INTERACTION OF CHLOROFORM WITH MONO- AND DIESTERS OF PIVALIC ACID

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The heat of mixing of chloroform with methyl pivalate, 2-methoxyethyl pivalate, ethylene dipivalate and 2,2′-oxydiethyl dipivalate was measured. In the range of very low chloroform concentrations the reduced heat of mixing of monoester does not almost differ from that of the respective diester. On the other hand, with increasing chloroform concentration the difference between the enthalpy of mixing of monoester and that of diester increases. Using the theory of the association equilibria, these facts can be interpreted by assuming that the thermodynamic parameters of the hydrogen bond of chloroform on the first protonacceptor site are the same for mono- and diester; for the latter, however, the bonding of chloroform on one site reduces the probability of bonding on the other site.

One of the main problems in the thermodynamics of polymer solutions is the question whether and how the interaction parameters of the polymer with the solvent are influenced by the incorporation of monomer repeat units in the polymer chain. If the solvent forms hydrogen bonds with the specific sites of the polymer, the problem can be formulated as follows: *1)* How do the equilibrium constants and bond energies of the solvent on the polymer sites differ from similar values for a monomeric model? *2)* Are the sites of the same polymer chain independent of each other, and consequently, can the global parameters of a simultaneous bond on n sites of the same chain be expressed exclusively in terms of the bond parameters on the individual sites? In our earlier communications we analyzed from this standpoint the heats of mixing of butyl methacrylate oligomers having different chain length with chloroform[1] and methanol[2]. This work reports a comparison between mono- and diesters. The heats of mixing of chloroform with methyl pivalate, 2-methoxyethyl pivalate, ethylene dipivalate and 2,2′-oxydiethyl dipivalate were measured. We shall regard ethylene dipivalate as a dimer of methyl pivalate, and 2,2′-oxydiethyl dipivalate as a mixed dimer of methyl pivalate and 2-methoxyethyl pivalate. The data are interpreted by using our version of the theory of association complexes adapted for polymer systems[3,4].

THEORETICAL

In order to characterize the asymmetry of the concentration dependence of the enthalpy of mixing, ΔH_M, we define the reduced heat (cf. also[1])

$$q_r = -\Delta H_M / (n_A + a n_B) \, x_A x_B \tag{1}$$

and its limiting values

$$q_r(A) = (q_r)_{x_A = 1} = -(\Delta H_M / a n_B)_{x_A = 1} , \tag{2a}$$

$$q_r(B) = (q_r)_{x_B = 1} = -(\Delta H_M / n_A)_{x_B = 1} , \tag{2b}$$

where n_A, n_B are the amounts of substance of the components A and B, and a is the number of monomer units in the molecule B; the component A will always be a monomer. The symbols x_A, x_B are used to designate the mole fraction of monomer units,

$$x_A = n_A / (n_A + a n_B) ; \quad x_B = 1 - x_A \tag{3}$$

(only for $a = 1$ x_A has the meaning of a true mole fraction).

If the molecule of the component B contains c protonacceptor sites, complexes $A_i B$ $(1 \leqq i \leqq c)$ can also exist in a mixture with the protondonor along with the simple molecules A and B. If a mixture of these species obeys the Flory–Huggins equation and if the van der Waals interaction component is not affected by the complex formation, an equilibrium equation[3,4]

$$v_i = K_i p_A^i p_B , \tag{4}$$

is valid; here, $v_i = n_i / (n_A + r n_B)$ is concentration of the complex $A_i B$ in mol per one mol of lattice sites (r is the number of sites in the lattice occupied by the molecule B), p_A, p_B are similar concentrations of simple unassociated molecules. For the sum of concentrations of all formations it holds

$$\sum v = p_A + p_B X(p_A) ; \quad X(p_A) = 1 + \sum_{i=1}^{c} K_i p_A^i . \tag{5}$$

For the stoichiometric concentrations of the components A and B and for the reduced heat it holds

$$v_A = p_A + p_B \sum_i i K_i p_A^i = p_A + v_B (\partial \ln X / \partial \ln p_A) , \tag{6}$$

$$v_B = p_B X(p_A) , \tag{7}$$

$$q_r = (p_B / a x_A v_B) \sum_i E_i K_i p_A^i = (a x_A)^{-1} \left(\partial \ln X / \partial (RT)^{-1} \right) , \tag{8}$$

where $E_i = \partial \ln K_i / \partial (RT)^{-1}$ is the energy released in the formation of the complex A_iB. The contribution of nonspecific interactions to the reduced heat is not included in Eq. (8), because it will not be considered in our comparative studies.

In the simplest case, when the monomer molecule B contains a single solvation site having the equilibrium constant η and the energy ε and occupies a single site in the latice, it holds

$$X(p_A) = 1 + \eta p_A \,, \tag{9}$$

$$v_A = p_A + v_B \eta p_A / (1 + \eta p_A) \,, \tag{10}$$

$$q_r = \varepsilon \eta (p_A / x_A) / (1 + \eta p_A) \,. \tag{11}$$

In Eqs (10) and (11) the dependence of q_r on v_A is expressed through the parameter p_A. The equations for the limiting values of q_r are

$$q_r(A) = \varepsilon \eta / (1 + \eta) \,, \tag{12}$$

$$q_r(B) = \varepsilon \eta / (r + \eta) \,. \tag{13}$$

If the molecule B consists of a structure units and contains c mutually independent sites, then

$$X(p_A) = \prod_{j=1}^{c} (1 + \eta_j p_A) \,, \tag{14}$$

$$v_A = p_A + v_B \sum_j [\eta_j p_A / (1 + \eta_j p_A)] \,, \tag{15}$$

$$q_r = (a x_A)^{-1} \sum_j [\varepsilon_j \eta_j p_A / (1 + \eta_j p_A)] \,, \tag{16}$$

$$q_r(A) = a^{-1} \sum_j [\varepsilon_j \eta_j / (1 + \eta_j)] \,, \tag{17}$$

$$q_r(B) = (\sum_j \varepsilon_j \eta_j) / (r + \sum_j \eta_j) \,, \tag{18}$$

where η_j and ε_j respectively are the equilibrium constant and energy of the j-th site. If $c = 2$, then the global equilibrium constants for the formation of the complexes AB and A_2B defined by Eq. (4) can be expressed as $K_1 = \eta_1 + \eta_2$; $K_2 = \eta_1 \eta_2$. This can be seen from a comparison of Eq. (5) with Eq. (14). If, however, the sites are not mutually independent (if both molecules A in the complex A_2B affect each other), we must write $K_2 = \gamma \eta_1 \eta_2$, where $\gamma \neq 1$, and so

$$X(p_A) = 1 + (\eta_1 + \eta_2) p_A + \gamma \eta_1 \eta_2 p_A^2 \,, \tag{19}$$

$$q_r(\mathrm{A}) = \frac{\varepsilon_1\eta_1 + \varepsilon_2\eta_2 + (\varepsilon_1 + \varepsilon_2 + \Delta\varepsilon)\,\gamma\eta_1\eta_2}{a(1 + \eta_1 + \eta_2 + \gamma\eta_1\eta_2)}\,, \qquad (20)$$

$$q_r(\mathrm{B}) = \frac{\varepsilon_1\eta_1 + \varepsilon_2\eta_2}{r + \eta_1 + \eta_2}\,. \qquad (21)$$

Here, $\Delta\varepsilon = \partial \ln \gamma/\partial(\boldsymbol{R}T)^{-1}$. It is obvious that the parameters γ and $\Delta\varepsilon$ express the mutual influence of the molecules A bonded on the same molecule B.

EXPERIMENTAL

Chemicals

Methyl pivalate was prepared by adding dropwise pivaloyl chloride (112·62 g, 0·934 mol) to a boiling anhydrous methanol, reagent grade (60 cm³, 47·52 g, 1·48 mol) with exclusion of air moisture. The product thus obtained was purified by a standard procedure[5] and distilled on a BICHI column (30 тр); the fraction 100·5—102·0°C was collected (in ref.[6], b.p. 99·5°C/97·4 kPa). The purity of the product determined by gas chromatography was 99·95%.

Ethylene dipivalate and 2,2′-oxydiethyl dipivalate were prepared by a procedure described earlier[7] consisting in the azeotropic esterification of the respective hydroxy compounds with pivalic acid in chloroform by using a strong acid cation exchanger as catalyst. The products obtained by distillation were purified by partition chromatography on silicagel soaked with water using hexane and benzene as solvents. The purity of both diesters according to the gas chromatographic analysis was higher than 99·9%.

2-Methoxyethyl pivalate. Pivaloyl chloride (222 g, 1·84 mol) was added with stirring to a mixture of benzene, reagent grade (185 cm³), pyridine, reagent grade (150 cm³, 1·86 mol), and 2-methoxyethanol, reagent grade (146 cm³, 1·85 mol). The mixture was heated to boil for 2 h. On cooling, the reaction mixture was extracted with 2 . 100 cm³ of water acidified to pH 2; the water extracts were "countercurrently" extracted with 2 . 50 ml of benzene. The benzene extracts were returned to the reaction mixture, which was shaken with a 10% solution of sodium carbonate, extracted with water and a 50% solution of CaCl₂ and eventually dried by adding anhydrous CaCl₂. Rectification yielded a product having a b.p. 58·0°C/800 Pa (in ref.[8], b.p. 60·2°C/1·32 kPa), purity (GLC) 99·9%.

Chloroform, anal. grade, was freed from traces of carbonyl compounds by boiling with 2,4-dinitrophenylhydrazine and concentrated HCl for 10 h, followed by column distillation[9].

Procedure

The heats of mixing were measured in Calvet's calorimeter (Setaram, Lyon, France) in a stainless steel mixing vessel with a 0·01 mm Ni membrane[10]. The vessels were always filled so as to make the corrections for the vapour space negligible. The thermal effect was determined by means of a constant obtained by electrical calibration and by means of an area determined by an electronic integrator with a reproducibility of ±0·2%.

RESULTS AND DISCUSSION

The dependence of the heats of mixing (J/cm^3) on the volume fraction of pivalate, φ_B, has been described by the Redlich–Kister series expansion

$$\Delta H_M/V = \varphi_A \varphi_B \sum_{n=0}^{n} C_n (1-2\varphi_B)^n . \qquad (22)$$

The expansion constants 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 using Fisher's test[11] on a 95% significance level (Table I).

By using equations given in the Theoretical, the following rules can be derived:

1) If a identical monomer units are joined to form a chain so that the parameters η and ε of their sites remain unchanged and $\gamma = 1$, then the curve $q_r(x_B)$ of the a-mer is identical with the curve $q_r(x_B)$ of the monomer, if x_A, x_B are defined by Eq. *(3)*. As a consequence, curves *1* and *4* in Fig. 1 can be related to any member in the series of oligomers; for instance, in the table included in Fig. 1 the parameters of both the monomer and dimer are given for these curves.

If, however, different compounds of the series differ as to their η and ε values, this is reflected in the total course of the curve, as can be seen from a comparison of curves *1* and *4*.

The above statement can be proved if we put $\varepsilon_j = \varepsilon$, $\eta_j = \eta$ in Eqs *(15)* and *(16)* for all j, and also $c = ac_0$, where c_0 is the number of sites in the monomer unit. Then we obtain equations containing only ε, η, c_0, but not a. By the same substitution Eqs *(17)* and *(18)* become

$$q_r(A) = c_0 \varepsilon \eta/(1 + \eta) , \quad q_r(B) = \varepsilon \eta/(r_0/c_0 + \eta) , \qquad (23)$$

where r_0 is the number of lattice sites occupied by the monomer unit. Eqs *(23)* also confirm such statements.

TABLE I

Redlich-Kister Constants (Eq. *(22)*) for Systems Chloroform (A)–Pivalic Acid Esters (B)
  s Weighted standard deviation.

Component B	C_0	C_1	C_2	s
Methyl pivalate	−78·8	+10·4	+13·2	0·6
2-Methoxyethyl pivalate	−92·9	+ 4·5	+15·0	0·4
Ethylene dipivalate	−73·8	+ 9·6	+12·0	1·9
2,2′-Oxydiethyl dipivalate	−82·2	+ 7·7	+11·8	2·0

2) A similar rule holds in good approximation also for the case when the monomer units in the chain are not identical. In such case it follows from Eq. *(17)* that $q_r(A)$ of the oligomer is equal to the arithmetic mean from the $q_r(A)$ values of the individual monomeric compounds. Eq. *(18)* is valid for $q_r(B)$, but the value of the latter differs by several per cent at utmost from the arithmetic mean from the $q_r(B)$ values of the individual monomers.

3) If the bonding sites of the oligomeric chain interfere with each other, so that $\gamma \neq 1$, $\Delta\varepsilon \neq 0$, $q_r(B)$ is not influenced by this, as shown by Eq. *(21)*. On the other hand, the other limiting value given by Eq. *(20)* decreases with decreasing γ and $\Delta\varepsilon$; this behaviour is illustrated by curves *1, 2, 3* in Fig. 1.

Let us now compare (Fig. 2) the curve obtained for ethylene dipivalate with that for methyl pivalate and the dependence for 2,2′-oxyethyl dipivalate with the curve representing the average from the q_r values for both monoesters. The ratio of the $q_r(A)$ values of the dimer to those of the monomer in the former case is $0.94 \pm 0.02_5$, while in the latter it is $0.99 \pm 0.02_5$; for $q_r(B)$ the respective ratios are 0.83 ± 0.02 and 0.86 ± 0.02. Hence, by using rules *1)–3)*, the main conclusion can be derived:
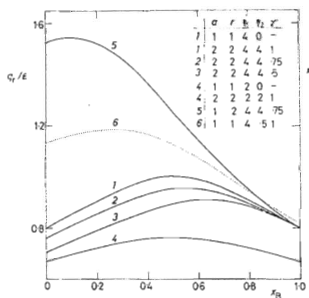

Fig. 1

Reduced Heats of Mixing Calculated from Equations Given in the Theoretical

Parameters of model systems are given in the right top corner. Assumed that $\varepsilon_1 = \varepsilon_2 = \varepsilon$, $\Delta\varepsilon = 0$.
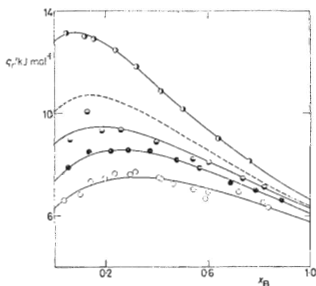
Fig. 2

Reduced Heats of Mixing Per One Mol of Monomer Unit Depending on the Molar Fraction of Monomer Units

Pivalates: ● methyl, ◑ 2-methoxyethyl, ○ ethylene di-, ◔ 2,2′-oxydiethyl di-. Full line — calculated from Eq. *(1)* with constants given in Table I and transformed from volume into molar coordinates. Broken line — average values for methyl and 2-methoxyethyl pivalate.

The constants ε and η for the bonding sites in the dimer are only insignificantly lower than in the monomer, but in the case of a simultaneous occupation of sites on both monomer units their mutual negative interaction becomes operative $(\gamma < 1, \Delta\varepsilon < 0)$. A similar result was obtained by analyzing our data on the heats of mixing of oligomers of butyl methacrylate with chloroform[1]. It is noteworthy that such similarity was found for two series of esters differing in the topological structure of the molecule.

The curves of model systems shown in Fig. 1 are not intended to give a quantitative picture of the experimental dependences, but to elucidate qualitatively the relations between them. Calculation or estimation of the parameters γ and $\Delta\varepsilon$ from our calorimetric data would require the knowledge of other parameters, namely, of the equilibrium constant η and of the effect (if any) of nonspecific interactions on it, and also of the contribution of nonspecific interactions to the heat of mixing as a function of concentration. Our conclusions, on the other hand, are based only on an analysis of the difference between q_r of the monomer and dimer, with the only assumption that the nonspecific interactions contribute to the reduced heat of mixing to the same extent for both the monomer and dimer.

Let us now deal with both monoesters, that is, methyl pivalate and 2-methoxyethyl pivalate. The considerable difference between both curves (Fig. 2) is obviously due to the fact that 2-methoxyethyl pivalate contains also the ether oxygen, the bonding parameters of which for chloroform will not greatly differ from those of the carboxylic group. The relationship between both dependences is qualitatively illustrated by the theoretically calculated curves 1 and 5 in Fig. 1. In the system characterized by curve 5 the acceptor possesses a double number of sites and a double molar volume; since, however, it models the monoester 2-methoxyethyl pivalate, it is treated as a monomer, consequently, $a = 1$. (Let it be noticed that if we put here $a = 2$, curve 5 becomes curve 2, $q_r(A)$ of which is half that of curve 5; this also follows from Eq. (17)).

If the experimental dependence of q_r for methyl pivalate is compared with the model functions represented by curves 1 and 6 in Fig. 1, it can be seen that one of the possible explanations of the asymmetry of the experimental dependence could consist in a view that the ester group is able to bind two chloroform molecules; the bond with the second molecule will of course be much weaker. Rules 1), 2) and 3) can be formulated in a more general manner also for a case that the monomer unit contains several nonequivalent mutually interfering sites. Thus, our conclusions concerning the relationship between the dimer and monomer are not endangered, even if there is more than one site in the monomer unit.

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