HEATS OF MIXING OF THE TERNARY SYSTEMS 1-PROPANOL–n-ALKANE–CYCLOHEXANE*

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Heats of mixing H^E were measured at the temperature of 298·15 K in the ternary systems 1-propanol–n-hexane–cyclohexane, 1-propanol–n-heptane–cyclohexane and 1-propanol–n-octane–cyclohexane along three pseudobinary chords and in the binary system 1-propanol–n-hexane. The measured values of the ternary excess enthalpies were correlated by the Scatchard equation for one polar component and by the SSF equation in pseudobinary mixtures. A very good agreement with the experiments was attained on computing the enthalpies of mixing by the group-contribution method. Qualitatively the same results were found on applying the modified Renon–Prausnitz model of continuously associated solution. The combination of the Renon–Prausnitz model with the group-contribution method did not yield a more conspicuous improvement.

In foregoing two papers[1,2] we have carried out an analysis and an extensive test of the prediction and correlation relations for concentration dependences of excess enthalpies of binary and ternary systems.

The knowledge obtained is general and allows to determine the most suitable type of correlation according to the physico-chemical character of substances.

The aim of our previous studies has been to apply some models of liquid solutions[3,4] to describe quantitatively the concentration and, if need be, also the temperature course of heats of mixing for systems of the alcohol–saturated hydrocarbon type. A particular standpoint was always the requirement that the final relations should contain as few parameters determined on the basis of experimental data as possible and stem rather from the properties of pure substances or allow to transfer the information from one system to similar ones. It was well satisfied by the Brown–Smith–Fock theory of homomorphous mixtures in series of n-alcohols and cyclohexane[5] and methylcyclohexane[6] or the Liebermann–Wilhelm model of associated solution in mixtures of 1-propanol and 2-propanol with cyclohexane[7]. No less favourable results were attained on applying the method of group contributions (of the Barker quasi-lattice model[8]).

In ternary mixtures, where the measurement of enthalpies of mixing is more time-consuming and difficult, the prediction and correlation methods acquire clearly their importance.

In this work we have riveted our attention upon the method of group contribution[8] making it possible to calculate excess enthalpies of similar systems only from the values of H^E for single basal system and to the Renon–Prausnitz model[9] with a simple form of the physical term[10] which requires theoretically an only experimental data point in each of constituent binaries.

A logical complement of the work was the comparison of experimental values with the values calculated from the Scatchard relation for one polar component[11] and from the SSF equation[12] modified for pseudobinary mixtures.

THEORETICAL

Group-Contribution Method

On the basis of the Solution-of-Groups Concept[13] a relation was derived[8] making it possible to convert (predict) enthalpies of mixing between systems of the type: arbitrary invariable component + n-alkane.

This method can be extended also to the ternary systems with two arbitrary components and n-alkane[14]. If we designate the mole fractions in the basal system by x_i and those in the predicted system x_i' with subscript $i = 2$ for n-alkane and $i = 1, 3$ for the remaining components then on condition

$$x_3/x_1 = x_3'/x_1' = \text{const},$$

we have for the predicted heat of mixing $H^{E'}(x_2')$

$$H^{E'}(x_2') = \frac{x_1'}{x_1} H^E(x_2), \qquad (1)$$

where $H^E(x_2)$ is the enthalpy of mixing of the basal pseudobinary system $(x_3/x_1 = \text{const})$ at a concentration x_2.

Here and below, the molar heat of mixing divided by RT, *i.e.* (H^E/RT), is implied in the term heat of mixing H^E.

For mole fractions of the basal and predicted systems hold further

$$x_1/x_1' = (1 - x_2')/(1 - x_2), \qquad (2a)$$

$$x_2 = x_2'/[C + x_2'(1 - C)], \qquad (2b)$$

$$C = Q_2/Q_2'. \qquad (2c)$$

The number of the surface contact points Q_2, Q_2' is determined from the relations

$$Q_2 = rz - 2r + 2, \tag{3a}$$

$$r = n_c/2 + 1, \tag{3b}$$

where r is the number of segments of the molecule and n_c the number of carbon atoms in n-alkane; z is the coordination number $(z = 6)$.

Renon–Prausnitz Association Model

Since the Renon–Prausnitz model[9] has been discussed[7] by us formerly in detail, we present here only the final relations.

The excess enthalpy is expressed as a sum of the chemical H_C^E and physical H_P^E terms

$$H^E = H_C^E + H_P^E. \tag{4}$$

From the mentioned model it follows

$$H_C^E = K\,\Delta H^0 x_1(\phi_{B1} - \phi_{B1}^*). \tag{5}$$

Here

$$\phi_{B1} = \frac{4\phi_1}{[1 + \sqrt{(1 + 4K\phi_1)}]^2}, \quad \phi_{B1}^* = \frac{4}{[1 + \sqrt{(1 + 4K)}]^2},$$

$\phi_1(x_1)$ is the volume (mole) fraction of alcohol, K and ΔH^0 are the association equilibrium constant and the standard enthalpy of association, respectively. Eq. (5) holds then also for the ternary systems of our type (see below).

Unlike Renon and Prausnitz who expressed the term H_P^E for binary systems by an equation of the van Laar type[15] and Liebermann and Wilhelm[4] who stemed from the Bruin equation[16], we have used the relation[10]

$$H_P^E = (x_1 S_1 + x_2 S_2)\,\xi_1 \xi_2 h_{12}, \tag{6}$$

where

$$\xi_1 = x_1 S_1/(x_1 S_1 + x_2 S_2), \quad \xi_2 = 1 - \xi_1.$$

The quantities S_1 and S_2 characterize the size of molecule of both components and are interpreted in this work as a measure of surface of the given molecule, $S_1 = kV_1^{2/3}$, $S_2 = kV_2^{2/3}$. V_1 and V_2 are molar volumes of pure components. We have chosen $k = 1\ \text{mol}^{3/2}$ for the sake of simplicity. The parameter h_{12} has the meaning of the exchange energy related to the surface unit.

For ternary mixtures Eq. (6) turns to the form

$$H_P^E = (x_1 S_1 + x_2 S_2 + x_3 S_3)(\xi_1 \xi_2 h_{12} + \xi_1 \xi_3 h_{13} + \xi_2 \xi_3 h_{23}). \qquad (7)$$

The parameters h_{ij} are evaluated from the respective binary systems and consequently it is sufficient to have in the limiting case a single data point H^E for each constituent binary to predict the concentration dependence of heat of mixing in the ternary systems of this type.

EXPERIMENTAL

The substances used were purified by the methods[5,6] described previously where the comparison of some physical constants with the literature data is given, too.

The heats of mixing were measured in an isothermal calorimeter of our own design. The calorimeter with control systems and the technique of measurement have been described in detail formerly[7].

RESULTS AND DISCUSSION

The concentration dependence of enthalpy of mixing of three ternary systems of the type 1-propanol–n-alkane–cyclohexane for n-hexane, n-heptane and n-octane was measured.

The measurements were carried out at the temperature of 298·15 K along the lines of constant ratios of mole fractions x_3/x_1. The value of this ratio amounted to 0·3349, 1·0008 and 2·9809. n-Alkane was always gradually added to the initial mixture of 1-propanol and cyclohexane and the excess enthalpy of the final mixture was calculated from the heats of dilution.

The formely carried out testing of the calorimeter with selected systems proved the estimated error in measurement 0·5% for heats higher than 400 J mol^{-1}. For lower values of heats the error did not exceed 1%. The reproducibility of measurement was better than 0·3%.

The experimental data for all nine pseudobinary mixtures are given in Table I and for the ratio $x_3/x_1 = 0·3349$ illustrated in Fig. 1. (All the values are given in the dimensionless form $H^E \equiv h^E/RT$.) It is evident from Fig. 1 and Table I that all the curves $H^E(x_2)$ go through a maximum whose position shifts to lower values of concentration of n-alkane with increasing value x_3/x_1. Also the length of the n-alkane chain manifests itself clearly in the height of the maximum.

The measured heats of mixing in the 1-propanol–n-hexane system at the temperature of 298·15 K are presented in Table II. The values published by Brown, Fock and Smith[3] are systematically 2—3% higher. With regard to a low number of their measurements (8 values) in a narrow concentration range and about four times larger error of the calorimeter used by them, we believe that our data are more probable.

This is also proved by the very good representation of the measured data by the SSF equation (see below). The differences between calculated and measured H^E are in the third and sixth columns of Table II.

Data for the other binary systems were taken from the literature.

Correlation Relations

For the first prediction method given in the theoretical part it is necessary to know the analytical expression of concentration dependence of binary heats of mixing. Likewise it is desirable to find a first-rate correlation relation for every ternary system to be able to determine enthalpies of mixing also for other compositions than those measured.

With this aim we have tested[17] all relations discussed elsewhere[1] and found in agreement with previous knowledge that the SSF equation[12] is most suitable for binary and pseudodbinary systems with 1-propanol. It has the form for the binary systems 1-propanol(1)–n-alkane(2) and 1-propanol(1)–cyclohexane(3):

$$H_{ij}^E = x_i x_j \sum_{k=1}^{p/2} A_k \left(\frac{x_i}{a_k} + a_k x_j \right)^{-2}, \tag{8}$$

where $i = 1$ and $j = 2, 3$; p is the number of constants A_k, a_k.

For pseudobinary systems we have

$$H_{123}^E = (1 - x_2) x_2 \sum_{k=1}^{p/2} A_k \left(\frac{1 - x_2}{a_k} + a_k x_2 \right)^{-2} + (1 - x_2) H_{13}^E. \tag{9}$$

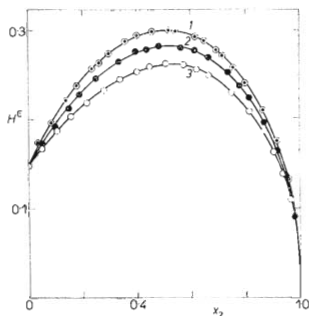

FIG. 1

Heat of mixing H^E in the 1-propanol(1)--n-alkane(2)–cyclohexane(3) systems at the temperature of 298·15 K and $x_3/x_1 = 0\cdot3349$. Experimental points: *1* n-octane, *2* n-heptane, *3* n-hexane; curves calculated from Eq. (9)

TABLE I

The concentration dependence of heats of mixing H^E in the 1-propanol(1)–n-alkane(2)–cyclohexane(3) systems at the temperature of 298·15 K

x_1	x_2	x_3/x_1	H^E	$\delta \cdot 10^{4\ a}$		
				a	b	c
			n-Hexane			
0·7077	0·0552	0·3349	0·1679	— 1	—11	41
0·6669	0·1097		0·1867	— 1	—16	40
0·6261	0·1642		0·2037	— 2	—17	36
0·5853	0·2186		0·2182	1	—21	37
0·5410	0·2778		0·2325	— 1	—16	30
0·4925	0·3425		0·2441	6	—21	33
0·4443	0·4069		0·2541	2	—10	21
0·4061	0·4579		0·2601	— 6	5	7
0·3661	0·5113		0·2623	— 4	4	10
0·3152	0·5792		0·2616	— 4	8	10
0·2749	0·6330		0·2567	0	4	19
0·2441	0·6741		0·2502	6	— 2	30
0·1832	0·7555		0·2311	5	— 7	42
0·1354	0·8193		0·2091	— 1	— 5	33
0·0995	0·8672		0·1879	— 9	0	— 1
0·0675	0·9099		0·1630	— 1	— 8	— 54
0·0434	0·9420		0·1385	8	2	— 3
0·0241	0·9678		0·1100	4	2	89
0·4797	0·0402	1·0008	0·2476	1	17	— 29
0·4610	0·0777		0·2572	2	20	— 38
0·4376	0·1245		0·2675	— 1	23	— 47
0·4109	0·1779		0·2765	— 1	23	— 48
0·3842	0·2313		0·2827	0	18	— 41
0·3506	0·2986		0·2871	2	1	— 27
0·3301	0·3396		0·2885	— 2	8	— 13
0·3020	0·3957		0·2877	— 3	9	— 7
0·2689	0·4620		0·2826	6	— 4	20
0·2325	0·5348		0·2750	— 5	4	29
0·1895	0·6209		0·2579	5	— 8	57
0·1522	0·6954		0·2391	1	— 5	59
0·1354	0·7290		0·2290	— 2	— 2	53
0·1194	0·7611		0·2182	— 5	0	43
0·0889	0·8221		0·1936	0	12	28
0·0635	0·8729		0·1688	7	—17	— 35
0·0394	0·9211		0·1412	— 6	2	—132
0·0177	0·9646		0·0975	1	4	—180

TABLE I

(*Continued*)

x_1	x_2	x_3/x_1	H^E	$\delta \cdot 10^4$ [a]		
				a	b	c
		n-Hexane				
0·2391	0·0480	2·9809	0·2545	—11	8	— 51
0·2269	0·0966		0·2641	— 7	6	— 57
0·2119	0·1565		0·2721	— 1	1	— 51
0·2033	0·1905		0·2753	— 2	1	— 47
0·1872	0·2549		0·2773	6	—10	— 24
0·1718	0·3160		0·2769	4	— 8	— 8
0·1598	0·3637		0·2738	8	—10	4
0·1536	0·3884		0·2717	8	—14	20
0·1370	0·4548		0·2656	— 8	2	22
0·1177	0·5314		0·2531	— 8	5	34
0·1104	0·5606		0·2474	— 9	6	34
0·0896	0·6432		0·2270	3	— 3	36
0·0712	0·7164		0·2066	0	2	3
0·0487	0·8060		0·1734	13	—16	— 46
0·0302	0·8798		0·1399	— 7	— 6	—128
0·0189	0·9246		0·1112	— 7	12	—169
0·0117	0·9535		0·0861	8	44	—181
0·0050	0·9800		0·0574	— 2	143	—209
		n-Heptane				
0·7104	0·0517	0·3349	0·1725	— 6	— 7	30
0·6751	0·0988		0·1929	— 4	—15	28
0·6397	0·1461		0·2113	— 2	—20	26
0·6045	0·1930		0·2273	2	—26	28
0·5591	0·2536		0·2450	6	—30	31
0·4954	0·3387		0·2639	11	—36	39
0·4492	0·4003		0·2754	— 7	—24	36
0·4204	0·4388		0·2792	— 5	—19	33
0·3858	0·4850		0·2816	0	—22	44
0·3243	0·5671		0·2815	— 5	—11	51
0·2821	0·6234		0·2756	4	—11	69
0·2488	0·6679		0·2695	— 4	— 1	68
0·1966	0·7376		0·2520	5	— 4	84
0·1635	0·7817		0·2378	2	1	77
0·1366	0·8177		0·2232	3	— 2	67
0·0950	0·8732		0·1965	— 7	— 1	12
0·0602	0·9196		0·1661	— 2	—10	— 69
0·0367	0·9510		0·1374	6	5	— 85
0·0151	0·9799		0·0912	— 3	60	—193

TABLE I
(*Continued*)

x_1	x_2	x_3/x_1	H^E	$\delta \cdot 10^4$ [a]		
				a	b	c

n-Heptane

0·4778	0·0441	1·0008	0·2530	— 1	21	— 36
0·4574	0·0848		0·2673	— 8	33	— 56
0·4345	0·1307		0·2792	0	27	— 54
0·4155	0·1687		0·2867	10	16	— 43
0·3895	0·2207		0·2977	— 9	33	— 57
0·3625	0·2748		0·3028	2	16	— 33
0·3349	0·3300		0·3050	11	— 1	— 6
0·3058	0·3892		0·3067	— 7	7	0
0·2890	0·4218		0·3049	— 3	— 1	18
0·2472	0·5055		0·2968	— 2	— 9	51
0·2031	0·5936		0·2815	0	—10	77
0·1592	0·6814		0·2595	1	— 4	82
0·1161	0·7678		0·2303	4	2	57
0·0803	0·8393		0·1999	6	9	— 11
0·0506	0·8988		0·1651	3	— 3	— 89
0·0256	0·9488		0·1239	0	36	—186
0·2400	0·0447	2·9809	0·2574	2	8	— 53
0·2292	0·0876		0·2695	2	13	— 63
0·2181	0·1317		0·2794	— 3	20	— 68
0·2076	0·1737		0·2856	— 2	16	— 58
0·1948	0·2247		0·2903	0	11	— 40
0·1774	0·2937		0·2926	— 1	7	— 15
0·1597	0·3644		0·2897	7	— 4	18
0·1441	0·4265		0·2854	— 3	4	25
0·1314	0·4771		0·2788	— 2	2	36
0·1189	0·5268		0·2705	— 3	2	40
0·0968	0·6147		0·2503	4	— 9	43
0·0786	0·6871		0·2302	— 1	— 7	17
0·0598	0·7619		0·2042	— 3	— 8	— 26
0·0461	0·8165		0·1810	1	— 7	— 68
0·0322	0·8719		0·1528	5	10	—124
0·0194	0·9228		0·1200	— 5	67	—188
0·0126	0·9500		0·0940	— 2	72	—150
0·0075	0·9703		0·0664	4	94	—148

TABLE I
(Continued)

x_1	x_2	x_3/x_1	H^E	$\delta \cdot 10^{4\,a}$		
				a	b	c

n-Octane

x_1	x_2	x_3/x_1	H^E	a	b	c
0·7161	0·0440	0·3349	0·1737	− 5	2	18
0·6845	0·0863		0·1955	2	− 5	14
0·6462	0·1373		0·2199	− 5	− 1	2
0·6137	0·1808		0·2365	5	−12	12
0·5701	0·2390		0·2573	− 3	− 6	8
0·5514	0·2639		0·2637	7	−14	14
0·5239	0·3006		0·2731	9	−19	28
0·4796	0·3598		0·2871	− 7	− 4	22
0·4470	0·4033		0·2943	−11	1	25
0·4041	0·4605		0·2993	− 5	− 7	42
0·3557	0·5252		0·2998	7	−10	58
0·3421	0·5433		0·2992	9	−24	74
0·2802	0·6260		0·2928	− 2	−17	83
0·2584	0·6551		0·2880	− 3	−17	88
0·2256	0·6988		0·2788	− 9	−10	90
0·2095	0·7203		0·2711	10	−29	112
0·1798	0·7600		0·2587	5	−20	107
0·1458	0·8053		0·2418	− 4	3	81
0·0994	0·8673		0·2113	− 7	35	21
0·0602	0·9196		0·1753	7	46	− 76
0·0295	0·9606		0·1315	− 2	34	−183
0·4798	0·0401	1·0008	0·2546	− 1	19	− 35
0·4638	0·0721		0·2679	− 4	23	− 48
0·4466	0·1064		0·2796	1	19	− 49
0·4267	0·1462		0·2915	− 1	16	− 49
0·4003	0·1991		0·3033	3	5	− 35
0·3717	0·2563		0·3126	2	− 3	− 18
0·3286	0·3426		0·3189	5	−20	20
0·2974	0·4049		0·3201	− 8	−15	34
0·2110	0·5778		0·2995	1	−20	95
0·1683	0·6632		0·2792	0	− 2	97
0·1341	0·7317		0·2568	2	14	83
0·0986	0·8028		0·2278	0	35	38
0·0671	0·8658		0·1957	− 5	52	− 45
0·0426	0·9147		0·1623	4	48	−132
0·0152	0·9696		0·1002	− 1	50	−114

TABLE I
(*Continued*)

x_1	x_2	x_3/x_1	H^E	$\delta \cdot 10^4$ [a]		
				a	b	c

n-Octane

x_1	x_2	x_3/x_1	H^E	a	b	c
0·2410	0·0407	2·9809	0·2590	1	4	— 52
0·2313	0·0794		0·2727	0	5	— 64
0·2221	0·1157		0·2827	1	1	— 63
0·2112	0·1591		0·2921	— 2	— 2	— 56
0·1985	0·2099		0·2992	0	— 9	— 37
0·1831	0·2712		0·3041	— 3	— 9	— 15
0·1656	0·3406		0·3035	7	—15	22
0·1489	0·4072		0·3006	— 2	4	33
0·1382	0·4500		0·2959	— 2	10	44
0·1246	0·5039		0·2879	— 2	22	51
0·1016	0·5957		0·2678	4	31	56
0·0876	0·6513		0·2528	1	40	41
0·0754	0·6998		0·2376	— 3	46	17
0·0529	0·7894		0·2030	— 2	46	— 49
0·0379	0·8492		0·1737	2	39	—109
0·0250	0·9003		0·1420	3	38	—168
0·0151	0·9400		0·1084	— 7	3	—141
0·0068	0·9730		0·0624	4	27	—128

[a] δ is the deviation between calculated and measured H^E; a corresponds to the representation of pseudobinary chord (Eq. (9)), b to the ternary correlation (Eq. (11)), c to the Renon–Prausnitz model (Eqs (4), (5) and (7)).

Here H_{13}^E is the excess enthalpy of the 1-propanol(1)–cyclohexane(3) mixture at a given constant ratio x_3/x_1.

The number of constants in Eqs (8) and (9) was set to six with regard to the F-test[1].

The constants of Eq. (8) are given for each system in Table III along with the reference to the source of experimental H^E data and with the standard deviation of correlation. The method of computing the constants was described previously[1].

Success of the SSF equation for pseudobinary systems is illustrated by the curves in Fig. 1 and by deviations δ in the fifth column of Table I. The constants of Eq. (9) for all nine pseudobinary systems are presented in the original work[17].

TABLE II

The dependence of heat of mixing H^E in the 1-propanol(1)–n-hexane(2) system on the mole fraction of alcohol at the temperature of 298·15 K

x_1	H^E	$\delta \cdot 10^{4\ a}$	x_1	H^E	$\delta \cdot 10^{4\ a}$
0·0251	0·1098	−2	0·4608	0·2258	−7
0·0525	0·1448	6	0·5146	0·2144	−4
0·0847	0·1711	−8	0·5655	0·2011	0
0·1208	0·1910	3	0·6316	0·1802	−3
0·1533	0·2060	3	0·6869	0·1600	−1
0·1965	0·2221	−0	0·7421	0·1374	2
0·2297	0·2285	6	0·7879	0·1169	15
0·2786	0·2366	−3	0·8505	0·0862	−4
0·3490	0·2375	7	0·8963	0·0618	−6
0·4098	0·2330	4	0·9470	0·0327	−5

[a] δ is the deviation between calculated and measured H^E.

TABLE III

The systems 1-propanol(1)–n-alkane(2)–cyclohexane(3). The values of constants in Eqs (8) and (10)

Data	System i − j						
	$1 + 2^a$	$1 + 2^b$	$1 + 2^c$	$1 + 3$	$2^a + 3$	$2^b + 3$	$2^c + 3$
Ref.	[d]	22	22	7	23	24	23
Eq.	(8)	(8)	(8)	(8)	(10)	(10)	(10)
A_1	0·6581	0·7908	0·7740	0·4544	0·3492	0·3892	0·4157
a_1	0·6674	0·7443	0·6645	1·0149	—	—	—
A_2	0·2896	0·2043	0·2874	0·5586	−0·1039	−0·0981	−0·1539
a_2	0·1913	1·3138	0·1847	0·6311	—	—	—
A_3	0·2737	0·3333	0·3750	0·2246	0·0313	0·0464	0·0752
a_3	1·1108	0·2177	1·2704	0·1828	—	—	—
A_4	—	—	—	—	—	−0·0561	—
$\sigma \cdot 10^{4\ a}$	7	3	12	9	2	4	5

[a] n-Hexane, [b] n-heptane, [c] n-octane, [d] this work, [e] σ is standard deviation.

The Redlich–Kister polynomial expansion[18]

$$H_{23}^E = x_2 x_3 \sum_{k=1}^{p} A_k (x_2 - x_3)^{k-1} \tag{10}$$

has appeared to be the most suitable for correlations of the concentration dependence of H^E function of the binary mixtures of cyclohexane(3) with n-hydrocarbons(2).

The constants A_k calculated by the least-squares method and the standard deviations σ are given in Table III for all three systems.

The best results of 26 correlation equations for the concentration dependence of heats of mixing of ternary systems[2] have been yielded by the Scatchard relation for the case that one component of the mixture is polar[11]:

$$H_{123}^E = \frac{x_2}{1 - x_1} H_{12}^E(x_1, 1 - x_1) + \frac{x_3}{1 - x_1} H_{13}^E(x_1, 1 - x_1) +$$

$$+ \frac{x_2 x_3}{x_2^{23} x_3^{23}} H_{23}^E(x_2^{23}, x_3^{23}) + H_T^E. \tag{11}$$

Here

$$x_2^{23} = (1 + x_2 - x_3)/2, \quad x_3^{23} = 1 - x_2^{23},$$

where x_1, x_2, x_3 are the mole fractions of components in ternary mixture.

The ternary term H_T^E is usually given in the form[2]

$$H_T^E = x_1 x_2 x_3 (A + Bx_1 + Cx_2) \tag{12}$$

with the constants A, B, C.

In our computations[17], the effect of the terms Bx_1 and Cx_2 has appeared to be unsubstantial (the F-test was used) and therefore we have set $B = C = 0$. The optimum values of the constant A are 0·0955 (n-hexane), 0·1866 (n-heptane) and 0·2675 (n-octane).

The deviations of excess enthalpies calculated from Eq. (11) from experimental data are given in the sixth column of Table I.

The values of mean (δ) and standard (σ) deviations have been 0·0012 and 0·0024 (n-hexane), 0·0016 and 0·0024 (n-heptane), 0·0019 and 0·0025 (n-octane).

On neglecting the term H_T^E, Eq. (11) enables to predict the ternary H^E from excess enthalpies of the constituent binaries. The result is worse than that obtained by correlation (mean deviations $2-3$ times larger) but still in relation of accuracy of chemical-engineering calculations.

Group-Contribution Method

By inserting Eq. (9) for basal pseudobinary mixture and relations (2) and (3) into Eq. (1) we have got heats of mixing of two remaining pseudobinaries (for the same ratio x_3/x_1).

The standard deviations of predictions for successive cyclic choice of the basal system are summarized in Table IV. With regard to simplicity of the method, the results of prediction are very satisfactory and for neighbouring n-alkanes comparable with the correlation according to Eq. (11).

Renon–Prausnitz Association Model

In accordance with Renon and Prausnitz[9] we accepted first the value of association constant $K = 90$ (at 323·15 K) and of standard enthalpy of association $\Delta H^0 = -10$. The given value of the parameter K gave, however, an unreal course of the concentration dependence of finally calculated physical term H_P^E. The curve $H_P^E(x_1)$ showed three extremes and in a part of concentration range the H_P^E values were even negative. A qualitative justification can be sought in a number of simplifying assumptions included in deriving the model which are fulfilled only partly at lower concentrations

TABLE IV

The systems 1-propanol(1)–n-alkane(2)–cyclohexane(3). The prediction of excess enthalpies at the temperature of 298·15 K by means of the group-contribution method

Basal system		n-hexane		n-heptane		n-octane	
		a	b	a	b	a	b
n-Hexane	c			45	39	83	69
	d			51	47	68	58
	e			53	51	83	78
n-Heptane	c	45	40			34	28
	d	48	43			20	15
	e	54	52			26	24
n-Octane	c	76	65	32	27		
	d	67	56	20	16		
	e	78	73	25	22		

[a] Group-contribution method, [b] combination of the Renon–Prausnitz model with the group-contribution method, [c] values of standard deviation $\sigma \cdot 10^4$ for the ratio $x_3/x_1 = 0\cdot3349$, [d] for $x_3/x_1 = 1\cdot0008$, [e] for $x_3/x_1 = 2\cdot9809$.

of alcohol. In spite of it we tried to adjust the parameter K so that the standard deviation of correlation of binary systems 1-propanol–n-alkane (the systems cited above were complemented by those of 1-propanol with n-nonane[19] and n-decane[20]) in terms of Eqs (4), (5) and (6) should be as small as possible. The adjusted value $K = 105$ (at 323·15 K) showed even then three extremes on the $H_P^E(x_1)$ curve but the physical term was already positive in the entire concentration range and the standard deviation of correlation was reduced to about one half.

The calculated optimum values of exchange energies h_{12}, h_{13}, h_{23} for the readjusted value of association constant K were used for estimating heats of mixing of single ternary mixtures. The results of these computations given in the seventh column of Table I were obtained by using the following parameters (densities of pure substances were taken from ref.[21]):

$$K\ (323{\cdot}15\ \text{K}) = 105, \quad \Delta H^0 = -10$$

$$S_1 = 75{\cdot}13 \cdot 10^{-4}\ \text{m}^2, \quad S_3 = 22{\cdot}78 \cdot 10^{-4}\ \text{m}^2, \quad h_{13} = 127\ \text{m}^{-2}$$

$$S_2 = 25{\cdot}87 \cdot 10^{-4}\ \text{m}^2, \quad h_{12} = 37\ \text{m}^{-2}, \qquad h_{23} = 147\ \text{m}^{-2}\ (\text{n-hexane})$$

$$S_2 = 27{\cdot}91 \cdot 10^{-4}\ \text{m}^2, \quad h_{12} = 51\ \text{m}^{-2}, \qquad h_{23} = 159\ \text{m}^{-2}\ (\text{n-heptane})$$

$$S_2 = 29{\cdot}80 \cdot 10^{-4}\ \text{m}^2, \quad h_{12} = 56\ \text{m}^{-2}, \qquad h_{23} = 168\ \text{m}^{-2}\ (\text{n-octane})$$

The mean and standard deviations from measured H^E were as follows: 0·0052 and 0·0075 (n-hexane); 0·0057 and 0·0074 (n-heptane); 0·0060 and 0·0078 (n-octane).

Considering that every ternary system is described by only three binary adjustable parameters h_{ij} (we do not include K and ΔH^0 which are identical for the same alcohol in different non-polar solvents) the quality of prediction is very good.

In conclusion of this study we verified quantitatively the possibilities of combination of the Renon–Prausnitz model with the group-contribution method.

There is namely the possibility to carry out the conversion of the line of constant x_3/x_1 ratio not by applying Eq. (1) to the total excess enthalpy of basal ternary system but only to its physical part and to calculate finally the chemical term of the predicted system from Eq. (5).

The results of this procedure are included in Table IV.

It can be seen that the method described yields only slightly better results than the group-contribution method itself.

Thus it seems that the Renon–Prausnitz model does not lead to a significant improvement of quality of prediction and that it is possible to recommend for further applications the group-contribution method itself which is simpler and does not require the prior knowledge of association constant and standard enthalpy of association.

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Translated by J. Linek.