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Ultrasonic Relaxation and Infrared Spectra of H-Bond Polymerized Benzyl Alcohol

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The hydrogen bond association of benzyl alcohol dissolved in cyclohexane has been investigated by means of ultrasonic absorption in the frequency range 4–50 Mc and by means of infrared spectroscopy. The sound absorption data show a relaxation which is described by a single relaxation time. The concentration dependence of this relaxation time in the concentration range 0.02–0.10 M is in agreement with the assumption that only a monomer-dimer equilibrium exists. This model is contradicted, however, by the infrared spectra. It is shown that a general association model with several species present might cause a relaxation time with the observed concentration dependence, and that this model is in agreement with the infrared data. The equilibrium constants and rate constants for this mechanism are evaluated.

The nature of the molecular hydrogen bond association of alcohols is of particular interest because water and alcohols resemble each other in hydrogen bonding facility. To a large extent the knowledge of the equilibrium properties of the alcohol association is based on infrared and NMR studies. Several of these are concerned with sterically hindered alcohols for which the association model is assumed to be simple, *i.e.* formation of dimers only,[1–3] formation of trimers only,[4] or formation of tetramers only.[5] The disagreement in these papers about which is the most valid association model seems to be caused by the fact that within experimental error the data can be described by several contradictory models.[6] The conclusion is that for alcohols a general association model with several species present is correct. The association can be described in terms of equilibria between polymeric species and tends to decrease with increasing molecular weight and in the sequence primary alcohol, secondary alcohol, tertiary alcohol. Although there is general agreement on this main feature of the alcohol association, precise knowledge about the polymeric entities is lacking.

Most investigations published so far deal with equilibrium properties and very few deal with the kinetics of alcohol association despite the fact that the

rate constants involved are primary factors in the molecular association. Although the determination of the relaxation time by ultrasonic measurements has been applied in investigation hydrogen bond kinetics,[7-9] to our knowledge it has not yet been used on a sterically hindered primary alcohol.

In this paper we present and interpret the relaxation spectra of benzyl alcohol dissolved in cyclohexane. From the point of view of the hydrogen bonding cyclohexane is probably a more inert solvent than carbon tetrachloride. Since infrared spectra for benzyl alcohol in the literature are reported for carbon tetrachloride solutions only,[10] we furthermore present and interpret the infrared spectra of benzyl alcohol dissolved in cyclohexane. The results obtained from the two different techniques are combined.

ULTRASONIC RELAXATION

The sound absorption caused by the relaxation of a single reaction is described by the following equation:

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

where α is the sound absorption coefficient, ν the frequency of sound, τ the relaxation time, and A the amplitude factor, a parameter given by the thermodynamics of the system. B is the background absorption, that means the value of α/ν^2 of the solution at frequencies high enough for the absorption due to the chemical reaction to be negligible.

The fact that some sound absorption data fit eqn. (1) does not necessarily mean that the relaxation is caused by a single reaction step. The possibility of having several reaction steps with relaxation times giving a very narrow relaxation spectrum always exists. This point becomes important if a kinetic interpretation of the measured relaxation time is desired. In fact this interpretation depends strictly on the detailed mechanism to which the observed relaxation is attributed.

If the reaction which causes the relaxation is a single step dimerization according to the scheme

$$A + A \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2 \tag{2}$$

where k_{12} and k_{21} are the forward and backward rate constants, respectively, the kinetic interpretation of the relaxation time, τ, becomes:

$$(1/\tau)^2 = 8k_{12}k_{21}\,C + {k_{21}}^2 \tag{3}$$

where C is the overall concentration. From eqn. (3) it is seen that a graph of $(1/\tau)^2$ *vs.* C is a straight line from which the rate constants can be calculated.

Even when some experimentally determined values of $(1/\tau)^2$ plotted *vs.* C can be fitted by a straight line one cannot infer, however, that the reaction mechanism is a single step dimerization. If the relaxation is caused by a two step dimerization, for instance that of forming a doubly bonded dimer, the kinetic interpretation of the relaxation time under certain conditions becomes [11]

$$(1/\tau)^2+U(1/\tau) = V\ C+S \tag{4}$$

where U, V, and S are different combinations of the rate constants involved. If the rate constants of the mechanism fulfil the requirement

$$1/\tau \geq 10\ U \tag{5}$$

then the graph of $(1/\tau)^2$ *vs.* C is a straight line. The parameters k_{12} and k_{21} obtained from the slope and intercept of this line using eqn. (3) do not represent rate constants for a single reaction, however, they are combinations of the four rate constants involved in the two step mechanism. This point of view has recently been extented to a multistep mechanism and has been applied to the polymerization of *N*-methylacetamide, which forms hydrogen bonded chain polymers.[12]

The polymerization model often used for alcohols is

$$\begin{array}{l} A_1+A_1 \rightleftharpoons A_2 \\ A_2+A_1 \rightleftharpoons A_3 \\ \quad\cdot\quad\cdot\quad\cdot \\ \quad\cdot\quad\cdot\quad\cdot \\ A_n+A_1 \rightleftharpoons A_{n+1} \end{array} \tag{6}$$

where A_i denotes a polymer with i molecules of alcohol. We have assumed a finite number of reaction steps. This assumption is immaterial and will be discussed later.

So far this model has been applied to data obtained by equilibrium studies only, and the interpretation is based on the assumption that the equilibrium constant for the first dimerization step (K_1) is different from that relating to subsequent steps (K_n), but the latter may be taken as independent of n. In analogy with this the forward and reverse rate constants in all but the first reaction steps are assumed to be independent of the degree of polymerization. The kinetics of the model is described by the following $n+1$ differential equations

$$\begin{aligned}
(\dot{A}_1) &= -2k_1(A_1)^2-k_n(A_1)\sum_{i=2}^{n}(A_i)+k_{-n}\sum_{i=3}^{n+1}(A_i)+2k_{-1}(A_2) \\
(\dot{A}_2) &= k_1(A_1)^2-k_{-1}(A_2)-k_n(A_1)(A_2)+k_{-n}(A_3) \\
(\dot{A}_3) &= k_n(A_1)(A_2)-k_{-n}(A_3)-k_n(A_1)(A_3)+k_{-n}(A_4) \\
&\vdots \\
(\dot{A}_i) &= k_n(A_1)(A_{i-1})-k_{-n}(A_i)-k_n(A_1)(A_i)+k_{-n}(A_{i+1}) \\
&\vdots \\
(\dot{A}_{n+1}) &= k_n(A_1)(A_n)-k_{-n}(A_{n+1})
\end{aligned} \tag{7}$$

where k_1 and k_{-1} are the forward and reverse rate constants, respectively, for the first reaction step while k_n and k_{-n} are the forward and reverse rate constants, respectively, for the remaining steps. n is the number of reaction steps, (A_i) is the molar concentration of component A_i, and $(\dot{A}_i)=\mathrm{d}(A_i)/\mathrm{d}t$.

When sound propagates in the system originally in equilibrium, a small variation in (A_i) occurs which we denote by a_i,

$$a_i = (A_i) - (A_i)^0 \tag{8}$$

$(A_i)^0$ is the equilibrium concentration of component A_i. By introducing eqn. (8) in eqn. (7) and by neglecting higher order terms in a we obtain the following differential equation for $a_1, a_2, \cdots, a_{n+1}$, which for convenience is written as a matrix equation (9)

$$\begin{Bmatrix} \dot{a}_1 \\ \dot{a}_2 \\ \dot{a}_3 \\ \dot{a}_4 \\ \vdots \\ \dot{a}_{n+1} \end{Bmatrix} = -k_{-n} \begin{Bmatrix} 4K_1(A_1)^0 \frac{k_{-1}}{k_{-n}} + \sum_{i=2}^{n} K_n(A_i)^0 & K_n(A_1)^0 - 2\frac{k_{-1}}{k_{-n}} & K_n(A_1)^0 - 1 & K_n(A_1)^0 - 1 \cdots - 1 \\ K_n(A_2)^0 - 2(A_1)^0 \frac{k_{-1}}{k_{-n}} & K_n(A_1)^0 + \frac{k_{-1}}{k_{-n}} & 1 & 0 \\ K_n(A_3)^0 - K_n(A_2)^0 & -K_n(A_1)^0 & K_n(A_1)^0 + 1 & -1 \\ K_n(A_4)^0 - K_n(A_3)^0 & 0 & -K_n(A_1)^0 & K_n(A_1)^0 + 1 \\ \vdots & & \vdots & \\ -K_n(A_n)^0 & & & 1 \end{Bmatrix} \begin{Bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ \\ a_{n+1} \end{Bmatrix}$$

The relaxation times for this system are given by the eigenvalues of the matrix. Note that the way the matrix is written we have

$$\dot{a} = -k_{-n}\, \mathbf{A}\, a \tag{10}$$

in which the matrix **A** only depends on the equilibrium properties of the system. If these properties can be determined independently for instance by infrared measurements the eigenvalues can be calculated and presumably some information about k_{-n}, the common value of the rate constants for depolymerization, can be obtained.

We shall now describe how the equilibrium constants may be determined using the infrared spectra of the solution.

INFRARED SPECTRA

The infrared spectra of different mixtures of benzyl alcohol and cyclohexane have been measured in order to determine the equilibrium constants for the hydrogen bond association of benzyl alcohol. Using the equilibrium conditions between the various orders of complexes according to the polymerization mechanism we get [10]

$$\frac{1}{K_n} = \frac{\gamma\, C}{2[(1/K_1) - Q]} \left[\frac{2}{K_1} - \frac{Q}{2} + \sqrt{\frac{2Q}{K_1} + \frac{Q^2}{4}} \right] \tag{11}$$

where γ is the fraction of the total concentration present as unassociated material, and

$$Q = 2\gamma^2 C/(1-\gamma) \tag{12}$$

Since

$$\lim_{C \to 0} \left(\frac{Q}{2}\right) = \frac{1}{2K_1} \tag{13}$$

K_1 may be evaluated by plotting Q *vs.* C and by extrapolating to zero concentration. When K_1 is known K_n can be calculated from eqn. (10), using the experimental values of γ and C. In order to get a value for γ from the measured infrared spectra one must assume the absorption due to the free hydroxyl group to be caused by the unassociated alcohol present in the solution.

EXPERIMENTAL

The benzyl alcohol used was the purest grade obtainable. All the experiments were performed at 15.0±0.1°C. The sound absorption coefficients of the solutions were measured at 4.50, 9.50, 13.50, 22.50, 28.50, and 47.50 Mc by means of a pulse-method described earlier.[18] The concentration of benzyl alcohol was between 0.02 and 0.1 M. The sound absorption coefficient of pure cyclohexane divided by the frequency squared, was found to be independent of the frequency in the frequency range used. From the absorption data and eqn. (1) the best theoretical curves and relaxation frequencies are calculated using an iterative least squares method. The coefficients of variation were smaller than 3 %. The infrared absorption data in the region 3000–4000 cm^{-1} were obtained on a Beckman Model IR9 spectrometer equipped with a thermostat keeping the sample at 15.0±0.1°C. A CaF_2 cell with a pathlength of 0.1 mm was used.

RESULTS

The infrared spectra used for calculation of the equilibrium constants are shown in Fig. 1. It is seen that the peak commonly ascribed to the free hydroxyl group is relatively small and consequently the results obtained are somewhat uncertain. The equilibrium constants obtained are given in Table 1 together with the equilibrium constants reported in the literature [10] for benzyl alcohol dissolved in carbon tetrachloride. The distribution of the alcohol on the different polymers is calculated from the equilibrium constants and shown in Fig. 2. This distribution shows that less than 3 % of the alcohol exists as polymers with 5 or more units. Even though the maximum degree of polymerization in principle is not a finite number, it will thus presumably be a good approximation to put $n=4$. The matrix, **A**, is then a 4 by 4 matrix.

Table 1. Equilibrium constants for the polymerization of benzyl alcohol calculated from the infrared data.

Benzyl alcohol dissolved in cyclohexane		Benzyl alcohol dissolved in carbon tetrachloride	
K_1 M^{-1}	K_n M^{-1}	K_1 M^{-1}	K_n M^{-1}
2.5	5.0	1.3	3.0

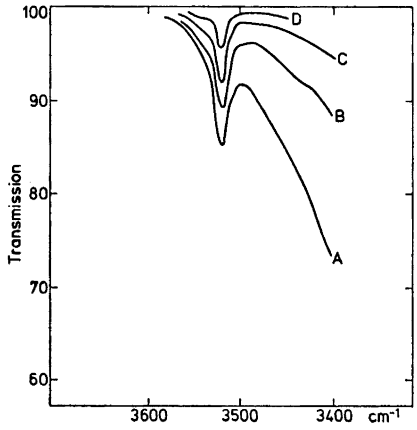

Fig. 1. A representative part of the 12 IR spectra used of benzyl alcohol dissolved in cyclohexane at 15°C. *A*: 0.5253 M, *B*: 0.2101 M, *C*: 0.1051 M, *D*: 0.0373 M.

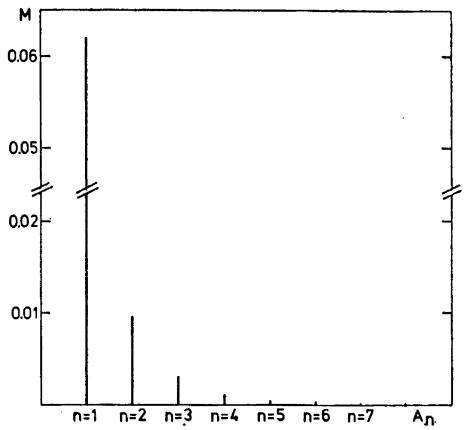

Fig. 2. The distribution of benzyl alcohol on the different polymeric species for a 0.098 M benzyl alcohol in cyclohexane.

Table 2 lists the eigenvalues of this matrix calculated for different overall concentrations of alcohol by using the equilibrium constants and the assumption that $k_{-1}=k_{-n}$.

Table 2. The eigenvalues of the coefficient matrix.

C M	$-\lambda_1$	$-\lambda_2$	$-\lambda_3$	$-\lambda_4$
0.0980	2.13	1.43	0.76	0
0.0518	1.85	1.28	0.69	0
0.0406	1.76	1.24	0.69	0
0.0242	1.58	1.15	0.70	0

The frequency dependence of the ultrasonic absorption divided by the frequency squared is shown in Fig. 3 for four different concentration of benzyl alcohol. It appears that a relaxation occurs in the frequency range 4—50 Mc. This relaxation is described by eqn. (1) and consequently by one relaxation time only. Table 3 lists the relaxation times obtained by fitting the data to eqn. (1). The plot of $(1/\tau)^2$ *vs.* C is shown in Fig. 4.

DISCUSSION

If the observed relaxation is attributed to the hydrogen bond association of benzyl alcohol, the fact that within experimental error $(1/\tau)^2$ is linear in C means that the ultrasonic data may be interpreted assuming a monomer-dimer

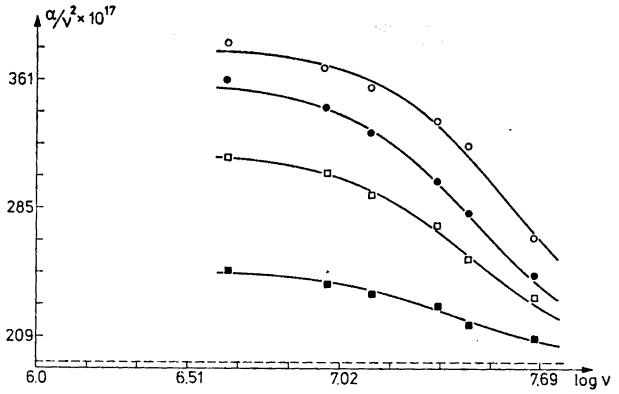

Fig. 3. The sound absorption coefficient at 15°C divided by the frequency squared is plotted *vs.* the logarithm of the frequency for benzyl alcohol dissolved in cyclohexane. ■: 0.0240 M, □: 0.0406 M, ●: 0.0517, ○: 0.0980 M. The curves drawn are the best theoretical curves obtained by fitting the data to eqn. (1).

Table 3. The relaxation times obtained at the different concentrations used.

C M	τ sec
0.0980	4.21×10^{-9}
0.0518	5.32×10^{-9}
0.0406	5.55×10^{-9}
0.0242	6.36×10^{-9}

equilibrium only. This model does not apply, however, to the infrared data, neither does it agree with the general point of view of the alcohol association. The question then arises whether or not the polymerization model under any conditions can be in agreement with the measured relaxation data. First we consider the requirements which are necessary for the polymerization model to be able to cause one relaxation time only. Then we check whether or not this relaxation time depends on the concentration in the same way as the measured relaxation time does.

If the polymerization model causes a spectrum of relaxation times, the average relaxation time is given by:

$$\frac{1}{\tau_{av}} = k_{-n} \frac{\sum -(\lambda_i)\beta_i}{\sum \beta_i} \tag{14}$$

where λ_i is the eigenvalue number i in the coefficient matrix, **A**, and β_i is the amplitude factor connected with λ_i. In order for the spectrum to fit the one relaxation time equation, eqn. (1), the eigenvalues must either be approximately equal or the amplitude factor for a particular eigenvalue must dominate. This means that either

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_{av}} = -k_{-n}\ \lambda_{av} \tag{15}$$

or

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_{av}} = -\ k_{-n}\lambda_j \tag{16}$$

From the values listed in Table 2 it is seen that the eigenvalues of the coefficient matrix differ with more than 100 %. Consequently, the approximation given by eqn. (15) does not apply.

If the approximation given by eqn. (16) is used the concentration dependence of $1/\tau_{obs}$ can be compared with the concentration dependence of the different eigenvalues ($j=1$, 2, and 3). It turns out that the eigenvalue λ_1 shows approximately the same variation as $1/\tau_{obs}$. Consequently we assume the proportionality factor between λ_1 and $1/\tau_{obs}$ to be equal to k_{-n}. Fig. 4 shows the graph of $(1/\tau_{obs})^2$ *vs.* C and $(k_{-n}\ \lambda_1)^2$ *vs.* C, and it is seen that within experimental error also $(k_{-n}\ \lambda_1)^2$ is linear in C in the concentration range investigated. By using the values of k_{-n} and the equilibrium constants, k_1 and k_n, can be calculated. The results are given in Table 4.

In the present work the alcohol concentration is changed by a factor of 4. Although a larger concentration range in general would be desirable most

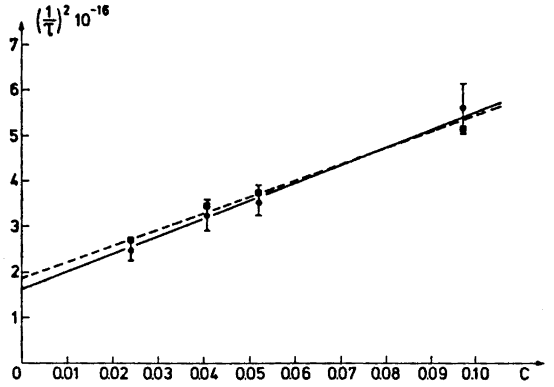

Fig. 4. (———) The dependence of the reciprocal of the relaxation time squared on the over all concentration of alcohol. (– – –) The dependence of $(k_{-n}\ \lambda_1)^2$ on the over all concentration.

Table 4. The obtained values of the rate constants.

k_1 M^{-1} sec^{-1}	k_n M^{-1} sec^{-1}	k_{-n} sec^{-1}
2.5×10^8	5.0×10^8	1.0×10^8

ultrasonic investigations of the hydrogen bond association of different compounds dissolved in inert solvents use a concentration variation of this order of magnitude. The main reasons for this are that 1) the sensitivity of the measuring technique is not yet improved enough for very low concentrations to be investigated and 2) that the solubility and requirement about ideal behaviour of the solutions very often set an upper limit for the concentration range.

If the present investigation covered a considerably larger concentration range we would expect the plot of $(1/\tau_{obs})^2$ *vs.* C to show a curvature. This point, however, is open to future investigations.

CONCLUSION

The infrared spectra as well as the relaxation spectra performed on benzyl alcohol dissolved in cyclohexane are in agreement with the generally accepted polymerization model for alcohol association. Assuming the association and dissociation rate constants to be independent of the degree of polymerization for all processes beyond the dimerization, it is possible to calculate approximate values of the rate constants involved by combining the information obtained from the two different techniques. The fact that the relaxation data can be fitted to a simpler model, in which dimerization only is assumed, shows how careful one should be in interpreting ultrasonic absorption data.

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