ACTA CHEMICA SCANDINAVICA 26 (1972) 2100–2112

Interaction Between Unlike Nonpolar Molecules: Correction of the Geometric Mean Rule. Part 3. Energies of Mixing

E. SONNICH THOMSEN

The Royal Danish School of Pharmacy, Chemical Laboratory A, 2100 Copenhagen Ø, Denmark

Combined use of the refined version of the solubility parameter theory and the geometric mean rule corrections evaluated in part 1 and part 2 (*Acta Chem. Scand.* **25** (1971) 260 and 265) makes it possible to account for energies of mixing of nonpolar liquids. The average numerical deviation between observed and calculated energies for equimolal mixtures for 31 systems (including 6 cryogenic and 3 fluorocarbon systems) is 12 cal/mol. Kihara $(6-n)$ potential functions are used for large molecules, *e.g.* octamethyl-cyclotetrasiloxane. No adjustable parameters are used but experimental excess volumes are needed for the calculations. Systems with chain molecules or with specific non-dispersion forces are not covered by the method. 41 additional systems are described in which specific forces act. The systematic deviations between observed and calculated energies of mixing indicate approximately the magnitudes of these specific forces.

The first paper [1] in this series (referred to as **1**) gave the basic formulae for correcting the geometric mean rules for calculating interactions between unlike molecules from those between the like molecules involved. In order to get numerical results, some correlations were evaluated in the second paper [2] (referred to as **2**) based on properties, *e.g.* critical temperatures, of gaseous mixtures. It turned out that it was possible to account for deviations from the geometric mean rules with almost the same precision as the original data used.

To investigate the general applicability of the method, properties which were not used in the first two papers should be considered. Energies of mixing (excess energies) of liquid systems will be the subject of this test. Contributions to these energies arising from specific forces (*e.g.* those between aromatic molecules and carbon tetrachloride) are causing systematic deviations which are described in a special section of this paper.

SOLUBILITY PARAMETER THEORY

The refined version of the solubility parameter equation for calculating energies of mixing was derived by Reed.[3] It may without further approximations be circumscribed into

$$\Delta e^{M} = \bar{\phi}_1\bar{\phi}_2\, v^{m}\,(\delta_1\beta_1 - \delta_2\beta_2)^2 + 2\bar{\phi}_1\bar{\phi}_2\, v^{m}\,\delta_1\delta_2\,(\beta_1\beta_2 - f) \quad (1)$$

with

$$v^{m} \equiv x_1v_1 + x_2v_2 + v^{E} \quad (2)$$

$$\bar{\phi}_1 \equiv x_1v_1/v^{m};\ \bar{\phi}_2 \equiv x_2v_2/v^{m} \quad (3)$$

$$\beta_1 \equiv [(1-\bar{\phi}_1)/\bar{\phi}_2]^{1/2};\ \beta_2 \equiv [(1-\bar{\phi}_2)/\bar{\phi}_1]^{1/2} \quad (4)$$

The solubility parameter, δ, is defined as the square root of the potential energy per unit volume. v and v^{E} are the molal volume and the experimental excess molal volume, respectively. x is the mol fraction, and f is the correction factor to the geometric mean rule for potential energies.

There are two advantages of eqn. (1) compared to Reeds equation. First, excess volumes are used instead of partial molal volumes, so that the equation can be used at one single concentration, say $x=1/2$, if v^{E} is determined at this concentration only. Second, the normal definition [4] of the solubility parameter is maintained.

The usual assumptions have been made in deriving eqn. (1): spherical nonpolar molecules, random mixing, and additivity of potential energies. Furthermore, when f is calculated according to **1** and **2**, dispersion forces alone are considered.

It should be noticed, that for $v^{E}=0$ and $f=1$ simultaneously, eqn. (1) gives the classical solubility parameter equation.[4]

GEOMETRIC MEAN CORRECTION

The correction factor f is a product of several factors (**1**, eqn. (19)):

$$f = f_I\, f_\alpha\, f_d\, f_n\, f_\psi \quad (5)$$

It is assumed in the following that f_ψ (**1**, eqn. (15) and (20)) is equal to one, which means that the influence of liquid structure is the same in the mixture and in the pure liquids. Hildebrand, Prausnitz and Scott [4] use $(1-\mathscr{l}_{12})$ for the product of the correction factors of eqn. (5), whereas $(1-k_{12})$ is used for $f_I f_\alpha f_d^2 f_N$, **1**, eqn. (11).

The equations in **1** and **2** were derived for Lennard-Jones $(6-n)$ potentials. As some of the mixtures in this paper involve rather large molecules however, the equations are rederived for Kihara $(6-n)$ potentials with core diameters a:

$$u(r) = \frac{\varepsilon n}{n-6}\left(\frac{n}{6}\right)\uparrow\left(\frac{6}{n-6}\right)\left[\left(\frac{\sigma-a}{r-a}\right)^{n} - \left(\frac{\sigma-a}{r-a}\right)^{6}\right] \quad (6)$$

in which $(A)\uparrow(B)$ means A^{B}. With the exception of a ($\neq a$ from **1**, eqn. (24)), the notation follows **1** and **2**. The use of a Kihara potential means that inter-

actions take place between the surface parts of the molecules. This was suggested by Hildebrand.[5]

The derivations are analogous to those of **1** and **2**; only the following equations are changed compared to these papers:

$$f_d \equiv ([(d_1^0 - a_1)(d_2^0 - a_2)]^{1/2}/(d_{12} - a_{12}))^3$$

(compare **1**, eqn. (12)) (7)

$$q \equiv 3n\left(\frac{n}{6}\right)\uparrow\left(\frac{3}{n-6}\right)\left[\frac{1}{3(n-3)} + \frac{a/(\sigma-a)}{2\,(n-2)} + \frac{[a/(\sigma-a)]^2}{5\,(n-1)}\right]$$

(compare **1**, eqn. (17)) (8)

$$\sigma = a + (d - a)\left(\frac{n}{6}\right)\uparrow\left(-\frac{1}{n-6}\right) \tag{9}$$

$$a_{12} = (a_1 + a_2)/2;\ d_{12} = (d_1^0 + d_2^0)/2;\ \sigma_{12} \neq (\sigma_1 + \sigma_2)/2 \tag{10}$$

Furthermore:

$$n^0 = 6 + 0.145v^0(1 - (a/d^0))^3$$

(compare **2**, eqn. (1)) (11)

$$\varkappa = \varkappa_{a=0}\ (1 - (a/d^0)) \tag{12}$$

$$d^0 = (v^0\ 10^{24}\sqrt{2}/N_0)^{1/3} \tag{13}$$

Excess refractive indices are related to y ($n_D^E \cong -4x_1x_2y$); in order to find y as a function of concentration we consider the equations analogous to **2**, eqn. (5):

$$\eta_1 = \eta_1^0 - 4x_2^2\,y \tag{14a}$$

$$\eta_2 = \eta_2^0 - 4x_1^2\,y \tag{14b}$$

η_1 and η_2 are substituted into **2**, eqn. (6), and the equation is solved with respect to y. Next, the experimental refractive indices n_D (which in this paper are always related to the polarisabilities by the Lorentz-Lorenz equation) are used for η^0 so that

$$y = \frac{\Delta(1/U)\,\Delta(n_D U)\,[0.0563 - 0.0883\,(|\Delta\varkappa|/(\varkappa_1 + \varkappa_2))^{1/3}]}{1 - 4\Delta(1/U)(U_2x_1^2 - U_1x_2^2)[0.0563 - 0.0883(|\Delta\varkappa|/(\varkappa_1 + \varkappa_2))^{1/3}]} \tag{15}$$

Preliminary calculations suggest that $a = 0$ for molecules smaller than neopentane ($d^0 \cong 5.9$ Å). With this assumption, a-values for the larger molecules were determined by minimizing the calculated excess energies (this corresponds to minimizing free energies because excess entropies are relatively unaffected by changes in a). It turned out that the "interaction shells" are of constant thickness so that

Table 1. The data for the pure substances.

	temp.	$\varkappa_{a=0}$	v (cm³/mol) *a*	v^0 (cm³/mol) *c*	δ (cal/cm³)$^{1/2}$ *a*	I (eV) *b*	$\alpha^0 \times 10^{24}$ (cm³/mol) *a,j,o*	a (Å) *d*
Ar	84.0 K	6	28.21	21.86	7.09	15.755	1.6264	0
	91.0	6	29.14	21.86	6.85	15.755	1.6264	0
	115.8	6	33.2	21.86	5.90	15.755	1.6264	0
Kr [k]	115.8	6	34.22	27.09	7.57	13.996	2.4559	0
N_2	77.0	6	34.63	26.19	5.89	15.60	1.734	0
	84.0	6	36.06	26.19	5.63	15.60	1.734	0
O_2	77.0	8	26.51	21.80	7.70	12.21	1.561	0
	84.0	8	27.27	21.80	7.46	12.21	1.561	0
CO [l]	90.7	8	37.24	26.71	5.63	14.01	1.926	0
CH_4	90.7	8	35.30	26.26	7.36	12.99	2.699	0
	91.0	8	35.36	26.26	7.35	12.99	2.699	0
n-C_6H_{14}	20°C	38	130.67	101.1	7.34	10.48	11.85	0
	25	38	131.57	101.1	7.27	10.48	11.86	0
	30	38	132.49	101.1	7.20	10.48	11.87	0
	35	38	133.43	101.1	7.13	10.48	11.89	0
n-C_7H_{16}	20	44	146.59	116.1	7.45	10.35	13.70	0
	25	44	147.51	116.1	7.43	10.35	13.70	0
	30	44	148.43	116.1	7.41	10.35	13.71	0
n-C_8H_{18}	20	50	162.59	131.0	7.57	10.24	15.53	0
	30	50	164.45	131.0	7.53	10.24	15.54	0
neo-C_5H_{12}	0	32	118.03	86.1	6.53	10.29	11.00	0.000
i-C_8H_{18}	20	50	165.09	130.9	6.91	9.86 [h]	15.56	0.850
	25	50	166.07	130.9	6.85	9.86 [h]	15.565	0.850
			±0.01	±0.2	±0.02	±0.05	±0.005	
	30	50	167.06	130.9	6.80	9.86 [h]	15.57	0.850
c-C_5H_{10}	25	30	94.71	74.3	8.10	10.53	9.17	0
c-C_6H_{12}	20	36	108.10	86.2	8.26	9.88	10.98	0
	25	36	108.75	86.2	8.19	9.88	10.986	0
			±0.02	±0.2	±0.02	±0.02	±0.003	
	40	36	110.79	86.2	8.00	9.88	11.00	0
	70	36	115.25	86.2	7.59	9.88	11.05	0
c-C_7H_{14}	25	42	121.61	101.5	8.50	9.88 [i]	12.78	0.299
c-C_8H_{16}	25	48	134.94	116.0	8.63	10.08 [i]	14.54	0.582
c-$C_6H_{11}CH_3$	20	42	127.61	102.1	7.88	9.85	12.88	0.312
	25	42	128.33	102.1	7.83	9.85	12.88	0.312
	65	42	134.59	102.1	7.37	9.85	12.95	0.312
C_6H_6	20	30	88.86	71.3	9.23	9.21	10.38	0
	25	30	89.40	71.3	9.16	9.21	10.38	0
	40	30	91.07	71.3	8.93	9.21	10.41	0
	70	30	94.69	71.3	8.48	9.21	10.46	0
$C_6H_5CH_3$	25	36	106.85	85.9	8.91	8.82	12.33	0
o-$C_6H_4(CH_3)_2$	25	42	121.19	100.4	8.99	8.58	14.20	0.277
	30	42	121.81	100.4	8.93	8.58	14.20	0.277
m-$C_6H_4(CH_3)_2$	25	42	123.46	100.4	8.82	8.58	14.26	0.277
	30	42	124.07	100.4	8.76	8.58	14.26	0.277
p-$C_6H_4(CH_3)_2$	25	42	123.93	100.4	8.77	8.48	14.28	0.277
1,3,5-$C_6H_3(CH_3)_3$	30	48	140.23	114.9	8.72	8.39	16.19	0.561
$(C_6H_5)_2$	70	58	155.28	129.4	9.42 [e]	8.3 [j]	20.82	0.822
CCl_4	0	24	94.21	77.1	8.97	11.47	10.45	0
	20	24	96.49	77.1	8.69	11.47	10.48	0

Table 1. Continued.

CCl_4	25°C	24	97.08	77.1	8.62	11.47	10.484	0
			±0.01	±0.2	±0.02	±0.01	±0.004	
	30	24	97.69	77.1	8.55	11.47	10.49	0
	40	24	98.91	77.1	8.41	11.47	10.51	0
	70	24	102.88	77.1	7.99	11.47	10.57	0
$SiCl_4$	20	24	114.64	89.4	7.62	11.60	11.37	0.043
	25	24	115.47	89.4	7.56	11.60	11.37	0.043
$TiCl_4$	20	24	109.80	86.8	8.74	11.7	15.03 [e]	0
$SnCl_4$	20	24	116.92	92.5	8.79	11.6 [e]	13.90	0.111
Br_2 [m]	20	10	51.25	44.2	11.49	10.55	6.43	0
C_2Cl_4	25	28	103.22	79.4	9.3	19.32	12.09	0
OMCTS[n]	25	88	312.12	255 [e]	6.40	9.5 [e]	29.58	2.528
$n\text{-}C_6F_{14}$	25	94	202.47	146.7	5.85	20.1 [f]	12.61	1.110
	35	94	205.98	146.7	5.70	20.1 [f]	12.62	1.110
$n\text{-}C_7F_{16}$	25	108	225.72	168.10	5.81	19.96 [f,g]	14.56	1.435
			±0.6	±0.04	±0.15	±0.2	±0.06	
	30	108	227.56	168.10	5.74	19.96 [f,g]	14.57	1.435
$c\text{-}C_6F_{11}CF_3$	65	98	209.2	148.4	5.73	18.93 [f]	13.55	1.137

[a] Data reported by the authors who determined excess volumes or enthalpies are preferred; beside these, data from Selected Values,[17,18] Timmermans,[19,20] Reed,[21] Rowlinson,[22] and Beilstein are used unless otherwise stated. [b] Vedeneyev *et al.*[23] [c] Sugden.[24] [d] eqn. (16); see text for n-alkanes. [e] estimated values. [f] eqn. (17). [g] Walkley *et al.*[25] use (but question) $I = 12.08$ eV from a report by Watanabe and Nakayama[26] which was apparently not published. [h] Streitwieser.[27] [i] Jannes and Puttemans.[28] [j] Landolt-Börnstein. [k] Gmelin. [l] Davies *et al.*[29] [m] Mellor. [n] OMCTS is octamethyl-cyclo-tetrasiloxane; data from Marsh.[12,31] [o] Moelwyn-Hughes,[33] p. 383.

$$a = \begin{cases} 0 & \text{for } d^0 < 5.9 \text{ Å} \quad (16a) \\ d^0 - 5.900 & \text{for } d^0 \geq 5.9 \text{ Å} \quad (16b) \end{cases}$$

(The correlation coefficient for eqn. (16b) is 0.975).

Exceptions from eqn. (16) are the normal alkanes, which cannot be described adequately with a spherosymmetric potential function. The assumption of $a = 0$ is preferred for such systems in this paper, but even then systematic deviations are seen for mixtures with n-alkanes higher than approximately C_7. Take as an example far beyond the range of this theory the energy of mixing of carbon tetrachloride + hexadecane which is 133 cal/mol (25°C, $x = 0.5$) [6] whereas 380 cal/mol and −20 cal/mol are calculated with $a = 0$ and $a \neq 0$, respectively. On the contrary, the perfluoro-n-alkanes seem to follow eqn. (16).

The data for the pure substances are shown in Table 1. The ionisation potentials for the fluorocarbons are not known. They are estimated from

$$I \text{ (eV)} = 1.729 \times 10^{-24} v^0/\alpha^0 \quad (17)$$

(correlation coefficient = 0.999) which is based on the properties of F_2, CF_4, SiF_4, and SF_6 (*cf.* Reed [7]).

The only property of the mixture which is used in the calculations is the experimental excess molal volume, shown in Tables 2 – 6. It should be stressed, that no adjustable parameters appear in the calculations.

EFFECT OF DISPERSION FORCES

The calculated energies of mixing are compared to the experimental ones in Table 2 ($a=0$) and in Table 3 (a_1 and/or $a_2 \neq 0$). 31 different systems are described, some of which are calculated at more than one temperature; a

Table 2. Excess energies (dispersion forces), $a=0$, for equimolal mixtures.

1	2	temp.	v^E(exptl.) (cm³/mol)	f ($x=0.5$)	Δe^M (cal/mol, $x=0.5$) calc.	exptl.
Ar	Kr	115.77 K	−0.52 [a]	0.9906	7	17 ± 4 [a]
Ar	CH_4	91	0.18 [b]	0.9817	26	25 [b]
Ar	N_2	84	−0.18 [c]	1.0012	9	12 [c]
Ar	O_2	84	0.14 [c]	0.9707	29	14 [c]
N_2	O_2	77	−0.21 [d]	0.9815	28	11 [d]
CH_4	CO	90.7	−0.33 [b,e]	0.9946	18	25 [b]
n-C_6H_{14}	c-C_6H_{12}	20°C	0.15 [q]	1.0003	33[35]æ	52 [g] 53 [h,p]
		25	0.23 [g]	1.0003	38	52 [h,i,p,y]
n-C_7H_{16}	c-C_6H_{12}	20	0.30 [q]	1.0000	39[32]æ	51[g]
		25	0.34 [g]	1.0000	39	57 [f,j]
c-C_5H_{10}	c-C_6H_{12}	25	0.04 [r]	0.9994	5	6 (20°C)[m] 7[i]
n-C_6H_{14}	CCl_4	30	0.03 [u]	0.9947	72[61]æ	73 [h]
n-C_7H_{16}	CCl_4	20	0.19 [v]; 0.27 [z]	0.9923	84[57]æ; 91	83 [h]
		30	0.19 [v]	0.9923	78	78 [h]
n-C_8H_{18}	CCl_4	20	0.31 [v]; 0.35 [z]	0.9887	102[50]æ; 105	87 [h]
		30	0.31 [v]	0.9887	96	82 [h]
c-C_5H_{10}	CCl_4	25	−0.03 [r,w]	0.9957	18	18 [w] 19 [i]
c-C_6H_{12}	CCl_4	20	0.16 [n]	0.9943	37	40 [h,i,o]
		25	0.16 [r]	0.9943	37	40[h,i,j]
		40	0.16 [q]	0.9943	35	37 [i]
		70	0.17 [q]	0.9943	34	(33) [i]
neo-C_5H_{12}	CCl_4	0	−0.55 [s]	0.9956	137	92 [h] 75 ± 5[t]
C_2Cl_4	c-C_5H_{10}	25	−0.01 [k]	0.9968	47	56 [k]
C_2Cl_4	CCl_4	25	0.02 [x]	0.9984	19	16 [x]
Br_2	CCl_4	20	0.51 [l]	0.9892	215	218 (23°C)[l]

[a] Davies *et al.*[29] [b] Lambert and Simon.[34] [c] Pool *et al.*[35] [d] Knobler *et al.*[36] [e] Mathot *et al.*[37] [f] Lundberg.[38] [g] Mathieson and Thynne.[39] [h] Harsted.[6] [i] Ewing and Marsh.[9] [j] Sturtevant and Lyons.[8] [k] Polak *et al.*[40] [l] Barthel.[41] [m] Dias d'Almeida *et al.*[42] [n] Kehlen and Sackmann.[43] [o] Kehlen and Sackmann.[44] [p] Marsh and Stokes.[30] [q] quoted from Ref. 14. [r] Bellemans.[50] [s] Mathot and Desmyter.[51] [t] Englert-Chwoles.[11] [u] estimated from Ref. 52. [v] Jain *et al.*[52] [w] Boublik *et al.*[53] [x] Poon and Lu.[54] [y] Murakami and Benson.[81] [z] Rodger *et al.*[57] æ values in [] are calculated with a for the normal alkanes from eqn. (16).

total of 42 calculations are performed. Statistical analysis was carried out for the 31 systems from these two tables (results for more than one temperature for the same system were preaveraged). The average numerical deviation between experimental and calculated energies is 12 cal/mol (standard deviation: 15 cal/mol), and the correlation coefficient is 0.993. The deviations for 84 % of the systems are within ± 20 cal/mol.

To investigate the influence of errors from the input data, detailed analyses were carried out for two systems at 25°C and $x=0.5$. The estimated errors of the parameters are listed in Table 1.

Table 3. Excess energies (dispersion forces), a_1 and/or $a_2 \neq 0$, for equimolal mixtures.

1	2	temp. (°C)	v^E(exptl.) (cm³/mol)	$f(a \neq 0)$ ($x = 0.5$)	Δe^M (cal/mol, $x = 0.5$) calc. $a = 0$	calc. $a \neq 0$	exptl.
i-C_8H_{18}	n-C_6H_{18}	20	−0.05 [r]	0.9934	14	44	6 (25°C) [q]
n-C_7H_{16}	c-$C_6H_{11}CH_3$	20	−0.01 [o]	0.9982	5	13	8 (25°C) [f] 9 [o]
i-C_8H_{18}	c-C_6H_{12}	25	0.01 [n]	1.0026	68	49	43 (30°C) [f,h]
c-C_6H_{12}	c-$C_6H_{11}CH_3$	25	0.02 [l]	1.0006	5	3	4 (20°C) [h]
i-C_8H_{18}	CCl_4	20	0.15 [a]	1.0014	147	100	95 [h]
		25	0.19 [n]	1.0014	147	101	94 [h]
c-$C_6H_{11}CH_3$	CCl_4	20	0.10 [a]	0.9965	51	38	38 [h]
$SiCl_4$	c-C_6H_{12}	20	0.21 [d]	0.9928	48	49	51 [o]
$SiCl_4$	CCl_4	20	0.05 [m]	0.9997	35	34	42 [p]
		25	0.05 [m]	0.9997	34	34	40 [p]
OMCTS	c-C_5H_{10}	25	0.05 [c]	1.0178	302	40	51 [b]
OMCTS	CCl_4	25	−0.25 [c]	1.0192	396	91	39 [g,h]
n-C_6H_{14}	n-C_6F_{14}	25	4.84 [j]	0.9253	615	520	516 [i]
		35	5.38 [i]	0.9247	615	528	516 [i]
i-C_8H_{18}	n-C_7F_{16}	25	5.08 [k]	0.9230	521	531	505 [i]
		30	5.30 [k]	0.9228	524	534	505 [i]
c-$C_6H_{11}CH_3$	c-$C_6F_{11}CF_3$	65	7.3 [e]	0.9310	673	623	(670 [e])

[a] Rodger *et al.*[57] [b] Marsh.[49] [c] Levien and Marsh.[46] [d] Kehlen and Sackmann.[43] [e] Dyke *et al.*[13] [f] Lundberg.[38] [g] Marsh and Tomlins.[12] [h] Harsted.[6] [i] Williamson and Scott.[10] [j] Bedford and Dunlap.[55] [k] Reed and Taylor.[56] [l] Roveillo and Gomel.[58] [m] Sackmann and Arnold.[59] [n] Washington and Battino.[62] [o] Brandt and Röck.[63] [p] Kolbe and Sackmann.[64] [q] Sturtevant and Lyons.[8] [r] Timmermans.[78]

For carbon tetrachloride + cyclohexane this analysis resulted in ± 1.0 cal/mol (of which ± 0.7 cal/mol comes from an estimated error of ± 0.01 cm³/mol for v^E). For isooctane + perfluoroheptane was found ± 19.9 cal/mol (here ± 17.8 cal/mol comes from an estimated error of ± 0.5 cm³/mol for v^E).

Beside these errors, the experimental energies of mixing used for comparison might be more or less precise. Whereas the experimental excess energy for carbon tetrachloride + cyclohexane is undoubtedly good within a fraction of 1 cal/mol,[6,8,9], an error of about ± 4 − 5 cal/mol is revealed by the least square curve fitting for isooctane + perfluoroheptane [10] (possible additional systematic errors are not disclosed by this fitting).

Furthermore, it was found that $d\Delta e^M(\text{calc.})/df$ and $d\Delta e^M(\text{calc.})/dv^E$ (exptl.) are -0.36×10^4 cal/mol and 70 cal/cm³, respectively, for carbon tetrachloride + cyclohexane, and -0.37×10^4 cal/mol and 36 cal/cm³, respectively, for isooctane + perfluoroheptane.

The deviation of 137 − 75 = 62 cal/mol for neopentane + carbon tetrachloride [11] urged us to repeat this determination;[6] the deviation remained unexplained but was reduced to 137 − 92 = 45 cal/mol. The deviation for octamethyl-cyclotetrasiloxane (OMCTS) + carbon tetrachloride (91 − 39 = 52 cal/mol) is not caused by experimental error: we [6] confirmed the measurements of Marsh and Tomlins.[12] (It should be borne in mind that the properties of pure OMCTS are some of the less established.)

In the case of the fluorocarbon systems, there might be non-random-mixing effects as well as systematic errors because of the estimated ionisation potentials, eqn. (17), and, furthermore, the energy of mixing for methylcyclohexane + perfluoromethyl-cyclohexane originates from free energy calculations combined with only two calorimetric measurements ($x \neq 0.5$) at 80°C.[13]

On the whole it seems possible to use the solubility parameter equation to calculate energies of mixing on the following conditions: (a) experimental excess volumes should be used, (b) only dispersion forces should act, (c) the geometric mean rule should be properly corrected, (d) the molecules should be spherical or nearly spherical, and (e) random mixing, additivity of potential energies, and similar structures in the mixture and in the pure liquids ($f_\psi = 1$) should be likely.

Table 4. Excess energies (specific forces and dispersion forces), for equimolal mixtures.

1	2	temp. (°C)	v^E(exptl.) (cm³/mol)	$f(a \neq 0)$ ($x = 0.5$)	Δe^M (cal/mol, $x = 0.5$) calc.	exptl.
C_6H_6	n-C_6H_{14}	25	0.46 [a]	1.0012	120	205 (20°C) [a]
C_6H_6	n-C_7H_{16}	25	0.60 [a]	0.9990	126	221 [f]
C_6H_6	i-C_8H_{18}	25	0.59 [m]	1.0071	162	237 [f]
C_6H_6	c-C_5H_{10}	25	0.30 [n]	1.0008	45	151 [n]
C_6H_6	c-C_6H_{12}	20	0.61 [p]	1.0006	66	196 [a]
		25	0.65 [d]	1.0006	69	191 [f,g,u]
		40	0.66 [o]	1.0007	66	180 [q]
		70	0.67 [o]	1.0007	61	155 [q]
C_6H_6	c-C_7H_{14}	25	0.67 [n]	1.0028	51	181 [n]
C_6H_6	c-C_8H_{16}	25	0.58 [n]	1.0049	31	191 [n]
C_6H_6	OMCTS	25	−0.01 [e]	1.0226	171	190 [i]
$C_6H_5CH_3$	n-C_7H_{16}	25	0.16 [r]	1.0017	71	132 [f]
$C_6H_5CH_3$	i-C_8H_{18}	25	0.08 (28°C) [k]	1.0043	124	149 (30°C) [k]
$C_6H_5CH_3$	c-C_5H_{10}	25	0.08 [n]	0.9971	32	87 [n]
$C_6H_5CH_3$	c-C_6H_{12}	25	0.57 [n]	1.0008	52	149 [n]
$C_6H_5CH_3$	c-$C_6H_{11}CH_3$	25	0.37 [s]	1.0017	53	125 [s]
$C_6H_5CH_3$	c-C_7H_{14}	25	0.53 [n]	1.0019	36	141 [n]
$C_6H_5CH_3$	c-C_8H_{16}	25	0.51 [n]	1.0034	24	148 [n]
m-$C_6H_4(CH_3)_2$	c-C_6H_{12}	25	0.7 (34°C) [t]	0.9991	66	137 [f]
$TiCl_4$	c-C_6H_{12}	20	0.21 [b]	0.9828	89	60 [c]
$TiCl_4$	CCl_4	20	0.08 [j]	0.9963	20	42 [l]
$TiCl_4$	$SiCl_4$	20	−0.38 [j]	0.9980	17	38 [l]
$SnCl_4$	c-C_6H_{12}	20	0.92 [b]	0.9856	132	148 [c]
$SnCl_4$	CCl_4	20	0.46 [j]	0.9974	46	69 [l]
$SnCl_4$	$SiCl_4$	20	0.13 [j]	0.9985	54	64 [l]

[a] Mathieson and Thynne.[39] [b] Kehlen and Sackmann.[43] [c] Kehlen and Sackmann.[44] [d] Stokes *et al.*[45] [e] Levien and Marsh.[46] [f] Lundberg.[38] [g] Stokes *et al.*[47] [h] Harsted.[6] [i] Marsh and Tomlins.[12] [j] Sackmann and Arnold.[59] [k] Prengle *et al.*[61] [l] Kolbe and Sackmann.[64] [m] Danusso.[65] [n] Watson *et al.*[66] [o] Wood and Austin.[67] [p] Suri and Ramakrishna.[68] [q] estimated by Abe and Flory.[14] [r] Tsao and Smith.[69] [s] Wóycicki and Sadowska.[70] [t] Reddy *et al.*[71] [u] Murakami and Benson.[81]

Table 5. Excess energies (specific forces and dispersion forces), for equimolal mixtures.

1	2	temp. (°C)	v^E(exptl.) (cm³/mol)	$f(a \neq 0)$ ($x = 0.5$)	Δe^M (cal/mol, $x = 0.5$) calc.	exptl.
CCl_4	C_6H_6	25	0.00 [a]	0.9966	20	27 [b] 28 [k]
		40	0.03 [d]	0.9966	21	31 [c]
		70	0.11 [h]	0.9966	25	35 [c]
CCl_4	$C_6H_5CH_3$	25	−0.04 [d,f]	0.9936	24	−4 [j]
CCl_4	o-$C_6H_4(CH_3)_2$	30	0.00 [g]; 0.10 [d]	0.9939	29; 37	−5 [g,j]
CCl_4	m-$C_6H_4(CH_3)_2$	30	0.10 [g]; 0.16 [d]	0.9940	33; 38	6 [g] 2 [j]
CCl_4	p-$C_6H_4(CH_3)_2$	25	0.03 [f]; 0.08 [d]	0.9936	29; 33	−17 [j]
CCl_4	1,3,5-$C_6H_3(CH_3)_2$	30	0.33 [e]; 0.46 [d]	0.9951	46; 56	25 [e,j]

[a] Levien and Marsh.[46] [b] Stokes *et al.*[47] [c] interpolated and extrapolated from data of Stokes *et al.*[47] and Ewing *et al.*[48] [d] Schmack and Bittrich.[60] [e] Nath and Yadava.[72] [f] Rastogi *et al.*[73] [g] Rastogi *et al.*[74] [h] Staveley *et al.*[75] and Wood and Brusie.[76] [i] Howell and Stubley.[77] [j] McGlashan *et al.*[15] [k] Murakami and Benson.[81]

SPECIFIC FORCES

When systematic deviations between experimental and calculated energies of mixing are observed, one or more of the above conditions are violated.

Mixtures of aromatic hydrocarbons with aliphatic ones (and with OMCTS) exhibit calculated excess energies which are too low by typically 60 − 130 cal/mol; see Table 4. Apparently, the reason is that specific forces between the aromatic molecules are destroyed when these liquids are diluted; this contributes positively to the excess energies. This point of view is supported by Abe and Flory [14] who suggest "an ordered arrangement in pure benzene which is dissipated by mixing".

On the other hand, Table 5 shows that comparatively small deviations are found for mixtures of aromatic molecules with carbon tetrachloride. We know [15] that specific forces exist between, *e.g.* benzene and carbon tetrachloride; this means that the positive contribution to the excess energy of the destroyed "aromatic forces" is nearly compensated for by the specific forces established between the unlike molecules.

In this particular case the result happens to be an agreement between experimental and calculated energies, but it is obvious that the agreement is jeopardized when the "strength" of the forces are changed by going to other aromatic molecules. McGlashan *et al.*[15] discuss the significance of the "strength" of a complex and stress that it is important to specify whether it is related to enthalpies or to equilibrium constants.

Next, it should be expected that "aromatic forces" can be reestablished between unlike aromatic molecules, and that these forces should − but only approximately − compensate for the two dilution effects. This is illustrated in Table 6.

It is not immediately possible from the results of this paper to make any quantitative conclusions as to the "strengths" (expressed as enthalpies) of the "aromatic forces". The reason is that the experimental excess volumes, which are used in the calculations depend strongly on these forces: whereas v^E for

Table 6. Excess energies (specific forces and dispersion forces), for equimolal mixtures.

1	2	temp. (°C)	v^E(exptl.) (cm³/mol)	$f(a \neq 0)$ ($x = 0.5$)	Δe^M (cal/mol, $x = 0.5$) calc.	exptl.
C_6H_6	$C_6H_5CH_3$	25	0.09 [f]	0.9995	11	16 [d,f]
C_6H_6	o-$C_6H_4(CH_3)_2$	25	0.25 [e]	1.0006	19	52 [e]
C_6H_6	m-$C_6H_4(CH_3)_2$	25	0.29 [e]	1.0006	24	53 [e]
C_6H_6	p-$C_6H_4(CH_3)_2$	25	0.21 [e]	1.0003	19	39 [e]
C_6H_6	1,3,5-$C_6H_3(CH_3)_3$	30	0.53 [c]	1.0021	35	92 [c]
C_6H_6	$(C_6H_5)_2$	70	−0.3 [h]	1.0034	−15	34 [i]
$C_6H_5CH_3$	o-$C_6H_4(CH_3)_2$	25	0.04 [f]	1.0004	2	11 [d,f]
$C_6H_5CH_3$	m-$C_6H_4(CH_3)_2$	25	0.05 [f]	1.0004	3	10 [f]
$C_6H_5CH_3$	p-$C_6H_4(CH_3)_2$	25	0.02 [f]	1.0003	1	5 [f]
o-$C_6H_4(CH_3)_2$	m-$C_6H_4(CH_3)_2$	25	0.00 [g]	1.0000	1	3 [g]
o-$C_6H_4(CH_3)_2$	p-$C_6H_4(CH_3)_2$	25	−0.01 [g]	1.0000	1	1 [d] 2 [g]
m-$C_6H_4(CH_3)_2$	p-$C_6H_4(CH_3)_2$	25	−0.01 [g]	1.0000	−1	−2 [g]
$TiCl_4$	$SnCl_4$	20	0.08 [b]	1.0001	6	46 [a]

[a] Kolbe and Sackmann.[64] [b] Sackmann and Arnold.[59] [c] Nath and Yadava.[72] [d] Sturtevant and Lyons.[8] [e] Singh *et al.*[79] [f] Murakami *et al.*[80] [g] Lam *et al.*[82] [h] Marechal.[83] [i] Kortüm *et al.*[84]

ordinary mixtures (excluding fluorocarbon systems) at room temperature are typically close to 0.1 cm³/mol, the corresponding values for mixtures of aromatic hydrocarbons with aliphatic ones are increased to about 0.4 cm³/mol. Thus, the calculated excess energies include an indefinite fraction of the contributions from the "aromatic forces".

Three ways can be proposed to evade this dilemma. First, one could in the calculations use excess volumes for systems for which the aromatic liquid is replaced by a nonpolar, nonaromatic liquid (or a mixture of two or more such liquids) with the same properties as the aromatic one. So far it has been impossible to find such liquids.

Second, excess volumes calculated from a theory which takes into account only dispersion forces could be used. As this theory should not be based on experimental properties of the actual system, say Δe^M, it is apparently difficult to indicate such a theory.

Third, one could use a version [60] of the homomorph concept so that v^E for C_6H_6+"X" is replaced by v^E for c-C_6H_{12}+"X", v^E for $C_6H_5CH_3$+"X" by v^E for c-$C_6H_{11}CH_3$+"X", *etc.* at the same concentration and temperature. Calculations with the available data for 5 benzene- and 3 toluene-systems indicate that the previous difference between experimental and calculated excess energies (typically 60 – 130 cal/mol) is increased by 30 % on the average. This energy compares favourably with the energy of the benzene-benzene complex obtained by Schuler [16] from the effect of pressure on the absorption spectrum of dilute solutions in isooctane. To compare his value (170 – 221 cal/mol) with the one obtained here, the former should be divided by 4 because approximately half of the benzene-benzene contacts are destroyed in one half mole benzene in the equimolal mixture.

Finally, systems including titanium tetrachloride or tin tetrachloride exhibit systematic deviations. With one exception (titanium tetrachloride + cyclohexane) the calculated excess energies are between 10 and 23 cal/mol lower than the experimental ones (Table 4). Although the limitations of the theory are approached this might suggest that extremely weak specific forces exist in these two liquids, possibly similar to those in Al_2Cl_6. On the other hand, these forces are not reestablished between tin tetrachloride and titanium tetrachloride so that the two dilution effects together give the deviation $(46 - 6 = 40$ cal/mol) for this system, see Table 6.

Acknowledgements. The author is grateful to Professor J. Chr. Gjaldbæk for kind interest and to *The Royal Danish School of Pharmacy* and *Statens naturvidenskabelige Forskningsråd* for financial support.

REFERENCES

1. Thomsen, E. S. *Acta Chem. Scand.* **25** (1971) 260.
2. Thomsen, E. S. *Acta Chem. Scand.* **25** (1971) 265.
3. Reed III, T. M. *J. Phys. Chem.* **59** (1955) 425.
4. Hildebrand, J. H., Prausnitz, J. M. and Scott, R. L. *Regular and Related Solutions*, van Nostrand Reinhold Co., New York 1970.
5. Hildebrand, J. H. and Scott, R. L. *Regular Solutions*, Prentice-Hall, New Jersey 1962, p. 123.
6. Harsted, B. *To be published.*
7. Reed III, T. M. *J. Phys. Chem.* **59** (1955) 428.
8. Sturtevant, J. M. and Lyons, P. A. *J. Chem. Thermodynamics* **1** (1969) 201.
9. Ewing, M. B. and Marsh, K. N. *J. Chem. Thermodynamics* **2** (1970) 351.
10. Williamson, A. G. and Scott, R. L. *J. Phys. Chem.* **65** (1961) 275.
11. Englert-Chwoles, A. *J. Chem. Phys.* **23** (1955) 1168.
12. Marsh, K. N. and Tomlins, R. P. *Trans. Faraday Soc.* **66** (1970) 783.
13. Dyke, D. E. L., Rowlinson, J. S. and Thacker, R. *Trans. Faraday Soc.* **55** (1959) 903.
14. Abe, A. and Flory, P. J. *J. Am. Chem. Soc.* **87** (1965) 1838.
15. McGlashan, M. L., Stubley, D. and Watts, H. *J. Chem. Soc.* **A 1969** 673.
16. Schuler, K. E. *J. Chem. Phys.* **21** (1953) 765.
17. National Bureau of Standards, *Selected Values of Properties of Hydrocarbons*, C 461, Washington 1947.
18. American Petroleum Institute, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Research Project 44, Carnegie Press, Pittsburg 1953.
19. Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, New York 1950.
20. Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*, Vol. II, Elsevier, Amsterdam 1965.
21. Reed III, T. M. *Fluorine Chemistry* **5** (1963) 133.
22. Rowlinson, J. S. *Liquids and Liquid Mixtures*, 2nd Ed., Butterworth, London 1969.
23. Vedeneyev, V. I., Gurvich, L. V., Kondrat'yev, V. N., Medvedev, V. A. and Frankevich, Y. L. *Bond Energies, Ionization Potentials, and Electron Affinities*, Edward Arnold Publ., London 1966.
24. Sugden, S. *J. Chem. Soc.* **1927** 1780 and 1786.
25. Walkley, J., Glew, D. N. and Hildebrand, J. H. *J. Chem. Phys.* **33** (1960) 621.
26. Watanabe, K. and Nakayama, T. *Tech. Rept.* 1-a, Ordnance Project. (Quoted from Ref. 25.)
27. Streitwieser, A. *Progr. Phys. Org. Chem.* **1** (1963) 1.
28. Jannes, G. and Puttemans, J. P. *Bull. Soc. Chim. Belges* **80** (1971) 133.
29. Davies, R. H., Duncan, A. G., Saville, G. and Staveley, L. A. K. *Trans. Faraday Soc.* **63** (1967) 855.
30. Marsh, K. N. and Stokes, R. H. *J. Chem. Thermodynamics* **1** (1969) 223.

31. Marsh, K. N. *Trans. Faraday Soc.* **64** (1968) 883.
32. Ross, M. and Hildebrand, J. H. *J. Phys. Chem.* **67** (1963) 1301.
33. Moelwyn-Hughes, E. A. *Physical Chemistry*, 2nd Ed., Macmillan, New York 1964.
34. Lambert, M. and Simon, M. *Physica* **28** (1962) 1191.
35. Pool, R. A. H., Saville, G., Herrington, T. M., Shields, B. D. C. and Staveley, L. A. K. *Trans. Faraday Soc.* **58** (1962) 1692.
36. Knobler, C. M., Knaap, H. F. P. and Beenakker, J. J. M. *Physica* **26** (1960) 142.
37. Mathot, V., Staveley, L. A. K., Young, J. A. and Parsonage, M. G. *Trans. Faraday Soc.* **52** (1956) 1488.
38. Lundberg, G. W. *J. Chem. Eng. Data* **9** (1964) 193.
39. Mathieson, A. R. and Thynne, J. C. J. *J. Chem. Soc.* **1956** 3708.
40. Polak, J., Murakami, S., Lam, V. T. and Benson, G. C. *J. Chem. Eng. Data* **15** (1970) 323.
41. Barthel, C. *Bull. Soc. Chim. France* **1970** 2488.
42. Dias d'Almeida, M., Fernandez-Garcia, J. G. and Boissonnas, C. G. *Helv. Chim. Acta* **53** (1970) 1389.
43. Kehlen, H. and Sackmann, H. *Z. Phys. Chem. Neue Folge* **50** (1966) 144.
44. Kehlen, H. and Sackmann, H. *Z. Phys. Chem., Neue Folge* **50** (1966) 135.
45. Stokes, R. H., Levien, B. J. and Marsh, K. N. *J. Chem. Thermodynamics* **2** (1970) 43.
46. Levien, B. J. and Marsh, K. N. *J. Chem. Thermodynamics* **2** (1970) 227.
47. Stokes, R. H., Marsh, K. N. and Tomlins, R. P. *J. Chem. Thermodynamics* **1** (1969) 211.
48. Ewing, M. B., Marsh, K. N., Stokes, R. H. and Tomlins, R. P. *J. Chem. Thermodynamics* **2** (1970) 297.
49. Marsh, K. N. *J. Chem. Thermodynamics* **2** (1970) 359.
50. Bellemans, A. *Bull. Soc. Chim. Belges* **66** (1957) 636.
51. Mathot, V. and Desmyter, A. *J. Chem. Phys.* **21** (1953) 782.
52. Jain, D. V. S., Lark, B. S., Chamak, S. S. and Chander, P. *Indian J. Chem.* **8** (1970) 66.
53. Boublik, T., Lam, V. T., Murakami, S. and Benson, G. C. *J. Phys. Chem.* **73** (1969) 2356.
54. Poon, D. P. L. and Lu, B. C.-Y. *J. Chem. Eng. Data* **13** (1968) 435.
55. Bedford, R. G. and Dunlap, R. D. *J. Am. Chem. Soc.* **80** (1958) 282.
56. Reed III, T. M. and Taylor, T. E. *J. Phys. Chem.* **65** (1959) 58.
57. Rodger, J. A., Hsu, C. C. and Furter, W. F. *J. Chem. Eng. Data* **14** (1969) 362.
58. Roveillo, J. and Gomel, M. *C. R. Acad. Sci. Paris* **226 C** (1968) 845.
59. Sackmann, H. and Arnold, H. *Z. Elektrochem.* **63** (1959) 565.
60. Schmack, G. and Bittrich, H. J. *J. prakt. Chem.* **312** (1970) 730.
61. Prengle, H. W., Felton, E. G. and Pike, M. A. *J. Chem. Eng. Data* **12** (1967) 193.
62. Washington, E. L. and Battino, R. *J. Phys. Chem.* **72** (1968) 4496.
63. Brandt, H. and Röck, H. *Chem.—Ing.—Techn.* **29** (1957) 397.
64. Kolbe, A. and Sackmann, H. *Z. Phys. Chem., Neue Folge* **31** (1962) 281.
65. Danusso, F. *Atti Accad. Nazl. Lincei* **17** (1954) 109.
66. Watson, A. E. P., McLure, I. A., Bennett, J. E. and Benson, G. C. *J. Phys. Chem.* **69** (1965) 2753.
67. Wood, S. E. and Austin, A. E. *J. Am. Chem. Soc.* **67** (1945) 480.
68. Suri, S. K. and Ramakrishna, V. *Indian J. Chem.* **7** (1969) 490.
69. Tsao, C. C. and Smith, J. M. *Chem. Eng. Progr. Sympos. Ser.* **49** (1953) 107.
70. Wóycicki, W. and Sadowska, K. W. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **16** (1968) 147.
71. Reddy, K. C., Subrahmanyam, S. V. and Bhimasenachar, J. *J. Phys. Soc. Japan* **19** (1964) 559.
72. Nath, J. and Yadava, R. B. *Indian J. Chem.* **9** (1971) 45.
73. Rastogi, R. P., Nath, J. and Misra, J. *J. Phys. Chem.* **71** (1967) 1277.
74. Rastogi, R. P., Nath, J. and Misra, J. *J. Phys. Chem.* **71** (1967) 2524.
75. Staveley, L. A. K., Tupman, W. I. and Hart, K. R. *Trans. Faraday Soc.* **51** (1955) 323.
76. Wood, S. E. and Brusie, J. P. *J. Am. Chem. Soc.* **65** (1943) 1891.
77. Howell, P. J. and Stubley, D. *J. Chem. Soc.* **A 1969** 2489.

78. Timmermans, J. *The Physico-Chemical Constants of Binary Systems in Concentrated Solution*, Vol. 1, Interscience, New York 1959, p. 79.
79. Singh, J., Pflug, H. D. and Benson, G. C. *J. Phys. Chem.* **72** (1968) 1939.
80. Murakami, S., Lam, V. T. and Benson, G. C. *J. Chem. Thermodynamics* **1** (1969) 397.
81. Murakami, S. and Benson, G. C. *J. Chem. Thermodynamics* **1** (1969) 559.
82. Lam, V. T., Murakami, S. and Benson, G. C. *J. Chem. Thermodynamics* **2** (1970) 17.
83. Marechal, J. *Bull. Soc. Chim. Belges* **61** (1952) 149.
84. Kortüm, G., Dreesen, G. and Freier, H.-J. *Z. Naturforsch.* **8a** (1953) 546.

Received October 4, 1971.