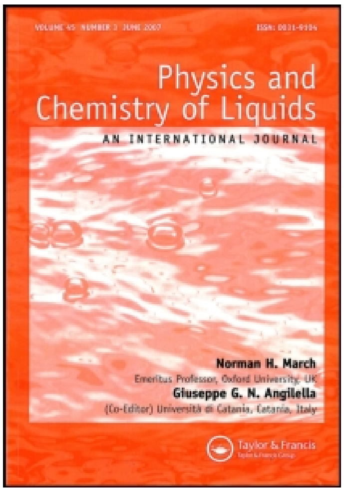

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Application of Two Hard Sphere Equations of State to Some Binary Non-Electrolyte Liquid Mixtures

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Experimental excess volumes V^E for 23 binary liquid mixtures consisting of polar (ethers, alcohols, amines or chloride hydrocarbons) + non polar components are compared with theoretical predictions of the equations of state of Snider and Herrington, and Guggenheim. The former predicts satisfactorily the sign of experimental V^E values in most of the cases, while the latter gives systematically large negative values. The one-fluid and two-fluid relations do not differ generally in their results.

INTRODUCTION

The fluid model of hard spheres has been extensively applied to binary liquid mixtures, the components of which have approximately a globular shape. In this paper we have applied it to more complicated mixtures with components of different shape, size and polarity. We have used two equations of state:

I) That of Snider and Herrington,[1] which has been obtained from the hard sphere equation of state of Reiss, Frisch and Lebowitz[2] modified by Longuet-Higgins and Widom.[3] This transformed equation of state has been successfully applied by Marsh[4] to mixtures of large globular molecules and by Snider and Herrington[1] to mixtures composed of small non-polar molecules. Subach and Kong[5] have also used this equation with mixtures of non-polar and significantly different molecules in size and shape.

II) That of Guggenheim[6] together with the van der Waals "one-fluid" and "two fluids" relations first used by Leland, Rowlinson, and Sather.[7] Leland *et al.*[8] and Marsh *et al.*[9] have also used the van der Waals "two-fluids" relations, and obtained substantially better agreement with the experimental results for simple systems than they did with the corresponding one-fluid theories. Marsh[4] has applied this prescription to mixtures of large globular molecules.

EQUATIONS AND CALCULATIONS

I) The modified equation of state used by Snider and Herrington is:

$$\frac{P}{nkT} = \phi(Y) - \frac{an}{kT} \tag{1}$$

where P is the pressure, n is the number density, k is Boltzmann's constant, T is the thermodynamic temperature, a is the van der Waals parameter, $\phi(Y)$ is

$$\phi(Y) = \frac{1 + Y + Y^2}{(1 - Y)^3} \tag{2}$$

where

$$Y = \frac{\pi r^3 n}{6} \tag{3}$$

and r is the hard sphere diameter. The function of density $\phi(Y)$ is the pressure of a hard sphere assembly at the same temperature and density as the model fluid.

The equation of state for binary mixtures is based on a generalization of $\phi(Y)$ to a binary mixture and on the configurational internal energy for mixing[10]

$$\frac{P}{n_m kT} = \phi_m(Y_m, x) - \frac{a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2}{kT} n_m \tag{4}$$

where a_{11} and a_{22} are the pure component parameters and a_{12} is the mixing parameters, n_m is the over-all density of the mixture, x_1 and x_2 are the respective mole fractions. $\phi_m(Y_m, x)$ is[1]

$$\phi_m = \frac{1 + Y_m + Y_m^2}{(1 - Y_m)^2} - \frac{3Y_m}{(1 - Y_m)^3} \cdot \frac{x_1x_2(r_1 - r_2)^2}{x_1r_1^3 + x_2r_2^3} \left(r_1 + r_2 + Y_m r_1 r_2 \frac{x_1r_1^2 + x_2r_2^2}{x_1r_1^3 + x_2r_2^3}\right) \tag{5}$$

and

$$Y_m = \frac{(x_1r_1^3 + x_2r_2^3)}{6} n_m \tag{6}$$

The respective equations for the excess functions are[4]

$$\frac{H^E}{NkT} = \sum_{i=1,2} x_i \left[\left(\frac{2P_m}{n_m kT} - \phi_m(Y_m, x) \right) - \left(\frac{2P_i}{n_i kT} - \phi(Y_i) \right) \right] \tag{7}$$

$$\frac{V^E}{N} = \frac{\pi}{6} \sum_{i=1,2} x_i r_i^3 (Y_m^{-1} - Y_i^{-1}) \tag{8}$$

The Y and r parameters of Eq. (1) can be determined from heat of vaporization data at the boiling-point by equations[4]

$$\frac{H_v}{NkT} = -\ln \frac{P}{nkT} - \ln(1 - Y) + \frac{3}{2} Y \frac{2 - Y}{(1 - Y)^2} \qquad \text{(Method A)} \tag{9}$$

$$\frac{H_v}{NkT} = \phi(Y) + 1 \qquad \text{(Method B)} \tag{10}$$

In Table I we give the necessary data for pure components at the boiling point used in the calculations.

With the known Y_s we have obtained firstly $\phi(Y)$ by Eq. (2), and then the van der Waals parameter a by Eq. (1).

TABLE I

Boiling-points data for the pure components

Component	$\Delta H_v / J\ \text{mol}^{-1}$	$V/m^3\ \text{mol}^{-1}\ 10^{-6}$	T/K	P/atm
benzene[5]	30765	96.09	353.35	1
tetrachloromethane[5]	30018	103.74	349.81	1
c-hexane[5]	33037	108.75	298.15	0.128
2-Cl 2-Methyl propane	32000[a]	112.32[b]	323.55	1
2-Cl propane	26514[11]	97.41[b]	308.00	1
2-Cl butane	30900[a]	115.09[b]	351.60	1
1-Cl pentane	33300[11]	138.81[b]	380.90	1
n-hexane[5]	29481	136.46	340.00	0.95
furan	27087[11]	72.4[b]	304.30	1
1-4 dioxane	35773[11]	86.5[b]	374.30	1
tetrahydrofuran	29648[c]	83.7[b]	337.00	1
tetrahydropyran	31748[c]	100.90[b]	361.00	1
methanol	35300[13]	342.44[b]	337.8	1
propanol	40480[13]	80.77[b]	370.4	1
terbutanol	39664[13]	103.45[b]	355.6	1
terbutylamine	29526[d]	102.84[b]	317.6	1
diethylamine	32843[a]	113.98[b]	329.1	1
aniline	40639[13]	101.25[b]	457.6	1

[a] Calculated from dT/dP data (Ref. 11).
[b] Calculated by Benson's method (Ref. 12).
[c] Calculated by Pitzer's method (Ref. 12).
[d] Calculated by Antoine's equation (Ref. 14).

Using the r and a parameters previously calculated, the molar volumes at the working temperature are obtained from Eq. (1), leaving aside the term in pressure. After this we obtain $\phi(Y)$ by means of the same Eq. (1).

In Table II are set out the heat of mixing data H^E for different mixtures of polar + non-polar components. $\phi(Y)$ and H^E are substituted in Eq. (7), in order to calculate ϕ_m at mole fraction $x = 0.5$ (leaving aside the term in P).

By replacing ϕ_m in Eq. (5) and solving this equation for Y_m we can evaluate V^E by Eq. (8). In Table III the calculated V^E values are compared with our experimental ones[9,10]

II) For the Guggenheim equation of state

$$\phi(Y) = (1 - Y)^{-4}, \tag{11}$$

where

$$Y = b/4V$$

The parameter b of the pure substance is evaluated by solving the equation:

$$\phi(Y)^c - V^c\left[\frac{\partial\phi(Y)}{\partial V}\right]_T^c - (V^c)^2\left[\frac{\partial^2\phi(Y)}{V^2}\right]_T^c = 0 \tag{12}$$

TABLE II

H^E data at mole fraction $x = 0.5$

Mixture	T/K	$H^E/J\ \mathrm{mol}^{-1}$
2-Cl 2-Me propane + benzene[15]	303.15	127.8
2-Cl 2-Me propane + tetrachloromethane[15]	303.15	52.9
2-Cl 2-Me propane + c-hexane[15]	303.15	488
2-Cl propane + c-hexane[15]	303.15	608
2-Cl butane + c-hexane[15]	303.15	529
1-Cl pentane + c-hexane[15]	303.15	499
furan + tetrachloromethane[16]	303.15	316
1-4dioxane + tetrachloromethane[16]	303.15	−237
tetrahydrofuran + tetrachloromethane[16]	303.15	−722
tetrahydropyran + tetrachloromethane[16]	303.15	−715
furan + n-hexane[16]	303.15	1150
1-4dioxane + n-hexane[16]	303.15	1594
tetrahydrofuran + n-hexane[16]	303.15	738
tetrahydropyran + n-hexane[16]	303.15	561
methanol + tetrachloromethane[17]	298.15	207
propanol + tetrachloromethane[17]	298.15	321
terbutanol + tetrachloromethane[18]	303.15	941
terbutilamine + tetrachloromethane[21]	303.15	59
aniline + tetrachloromethane[19]	298.15	280
terbutanol + benzene[18]	303.15	1572
terbutylamine + benzene[21]	303.15	540
aniline + benzene[19]	298.15	172
diethylamine + benzene[20]	298.15	332

and the parameter a is given by

$$a = \frac{RT^cV^c}{2}\left\{\phi(Y)^c - V^c\left[\frac{\partial\phi(Y)}{\partial V}\right]_T^c\right\} \tag{13}$$

where T^c and V^c are respectively the critical temperature and critical volume.

The interaction parameters a_{AB} and b_{AB} are obtained from the Berthelot and Lorenz combining rules.

$$\frac{a_{AB}}{b_{AB}} = \left[\frac{a_A}{b_A}\frac{a_B}{b_B}\right]^{1/2}\mathscr{E} \tag{14}$$

$$b_{AB} = [\tfrac{1}{2}(b_A^{1/3} + b_B^{1/3})]^3 \tag{15}$$

The deviations from these rules are expressed in terms of $\mathscr{E}$.

The parameters $a(x)$ and $b(x)$, characterizing the equivalent substances for the composition x, and the analogous two-fluids parameters $a_1(x)$, $a_2(x)$, $b_1(x)$ and $b_2(x)$, are defined by the corresponding van der Waals approximation:

$$b(x) = x^2b_A + 2x(1 - x)b_{AB} + (1 - x)^2b_B \qquad \text{(1F)}$$

$$a(x) = x^2a_A + 2x(1 - x)a_{AB} + (1 - x)^2a_B \qquad \text{(1F)}$$

$$a_1(x) = xa_A + (1 - x)a_{AB} \qquad \text{(2F)}$$

$$a_2(x) = (1 - x)a_B + xa_{AB} \qquad \text{(2F)}$$

$$b_1(x) = xb_A + (1 - x)b_{AB} \qquad \text{(2F)}$$

$$b_2(x) = (1 - x)b_B + xb_{AB} \qquad \text{(2F)}$$

The molar volume of the mixture is given by the appropriate roots of the equation of state.

The respective equations for the excess functions are:

$$\text{(1F)} \qquad H^E = -\frac{a(x)}{V} + x\,\frac{a_A}{V_A} + (1 - x)\frac{a_B}{V_B} \tag{16}$$

$$\text{(1F)} \qquad V^E = V_m - xV_A - (1 - x)V_B \tag{17}$$

V_m is the molar volume of the mixture.

$$\text{(2F)} \qquad H^E = x\left[-\frac{a_1}{V_1} + \frac{a_A}{V_A}\right] + (1 - x) - \frac{a_2}{V_2} + \frac{a_B}{V_B} \tag{18}$$

$$\text{(2F)} \qquad V^E = x(V_1 - V_A) + (1 - x)(V_2 - V_B) \tag{19}$$

Subscripts 1 and 2 refer to the equivalent fluids 1 and 2.

In our calculations the experimental values for H^E were used for evaluation of $\mathscr{E}$.

TABLE III

Calculated and experimental V^E values ($x = 0.5$)

Mixture	Snider and Herrington		Guggenheim		
	$V^E_{cal}(A)$	$V^E_{cal}(B)$	$V^E_{cal}(1F)$	$V^E_{cal}(2F)$	$V^E_{exp}/10^{-9}\ m^3\ mol^{-1}$
2-Cl 2-Methyl propane + benzene	−33	83	−8120	−8110	−254[15]
2-Cl 2-Methyl propane + tetrachloromethane	−244	65	−8750	−8740	−304[15]
2-Cl 2-Methyl propane + c-hexane	26	578	−7890	−7900	113[15]
2-Cl propane + c-hexane	354	693	−4660	−4630	286[15]
2-Cl butane + c-hexane	357	623	−5380	−5380	391[15]
1-Cl pentane + c-hexane	492	601	−5860	−5650	456[15]
furan + tetrachloromethane	232	359	−5600	−5030	498[16]
1-4-dioxane + *tetrachloromethane*	−871	−664	−8680	−9060	−290[16]
tetrahydrofuran + tetrachloromethane	−501	−705	−6820	−8080	−560[16]
tetrahydropyran + tetrachloromethane	−517	−720	−8610	−9890	−510[16]
furan + n-hexane	884	1323	−5830	−2920	1020[16]
1-4-dioxane + n-hexane	−499	119	−9270	−5100	470[16]
tetrahydrofuran + n-hexane	410	489	−7210	−5370	160[16]
tetrahydropyran + n-hexane	125	131	−8670	−7090	60[16]
methanol + tetrachloromethane	−1890	−1310	−5890	−5850	−41[22]
propanol + tetrachloromethane	−2080	−700	−5700	−5210	−100[22]
terbutanol + tetrachloromethane	−1440	−410	−4730	−2700	623[23]
aniline + tetrachloromethane	−580	−740	−9740	−9070	−320[19]
terbutanol + benzene	−760	1080	−4050	−730	672[23]
terbutilamine + benzene	340	440	−7500	−6110	31[21]
aniline + benzene	−360	−500	−8800	−8380	−240[19]
diethylamine + benzene	70	280	−4530	−3730	31[20]
terbutylamine + tetrachloromethane	0	30	−8010	−7720	−313[21]

TABLE IV

a_{12} values calculated from Eq. (20) as compared with those obtained from experimental H^E

Mixture	(Method A) $a_{12}/J\ m^3\ mol^{-2}$		(Method B) $a_{12}/J\ m^3\ mol^{-2}$	
	Using Eq. (20)	Using H^E	Using Eq. (20)	Using H^E
2 Cl, 2-Me propane + benzene	4.48	4.44	2.95	2.94
2 Cl, 2 Me propane + tetrachloromethane	4.58	4.57	3.03	3.02
2 Cl, 2 Me propane + cyclohexane	5.06	5.00	3.29	3.21
2 Cl propane + cyclohexane	3.75	3.65	2.79	2.70
2 Cl butane + cyclohexane	4.51	4.42	3.27	3.19
1 Cl pentane + cyclohexane	5.20	5.11	3.73	3.65
furan + tetrachloromethane	2.94	2.90	2.25	2.21
1,4-dioxane + tetrachloromethane	3.94	4.04	2.82	2.88
tetrahydrofuran + tetrachloromethane	3.27	3.36	2.52	2.61
tetrahydropyran + tetrachloromethane	3.79	3.90	2.86	2.95
furan + n-hexane	3.55	3.38	2.59	2.53
1,4 dioxane + n-hexane	4.72	4.64	3.23	3.09
tetrahydrofuran + n-hexane	3.93	3.83	2.89	2.81
tetrahydropyran + n-hexane	4.54	4.48	3.26	3.20
methanol + tetrachloromethane	2.85	3.07	2.02	2.12
propanol + tetrachloromethane	4.55	4.75	2.92	2.93
terbutanol + tetrachloromethane	5.34	5.33	3.27	3.14
terbutilamine + tetrachloromethane	3.97	3.95	2.79	2.78
aniline + tetrachloromethane	4.18	4.20	3.24	3.24
terbutanol + benzene	5.22	5.06	3.19	2.97
terbutylamine + benzene	3.87	3.79	2.72	2.65
aniline + benzene	4.09	4.09	3.16	3.16
diethylamine + benzene	4.56	4.49	3.02	2.97

DISCUSSION

As can be seen from Table III, the applied equation of Snider and Herrington predicts correctly the sign of experimental values of V^E in all the cases, except in that of 1-4-dioxane + *n*-hexane with Method A and 2-Cl 2-Methyl propane + benzene, and + tetrachloromethane with Method B. On the whole, Method A seems to have better predictive properties than Method B. The best agreement is obtained with systems in which tetrachloromethane and cyclohexane are involved.

It is interesting to compare the a_{12} values obtained from the experimental H^Es with those derived from the combining rule:

$$a_{12} = \left[\frac{a_{11}a_{22}}{r_1^3 r_2^3}\right]^{1/2}\left[\frac{r_1 + r_2}{2}\right]^3 \tag{20}$$

In Table IV both sets of values are set out, and, as can be observed, the agreement is generally good, what constitutes a further support of the model.

On the other hand, the excess volumes predicted by Guggenheim's equation have systematically large negative values, which never agree with the experimental ones, even in sign in most of the cases. The one-fluid and two-fluids relations do not differ generally in their results.

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