

HEATS OF MIXING OF CYCLOHEXANE WITH 1-PROPANOL AND 2-PROPANOL*

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The concentration dependences of excess enthalpies of the binary systems cyclohexane-1-propanol and cyclohexane-2-propanol were measured in an isothermal calorimeter at six temperatures in the range of 25–50°C. For the quantitative description of the concentration and temperature dependences of heats of mixing, the Liebermann-Wilhelm model of associated solution was used extended by the assumption of polynomial temperature dependence of the interaction parameter. It follows from the comparison of chemical and physical contribution to the excess enthalpy that heats of mixing in the system with 1-propanol are given mostly by a specific interaction of hydrogen bond. The excess Gibbs energies were estimated using an interaction parameter calculated from heats of mixing. The values obtained are systematically higher and have rather semi-quantitative character.

In the last 25 years, an increasing effort can be noted to interpret quantitatively the mixing process of a component which forms in pure state associates of different order (alcohols) with an inert solvent (saturated hydrocarbons). The formation and breakdown of the associates is regarded as a succession of chemical reactions.

The first more general model of continuous associated solution was derived by Kretschmer and Wiebe¹. The models reported during next years follow it more or less and therefore the fundamental assumptions for their derivation are given below: 1) The alcohol exists in the form of linear associates B_1, B_2, \dots, B_n which result from the hydrogen bridge formation. The formation of the associates is described by the system of equations of the type

$$B_1 + B_{n-1} = B_n.$$

2) The association constant K depends neither on the degree of association nor on the inert solvent. 3) The molar volume of an n -mer is equal to the product of degree of association and molar volume of monomer. 4) The ratio of molar volumes of pure components does not depend on temperature. 5) The standard heat ΔH^0 of hydrogen bond depends neither on temperature nor on degree of association. 6) The mutual interactions of n -mers and their interactions with the solvent molecules are of physical nature only (therefore analogous to those in non-associating mixtures). 7) The excess Gibbs energy G^E can be divided into the chemical part G_c^E given by the formation of associates and the physical part G_p^E following from the above-mentioned physical interactions.

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The work by Kretschmer and Wiebe was resumed by Renon and Prausnitz² in 1967. Their final relations are in substance analogous to the conclusions due to Kretschmer and Wiebe but they are derived in a much more lucid way. Moreover, they also consider the temperature dependence of the interaction parameter of the G_p^E part, however, at the cost of another constant unknown in advance. The procedure which chose Liebermann and Wilhelm³ does not suffer from this disadvantage and allows to predict the excess functions H^E and G^E from one experimental point.

THEORETICAL

Liebermann and Wilhelm retained the G_c^E part the same as that in the Renon and Prausnitz model (for the sake of lucidity, the same symbolism is used and only final expressions are given; for details see papers cited):

$$G_c^E = x_A \ln \frac{\Phi_A}{x_A} + x_B \ln \frac{\Phi_{B1}}{\Phi_{B1}^* x_B} + K x_B (\Phi_{B1} - \Phi_{B1}^*). \quad (1)$$

Here

$$\Phi_{B1} = \frac{4\Phi_B}{[1 + \sqrt{(1 + 4K\Phi_B)}]^2}, \quad \Phi_{B1}^* = \lim_{x_B \rightarrow 1} \Phi_{B1},$$

where Φ_B , x_B are the volume fraction and mole fraction of alcohol, respectively, the same symbols with subscript A stand for saturated hydrocarbon, K is the equilibrium association constant.

To express the contribution G_p^E they used a simplified equation proposed by Bruin⁴

$$G_p^E = \frac{-2RTx_A x_B \ln A}{(x_A + x_B A)(x_B + x_A A)}, \quad (2)$$

where A is the parameter dependent on temperature only.

The total excess Gibbs energy is then equal

$$G^E = G_c^E + G_p^E. \quad (3)$$

From the relation

$$H^E = -T^2 \frac{\partial}{\partial T} \left(\frac{G^E}{T} \right)_{p,x} \quad (4)$$

and from Eqs (1) and (2) we obtain the corresponding contributions to heats of mixing:

$$H_c^E = K \Delta H^0 x_B (\Phi_{B1} - \Phi_{B1}^*), \quad (5)$$

$$H_p^E = \frac{ACG_p^E \ln A}{1 - \ln A} \left(\frac{x_B}{x_A + x_B A} + \frac{x_A}{x_B + x_A A} - \frac{1}{A \ln A} \right), \quad (6)$$

where

$$C = 2 - \frac{2AK \Delta H^0}{RT \ln A} \left(\frac{V_A/V_B}{\sqrt{(1+4K)[1+\sqrt{(1+4K)}]^2}} \right), \quad (7)$$

V_A , V_B are the molar volumes of hydrocarbon and alcohol.

The total heat of mixing is then

$$H^E = H_c^E + H_p^E. \quad (8)$$

To verify the Liebermann–Wilhelm model (hereinafter LW-model only) the authors have calculated the respective parameters A for $x_B = 0.5$ and the corresponding G^E for nine binary systems and from them, heats of mixing at the same concentration. The values of K and ΔH^0 have been taken over from the cited work of Renon and Prausnitz². The difference from the experimental data on H^E has been from several to twenty per cent. With regard to the variety of sources of the experimental H^E values, in some cases of unwarranted quality, the result can be estimated favourably.

For a more unambiguous judgement it has seemed therefore more convenient to calculate the parameter A from heat of mixing, to carry out the comparison of calculations with direct measurements in the whole concentration range and at more temperatures and just from the H^E values calculated concentration and temperature course of the G^E function to compare with available literature data. For this purpose the systems cyclohexane–1-propanol and cyclohexane–2-propanol have been chosen.

EXPERIMENTAL

Cyclohexane and 1-propanol have been purified in the previously described ways⁵. Their boiling points, refractive indices and densities have been identical with the values given there.

2-Propanol, analytical reagent grade, has been distilled with benzene⁶ first and the remainder of water has been removed by molecular sieves Nalsit A4. Its physical constants have been as follows: $n_{\text{bp}} = 82.3^\circ\text{C}$ (ref.⁷ 82.23°C), $n_D^{25} 1.3748$ (ref.⁸ 1.3748), $d_4^{25} 0.78091$ (ref.⁹ 0.78093).

All the substances have been stored over a layer of molecular sieves. The water content of all substances has been lower than 0.004 mass %.

The heats of mixing have been measured in an isothermal calorimeter of our own design. The calorimeter with control circuits and the technique of measurements have already been described¹⁰ in detail formerly. Only the heating circuit of mixing vessel has been complemented by a five-level source of constant current¹¹.

RESULTS AND DISCUSSION

The heats of mixing have been measured for both systems in the whole concentration range at temperatures of 25, 30, 35, 40, 45 and 50°C. The measured values are given in Table I. For the values of H^E within 500–1000 J mol⁻¹, the error of measurement has amounted to 0.5–0.2%. At the concentration ends the error has reached about 2%.

The heats of mixing of cyclohexane with 1-propanol have been measured at 25°C by Nagata¹². His data and those measured in this work are in surprisingly excellent agreement; the differences of H^E are within the limits of measuring errors of both calorimeters.

For the cyclohexane-2-propanol system, the data of Nagata and Ohta¹³ for temperatures of 35 and 45°C are available in the literature. We can again state very good agreement with our measurements, only at a temperature of 35°C, their values are systematically 1–2% higher for $x_B > 0.5$.

It can be also seen in Table I that the temperature dependence of H^E is nonlinear and comparatively large for both systems. For instance, in the system with 1-propanol, H^E (25°C) = 627 J mol⁻¹ and H^E (50°C) = 952 J mol⁻¹ for $x_B = 0.4$. Similarly at the same concentration and 30°C, the excess molar heat capacity $c_p^E = 11.8$ J K⁻¹ mol⁻¹ and at 45°C, $c_p^E = 15$ J K⁻¹ mol⁻¹. For the system with 2-propanol, H^E are roughly 200–250 J mol⁻¹ higher than for 1-propanol. The concentration course of H^E is here also rather more symmetric (the maximum corresponds to $x_B \approx 0.42$ compared to 0.35 for 1-propanol). The heat of mixing also increases more distinctly with temperature as it can be seen from the excess molar heat capacities: c_p^E (30°C) = 13.8 J K⁻¹ mol⁻¹, c_p^E (45°C) = 16 J K⁻¹ mol⁻¹.

Heat of Mixing

In agreement with Liebermann and Wilhelm³, the values of K and ΔH^0 have been taken over from the work by Renon and Prausnitz². The ratio of molar volumes V_B/V_A has been calculated from the temperature dependences of densities⁶ of respective substances. Consistently with the above-mentioned assumptions the average value has been taken which has differed only by 0.5% from those for pure substances.

However, preliminary calculations have shown that the original value of K for 2-propanol is too low and therefore, by analogy with the subsequent corrected data¹⁴ for other alcohols, the constant K has been increased to 80.

The calculations have been carried out with the following set of constants:

$$\text{1-propanol: } K(50^\circ\text{C}) = 90, \quad \Delta H^0 = -25.1 \text{ kJ mol}^{-1}, \quad V_B/V_A = 0.6883;$$

$$\text{2-propanol: } K(50^\circ\text{C}) = 80, \quad \Delta H^0 = -25.1 \text{ kJ mol}^{-1}, \quad V_B/V_A = 0.7060.$$

For both systems, the values of parameter A have been calculated from Eqs (5)–(8)

TABLE I

Dependence of Heat of Mixing H^E ($J mol^{-1}$) in Systems Cyclohexane(A)-1-Propanol(B) and -2-Propanol(B) on Mole Fraction at Various Temperatures

x_B	H^E	δ	x_B	H^E	δ
1-Propanol					
25°C					
0.0452	314.5	0.05	0.4562	602.9	1.32
0.0858	406.7	-4.90	0.4729	596.8	1.58
0.1173	460.5	-5.36	0.4951	585.5	1.62
0.1295	485.0	-3.73	0.5191	573.9	2.05
0.1390	497.1	-3.90	0.5517	549.1	1.52
0.1680	532.1	-3.32	0.5836	526.0	1.69
0.1996	562.9	-2.53	0.6476	468.8	1.43
0.2064	569.2	-2.25	0.6918	424.7	1.46
0.2619	600.5	-1.62	0.7502	363.0	2.42
0.3036	616.9	-0.53	0.7918	314.9	3.47
0.3126	621.5	0.05	0.8540	229.1	3.03
0.3670	620.6	0.06	0.9206	133.0	4.72
0.3745	620.2	0.17			
30°C					
0.0805	446.6	-0.12	0.5126	625.5	0.72
0.1003	482.7	-2.00	0.5648	584.0	0.08
0.1273	530.7	-2.13	0.6282	528.6	0.19
0.1632	580.2	-1.89	0.6593	497.4	0.24
0.1984	614.2	-1.98	0.6946	455.6	-0.42
0.2189	634.8	-1.13	0.7581	380.1	-0.02
0.2518	656.6	-0.63	0.8128	305.6	-0.06
0.3067	673.6	-0.55	0.8438	260.6	0.01
0.3782	674.0	-0.37	0.8797	207.2	0.84
0.4262	665.8	0.26	0.9080	161.3	0.81
0.4632	652.3	0.56			
35°C					
0.0493	409.7	7.96	0.5222	674.8	0.02
0.0781	483.1	1.82	0.5701	634.5	-0.31
0.1038	541.5	0.50	0.6280	576.5	-0.71
0.1274	583.5	-0.38	0.6652	532.6	-1.27
0.1542	621.0	-1.20	0.7013	488.8	-1.38
0.1982	669.8	-1.52	0.7440	428.5	-2.46
0.2203	692.4	-0.94	0.7801	377.7	-2.56
0.2660	720.8	-0.74	0.8189	319.0	-2.83

TABLE I
 (Continued)

x_B	H^E	δ	x_B	H^E	δ
35°C					
0.3077	735.5	-0.49	0.8540	265.0	-2.24
0.3795	738.2	-0.17	0.9046	179.8	-1.83
0.4300	725.8	0.03	0.9431	111.5	-0.38
0.4689	708.6	0.10			
40°C					
0.0602	488.6	8.49	0.5360	726.0	-0.36
0.1078	603.1	2.25	0.5637	699.9	-0.65
0.1397	664.2	1.38	0.5903	670.1	-1.29
0.1982	738.8	0.23	0.6122	639.8	-2.48
0.2410	778.9	0.54	0.6604	585.1	-2.42
0.3036	803.9	-0.02	0.7181	505.0	-3.33
0.3527	810.4	0.07	0.7672	431.1	-3.86
0.3786	807.5	-0.01	0.8110	360.7	-4.11
0.4255	796.8	0.20	0.8574	280.2	-4.51
0.4605	781.4	0.24	0.9195	164.5	-4.83
0.5100	744.2	-0.60			
45°C					
0.0532	507.9	12.01	0.5483	782.1	-0.69
0.0906	623.0	6.02	0.5703	755.6	-1.38
0.1365	718.8	2.63	0.6091	707.2	-2.33
0.1715	777.5	2.03	0.6371	671.1	-2.74
0.2152	827.3	1.23	0.6438	663.0	-2.69
0.2457	846.7	0.29	0.6758	615.5	-3.56
0.2680	868.0	1.02	0.7099	561.4	-4.58
0.3046	880.2	0.56	0.7459	508.3	-4.18
0.3413	884.4	0.23	0.7731	458.0	-5.49
0.3780	883.5	0.25	0.8038	403.0	-6.12
0.4275	869.9	0.20	0.8242	364.3	-6.81
0.4642	851.2	0.07	0.8741	272.6	-5.98
0.5096	815.0	-0.65	0.9215	172.7	-7.81
0.5133	805.9	-1.43			
50°C					
0.0763	641.5	10.25	0.4682	919.6	-0.76
0.1105	730.7	5.89	0.5210	875.4	-1.38
0.1399	794.2	4.23	0.5677	819.4	-2.74

TABLE I
(Continued)

x_B	H^E	δ	x_B	H^E	δ
50°C					
0.1671	843.0	3.42	0.6202	750.0	-3.88
0.1970	867.6	3.02	0.6567	695.0	-4.83
0.2510	932.0	1.37	0.6954	634.0	-5.53
0.2987	952.2	0.39	0.7432	550.8	-6.53
0.3655	958.0	-0.30	0.7953	454.4	-7.43
0.3772	956.6	-0.36	0.8403	363.1	-8.57
0.4189	947.3	-0.33	0.8975	241.3	-9.36
0.4447	931.1	-0.91	0.9411	144.5	-8.23
2-Propanol					
25°C					
0.0613	415.7	-2.29	0.5148	797.4	1.83
0.1053	530.1	-5.25	0.5633	760.6	1.87
0.1490	617.9	-5.26	0.5990	723.4	1.40
0.1680	648.7	-5.17	0.6351	683.2	1.28
0.1949	695.4	-3.60	0.6662	643.2	0.98
0.2238	732.1	-2.95	0.7030	593.2	0.96
0.2501	759.1	-2.46	0.7599	508.6	1.53
0.3018	805.9	-0.55	0.8109	417.7	1.21
0.3405	822.3	-0.13	0.8536	335.4	1.23
0.3825	833.1	0.65	0.8854	267.5	0.49
0.4087	835.8	1.23	0.9204	192.6	1.26
0.4536	827.2	1.61			
30°C					
0.0620	456.6	-0.44	0.5129	861.9	1.28
0.1065	585.1	-3.19	0.5608	824.1	1.39
0.1453	669.4	-3.72	0.5967	784.1	0.90
0.1678	711.8	-3.43	0.6348	735.0	0.27
0.1983	760.0	-3.04	0.6702	688.1	0.24
0.2440	819.8	-1.95	0.7057	639.4	0.79
0.3028	871.2	-0.77	0.7615	546.5	0.87
0.3325	887.6	-0.24	0.8251	424.3	0.93
0.3753	900.7	0.42	0.8559	357.4	0.52
0.4117	903.5	0.99	0.9219	203.9	0.22
0.4600	892.3	1.36			

TABLE I
(Continued)

x_B	H^E	δ	x_B	H^E	δ
35°C					
0.0625	510.7	3.64	0.4241	970.8	0.70
0.0956	610.5	-0.65	0.4588	963.0	1.13
0.1061	639.2	-1.16	0.5102	936.0	1.47
0.1302	691.8	-2.82	0.5639	886.3	1.14
0.1503	738.2	-2.57	0.6079	829.2	0.16
0.1978	822.4	-2.46	0.6426	783.5	0.05
0.2484	886.6	-2.14	0.6817	726.1	0.03
0.2762	915.5	-1.58	0.7036	692.5	0.26
0.3039	938.6	-1.00	0.7557	603.3	0.84
0.3403	958.1	-0.51	0.8185	469.6	-0.15
0.3784	966.8	-0.22	0.8592	370.8	-1.92
0.3878	971.8	0.29	0.9076	256.8	-0.57
40°C					
0.0519	513.9	8.18	0.5047	1 011.0	1.19
0.0886	648.3	2.54	0.5449	974.6	0.99
0.1189	729.3	-0.17	0.5849	934.5	1.31
0.1498	802.2	-1.06	0.6120	890.2	0.19
0.1755	849.8	-1.81	0.6621	815.9	-0.02
0.2002	891.9	-1.90	0.7026	741.5	-0.90
0.2191	920.8	-1.79	0.7360	682.1	-0.57
0.2489	960.8	-1.40	0.7671	624.1	0.15
0.2984	1 007.8	-0.90	0.8212	494.1	-1.68
0.3098	1 014.9	-0.87	0.8538	410.6	-2.95
0.3403	1 032.7	-0.42	0.8901	322.2	-1.72
0.3802	1 045.5	0.14	0.9488	157.1	-2.03
0.4509	1 042.2	1.16			
45°C					
0.0811	677.8	5.21	0.5350	1 060.0	1.02
0.1267	811.2	0.89	0.5615	1 031.7	0.98
0.1563	877.3	-0.67	0.5976	982.8	0.56
0.1965	954.1	-1.39	0.6378	920.3	0.10
0.2252	1 000.2	-1.38	0.6758	852.1	-0.49
0.2584	1 044.8	-1.09	0.7091	787.7	-0.87
0.3027	1 092.2	-0.27	0.7502	701.1	-1.27
0.3355	1 110.2	-0.22	0.7862	624.1	-0.71
0.3868	1 123.6	0.08	0.8268	520.9	-1.42

TABLE I
(Continued)

x_B	H^E	δ	x_B	H^E	δ
45°C					
0.4241	1 124.5	0.59	0.8694	408.5	-1.24
0.4569	1 115.8	0.90	0.9193	262.8	-1.47
0.5113	1 081.5	1.03			
50°C					
0.0459	565.0	13.06	0.5044	1 168.4	1.12
0.0814	731.3	6.55	0.5618	1 107.7	0.95
0.1025	811.2	4.89	0.6026	1 048.7	0.52
0.1274	879.1	2.31	0.6405	985.3	0.14
0.1607	966.6	1.34	0.6731	922.6	-0.38
0.1981	1 031.9	-0.47	0.7084	855.6	-0.09
0.2472	1 109.8	-0.58	0.7491	764.5	-0.30
0.2752	1 142.8	-0.53	0.7871	672.0	-0.38
0.3053	1 168.9	-0.51	0.8265	562.4	-1.34
0.3401	1 189.1	-0.44	0.8714	436.3	-0.78
0.3732	1 199.2	-0.32	0.9031	339.0	-0.46
0.4241	1 202.8	0.28	0.9388	216.7	-2.32
0.4611	1 192.2	0.63			

δ Deviation between measured and calculated H^E related to the measured value (%).

for single measurements by an iterative procedure on a computer HP 2116 B. With regard to the requirement to describe heats of mixing in the region about their maximum, the average value of A has been established for $x_B \in (0.2, 0.6)$. From the temperature dependence of the average parameter A it has been found that for the system with 1-propanol, it is possible to express A as

$$A = 0.4432 + 4.6946 \cdot 10^{-3}T - 11.0 \cdot 10^{-6}T^2 \quad (9)$$

and for 2-propanol

$$A = 1.3982 - 1.9666 \cdot 10^{-3}T. \quad (10)$$

To judge quantitatively the LW-model, the excess enthalpies have been calculated from Eqs (5)–(10) for measured values of mole fractions and the results have been mutually compared. In the third and fourth columns of Table I, the per cent deviations between measured and calculated H^E are given. For the first system, the results

are very satisfactory excepting the region of lower alcohol concentrations ($x_B < 0.2$) and temperature of 50°C. For better visualization, the mean absolute deviations (in %) are given calculated from all the experimental points. For the individual sets with increasing temperature, they have the following values: 2.19, 0.72, 1.38, 1.99, 3.07, 4.08. Approximately the same holds for the second set. Thanks to higher values of H^E , the mean absolute per cent deviations are more favourable (1.96, 1.28, 1.14, 1.44, 1.04, 1.63).

Moreover, from Table I it is evident that practically the same results would be obtained when calculating the parameter A (for the given temperature) from one measurement at the maximum of H^E .

In the end if we judge the results simultaneously from the point of view of the concentration and temperature dependence, the LW-model represents 139 experimental values of heats of mixing in the cyclohexane-1-propanol system in terms of three constants of Eq. (9) with a standard deviation of 16.6 J mol⁻¹ and a mean absolute deviation of 2.3%; in the cyclohexane-2-propanol system, 141 data on H^E with the deviations of 14.4 J mol⁻¹ and 1.42%, in terms of two constants of Eq. (10).

To complete the entirety of the LW-model judgement the comparison of both contributions H_c^E and H_p^E has been carried out, too. In one of our previous works⁵ it was found that for lower alcohols the heats of mixing are given mostly by specific interactions of hydroxylic group. The small values of heats of mixing of propane with cyclohexane calculated from the Barker model¹⁵ also corresponded to it. Since all the models of associated solutions assume an additive relation analogous to Eq. (8) we can explicitly express the ratio of specific and unspecific interactions for the LW-model as well. The values of H_c^E and H_p^E for $x_B = 0.4$ calculated from Eqs (5)–(10) are compared in Table II.

In the cyclohexane-1-propanol system the contribution H_p^E increases with temperature from 17.5 to 25.3% of the total H^E . For the second system this contribution is greater (at 25°C twofold) but changes only little with temperature. The higher values of H^E for 2-propanol are consequently explainable by an increased ratio of non-specific interactions. The reason is probably in different spatial arrangement of CH₃ and CH₂ groups of both alcohols.

Excess Gibbs Energy

The isothermal vapour-liquid equilibrium in the cyclohexane-1-propanol system has been measured at temperatures of 49.86 and 59.71°C by Brzostowski and Warycha¹⁶ and at temperatures 55 and 65°C by Strubl and coworkers¹⁷. From Eqs (1)–(3) and (9), the excess Gibbs energies were calculated¹⁸ for these temperatures and corresponding concentrations and compared with the data of the authors cited above. All the calculated values have been systematically higher even if they have represented the position of maximum and the course of G^E curve. For the tempera-

tures 49.86 and 55°C, the average absolute deviation has been practically the same (11.8 and 11.2%, respectively). At higher temperatures, it has grown up to the value of 25.8% at 65°C. The main reason has been probably the extrapolation of Eq. (9) outside the range of its validity.

The vapour-liquid equilibrium in the cyclohexane-2-propanol system was measured at 50 and 60°C by Nagata and coworkers⁸. The G^E values calculated from the LW-model and from Eq. (10) have been again at all concentrations higher than the experimental values. In spite of a small number of measurements (9 and 10, respectively) the found deviations (20.6 and 30.9%) are too high.

With regard to the comparative simplicity of the LW-model we can, however, consider the results for both systems to be sufficient for a semiquantitative estimation of G^E .

Heats of Mixing with n-Alkanes

For a more extensive judgement of the LW-model, the calculations have been carried out of heats of mixing for 6 systems published in the literature whose one component is 1-propanol or 2-propanol, respectively, and the second is n-alkane. The data used have not been assorted and smoothed in any way. The parameter A has

TABLE II
Comparison of Contributions H_c^E and H_p^E ($J\ mol^{-1}$) for $x_B = 0.4$

$t, ^\circ C$	H^E	H_c^E	H_p^E	$H_p^E/H^E, \%$
1-Propanol				
25	614.0	506.7	107.3	17.5
30	671.9	546.0	125.9	18.7
35	735.2	586.5	148.7	20.2
40	803.3	628.1	175.2	21.8
45	877.0	670.6	206.4	23.5
50	956.0	714.0	242.0	25.3
2-Propanol				
25	826.6	524.0	302.7	36.6
30	896.1	564.3	331.8	37.0
35	968.2	605.9	362.4	37.4
40	1 043.4	648.4	395.0	37.8
45	1 122.2	691.9	430.2	38.3
50	1 203.6	736.3	467.3	38.8

been calculated as an average value from the range of $x_B \in \langle 0.1, 0.9 \rangle$. The results are summarized in Table III.

The calculated results are, except for the system with n-tetradecane, very favourable and in full agreement with the results obtained in this work. The great deviations for the 1-propanol-n-tetradecane system originate probably from the fact that the assumptions of the LW-model cease to be valid with increasing hydrocarbon chain. Similar differences were found by Nagata¹² as well. The same found out Dohnal¹⁹ when applying the Barker model with hydrocarbon as one component. Patterson and coworkers²⁰ explain it by the difference of the hydrocarbon structure in a pure state and in a mixture.

TABLE III
Calculation of Heats of Mixing from LW-Model for n-Alkanes with 1-Propanol and 2-Propanol

System	$t, ^\circ\text{C}$	m^a	A	$\delta, \%$	Ref.
n-Hexane + 1-propanol	25	8	0.8715	3.27	21
	35	8	0.8494	0.90	
	45	8	0.8221	2.90	
n-Hexane + 2-propanol	25	7	0.8170	8.03	22
n-Heptane + 1-propanol	30	12	0.8533	3.22	23
	45	12	0.8124	2.40	
	20	9	0.8760	5.31	24
	25	10	0.8671	4.25	
	30	10	0.8556	3.01	
n-Heptane + 2-propanol	35	16	0.8097	4.75	25
	45	17	0.7676	1.91	
	60	15	0.7305	1.82	
n-Octane + 1-propanol	20	9	0.8638	5.24	24
	25	10	0.8552	5.04	
	30	11	0.8454	5.46	
n-Tetradecane + 1-propanol	20	9	0.8198	13.06	24
	25	9	0.8066	10.37	
	30	10	0.7862	7.40	

^a Number of measurements.

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