SPECIFIC INTERACTIONS IN SOLUTIONS OF POLYMERS. V.*

AN INTERPRETATION OF THE ENTHALPIES OF MIXING OF CHLOROFORM WITH BUTYL METHACRYLATE OLIGOMERS IN TERMS OF BARKER's THEORY

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The heat of mixing of poly(butyl methacrylate) with chloroform was measured and interpreted together with the results of earlier measurements of the heats of mixing of butyl methacrylate oligomers with chloroform in terms of Barker's lattice theory. The number of adjustable energetic parameters was reduced to minimum by using parameters corresponding particularly to non-specific interactions and taken from simpler systems (*e.g.*, from the series chloroform–n-alkanes). It was found, however, that no completely universal energetic parameters could be found in the systems under investigation, but that the energy corresponding to a specific interaction of the acidic hydrogen of chloroform with the ester group had to be adjusted individually. This finding can be explained by the fact that Barker's theory takes into account neither the conformational structure nor the mutual interaction of the solvated sorption centres of more complex oligomer and polymer molecules.

In a preceding paper[1] the enthalpies of mixing of the butyl methacrylate oligomers with chloroform measured by us were interpreted in terms of the theory of association equilibria[2,3]. In this paper we shall try to interpret the results in terms of Barker's theory. In Barker's theory[4,5], similarly to other lattice theories of polymer solutions, one divides the molecules of the components involved into segments which occupy just one lattice site on a lattice with the coordination number z; the values of the thermodynamic functions of mixing are regarded as a result of the energetic interactions of the surface atoms or groups. The probability of their mutual contacts is also controlled by these interactions. Consequently, one cannot speak about random mixing any more.

THEORETICAL

For the total surface $q_1 z$ of a molecule of component I it holds

$$q_1 z = r_1(z - 2) + 2 , \qquad (1)$$

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where r_1 is the number of segments in a molecule of I and z is the coordination number of the lattice. In Barker's theory, this surface is resolved into the sum of surfaces Q_k^I of the individual classes of the contact points present in the molecule of I, according to

$$q_1 z = \sum_{k=1}^{n} Q_k^I . \tag{2}$$

It is assumed at the same time that the interaction energy U_{kt}^{II} between the contact points of the same class is zero and the interaction energies between these and any contact point of some different class are the same for all contact points of the given class. Thus, for each model of a real solution one has to determine: (a) types of the interacting surfaces (atoms or groups) (i.e., to define the respective classes of contact), (b) their magnitudes (relatively, by the number of the contact points of the given class per molecule), and (c) interaction energies U_{kt}^{II} of the individual possible contacts belonging to different classes (superscripts designate components to which the contact points designated by the corresponding subscripts have been assigned).*

It was found that the given binary mixture could be described to advantage by a matrix representation of the participating interaction energies in the form

$$\mathbf{T} = \begin{bmatrix} \eta_{11}^{AA} & , \ldots, \eta_{1m}^{AA}, & \eta_{1,m+1}^{A\,B} & , \ldots, \eta_{1,m+n}^{A\,B} \\ \cdots\cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots\cdots \\ \eta_{m1}^{AA} & , \ldots, \eta_{mm}^{AA}, & \eta_{m,m+1}^{A\,B} & , \ldots, \eta_{m,m+n}^{A\,B} \\ \hline \eta_{m+1,1}^{B\quad A} & , \ldots, \eta_{m+1,m}^{B\quad A}, & \eta_{m+1,m+1}^{B\quad B} & , \ldots, \eta_{m+1,m+n}^{B\quad B} \\ \cdots\cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots\cdots \\ \eta_{m+n,1}^{B\quad A} & , \ldots, \eta_{m+n,m}^{B\quad A}, & \eta_{m+n,m+1}^{B\quad B} & , \ldots, \eta_{m+n,m+n}^{B\quad B} \end{bmatrix}, \tag{3a}$$

where the quantities

$$\eta_{kt}^{II} = \exp\left(-U_{kt}^{II}/RT\right) \tag{3b}$$

are sometimes called the Boltzmann factors in statistical thermodynamics. From the independence of energy interactions of the order of the participating particles follows the symmetric character of the matrix $\mathbf{T}$. All the diagonal elements of the matrix $\mathbf{T}$ are equal to unity, since according to the definition the interaction energy is zero within the same class of contacts. Broken lines in Eq. (3a) divide the matrix $\mathbf{T}$ into four submatrices so that the elements in diagonal blocks express interactions between

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* Since at present only data on the enthalpies of mixing are complete in the series of systems investigated by us, U_{kt}^{II} will have the character of internal energy and not of free energy, as would be required by a more recent version of Barker's theory[5].

molecules of the same components, and the elements of off-diagonal blocks express interactions of the classes of contacts belonging to different components. With respect to the symmetry of the matrix $\boldsymbol{T}$ it is sufficient if only its upper triangular part will be given further, involving $(m + n)(m + n - 1)/2$ of undetermined energetic parameters, where m is the number of classes of the contact points for the component A and n is the corresponding number of classes of the contact points for the component B.

Now we shall introduce the quantities X_k^I characterizing the frequency of the corresponding contacts between the contact points from different classes of contact in terms of the equations

$$N_{kt}^{IJ} = 2\eta_{kt}^{IJ}X_k^I X_t^J N, \quad N_{kk}^{II} = (X_k^I)^2 N, \qquad (4a,b)$$

where N_{kt}^{IJ} designates the number of contacts between the contact points of the class k from a molecule I and those of the class t of a molecule J in a system with N molecules on the whole. Let $\boldsymbol{x}$ stand for the column vector the elements of which are the just introduced quantities X_k^I, while the matrix $\boldsymbol{L}$ is a diagonal matrix whose diagonal elements are also X_k^I; then for the given binary system the equations of quasichemical equilibrium between the individual classes of surface contacts (cf. Eqs (4a,b)) can be combined with the balance equations (representing the connections to the total composition of mixture) into a single system of nonlinear equations

$$\boldsymbol{L}\,\boldsymbol{Tx} - \boldsymbol{b} = \boldsymbol{0}, \qquad (5)$$

where $\boldsymbol{b}$ is the $(m + n)$-dimensional column vector with the components $Q_k^A x_A/2$ for $k = 1, ..., m$ and $Q_k^B x_B/2$ for $k = m + 1, ..., m + n$ and x_A and x_B are the respective mole fractions of the components A and B. Similarly, quantities X_k^I are arranged into vector $\boldsymbol{x}$ or into matrix $\boldsymbol{L}$.

The values of X_k^A, $k = 1, ..., m$ and X_k^B, $k = m + 1, ..., m + n$ obtained by solving the nonlinear system of equations (5) by means of Newton and Raphson's method are then substituted into the relationship for the enthalpy of mixing derived by Barker[4]:

$$\Delta H_M = 2\Big\{ \sum_{j=1}^{m-1} \sum_{k>j}^{m} (X_j^A X_k^A - x_A X_j^{A1} X_k^{A1})\,\eta_{jk}^{AA} U_{jk}^{AA} +$$

$$+ \sum_{j=m+1}^{m+n-1} \sum_{k>j}^{m+n} (X_j^B X_k^B - x_B X_j^{B1} X_k^{B1})\,\eta_{jk}^{BB} U_{jk}^{BB} +$$

$$+ \sum_{j=1}^{m} \sum_{k=m+1}^{m+n} X_j^A X_k^B \eta_{jk}^{AB} U_{jk}^{AB} \Big\}, \qquad (6)$$

where X_j^{A1} or X_k^{B1} respectively are the values of X_j^A or X_k^B obtained by solving the

systems of equations (5) in the concentration limits (*i.e.* for $x_A = 1$ or $x_B = 1$). The first two terms of Eq. (6) represent a change in enthalpy connected with the transfer of pure components into solution; the third term expresses a change in enthalpy accompanying interactions between the surface contact points belonging to different components of the system.

The system of equations (5) can be solved analytically assuming random mixing when all elements of the matrix T equal unity. In this case the solutions $*X_k^I$ are given by expressions

$$*X_k^I = (b'u)^{-1/2} Q_k^I x_I/2 , \quad k = 1, ..., m \quad \text{for} \quad I \equiv A ,$$
$$k = m + 1, ..., m + n \quad \text{for} \quad I \equiv B , \qquad (7)$$

where b' is the row vector due to the transposition of the vector b and u is a unit $(m + n)$-dimensional column vector. The values of $*X_k^I$ thus calculated were used as the starting approximations for the numerical solution of (5) at the same composition of the binary system and the same surfaces of the contact points involved.

Determination of structure parameters. Similarly to the majority of other authors who have used Barker's theory we chose the lattice coordination number $z = 4$. The number of contact points of the respective classes was determined in accordance with a procedure first introduced by Goates and coworkers[6], by assigning one, two and three contact points to the hydrogen, oxygen, and chlorine atoms respectively. Thus, for instance, the class of the oxygen atoms of the ester group of butyl isobutyrate owns four contact point, *i.e.* $Q_O^B = 4$. These quantities are given by the chemical structure of the components of the mixture, and are therefore called structure parameters.

TABLE I
Structure Parameters of the Compounds Used ($Y = $ n-$C_4H_9O.CO.C(CH_3).CH_2$)

Compound	r	Q_h	Q_{Cl}	Q_R	Q_O	$Q_{O'}$
$CHCl_3$	4	1	9	—	—	—
CCl_4	5	—	12	—	—	—
C_nH_{2n+2}	n	—	—	$2n + 2$	—	—
$(C_nH_{2n+1})_2O$	$2n + 1$	—	—	$4n + 2$	2	—
HYH	9	—	—	16	—	4
n-C_4H_9OYH	14	—	—	24	2	4
n-$C_4H_9OY_2H$	23	—	—	38	2	8
n-$C_4H_9OY_3H$	32	—	—	52	2	12
n-$C_4H_9OY_4H$	41	—	—	66	2	16
n-$C_4H_9OY_{69}H$	626	—	—	976	2	276

Determination of energetic parameters. The only remaining adjustable parameters are inter-action energy values which become operative if contact points of different classes get into contact. If it is our aim to give an adequate picture of the experimental course of ΔH_M only for one single binary system regardless of correlation with the other similar systems, it is sufficient to choose the corresponding energetic parameters U_{kt}^{IJ} so that the sum of squared deviations between the calculated and experimental ΔH_M would be minimum. However, practical applications of this so-called "best-fit" method have revealed that the given experimental data can equally well be represented by several completely different sets of energetic parameters; moreover, sometimes not even the sign of particular energies coincides with that which would correspond to the chemical nature of the respective interaction[7] (*e.g.*, measurements of ΔH_M of the mixtures CCl_4–7,14-dioxa-cosane show that $U_{ClO}^{A,B} < 0$, but the "best-fit" method yielded $U_{ClO}^{A,B} > 0$). Besides, the above procedure also makes impossible any prediction of the course of ΔH_M in analogous systems. We believe that one of the routes that leads to physically better founded interaction energy values consists in studies proceeding step by step from rather simple to more complicated systems. In a very idealized form, such procedure would first mean describing systems with a single type of interactions, then substituting the energy found into equations for a system with two types of interactions and adjusting the remaining energy, then investigating systems with three types of interactions, two of which have been determined in the step immediately preceding, *etc.* However, to follow the above procedure consistently would mean to cope with the lack of experimental data, and also with the fact that in more complicated, particularly polymer molecules there is mutual influence between the contact points of the same molecule. It will be shown in the Discussion of this and a forthcoming[8] paper what types of compromises between the procedures outlined here must be chosen to obtain the most adequate representation of the experimental data in some structurally logical series of systems while taking into account the results of the studies of simpler systems involving only some of the energetic interactions.

EXPERIMENTAL

Materials. The oligomers of butyl methacrylate were prepared by anionic oligomerization[9,10] (*cf.* also ref.[1]). Poly(butyl methacrylate) (formula $C_4H_9OY_{69}H$ where Y = —$CH_2.\overset{|}{C}(CH_3)$.

.$CO.OC_4H_9$, determined from the viscosity measurements of molecular weight) was prepared by the anionic polymerization of butyl methacrylate initiated with sodium butoxide without solvent at 65°C. After one hour the mixture was inhibited with acetic acid and diluted with hexane. The polymer was then precipitated with methanol, the precipitate dried *in vacuo* at 40–45°C to constant weight. Chloroform, analytical purity grade (Lachema, Brno) was freed from traces of carbonyl compounds by boiling several hours with 2,4-dinitrophenylhydrazine[11] and distilled on a packed column with approx. 40 TP (physical constants of chloroform are given in ref.[1]).

Heats of mixing. Since the polymer was in the rubberlike state, the same procedure as for oligomers could also be used for measuring ΔH_M.

RESULTS AND DISCUSSION

The ΔH_M of chloroform with butyl methacrylate oligomers have been published in an earlier paper[1]. ΔH_M of the system chloroform(A)–polymer(B) in the range of the volume fractions $v_B \in (0; 0.62)$ can be described in terms of Redlich's and Kister's equation on the basis of volume fractions with the constants $C_0 = -76.831$ and $C_1 = 29.886$ and a residual standard deviation $s = 2.5$ J/ml.

In the system chloroform(A)–butyl methacrylate oligomers(B) we shall distinguish five classes of contact points on the whole, in accordance with their chemical formulas (*cf.*[1], Table I): h = acidic hydrogen atom of chloroform, Cl = chlorine atom of chloroform, R = alkyl hydrogen, O = ether oxygen and O′ = ester oxygen of the oligomer. Both oxygen atoms of the ester groups are placed in the same class of contacts with respect to the resonance delocalization of their free electron pairs. The corresponding structure parameters are summarized in Table I. In this case, then, $m = 2$, $n = 3$, and the matrix $\mathbf{T}$ is of the 5 . 5 type. Its upper triangular part has the form

$$
\begin{array}{cccc}
\eta_{hCl}^{AA} & \eta_{hR}^{AB} & \eta_{hO}^{AB} & \eta_{hO'}^{AB} \\[4pt]
 & \eta_{ClR}^{AB} & \eta_{ClO}^{AB} & \eta_{ClO'}^{AB} \\[4pt]
 & & \eta_{RO}^{BB} & \eta_{RO'}^{BB} \\[4pt]
 & & & \eta_{OO'}^{BB} \, .
\end{array} \tag{8}
$$

Consequently, for the thermodynamic description of the enthalpic behaviour of the above series of systems, 10 energetic parameters are needed which in principle can all be determined on the basis of data on simpler systems. We regard the system $CHCl_3(A)$–$CCl_4(B)$ as the basic one; its heat of mixing was determined by Cheesman and coworkers[12,13] and by Adcock and McGlashan[14]. The treatment of their experimental data showed that for the description of the enthalpic behaviour of the system it is not sufficient to know the energy U_{hCl}^{AA} alone — the difference between the chlorine atoms in chloroform and tetrachloromethane must also be taken into account (the energy values found by us by using the "best-fit" method were as follows: $U_{hCl}^{AA} = -236\ \text{Jmol}^{-1}$, $U_{hCl}^{AB} = 1266\ \text{Jmol}^{-1}$ and $U_{ClCl}^{AB} = -25\ \text{Jmol}^{-1}$), which was qualitatively pointed out also by Kehiaian[15]. The agreement with the experiment can be seen in Fig. 1. The great difference between the interaction energies U_{hCl}^{AA} and U_{hCl}^{AB} clearly indicates that a mechanical transfer of the interaction energies from systems with CCl_4 to those with $CHCl_3$ is not justified. A theoretical reason can probably be seen in the ability of the acidic hydrogen to form a "charge-transfer" complex with the chlorine atom of $CHCl_3$, but not with the chlorine atom of CCl_4.

Two possibilities emerge for the determination of the energy U_{hR}^{AB} : (*1*) to take over the value of U_{hCl}^{AA} from the system $CHCl_3$–CCl_4 and the energy U_{ClR}^{AB} determined from ΔH_M in the system CCl_4–heptane[1,16] and from the data on the system $CHCl_3$–heptane[1,17] to determine eventually U_{hR}^{AB} by the "best-fit" method; (*2*) to take over only the value of U_{hCl}^{AA} and to determine the remaining energies U_{hR}^{AB} and U_{ClR}^{AB} from the enthalpic data on the systems of the series $CHCl_3(A)$–n-alkanes(B). The energy U_{hR}^{AB} was determined so as to represent adequately both the position and the value of the maximum on the concentration dependence of ΔH_M, while U_{ClR}^{AB} was at the same time adjusted so as to reproduce the course of ΔH_M for larger mole fractions of $CHCl_3$.

The fact that the interaction energies thus found reflected approximately equally well the data for the mixtures of $CHCl_3$ both with heptane and with n-hexadecane[1,17] (Fig. 1) support the physical justification of the parameters determined. With respect to the difference in the chlorine atoms of $CHCl_3$ and CCl_4 described above, we preferred in our work the latter of the two methods.

The interaction energy of the alkyl hydrogen atoms with the ether oxygen was determined from the experimental ΔH_M in the system dibutyl ether–heptane[18]. Similarly, the energy $U_{RO'}^{BB}$ was also determined from the experimental ΔH_M of the mixtures of butyl isobutyrate and heptane[1] (Fig. 2). The remaining energies U_{hO}^{AB} and U_{ClO}^{AB} or $U_{hO'}^{AB}$ and $U_{ClO'}^{AB}$, respectively were adjusted so as to reflect the experimental heats of mixing in the systems $CHCl_3$–dibutyl ether[19] or $CHCl_3$–butyl isobutyrate[1] (Fig. 3a). The value found on the basis of ΔH_M of the system CCl_4–dibutyl ether[19] was chosen to be the initial approximation of the energies U_{ClO}^{AB} and $U_{ClO'}^{AB}$, since the data on the system CCl_4–ethyl acetate[20] were considered to be inconsistent. Finally, the energy $U_{OO'}^{BB}$ was taken to be zero.
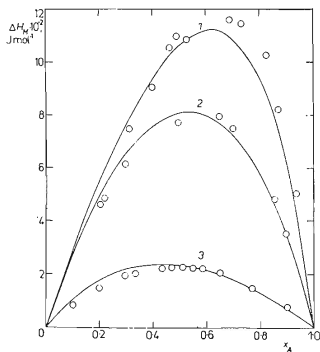

FIG. 1

Enthalpies of Mixing of the Mixtures of $CHCl_3$(A) and n-$C_{16}H_{34}$ (1) n-C_7H_{16} (2) and CCl_4 (3) (components B)

The curves represent the values calculated according to Barker's theory with the structure and energetic parameters given in Tables I and II.
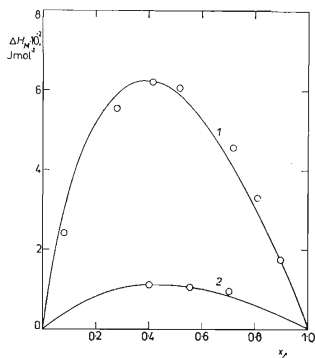
FIG. 2

Enthalpies of Mixing of the Mixtures of Heptane (B) and Butyl Isobutyrate (1) and Dibutyl Ether (2) (components A)

Meaning of curves cf. Fig. 1.

   Thus, by using the above procedures we determined all interaction energies for the series of the systems chloroform–butyl methacrylate oligomers (Fig. 3a). However, the comparison of the courses of ΔH_M calculated therefrom for the individual members of the series with the heats of mixing found experimentally revealed that these values are not quite universal for all members of the series. Since the compounds investigated in this work differ mainly by the number of the ester groups in their molecules, we decided to carry out an additional adjustment of the U_{hO}^{AB}, values for each system individually so as to describe the dependences of ΔH_M on the composition of the mixtures in the best possible way. The values of the parameter U_{hO}^{AB} thus adjusted are then given in the last column of Table II and were used for the calculation of full curves in Fig. 3a. The absolute value of this energy for the mixture of $CHCl_3$ with the so-called monomer n-C_4H_9OYH (Y = n-$C_4H_9O.CO.C(CH_3)$.

.CH_2) is essentially lower (Table II) than for the corresponding mixture with butyl

isobutyrate, which is probably due to the positive induction effect (repulsion of electrons) of the isopropyl group. This effect, which considerably raises the proton — acceptor power of the adjacent ester group is somewhat reduced in the molecule
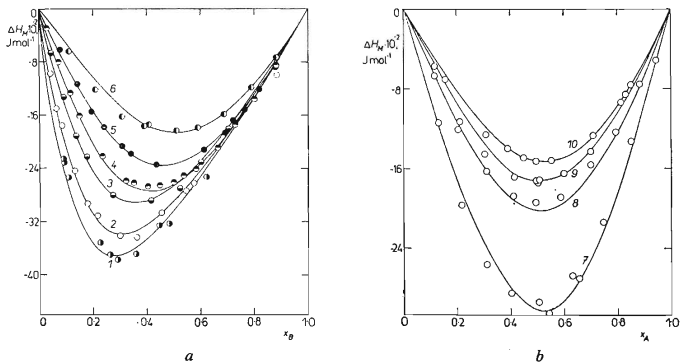

Fɪɢ. 3

Enthalpies of Mixing of the Mixtures of Chloroform (A) and Butyl Methacrylate Oligomers (a) and Ethers (b)

   The curves represent calculated values (Fig. 1) for the components B (Y = n-C_4H_9O. .$CO.C(CH_2H_3).CC_4$)n-: 1 H_9OY_4H, 2 n-$C_4H_9OY_3H$, 3 n-$C_4H_9OY_2H$, 4 n-$C_4H_9.OYH$, 5 HYH, 6 (n-$C_4H_9)_2O$, 7 (i-$C_3H_7)_2O$, 8 (n-$C_3H_7)_2O$, 9 (n-$C_5H_{11})_2O$, 10 (t-$C_4H_9)_2O$.

of the monomer by the presence of the n-$C_4H_9O.CH_2$-group in place of the methyl group. The effect of the isopropyl group mentioned above was also observed when we compared the values of U_{hO}^{AB} obtained from the available heats of mixing in the series of systems $CHCl_3(A)$–ethers(B)[19] (Fig. 3b) assuming that the other interaction energies are the same as in the tabulated case of the system $CHCl_3$–dibutyl ether (Table II). Thus, U_{hO}^{AB} for diisopropyl ether equalled $-7930\ Jmol^{-1}$ while for dipropyl ether and diamyl ether the value of U_{hO}^{AB} found for dibutyl ether was satisfactory. On the other hand, for the system $CHCl_3$–ditert-butyl ether we obtained $U_{hO}^{AB} = -6011\ Jmol^{-1}$, probably due to steric hindrances. The negative induction effect of the butoxy group in the monomer probably also contributes to the relatively great difference of $U_{hO'}^{AB}$ between isobutyrate and monomer.

The further decrease in the absolute value $|U_{hO'}^{AB}|$ proceeding from monomer to dimer is probably already connected with the negative interaction of two adjacent

TABLE II

Interaction Energies (in J/mol) Valid for the Binary Systems Under Discussion
(Y = n-$C_4H_9.CO.C(CH_3).CH_2$)   R' = propyl, butyl or amyl.

Component B	U_{hCl}^{AA}	U_{ClR}^{AB}	U_{hR}^{AB}	U_{RO}^{BB}	$U_{RO'}^{BB}$	U_{ClO}^{AB}	$U_{ClO'}^{AB}$	U_{hO}^{AB}	$U_{hO'}^{AB}$
Component A–tetrachloromethane									
n-C_7H_{16}	—	104	—	—	—	—	—	—	—
(n-$C_4H_9)_2$O	—	104	—	1 350	—	−214	—	—	—
Component A–heptane									
(n-$C_4H_9)_2$O	—	—	—	1 350	—	—	—	—	—
HYH	—	—	—	—	2 334	—	—	—	—
Component A–chloroform									
n-C_7H_{16}	−236	175	1 266	—	—	—	—	—	—
R_2'O	−236	175	1 266	1 350	—	−553	—	−6 542	—
(i-$C_3H_7)_2$O	−236	175	1 266	1 350	—	−553	—	−7 930	—
(t-$C_4H_9)_2$O	−236	175	1 266	1 350	—	−553	—	−6 011	—
HYH	−236	175	1 266	—	2 334	—	−410	—	−4 824
n-C_4H_9OYH	−236	175	1 266	1 350	2 334	−553	−410	−6 542	−3 437
n-$C_4H_9OY_2H$	−236	175	1 266	1 350	2 334	−553	−410	−6 542	−3 106
n-$C_4H_9OY_3H$	−236	175	1 266	1 350	2 334	−553	−410	−6 542	−3 729
n-$C_4H_9OY_4H$	−236	175	1 266	1 350	2 334	−553	−410	−6 542	−3 990
n-$C_4H_9OY_{69}H$	−236	175	1 266	1 350	2 334	−553	−410	−6 542	−3 729

solvated centres, as has also been demonstrated by means of infrared spectra[21]. However, the opposite effect of shielding of the negative induction effect of the butoxy group on more remote methacrylate monomer units competes with the above interaction; it probably also causes an increase in $|U_{hO'}^{AB}|$ when passing from dimer to tetramer. The lower value found for the polymer (Fig. 4) compared to tetramer is obviously related to the presence of nonsolvated centres in the polymer, which is probably also due to the backcoiling of the polymer chains.

In conclusion, let us also suggest the likely cause why Barker's theory gives lower strength values of the hydrogen bonds compared to values obtained from both the spectral and enthalpic data on the assumption that one proton-acceptor centre of the molecule B (*e.g.* the ester group) binds one molecule of the proton-donor at the utmost, and that the mixture thus obtained behaves in an ideal way (model of an ideally associated solution). According to these papers[22–24], the enthalpy of formation of the hydrogen bonds between chloroform and ethers equals -12000 to -18000 Jmol^{-1}, and that between chloroform and esters[2] approx. -8000 Jmol^{-1}, which are values differing considerably from those given in Table II. It can be seen from the surfaces of the contact points O and O' chosen above that the treatment in terms of Barker's theory assumes the bonding of two or four chloroform molecules respectively to one ether or ester group of the polymer. Indeed, the model calculations of the course of ΔH_M in the system CHCl$_3$–butyl isobutyrate showed, assuming a reduced number of contact points in the class of contacts O'($Q_{O'}^B <$ < 4), that to represent the experimental results obtained in the above system a substantially higher $|U_{hO'}^{AB}|$ must be chosen. If we consider, for instance, that only three contact points O' are pertinent to the ester group, we obtain $U_{hO'}^{AB} = -6157$ Jmol^{-1}. Similarly, for 2 contact points one obtains $U_{hO'}^{AB} = -7445$ Jmol^{-1}; finally, $U_{hO'}^{AB} = -8037$ Jmol^{-1} obtained assuming a single contact point is already very close to the above values of the enthalpy of formation of hydrogen bond between chloroform and ester. Let it also be mentioned that simultaneously with the energy $U_{hO'}^{AB}$, the energy $U_{RO'}^{BB}$ was also varied so as to best reflect the data on the system butyl isobutyrate–
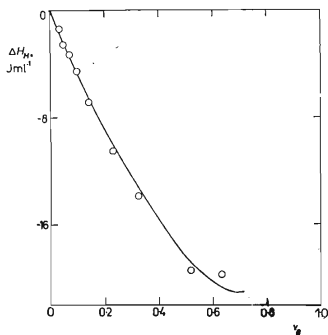

Fig. 4

Enthalpies of Mixing of the Mixtures of CHCl$_3$ (A) and n-C$_4$H$_9$OY$_{69}$H (B) Depending on the Volume Fraction of the Polymer v_B

(Y = n-C$_4$H$_9$O.CO.C(CH$_3$).CH$_2$). The curve represents calculated values, *cf.* Fig. 1.

–heptane. However, for the case of a single contact O′ in the ester molecule no perfect accordance with the experiment in the latter system could be attained any more. It seems that the changes in Q_O^B, just described should be accompanied by changes in relative surfaces of the other classes of contacts of the given molecule. Such procedure, however, would lead to too great an increase in the number of adjustable parameters of Barker's theory, which would be at variance with what we have in mind. Moreover, the fact cannot be neglected that not even from the physical viewpoint can the energetic parameters of Barker's theory be identified with the solvation energies appearing in the theory of association equilibria, and that the application of Barker's theory to polymer systems consists in a simultaneous simulation of the solvation equilibria and of the mutual influence of sorption centres of the polymer by a set of energies between isolated surface contact points. In spite of all this, however, Barker's theory seems to be useful for a semiquantitative forecast of the concentration dependence of the enthalpies of mixing from the chemical structure of the components involved in the respective binary mixtures, especially for low-molecular weight mixtures (*e.g.* in the series of the systems chloroform–di-n-alkyl ethers, the same energetic parameters hold for ΔH_M measured so far).

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