3684 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 3684—3687 (1981) [Vol. 54, No. 12

A Theoretical Approach to the Dielectric Relaxation of Alcohol Solutions. II.[1] The Effect of Dilution with Inert Solvents on the Principal Relaxation Times of Primary Alcohols

Ryuichi MINAMI, Koichi ITOH,* Hiroaki TAKAHASHI, and Keniti HIGASI
Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo 160

(Received May 8, 1981)

The concentration dependence of the principal relaxation times, τ_P, of primary alcohol/inert solvent solutions are analyzed based on the equation,

$$\tau_p = 2(1+Kx_A)\tau_H,$$

where x_A is the alcohol mole fraction, K the equilibrium constant corresponding to the formation of hydrogen bonded multimers, and τ_H the time constant characterizing the rotational activation process of the terminal OH groups of the multimers. By applying Eyring's absolute rate theory to the activation process, we calculated τ_P as a function of temperature and alcohol concentration. The results reproduce quite well the τ_P values observed for the ethanol/cyclohexane, 1-hexanol/cyclohexane, and 1-propanol/benzene solutions.

In the preceding papers[1,2] we studied the dielectric relaxation processes of pure alcohols and alcohol solutions by assuming the association equilibrium between hydrogen bonded chain multimers. The dipole inversion arising from the cooperative rotation of the OH groups of the multimers was considered to be the main mechanism of the dipole relaxation. To the dipole inversion process we applied the stochastic model of one-dimensional random walk with two absorption walls[3] and found that the relaxation time of an n-mer is given by

$$\tau_n = (1+n)\tau_H. \tag{1}$$

Here τ_H is the reciprocal of the rate constant in which the terminal hydroxyl groups of the n-mer are activated rotationally. The dielectric relaxation observed for liquid alcohols and alcohol solutions was considered to be the sum of the contributions from the dipole relaxation of each n-mer. Using Eq. 1 together with the stoichiometric relationships for the association equilibrium,[4,5] we obtained analytical equations for the dielectric dispersions of pure alcohols and alcohol solutions. It is well known that in a low-frequency region most of alcohols and alcohol solutions show a dielectric dispersion which conforms very well to the simple relaxation pattern of Debye.[6,7] Assuming that the above-mentioned analytical formula under the low frequency limit ($\omega \rightarrow 0$) can express the relaxation time corresponding to this dispersion (This has often been called as the principal relaxation time. In this paper we abbreviate it as τ_P.), we obtained τ_P as a function of K, K_b, and x_A, where K is the equilibrium constant of the formation of chain multimers, K_b the constant of the association between the chain-multimers and a solvent with a hydrogen-bonding capacity, and x_A is the mole fraction of alcohols.[1] From the result we successfully estimated the change in the principal relaxation times of primary alcohols due to dilution with solvents having a hydrogen-bond acceptor as well as with inert solvents.[8,9] In the case of alcohol/inert solvent systems we can put $K_b=0$, which leads to the following equation:

$$\tau_p = \frac{\tau_1}{(1+Kx_A)^2} + 2\left\{1 + Kx_A - \frac{1}{(1+Kx_A)^2}\right\}\tau_H, \tag{2}$$

where τ_1 is the dipole relaxation time of alcohol monomers. Under the condition of $Kx_A \gg 1$, the equation can be approximated by

$$\tau_p = 2(1+Kx_A)\tau_H. \tag{3}$$

In the previous paper[1] we reported that the formula well represents the τ_P *vs.* x_A curves observed for 1-propanol/benzene and 1-butanol/benzene solutions.[8,10] For the cyclohexane solutions of primary alcohols, however, Sagal[11] and Komooka[12] observed a maximum in the τ_P *vs.* x_A curves. As stated previously, in order to explain these results it is necessary to consider the dependence of τ_H in Eq. 3 upon the atmosphere surrounding alcohol molecules or, rather, surrounding the end OH groups of the molecule. In this paper, we studied thermodynamics of the dilution effect of τ_H and discussed the variation of τ_P with x_A in further detail.

Thermodynamic Treatment on τ_P

The mechanism in which the hydroxyl group of one of the two terminal segments of multimers is brought into a rotational transition state can be regarded as a single relaxation process. Therefore, we can apply Eyring's absolute rate theory[13] to this process and get the equation,

$$\tau_H = \frac{h}{k_BT}\exp\left(-\frac{\Delta S^{\neq}}{R} + \frac{\Delta H^{\neq}}{RT}\right), \tag{4}$$

where h and k_B are the Planck and Boltzmann constants, respectively. $\Delta S^{\neq}$ the activation entropy, and $\Delta H^{\neq}$ the activation enthalpy.

As we are interested in the systems where the mole fraction of alcohols, x_A, is larger than 0.5, we can make a further approximation to Eq. 3 as follows:

$$\begin{aligned}\tau_p &= 2Kx_A\tau_H \\ &= 2K(1-x_B)\cdot\tau_H(x_B),\end{aligned} \tag{5}$$

where x_B $(=1-x_A)$ is the mole fraction of an inert solvent B. In the last equation, τ_H is represented as a function of x_B to take the dilution effect on τ_H into consideration. This means that $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in Eq. 4 are also a function of x_B. Substitution of Eq. 4 into Eq. 5 yields the following formula for τ_P:

$$\tau_P = \frac{2h(1-x_B)}{k_B T} \times \exp\left\{-\frac{-\Delta S^\circ+\Delta S^{\ast}(x_B)}{R} + \frac{-\Delta H^\circ+\Delta H^{\ast}(x_B)}{RT}\right\}. \quad (6)$$

In this expression we used the fact that the equilibrium constant K can be expressed as

$$K = \exp\left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\right), \quad (7)$$

where ΔS° and ΔH° are the entropy and enthalpy changes, respectively, due to the hydrogen-bond formation between multimers and a monomer. Equation 6 can be simplified to the equation,

$$\tau_p = \frac{A(x_B)}{T} \exp\left\{\frac{E_a(x_B)}{RT}\right\}, \quad (8)$$

by defining $E_a(x_B)$ and $A(x_B)$ as follows,

$$E_a(x_B) \equiv -\Delta H^\circ + \Delta H^{\ast}(x_B), \quad (9)$$

$$A(x_B) \equiv \frac{2h(1-x_B)}{k_B} \exp\left\{\frac{\Delta S^\circ - \Delta S^{\ast}(x_B)}{R}\right\}. \quad (10)$$

According to Eq. 8, the plot of $\ln(T \cdot \tau_P)$ against $1/T$ is represented as a straight line with the slope of $E_a(x_B)/R$ and the point of intersection with the vertical axis at $\ln\{A(x_B)\}$.[14,15] On the basis of these results we obtained the values of $E_a(x_B)$ and $A(x_B)$ as functions of x_B for ethanol/cyclohexane,[11] 1-hexanol/cyclohexane,[12] 1-octanol/cyclohexane,[12] and 1-propanol/benzene[16] solutions. Figures 1 and 2 were obtained by plotting $E_a(x_B)$ and $\ln\{A(x_B)/(1-x_B)\}$ against x_B, respectively. Each set of the plots conforms very well to a straight line especially in the region where $x_B<0.5$, indicating that $E_a(x_B)$ and $\ln\{A(x_B)/(1-x_B)\}$ can be approximated by the linear equations,

$$E_a(x_B) = E_a(0) + \alpha x_B, \quad (11)$$

$$\ln\{A(x_B)/(1-x_B)\} = \ln\{A(0)\} - \beta x_B/R, \quad (12)$$

where α and β are the constants characteristic of the solution in question. Equations 9 and 10 give the followings for pure alcohols ($x_B=0$),

$$E_a(0) = -\Delta H^\circ + \Delta H^{\ast}(0), \quad (13)$$

$$A(0) = \frac{2h}{k_B} \exp\left\{\frac{\Delta S^\circ - \Delta S^{\ast}(0)}{R}\right\}. \quad (14)$$

Using the above together with Eqs. 11 and 12, we can rewrite Eq. 6 to the following equation, which expresses τ_P explicitly as a function of x_B and T.

$$\tau_p = \frac{(1-x_B)A(0)}{T} \exp\left\{\frac{E_a(0)}{RT} - \left(\frac{\beta}{R} - \frac{\alpha}{RT}\right)x_B\right\} \quad (15)$$

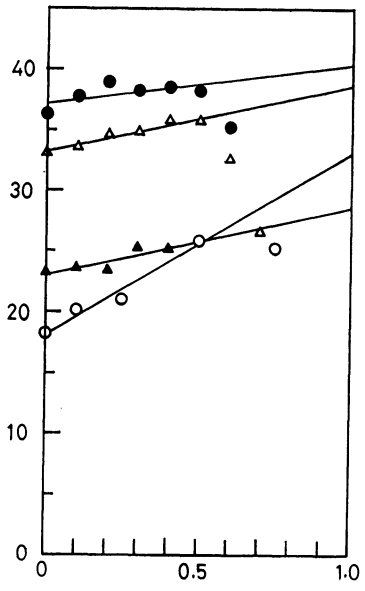

Fig. 1. Variation of E_a with the concentration of inert solvent, x_B, for the ethanol/cyclohexane (○), 1-hexanol/cyclohexane (△), 1-octanol/cyclohexane (●), and 1-propanol/benzene (▲) solutions. The straight lines are drawn to obtain the best fit with the data in the region of $x_B<0.5$ (see text.).

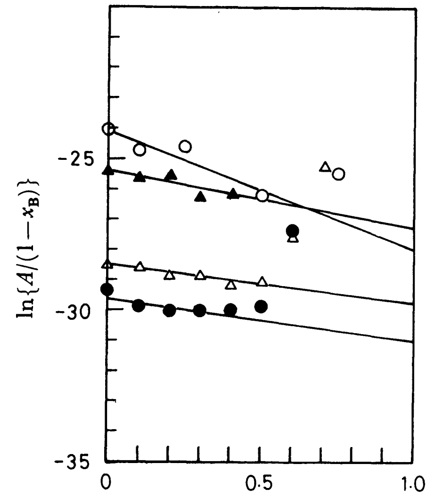

Fig. 2. $\ln\{A/(1-x_B)\}$ *vs.* x_B. The symbols have the same meaning as those in Fig. 1.

Results and Discussion

Using the least-squares method we determined $E_a(0)$, α, $A(0)$, and β from Figs. 1 and 2. The results are given in Table 1. Inserting the $E_a(0)$, α, $A(0)$ and β values into Eq. 15, we calculated τ_P as a function of x_B and T for each set of the alcohol solutions listed in Table 1. The results are depicted by solid curves in Figs. 3, 4, and 5, where the observed values of τ_P are also included.

Figures 3, 4, and 5 show that the result of calculation for the region of $x_B<0.5$ well reproduces each set of the τ_P *vs.* x_B plots observed at various temperatures. In the region where x_B is larger than 0.5, however, the

TABLE 1. ESTIMATED VALUES FOR THE PARAMETERS $E_a(0)$, α, $A(0)$, AND β IN EQS. 11 AND 12

Alcohol/Solvent	$E_a(0)$ kJ mol^{-1}	α kJ mol^{-1}	$A(0)$ ps K	β J K^{-1}mol^{-1}
Ethanol/Cyclohexane[11]	18.0	15.1	36.4	33.1
1-Hexanol/Cyclohexane[12]	33.1	5.9	0.41	10.5
1-Octanol/Cyclohexane[12]	36.8	5.0	0.13	11.7
1-Propanol/Benzene[16]	23.0	5.9	9.0	15.5

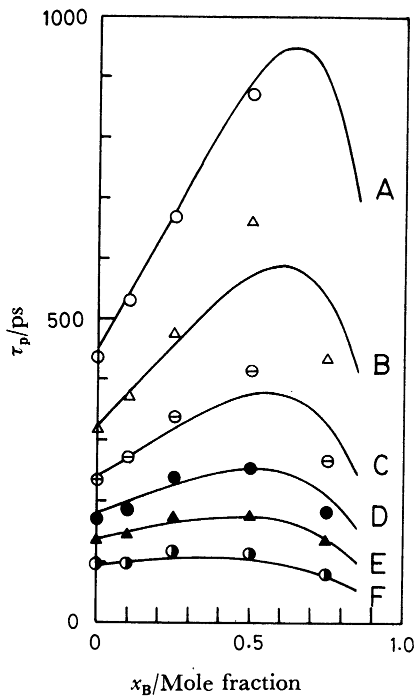

Fig. 3. Variation of τ_p with x_B for the ethanol/cyclohexane solutions. The solid lines show τ_p *vs.* x_B calculated by the use of Eq. 15 with the parameter values given in Table 1. Each set of points show the τ_p values observed at the following temperature.[11]
(A, ○): 268 K, (B, △): 278 K, (C, ⊖): 288 K, (D, ●): 298 K, (E, ▲): 308 K, (F, ◑): 323 K.

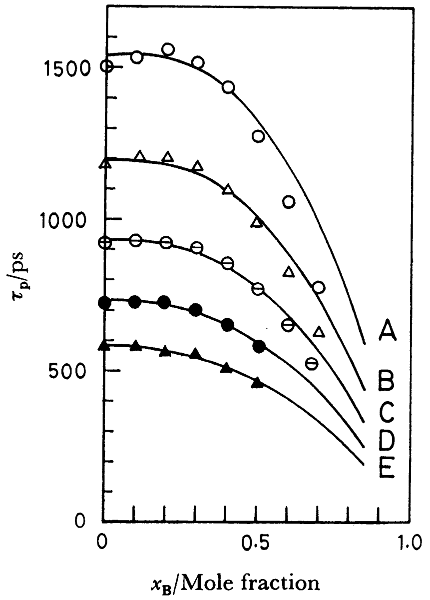

Fig. 4. τ_p *vs.* x_B for the 1-hexanol/cyclohexane solutions. The solid lines show τ_p *vs.* x_B calculated by the use of Eq. 15 with the parameter values given in Table 1. Each set of points show the τ_p values observed at the following temperature.[12]
(A, ○): 288 K, (B, △): 293 K, (C, ⊖): 298 K, (D, ●): 303 K, (E, ▲): 308 K.

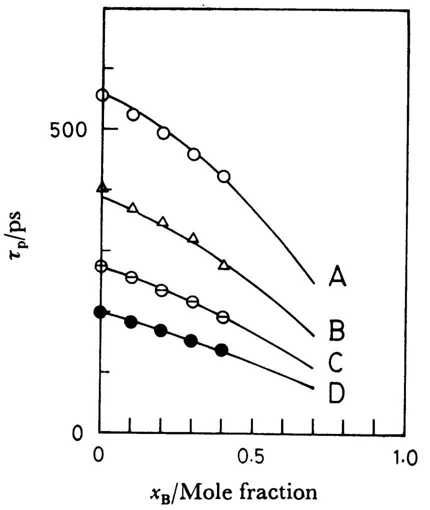

Fig. 5. τ_p *vs.* x_B for the 1-propanol/benzene solutions. The solid lines show τ_p *vs.* x_B calculated by the use of Eq. 15 with the parameter values given in Table 1. Each set of points show the τ_p values observed at the following temperature.[16]
(A, ○): 283 K, (B, △): 293 K, (C, ⊖): 303 K, (D, ●): 313 K.

results of calculation especially for the ethanol/cyclohexane (Fig. 3), 1-hexanol/cyclohexane (Fig. 4), and 1-octanol/cyclohexane solutions are not in good agreements with the data already reported.[11,12] In this region the approximate equations, (5), (11), and (12), cannot be applied to the systems in question. This is one of the main reasons for the deviation of the theoretical curves from the experimental data. In spite of such a deviation, the theoretical curves in Figs. 3 and 4 clearly predict the observations that the principal dielectric relaxation times of ethanol and 1-hexanol increase on the initial addition of cyclohexane, reach a maximum and then decrease. This result demonstrates the validity of our model proposed to the dielectric relaxation process of alcohol solutions.

From Eq. 3 it can be concluded that the principal relaxation times of alcohol solutions are determined by two factors. The first one is $(1+Kx_A)$, which depends on the distribution of chain lengths of hydrogen-bonded multimers,[17] and the other is τ_H. In the previous paper[1] we assumed that τ_H is constant. Using the thermodynamics of τ_H, which was explained in the preceding section, we can now discuss the dilution and temperature effects of τ_P in further detail.

Equation 9 indicates that the activation energy $E_a(x_B)$ is the sum of ΔH^* (the rotational activation energy of the terminal OH groups of hydrogen-bonded chain multimers) and $-\Delta H^\circ$ (the enthalpy change in the hydrogen-bond formation between chain-multimers and monomers). As the $-\Delta H^\circ$ values are in the region from 16 to 25 kJ/mol,[18] it is clear, from the $E_a(0)$ values listed in Table 1, that $\Delta H^*(0)$ of 1-hexanol and 1-octanol are larger than those of ethanol and 1-propanol; *i.e.*, the larger the hydrocarbon skelton of a primary alcohol is, the larger $\Delta H^*(0)$ becomes. The explanation for this can be given by a mechanism in which a third alcohol molecule approaches with its oxygen atom oriented favorably to activate the OH group of the terminal molecule hydrogen-bonded to the neighboring one. With the increase in the size of the alcohol molecules the proximate presence of the hydrogen-acceptor atom to the terminal OH group becomes more and more scarce, causing the increase in the value of $\Delta H^{*}(0)$. In a similar manner we can explain the positive α values for the primary alcohols listed in Table 1. The addition of solvents such as cyclohexane and benzene to primary alcohols is considered to decrease the probability of the approach of an alcohol molecule near the terminal OH group, making it rotational activation more difficult. This will cause the increase in ΔH^{*} for the primary alcohol solutions.

Based on the activation energies observed for the ethanol/cyclohexane solutions and various pure alcohols, Sagal(11) proposed a mechanism to the dielectric relaxation process of alcohols. In his model the main mechanism of the relaxation is a switching process of hydrogen bonds. The reasoning for the explanation of the dependence of activation energy on the molecular size and shape of alcohols is similar to that given in this paper. Sagal, however, neither gave any explicit model to the structure of liquid alcohols and alcohol solutions, nor specify the OH group to any particular part of the structure. Therefore, although Sagal also noted that the energy necessary to reorient an OH group ($E_a(x_B)$) should be greater than that required to break a hydrogen bond ($-\Delta H^{\circ}$), he discussed the relationship between these two energies rather ambiguously.

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