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The H-Bond Association of Alcohols and the Effect of Steric Hindrance on the Relaxation Spectra

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The ultrasonic relaxation spectra in the frequency range 10 – 300 MC and the infrared spectra in the range 3000 – 4000 cm^{-1} have been obtained at 15°C for normal butyl alcohol dissolved in cyclohexane in the concentration range 0.04 – 0.30 M. The spectra are attributed to a hydrogen bond association of the alcohol and the extent to which different reaction mechanisms describe the experiments is discussed. The multistep mechanism which describes experiments of the above mentioned type for *N*-methylacetamide dissolved in carbon tetrachloride does not describe the alcohol association to the same degree of accuracy. This is attributed to a difference between the molecular association mechanism of alcohols and amides and the nature of this difference is discussed.

The effect of steric hindrance on the relaxation spectra is illustrated by comparing the results obtained for normal butyl alcohol with the previously published relaxation spectra of tertiary butyl alcohol.

The hydrogen bond association of alcohols has been investigated by a variety of different techniques, which give information about the equilibrium properties of the systems.[1–4] Although the alcohol association has been described in terms of different association mechanisms it seems likely that for alcohols dissolved in inert solvents a general association mechanism which consists of several equilibria between monomers and polymers is the most probable.[5]

Kinetic investigations of the alcohol association by means of the ultrasonic absorption technique have also been reported,[6–8] but only recently an attempt has been made to interpret the ultrasonic relaxation spectra in terms of the multistep mechanism mentioned above. Thus the relaxation spectra of benzyl alcohol [9] and tertiary butyl alcohol [10] dissolved in cyclohexane have been interpreted in terms of this multistep mechanism with the result that approximate values of the common depolymerization rate constants are obtained. The interpretation is based on the assumption that a particular one of the individual relaxation times involved in the multistep mechanism is connected

with a dominating relaxation strength and consequently is responsible for the observed relaxation. This approximation does not explain the fact that the relaxation strength passes through a maximum with increasing overall concentration of alcohol. It has recently been shown, however, that a modification of the approximation may lead to an explanation of this maximum.[11] This modification, which so far has been used to explain the relaxation spectra obtained from *N*-methylacetamide dissolved in carbon tetrachloride, involves that the experimentally observed relaxation is the higher frequency part of the relaxation spectrum of the multistep mechanism.

The experimentally observed maximum in the relaxation strength has been considered as a main point in several papers which are concerned with the ultrasonic absorption in the low frequency end of the relaxation spectrum of alcohols dissolved in inert solvents. Recently Lang and Zana [6] have pointed out that a qualitative explanation of this feature can be obtained by considering the theoretical expression of the relaxation strength for the following reaction mechanism

$$3\,A_1 \rightleftharpoons A_3 \tag{1}$$

Since a trimolecular collision is quite improbable this point seems to be of less interest. However, the authors suggest that a quantitative explanation can be obtained on the basis of the following mechanism

$$\begin{aligned} A_1 + A_1 &\rightleftharpoons A_2 \\ A_1 + A_2 &\rightleftharpoons A_3 \end{aligned} \tag{2}$$

Thus it is the contention of Lang and Zana that the relaxation strength for this mechanism also passes through a maximum with increasing overall concentration of alcohol.

In this paper the extent to which the different association models describe the self-association of alcohols will be discussed. The infrared and the ultrasonic relaxation spectra of tertiary butyl alcohol dissolved in cyclohexane previously published [10] as well as the infrared and ultrasonic relaxation spectra of normal butyl alcohol dissolved in cyclohexane presented in this paper form the background for this discussion. Finally the effect of steric hindrance in the relaxation spectra of alcohol association is discussed.

ULTRASONIC ABSORPTION

The sound absorption coefficient, α, divided by the sound frequency squared, ν^2, is given by the following equation

$$\frac{\alpha}{\nu^2} = \frac{\pi}{U\nu} \tan \phi \tag{3}$$

where U is the sound velocity, and ϕ is the phase lag between the pressure wave and the density wave produced when the sound propagates through the medium. This phase lag is given by the following equation

$$\tan \phi = \frac{\mathrm{Im}(\delta P/\delta V)_S}{\mathrm{Re}(\delta P/\delta V)_S} \tag{4}$$

and the correlation between the frequency dependence of α/ν^2 and the thermodynamic and kinetic parameters for a given chemical reaction is obtained by developing the expression of tan ϕ in terms of these parameters for the chemical reaction in question. The procedure to follow is the one which generally is used in the thermodynamics of irreversible processes. The procedure is worked out in detail only for a chemical reaction which consists of a single elementary reaction step,[12,13] but recently it has been worked out for a chemical reaction which consists of an infinite number of elementary reaction steps.[14] If the procedure is used for the two step mechanism given by eqn. (2) the following expression is obtained for $(\delta P/\delta V)_S$

$$\left(\frac{\delta P}{\delta V}\right)_S \approx \frac{\Delta P}{\Delta V} = \frac{\psi_1 D_3 + \psi_2(D_1/V) + [\psi_1 D_4 + \psi_2(D_2/V)]\mathrm{i}\omega}{-[\psi_3 D_3 + \psi_4(D_1/V)] - [\psi_3 D_4 + \psi_4(D_2/V)]\mathrm{i}\omega} \tag{5}$$

where

$$\psi_1 = \frac{\Delta H^{\circ 2}}{RT^2} - l\,\Delta H^\circ \tag{6}$$

$$\psi_2 = C_V + \frac{Vl^2T}{\beta_T} = C_P \tag{7}$$

$$\psi_3 = V\beta_T \frac{\Delta H^{\circ 2}}{RT^2} \tag{8}$$

$$\psi_4 = V\beta_T C_V \tag{9}$$

$$D_1 = \left(q_1 q_3 - q_2^2 - \frac{\omega^2}{k_1 k_{-2}[A_1]^2[A_3]}\right) \tag{10}$$

$$D_2 = \frac{q_1}{k_{-2}K_1K_2[A_1]^3} + \frac{q_3}{K_1 k_{-1}[A_1]^2} \tag{11}$$

$$D_3 = q_3 + \frac{3}{K_1[A_1]^2} \tag{12}$$

$$D_4 = \frac{1}{k_{-2}K_1K_2[A_1]^3} + \frac{1}{k_1[A_1]^2} \tag{13}$$

$$q_1 = \frac{4K_1[A_1]+1}{K_1[A_1]^2} \tag{14}$$

$$q_2 = \frac{1-2K_1[A_1]}{K_1[A_1]^2} \tag{15}$$

$$q_3 = \frac{1+K_2[A_1]+K_1K_2[A_1]^2}{K_1K_2\,[A_1]^3} \tag{16}$$

R is the gas constant, l is the thermal expansion coefficient, C_P and C_V are the heat capacities, β_T is the isothermal compressibility, K_1 and K_2 are the

equilibrium constants for the first and second reaction step, respectively, k_1 and k_2 are the forward rate constants for the first and second reaction step, respectively, and k_{-1} and k_{-2} are the corresponding reverse rate constants, [X] denotes the molar equilibrium concentration of component X. Finally we assume that the standard volume change due to the two reaction steps is negligible and that the standard enthalpy change for the first and second reaction step are equal ($\Delta H_1^\circ = \Delta H_2^\circ = \Delta H^\circ$).

In order to obtain the expression for tan ϕ the ratio of the imaginary part to the real part of eqn. (5) is expressed. In the limit $\nu \to 0$ this ratio is equal to the relaxation strength, A, which can be written in the following way.

$$A = \lim_{\nu \to 0} \frac{\pi}{U\nu} \tan\phi = \frac{(2\pi^2/U)(\psi_2\psi_3 - \psi_1\psi_4)(D_2D_3 - D_1'D_4)}{V\psi_1\psi_3 D_3^2 + [(\psi_2\psi_4)/V]D_1'^2 + (\psi_1\psi_4 + \psi_2\psi_3)D_1'D_3} \tag{17}$$

in which

$$D_1' = (q_1q_3 - q_2^2) \tag{18}$$

Using eqns. (6) – (9) it is seen that

$$\psi_2\psi_3 - \psi_1\psi_4 \simeq V\beta_T \frac{\Delta H^{\circ 2}}{RT^2}(C_P - C_V) \tag{19}$$

$$\psi_1\psi_4 + \psi_2\psi_3 \simeq V\beta_T \frac{\Delta H^\circ}{RT^2}(C_P + C_V) \tag{20}$$

$$\psi_1\psi_3 \simeq V\beta_T\left(\frac{\Delta H^{\circ 2}}{RT^2}\right)^2 \tag{21}$$

Consequently eqn. (17) can be rewritten as

$$A = \frac{2\pi^2 V(C_P - C_V)\Delta H^{\circ 2}}{U \quad RT^2} \frac{D_2D_3 - D_1'D_4}{\left(\frac{\Delta H^{\circ 2}}{RT^2}\right)^2 V^2 D_3^2 + C_PC_VD_1'^2 + V\frac{\Delta H^{\circ 2}}{RT^2}(C_V + C_P)D_1'D_3} \tag{22}$$

Very often one attempts to express the relaxation strength as a product of two functions of which one depends on the thermodynamic parameters of the system only, while the other contains kinetic parameters and equilibrium concentrations only. Whether or not this way of expressing the relaxation strength is a reasonable approximation for eqn. (22) depends on the actual order of magnitude of D_3^2, $D_1'^2$, and $D_1'D_3$. From the values given in Table 1 it turns out that for tertiary and normal butyl alcohol dissolved in cyclohexane the relaxation strength in the concentration range 0.04 – 0.3 M can be written as

$$A = QZ \tag{23}$$

where

$$Q = \frac{2\pi^2 V(C_P - C_V)\Delta H^{\circ 2}}{U\,RT^2 C_P C_V} \tag{24}$$

and

Table 1. The values of the different functions involved in the expression of the relaxation strength given by eqn. (22). Values of tertiary butyl alcohol are given in parentheses.

C	q_1	q_2	q_3	D_1'	$D_2 k_r$	D_3	$D_4 k_r$	$Z k_r$
0.0253 (0.0218)	680 (1589)	381 (1289)	3780 (11220)	2.43×10^{6} (1.62×10^{7})	4.03×10^{6} (3.11×10^{7})	5220 (15400)	3729 (11200)	2.06×10^{-3} (1.13×10^{-3})
0.0437 (0.0496)	347 (751)	147 (551)	1210 (3548)	3.98×10^{5} (2.36×10^{6})	5.93×10^{5} (4.37×10^{6})	1851 (5399)	1176 (3515)	3.97×10^{-3} (2.73×10^{-3})
0.0686 (0.0678)	220 (447)	70.2 (297)	551 (1595)	1.16×10^{5} (6.25×10^{5})	1.56×10^{5} (1.10×10^{6})	912 (2636)	526 (1570)	6.03×10^{-3} (4.92×10^{-3})
0.1037 (0.0910)	157 (302)	3.69 (182)	305 (868)	4.65×10^{4} (2.29×10^{5})	5.61×10^{4} $(3.82\times10^{5}$	536 (1535)	285 (848)	7.77×10^{-3} (7.40×10^{-3})
0.1542 (0.1684)	120 (221)	20.1 (121)	190 (533)	2.24×10^{4} $(1.03\times10^{5}$	2.46×10^{4} (1.62×10^{5})	351 (996)	174 (517)	9.41×10^{-3} (1.05×10^{-2})
0.2325 (0.2423)	96.4 (171)	10.7 (84.8)	129 (356)	1.23×10^{4} (5.35×10^{4})	1.24×10^{4} (7.92×10^{4})	247 (696)	115 (342)	1.08×10^{-2} (1.29×10^{-2})
0.3615 (0.3760)	80.0 (137)	5.05 (61.8)	93.3 (252)	7.44×10^{3} (3.07×10^{4})	6.87×10^{3} (4.28×10^{4})	183 (513)	80.8 (240)	1.19×10^{-2} (1.54×10^{-2})

$$Z = \frac{D_2D_3 - D_1'D_4}{D_1'^2} \tag{25}$$

If it furthermore is assumed that the reverse rate constants for the two elementary reaction steps are equal to k_r, combination of eqn. (25) and eqns. (10) – (16) gives

$$Z = \frac{1}{k_r} \frac{\left(\frac{q_1}{[A_3]} + \frac{q_3}{[A_2]}\right)\left(q_3 + \frac{3}{[A_2]}\right) - (q_1q_3 - q_2^2)\left(\frac{1}{[A_3]} + \frac{1}{[A_2]}\right)}{(q_1q_3 - q_2^2)^2} \tag{26}$$

Hence it is seen that the concentration dependence of Z and consequently the concentration dependence of the relaxation strength for the two step mechanism can be calculated from eqn. (26) if the equilibrium constants are known.

The argument given above shows that the relaxation strength even for a relatively simple reaction mechanism is a very complicated expression which can be given in a relatively simple way only if several approximations are introduced. The validity of these approximations as well as the validity of the approximations introduced in the relaxation theory in general are restricted to very dilute solutions. In this particular case to solutions with an alcohol concentration smaller than about 0.3 M.

If the concentration dependence of the relaxation strength predicted from the two step mechanism does not agree with the actually measured concentration dependence of the relaxation strength the two step mechanism must be given up as a plausible explanation of the alcohol association, and a new mechanism must be proposed. In order to treat the simplest possible mechanism one could try just to extend the two step mechanism to a three step mechanism taking up to tetramers into account. Although an approximation of this type may be reasonable in a certain concentration range the extent to which it is fulfilled depends on the overall concentration because the probability of having higher polymers present increases with increasing concentration. It is therefore not a good idea to compare the concentration dependence predicted from a theoretical expression derived on the basis of an approximation of this type with the experiments. It is presumably a better approximation to involve in the mechanism that the degree of polymerization is a function of the overall concentration. This means a reaction mechanism of the following type

$$\begin{aligned} A_1 + A_1 &\rightleftharpoons A_2 \\ A_1 + A_2 &\rightleftharpoons A_3 \\ &\vdots \\ A_1 + A_i &\rightleftharpoons A_{i+1} \end{aligned} \tag{27}$$

in which i is considered as a function of the overall concentration. This mechanism has been used recently [9–11] and the dependence of i on the concentration is based on a distribution function giving the distribution of alcohol on the different polymeric species present in the solution. The distribution

function can be developed from the infrared spectra of the solutions. The interpretation of the infrared spectra is based on the assumption that the equilibrium constant for the dimerization step, K_1 is different from that of subsequent steps, K_n, and that the latter may be taken as independent of i. The number of steps is considered as being infinitly large when the sums of the different coefficient series which are needed to correlate the monomer concentration with the equilibrium constants and the overall concentration are evaluated. Whenever an actual value of i is needed we use $i = i^+$, where i^+ is defined

$$\sum_{i=1}^{i=i^+} \Phi(i) \geqslant 0.99 \tag{28}$$

where

$$\Phi(1) = \frac{[A_1]}{\sum_j [A_j]} \tag{29}$$

and

$$\Phi(i) = \frac{K_1}{K_n^2 \sum_j [A_j]} (K_n [A_1]^i) \text{ for } i > 1 \tag{30}$$

The theoretical expression of the relaxation spectrum of the multistep mechanism is given by the following equation[11,14]

$$\frac{\alpha}{\nu^2} = Q \sum_{i=1}^{i=i^+} \frac{\Psi_i^2}{\lambda_i^2 + (2\pi/k_{-n})^2 \nu^2} + B \tag{31}$$

In order to obtain this equation we assume that all but the first of the forward rate constants are equal and that all the reverse rate constants are equal to k_{-n}. If it furthermore is assumed that all the enthalpies of reaction are equal to $\Delta H°$, Q is given by eqn. (24). Ψ_i is the element number i in a vector the elements of which can be calculated from K_1, K_n, k_{-n}, and the overall concentration, C. λ_i is the eigenvalue number i in the previously published coefficient matrix of the differential equations which describe the kinetics of the system when it is perturbed by ultrasound.[9] Since the eigenvalues can be calculated from K_1, K_n, and C, it is seen that eqn. (31) contains three unknown parameters, namely k_{-n}, Q and B, provided the equilibrium constants are known from the infrared measurements. Thus the theoretical expression for the relaxation spectrum of the multistep mechanism is reduced to contain the same number of independent parameters as the generally used relaxation equation involving one relaxation time, namely

$$\frac{\alpha}{\nu^2} = \frac{A'}{1 + (2\pi\tau'\nu)^2} + B \tag{32}$$

where A' and τ' are the apparent relaxation strength and relaxation time, respectively.

INFRARED ABSORPTION

The equilibrium constants for the multistep mechanism given by eqn. (27) may be evaluated from the infrared spectra of the solutions. By assuming that only unassociated alcohol contributes to the OH stretching band at 3627 cm^{-1} the fraction of the alcohol concentration which exists as monomers, γ, may be calculated. If we define

$$w = \frac{1-\gamma}{2\gamma^2 C} \tag{33}$$

then K_1 may be found by extrapolating a plot of w^{-1} *vs.* C to $C=0$ since

$$\lim_{C\to 0} w^{-1} = K_1^{-1} \tag{34}$$

An expression of K_n may be obtained by combining eqn. (33) with the definitions of K_1 and K_n and the expression

$$C = \sum_{i=1}^{\infty} i[A_i] \tag{35}$$

From this the following equation results [9]

$$\frac{1}{K_n} = \frac{\gamma C}{2(K_1 - w)} \left[4w - K_1 + \sqrt{2K_1 w + 4K_1^2}\right] \tag{36}$$

EXPERIMENTAL

The normal butyl alcohol was the purest grade obtainable and before use it was dried over Linde 4 Å molecular sieves. The sound absorption coefficients of the solutions were measured at 15.0 ± 0.02°C in the frequency range 10 – 300 MC. The sound absorption coefficient divided by the frequency squared of pure cyclohexane was found to be independent of the frequency in the range 10 – 100 MC. At higher frequencies a slight decrease in α/ν^2 was observed. This decrease was taken into account when the absorptions of the solutions were calculated.

The infrared spectra in the region 3000 – 4000 cm^{-1} were measured on a Beckman Model IR 9 spectrometer equipped with a thermostat keeping the sample at 15.0 ± 0.1°C. An NaF cell with a pathlength of 1.0 mm was used.

RESULTS

A representative number of the 10 infrared spectra used in the calculation of the equilibrium constants are shown in Fig. 1. The equilibrium constants obtained are given in Table 2. By using these equilibrium constants the

Table 2. The equilibrium constants at 15°C for normal butyl alcohol dissolved in cyclohexane. The results for tertiary butyl alcohol are given in parentheses.

K_1 M^{-1}	K_n M^{-1}
5.2 (1.8)	7.4 (7.1)

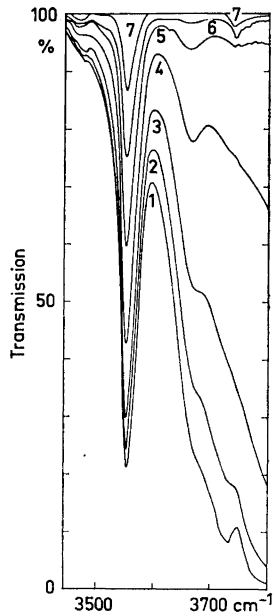

Fig. 1. Seven infrared spectra used in calculating the equilibrium constants.

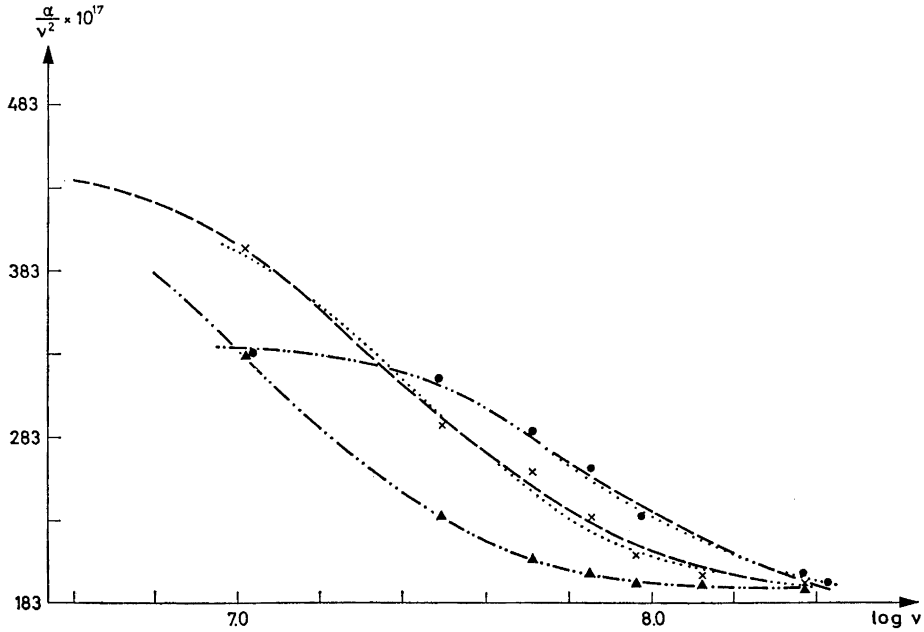

Fig. 2. Ultrasonic relaxation spectra of normal butyl alcohol dissolved in cyclohexane. ▲, 0.0460 M, ×, 0.0980 M. ●, 0.2200 M. The best theoretical curves obtained by fitting the experimental data to eqns. (32) and (31) are given by the signatures (— — —) and (· · · · · ·), respectively.

concentration dependence of the Z-factor given by eqn. (26) is calculated. Table 1 shows the results. The frequency dependence of α/ν^2 for three different solutions are given in Fig. 2. The observed relaxation can be described by a single relaxation time by means of eqn. (32). The goodness of fit parameter, F,[15] and the values of A', τ', and B obtained by a least square fitting procedure of eqn. (32) to the experimental results are given in Table 3 together with the previously published results for tertiary butyl alcohol. The best theoretical curves obtained by fitting the data to the expression for the relaxation spectrum

Table 3. Ultrasonic relaxation parameters and goodness of fit parameter, F, resulting from fitting the data from normal butyl alcohol to eqn. (32). Results of tertiary butyl alcohol are given in parentheses.

C M	$A' \times 10^{17}$ sec^2 cm^{-1}	$B \times 10^{17}$ sec^2 cm^{-1}	$\tau' \times 10^8$ sec	F
0.0460	192	189	0.920	0.3
(0.0467)	(108)	(184)	(0.743)	(0.6)
0.0980	225	191	0.530	1.3
(0.0752)	(165)	(183)	(0.556)	(0.6)
0.1430	203	174	0.289	1.2
(0.1144)	(195)	(183)	(0.415)	(0.5)
0.2200	155	184	0.229	1.2
(0.1928)	(175)	(200)	(0.287)	(1.2)
0.3040	122	183	0.168	1.2
(0.3128)	(163)	(190)	(0.217)	(1.1)

Table 4. Ultrasonic parameters resulting form fitting the data for normal butyl alcohol to eqn. (31). Results of tertiary butyl alcohol are given in parentheses.

C M	$B \times 10^{17}$ sec^2 cm^{-1}	$Q \times 10^5$ (see eqn. (24))	$k_{-n} \times 10^8$ sec^{-1}
0.0460	188	3.49	1.1
(0.0467)	(184)	(2.81)	(2.3)
0.0980	183	3.06	2.9
(0.0752)	(180)	(2.50)	(3.7)
0.1430	150	4.77	8.4
(0.1144)	(171)	(2.46)	(6.4)
0.2200	153	4.23	16.6
(0.1924)	(175)	(2.44)	(14.0)
0.3040	145	5.04	36.2
(0.3128)	(141)	(3.66)	(35.9)

for the multistep mechanism are also shown in Fig. 2. The values of Q, k_{-n}, and B obtained by this procedure are given in Table 4 together with the values which are obtained when the same procedure is applied to the previously published relaxation spectra of tertiary butyl alcohol.

DISCUSSION

Table 1 shows that the relaxation strength for the two step mechanism given by eqn. (2) is a monotonically increasing function of the overall concentration of alcohol in the concentration range considered. Table 3 shows that the value of the apparent relaxation strength, A', passes through a maximum with increasing overall concentration in the concentration range considered. Consequently the relaxation strength obtained from eqn. (32) cannot be the relaxation strength for the two step mechanism, which then must be given up as a plausible explanation of the observed relaxation.

Fig. 2 shows furthermore that the theoretical expression for the multistep mechanism given by eqn. (27) also describes the measured relaxation. Table 4 gives the values of k_{-n}, Q, and B obtained. It is seen that the value of k_{-n} depends on the overall concentration. A fitting procedure taking all the relaxation spectra at the different concentrations into account at the same time does not work out at all for the data obtained. This result is very diferent from the result obtained for N-methylacetamide dissolved in carbon tetrachloride.[11,16–18] Thus the infrared spectra and the relaxation spectra for this system agree with the multistep mechanism when it is treated the way described in this paper. Consequently neither normal nor tertiary butyl alcohol associate in the same way as N-methylacetamide. The nature of the molecular association of N-methylacetamide is that long hydrogen bonded chains are formed and that these chains increase and decrease by adding and removing end groups, respectively. This nature of the association is implicitly involved when the association mechanism given by eqn. (27) is used as a detailed reaction mechanism. Thus this mechanism neglects all the elementary reaction steps of the following type

$$A_i + A_j \rightleftharpoons A_{i+j} \tag{37}$$

$$i,j = 2,3,\ldots \tag{38}$$

It may be a reasonable approximation to neglect these elementary reaction steps as long as the probability of having a collision between a monomer and a polymer is considerably larger than the probability of having a collision between two polymers, *i.e.* as long as

$$[A_1] \gg \sum_{j>1} [A_j] \tag{39}$$

From Table 5 it is seen that the concentration range in which this requirement is fulfilled for normal butyl alcohol roughly corresponds to the concentration range in which the reverse rate constant is found to be independent of the overall concentration.

Table 5. The molar concentration of monomers and polymers calculated for different over all concentrations of normal butyl alcohol. Results of tertiary butyl alcohol are given in parentheses.

C M	$[A_1]$ M	$\sum_{i=2}[A_i]$ M	$[A_1]/\sum[A_i]$
0.0253 (0.0218)	0.0200 (0.0200)	0.0024 (0.0008)	8.3 (2.5)
0.0437 (0.0496)	0.0300 (0.0400)	0.0060 (0.0040)	5.0 (10)
0.0686 (0.0678)	0.0400 (0.0500)	0.0118 (0.0070)	3.4 (7.1)
0.1034 (0.0910)	0.0500 (0.0600)	0.0206 (0.0113)	2.4 (5.3)
0.1542 (0.1684)	0.0600 (0.0800)	0.0337 (0.0267)	1.8 (3.0)
0.2325 (0.2423)	0.0700 (0.0900)	0.0529 (0.0403)	1.3 (2.2)
0.3615 (0.3760)	0.0800 (0.1000)	0.0816 (0.0620)	1.0 (1.6)

The effect of the steric hindrance on the association of the alcohols appears from the difference between the equilibrium constants given in Table 2. The influence of the steric hindrance on the relaxation spectra can be correlated with this effect since the number of elementary reaction steps involved in the multistep mechanism at a given overall concentration increases with increasing equilibrium constants. The value of the relaxation time obtained by fitting the data to eqn. (32) is to consider as a weighted average value of the individual relaxation times involved in the mechanism according to the equation

$$\frac{1}{\tau'} = \sum_{i=1}^{i=i^+} \beta_i \frac{1}{\tau_i} \Big/ \sum_{i=1}^{i=i^+} \beta_i$$

Thus one would expect a steric hindrance to cause a decrease in the value of $1/\tau'$. Fig. 3 shows the values of $1/\tau'$ for the two different alcohols and the above mentioned trend is noticed at concentrations larger than 0.1 M.

CONCLUSION

It is well known that a single elementary reaction step in which three monomers recombine and form a trimer predicts that the relaxation strength passes through a maximum with increasing overall concentration. This does not necessarily mean as it has been suggested in the literature recently that

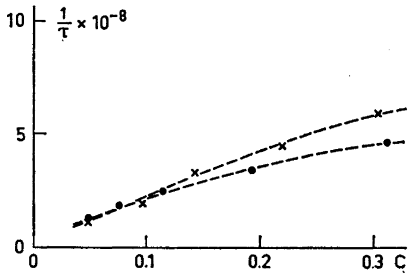

Fig. 3. The reciprocal relaxation time for tertiary and normal butyl alcohol dissolved in cyclohexane plotted against the overall concentration. ×, normal butyl alcohol. ●, tertiary butyl alcohol.

a two step mechanism taking up to trimers into account also predicts this concentration dependence of the relaxation strength.

It is shown that the theoretical expression of the relaxation strength of the two step mechanism is rather complicated and only develops into a useful form when several approximations are introduced. The validity of these approximations is limited to a certain concentration range, and this again limits the use of the concentration dependence of the relaxation strength in clearing up the kinetics of a chemical reaction. The one relaxation time equation, eqn. (32), as well as the theoretical three parameter expression for the multistep mechanism in which the largest polymer present is considered as a function of the overall concentration describe the experimental results for tertiary and normal butyl alcohol. The multistep mechanism gives consistent results at low alcohol concentration only. By comparing this behaviour with the association of *N*-methylacetamide dissolved in carbon tetrachloride it may be concluded that the nature of the molecular association of alcohols is different from that of amides, although the equilibrium properties of the two systems can be described by the same mechanism. An explanation may be that for alcohols all sorts of polymer/polymer interactions take place while for amides the polymers increase and decrease by adding and removing monomer units, respectively.

Finally it is shown that the effect of steric hindrance on the relaxation spectra causes a decrease in the obtained value of $1/\tau'$. The difference between the value of $1/\tau'$ obtained from normal and tertiary butyl alcohol becomes noticeable at concentrations larger than about 0.1 M.

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