

PARAMETERS OF THE BENDER EQUATION OF STATE FOR CHLORO DERIVATIVES OF METHANE AND CHLOROBENZENE

Ivan CIBULKA^{1,*}, Lubomír HNĚDKOVSKÝ² and Květoslav RŮŽIČKA³

Department of Physical Chemistry, Institute of Chemical Technology, Prague, 166 28 Prague 6, Czech Republic; e-mail: ¹ ivan.cibulka@vscht.cz, ² lubomir.hnedkovsky@vscht.cz, ³ kvetoslav.ruzicka@vscht.cz

Received December 27, 2000

Accepted April 17, 2001

Values of adjustable parameters of the Bender equation of state evaluated for chloromethane, dichloromethane, trichloromethane, tetrachloromethane, and chlorobenzene from published experimental data are presented. Experimental data employed in the evaluation included the data on state behaviour (p - ρ - T) of fluid phases, vapour-liquid equilibrium data (saturated vapour pressures and orthobaric densities), second virial coefficients, and the coordinates of the gas-liquid critical point. The description of second virial coefficient by the equation of state is examined.

Keywords: Equation of state; Second virial coefficient; Chloromethanes; Chlorobenzene.

An extensive database of original published experimental data on state behaviour of pure fluids ($\rho(p, T)$ -data, second virial coefficients) has been developed recently in the laboratory of the authors. The goal of this activity is (i) a collection of available experimental data, and (ii) a critical evaluation of adjustable parameters (constants) of a properly selected equation of state which might be employed for generation of recommended state-behaviour data or calculation of other thermodynamic properties.

One of the equations of state employed in connection with the above database is the Bender equation of state^{1,2}, which may be written in terms of the compressibility factor z as a function of density ρ and temperature T with twenty adjustable parameters (constants) a_k

$$z = \frac{pV}{nRT} = \frac{pM}{RT\rho} = 1 + B\frac{\rho}{R} + C\frac{\rho^2}{R} + D\frac{\rho^3}{R} + E\frac{\rho^4}{R} + F\frac{\rho^5}{R} + (G + H\rho^2)\frac{\rho^2}{R} e^{-\frac{\rho^2}{a_{20}^2}}, \quad (1)$$

where

$$B = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} + \frac{a_4}{T^3} + \frac{a_5}{T^4}, \quad C = a_6 + \frac{a_7}{T} + \frac{a_8}{T^2}, \quad D = a_9 + \frac{a_{10}}{T}, \quad (2)$$

$$E = a_{11} + \frac{a_{12}}{T}, \quad F = \frac{a_{13}}{T}, \quad G = \frac{a_{14}}{T^3} + \frac{a_{15}}{T^4} + \frac{a_{16}}{T^5}, \quad H = \frac{a_{17}}{T^3} + \frac{a_{18}}{T^4} + \frac{a_{19}}{T^5},$$

and R is the gas constant. With the recommended approximation^{1,2} $a_{20} = \rho_c$, where ρ_c is the critical density, which was adopted for this work, Eq. (1) is a linear function of parameters $\vec{a} = \{a_k\}$, $k = 1, \dots, 19$. The function B is related to the second virial coefficient $B_V = \psi B$, where ψ is a constant whose value depends on both the molar mass of the substance and the units used.

EVALUATION METHOD

A method of the evaluation of the equation-of-state parameters was described in detail in our previous paper³ along with the tests on data for methane and pentane. The method is based on minimisation of the objective function, which can be written as a sum of terms related to the individual data groups (G, vapour/gas; L, liquid; VLE, vapour-liquid equilibrium curve; V, second virial coefficient; CP, gas-liquid critical point)

$$\phi(\vec{a}, \vec{\lambda}) = \alpha_G w_G \phi_G + \alpha_L w_L \phi_L + \alpha_{VLE} w_{VLE} \phi_{VLE} + \alpha_V w_V \phi_V + \alpha_{CP} \phi_{CP}, \quad (3)$$

where

$$\phi_G = \sum_{j=1}^{N_G} w_{z,j} \left[z_j^{(G)} - z(\vec{a}, T_j, \rho_j^{(G)}) \right]^2 \quad (4)$$

and

$$\phi_L = \sum_{k=1}^{N_L} w_{z,k} \left[z_k^{(L)} - z(\vec{a}, T_k, \rho_k^{(L)}) \right]^2 \quad (5)$$

are the sums of weighted fit residuals in compressibility factor corresponding to vapour/gas (G data) and liquid phase (L data) in the single-phase regions, respectively. The third term in Eq. (3)

$$\phi_{\text{VLE}} = \sum_{i=1}^{N_{\text{VLE}}} w_{\text{VL},i} \left\{ \left[p(\bar{a}, \rho_{\text{sat},i}^{(\text{L})}, T_i) - p_{\text{sat}}(T_i) \right]^2 + \left[p(\bar{a}, \rho_{\text{sat},i}^{(\text{G})}, T_i) - p_{\text{sat}}(T_i) \right]^2 + \right. \\ \left. + \frac{1}{\left(\frac{1}{(\rho_{\text{sat},i}^{(\text{L})})^2} + \frac{1}{(\rho_{\text{sat},i}^{(\text{G})})^2} \right) \left(\frac{M}{RT_i} \right)^2} \left[\ln f(\bar{a}, \rho_{\text{sat},i}^{(\text{L})}, T_i) - \ln f(\bar{a}, \rho_{\text{sat},i}^{(\text{G})}, T_i) \right]^2 \right\} \quad (6)$$

is the sum of weighted deviations between the calculated and experimental saturated vapour pressure and deviations between the calculated fugacities of liquid and vapour phases in equilibrium (VLE data). Second virial coefficient data (V data) are incorporated into Eq. (3) as the sum of weighted deviations between experimental and calculated second virial coefficients

$$\phi_{\text{V}} = \sum_{m=1}^{N_{\text{V}}} w_{\text{V},m} \left[B_{\text{V},m} - B_{\text{V}}(\bar{a}, T_m) \right]^2. \quad (7)$$

The last term (CP data)

$$\phi_{\text{CP}} = \left\{ \lambda_1 \left[z(\bar{a}, T_c, \rho_c) - z_c \right] + \lambda_2 \left[\frac{\partial p(\bar{a}, T, V)}{\partial V} \right]_{T,\text{CP}} + \lambda_3 \left[\frac{\partial^2 p(\bar{a}, T, V)}{\partial V^2} \right]_{T,\text{CP}} \right\}, \quad (8)$$

where λ_1 , λ_2 , λ_3 are the Lagrange multipliers introduces the conditions (constraints) that apply at the gas-liquid critical point.

Individual terms in Eq. (3) can be incorporated into calculations by varying coefficients α_i : a particular data group ($i = \text{G, L, VLE, V, CP}$) may be retained in the calculations ($\alpha_i = 1$) or rejected ($\alpha_i = 0$), *i.e.*, the inclusion of the data groups may be characterised by the vector $\{\alpha_i\} = (\alpha_{\text{G}}, \alpha_{\text{L}}, \alpha_{\text{VLE}}, \alpha_{\text{V}}, \alpha_{\text{CP}})$. Group weight factors w_i in Eq. (3) for individual data groups ($i = \text{G, L, VLE, V}$) were employed for balancing mutual weights among the data groups. The default setting was derived from the number of retained data points in the data groups. Statistical weights of individual data points, $w_{z,k}$, $w_{z,k}$ and $w_{\text{V},m}$ in the summations (4), (5), and (7) are given by formulas

$$w_{z,j} = \omega_j / (\delta z_j)^2, \quad w_{z,k} = \omega_k / (\delta z_k)^2, \quad w_{V,m} = \omega_m / (\delta B_{V,m})^2, \quad (9)$$

where the experimental uncertainties of compressibility factor δz_j , δz_j and of second virial coefficient $\delta B_{V,m}$, were derived from the information recorded in the database of original experimental data. Quantities ω_j , ω_m make it possible to change the weights of individual data points by changing the value of ω of each data point (default setting is $\omega = 1$; $\omega > 0$ and $\omega = 0$ holds for retained and rejected data points, respectively). The summations (4), (5), and (7) are performed over retained data points.

The term ϕ_{VLE} (Eq. (6)) represents the data along the vapour–liquid equilibrium line and minimises the deviations between the saturated vapour pressure calculated for both phases from the equation of state and experimental saturated vapour pressure $p_{\text{sat}}(T_i)$, as well as the deviations between calculated fugacities of liquid and vapour on the vapour–liquid equilibrium line. Weights of the data points along the equilibrium line are given by the formula

$$w_{VL,i} = \omega_i / \{ \delta p_{\text{sat}}(T_i) \}^2 = \omega_i / \{ p_{\text{sat}}(T_i) \delta_r [p_{\text{sat}}(T_i)] \}^2, \quad (10)$$

where ω_i plays a similar role to that in Eq. (9). Since saturated pressure data were represented by a smoothing function (see below), its relative uncertainty $\delta_r [p_{\text{sat}}(T_i)]$ was assumed to be a constant derived from the average deviation of the vapour pressure fit. The uncertainty of the fugacity term is related to the uncertainty of saturated pressure using a general thermodynamic formula $\delta \ln f = (\partial \ln f / \partial p)_T \delta p = V_m / (RT) \delta p = M / (RTp) \delta p$. It is obvious that the conditions valid for vapour liquid equilibrium are not fulfilled exactly here but only within the minimised deviations (Eq. (6)). Exact calculations of vapour–liquid equilibrium ($p_{\text{sat,calc}}$, $\rho_{\text{sat,calc}}^{(G)}$, and $\rho_{\text{sat,calc}}^{(L)}$) based on the equilibrium conditions

$$p(\bar{a}, T, \rho_{\text{sat,calc}}^{(G)}) = p(\bar{a}, T, \rho_{\text{sat,calc}}^{(L)}), \quad f(\bar{a}, T, \rho_{\text{sat,calc}}^{(G)}) = f(\bar{a}, T, \rho_{\text{sat,calc}}^{(L)}) \quad (11)$$

were performed for each set of parameters $\bar{a} = \{a_k\}$ as obtained from the objective function (3) using a modified Newton method⁴. The deviations of calculated saturated vapour pressure and orthobaric densities from experi-

mental data employed as the input for the objective function (3) were then evaluated.

EXPERIMENTAL DATA

An overview of experimental data employed for the evaluation of the parameters of Eq. (1) for substances under investigation is summarised in Table I. Attention was paid to avoid duplication of data in the cases with $\alpha_G = \alpha_V = 1$, where second virial coefficients were evaluated from p - ρ - T data of gases and vapours at low pressures retained in the G-data group. Original p - ρ - T data were preferred, whenever possible, to avoid an influence of a method used by researchers in evaluation of virial coefficients.

Saturated vapour pressure and saturated liquid density data were presented by smoothing functions either available in the literature (vapour pressure) or obtained by a fit of recommended data (liquid density). The references to the sources are also given in Table I. The respective values were calculated from the functions at temperatures of data for saturated vapour density. Other data were direct experimental values taken from the database. No experimental data for saturated vapour density were found for dichloromethane. Since the vapour-liquid equilibrium curve is substantial for correct description of the p - ρ - T surface, the saturated vapour densities were calculated from the experimental values of second virial coefficient for experimental temperatures and corresponding saturated vapour pressure, *i.e.* from the equation $p_{\text{sat}}M/(\rho_{\text{sat}}RT) = 1 + \{B_V(T)/M\}\rho_{\text{sat}}$. The upper temperature limit was selected as $T_{\text{max}} = 0.8T_c$. Therefore the VLE-data and V-data groups for this substance are interrelated.

Particular attention was paid to extrapolation capabilities of the Bender equation to the regions where no experimental data were available. As one of the tests, extrapolation of second virial coefficient toward high temperatures can be considered. Seldom the temperature range of experimental data in vapour/gas phase (G data, V data) reaches the high-temperature region, where the second virial coefficient crosses the zero value (at the Boyle temperature for which $T_B \approx 2.5T_c$ is a crude approximation). Therefore, the second virial coefficients extrapolated above the highest experimental temperature usually pass through a maximum, where the virial coefficient is still negative (see below). Thus the correct description of the Boyle temperature may increase the prediction reliability in the range between the highest temperature of data and the Boyle temperature. No data for the substances investigated in this work approach the range close to the Boyle temperature. Since the Boyle temperature could not be evaluated from ex-

TABLE I

List of experimental data and the temperature and pressure ranges used for evaluation of the parameters of the Bender equation of state

Data Source	Range of T K	Range of p MPa	Numbers of values	
Chloromethane				
G	Guye (1909) ref. ⁸	273	0.1	1
	Shorthose (1924) ref. ⁹	273	0.1	4
	Tanner (1939) ref. ¹⁰	233–500	0.041–1.38	185
	Hsu (1964) ref. ¹¹	308–498	0.1–31.41	356
	Suh (1967) ref. ¹²	473–623	0.1–34.45	140
	Mansoorian (1981) ref. ¹³	323–473	0.1–15.00	106
	Total	233–623	0.1–34.45	792
L	Hsu (1964) ref. ¹¹	308–413	0.8–31.5	132
	Kumagai (1978) ref. ¹⁴	253–313	28.7–159.5	30
	Total	253–413	0.8–159.5	162
VLE				
Saturated vapour pressure:				
	McGarry (1983) ref. ¹⁵	233–403	0.049–5.4	35
Saturated liquid density:				
	TRC Tables (1973, 1981) refs ^{16,17}	233–403	0.049–5.4	35
Saturated vapour density:				
	Tanner (1939) ref. ¹⁰	233–322	0.049–1.08	15
	Hsu (1964) ref. ¹¹	308–403	0.75–5.4	20
	Total	233–403	0.049–5.4	35
V	Hamann (1952) ref. ¹⁸	293–353		17
	Reeves (1958) ref. ¹⁹	295		1
	Blythe (1960) ref. ²⁰	295		1
	Bottomley (1967) ref. ²¹	276–427		9
	Lichtenthaler (1969) ref. ²²	288–313		5
	Eubank (1985) ref. ²³	323–473		7
	Total	276–473		40
CP ^a	CDATA ref. ²⁴	$T_c = 416.25$	$p_c = 6.679$	$\rho_c = 363.220 \text{ kg m}^{-3}$

TABLE I
(Continued)

Data Source	Range of T K	Range of p MPa	Numbers of values
Dichloromethane			
G Singh (1979) ref. ²⁵	349–510	0.011–1.184	113
L Burkat (1975) ref. ²⁶	293–298	1.0–10.0	20
Kumagai (1982) ref. ²⁷	298–348	10.1–101.3	21
Easteal (1985) ref. ²⁸	298	50.0–100.0	2
Baonza (1991) ref. ²⁹	298	0.6–102.0	25
Total	293–348	0.6–102.0	68
VLE			
Saturated vapour pressure:			
McGarry (1983) ref. ¹⁵	288–403	0.038–1.115	24
Saturated liquid density:			
TRC Tables (1973) ref. ¹⁶	288–403	0.038–1.115	24
Saturated vapour density ^b :			
Fog (1953) ref. ³⁰	288–353	0.038–0.347	5
Perez (1958) ref. ³¹	323–398	0.142–1.005	4
Raetzsch (1968) ref. ³²	303–333	0.070–0.195	3
Singh (1986) ref. ³³	349–390	0.314–0.841	3
Wormald (1998) ref. ³⁴	323–403	0.142–1.115	9
Total	288–403	0.038–1.115	24
V Fog (1953) ref. ³⁰	288–353		5
Perez (1958) ref. ³¹	323–423		5
Raetzsch (1968) ref. ³²	303–333		3
Singh (1986) ref. ³³	349–510		10
Wormald (1998) ref. ³⁴	323–423		11
Total	288–510		34
CP ^a CDATA ref. ²⁴	$T_c = 510.00$	$p_c = 6.080$	$\rho_c = 440.065 \text{ kg m}^{-3}$
Trichloromethane			
G Buckinham (1961) ref. ³⁵	353	0.015–0.016	3
L Burkat (1975) ref. ²⁶	293–298	1.0–10.0	20
Kumagai (1982) ref. ²⁷	273–348	10.8–98.7	27
Easteal (1984) ref. ³⁶	298	50.0–250.0	5
Easteal (1985) ref. ²⁸	298	25.0–100.0	3
Nhu (1987) ref. ³⁷	293	2.0–10.0	5
Total	273–348	1.0–250.0	60

TABLE I
 (Continued)

Data Source	Range of T K	Range of p MPa	Numbers of values	
Trichloromethane				
VLE				
Saturated vapour pressure:				
McGarry (1983) ref. ¹⁵	385–511	0.41–3.83	18	
Saturated liquid density:				
TRC Tables (1973) ref. ¹⁶	385–511	0.41–3.83	18	
Saturated vapour density:				
Campbell (1968) ref. ³⁸	385–511	0.41–3.83	18	
V	Zaalishvili (1960) ref. ³⁹	338–358	3	
	Zaalishvili (1961) ref. ⁴⁰	333–363	4	
	Zaalishvili (1965) ref. ⁴¹	353–383	4	
	Philippe (1971) ref. ⁴²	293–328	5	
	Abuselme (1989) ref. ⁴³	358	2	
	Doyle (1998) ref. ⁴⁴	333–423	12	
	Total	293–423	30	
CP ^a	CDATA ref. ²⁴	$T_c = 536.40$	$p_c = 5.470$	$\rho_c = 499.487 \text{ kg m}^{-3}$
Tetrachloromethane				
G	–	–	–	
L	Holder (1962) ref. ⁴⁵	298–348	1.0–10.0	50
	Schamp (1965) ref. ⁴⁶	298	20.0–90.0	8
	Mopsik (1969) ref. ⁴⁷	273–323	10.2–197.7	21
	Rogers (1973) ref. ⁴⁸	298	1.0–10.0	10
	Burkat (1975) ref. ²⁶	293–298	1.0–10.0	20
	Benson (1976) ref. ⁴⁹	273–413	0.4–172.6	322
	Holzappel (1987) ref. ⁵⁰	293	2.0–10.0	5
	Lainez (1987) ref. ⁵¹	330–409	2.5–55.7	109
	Total	273–413	0.4–197.7	545

TABLE I
(Continued)

Data Source	Range of T K	Range of p MPa	Numbers of values
Tetrachloromethane			
VLE			
Saturated vapour pressure:			
McGarry (1983) ref. ¹⁵	343–551	0.082–4.266	114
Saturated liquid density:			
TRC Tables (1973) ref. ¹⁶	343–551	0.082–4.266	114
Saturated vapour pressure:			
Young (1891) ref. ⁵²	353–543	0.149–3.854	48
Young (1891) ref. ⁵³	433–543	0.735–3.854	12
Young (1910) ref. ⁵⁴	343–543	0.082–3.854	20
Campbell (1969) ref. ⁵⁵	401–551	0.386–4.266	34
Total	343–551	0.082–4.266	114
V			
Francis (1955) ref. ⁵⁶	316–343		5
Perez (1964) ref. ⁵⁷	354–399		3
Jain (1970) ref. ⁵⁸	298–313		4
Wormald (1996) ref. ⁵⁹	333–413		6
Total	298–413		18
CP ^a	$T_c = 556.40$	$p_c = 4.560$	$\rho_c = 557.327 \text{ kg m}^{-3}$
Chlorobenzene			
G			
Agaev (1976) ref. ⁶⁰	463–633	0.172–4.550	158
Ahlmeyer (1982) ref. ⁶¹	439–625	0.064–0.207	39
Total	439–633	0.064–4.550	197
L			
Gibson (1939) ref. ⁶²	298–338	50.0–100.0	6
Gibson (1939) ref. ⁶³	298–358	25.0–100.0	16
Agaev (1973) ref. ⁶⁴	308–583	0.6–32.5	101
Takagi (1982) ref. ⁶⁵	303	10.0–190.0	19
Kashiwagi (1983) ref. ⁶⁶	298–398	12.3–98.2	35
Abdullaev (1984) ref. ⁶⁷	298–523	1.3–50.0	68
Easteal (1997) ref. ⁶⁸	278–338	1.9–283	138
Total	278–583	0.6–283	383

TABLE I
 (Continued)

Data Source	Range of T K	Range of p MPa	Numbers of values
Chlorobenzene			
VLE			
Saturated vapour pressure:			
McGarry (1983) ref. ¹⁵	403–553	0.097–1.694	21
Saturated liquid density:			
TRC Tables (1990) ref. ⁶⁹	403–553	0.097–1.694	21
Saturated vapour pressure:			
Young (1910) ref. ⁵⁴	403–553	0.097–1.694	16
Agaev (1976) ref. ⁶⁰	463–543	0.389–1.474	5
Total	403–553	0.097–1.694	21
V	–	–	–
CP ^a	CDATA ref. ²⁴	$T_c = 632.40$	$p_c = 4.520$ $\rho_c = 365.451 \text{ kg m}^{-3}$

^a Critical densities are given with three decimal places as calculated from rounded values of molar critical volume recorded in database CDATA. ^b See the text.

perimental data, the estimates were obtained using Tsonopoulos⁵ and Weber⁶ methods (examination of these methods when applied to haloalkanes was presented recently by Dymond⁷). Both methods yielded similar values: chloromethane $T_B = 1021$ K, dichloromethane $T_B = 1223$ K, trichloromethane $T_B = 1273$ K, tetrachloromethane $T_B = 1339$ K, chlorobenzene $T_B = 1480$ K.

The values above were included in the evaluation of the equation-of-state parameters as additional experimental data points with zero values of second virial coefficient at $T = T_B$ and a high (though variable) statistical weight was attributed to this data point. Since the values of the Boyle temperature were estimated, an alternative procedure to include the Boyle temperature into the objective function (3) as a constraint using additional Lagrange coefficient was not employed.

RESULTS

Values of parameters of the Bender equation of state (Eqs (1) and (2)) are summarised in Table II along with the statistical characteristics of the fits and calculated values of the Boyle temperature. The data listed in Table I and estimated values of the Boyle temperature were employed for the fits. The group weight factors w_i (Eq. (3)) were set to values for which $N_i w_i$ was a constant same for all data groups except for the L-data group. It was observed that the dependence of the deviations of single-phase liquid data (L data) on w_L is very flat while the effect on other data groups (particularly vapour-liquid equilibrium) is much more pronounced. Therefore the group weight factor w_L was set to the value in the interval from 0.01 to 0.05, regardless of the number of data points N_L .

Data used for chloromethane were found to be mutually consistent. A fit of the VLE data, *i.e.* with $\{\alpha_{ij}\} = (0, 0, 1, 0, 0)$, after rejecting two data points¹¹ close to critical temperature (408.15 and 413.15 K), resulted in very small deviations between the calculated critical point (obtained by solving the second and third constraint of Eq. (8) (for details, see ref.³)) and the experimental one ($\delta_{r,z_c} = 4.08\%$, $\delta T_c = 0.92$ K, and $\delta_{r,\rho_c} = -1.44\%$). Values of second virial coefficient, extrapolated from the fit where the estimated value of the Boyle temperature was not used, are in qualitative agreement with the course obtained using Tsionopoulos⁵ and Weber⁶ estimation methods (see Fig. 1a). The agreement is better for the final fit (Table II and Fig. 1a), where the estimated value of the Boyle temperature was included in the input data. Deviations of all experimental values of second virial coefficient from those calculated from equation of state are less than ± 10 cm³ mol⁻¹ (see Fig. 2).

The experimental values of the second virial coefficient for dichloromethane are in mutual agreement and consistent with the single-phase gas/vapour data (the fit with $\{\alpha_{ij}\} = (0, 0, 0, 1, 0)$ resulted in $\text{RMSD}_r(B_V) = 2.6\%$; the same deviation was obtained for the fit with $\{\alpha_{ij}\} = (1, 0, 0, 1, 0)$). Therefore all virial data were used to calculate saturated vapour densities (see above) up to temperature 403 K. The deviations at the critical point for a tentative fit of VLE data $\{\alpha_{ij}\} = (0, 0, 1, 0, 0)$ were rather high ($\delta_{r,z_c} = -27.2\%$, $\delta T_c = 12.1$ K, $\delta_{r,\rho_c} = 8.3\%$), but the highest temperature of the VLE data is more than 100 K below the critical temperature and thus the extrapolation is rather uncertain. The fit with $\{\alpha_{ij}\} = (0, 0, 1, 0, 1)$ resulted in the same deviations of equilibrium data as that with $\{\alpha_{ij}\} = (0, 0, 1, 0, 0)$ which supports the conclusion that saturated vapour density values calculated from experimental second virial coefficients are consistent with coordinates

TABLE II

Parameters of the Bender equation of state (Eqs (1) and (2))^a for the fits, where all data listed in Table I and the values of the Boyle temperature (see the text) were included in the input data

Parameter	Chloromethane	Dichloromethane
$a_1 \cdot 10^2$	1.67228730	1.89670782
$a_2 \cdot 10^{-1}$	-1.96855018	-3.20519613
$a_3 \cdot 10^{-3}$	4.82028480	14.8819077
$a_4 \cdot 10^{-6}$	-2.31954724	-5.18487212
$a_5 \cdot 10^{-8}$	1.24633584	2.82642610
$a_6 \cdot 10^5$	3.27640851	1.94607501
$a_7 \cdot 10^2$	-1.49078577	-0.817723184
a_8	9.64018373	14.5364065
$a_9 \cdot 10^8$	-3.94160512	-1.57208295
$a_{10} \cdot 10^5$	-0.208807749	-4.25890308
$a_{11} \cdot 10^{11}$	8.94338028	5.89922840
$a_{12} \cdot 10^8$	-4.70956953	-0.640895447
$a_{13} \cdot 10^{11}$	2.76405216	0.598978188
$a_{14} \cdot 10^{-3}$	-9.97315298	99.0883690
$a_{15} \cdot 10^{-6}$	7.08002424	-95.1485848
$a_{16} \cdot 10^{-9}$	-1.27837440	21.6327447
$a_{17} \cdot 10^2$	1.83100458	-53.1277005
$a_{18} \cdot 10^{-1}$	-2.22409369	48.8274694
$a_{19} \cdot 10^{-3}$	7.06642637	-108.765870
$a_{20} \cdot 10^{-2}$	3.63220	4.40065
G data:		
RMSD(z)	0.0033	0.00022
RMSD _r (z), %	0.44	0.024
L data:		
RMSD(z)	0.0139	0.0202
RMSD _r (z), %	2.70	2.63
VLE data:		
RMSD _r ($p_{\text{sat,liq}}$), %	0.31	0.52
RMSD _r ($p_{\text{sat,vap}}$), %	0.70	0.42
exact VLE: RMSD _r (p_{sat}), %	0.58	0.50
RMSD _r ($p_{\text{sat,liq}}$), %	0.013	0.0013
RMSD _r ($p_{\text{sat,vap}}$), %	0.53	0.46
V data:		
RMSD(B_v), cm ³ mol ⁻¹	3.9	14.8
RMSD _r (B_v), %	1.22	2.33
T_B , K	1 021	1 223

TABLE II
(Continued)

Parameter	Trichloromethane	Tetrachloromethane
$a_1 \cdot 10^2$	-3.87797282	-1.17515560
$a_2 \cdot 10^{-1}$	8.80848273	3.19351471
$a_3 \cdot 10^{-3}$	-57.0148499	-23.8676509
$a_4 \cdot 10^{-6}$	10.3936816	3.11112250
$a_5 \cdot 10^{-8}$	-7.08247367	-2.62479170
$a_6 \cdot 10^5$	2.68637548	4.31981757
$a_7 \cdot 10^2$	-2.36395625	-4.29076004
a_8	-1.58995312	6.11291927
$a_9 \cdot 10^8$	-11.6260048	-8.41082793
$a_{10} \cdot 10^5$	11.1129321	8.45248816
$a_{11} \cdot 10^{11}$	5.02700241	4.78615991
$a_{12} \cdot 10^8$	-7.83383332	-6.73582348
$a_{13} \cdot 10^{11}$	1.91220565	1.61931794
$a_{14} \cdot 10^{-3}$	-656.407213	-2.81455369
$a_{15} \cdot 10^{-6}$	665.295067	0.911881832
$a_{16} \cdot 10^{-9}$	-168.061380	0.703325463
$a_{17} \cdot 10^2$	449.539809	-5.06574337
$a_{18} \cdot 10^{-1}$	-467.237100	4.84739115
$a_{19} \cdot 10^{-3}$	1 214.34964	-10.7308346
$a_{20} \cdot 10^{-2}$	3.65451	5.57327
G data:		
RMSD(z)	0.0015	-
RMSD _r (z), %	0.15	-
L data:		
RMSD(z)	0.0268	0.01856
RMSD _r (z), %	1.14	2.13
VLE data:		
RMSD _r ($p_{\text{sat,liq}}$), %	0.38	0.34
RMSD _r ($p_{\text{sat,vap}}$), %	2.30	1.21
exact VLE: RMSD _r (p_{sat}), %	1.72	0.821
RMSD _r ($p_{\text{sat,liq}}$), %	0.086	0.067
RMSD _r ($p_{\text{sat,vap}}$), %	3.87	1.66
V data:		
RMSD(B_v), cm ³ mol ⁻¹	45.2	42.9
RMSD _r (B_v), %	4.30	4.04
T_B , K	761	1 239

TABLE II
 (Continued)

Parameter	Chlorobenzene
$a_1 \cdot 10^2$	-2.99842636
$a_2 \cdot 10^{-1}$	9.30512681
$a_3 \cdot 10^{-3}$	-83.6725324
$a_4 \cdot 10^{-6}$	18.0672405
$a_5 \cdot 10^{-8}$	-12.5244961
$a_6 \cdot 10^5$	-0.405297844
$a_7 \cdot 10^2$	2.17830024
a_8	-14.3597283
$a_9 \cdot 10^8$	-14.0113322
$a_{10} \cdot 10^5$	17.6199759
$a_{11} \cdot 10^{11}$	7.09303779
$a_{12} \cdot 10^8$	-18.5446793
$a_{13} \cdot 10^{11}$	8.45516905
$a_{14} \cdot 10^{-3}$	-99.3648153
$a_{15} \cdot 10^{-6}$	113.235171
$a_{16} \cdot 10^{-9}$	-29.9986470
$a_{17} \cdot 10^2$	7.38461249
$a_{18} \cdot 10^{-1}$	-17.5095010
$a_{19} \cdot 10^{-3}$	88.0885205
$a_{20} \cdot 10^{-2}$	3.65451
G data:	
RMSD(z)	0.0023
RMSD _r (z), %	0.36
L data:	
RMSD(z)	0.0348
RMSD _r (z), %	2.042
VLE data:	
RMSD _r ($p_{\text{sat,liq}}$), %	0.62
RMSD _r ($p_{\text{sat,vap}}$), %	0.72
exact VLE: RMSD _r (p_{sat}), %	0.68
RMSD _r ($\rho_{\text{sat,liq}}$), %	0.006
RMSD _r ($\rho_{\text{sat,vap}}$), %	1.16
V data:	
RMSD(B_v), cm ³ mol ⁻¹	-
RMSD _r (B_v), %	-
T_B , K	1 351

^a The values of parameters $\{a_k\}$ correspond to T in K and p in kg m⁻³.

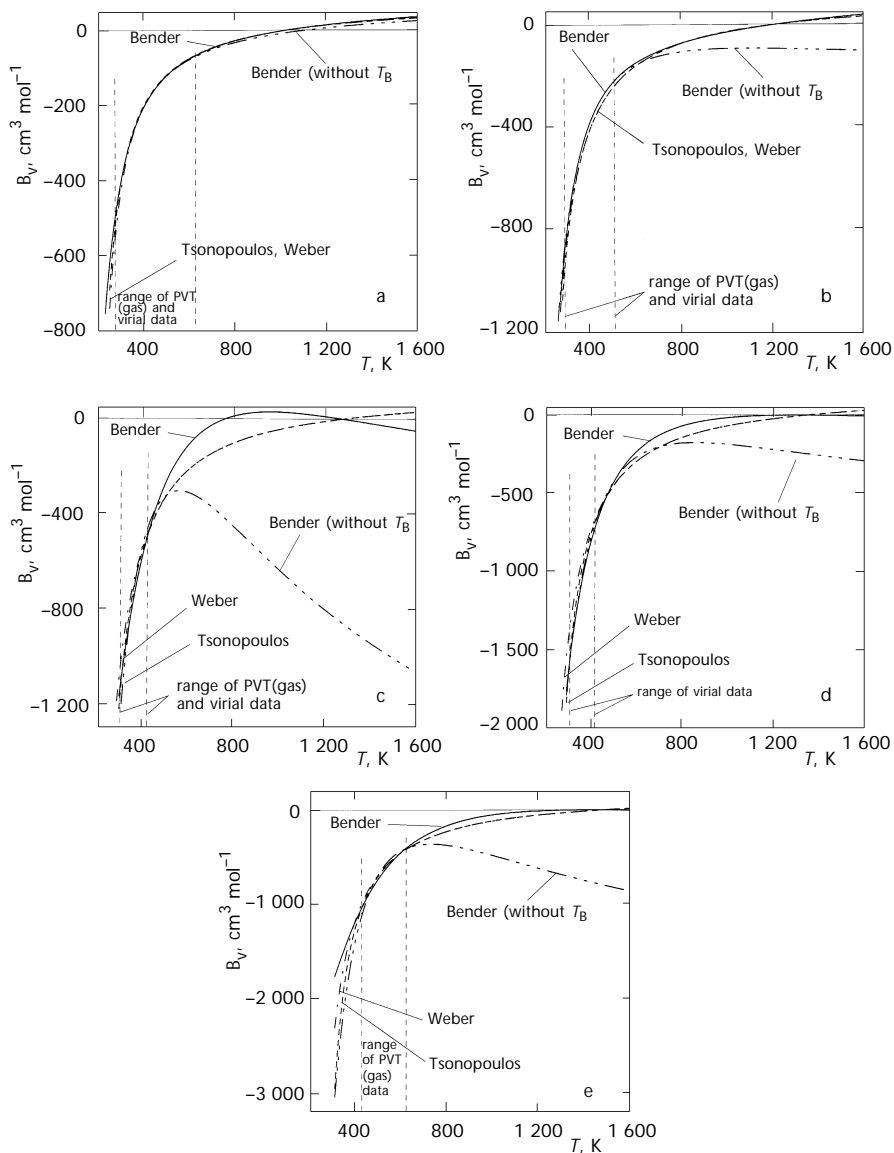


FIG. 1

Dependence of second virial coefficient on temperature: chloromethane (a), dichloromethane (b), trichloromethane (c), tetrachloromethane (d), and chlorobenzene (e). Bender: calculated using the parameters $\{a_k\}$, $k = 1, 2, \dots, 5$ from Table II; Bender (without T_B): calculated from the parameters $\{a_k\}$, $k = 1, 2, \dots, 5$ of the tentative fit where the Boyle temperature was not used; Tsonopoulos: estimated by the Tsonopoulos method⁵; Weber: estimated by the Weber method⁶

of the critical point. The Boyle temperature predicted from the fit with $\{\alpha_{ij}\} = (1, 0, 1, 1, 1)$ was 1 097 K (about 130 K below the estimated value). Inclusion of L data, however, led to the fit, where no Boyle temperature was found in the realistic temperature range (see Fig. 1b) and the deviations along the VLE curve doubled. The final fit ($\{\alpha_{ij}\} = (1, 1, 1, 1, 1)$; Table II and Fig. 1b) gives a correct Boyle temperature. Deviations of experimental values of second virial coefficient from the calculated ones are randomly scattered and lower than $\pm 25 \text{ cm}^3 \text{ mol}^{-1}$ except for two data points at low temperatures (see Fig. 2). It is worth mentioning that in the range from 300 to 700 K, the Bender equation based on experimental data gives higher (less negative) values of the second virial coefficient than the estimation methods^{5,6}.

Data available for trichloromethane are scarce and seem to be inconsistent. One set with only three values at low pressures was available for the single-phase gas (G data). Full-range fit of VLE data³⁸ (374.55–535.95 K, $\{\alpha_{ij}\} = (0, 0, 1, 0, 0)$) yielded rather high deviations at the critical point ($\delta_{r,z_c} = -9.6\%$, $\delta T_c = 0.11 \text{ K}$, $\delta_r \rho_c = 9.0\%$). For a tentative fit with $\{\alpha_{ij}\} = (0, 0, 1, 0, 1)$, the data points in the temperature range close to T_c (518–536 K) were rejected due to large deviations. Experimental virial coefficients are in mutual agreement except for the data of Francis and McGlashan⁵⁶ which were rejected due to large negative deviations (up to $-100 \text{ cm}^3 \text{ mol}^{-1}$) from other data at temperatures around 400 K. The data of Philippe *et al.*⁴²

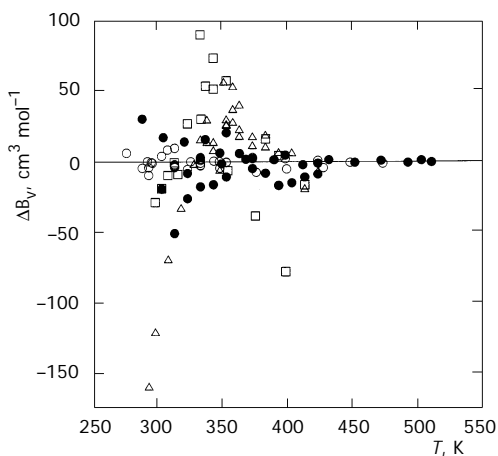


FIG. 2

Deviations of second virial coefficient $\Delta B_V = B_V(\text{exp}) - B_V(\text{calc})$: \circ chloromethane, \bullet dichloromethane, Δ trichloromethane, \square tetrachloromethane

that exhibit rather large negative deviations for $T < 300$ K (Fig. 2) were retained in the final fit since no other data were available in low temperature range. Virial coefficients calculated from the final fit (Table II and Fig. 1c) are in accordance with those resulting from the estimation methods^{5,6} within the temperature range of experimental data, which is, compared to chloromethane and dichloromethane, rather narrow. Extrapolation toward higher temperatures gives an incorrect Boyle temperature even for the final fit (Table II), where the estimated value was employed (from Fig. 1c it can be seen that the full line crosses zero value of the virial coefficient twice). Extrapolation from the fit without the Boyle temperature in the input data gives unrealistic values of the virial coefficient (see Fig. 1c). Higher order parameters $\bar{a} = \{a_k\}$, $k > 13$ are, compared to those for other substances, much more interrelated (Table II) as a consequence of insufficient input experimental data. Need for new experimental data for trichloromethane in wider T , p ranges is obvious.

No data for the single-phase gas (G data) were available for tetrachloromethane contrary to relatively large number of values for saturated vapour density. After the data close to the critical point (553.15–554.35 K) were rejected due to large deviations, a very good agreement between the calculated and experimental critical point ($\delta_r z_c = -1.8\%$, $\delta T_c = 2.17$ K, $\delta_r \rho_c = 0.42\%$) was obtained from the fit with $\{\alpha_j\} = (0, 0, 1, 0, 0)$. A fit of virial coefficient data ($\{\alpha_j\} = (0, 0, 0, 1, 0)$) yielded a deviation in virial coefficients $\text{RMSD}_r(B_V) = 3.0\%$ that increased to 4% when all available data groups were included (see Table II). Deviations between experimental and calculated virial coefficients are lower than ± 100 cm³ mol⁻¹ (Fig. 2). Extrapolation of virial coefficients to higher temperatures is somewhat better than in the case of trichloromethane; however, the values in the range from about 500 K to T_b are higher (less negative) than those calculated using the estimation methods^{5,6}.

No virial coefficient data were used for chlorobenzene. On the other hand there were two rather large sets of data available for single-phase vapour/gas which seem mutually consistent. Good consistence of the vapour-liquid equilibrium data with coordinates of the critical point was achieved after the data⁶⁰ in the range 563–628 K were rejected. Extrapolation of the second virial coefficient to high temperatures is substantially improved by inclusion of the estimated Boyle temperature into the input data (see Table II and Fig. 1e). It is worth noting that the extrapolation to low temperatures yields higher (less negative) second virial coefficients than the estimation methods^{5,6}. The reason might issue from the fact that the low-temperature limit of the data on the vapour/gas side (single-phase

vapour/gas and saturated vapour density) is somewhat higher (403 K) than for other chlorinated hydrocarbons investigated here and thus the region with large dB_V/dT is not covered by experimental data. Nevertheless, the values of the second virial coefficient calculated from the equation of state in the temperature range of experimental data are in agreement with those obtained from the estimation methods^{5,6} despite the fact that no virial coefficients were included in the input data used for the evaluation of the equation-of-state parameters.

CONCLUSIONS

The available experimental data on state behaviour of fluid phases for five chlorinated hydrocarbons were evaluated into the form of the Bender equation of state. Best results were obtained for substances, where sufficient number of experimental data was available (chloromethane, dichloromethane). On the other hand, a reasonable description of state behaviour using obtained parameters of equation of state cannot be expected for trichloromethane due to lack of experimental data.

It was demonstrated that good description of experimental second virial coefficients can be obtained using the parameters of the Bender equation. The results indicate that the parameters $\{a_k\}$, $k = 1, 2, \dots, 5$ are predominantly influenced by low-density p - ρ - T and second virial coefficient data while those of higher order terms (C , D , ..., Eq. (1)) by data at higher densities. This observation is in accordance with the results of the tests presented in our previous paper³ and with the conclusions of Malijevský and Hujo⁷⁰. On the other hand, if vapour/gas data (p - ρ - T and B_V) cover a narrow temperature interval at lower temperatures, where the curvature of the dependence $B_V(T)$ is moderate, then the parameters $\{a_k\}$, $k = 1, 2, \dots, 5$ are more interrelated ("too many parameters for a simple-shape dependence") and influenced by data at higher densities (dense gas, liquid). Extrapolations of the virial coefficient to high temperatures are highly unreliable in these cases. The inclusion of the Boyle temperature into the input data may lead to a significant improvement of extrapolations to high temperatures.

The vapour-liquid equilibrium curve, calculated from the phase equilibrium conditions for the equation-of-state parameters obtained using the present method, is described very satisfactorily except for trichloromethane. The deviations are close to experimental uncertainties.

The values of the compressibility factor in the liquid region cover a much broader interval (compared to the gas phase); they may span several orders of magnitude while the values of liquid density are of the order 10^3 to

10^4 kg m^{-3} . The slopes of isotherms $(\partial z/\partial \rho)_T$ are large in the dense fluid region which may lead to an increasing of interrelation among the parameters of the equation of state. The description of a single-phase compressed liquid by the Bender equation of state is therefore rather worse (particularly at low-pressures where the compressibility factor is of the magnitude 10^{-3}) than by simple empirical equations designed especially for the liquid phase (e.g., the Tait equation⁷¹) which are mostly fitted to experimental data in the form $\rho(T, p)$. It is, however, advisable to include liquid-phase p - ρ - T data in the evaluation of the equation-of-state parameters whenever possible since in their absence, an incorrect (negative) derivative $(\partial p/\partial \rho)_T$ may appear on the liquid side of the vapour-liquid equilibrium curve when vapour/gas (G) and equilibrium (VLE) data only are included³.

The reliability of extrapolations beyond the ranges of input experimental data could be improved by inclusion of other than state-behaviour data, e.g. heat capacities or speed of sound data. A search in available data sources revealed, however, that experimental data are available mostly for liquid phase at moderate pressures while the gaps in present data are predominantly in the high-pressure high-temperature ranges (dense supercritical gas).

LIST OF SYMBOLS

a_i	adjustable parameters of the Bender equation of state
B_v	second virial coefficient
f	fugacity
M	molar mass
n	number of moles
N	number of values (data points)
p	pressure
R	universal gas constant ($R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1}$)
RMSD	root mean square deviation ($\text{RMSD}(X) = \{\sum(X_{\text{calc}} - X_{\text{exp}})^2/N\}^{1/2}$)
RMSD_r	relative root mean square deviation ($\text{RMSD}_r(X) = \{\sum(X_{\text{calc}}/X_{\text{exp}} - 1)^2/N\}^{1/2}$)
T	temperature
V, V_m	volume, molar volume
w	data group weight factor
z	compressibility factor
α	data group inclusion parameter
δ	experimental uncertainty, deviation
ϕ	objective function
λ	Lagrange multiplier
ρ	mass density
ω	preselected weighting factor of a data point
ψ	constant

Subscripts

B	Boyle
c	critical
calc	calculated
CP	critical point data group
G	single-phase gas/vapour data group
<i>i, j, k, m</i>	experimental data point (<i>i</i> -th, <i>j</i> -th, . . .)
L	single-phase liquid data group
r	relative
sat	saturated
VLE	vapour-liquid equilibrium data group
V	second virial coefficient data group

Superscripts

(G)	gas/vapour
(L)	liquid

This work was supported by the Grant Agency of the Czech Republic (grant No. 203/98/0134) and partially by the Czech Ministry of Education, Youth and Sports (fund MSM 223400008).

REFERENCES

1. Bender E.: *Cryogenics* **1975**, 15, 667.
2. Teja A. S., Singh A.: *Cryogenics* **1977**, 17, 591.
3. Cibulka I., Kováčiková J., Hnědkovský L., Novák J. P.: *Fluid Phase Equilib.* **2001**, 180, 27.
4. Novák J. P., Malihevský A., Cibulka I.: *Collect. Czech. Chem. Commun.* **1999**, 64, 1087.
5. Tsonopoulos C.: *AIChE J.* **1974**, 20, 263.
6. Weber L. A.: *Int. J. Thermophys.* **1994**, 15, 461.
7. Dymond J. H.: *Fluid Phase Equilib.* **2000**, 174, 13.
8. Guye P. A.: *Bull. Soc. Chim. Fr.* **1909**, 339.
9. Shorthose D. N.: *G. B. Dep. Sci. Ind. Res., Food Invest. Board, Spec. Rep.* **1924**, 19, 1.
10. Tanner H. G., Benning A. F., Mathewson W. F.: *Ind. Eng. Chem.* **1939**, 31, 878.
11. Hsu C. C., McKetta J. J.: *J. Chem. Eng. Data* **1964**, 9, 45.
12. Suh K. W., Storvick T. S.: *AIChE J.* **1967**, 13, 231.
13. Mansoorian H., Hall K. R., Holste J. C., Eubank P. T.: *J. Chem. Thermodyn.* **1981**, 13, 1001.
14. Kumagai A., Iwasaki H.: *J. Chem. Eng. Data* **1978**, 23, 193.
15. McGarry J.: *Ind. Eng. Chem., Process Des. Dev.* **1983**, 22, 313.
16. TRC Tables 23-10-2-(10.011)-d. C-Cl-H. Chloroalkanes, C1 and C2. *TRC Thermodynamic Tables-Nonhydrocarbons*, p. 7240. Thermodynamics Research Center, The Texas A&M University System, College Station (TX) 1973.
17. TRC Tables 23-10-2-(1.013)-d. C-Cl-H. Monochloroalkanes, C1 to C5. *TRC Thermodynamic Tables-Nonhydrocarbons*, p. 7040. Thermodynamics Research Center, The Texas A&M University System, College Station (TX) 1981.
18. Hamann S. D., Pearse J. F.: *Trans. Faraday Soc.* **1952**, 48, 101.

19. Reeves C. G., Whytlaw-Gray R., Bottomley G. A.: *Nature* **1958**, 181, 1004.
20. Blythe A. R., Lambert J. D., Petter P. J., Spoel H.: *Proc. R. Soc. London, Ser. A* **1960**, 255, 427.
21. Bottomley G. A., Spurling T. H.: *Aust. J. Chem.* **1967**, 20, 1789.
22. Lichtenthaler R. N., Schaefer K.: *Ber. Bunsen-Ges. Phys. Chem.* **1969**, 73, 42.
23. Eubank P. T., Kreglewski A., Hall K. R., Holste J. C., Mansoorian H.: *AIChE J.* **1985**, 31, 849.
24. *CDATA Database of Physical and Transport Properties of Pure Fluids*. Department of Physical Chemistry, Institute of Chemical Technology, Prague and FIZ CHEMIE GmbH, Berlin 1993.
25. Singh R. P., Kudchadker A. P.: *J. Chem. Thermodyn.* **1979**, 11, 205.
26. Burkat R. K., Richard A. J.: *J. Chem. Thermodyn.* **1975**, 7, 271.
27. Kumagai A., Takahashi S.: *Chem. Lett.* **1982**, 971.
28. Eastal A. J., Woolf L. A.: *Int. J. Thermophys.* **1985**, 6, 331.
29. Baonza V. G., Caceres A. M., Arsuaga F. J., Nunez Delgado J.: *J. Chem. Thermodyn.* **1991**, 23, 231.
30. Fogg P. G. T., Hanks P. A., Lambert J. D.: *Proc. R. Soc. London, Ser. A* **1953**, 219, 490.
31. Perez Masia A., Diaz Pena M.: *An. Quim. Fis.* **1958**, 54, 661.
32. Raetzsch M.: *Z. Phys. Chem. (Leipzig)* **1968**, 238, 321.
33. Singh R. P.: *J. Chem. Eng. Data* **1986**, 31, 462.
34. Wormald C. J., Johnson P. W.: *J. Chem. Thermodyn.* **1998**, 30, 1235.
35. Buckingham A. D., Raab R. E.: *J. Chem. Soc.* **1961**, 5511.
36. Eastal A. J., Woolf L. A.: *J. Chem. Thermodyn.* **1984**, 16, 391.
37. Nhu N. V., Bhat S. N., Kohler F.: *Ber. Bunsen-Ges. Phys. Chem.* **1987**, 91, 525.
38. Campbell A. N., Chatterjee R. M.: *Can. J. Chem.* **1968**, 46, 575.
39. Zaalishvili S. D., Kolysko L. E.: *Zh. Fiz. Khim.* **1960**, 34, 2596.
40. Zaalishvili S. D., Kolysko L. E.: *Zh. Fiz. Khim.* **1961**, 35, 2613.
41. Zaalishvili S. D., Belousova Z. S., Kolysko L. E.: *Zh. Fiz. Khim.* **1965**, 39, 447.
42. Philippe R., Jose J., Clechet P.: *Bull. Soc. Chim. Fr.* **1971**, 2866.
43. Abuselme J. A., Vera J. H.: *Fluid Phase Equilib.* **1989**, 45, 287.
44. Doyle J. A., Hutchings D. J., Lancaster N. M., Wormald C. J.: *J. Chem. Soc., Faraday Trans.* **1998**, 94, 1263.
45. Holder G. A., Whalley E.: *Trans. Faraday Soc.* **1962**, 58, 2095.
46. Schamp H. W., Hastings J. R., Weissman S.: *Phys. Fluids* **1965**, 8, 8.
47. Mopsik F. I.: *J. Chem. Phys.* **1969**, 50, 2559.
48. Rogers K. S., Burkat R., Richard A. J.: *Can. J. Chem.* **1973**, 51, 1183.
49. Benson M. S., Winnick J.: *J. Chem. Eng. Data* **1976**, 21, 432.
50. Holzapfel K., Goetze G., Demiriz A. M., Kohler F.: *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1987**(1), 30.
51. Lainez A., Miller J. F., Zollweg J. A., Streett W. B.: *J. Chem. Thermodyn.* **1987**, 19, 1251.
52. Young S.: *J. Chem. Soc.* **1891**, 903.
53. Young S.: *J. Chem. Soc.* **1891**, 37.
54. Young S.: *Sci. Proc. R. Dublin Soc.* **1910**, 12, 374.
55. Campbell A. N., Chatterjee R. M.: *Can. J. Chem.* **1969**, 47, 3893.
56. Francis P. G., McGlashan M. L.: *Trans. Faraday Soc.* **1955**, 51, 593.
57. Perez Masia A., Diaz Pena M., Burriel Lluna J. A.: *An. Quim. Fis.* **1964**, 60, 229.
58. Jain D. V. S., Gupta V. K., Lark B. S.: *Indian J. Chem.* **1970**, 8, 815.

59. Wormald C. J., Lancaster N. M.: *J. Chem. Thermodyn.* **1996**, *28*, 245.
60. Agaev T. S., Kafarov T. E., Kerimov A. M.: *Zh. Fiz. Khim.* **1976**, *50*, 1901. (Data were taken from the deposited document VINITI No. 1196-76)
61. Ahlmeyer E., Bich E., Opel G., Schulze P., Vogel E.: *Z. Phys. Chem. (Leipzig)* **1982**, *263*, 519.
62. Gibson R. E., Loeffler O. H.: *J. Phys. Chem.* **1939**, *43*, 207.
63. Gibson R. E., Loeffler O. M.: *J. Am. Chem. Soc.* **1939**, *61*, 2515.
64. Agaev T. S., Kafarov T. A., Kerimov A. M.: *Izv. Akad. Nauk Azerb. SSR, Ser. Fiz.-Tekhn. Mat. Nauk* **1973**(3) 128.
65. Takagi T., Teranishi H.: *J. Chem. Thermodyn.* **1982**, *14*, 577.
66. Kashiwagi H., Fukunaga T., Tanaka Y., Kubota H., Makita T.: *J. Chem. Thermodyn.* **1983**, *15*, 567.
67. Abdullaev F. G., Dzhabiev Yu. A.: *Izv. Vyssh. Uchebn. Zaved., Neft Gaz* **1984**, *27*(8), 58.
68. Eastal A. J., Back P. J., Woolf L. A.: *J. Chem. Eng. Data* **1997**, *42*, 1261.
69. TRC Tables 23-10-(33.1001) to 23-10-2-(33.1001)-d. C-Cl to C-Cl-H. Chlorobenzenes, C6. *TRC Thermodynamic Tables-Nonhydrocarbons*, p. 7330. Thermodynamics Research Center, The Texas A&M University System, College Station (TX) 1990.
70. Malijevský A., Hujo T.: *Collect. Czech. Chem. Commun.* **2000**, *65*, 1464.
71. Cibulka I., Takagi T., Růžička K.: *J. Chem. Eng. Data* **2001**, *46*, 2.