HEATS OF MIXING OF NORMAL ALCOHOLS
WITH METHYLCYCLOHEXANE*

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Heats of mixing of n-alcohols (ethanol, propanol, butanol, hexanol, heptanol and octanol) and of n-hydrocarbons (hexane, heptane, and octane) with methylcyclohexane were measured at 25°C. The estimated error for systems containing alcohols is $0.5-1\%$, with hydrocarbons 2 J mol^{-1}. It was proved that the Brown-Fock–Smith theory of homomorphic mixtures can be applied also to binary systems of methylcyclohexane with n-alcohols.

In the last few years a considerable attention has been focused on studies of solutions containing associated components. To describe these systems, a number of models have been proposed which all have in common that they distinguish specific and nonspecific interactions between molecules. Interactions, characteristic of the given mixture, are usually denoted as specific, having most frequently the decisive effect on the extent and the course of the concentration dependence of the excess function of the system. All other force effects are included into the term non-specific interactions. In this way the total heat of mixing H^E can be assumed to consist of two active parts: the heat given by specific interactions in the solution and the contribution due to non-specific interactions.

At present a number of procedures is known[1,5] how to interpret both the mentioned contributions of the heat of mixing of binary mixtures of alcohols with hydrocarbons. A rather simple approach, chosen by Brown, Fock and Smith[6], has a clear advantage in comparison with other methods, particularly in that it makes possible to calculate (under certain assumptions) the heat of mixing in the whole homologous series of binary mixtures of associating components with a non-polar solvent only on the basis of known concentration dependences of the excess enthalpy of the lowest homologue.

With respect to the fact that the principle of the Brown–Fock and Smith theory (further on only BFS) has been discussed in detail in one of our previous publications[7], it can be only briefly characterized in terms of the final relations

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$$H^E/x_1 = \varphi(C) = \Phi(C) - (H_A - H_H), \tag{1}$$

$$\varphi(C) = (H_{AP}^E - H_{HP}^E)/x_1, \tag{2}$$

$$C = x_1/[x_1 N_A + (1 - x_1) N_P]. \tag{3}$$

The symbol H_{AP}^E means the molar heat of mixing of alcohol (at mole fraction x_1) with the given solvent, H_{HP}^E is the molar enthalpy of mixing of the homomorphic mixture (homomorphic hydrocarbon has the same number of carbon atoms in its molecule as the respective alcohol) which is identical with the contribution due to non-specific interactions, N_A and N_P are the numbers of mol of carbon in the alcohol and in the solvent, respectively and H_A and H_H are the molar enthalpies of alcohol and of the homomorphic hydrocarbon, respectively. According to the BFS theory the course of the function $\Phi(C)$ should be identical for all members of the homologous series. From the literature data it follows that Eq. (2) is very well fulfilled for n-hydrocarbons[6,8] and cyclohexane as solvent[7].

The earlier discussed connection of the BFS theory to the Barkers quasi-lattice model[7] indicated that Eq. (2) holds provided that two kinds of interaction prevail: specific interaction of the functional group of the alcohol and non-specific interaction of the alkyl group of the alcohol with CH_2 (CH_3) groups of the solvent. Therefore it was expected that the mentioned theory could be applied also to systems in which the solvent would be represented by methylcyclohexane instead of cyclohexane or hydrocarbons.

TABLE I

Index of Refraction and Specific Mass of the Substances Used

Substance	n_D^{25}		f_4^{25}, g . cm^{-3}	
	measured	literature	measured	literature
Ethanol	1·3592	1·35926[6]	0·78510	0·78511[6]
n-Propanol	1·3832	1·38312[6]	0·79992	0·79985[23]
n-Butanol	1·3974	1·3974[23]	0·80600	0·80590[23]
n-Hexanol	1·4160	1·41607[6]	0·81512	0·81531[6]
n-Heptanol	1·4223	1·4225[24]	0·81895	0·8186[24]
n-Octanol	1·4276	1·4276[24]	0·82241	0·82247[6]
Methylcyclohexane	1·4205	1·42058[25]	0·76510	0·76501[25]
n-Hexane	1·3721	1·37226[25]	0·65478	0·65481[25]
n-Heptane	1·3853	1·38511[25]	0·67960	0·67951[25]
n-Octane	1·3950	1·39505[25]	0·69853	0·69849[25]

EXPERIMENTAL

All alcohols used as well as the hexane used were purified as described earlier[7,9]. Methylcyclohexane, prepared by catalytic hydrogenation of toluene of the reagent grade purity, was after rectification directly used for measurements. n-Heptane (Lachema, Brno) was three times distilled on a column packed with stainless steel spirals. n-Octane (Laborchema, Apolda) was twice distilled on a 100-plate packed column and the medium fraction was taken. The index of refraction and the specific mass of all substances used for measurement are summarized in Table I as compared with the data from the literature.

All measurements were carried out at 25°C in an isothermal calorimeter of our own construction, the detailed description of which was given in the preceding paper[10].

RESULTS AND DISCUSSION

The measured values of enthalpies of mixing in dependence on the mole fraction of alcohol or of n-hydrocarbon are summarized in Table II. The estimated error of measurement for the values of excess enthalpy $200-600$ J . mol^{-1} is $0.5-1\%$, that for the heats of mixing of the order of tens J is 2 J . mol^{-1} maximum.

The data of Hwa and Ziegler[2] for ethanol–methylcyclohexane, calculated from the measured excess molar heats and from heats of mixing[11] at 35°C are in very good agreement with our measurements, exceeding the original expectations of the authors $(\pm 5\%)$. On the contrary, the data published by Nagata and Yamada[12] are by as much as 60 J . mol^{-1} higher, although the accordance in the range of maximum heats of mixing is fairly good (2%). In their case it is evidently a systematic error, caused by the calorimeter construction[13], which is supported also by the fact that the data of Brown and coworkers at 35°C are for $x_1 > 0.7$ lower than their
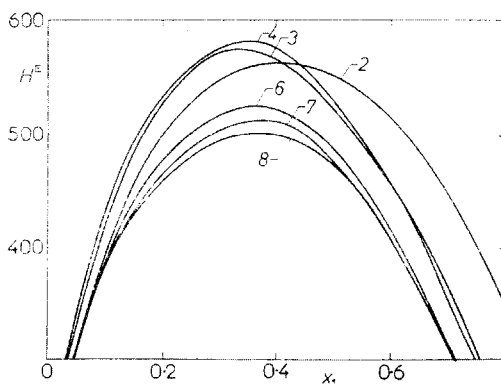

FIG. 1

Comparison of the Heats of Mixing, H^E (J . mol^{-1}) of n-Alcohols with Methylcyclohexane at 25°C

Numbers on the curves give the number of carbon atoms of the alcohol.

TABLE II

Dependence of the Heat of Mixing, H^E (J . mol^{-1}) in the Systems Methylcyclohexane(2) with n-Alcohols(1) or n-Hydrocarbons(1) at 25°C on Mole Fraction

x_1	H^E	x_1	H^E	x_1	H^E
		Ethanol			
0·0455	301·5	0·3354	558·9	0·6803	466·0
0·0600	324·5	0·3804	563·4	0·6898	451·5
0·1056	401·7	0·4374	558·5	0·7237	425·3
0·1314	437·0	0·4902	552·2	0·7798	367·4
0·1653	469·5	0·5711	527·4	0·8489	282·3
0·2045	498·9	0·6161	503·9	0·9014	202·0
0·2546	530·0	0·6382	487·3	0·9436	123·9
0·2914	542·5	0·6409	484·8		
		n-Propanol			
0·0246	255·4	0·3492	575·0	0·6267	434·0
0·0468	325·5	0·3588	574·6	0·6350	426·2
0·0935	419·1	0·4229	559·6	0·7086	352·0
0·1417	481·2	0·4727	535·9	0·7618	295·5
0·1845	524·2	0·5167	510·2	0·8452	203·0
0·2643	560·7	0·5613	482·8	0·9176	111·1
0·2795	563·1	0·6194	442·9		
		n-Butanol			
0·0208	225·2	0·3108	578·7	0·5788	473·0
0·0414	300·5	0·3929	577·6	0·6345	420·3
0·0822	382·7	0·4661	545·5	0·7006	350·5
0·1174	447·4	0·4759	544·5	0·7709	273·0
0·1613	491·9	0·5054	518·4	0·8230	213·0
0·2253	541·1	0·5150	518·0	0·8944	127·5
0·2540	556·8	0·5737	478·8	0·9401	70·1
		n-Hexanol			
0·0232	236·3	0·2611	505·6	0·5558	448·7
0·0459	305·6	0·2908	514·0	0·5808	426·8
0·0741	359·4	0·3211	522·4	0·6113	404·5
0·1092	397·0	0·3451	523·6	0·6364	379·1
0·1207	409·6	0·3686	524·0	0·6663	349·9
0·1280	418·5	0·3893	526·1	0·6769	334·9
0·1369	426·0	0·4297	515·8	0·7415	270·7
0·1472	435·4	0·4522	508·2	0·7952	217·0
0·1659	453·0	0·4533	509·5	0·8528	156·0
0·1952	472·9	0·4832	494·5	0·8938	110·0
0·2174	481·4	0·5059	479·7		
0·2320	491·5	0·5126	479·5		

TABLE II

(*Continued*)

x_1	H^E	x_1	H^E	x_1	H^E
			n-Heptanol		
0·0417	287·8	0·2879	498·0	0·5250	457·5
0·0528	306·1	0·3616	511·7	0·5776	430·6
0·0863	361·8	0·3804	512·5	0·6376	372·7
0·1093	389·9	0·4238	507·9	0·7140	297·0
0·1406	420·5	0·4696	489·3	0·7744	237·0
0·1789	451·8	0·4704	493·9	0·8535	152·1
0·2301	475·9	0·4762	487·0	0·9198	83·1
			n-Octanol		
0·0147	184·2	0·2967	494·6	0·6547	355·6
0·0290	246·0	0·3492	497·6	0·6949	316·5
0·0423	286·3	0·4422	493·0	0·7307	285·1
0·0585	323·8	0·4559	491·0	0·7952	214·7
0·0840	362·6	0·4997	472·6	0·8393	171·6
0·1148	395·7	0·5440	448·6	0·8813	127·0
0·1675	441·7	0·5702	431·0	0·9301	74·0
0·2269	471·1	0·6157	395·2		
			n-Hexane		
0·1476	5·2	0·4162	11·6	0·5467	12·4
0·2231	8·2	0·4402	12·2	0·6117	10·6
0·3031	9·6	0·4915	12·7	0·7259	8·5
0·3746	11·5	0·5025	11·2	0·8443	4·9
			n-Heptane		
0·1126	12·5	0·4610	30·6	0·6950	21·0
0·1712	17·5	0·5143	29·1	0·7908	14·0
0·2273	23·3	0·5780	26·0	0·8601	9·6
0·3521	28·8	0·5812	26·9	0·9319	4·7
0·4530	31·4	0·6331	23·5		
			n-Octane		
0·1102	15·8	0·4288	39·4	0·6785	29·3
0·1859	25·7	0·4499	40·2	0·7286	27·2
0·2248	29·1	0·4948	37·6	0·7931	19·4
0·2840	34·0	0·5615	36·9	0·8592	13·3
0·3397	36·5	0·5620	36·0		
0·3887	39·2	0·6064	34·7		

values measured at 25°C, although the heat of mixing increases with increasing temperature. The data of Lundberg[14], who studied the system n-heptane–methyl-cyclohexane, are over the whole concentration range systematically by as much as 4 J . mol^{-1} higher than the data published here. The difference is probably caused rather by the different way of evaluating the measured data than by the imperfect mixing in our measurements. The heats of mixing of the other systems have so far not been measured.

Fig. 1 shows the comparison of the composition dependences of the heats of mixing of individual alcohols with methylcyclohexane. On all curves, the maxima are shifted towards lower values of the mole fraction of alcohol, lying in the interval $x_1 = 0.33$ to 0·40. In the vicinity of the maximum the heat of mixing decreases with increasing number of carbon atoms in the alcohol molecule. In this respect, methylcyclohexane as a solvent behaves similarly to n-hexane, whereas with cyclohexane the heat of mixing increases towards higher alcohols. An exception is ethanol (and in a lower extent also propanol) whose heat of mixing in the maximum is lower than that of butanol. In contrast to this, for $x_1 > 0.5$, it has the highest values of H^E of all systems.

The system methanol–methycyclohexane is limitedly miscible at 25°C (see[15]) However, the measurements of Rant and coworkers[16] indicate that at temperatures higher than critical temperature of solution this anomaly also is valid. Also the volume of mixing (its values are positive with all systems) decreases with increasing carbon chain of the alcohol[17,18], however, in the sequence of $N_A = 2, 5, 3, 4, 6$. It is of course a question whether, owing to the rather laborious purification of n-pentanol, it is not rather an experimental error than an anomaly which could be otherwise hardly explained.

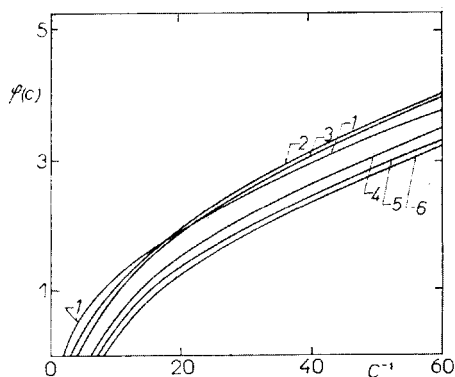A similar behaviour of systems with the lowest alcohols was also found with n-hydrocarbons[6,19,22] and with cyclohexane[7].

FIG. 2

Function $\varphi(C)$ (kJ . mol^{-1}) at 25°C

Methylcyclohexane with: 1 ethanol, 2 n-pro-panol, 3 n-butanol, 4 n-hexanol, 5 n-heptanol and 6 n-octanol.

To verify the validity of Eq. (1) even for lower alcohols, it is necessary to know the heats of mixing of their homomorphic mixtures. In this case the situation is even more complicated, since their values cannot be estimated by using the principle of congruence, as it is with n-hexane[6], or calculated from the quasi-lattice model, as with cyclohexane[9].

Therefore, in the first approximation, the value of H_{HP}^E was not taken into account for ethanol, propanol and butanol and the estimation of the validity of the BFS theory was restricted only to higher alcohols, where this disadvantage does not interfere. Moreover, it is sufficient to calculate $\varphi(C)$ at 1 atm and not at the saturation pressure of ethane (41·7 atm).

The values of $\varphi(C)$ for different alcohols are shown in Fig. 2. The curves of hexanol, heptanol and octanol are distinctly congruent within the limits of experimental errors, so that they can be identified by mutual shifting along the $\varphi(C)$ axis. This indicates that a single dependence $\Phi(C)$ can be set up for all systems in the series n-alcohol–methylcyclohexane. The curves for propanol and butanol are practically also congruent with the curves $\varphi(C)$ for $N_A = 6, 7, 8$, thus indicating that the heats of mixing of the respective homomorphic hydrocarbons will have small negative values. On the other hand, the same dependence for ethanol shows clearly that the heat of mixing of the homomorphic mixture is relatively great and negative, especially in the region $x_1 < < 0·5$. The situation is analogous to that of ethanol mixtures with n-hydrocarbons[6,8].

In terms of the BFS theory the course of the mixing curves in the region of maximum (Fig. 1) can be interpreted in the following way: during mixing of ethanol with methylcyclohexane, not only dissociation of hydrogen bonds (endothermic heat) but also a distinct interaction of the alkyl group of the alcohol with the methylcyclohexane molecule (exothermic heat) takes place. Propanol is less associated than ethanol[2] and consequently the heat absorbed in the destruction of its associated structure is less, too. Contrary to this, the non-specific interaction alkyl–methylcyclohexane is very low and therefore the resulting heat of mixing is higher than with ethanol. The difference in the association of propanol and butanol is not so great as in the case of ethanol and propanol. However, the increase of alkyl chain will be more manifested and the value H_{HP}^E will increase. This will result in a higher value of H^E than in the case of propanol. At lower concentration of butanol ($x_1 < 0·2$) the effect of dissociation prevails and the heat of mixing is lower. The number of hydrogen bonds decreases steeply towards higher alcohols, whereas the endothermic heat connected with interaction of alkyl with methylcyclohexane increases markedly more slowly. The result is that H^E decreases with increasing alkyl group of the alcohol.

As it has been demonstrated earlier[7], the advantage of Eq. (2) is that it makes possible to calculate the heats of mixing in the whole homologous series directly from the data of a single one system. The same procedure, as described in the cited paper[7] was applied to calculate the heats of mixing of the systems with heptanol and octanol from the values of $\Phi(C)$ for hexanol–methylcyclohexane. The calculated

values are compared with the smoothed experimental data, as shown in Figs 3 and 4. This comparison shows, for the whole concentration range, a mean absolute deviation $2 \cdot 1$ $(1 \cdot 1\%)$.
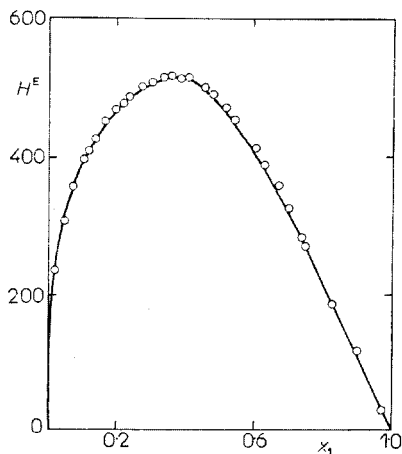

FIG. 3

Heat of Mixing, $H^E (\text{J . mol}^{-1})$ of the System n-Heptanol(1)–Methylcyclohexane(2) at 25°C
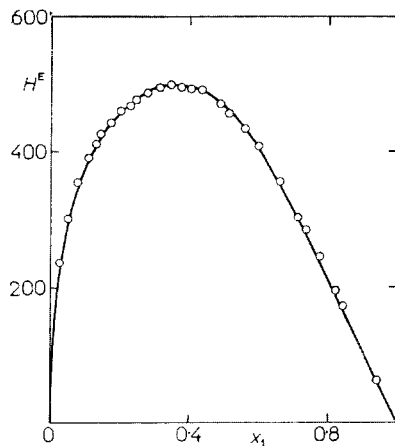 Points calculated according to the BFS theory, curve smoothed experimental data.

FIG. 4

Heat of Mixing, H^E (J mol^{-1}) of the System n-Octanol(1)–Methylcyclohexane(2) at 25°C
  Points calculated according to the BFS theory, curve smoothed experimental data.

From the results obtained the conclusion can be drawn that the heats of mixing in the systems n-alcohol–methylcyclohexane can be interpreted as the result of both specific interaction of the functional group of alcohol and the non-specific interactions of the type IS.

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