HEATS OF MIXING OF BUTANONE AND CHLOROFORM WITH ALKANES: TERNARY SYSTEMS

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A change in enthalpy was determined on the addition of alkane (component 3) to a mixture of the same volumes of 2-butanone (1) and chloroform (2), as a function of the resulting volume fraction of alkane. The alkanes used were the same as in the preceding paper dealing with binary systems, and the same order of alkanes was found according to the magnitude of heat effect. The heat of mixing of chloroform with 2-butanone was also ascertained. By analysing data from this paper and from the paper referred to above, it was possible to compare the ability of three theories to predict the behaviour of a ternary system using data provided by binary systems. The equation based on the simple lattice theory greatly overestimates the contribution of interaction between components 1 and 2; the departure from reality is independent of the alkane structure. The application of the equation-of-state theory has brought some improvement, due to the introduction of surface fractions instead of volume fractions. The Barker theory of quasichemical equilibria led to a prediction which was in a reasonable agreement with experimental results. This seems to suggest that nonrandom mixing is an important factor in the thermodynamics of polar mixtures.

In studying the thermodynamic properties of ternary liquid mixtures, one comes across a question whether the behaviour of a ternary mixture can be predicted using known properties of the three binary mixtures derived therefrom, and what the causes may be of possible deviations of the predicted behaviour from that observed experimentally. The question is important both in the rather general context of foreseeing properties of complicated systems basing on the knowledge of simpler ones, and also as a test of validity of the theory or empirical equation used in the prediction. In recent times[1], the thermodynamic properties of dilute solutions of nonpolar polymers in mixed nonpolar solvents have been interpreted in the terms of data on binary systems, using the Prigogine–Flory–Patterson theory, while a prediction based on the Flory–Huggins classical lattice theory[2–4] was not successful.

It seems that differences between calculations carried out on the basis of the classical lattice theory and experimental results are particularly large with systems containing polar components. In this paper, the heats of mixing of the system 2-butanone–chloroform (in a volume ratio 1 : 1) with four different alkanes are presented and discussed. The paper is a continuation of our preceding paper[5] dealing with the enthalpies of mixing of pure chloroform and butanone with the same alkanes. It was shown there, using data analysis, how the heat of mixing in binary mixtures of a polar

compound with alkane was affected by the size and shape of the alkane molecule. The same question should of course be answered for ternary systems 2-butanone––chloroform–alkane. In order to complete the series of binary systems, the heat of mixing of 2-butanone with chloroform was also measured. In a theoretical analysis of ternary data concentrated on the two problems formulated above, we employed the classical lattice theory, the Prigogine–Flory–Patterson theory and the Barker theory.

THEORETICAL

If a mixture of compounds 1 and 2 which has a composition given by the volume fractions φ'_1, φ'_2 is diluted with component 3, a ternary mixture of the composition φ_1, φ_2, φ_3, is obtained, in which

$$\varphi_i = \varphi'_i(1 - \varphi_3), \quad i = 1, 2. \tag{1}$$

A change in enthalpy in this process related to 1 ml of the resulting ternary mixture (ΔH_v) is given by

$$\Delta H_v = (\Delta H_v)_{123} - (1 - \varphi_3)(\Delta H_v)_{12}, \tag{2}$$

where $(\Delta H_v)_{123}$ and $(\Delta H_v)_{12}$ are the heats of mixing of pure compounds leading to formation of a ternary mixture of components 1, 2, 3, or of a binary mixture of components 1, 2; the two quantities are related by

$$(\Delta H_v)_{12} = \lim_{\varphi_3 \to 0} (\Delta H_v)_{123}. \tag{3}$$

The dependence of $(\Delta H_v)_{123}$ on the composition of the ternary mixture can be expressed by the equation

$$(\Delta H_v)_{123} = \varphi_1\varphi_2\alpha_{12} + \varphi_1\varphi_3\alpha_{13} + \varphi_2\varphi_3\alpha_{23} + \varphi_1\varphi_2\varphi_3\alpha_T. \tag{4}$$

The parameters α_{ij} can be obtained from the heats of mixing of the respective binary systems, *e.g.*

$$\alpha_{12} = (\Delta H_v)_{12}/\varphi'_1\varphi'_2. \tag{5}$$

The term with α_T expresses departures of the ternary system from the behaviour predicted using a simple combination of binary terms. Eqs (1) through (4) yield

$$\Delta H_v = \varphi_3(1 - \varphi_3)\left[\varphi'_1\alpha_{13} + \varphi'_2\alpha_{23} - \varphi'_1\varphi'_2\alpha_{12} + \varphi'_1\varphi'_2(1 - \varphi_3)\alpha_T\right]. \tag{6}$$

The calculation using Eq. (6) is unambiguous only if the parameters α_{ij} are independent of the composition of the respective binary systems. In most cases this is not so; the dependence of α_{ij} on the composition of a binary system is expressed, e.g., in terms of the Redlich–Kister series expansion

$$\alpha_{13} = \sum_{k=0}^{n} C_k(\varphi_1 - \varphi_3)^k = \sum_{k=0}^{n} C_k(1 - 2\varphi_3)^k = \sum_{k=0}^{n} C_k(2\varphi_1 - 1)^k. \qquad (7)$$

All three forms of the expansion are mutually equivalent in a binary system, but not in a ternary one, where $\varphi_1 + \varphi_3 < 1$. If, thus, one wants to use substitution from Eq. (7) into Eq. (6), the choice of the form of expansion suitable for a ternary mixture is intuitive to some extent and depends on the character of the system. In our case, dilution of a mixture of two polar components (1 and 2) with a nonpolar component (3) represents a process very similar to that investigated in the paper dealing with binary systems, i.e. mixing of a pure polar component 1 or 2 with a nonpolar component. In both cases the addition of an inert component causes one part of strong interactions between polar molecules to disappear, being replaced by weak interactions of polar molecules with nonpolar ones. In the second case, only interactions between like molecules disappear, which in the first case is accompanied by the disappearance of interactions between unlike molecules. We expect, therefore, that α_{13}, which in the binary system 1−3 is a function of $\varphi_1 - \varphi_3$, in our ternary system will be a function of the expression $(\varphi_1 + \varphi_2) - \varphi_3 = 1 - 2\varphi_3$, thus justifying the use of the second form of expansion (7). A similar reasoning holds for the parameter α_{23}. With the parameter α_{12} we regard $\alpha_{12} \equiv \alpha_{12}(\varphi_1')$ as a suitable expression.

Equations describing the change in enthalpy on the addition of a third component to the binary mixture may be derived using the Prigogine–Flory–Patterson theory. In Eqs (1) through (3), enthalpies related to the unit volume ΔH_v are replaced by values related to the unit hard-core volume ΔH_v^* (ref.[5]), while the volume fractions φ_i are replaced by the hard-core volume fractions ϕ_i. Eq. (5) from ref.[5] may be reformulated for a ternary system; by doing so, one obtains a relationship for $(\Delta H_v^*)_{123}$, which substitutes Eq. (4). By combining equations thus obtained, one arrives at a relationship for the heat of mixing of the system (1 + 2) with component 3

$$\Delta H_v^* = (\phi_1 P_1^* + \phi_2 P_2^*)\left[\tilde{U}(\tilde{T}_t) - \tilde{U}(\tilde{T}_{12})\right] + \phi_3 P_3^*\left[\tilde{U}(\tilde{T}_t) - \tilde{U}(\tilde{T}_3)\right] - $$
$$- (\phi_1 X_{13} + \phi_2 X_{23} - \phi_1 \Theta_2' X_{12})\,\Theta_3\,\tilde{U}(\tilde{T}_t) - \phi_1 \Theta_2' X_{12}\left[\tilde{U}(\tilde{T}_t) - \tilde{U}(\tilde{T}_{12})\right]. $$
$$\qquad (8)$$

Here, ϕ_i and Θ_i is the hard-core-volume and surface fraction of i-th component in the ternary system; Θ_i' is the surface fraction in the binary system (1 − 2), and $\tilde{T}_t$ is a reduced temperature of the ternary system:

$$\tilde{T}_t = \sum_i \phi_i P_i^* \tilde{T}_i / (\sum_i \phi_i P_i^* - \sum_i \sum_{j>i} \phi_i \Theta_j X_{ij}) \,. \qquad (9)$$

The reduced temperature of the binary system, $\tilde{T}_{12}$, is defined as $\tilde{T}_{12} = \lim_{\phi_3 \to 0} (\tilde{T}_t)$.

The other symbols have been explained in ref.[5]. In recalculating Eq (8) to the relationship $\Delta H_v(\varphi_i)$, it is then possible to use equations

$$\Delta H_v = \Delta H_v^* / (\sum_i \phi_i \tilde{V}_i) \,, \quad \varphi_j = \phi_j \tilde{V}_j / (\sum_i \phi_i \tilde{V}_i) \,. \qquad (10)$$

The Barker theory[6] is a suitable tool for interpreting the thermodynamic behaviour of systems with non-random mixing. If the surface of each molecule is divided into a set of interacting sites of different chemical nature, then according to Barker the enthalpy of the system can be expressed as a sum of contributions originating in the double contacts of various sites. For instance, contacts between sites of i-th and j-th type contribute by the term $2U_{ij}\eta_{ij}X_iX_j$, in which U_{ij} is the energy of one contact, $2\eta_{ij}$ is the equilibrium constant of formation of one ij contact at the expense of the contacts ii and jj, and X_i^2, X_j^2 give the number of contacts of the ii and jg types respectively in 1 mol of mixture. The values of X_i must be determined by solvin$j$ a set of n equations

$$X_i(X_i + \sum_{j \neq i} \eta_{ij}X_j) = q_{C,i}x_C/2 \quad i, j = 1, \ldots, n \,, \qquad (11)$$

where n gives the number of various types of contact sites, x_C is the mole fraction of the component to the molecule of which the site of i-th type is assigned, and $q_{C,i}$ gives the number of sites of i-th type in a molecule of component C. (A more detailed presentation of Barker's theory cf. ref.[6]).

For the enthalpy ΔH_M (J/mol) of dilution of the mixture $1-2$ with component 3 at the formation of 1 mol of ternary system, an equation

$$\Delta H_M = 2\{\sum_k \sum_{1 \neq k} U_{k1}\eta_{k1}[X_kX_1 - (1 - x_3) X_k'X_1'] +$$
$$\sum_r \sum_{s \neq r} U_{rs}\eta_{rs}[X_rX_s - x_3X_r^0X_s^0] + \sum_k \sum_r U_{kr}\eta_{kr}X_kX_r\} \qquad (12)$$

has been derived. Here, the subscripts, k, 1 denote the interaction sites of molecule; (1 or 2 respectively, the subscripts s, r denote those of molecules of component 3 X_k and X_k' respectively are related to the ternary system and binary mixture $(1-2)$, while X_r^0 relates to the pure component 3. Hence, in a general case three sets of equations must be solved, namely, for X_i $(i = 1, \ldots, n)$; for $X_k'(k = 1, \ldots, n')$, for X_r^0 $(r = 1, \ldots, n_3)$; it holds that $n = n' + n_3$.

The heat per volume unit is calculated using

$$\Delta H_v = \Delta H_M / \sum x_i V_i . \qquad (13)$$

EXPERIMENTAL

The chemicals and experimental procedure used have been described in a preceding paper[5].

RESULTS AND DISCUSSION

The measured heats of mixing of the mixture of 2-butanone(1) and chloroform(2) having the composition $\varphi_1' = 0.5$ with alkanes(3) were correlated by using the Redlich–Kister series expansion, similarly to the heats of mixing of pure polar components with alkanes in ref.[5]:

$$\Delta H_v = \varphi_3 (1 - \varphi_3) \sum_{k=0}^{n} C_k (1 - 2\varphi_3)^k . \qquad (14)$$

A similar series expansion, in which φ_3 was replaced by φ_2', was used for the binary mixture 2-butanone–chloroform. The constants of the series are summarized in Table I, the concentration dependences are plotted in Figs 1 and 2. Similarly to ref.[5],
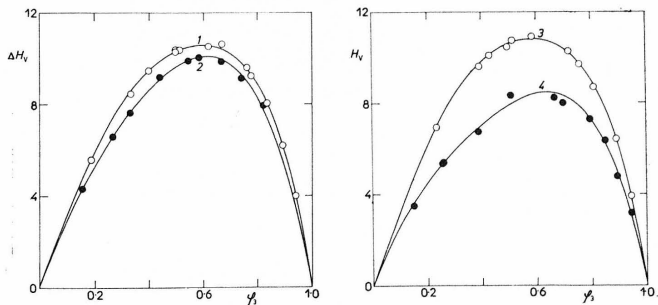

Fig. 1

Dependence of the Enthalpy of Mixing, ΔH_v (J cm^{-3}) of the System Butanone + Chloroform (vol. 1 : 1) with Alkane (component 3) on φ_3 at 25°C

Alkanes: *1* heptane, *2* trimethylpentane, *3* hexadecane, *4* heptamethylnonane. The curves correspond to the Redlich–Kister expansion, *cf.* (*14*) and Table I. Odd curves ○, even curves ●.

here too the heats of mixing decrease in the order hexadecane > heptane > trimethyl-pentane > heptamethylnonane.

The results are first analyzed on the basis of the classical lattice theory in a simple version, mathematically expressed by Eq. (6) after omitting the term with α_T. This equation includes the requirement of random mixing and the assumption that the extent of interaction contacts of the molecule is proportional to its volume. The first two terms in square brackets of Eq. (6) express the contribution of the contact formation between molecules of components 1 and 3, or 2 and 3; the third term describes the decrease in the number of contacts of type 1 — 2 in the case of dilution of the binary mixture with component 3. Using the above assumptions and also reasonings related to Eq. (7), we derived the subsequent equation, allowing a theoretical prediction of ΔH_v at $\varphi'_1 = 0.5$:

$$\Delta H_v = \varphi_3(1 - \varphi_3) \left\{ 0.5 \sum_{k=0}^{n} \left[(C_k)_{13} + (C_k)_{23} \right] (1 - 2\varphi_3)^k - 0.25(C_0)_{12} \right\}.$$

$$(15)$$

Here, $(C_k)_{ij}$ is k-th constant in the Redlich–Kister series expansion for a binary system consisting of components i and j; the constants $(C_k)_{13}$ and $(C_k)_{23}$ were taken from Table I in ref.[5], while the constant $(C_0)_{12}$ comes from Table I in this paper.
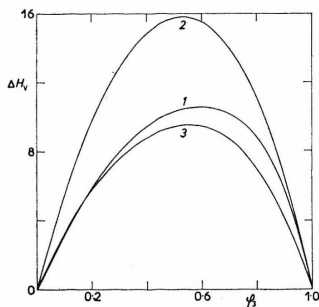

Fig. 3

Comparison of Experiment and Prediction According to the Classical Lattice Theory ΔH_v vs φ_3 for the system (butanone + + chloroform)–heptane: 1 experiment, 2 prediction according to Eq. (15), 3 prediction assuming $\alpha_{12} = 0$.

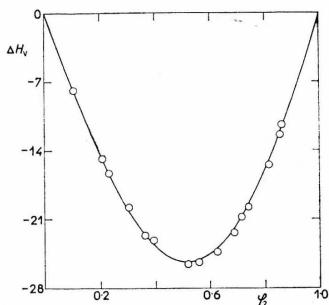Fig. 2

Dependence of ΔH_v (Jcm^{-3}) on φ_2 for the System Butanone(1)–Chloroform(2) at 25°C

The curve corresponds to the Redlich–Kister expansion.

As documented by Fig. 3, the ΔH_v values thus predicted (curve 2) are by 50% to 70% higher than those measured (curve 1). A better approximation consists in a prediction assuming $\alpha_{12} = (C_0)_{12} = 0$, in agreement with the assumed simple additivity of interactions $1 - 3$ and $2 - 3$ with interactions $1 - 2$ ruled out (curve 3). The main cause of departures of Eq. (15) from reality should probably be sought in that the loss of contacts of type $1 - 2$ in the case of dilution with component 3 is much lower than predicted by the simple lattice theory[1,2]. It should be pointed out that if the other forms of series expansion of (7) are used, namely, polynomials in $(\varphi_1 - \varphi_3)$ or $(2\varphi_1 - 1)$ instead of polynomials in $(1 - 2\varphi_3)$, the departures would be still larger.

Obviously, Eq. (6) can be used successfully only if one admits an empirical correction in the form of a term with α_T. We have therefore plotted in a diagram differences between the experimental value of $\Delta H_v/\varphi_3(1 - \varphi_3)$ and an analogous value calculated from Eq. (15), as a function of $(1 - \varphi_3)$; from Eq. (6), it is clear that for $\varphi_1' = 0.5$ this difference is $\alpha_T(1 - \varphi_3)/4$.

It can be seen in Fig. 4 that all four systems differing in the inert component 3 yielded, within the limits of experimental error, the same dependence of the product $\alpha_T(1 - \varphi_3)/4$ on $(1 - \varphi_3)$. As one had to expect, the dependence passes through the beginning of the coordinates, but it is not a straight line, so that α_T is a function of φ_3. To express this functional dependence, the Redlich–Kister series expansion

$$\alpha_T = \sum_{k=0}^{n} C_k(1 - 2\varphi_3)^k ; \qquad (16)$$

TABLE I

Constants C_i (J/cm^3) and Standard Deviation σ of the Redlich–Kister Series Expansion

Mixing	C_0	C_1	C_2	C_3	σ
$(1 + 2)^a$ + heptane	41·26	−11·09	13·07	−12·37	0·7
$(1 + 2)$ + hexadecane	42·50	− 9·53	13·41	−15·32	0·6
$(1 + 2)$ + branched alkane C$_8$^{b}	38·66	−15·34	10·04	—	0·8
$(1 + 2)$ + branched alkane C$_{16}$^{c}	31·64	−14·38	14·27	—	1·9
$1 + 2$	−101·24	9·53	17·38	—	2·0
Parameter α_T^{d}	−174·32	135·48	−94·88	—	—

[a] $(1 + 2)$ is the mixture of 2-butanone and chloroform in the 1 : 1 volume ratio. [b] 2,2,4-Trimethylpentane. [c] 2,2,4,4,6,8,8-Heptamethylnonane. [d] Defined using Eq. (6); common for all cases of mixing of $(1 + 2 -$ mixture) with alkane.

was used again. The constants of the series expansion are summarized in Table I. (It should be pointed out that the plot in Fig. 4 has been obtained by a linear combination of three different experimental curves for a given alkane. Consequently, the dependence on φ_3 could be considered only in that part of the concentration range, in which for each of the three experimental dependences a sufficient number of points was measured. This is why the dependence of α_T on φ_3 as expressed in terms of the series expansion (16) holds only in the range $1 - \varphi_3$ from 0 to 0·8).

As has been said in the introduction, the Prigogine–Flory–Patterson theory, also called the equation-of-state theory, allows to deal with nonpolar ternary mixtures along with binary mixtures without introducing any further parameters. In the case of the heats of dissolution of polymers in a mixture of two liquids, the large difference between values predicted on the basis of the classical lattice theory and of the equation-of-state theory is due to the fact that the former regards the intermolecular interaction as proportional to the volume, while the latter expresses the same interaction as proportional to the surface[1]. Compared with small molecules, macromolecules usually exhibit a considerably smaller s value (molecular surface-to-volume ratio). If, then, the interaction depends on the surface area, the decrease in the number of contacts between molecules of the solvent components 1 and 2, which occurs during dissolution of the polymer (component 3), is smaller than that predicted by the classical lattice theory; the same holds (in an absolute value) for the energetic contribution associated with it. Substitution of the volume fraction with the surface fraction did indeed lead in ref.[1] to results which agreed with experiment. This confirmed the correctness of the assumption that surface is the relevant quantity in contact interactions.

The Prigogine–Flory–Patterson theory also proved useful in the analysis of binary mixtures of a polar and nonpolar component, as described in the preceding paper[5]. We therefore calculated the theoretical ΔH_v values of ternary systems, using Eqs (8) through (10). Values given in Tables II and III of the preceding paper were substituted for the parameters of pure components and for the interaction parameters (X_{13} and X_{23}); for the interaction parameter butanone–chloroform, we obtained $X_{12} = -118·5$ J cm^{-3} from the results presented in this paper. Compared with the prediction based on the classical lattice theory, the calculation of ΔH_v of the ternary system was only a partial improvement; e.g., for $\varphi_3 = 0·5$ the departure from experimental values decreased approximately by one-twentieth with n-alkane systems and by one-sixth in the case of systems with strongly branched alkanes. A somewhat better result obtained with the branched alkanes may be explained by the fact that s value of the latter is still lower than that of linear alkanes (cf. Table II in the preceding paper[5]); on the other hand, however, the difference from s of butanone and chloroform is by far not so large as that existing between the majority of polymers and low--molecular weight compounds. Thus, if systems with polar compounds are concerned, the equation-of-state theory, useful as it might be in the comparative analysis

of binary mixtures, does not hold its ground in a more exacting test, such as an inter-
pretation of ternary systems. It is worth mentioning that in ref.[1], too, no agreement
with experiment could be obtained with the system chlorobenzene–heptane–poly-
isobutylene, where the first component is a polar one.

We believe that with systems containing strongly interacting polar groups no ran-
dom mixing can be assumed. We therefore treated our data for the system 2-butanone
(1)–chloroform(2)–heptane(3) also employing Barker's theory, which takes account
of nonrandom mixing. The following interaction sites were discerned on the surface
of molecules of the individual components (number of sites per molecule, q, given
in brackets, is given by the number of electron pairs not involved in the valency bonds):
For 2-butanone, inert hydrogen atoms (denoted R; $q = 8$) and the carbonyl group
(0; $q = 2$); for chloroform, hydrogen (H; $q = 1$) and chlorine (Cl; $q = 9$), and for
heptane, again inert hydrogen R ($q = 16$).

Since the sites R of 2-butanone are considered to be the same as the sites of heptane,
there are four types of sites on the whole which can form six types of binary contacts
(Table II). There are two thermodynamic characteristics per each type of contacts,
namely, η_{ij} and U_{ij}, or else, $F_{ij} = -RT \ln \eta_{ij}$ and U_{ij}. Hence, the number of inter-
action parameters (twelve) is much higher than that obtained with the equation-
-of-state theory. To avoid suspicion that the Barker theory must be more successful
because of the higher number of adjustable parameters, we determined the Barker
parameters of the interaction contacts using the largest possible data assembly
on binary systems and avoiding adjustment on the basis of the ternary system data.
In this way, the same conditions of application were observed in principle as in the
case of the two theories discussed before. The parameter η_{RO} was calculated from the
maximum G^E value of the mixture 2-butanone–hexane[7] (after recalculating experi-
mental data from 60° to 25°C); U_{RO} was determined from the maximum of H^E

TABLE II
Interaction Parameters of Group Contacts According to the Barker Theory

Contact ij	η_{ij}	F_{ij}, J/mol	U_{ij}, J/mol
RO	0·10	5 710	10 950
RCl	0·95	130	200
RH	0·93	185	580
HCl	1·00	0	−310
OCl	1·00	0	0
HO	4·0	−3 440	−7 160

of the same mixture[8] using η_{RO} just obtained. Both parameters were also satisfactory at H^E maximum of the system 2-butanone–heptane[5]. The parameters η_{HCl} and U_{HCl} were obtained by treating the activity[9] and enthalpy[10] data of the system chloroform–tetrachloromethane (chlorine sites of chloroform were distinguished from chlorine sites of CCl_4). The thermodynamic characteristics of the R—Cl and R—H contacts were obtained from the activity[11] and enthalpy[5] data of the system chloroform–heptane by the minimization of the sum of squares of deviations given by theory and of smoothed experimental data, using η_{HCl} and U_{HCl}. The parameters of the remaining contacts, H—O and O—Cl, had to be determined from data on the mixture 2-butanone–chloroform, where only H^E values measured by us were at disposal (Table I). For simplicity's sake, we put $\eta_{OCl} = 1$, $U_{OCl} = 0$; η_{HO} and U_{HO} were adjusted to the experimental H^E value for $x_1 = 0.5$ so as to observe the condition

$$F_{ij} = 0.5 U_{ij} \pm 250 \text{ J/mol}.$$

which is satisfied by the parameters of all types of contacts under consideration.

All values of η_{ij}, F_{ij} and U_{ij} thus obtained are summarized in Table II. They were used in calculating the theoretical dependence of ΔH_M on x_3 for mixing of the system 2-butanone–chloroform with heptane. As can be seen in Fig. 5, such prediction
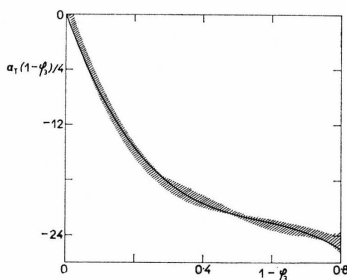

Fig. 4

Ternary Term of Eq. (16):

Plot of $\alpha_T (1 - \varphi_3)/4$ vs $(1 - \varphi_3)$

Curves for all systems studied lie in the hatched zone; a common curve is plotted which adequately characterizes all systems within the limits of experimental error.
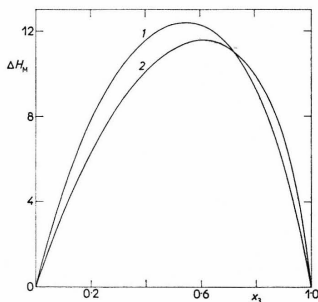
Fig. 5

Comparison of Experiment and Prediction

ΔH_M vs x_3 for the system (butanone + + chloroform)–heptane, 1 experiment, 2 prediction according to Barker's theory using parameters given in Table II.

reasonably agrees with experiment. This success of the Barker theory confirms the importance of non-random mixing in systems with strong interactions. In our system the conclusive role is obviously played by the negative sign of F_{HO} and by the high value of η_{HO} connected with it. Owing to the latter, the hydrogen bonds between the hydrogen atom of chloroform and the oxygen atom of ketone are split by the addition of alkane to a much smaller extent than it would follow from the conception of random mixing. This provides a more exact formulation of the hypothesis forwarded in the discussion on Fig. 3 and regarding the very low loss of the number of $1-2$ contacts after the addition of component 3.

Thus, the analysis of our data has shown that the prediction of the thermodynamic behaviour of a ternary system using binary data is not successful if carried out on the basis of a simple equation derived from the classical lattice theory. The difference between this prediction and experiment is considerable, but independent of the size and shape of the alkane molecule; consequently, the effect of the size and shape of the molecules on the enthalpy of mixing is the same in our case with both binary and ternary systems. The prediction is not considerably improved either by substituting volume fractions by surface fractions, or by taking into account the thermal expansion of the liquids used in mixing in accordance with the equation-of-state theory. It seems, however, that an almost complete fit with experiment can be reached if one bears in mind non-random mixing, which in polar systems is obviously a very important factor.

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