

## HEATS OF MIXING OF BUTANONE AND CHLOROFORM WITH ALKANES: BINARY SYSTEMS

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The heats of mixing of a polar compound (chloroform, 2-butanone) with two normal and two highly branched alkanes were determined at 25°C using the Calvet microcalorimeter. The magnitude of the measured heat of alkane with a polar compound decreases in the order hexadecane–heptane–2,2,4-trimethylpentane–2,2,4,4,6,8,8-heptamethylnonane. The interaction parameter  $X_{12}$  of the equation-of-state theory was calculated and the results were compared with those obtained by Lam and coworkers with mixtures of the same alkanes with cyclohexane and 2,2-dimethylbutane. The analysis leads to a conclusion that besides the predominant contribution due to the difference in polarities of the two components, a certain role is played by the effects of the size and shape of alkane molecules described by Patterson: namely, differences in the thermal expansion of the two components and a change in the correlation of molecular orientations during the mixing of liquid hexadecane with small or isotropic molecules.

Changes in the thermodynamic quantities which occur in mixing depend not only on the polarity and polarizability of molecules, but also on their size and shape. Recently, much attention has been devoted to the influence of the latter two factors on the heats of mixing of nonpolar liquids<sup>1</sup>. It has been proved that in addition to effects described in terms of the Prigogine–Flory–Patterson theory<sup>2,3</sup>, changes in the correlation of molecular orientation become operative in molecules with a sufficiently long hydrocarbon chain<sup>4</sup>. A question arises to what extent such factors are operative in polar systems in which the predominant contribution is due to *e.g.* dipole interactions or hydrogen bonds.

Our recent papers<sup>5</sup> are dealing with the effect of the number of proton-acceptor sites in molecules of oligomeric substances with various chain length on the heats of mixing with proton donors. As regards the effect exerted by the molecular size and shape *per se* on interactions in polar mixtures, it should be examined in the simplest possible systems, *e.g.* in a system of small polar molecules with alkanes of different molecular structure. This paper reports the measurement and interpretation of the heats of mixing of binary systems with chloroform or 2-butanone as one component and an either linear or highly-branched alkane as another. The other paper<sup>6</sup> is concerned with the enthalpy of mixing of a mixture of chloroform and butanone with the same alkanes.

## EXPERIMENTAL

Chloroform, heptane and hexadecane were identical with those used in ref.<sup>7</sup>. 2,2,4-Trimethylpentane, *purissimum* (Laborchemie, Apolda, GDR), was rectified on a 70 TP column packed with heligrad, and the narrow middle fraction was taken; the purity of the product according to gas-chromatographic analysis was 99.9%. 2,2,4,4,6,8,8-Heptamethylnonane was identical with the compound used in paper<sup>4</sup>. 2-Butanone, reagent grade (Reanal, Budapest, Hungary) was redistilled on a 40-plate packed column; the chromatographic purity of the narrow middle fraction used was 99.9%.

The heats of mixing were recorded in the Calvet microcalorimeter with mixing cells  $2 \times 3 \text{ cm}^3$  in volume and with a 0.01 mm nickel membrane<sup>8</sup>.

## RESULTS AND DISCUSSION

The dependence of the heats of mixing,  $\Delta H_v = \Delta H/V$  ( $\Delta H$  is the measured heat in J,  $V$  is the system volume in  $\text{cm}^3$ ,  $\Delta H_v$  is the heat of mixing in  $\text{J}/\text{cm}^3$ ), on the hydrocarbon volume fraction  $\varphi_2$  was expressed in terms of the Redlich-Kister series expansion

$$\Delta H_v = \varphi_2(1 - \varphi_2) \sum_{k=0}^n C_k(1 - 2\varphi_2)^k. \quad (1)$$

TABLE I

Constants  $C_i$  ( $\text{J}/\text{cm}^3$ ) and Standard Deviation  $\sigma$  of the Redlich and Kister Series Expansion (1) at 25°C

Component (2)	$C_0$	$C_1$	$C_2$	$C_3$	$\sigma$
Component (1)-chloroform					
Heptane <sup>a</sup>	30.30	- 1.98	-	-	0.8
Hexadecane <sup>b</sup>	33.43	- 5.38	5.68	17.26	1.3
2,2,4-Trimethylpentane	28.24	- 2.83	3.01	-	0.4
2,2,4,4,6,8,8-Heptamethylnonane	22.71	- 5.39	2.11	-	0.5
Component (1)-2-butanone					
Heptane	45.12	-12.58	10.99	-	1.2
Hexadecane	44.48	- 8.77	15.11	-13.99	0.8
2,2,4-Trimethylpentane	41.34	-10.84	11.40	- 8.91	0.6
2,2,4,4,6,8,8-Heptamethylnonane	33.99	- 6.30	15.42	-14.97	0.5

<sup>a</sup> Ref. 7, <sup>b</sup> Data from ref. 7 supplemented by new measurements.

The constants  $C_k$  were optimized by the least squares method, assuming a constant relative error in the heat of mixing. The optimal degree of the polynomial was selected by means of Fisher's test<sup>9</sup> on a 95% significance level. The constants are summarized in Table I; the dependences are plotted in Fig. 1. Our results obtained with the system chloroform–heptane<sup>7</sup>, and supplemented results for the mixture chloroform–hexa-

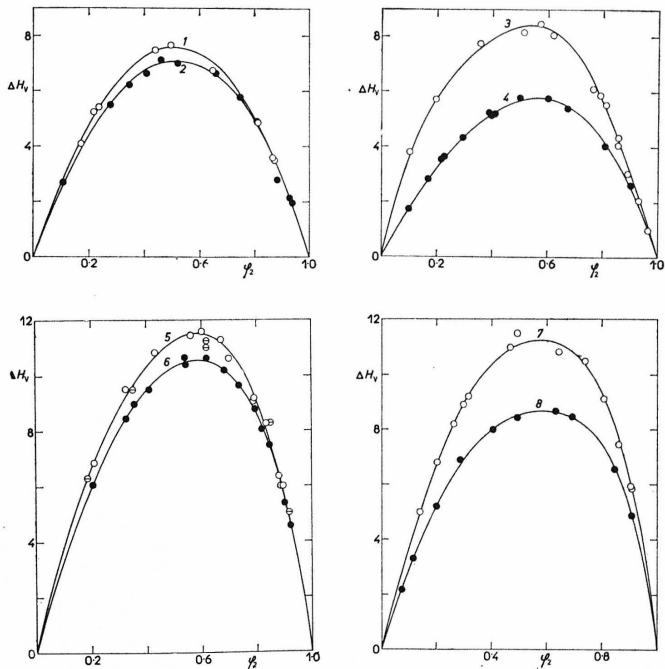


FIG. 1

Dependence of  $\Delta H_v$  ( $\text{Jcm}^{-3}$ ) on  $\phi_2$  at  $25^\circ\text{C}$

Systems: 1 chloroform(1)–heptane(2), 2 chloroform–trimethylpentane, 3 chloroform–hexadecane, 4 chloroform–heptamethylnonane, 5 2-butanone(1)–heptane(2), 6 2-butanone–trimethylpentane, 7 2-butanone–hexadecane, 8 2-butanone–heptamethylnonane. The curves correspond to the Redlich–Kister series expansion, cf. Eq. (1) and Table I; odd-numbered curves O, even-numbered curves ●, recalculated data according to ref.<sup>10</sup> ⊖.

decane<sup>7</sup>, are also included; results from ref.<sup>10</sup> are plotted in Fig. 1c for the sake of comparison. The heats of mixing of alkanes with chloroform related to the volume unit decrease in the order hexadecane > heptane > trimethylpentane > heptamethylnonane, *i.e.* in the same order as follows from ref.<sup>4</sup> for mixing of these alkanes with cyclohexane, 2,2-dimethylbutane and hexane. A similar conclusion holds for mixtures with 2-butanone, with the difference that hexadecane and heptane give almost identical heats. It follows from what has been said above that besides a strong positive thermal effect due to the difference in the polarity of alkanes, on the one hand, and of chloroform or 2-butanone on the other, factors which decide about the magnitude of  $\Delta H$  in nonpolar systems become operative in our systems in the second order. To make possible a more detailed comparison of our results with those presented in ref.<sup>4</sup>, we analyzed them in the terms of the Prigogine-Flory-Patterson theory<sup>2,3</sup>.

This theory, which is also called the equation-of-state theory, is based on an assumption of the validity of a universal equation of state for liquids

$$\tilde{V}_i = \tilde{V}(\tilde{T}_i, \tilde{P}_i), \quad (2)$$

in which the subscript  $i$  relates to pure components 1, 2 or to a mixture; the dimensionless "reduced" quantities are defined by

$$\tilde{V}_i = V/V_i^*, \quad \tilde{T}_i = T/T_i^*, \quad \tilde{P}_i = P/P_i^*. \quad (3)$$

Of the reduction parameters,  $V_i^*$  gives the hard-core volume (molar volume extrapolated to  $T = 0$ ),  $P_i^*$  indicates the cohesion energy density at  $T = 0$  and  $T_i^*$  is proportional to the ratio of cohesion energy to configurational entropy.

A universal relationship

$$\tilde{U}_i = \tilde{U}(\tilde{T}_i, \tilde{V}_i), \quad (4)$$

is valid, in which  $\tilde{U} = U/(P_i^* V_i^*)$  and  $U$  is the configurational part of internal energy. The change in enthalpy at mixing is then given by

$$\Delta H_v^* = \Phi_1 P_1^* [\tilde{U}(\tilde{T}_m) - \tilde{U}(\tilde{T}_1)] + \Phi_2 P_2^* [\tilde{U}(\tilde{T}_m) - \tilde{U}(\tilde{T}_2)] - \Phi_1 \Phi_2 X_{12} \tilde{U}(\tilde{T}_m), \quad (5)$$

where  $\Delta H_v^*$  is heat per unit hard-core volume,

$$\Delta H_v^* = \Delta H / (n_1 V_1^* + n_2 V_2^*), \quad (6)$$

$\Phi_1$  is the hard-core volume fraction,

$$\Phi_1 = n_1 V_1^* / (n_1 V_1^* + n_2 V_2^*) \quad (7)$$

( $n_1, n_2$  are amounts of substance) and  $\Theta_2$  is the surface fraction,

$$\Theta_2 = s_2\Phi_2/(s_1\Phi_1 + s_2\Phi_2) \quad (8)$$

( $s_i$  is the molecular surface-to-volume ratio). For the reduced temperature of mixture,  $\tilde{T}_m$ , it holds that

$$\tilde{T}_m = \frac{\Phi_1 P_1^* \tilde{T}_1 + \Phi_2 P_2^* \tilde{T}_2}{\Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1 \Theta_2 X_{12}} \quad (9)$$

In the Flory theory the functional relationship  $\tilde{U}(\tilde{T})$  is given by equations

$$\tilde{U} = -\tilde{V}^{-1}, \quad \tilde{T} = \tilde{V}^{-1} - \tilde{V}^{-4/3} \quad (10a,b)$$

The reduction parameters of pure compounds,  $V_i^*$ ,  $T_i^*$ ,  $P_i^*$ , must be calculated from the specific volume, thermal expansion and compressibility using equations given in ref.<sup>2</sup>; the results of these calculations are summarized in Table II.

The parameter  $X_{12}$  is a measure of the change in energy in contact formation between molecules 1 and 2 at the expense of contacts of type 1-1 and 2-2. This is an adjustable parameter, which must be calculated from experimental heat values. Eq. (5) contains  $X_{12}$  both explicitly and implicitly in the reduced temperature of mixture,  $\tilde{T}_m$ ; as a consequence,  $X_{12}$  was calculated by an iterative procedure.

TABLE II  
Parameters of Pure Components at 25°C

Compound	$\rho_{25}$ g/cm <sup>3</sup>	$P^*$ J/cm <sup>3</sup>	$V^*$ cm <sup>3</sup> /mol	$T^*$ K	$s$ nm <sup>-1</sup>
Chloroform <sup>a</sup>	1.47890	615	61.95	4 601	10.3 <sup>b</sup>
2-Butanone <sup>c</sup>	0.79985	582	68.73	4 559	10.0 <sup>b</sup>
Heptane <sup>d</sup>	0.67930	433	113.63	4 654	10.2 <sup>c</sup>
Hexadecane <sup>f</sup>	0.76969	463	239.69	5 549	9.0
2,2,4-Trimethylpentane <sup>f</sup>	0.68778	370	129.08	4 760	8.1
2,2,4,4,6,8,8-Heptamethylnonane <sup>f</sup>	0.78135	399	238.04	5 725	7.7

<sup>a</sup> The calculation was carried out using the density measured by us and  $\alpha$  and  $\gamma$  interpolated from data in ref.<sup>11</sup> to 25°C. <sup>b</sup> Calculated from  $V^*$  assuming spherical shape of the molecule. <sup>c</sup> Ref.<sup>12</sup>. <sup>d</sup>  $\alpha$  and  $\rho$  used from series expansion in ref.<sup>13</sup> and  $\gamma$  from data in ref.<sup>14</sup>. <sup>e</sup> Mean value from  $s$  values for hexane and octane in ref.<sup>4</sup>. <sup>f</sup>  $\rho$  from our measurements, the other data from ref.<sup>4</sup>.

The values thus calculated are summarized in Table III. The results of an approximate calculation using Eq. (6), ref.<sup>4</sup>, were used as the initial  $X_{12}$  values in the iteration. These values differed from the final ones by +0.15 at utmost, which corroborates the suitability of the approximation also for high  $X_{12}$  values. As has been expected, the  $X_{12}$  values determined with mixtures of chloroform or butanone with alkanes are considerably higher than with mixtures of nonpolar compounds (Table III). However, in comparing linear alkanes with branched ones similar differences are observed, independent of the fact whether the other component is a polar compound or some other alkane: hexadecane has its  $X_{12}$  values higher by some 10 J/cm<sup>3</sup> than its branched isomer, while for n-heptane  $X_{12}$  is almost the same as for 2,2,4-trimethylpentane.

If one starts with the equation-of-state theory, it is possible, by using  $X_{12}$  values given in Table III, to interpret the experimental results obtained by us as follows:

1) The last term in Eq. (5), the cohesion energy term (C.E.T.) represents a change in enthalpy according to the classical lattice theory; in other words, it expresses the difference in the cohesion energies of mixture and of original components, assuming that both the mixture and the original components have the same reduced temperature ( $T_m^*$ ), and that as a consequence the degree of thermal expansion does not change with mixing. The magnitude is proportional to the surface fraction  $\Theta_2$ , and is thus a function of the ratio of the specific surfaces of molecules,  $s_2/s_1$ . Owing to the isometric shape of their molecules, strongly branched alkanes have a lower  $s$  than chain-like n-alkanes (Table II). Consequently, with the former the cohesion energy term at  $\Phi_2$  0.5 and the same  $X_{12}$  should be roughly by 10% smaller than with the latter. In this way one may fully explain the difference between  $\Delta H$  of trimethyl-

TABLE III  
Interaction Parameter  $X_{12}$  (Jcm<sup>-3</sup>) Values for  $\Phi_2 = 0.5$

	According to ref. <sup>4</sup>		Our data	
	cyclohexane	2,2-dimethylbutane	chloroform	2-butanone
Heptane	(9.2) <sup>a</sup>	(0.9) <sup>a</sup>	37.5	54.5
Hexadecane	16.1	7.6	44.5	57.6
2,2,4-Trimethylpentane	7.3	0.0	39.2	56.2
2,2,4,4,6,8,8-Heptamethylnonane	5.4	1.0	33.7	48.7

<sup>a</sup> Mean value from the values for hexane and octane in ref.<sup>4</sup>.

pentane and heptane, but only partly the difference between heptamethylnonane and hexadecane (Figs 1a–d and Table I).

2) The sum of the first two terms on the right-hand side of Eq. (5) gives the term of the equation of state (E.S.T.), describing the influence of the difference between thermal expansion of mixture, on the one hand, and of both pure components, on the other. This term can be further divided into two subterms. The first subterm is given by the limit of E.S.T. for  $X_{12} = 0$ , and consequently represents that part of E.S.T. which depends only on the difference in the properties of pure components. Let this subterm be called E.S.T. I; in our system it is proportional to  $|\bar{T}_2 - \bar{T}_1|$ , and is thus affected by the size of the molecules. The other part of the term of the equation of state, E.S.T. II, characterizes the influence exerted by the parameter  $X_{12}$  on the reduced temperature of mixture, and thus on its thermal expansion (Eq. (9)).

It is clear from Table II that the reduced temperature of hydrocarbons  $C_7$ ,  $C_8$  is almost the same as that of chloroform and 2-butanone, and that consequently E.S.T. I in their mixtures is negligibly small. The reduced temperature of hydrocarbons with a longer chain,  $C_{16}$  in our case, is lower; E.S.T. I is negative, and for  $\Phi_2$  0.5 it amounts to 3–6% of  $\Delta H_v^*$ . Hence, the enthalpy of mixing of hydrocarbons  $C_7$ ,  $C_8$  should be somewhat higher than with  $C_{16}$ . This is fulfilled, if one compares both branched hydrocarbons (curves 2 and 4; 6 and 8). On the other hand, in the case of n-alkanes (curves 1 and 3, 5 and 7) the order with respect to size is an opposite one. The larger part of the term of the equation of state in the case of strongly interacting systems is given by E.S.T. II, which is positive, and in our case amounts to 26–28% of  $\Delta H_v^*$ . As regards C.E.T., the contribution of alkanes  $C_{16}$  to this term is 76–80%  $\Delta H_v^*$ , while that of lower alkanes is about 72%.

3) Patterson and coworkers<sup>4</sup> have shown that the difference in the content of methyl and methylene groups, which appears with branched and linear alkanes, does not lead to any significant differences in the values of  $X_{12}/P_1^*$ . It could be expected, therefore, that  $\Delta H$  would be affected only by the specific surface of molecules and by the reduced temperature of the alkane. In this case hexadecane should occupy a third place in the order of the heats of mixing of alkanes measured by us; in actual fact, however, it gives the highest values of the enthalpy of mixing. Patterson and coworkers<sup>4</sup> compared their calorimetric data on mixtures of alkanes with values of the apparent optical anisotropies of pure components determined by depolarized Rayleigh scattering, thus proving that in n-alkanes there exists a short-range correlation of molecular orientations. The degree of correlation increases with chain length; it is very small in heptane, but quite important in hexadecane. The correlation is cancelled in the mixing of n-alkanes with isotropic or small molecules; this is related with an endothermal effect, which is reflected in an increase of the parameter  $X_{12}$ . We believe that such explanation is valid also for the mixtures of hexadecane with polar liquids measured by us.

One may summarize, therefore, that the difference between the cohesion energies of mixture and of pure components characterized by the term  $X_{12}\Phi_1\Theta_2$ , depends on the specific surface of molecules; in  $\Delta H$  it is reflected both directly (C.E.T.) and through an influence on the degree of thermal expansion of the mixture (E.S.T. II). The effect of the difference  $\tilde{T}_2 - \tilde{T}_1$  is inferior (E.S.T.I), even though it may seem that it is operative to a somewhat larger extent than predicted by equations of the Flory theory. Moreover, in mixtures of hexadecane there is an endothermal contribution due to changes in the correlation of molecular orientations.

The equations used were derived assuming random mixing, which in mixtures with strong interactions is probably not fulfilled. In the case of a positive value of the interaction parameter the number of contacts between molecules of different components will obviously be lower than assumed; consequently, the product  $\Phi_1\Theta_2$  in Eqs (5) and (9) must be multiplied by a factor  $\alpha < 1$ , which is a function of composition and decreases with increasing  $X_{12}$ . Hence, the actual  $X_{12}$  values will be higher than those calculated, but the qualitative results of comparison between the individual mixtures and analyses of contributions of the individual influences will remain unaffected. As will be shown in a forthcoming paper<sup>6</sup>, much worse consequences ensue from neglecting nonrandom mixing in the treatment of ternary systems data, which is a much stricter test of the molecular theories of mixtures.

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