

**EXCESS VOLUMES AND EXCESS ENTHALPIES
OF THE MIXTURES TETRACHLOROMETHANE + CYCLOALKANE
AND TRICHLOROMETHANE + CYCLOALKANE:
CALCULATION IN TERMS OF EQUATIONS OF STATE
OF THE VAN DER WAALS TYPE**

Ivan CIBULKA and Robert HOLUB

*Department of Physical Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6*

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The excess volumes and excess enthalpies for equimolar compositions and a temperature of 298.15 K for the binary liquid mixtures of tetrachloromethane and trichloromethane with cyclopentane, cyclohexane, cycloheptane and cyclooctane were calculated in terms of equations of state of the van der Waals type, the Redlich-Kwong equation of state and an equation following from the Flory theory. The pure-component parameters were evaluated in three different ways. The equations of state with pure-component parameters determined from gas-liquid critical constants yielded poor agreement with experiment. The best agreement with experiment was yielded by the Snider-Herrington equation with the pure-component parameters evaluated from molar volumes and thermal pressure coefficients and by the Flory equation. The Frisch equation extended to mixtures by using the van der Waals one-fluid approximation gave a good agreement with experiment in case of mixtures of molecules of approximately the same size. The excess entropies and the values of temperature derivatives of excess functions were as well calculated and compared with available experimental data.

The use of equations of state in an analytical form is one of the means for describing the thermodynamic properties of liquids and liquid mixtures. The generalized van der Waals equation of state is often used of these equations. The applicability of equations of state of the van der Waals type for predicting the properties of liquid mixtures has been verified formerly for mixtures of simple^{1,2} and complex³⁻⁷ molecules. The aim of this work is to contribute to this verification, and to compare the calculated values of excess volumes and excess enthalpies of the mixtures of tetrachloromethane and trichloromethane with cycloalkanes with the experimental data which have been obtained formerly^{8,9} or taken from the literature¹⁰⁻¹².

The generalized van der Waals equation may be written in the form

$$PV/RT = z(y) - a/VRT, \quad y = b/4V, \quad (1)$$

where a and b are the temperature independent parameters and $z(y)$ is the compressibility factor of a system of hard particles. The first term on the right-hand side of Eq. (1) represents the re-

pulsive forces between molecules, the second term the attractive forces. Eq. (1) is formally identical with an equation of state of the first-order perturbation theories where the parameter a is given by a perturbation integral, and is, in general, a function of temperature and density of the system. However, the use of the perturbation theories in case of more complex molecules meets with difficulties connected especially with insufficient knowledge of intermolecular potential, and then the results obtained do not often correspond to the complexity of calculation. However, provided the parameters a and b in Eq. (1) are considered to be constant quantities whose values can be determined by adjusting to suitably chosen properties of pure substances, the calculations are considerably simplified. With regard to the expressions which are used for the repulsive term in Eq. (1) (see below) and to the theoretical basis of the equation, its use is, however, limited, strictly speaking, to spherical nonpolar molecules. Equation of state (1), however, comprises the above-mentioned simplification, for extending the equation to mixtures are used further approximations, and so this limitation loses to a certain extent its strictness. Eq. (1) may then be used not only for nonpolar spherical molecules^{1,2} but also for the molecules whose shape is more or less different from sphere³⁻⁷ and even for polar molecules³.

A number of expressions were proposed for the repulsive term in Eq. (1). For the original van der Waals equation the relation (2)

$$z(y) = (1 - 4y)^{-1} \quad (\text{vdW}) \quad (2)$$

holds. For $z(y)$ it is possible to use the results of theories of distribution functions for systems of hard spheres so resulting *e.g.* the Frisch equation¹³

$$z(y) = (1 + y + y^2)(1 - y)^{-3} \quad (\text{Fr}) \quad (3)$$

The equation of state which was obtained by Flory and coworkers¹⁴ may be written as well in the general form (1), where

$$z(y) = c(1 - y^{1/3})^{-1} \quad (\text{Fl}) \quad (4)$$

where c is the third parameter of the equation of state. The attractive term of Eq. (1) can also be modified. As an example of such an equation, the Redlich-Kwong equation of state¹⁵ may be presented

$$PV/RT = z(y) - a/[(V + b) RT^{3/2}], \quad (\text{RK}) \quad (5)$$

where the repulsive term is identical with the van der Waals term $z(y) = (1 - 4y)^{-1}$.

Eq. (1) combined with relations (2) and (3) and Eq. (5) can be extended to a mixture of components 1 and 2 by applying the van der Waals one-fluid approximation

$$a = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}, \quad (6)$$

$$b = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22}, \quad (7)$$

where the combination rules are used for the parameters a_{12} and b_{12} :

$$a_{12} = (1 - k_{12}) (a_{11} a_{22} / b_{11} b_{22})^{1/2} b_{12}, \quad (8)$$

$$b_{12} = (b_{11}^{1/3} + b_{22}^{1/3})^3 / 8. \quad (9)$$

The interaction parameter k_{12} is usually considered as an adjustable parameter.

Ewing and Marsh⁶ proposed for extension of the Flory equation in the form of (1) and (4) the relations

$$a = b(x_1^2 a_{11}/b_{11}^{1/3} + 2x_1 x_2 a_{12}/b_{12}^{1/3} + x_2^2 a_{22}/b_{22}^{1/3})/(x_1 b_{11}^{2/3} + x_2 b_{22}^{2/3}), \quad (10)$$

$$b = x_1 b_{11} + x_2 b_{22}. \quad (11)$$

For the parameter c it is possible to derive the relation

$$c = x_1 c_{11} + x_2 c_{22}. \quad (12)$$

The Frisch equation can be extended to mixtures as well in the way due to Snider and Herrington¹⁶ who used for $z(y)$ of the mixture the compressibility equation of state of the mixture of additive hard spheres¹⁷ which can be written in the form

$$z(y) = [1 + y + y^2 - 3y(\alpha_1 + \alpha_2 y)](1 - y)^{-3}, \quad (\text{SH}) \quad (13)$$

where

$$b = x_1 b_{11} + x_2 b_{22}, \quad (14)$$

$$\alpha_1 = x_1 x_2 (b_{11}^{1/3} - b_{22}^{1/3})^2 (b_{11}^{1/3} + b_{22}^{1/3})/b, \quad (15)$$

$$\alpha_2 = x_1 x_2 (b_{11} b_{22})^{1/3} (b_{11}^{1/3} - b_{22}^{1/3})^2 (b_{11}^{2/3} x_1 + b_{22}^{2/3} x_2)/b^2. \quad (16)$$

Eqs (6), (8) and (9) can be used for the parameter a .

The equations of state mentioned are equations with two or three parameters a , b , and c , respectively, for each component whose values can be determined from the properties of pure components. The interaction parameter k_{12} can then be adjusted so that the agreement between the calculated and experimental value of a chosen property of mixture should be attained, and in such a way determined value of interaction parameter can be further used for calculating the other properties of mixture.

RESULTS AND DISCUSSION

Three ways of evaluating the pure-component parameters were used in this work for all the equations of state except for the Flory equation:

1) From gas-liquid critical constants by using the conditions

$$(\partial P/\partial V)_{T_c} = (\partial^2 P/\partial V^2)_{T_c} = 0. \quad (17)$$

This way is further denoted (V_c, T_c) . For the Redlich-Kwong equation, the recommended relations $(\text{RK}(P_c, T_c))$

$$a = 0.4278RT_c^{5/2}/P_c, \quad b = 0.0867RT_c/P_c \quad (18)$$

were used as well.

2) From liquid molar volumes and enthalpies of vaporization at the temperature of 298.15 K. This way is designated by (V, H) .

3) From liquid molar volumes and mechanical properties at the temperature of 298.15 K. For this way (denoted (V, β)), it is suitable⁴ to employ the coefficient $\beta = (\partial P / \partial T)_V$, which can easily be calculated from isothermal compressibilities, κ , and thermal expansivities, α ($\beta = \alpha / \kappa$). The parameters of the Flory equation were calculated from liquid molar volumes of liquids and coefficients β and κ ($Fl(V, \beta, \kappa)$). The experimental values of the quantities used for evaluating the parameters of pure components are summarized in Table I.

The excess volumes, excess enthalpies and excess Gibbs energies of the mixtures investigated at the temperature of 298.15 K and negligible pressure were calculated. The interaction parameter k_{12} was adjusted so that the agreement of calculated and experimental value of excess enthalpy of equimolar mixture, $H^E(x = 0.5, 298.15 \text{ K})$ might be attained. As the experimental concentration dependences of excess enthalpy are nearly symmetrical, this way is acceptable. The calculations were carried out as well by using the Thiele²⁹ and Carnahan–Starling³⁰ equations, however, the results were very close to those obtained from the Frisch equation. Nor the extension of the Carnahan–Starling equation to mixture in terms of the Mansoori and coworkers³¹ relation led to essentially different results from those yielded by the Snider–Herrington equation. A two-fluid extension to mixture was also examined, however, results uniquely better or worse than those obtained in terms of the one-fluid approximation were not obtained.

The calculated excess volumes of equimolar mixtures are given in Table II along with the experimental values. The experimental values of excess Gibbs energy were found only for the mixtures $\text{CCl}_4 + \text{c-C}_5\text{H}_{10}$ ($G^E(x = 0.5, 298.15 \text{ K}) = 34.1 \text{ J mol}^{-1}$, ref.²⁸), $\text{CCl}_4 + \text{c-C}_6\text{H}_{12}$ ($G^E(x = 0.5, 298.15 \text{ K}) = 69.8 \text{ J mol}^{-1}$, ref.²⁸) and $\text{CHCl}_3 + \text{c-C}_5\text{H}_{10}$ ($G^E(x = 0.5, 298.15 \text{ K}) = 262.0 \text{ J mol}^{-1}$, ref.¹¹), and the comparison of the calculated and experimental values is therefore given only qualitatively (see below).

It is evident from Table II that all the equations (independently of the way of evaluating the pure component parameters) represent qualitatively the non-monotonic dependence of excess volume $V^E(x = 0.5, 298.15 \text{ K})$ on the number of carbon atoms in the cycloalkane molecule for the mixtures $\text{CCl}_4 + \text{c-C}_n\text{H}_{2n}$ ($n = 5, 6, 7, 8$). For the mixtures containing trichloromethane, this dependence is qualitatively brought out only by the Snider–Herrington equation (again independently of the way of evaluating the pure component parameters), the Flory, the van der Waals ($vdW(V_c, T_c)$) and by the Frisch ($Fr(V_c, T_c)$) equations. This behaviour can be caused partly by the polarity of trichloromethane but it seems that especially the effect of differences in sizes of the component molecules plays here the role. This assertion can be supported by comparing the results yielded by the Frisch and Snider–Herring-

TABLE I

Properties of pure components: Critical pressure P_c , critical temperature T_c , critical volume V_c , liquid molar volume V_l , enthalpy of vaporization ΔH_v , thermal pressure coefficient β , isothermal compressibility α^a

Component	P_c , MPa	T_c , K	V_c , cm ³ mol ⁻¹	V_l , cm ³ mol ⁻¹	ΔH_v , kJ mol ⁻¹	β , MPa K ⁻¹	α , TPa ⁻¹
Tetrachloromethane	4.56 (18)	556.4 (18)	276 (18)	97.084 ^b	32.40 (20)	1.160 ^c	1.055 ^d
Trichloromethane	5.47 (18)	536.4 (18)	239 (18)	80.677 ^b	31.14 (20)	1.274 ^c	996 (27)
Cyclopentane	4.51 (18)	511.7 (18)	260 (18)	94.717 ^b	28.52 (21)	1.010 (24)	1.331 (24)
Cyclohexane	4.07 (18)	553.5 (18)	308 (18)	108.75 ^b	33.02 (22)	1.075 (24)	1.130 (24)
Cycloheptane	3.82 (19)	604.2 (19)	354 (19)	121.70 ^b	38.53 (23)	1.154 (25)	992 (25)
Cyclooctane	3.56 (19)	647 (19)	408 (19)	134.86 ^b	43.35 (23)	1.222 (24)	803 (24)

^a The data on V_l , ΔH_v , β , α are for the temperature of 298.15 K; numbers in parentheses stand for the numbers of references; ^b mean values of literature data selected; ^c calculated from values of α and β , where α was obtained from the temperature dependence of density; ^d mean value from refs^{26,27}.

TABLE II

The calculated and experimental excess volumes V^E ($\text{cm}^3 \text{mol}^{-1}$) of the equimolar mixtures $\text{CCl}_4 + \text{c-C}_n\text{H}_{2n}$ and $\text{CHCl}_3 + \text{c-C}_n\text{H}_{2n}$ ($n = 5, 6, 7, 8$) at 298.15 K^a

Values	k_{12}	V^E $\text{cm}^3 \text{mol}^{-1}$	k_{12}	V^E $\text{cm}^3 \text{mol}^{-1}$
	$\text{CCl}_4 + \text{c-C}_5\text{H}_{10}$ $H^E = 79.7 \text{ J mol}^{-1}$ (10)		$\text{CCl}_4 + \text{c-C}_6\text{H}_{12}$ $H^E = 166.0 \text{ J mol}^{-1}$ (10)	
Experiment	—	−0.036(8)	—	0.166(8)
vdW(V_c, T_c)	0.01073	0.114	0.01986	0.340
RK(V_c, T_c)	0.00532	−0.039	0.00982	0.062
RK(P_c, T_c)	0.00571	−0.044	0.00982	0.078
Fr(V_c, T_c)	0.00536	0.036	0.00988	0.210
SH(V_c, T_c)	0.00521	0.042	0.00936	0.233
vdW(V, H)	0.00448	−0.016	0.01051	−0.002
RK(V, H)	0.00490	−0.029	0.00992	0.058
Fr(V, H)	0.00419	0.004	0.00808	0.126
SH(V, H)	0.00397	0.015	0.00740	0.161
vdW(V, β)	0.00347	−0.032	0.00981	−0.013
RK(V, β)	0.00250	−0.058	0.00744	−0.007
Fr(V, β)	0.00372	−0.036	0.00770	0.100
SH(V, β)	0.00346	−0.023	0.00693	0.139
Fl(V, β, κ)	0.00213	0.013	0.00728	0.137
	$\text{CCl}_4 + \text{c-C}_7\text{H}_{14}$ $H^E = 134.7 \text{ J mol}^{-1}$ (9)		$\text{CCl}_4 + \text{c-C}_8\text{H}_{16}$ $H^E = 109.2 \text{ J mol}^{-1}$ (9)	
Experiment	—	0.098(9)	—	0.020(8)
vdW(V_c, T_c)	0.02030	0.068	0.02525	−0.408
RK(V_c, T_c)	0.01367	−0.114	0.02232	−0.486
RK(P_c, T_c)	0.01400	−0.159	0.02279	−0.621
Fr(V_c, T_c)	0.01197	0.092	0.01762	−0.135
SH(V_c, T_c)	0.00922	0.220	0.01072	0.204
vdW(V, H)	0.01434	−0.211	0.02117	−0.555
RK(V, H)	0.01465	−0.185	0.02290	−0.589
Fr(V, H)	0.01245	−0.064	0.02019	−0.386
SH(V, H)	0.00860	0.147	0.01150	0.110
vdW(V, β)	0.01396	−0.235	0.02111	−0.613
RK(V, β)	0.01269	−0.250	0.02109	−0.677
Fr(V, β)	0.01278	−0.119	0.02195	−0.528
SH(V, β)	0.00864	0.106	0.01242	0.013
Fl(V, β, κ)	0.00720	0.108	0.00706	0.033

TABLE II
 (Continued)

Values	k_{12}	V^E $\text{cm}^3 \text{mol}^{-1}$	k_{12}	V^E $\text{cm}^3 \text{mol}^{-1}$
	$\text{CHCl}_3 + \text{c-C}_5\text{H}_{10}$ $H^E = 551.1 \text{ J mol}^{-1}$ (11)		$\text{CHCl}_3 + \text{c-C}_6\text{H}_{12}$ $H^E = 639.8 \text{ J mol}^{-1}$ (12)	
Experiment	—	0.312(8)	—	0.546(8)
vdW(V_c, T_c)	0.06792	1.361	0.07999	1.398
RK(V_c, T_c)	0.03404	0.319	0.04249	0.267
RK(P_c, T_c)	0.03295	0.289	0.04342	0.158
Fr(V_c, T_c)	0.03401	0.795	0.04133	0.882
SH(V_c, T_c)	0.03372	0.807	0.03862	0.999
vdW(V, H)	0.03220	0.043	0.04343	−0.139
RK(V, H)	0.03041	0.198	0.04100	0.095
Fr(V, H)	0.02479	0.363	0.03346	0.356
SH(V, H)	0.02401	0.398	0.02869	0.585
vdW(V, β)	0.03087	0.033	0.04352	−0.178
RK(V, β)	0.02182	0.037	0.03414	−0.150
Fr(V, β)	0.02386	0.337	0.03439	0.292
SH(V, β)	0.02295	0.378	0.02893	0.554
Fl(V, β, α)	0.02423	0.414	0.03037	0.543
	$\text{CHCl}_3 + \text{c-C}_7\text{H}_{14}$ $H^E = 610.3 \text{ J mol}^{-1}$ (9)		$\text{CHCl}_3 + \text{c-C}_8\text{H}_{16}$ $H^E = 578.7 \text{ J mol}^{-1}$ (9)	
Experiment	—	0.455(9)	—	0.359(8)
vdW(V_c, T_c)	0.08294	0.893	0.08932	0.200
RK(V_c, T_c)	0.04986	−0.065	0.06139	−0.590
RK(P_c, T_c)	0.05380	−0.318	0.06740	−1.019
Fr(V_c, T_c)	0.04587	0.663	0.05335	0.338
SH(V_c, T_c)	0.03921	0.961	0.04077	0.931
vdW(V, H)	0.05235	−0.520	0.06298	−1.028
RK(V, H)	0.05123	−0.315	0.06356	−0.877
Fr(V, H)	0.04256	0.062	0.05383	−0.370
SH(V, H)	0.03152	0.621	0.03522	0.616
vdW(V, β)	0.05307	−0.599	0.06488	−1.163
RK(V, β)	0.04575	−0.599	0.05971	−1.217
Fr(V, β)	0.04519	−0.087	0.05927	−0.647
SH(V, β)	0.03288	0.533	0.03833	0.450
Fl(V, β, α)	0.03114	0.526	0.03145	0.453

^a The interaction parameter k_{12} adjusted to $H^E = H_{\text{exp}}^E$ ($\alpha = 0.5, 298.15 \text{ K}$); numbers in parentheses stand for the numbers of references.

ton equations. It is evident from Table II that the excess volume calculated from the equations whose extension to mixtures is based on the one-fluid approximation decreases progressively with increasing difference in sizes of the component molecules. To characterize this difference, it is possible to use ratios of liquid molar volumes of pure components at 298.15 K, $V(\text{c-C}_n\text{H}_{2n})/V(\text{CCl}_4 \text{ or } \text{CHCl}_3)$, whose values are 0.976, 1.120, 1.254, 1.389 for the mixtures with tetrachloromethane, and 1.174, 1.348, 1.508, 1.572 for the mixtures with trichloromethane for n equal gradually to 5, 6, 7, 8. The Frisch and Snider–Herrington equations are mutually equivalent for $b_{11} = b_{22}$, and consequently yield approximately the same values of excess volume for mixtures of molecules of approximately the same size ($\text{CCl}_4 + \text{c-C}_5\text{H}_{10}$, $\text{CCl}_4 + \text{c-C}_6\text{H}_{12}$, $\text{CHCl}_3 + \text{c-C}_5\text{H}_{10}$). For the other mixtures, the difference between $V^E(\text{SH})$ and $V^E(\text{Fr})$ is the higher the more differ the sizes of the component molecules, and always $V^E(\text{SH}) > V^E(\text{Fr})$ holds. The van der Waals and Redlich–Kister equations suffer from the same shortcomings as the Frisch equation, however, it is evident that they describe excess volume rather worse than the Frisch one.

Further it is evident from Table II that the calculated values of excess volume depend strongly on the way of evaluating the parameters of pure components. The calculations carried out with the parameters evaluated from gas–liquid critical constants (V_c, T_c) or (P_c, T_c), respectively, have yielded excess volumes which are in poor agreement with experiment. This finding proves the conclusions which were arrived by Ewing and Marsh^{6,7} who found that for mixtures of components which did not pertain to the same group of homologues, the (V_c, T_c)-parameters gave substantially worse results than the parameters evaluated from the properties of pure liquids at the given temperature. It should be mentioned that even in the cases when the equations with (V_c, T_c)-parameters have predicted excess volumes fairly well, the molar volumes of mixtures at 298.15 K are not predicted correctly for the equations of state have yielded incorrect values of molar volumes of pure components at 298.15 K (mean deviations: $\text{vdW}(V_c, T_c) + 20\%$, $\text{RK}(V_c, T_c) - 9\%$, $\text{RK}(P_c, T_c) + 10\%$, $\text{Fr}(V_c, T_c) - 13\%$). An apparent reason for this behaviour is inability of the equations of state used to describe the entire region of the liquid state from the temperature of 298.15 K up to the critical point.

The best agreement with experiment has been given by the Snider–Herrington $\text{SH}(V, \beta)$ and Flory $\text{Fl}(V, \beta, \kappa)$ equations. For mixtures of molecules approximately comparable in sizes a good agreement with experiment has been yielded also by the Frisch $\text{Fr}(V, \beta)$ equation. The excess volumes calculated on using the (V, H)-parameters are mildly higher than those calculated on using the (V, β)-parameters. For all the equations of state it is possible to write

$$V^E(V_c, T_c) > V^E(V, H) > V^E(V, \beta). \quad (19)$$

The excess volumes calculated in terms of the Redlich–Kwong $\text{RK}(V_c, T_c)$ equa-

tion are rather better than the results in terms of the $RK(P_c, T_c)$ equation, and mostly they considerably differ from the values calculated in terms of the van der Waals $vdW(V_c, T_c)$ equation. On the other hand, the excess volumes calculated from the $vdW(V, H)$ and $vdW(V, \beta)$ equations are relatively close to the results of the $RK(V, H)$ and $RK(V, \beta)$ equations. This fact indicates that in these cases, excess volume and excess enthalpy are influenced only little by different forms of the attractive term in iEqs (1) and (5).

The values of temperature derivatives of excess quantities $(\partial V^E/\partial T)_P$, $c_P^E = (\partial H^E/\partial T)_P$, $S^E = -(\partial G^E/\partial T)_P = (H^E - G^E)/T$ for $x = 0.5$ and the temperature of 298.15 K were calculated. The parameters of pure components and the interaction parameter were considered as temperature independent. Considering that the interaction parameter was adjusted to the agreement of calculated and experimental value of excess enthalpy, the comparison of calculated values of excess entropy, S^E , with experiment can be considered at the same time as the comparison of values of excess Gibbs energy. Experimental data on the temperature derivatives of excess quantities at 298.15 K were found in the literature only for the mixtures $CCl_4 + c-C_5H_{10}$ (ref.^{10,28,32}), $CCl_4 + c-C_6H_{12}$ (ref.^{10,28,33,34}) and $CHCl_3 + c-C_5H_{10}$ (ref.¹¹, S^E only). Therefore it is more expedient to present the results only qualitatively.

The equations of state $SH(V, \beta)$, $SH(V, H)$, $Fr(V, H)$, $RK(V, H)$, $RK(V_c, T_c)$ and $RK(P_c, T_c)$ have yielded $(\partial V^E/\partial T)_P < 0$ for the mixtures $CCl_4 + c-C_5H_{10}$, $CCl_4 + c-C_8H_{16}$ and $(\partial V^E/\partial T)_P > 0$ for the other mixtures, $c_P^E < 0$ and $S^E > 0$ for all the mixtures. From the comparison with available experimental data it has followed that in these cases the equations of state predict correct signs of the temperature derivatives, the quantitative agreement, however, has not been very good. The Flory equation has given the same signs of $(\partial V^E/\partial T)_P$ and S^E as the above mentioned equations, however, for all the mixtures with the exception of $CCl_4 + c-C_8H_{16}$ it has yielded $c_P^E > 0$. The interrelations between the temperature derivatives obtained in terms of the individual equations of state and particular types of parameters of pure components can be summarized in the form of the following inequalities

$$c_P^E(\text{exp}) < c_P^E(\text{RK}) < c_P^E(\text{SH}) < c_P^E(\text{Fr}) < c_P^E(\text{vdW}) < c_P^E(\text{Fl}), \quad (20)$$

$$S^E(\text{exp}) > S^E(\text{RK}) > S^E(\text{SH}) > S^E(\text{Fr}) > S^E(\text{vdW}) > 0 \quad (21)$$

for the same type of evaluating the parameters of pure components and each mixture,

$$S^E(\text{exp}) > S^E(V_c, T_c) > S^E(V, H) > S^E(V, \beta) > 0 \quad (22)$$

for individual equations of state and each mixture, and

$$S^E(\text{Fl}(V, \beta, \kappa)) \approx S^E(\text{SH}(V, \beta)). \quad (23)$$

Analogous inequalities cannot be written for $(\partial V^E/\partial T)_p$ and for $c_p^E(V_c, T_c)$, (V, H) , (V, β) for they differ for the individual mixtures investigated.

If we compare the prediction of excess entropy in terms of the Redlich–Kwong and van der Waals equations, it is evident that the attraction term in Eq. (5) influences substantially the prediction of excess entropy. It is then possible to assume that by a convenient modification of the attractive term in Eq. (1) (*e.g.* by expressing the temperature dependence of the parameter a), it would be possible to improve the prediction of excess Gibbs energy without changing the prediction of excess volume very much. To verify this suggestion, however, it would be necessary to use experimental data of a larger set of mixtures.

Ševčík and coworkers¹¹ calculated excess quantities of the mixture $\text{CHCl}_3 + c\text{-C}_5\text{H}_{10}$ at 298.15 K in terms of the first-order perturbation theory using a mixture of hard convex bodies (pyramid and regular pentagon) as a reference system. They estimated the value of interaction parameter from ionization potentials of components ($k_{12} = 0.015$), and for $x = 0.5$ they obtained $V^E = 0.24 \text{ cm}^3 \text{ mol}^{-1}$, $H^E = 410 \text{ J mol}^{-1}$, $G^E = 257 \text{ J mol}^{-1}$. The Snider–Herrington equation $\text{SH}(V, \beta)$ used in this work yielded $V^E = 0.22 \text{ cm}^3 \text{ mol}^{-1}$, $H^E = 383 \text{ J mol}^{-1}$, $G^E = 261 \text{ J mol}^{-1}$ for $k_{12} = 0.015$ and $x = 0.5$ at the temperature of 298.15 K. Accordingly it is evident that the use of the repulsive term $(z(y))$ for nonspherical hard particles in Eq. (1) (and if need be, the perturbation theory for the attractive term) does not lead in this case to a significant improvement of prediction of excess quantities. Ewing and Marsh as well drew similar conclusions referring the nonsphericity of the component molecules in case of the mixtures of cycloalkanes with 2,3-dimethylbutane⁶ and binary mixtures of cycloalkanes⁷.

The Flory equation gave results close to those obtained from the Snider–Herrington $\text{SH}(V, \beta)$ equation, however, it requires three parameters for each component of mixture. Nevertheless, the main shortcomings of the Flory equation consist in the fact that for an ideal gas, *i.e.* for $V \rightarrow \infty$, $PV/RT \rightarrow c$ (for the components of mixtures examined, c is from the interval 1.0019 to 1.3906) and that for liquids, $y(\text{Flory})$ is higher than $y(\text{close packing}) = 0.74$. These shortcomings are, together with the ability of the Flory equation to describe the temperature dependence of excess quantities, discussed in the literature⁶.

CONCLUSION

Several equations of state were employed for calculating the excess quantities of binary liquid mixtures of tetrachloromethane and trichloromethane with cycloalkanes. The interaction parameter was adjusted to the agreement of excess enthalpy of equimolar mixture with experiment. The best prediction of excess volumes was yielded by the Snider–Herrington equation with parameters determined from molar volumes and mechanical properties of pure components and by the Flory equation.

In spite of a considerable polarity of trichloromethane molecules, the agreement of calculated and experimental values of excess volume of mixtures containing trichloromethane is relatively good, however, rather worse than that for mixtures with tetrachloromethane. For mixtures of molecules of approximately the same size, the Frisch equation gave results close to those obtained from the Snider–Herrington equation. All the equations of state with parameters determined from gas–liquid critical constants yielded poor prediction of excess volumes. On using the parameters of pure components determined from molar volumes and heats of vaporization, excess volumes slightly higher than those calculated on using the parameters evaluated from mechanical properties were obtained. It is to be summarized that the predominant importance for predicting excess volume has the choice of repulsive term of equation of state and the method of evaluating the parameters of pure components, and for mixtures of molecules of different size, then also the extension of equation of state to mixtures. The excess entropies and the values of temperature derivatives of excess quantities were also calculated and compared with available experimental data. Here the Redlich–Kwong equation seems to be the best.

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