloro-1,1,2,2-tetrafluoroethane (1)–benzene (2) binary system at different temperatures: 363 K (○); 383 K (●); 403 K (□); 423 K (■); (—) calculated results with the TBS EOS and binary parameters given in Table XII.

EOS) (*9*). Volume translation, as proposed by Péneloux et al. (*14*), has been introduced in PR EOS and RKS EOS. A brief description of all the preceding equations of state is given by Laugier et al. (*7*).

Values of adjusted pure component parameters using the objective function given by eq 3, for all equations of state are reported in Table IX. Parameters m and ζ_c are found identical to those given by Patel–Teja (*13*) for hydrocarbons. Parameters ζ_c, m, p, and d for TBS EOS given in ref 9 yield a representation of pressures and saturated liquid molar volumes which is worse than with parameters calculated through the correlation given in ref 9; parameters ζ_c, m, p,

Table VIII. Experimental P_{exp} and Calculated P_{cal} Pressures, Experimental $x_{1,exp}$, $x_{2,exp}$, and $x_{3,exp}$ Liquid Mole Fractions, Calculated $y_{1,cal}$ and $y_{2,cal}$ Vapor Mole Fractions, and Saturated Liquid Molar Volumes v^{LS} for the 1,2-Dichloro-1,1,2,2-tetrafluoroethane (1)–1,1,2-Trichloro-1,2,2-trifluoroethane (2)–Heptane (3) Mixture[a]

T/K	P_{exp}/MPa	$x_{1,exp}$	$\delta x/10^{-4}$	$x_{2,exp}$	$\delta x/10^{-4}$	$x_{3,exp}$	$\delta x/10^{-4}$	v^{LS}/(dm³·mol⁻¹)	δv^{LS}/(10⁻³ dm³·mol⁻¹)	P_{cal}[b]/MPa	$y_{1,cal}$[b]	$y_{2,cal}$[b]
363.2_0	0.815	0.6181_0	1	0.2881_4	0.6	0.0937_6	0.7	0.1395	0.2	0.809	0.8308	0.1492
363.2_5	0.549	0.3024_3	0.9	0.4999_7	1	0.1976_0	1	0.1411	0.2	0.544	0.6111	0.3426
363.1_5	0.560	0.3405_4	0.8	0.3822_7	0.8	0.2772_0	1	0.1435	0.2	0.559	0.6810	0.2584
378.2_0	1.102	0.6181_0	1	0.2881_4	0.6	0.0937_6	0.7	0.1455	0.2	1.094	0.8128	0.1630
378.1_5	0.747	0.3024_3	0.9	0.4999_7	1	0.1976_0	1	0.1460	0.2	0.740	0.5830	0.3625
378.1_5	0.761	0.3405_4	0.8	0.3822_7	0.8	0.2772_0	1	0.1484	0.2	0.758	0.6529	0.2749
393.2_5	1.457	0.6181_0	1	0.2881_4	0.6	0.0937_6	0.7	0.1530	0.2	1.448	0.7924	0.1780
393.1_0	0.994	0.3024_3	0.9	0.4999_7	1	0.1976_0	1	0.1516	0.2	0.985	0.5544	0.3818
393.2_5	1.009	0.3405_4	0.8	0.3822_7	0.8	0.2772_0	1	0.1542	0.2	1.006	0.6235	0.2910
408.2_0	1.884	0.6181_0	1	0.2881_4	0.6	0.0937_6	0.7	0.1632	0.2	1.873	0.7691	0.1946
408.1_0	1.290	0.3024_3	0.9	0.4999_7	1	0.1976_0	1	0.1584	0.2	1.284	0.5247	0.4008
408.0_5	1.304	0.3405_4	0.8	0.3822_7	0.8	0.2772_0	1	0.1610	0.2	1.299	0.5931	0.3065

[a] $\delta T = \pm 0.1$ K. $\delta P = \pm 0.005$ MPa. [b] Calculated values with TBS EOS and binary parameters given in Table XII.

Table IX. Critical Pressure P_c, Temperature T_c, Acentric Factor w, Critical Compressibility Z_c, and Rackett Compressibility Factor Z_{RA} Used in the Cubic Equations of State and New Parameter Values Used in the Patel–Teja (ζ_c, m) and Trebble–Bishnoi–Salim (ζ_c, m, p, d) Equations of State

							Patel–Teja		Trebble–Bishnoi–Salim			
substance	ref	P_c/MPa	T_c/K	w	Z_c	Z_{RA}	ξ_c	m	ξ_c	m	p	d/(dm³·mol⁻¹)
propane	15	4.242	369.80	0.1515	0.2810	0.276 64	0.3170	0.648 049	0.2903	0.8425	0.8405	0.0686
butane	15	3.796	425.20	0.1993	0.2749	0.273 31	0.3090	0.678 389	0.2904	1.0096	0.8525	0.0824
pentane	15	3.369	469.65	0.2510	0.2620	0.268 53	0.3080	0.746 470	0.2817	1.0288	0.9809	0.10877
hexane	15	2.969	507.40	0.2960	0.2600	0.263 55	0.3050	0.801 605	0.2766	1.1301	1.1864	0.1228
heptane	15	2.735	540.10	0.3510	0.2630	0.260 60	0.3050	0.868 856	0.2787	1.3071	1.1653	0.1413
benzene	15	4.898	562.20	0.2120	0.2705	0.269 67	0.3100	0.704 657	0.2870	1.0094	1.0096	0.0834
1,2-dichloro-1,1,2,2-tetrafluoroethane	16	3.26	418.85	0.255	0.275		0.3144	0.782 5	0.2887	1.1033	0.9523	0.1025
1,1,2-trichloro-1,2,2-trifluoroethane	16	3.41	487.26	0.252	0.274		0.3146	0.780 8	0.2903	1.1440	0.9388	0.1086

Table X. Values and T_r Validity Range of Adjusted e_i and e_{ij} Parameters for each Pure Substance in the Volume Translations Associated with the Soave's and Peng–Robinson's Equations of State

refrigerant	number of points used in adjustment	Soave e_i/ (10^{-2} dm^3·mol^{-1})	Peng–Robinson e_{i1}/ (dm^3·mol^{-1})	e_{i2}/ (10^{-3} dm^3·mol^{-1}·K^{-2})	e_{i3}/ (10^{-6} dm^3·mol^{-1}·K^{-2})	T_r range
propane	15[a]	0.5251	0.0937	−0.775	1.511	0.59–0.97
butane	16[a]	0.8003	0.1234	−0.869	1.460	0.71–0.96
pentane	17[a]	1.2229	0.2636	−1.564	2.281	0.66–0.98
hexane	11[b]	1.7520	0.1720	−0.986	1.413	0.61–0.96
heptane	11[a]	2.2660	0.3359	−1.708	2.164	0.66–0.94
benzene	23[a]	0.9640	0.1011	−0.543	0.701	0.59–0.98
1,2-dichloro-1,1,2,2-tetrafluoroethane	27[c]	0.8450	0.2842	−1.888	3.048	0.65–0.99
1,1,2-trichloro-1,2,2-trifluoroethane	23[c]	0.9890	0.1673	−1.039	1.539	0.65–0.99

[a] From ref 17. [b] From ref 18. [c] From ref 16.

Table XI. Relative Standard Deviations σ^R_P on Pressures and Saturated Liquid and Vapor Molar Volumes σ^R_{VLS} and σ^R_{VVS} for each Substance Associated with the Investigated Cubic Equations of State

substance	number of data	σ^R_P/% RKS	PR	PT	PTg	TBS	TBSg	σ^R_{VLS}/% RKS	RKS trans	PR	PR trans	PT	PTg	TBS	TBSg	σR_{VVS}/% RKS	PR	PT	PTg	TBS	TBSg
propane	15[a]	0.9	0.6	0.8	0.8	0.3	0.7	12.	8.3	5.9	1.4	2.6	2.7	2.1	4.2	1.1	1.4	1.4	1.0	2.9	2.3
butane	16[a]	1.2	0.5	0.5	0.6	0.4	0.7	13.	7.8	5.0	3.1	1.1	2.4	1.9	2.4	1.0	1.3	1.2	0.9	2.6	2.5
pentane	17[a]	1.3	0.4	0.9	0.9	0.2	0.5	17.	10.	6.3	1.6	2.3	2.5	2.4	3.8	1.7	1.1	1.3	1.4	2.5	2.8
hexane	11[b]	0.9	0.7	1.6	1.3	0.7	1.3	19.	9.1	5.9	0.8	2.7	3.9	1.4	1.5						
heptane	11[a]	1.7	0.8	0.8	1.2	0.4	0.4	19.	8.7	6.2	1.0	2.0	1.9	1.7	1.8	6.5	6.8	6.7	7.2	7.1	7.1
benzene	23[a]	1.0	0.8	1.2	0.9	0.5	1.0	14.	7.6	4.3	0.8	2.5	2.9	1.5	1.6	1.7	1.2	1.7	1.3	2.5	2.4
1,2-dichloro-1,1,2,2-tetrafluoroethane	27[c]	1.5	0.8	0.6	0.6	0.6	0.7	14.	10.	6.7	2.1	2.2	2.8	3.1	3.6	1.8	2.9	3.1	3.2	4.6	4.4
1,1,2-trichloro-1,2,2-trifluoroethane	23[c]	1.2	0.5	0.5	0.4	0.5	0.4	13.	8.2	6.0	2.1	2.1	2.7	2.8	2.9	1.1	2.1	2.5	2.6	3.3	3.3

[a] From ref 17. [b] From ref 18. [c] From ref 16.

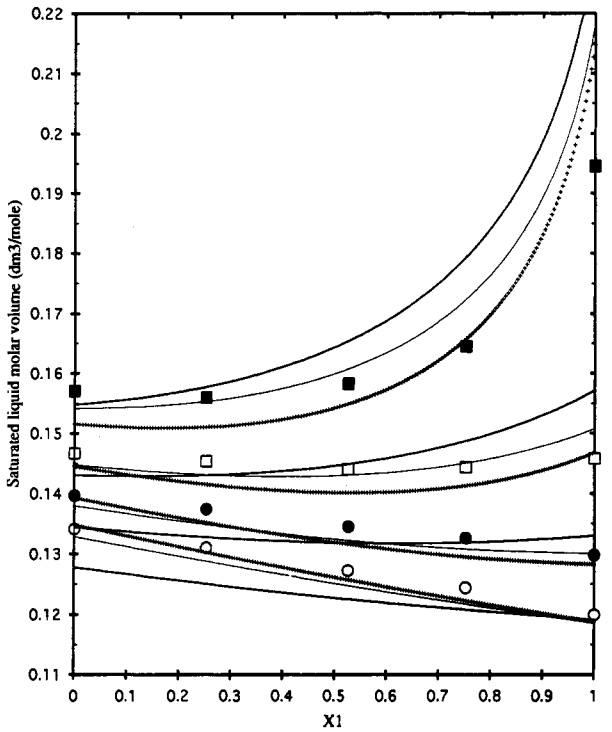

Figure 3. Saturated liquid molar volume versus composition equilibrium diagram for the butane (1)–1,1,2-trichloro-1,2,2-trifluoroethane (2) binary system at different temperatures: 363 K (○); 383 K (●); 403 K (□); 423 K (■); (thin line) calculated results with the TBS EOS; (thick line) calculated results with the PR EOS; (+) calculated results with the PR EOS and volume translation (binary parameters given in Table XII).

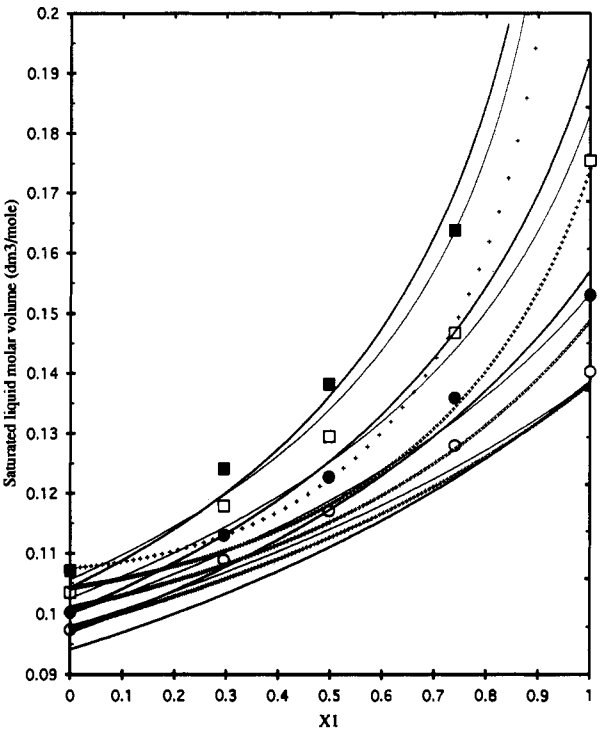

Figure 4. Saturated liquid molar volume versus composition equilibrium diagram for the 1,2-dichloro-1,1,2,2-tetrafluoroethane (1)–benzene (2) binary system at different temperatures: 363 K (○); 383 K (●); 403 K (□); 423 K (■); (thin line) calculated results with the TBS EOS; (thick line) calculated results with the PR EOS; (+) calculated results with the PR EOS and volume translation (binary parameters given in Table XII).

and d adjusted in this work for hydrocarbons have a very smooth dependence on the carbon atom number and perform better for our PVT data.

Volume translation parameters are given in Table X. For RKS EOS, the molar volume calculated from the regular equation of state, v_{cal}, is incremented by a translation term

Table XII. Relative Standard σ^R_P on Pressures and Saturated Liquid Molar Volumes σ^R_{VLS} for each Mixture Associated with the Investigated Cubic Equations of State

mixture	number of binary data	δ_{ij}						σ^R_P/%						σ^R_{VLS}/%							
		RKS	PR	PT	PTg	TBS	TBSg	RKS	PR	PT	PTg	TBS	TBSg	RKS	RKS trans	PR	PR trans	PT	PTg	TBS	TBSg
propane–1,2-dichloro-1,1,2,2-tetrafluoroethane[a]	12	0	0	0	0	0	0	6.6	7.2	8.6	8.4	7.5	7.2	14	8.4	3.6	5.3	2.6	3.2	2.6	1.9
		0.044	0.045	0.053	0.052	0.041	0.040	0.8	0.6	0.7	0.8	0.6	0.6	17	12.	6.2	1.8	2.8	2.3	3.5	4.8
propane–1,1,2-trichloro-1,2,2-trifluoroethane[a]	10	0	0	0	0	0	0	5.0	5.6	8.2	7.8	7.4	6.0	13	7.7	3.2	6.4	4.2	4.9	1.9	1.8
		0.025	0.027	0.040	0.038	0.032	0.026	1.0	0.7	0.7	0.7	0.9	0.8	15	9.6	4.4	4.6	3.7	3.8	2.5	3.7
butane–1,1,2-trichloro-1,2,2-trifluoroethane	12	0	0	0	0	0	0	3.5	4.5	5.7	5.4	5.1	5.1	13	7.1	3.5	10.	3.0	3.1	2.2	1.6
		0.019	0.024	0.029	0.027	0.024	0.024	0.5	0.3	1.2	1.4	0.2	0.2	14	8.4	4.0	8.9	1.2	1.7	2.1	2.1
1,2-dichloro-1,1,2,2-tetrafluoroethane–pentane	12	0	0	0	0	0	0	8.3	9.3	9.9	10.	9.9	9.7	12	5.9	2.9	6.3	3.8	3.6	4.1	5.1
		0.049	0.052	0.054	0.055	0.048	0.047	0.4	0.2	0.8	0.7	0.3	0.3	16	9.5	4.5	2.5	1.3	1.5	2.3	3.2
1,2-dichloro-1,1,2,2-tetrafluoroethane–hexane	12	0	0	0	0	0	0	9.8	11	12	12	11	11	11	5.8	2.4	8.5	5.7	5.3	4.5	4.1
		0.051	0.053	0.057	0.059	0.049	0.047	0.8	0.5	1.8	1.6	0.4	0.4	16	2.8	3.7	5.3	2.2	1.0	2.6	2.6
1,2-dichloro-1,1,2,2-tetrafluoroethane–benzene	12	0	0	0	0	0	0	9.5	11	12	12	13	12	8.3	2.6	5.3	9.8	8.2	7.8	4.9	3.9
		0.042	0.046	0.050	0.051	0.049	0.046	0.5	0.6	1.2	1.1	0.6	0.5	10	4.3	4.1	7.8	6.1	5.6	2.9	2.3
1,2-dichloro-1,1,2,2-tetrafluoroethane–heptane	12	0	0	0	0	0	0	13	14	15	15	15	14	11	1.9	2.8	6.6	5.0	5.6	3.7	2.9
		0.052	0.054	0.056	0.058	0.049	0.047	0.6	0.3	2.1	2.0	0.4	0.3	13	3.7	1.6	4.6	3.1	3.6	2.1	1.4
1,1,2-trichloro-1,2,2-trifluoroethane–heptane	12	0	0	0	0	0	0	6.7	7.5	6.8	7.4	7.2	6.9	12	1.2	2.4	1.1	1.3	2.3	1.7	1.1
		0.027	0.028	0.026	0.028	0.025	0.024	0.8	0.4	0.5	0.5	0.5	0.4	12	1.7	1.8	0.5	0.9	1.7	1.2	0.7
propane[a]–1,2-dichloro-1,1,2,2-tetrafluoroethane	12	0	0	0	0	0	0	6.1	6.8	9.2	9.0	8.1	7.0	13	7.4	3.1	7.0	4.2	5.2	2.5	1.5
	δ_{12}	0.044	0.045	0.054	0.053	0.026	0.041														
1,1,2-trichloro-1,2,2-trifluoroethane	δ_{13}	0.025	0.027	0.040	0.038	0.010	0.029	1.3	0.8	0.4	0.4	0.8	0.7	14	9.1	4.2	5.0	2.3	3.1	2.5	3.1
	δ_{23}	−0.002	0.004	0.008	0.008	0.009	0.007														
1,2-dichloro-1,1,2,2-tetrafluoroethane	12	0	0	0	0	0	0	4.4	5.6	6.5	6.7	6.7	6.0	11	3.2	3.2	5.1	3.3	4.4	2.8	2.2
	δ_{12}	−0.002	0.004	0.008	0.008	0.009	0.007														
1,1,2-trichloro-1,2,2-trifluoroethane–heptane	δ_{13}	0.052	0.054	0.056	0.058	0.049	0.047	0.8	0.7	1.5	1.4	0.7	0.7	12	4.3	2.3	3.8	2.0	2.9	1.7	1.1
	δ_{23}	0.027	0.028	0.026	0.028	0.025	0.024														

[a] From ref 6.

according to

$$v_{cal,t} = v_{cal} - \sum_i e_i x_i \tag{4}$$

with temperature-independent parameters e_i. For PR EOS, parameter e_i is taken as temperature dependent according to

$$e_i = \sum_{k=1}^{3} e_{ik} T^{k-1} \tag{5}$$

The objective function used when adjusting e_{ik} volume translation parameters was

$$Q = \sum_{j=1}^{n} \left(\frac{v^{LS}_{j,exp} - v^{LS}_{j,cal,t}}{v^{LS}_{j,exp}} \right)^2 \tag{6}$$

Table XI reports the quality of the pure component representation in terms of relative standard deviations defined as

$$\sigma^R_u = 100 \left[\sum_{j=1}^{n} \left(\frac{u_{j,exp} - u_{j,cal}}{u_{j,exp}} \right)^2 / (n-k) \right]^{1/2} \tag{7}$$

where u is either P or v^L, n is the number of experimental points, and k is the number of parameters used in the model.

Pressures for all mixtures are represented with any equation of state within 1%. Representation of saturated liquid molar volumes are generally within 2% with PT EOS and TBS EOS. PT EOS is better for saturated vapor volume representation.

For the limited set of PVT data of this work, PR EOS with volume translation is the best for representing simultaneously vapor pressures, saturated liquid molar volumes, and saturated vapor molar volumes. It must be noted that use of temperature-dependent translation terms (Salim and Trebble (9)) results in thermodynamic inconsistencies at elevated pressure. Introducing a volume translation with temperature-independent parameters e_i in RKS EOS improves the saturated liquid molar volume representation by a factor of about 2–5. This translation is carried out using a parameter e_i correlated as suggested by Péneloux et al. (14) to P_c, T_c, and Z_{RA} by the following empirical correlation:

$$e_i = 0.40768(RT_c/P_c)(0.29441 - Z_{RA}) \tag{8}$$

where P_c is the critical pressure, T_c is the critical temperature, R is the gas constant, and Z_{RA} is the Rackett factor given in Table IX. When Z_{RA} is not known, it is replaced by Z_c as proposed by Péneloux et al. (14).

The preceding formulation does not improve the quality of representation by the PR EOS. Then e_i parameters cannot be taken as temperature independent; e_{ik} parameters according to eq 5 are adjusted (3). RKS EOS gives about the same accuracy on v^{LS} as PR EOS if temperature-dependent e_i parameters are adjusted. For propane–1,1,2-trichloro-1,2,2-trifluoroethane and propane–1,2-dichloro-1,1,2,2-tetrafluoroethane mixtures, e_{ik} parameters have been adjusted on temperature ranges different (lower temperatures are now taken into account) from those in ref 6, leading to better representations.

The quality of representations for binary and ternary mixtures is given in Table XII. Pressures are well represented by all the equations of state as soon as temperature-independent binary interaction parameters are adjusted (deviations always less than 1% except with PT EOS where deviations can reach 2%). With a zero binary interaction

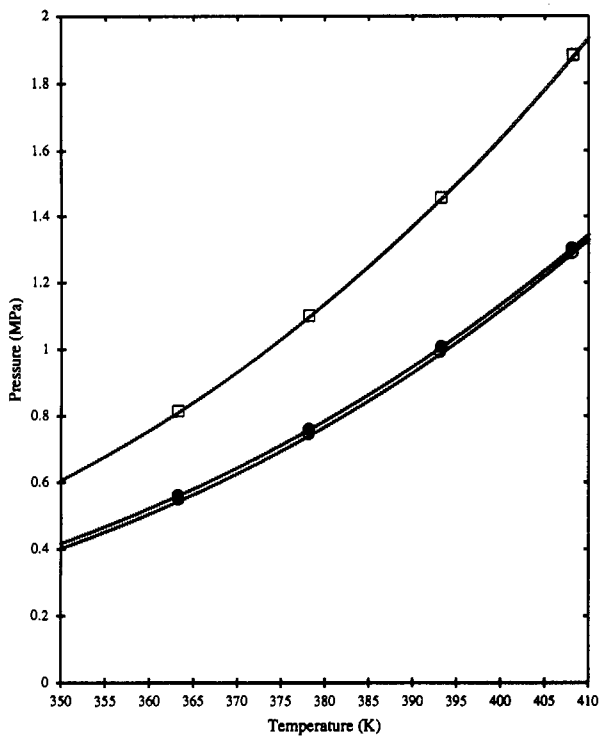

Figure 5. Pressure versus temperature diagram at different compositions for the 1,2-dichloro-1,1,2,2-tetrafluoroethane (1)–1,1,2-trichloro-1,2,2-trifluoroethane (2)–heptane (3) ternary system with compositions 34%:38%:28% (●); 30%:50%:20% (○); 62%:29%:9% (□): (—) calculated results with the TBS EOS; (+) calculated results with the PR EOS (binary parameters given in Table XII).

parameter, all equations are bad (deviations around 10%).

Saturated liquid molar volumes are generally best represented by PT EOS and TBS EOS. Generalization of these two equations does not have a significant influence on the quality of representations. For most of the studied mixtures, volume translations in combination with PR and RKS EOS have the defect of exaggerating nonideality effects.

For representing ternary mixture data, both solubilities and saturated molar volumes, the best equation is the TBS EOS in its generalized form, requiring the adjustment of the minimum number of parameters (see Table XII). Figure 5 shows the very good pressure representation.

The conclusion is, as in a previous paper (*7*), that the TBS EOS is the most suitable of the studied EOS for simultaneously representing pressures and saturated liquid molar volumes for binary and ternary mixtures of given composition and given temperature.

Glossary

d	parameter of TBS EOS
e_i, e_{ik}	pure component parameters in volume translation
h^P	displacement of the piston from its lower stopped position, m
k	number of parameters
m	parameter of temperature dependence (*7*)
m_i	mass of component i in the equilibrium cell, g
M	molar mass, g·mol^{-1}
n	number of experimental points
p	parameter of TBS EOS
P	pressure, MPa
Q	objective function
S	internal section of the equilibrium cell, m^2
T	temperature, K
v	molar volume, dm^3·mol^{-1}
V^M	maximum internal volume of the equilibrium cell, m^3
x	liquid mole fraction
y	vapor mole fraction
Z	compressibility factor

Superscripts

R	relative property
L	liquid property
S	saturated property
V	vapor property

Subscripts

c	critical property
cal	calculated property
exp	experimental property
i,j	components i and j
P	pressure property
r	reduced property
RA	Rackett property
t	EOS with translated volume
u	either P, V^L, or V^v
V	volume property

Greek Letters

δ	uncertainty
δ_{ij}	binary interaction parameter
ζ	compressibility factor generated by PT or TBS EOS
σ	standard deviation

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