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A Theoretical Approach to the Dielectric Relaxation of Alcohol Solutions

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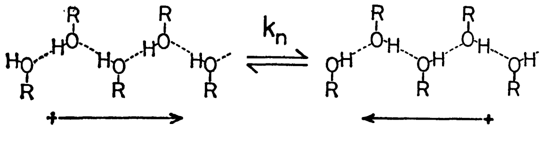
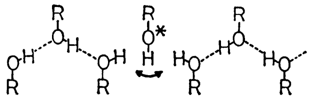
The dielectric relaxation mechanism of primary alcohols in solutions of various solvents with and without a hydrogen-bonding capacity was theoretically studied using the concept of the chemical equilibrium between hydrogen-bonded chain multimers and that between the multimers and solvents. The dipole-inversion processes originating from the successive rotation of the hydroxyl groups of the hydrogen-bonded multimers were considered to play the dominant role in the dielectric relaxation of alcohol solutions. By applying the one-dimensional random-walk process to the dipole inversion, we estimated the effect of dilution upon the dielectric relaxation times of primary alcohol in solution. The results of our calculation appear to explain the experimental data.

The dielectric relaxation of liquid alcohols was first studied by Mizushima[1] in 1926; since then, the theoretical explanation of its mechanism has become a long-standing problem which has never been solved clearly.[2-4] For the last decade some of the present authors have joined in examining the effect of dilution on the principal relaxation times of several alcohols, using inert solvents (*e.g.*, benzene) as well as those with functional groups (*e.g.*, pyridine and dioxane) as diluents.[5-8] In spite of these studies, it has still been difficult to give a simple molecular model for the dipole-inversion process of alcohol solutions in which various sorts of intermolecular hydrogen-bond interactions and steric hindrances are supposed to exist.[9] On the other hand, the theoretical explanation of the static dielectric constants of liquid alcohols has successfully been performed by several authors.[10-12] For example, Dannhauser[13] experimentally determined the values of the Kirkwood correlation factor,[11] *g*, for eight isomers of octanols and analyzed the data in terms of the thermodynamic equilibrium constants for cyclic-dimer and open-chain multimer formations.

Recently we ourselves proposed a new theoretical treatment of the dielectric relaxation process of pure liquid alcohols.[14] Following Dannhauser's treatment,[13] we assumed that liquid alcohol molecules exist in an association equilibrium involving both hydrogen-bonded cyclic dimers and open-chain *n*-mers, and, further, that each of the *n*-mers alters or reverses its dipole moment by the successive rotation of the indivisual hydroxyl group, as is shown in Scheme 1. This inversion process was assumed to be the main mechanism of the dipole relaxation of the hydrogen-bonded chain *n*-mers. Scheme 2 shows an intermediate state of the dipole inversion from the left multimer to the right one in Scheme 1. The hydroxyl group with an asterisk in Scheme 2 indicates a rotationally activated state. The dipole inversion of the *n*-mers is considered always to originate at the terminal molecules because, in order to activate one of the terminal segments, it needs to break only one hydrogen bond, while two hydrogen bonds must be broken to activate an intermediate segment. Therefore, the inversion process can be regarded as the most probable process by which the activated state propagates from the left end to the right end, or from the right end to the left end. In our treatment, we applied the one-dimensional random-walk model with two absorption walls to these dipole inversion processes,[15] and concluded that the relaxation time, τ_n, of the *n*-mer is given by:



Scheme 1.



Scheme 2.

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

where τ_H is the reciprocal of k_H, the rate in which the terminal hydroxyl groups of the *n*-mer are activated rotationally. By using Eq. 1 and the values of the thermodynamic equilibrium constants for the cyclic dimer and chain *n*-mer formations, we calculated the complex permitivities as a function of the angular frequency, ω, of the field. The results are in fair agreement with the dielectric dispersion observed for liquid 1-heptanol.[16]

Sack also developed a theory for the relaxation process of a system containing linear chains of dipoles and applied it to explain the high dielectric constants and losses of long-chain alcohols in the solid state.[17] He assumed that there exists, at most, one discontinuity where two anti-parallel arrangements of the hydroxyl groups of alcohols face each other, and that the wandering of this discontinuity along each chain is the main mechanism of the dipole relaxation. It was concluded that the effective relaxation time of a linear chain *n*-mer is proportional to $(n+1)^2$. This mechanism, however, cannot be applied to the dielectric relaxation process of liquid alcohols because, immediately after a discontinuous point appears, a pair of anti-parallel chains should separate and move away from each other in the liquid state.

In this paper we extend the above-mentioned theory to include the effect of the addition of inert solvents as well as those with functional groups, which form hydrogen bonds, on the dielectric relaxation mechanism of alcohols. We also give a theoretical prediction regarding the dilution effect on the relaxation times of alcohol solutions. The results are compared with the experimental data.

Stoichiometry of Association Equilibria between Alcohol Monomers and Multimers and between Multimers and Solvents

The binary solutions of primary alcohols and solvents are assumed to consist of alcohol monomers, A_1; solvent molecules, B; hydrogen-bonded cyclic dimers,[†] A_c; hydrogen-bonded open-chain n-mers, A_n, and, if B has proton-acceptor groups, open-chain n-mers hydrogen-bonded with the solvent at one end, A_nB. As is the case with pure alcohols, the association equilibria can be expressed as follows:

i) Cyclic dimer: $A_1 + A_1 \overset{K_c}{\rightleftharpoons} A_c$,

ii) open-chain n-mer: $A_{n-1} + A_1 \overset{K_n}{\rightleftharpoons} A_n \quad (n \geqq 2)$,

where K_c and K_n are the equilibrium constants of the formation of the cyclic dimer and the open-chain n-mer respectively. When the solvent molecule, B, can form a hydrogen bond with the hydroxyl group of alcohols, we also assume the following equilibrium between A_n and B:

iii) addition compound: $A_n + B \overset{K_{nb}}{\rightleftharpoons} A_nB \quad (n \geqq 1)$,

where K_{nb} is the equilibrium constant of the association between A_n and B. As the mole fraction of the solvent molecules with the hydrogen-bond capacity is increased, the average degree of the association of alcohol multimers is decreased. This can be seen in the following stoichiometric calculations.

The stoichiometric relationships for the association equilibria mentioned above have been studied extensively,[13] and the volume fractions[18] of A_1, A_c, A_n, A_nB, and B, which are expressed as ϕ_1, ϕ_c, ϕ_n, ϕ_{nb}, and ϕ_b, are related to each other by the following equations:

$$\left.\begin{aligned} \phi_c &= K_c\phi_1^2, \\ \phi_n &= (K\phi_1)^{n-1}\phi_1, \\ \phi_{nb} &= (K\phi_1)^{n-1}\phi_1 K_b \phi_b, \end{aligned}\right\} \tag{2}$$

where we assumed that:[19]

$$K \equiv K_2 = K_3 \ldots = K_n = \ldots,$$

and

$$K_b \equiv K_{1b} = K_{2b} = \ldots = K_{nb} = \ldots .$$

The sum of the volume fractions is equal to one, giving this equation:

$$\sum_{n=1}^{\infty} \phi_n + \phi_c + \sum_{n=1}^{\infty} \phi_{nb} + \phi_b = 1. \tag{3}$$

The total mole fraction of the solvent B, x_B, can be expressed as follows:

$$\sum_{n=1}^{\infty} \phi_{nb}/(n+1) + \phi_b = x_B. \tag{4}$$

From Eqs. 2, 3, and 4, we derive the following transcendental equations:

$$(1+K_b\phi_b)\phi_1/(1-K\phi_1) + K_c\phi_1^2 + \phi_b = 1, \tag{5}$$

$$\phi_b - \{\ln(1-K\phi_1) + K\phi_1\}K_b\phi_b/K^2\phi_1 = x_B. \tag{6}$$

The numerical calculations[20] using Eqs. 5 and 6 give the ϕ_1 and ϕ_b values as functions of x_B for the assumed K, K_c, and K_b values. On the substitution of the ϕ_1 and ϕ_b values into Eq. 2 we can obtain the ϕ_c, ϕ_n, and ϕ_{nb} values as functions of x_B.

Dielectric Relaxation of Alcohol Solutions

The dielectric dispersion observed for alcohol solutions is the sum of the contributions from the dielectric relaxations of A_n, A_nB, and A_1 (and B, if it is a polar molecule.) The cyclic dimer A_c has no permanent dipole moment, and it does not contribute to the dielectric dispersion. The dielectric relaxation times of all the polar solvent molecules are, in general, very much smaller than those of the multimers. For this reason, the contribution from the solvent can also be neglected. We applied the one-dimensional random walk model also to the dipole inversion process of A_nB. The mechanism of its stochastic process, however, is a little different from that of the dipole inversion process of A_n. The reason for this is that activating the alcohol segment neighboring B requires a mechanism different from that required to activate one of the end segments in A_n. Therefore, we use the $\tau_{H'}$, symbol for the activation of the alcohol segments at the ends of A_nB instead of the symbol, τ_H, for the activation of the end segment of A_n. The relaxation time of the dipole inversion of A_nB, τ_{nb}, is expressed by:

$$\tau_{nb} = (n+1)\tau_{H'}. \tag{7}$$

The weights of the contributions of the multimers, A_n and A_nB, to the dielectric dispersion are proportional to the values of ϕ_n/n and $\phi_{nb}/(n+1)$, which represent the proportions of A_n and A_nB respectively, and are also proportional to the expected values of their squared dipole moments, $\langle \boldsymbol{\mu}_n^2 \rangle$ and $\langle \boldsymbol{\mu}_{nb}^2 \rangle$ respectively. In this paper we assume that $\boldsymbol{\mu}_n$ is approximately equal to $\boldsymbol{\mu}_{nb}$ and that $\langle \boldsymbol{\mu}_n^2 \rangle$ is proportional to n^2.[††] On the basis of these considerations, we obtain the following equations:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = Z^{-1}\left\{\frac{\phi_1}{1+i\omega\tau_1} + \sum_{n=2}^{\infty}\frac{n\phi_n}{1+i\omega(n+1)\tau_H} + \sum_{n=1}^{\infty}\frac{n^2\phi_{nb}/(n+1)}{1+i\omega(n+1)\tau_{H'}}\right\}, \tag{8a}$$

$$\begin{aligned} Z &\equiv \sum_{n=1}^{\infty}(n\phi_n + n^2\phi_{nb}/(n+1)) \\ &= \phi_1/(1-K\phi_1)^2 + K_b\phi_b[K\phi_1^2/(1-K\phi_1)^2 \\ &\qquad -\{\ln(1-K\phi_1) + K\phi_1\}/K^2\phi_1], \end{aligned} \tag{8b}$$

where ε^*, ε_0, and ε_∞ are the complex, static, and limiting high-frequency permitivities respectively.

[†] Cyclic trimers, cyclic tetramers, *etc.* are not considered here, after Dannhauser.[13]

[††] For an extremely large n, $\langle \boldsymbol{\mu}_n^2 \rangle$ and $\langle \boldsymbol{\mu}_{nb}^2 \rangle$ would be proportional to n instead of n^2.[21] Our calculation, however, indicates that the average numbers $\langle n \rangle$, are 6.6, 8.7, and 10.8 for K=20, 30, and 40 respectively. For A_n and A_{nb} with these small n values, it is reasonable to assume that $\langle \boldsymbol{\mu}_n^2 \rangle$ and $\langle \boldsymbol{\mu}_{nb}^2 \rangle$ are proportional to n^2,

As is well known, the dielectric constants and losses of most of the liquid alcohols measured in the low-frequency region conform very well to the simple relaxation pattern of Debye. (This dispersion is often called "the principal dielectric dispersion", and the relaxation time corresponding to this dispersion, "the principal relaxation time".) On the other hand, some strong deviation from the simple Debye dispersion have been detected in the high-frequency region.[3] If we limit our discussion only to the low-frequency dispersions or the principal dispersions, we can express the measured complex permitivities of alcohol solutions by the well-known Debye equation:

$$(\varepsilon^* - \varepsilon_\infty)/(\varepsilon_0 - \varepsilon_\infty) = 1/(1+i\omega\tau_p), \tag{9}$$

where τ_p is the principal relaxation time. By equating the right-hand side of Eq. 8a to that of Eq. 9, τ_p can be calculated as a function of ω. The results of calculation for several sets of the assumed values of K, K_b, K_c, and τ_H (assuming that τ_H is equal to $\tau_{H'}$) indicate that the calculated values of τ_p do not depend on ω so long as ω is less than $1/\tau_H$. On the basis of this result, we obtained the analytical equation of τ_p at the low-frequency limit(: $\omega \to 0$) as follows:

$$\begin{aligned}\tau_p &= Z^{-1}\left\{\sum_{n=2}^{\infty} n(n+1)\tau_H\phi_n + \sum_{n=1}^{\infty} n^2\tau_H\phi_{nb}\right\} \\ &= (\tau_H\phi_1/Z)[\{2+(1+K\phi_1)K_b\phi_b\}/(1-K\phi_1)^3-2], \end{aligned} \tag{10}$$

where the contribution of alcohol monomers to the dielectric dispersion is neglected because τ_1 is much smaller than τ_n and τ_{nb} ($n \geqq 2$). This equation allows us to calculate the principal dielectric relaxation times of alcohol solutions for the assumed K, K_b, K_c, and τ_H values.

Effect of Dilution on Dielectric Relaxation Times of Alcohol Solutions

When an inert solvent is used as a diluent of alcohol solution, it can be assumed that K_b is equal to zero. Since primary alcohols associate strongly with each other, K is expected to be much larger than one, giving the condition $K \cdot x_A \gg 1$ (x_A denotes the total mole fraction of alcohol molecules, *viz.*, $x_A = 1 - x_B$; its value is set so as to be always larger than 1/2.) A tentative assumption that K_c is equal to zero is also made because the K_c value of primary alcohol was experimentally found to be much smaller than the K value, and also because the cyclic dimers do not contribute to the dielectric dispersion of alcohol solutions.[13] Under these conditions, we can derive the analytical expression for ϕ_1 from Eqs. 5 and 6:

$$\phi_1 = x_A/(1+Kx_A). \tag{11}$$

On the substitution of Eq. 11 into Eq. 10, we obtain an approximate expression for τ_p defined by Eq. 9:

$$\tau_p = 2(1+Kx_A)\tau_H. \tag{12}$$

As can be seen from Fig. 1, the observed principal dielectric relaxation times of 1-propanol decrease linearly as the mole fractions of benzene are increased. From the variation in the observed principal dielectric relaxation times of 1-propanol and 1-butanol caused by the addition of benzene,[5,6] we can determine the values of K and τ_H. The results are summarized in Table 1.[22]

When the solvent has a functional group or groups which form a hydrogen bond or bonds with alcohols, K_b becomes much different from zero. In this case, we must use Eq. 10 in order to estimate the principal relaxation times of the solutions. Assuming that K is equal to 30 (*cf.* Table 1), we calculated the principal relaxation times of 1-propanol as functions of x_B, while varying the K_b from 0.5 to 30.0. The results are

TABLE 1. EXPERIMENTAL PRINCIPAL RELAXATION TIMES, τ_p, FOR AN ALCOHOL/BENZENE MIXTURE AND ESTIMATED VALUES OF K AND τ_H[a)]

1-Propanol (25 °C)[b)]		1-Butanol (25°C)[b)]	
x_A[c)]	τ_p/ps	x_A	τ_p/ps
1.0	338	1.0	504
0.920	324	0.899	472
0.886	294	0.806	422
0.788	279	0.670	353
0.691	235	0.620	314
K	τ_H/ps	K	τ_H/ps
30	5.5	41	6.1

a) The values of K and τ_H are evaluated by using the least-squares method applied to Eq. 12. b) Ref. 6. c) Mole fraction of alcohol.

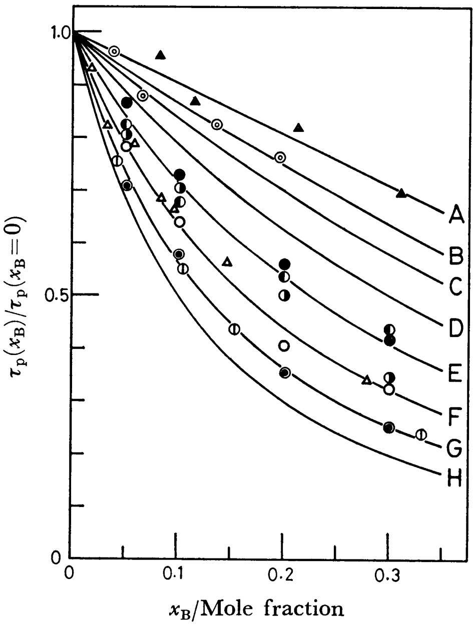


Fig. 1. Variation of principal dielectric relaxation times due to dilution with various solvents. Solid curves are theoretical results obtained from Eq. 10 with $K=30$ and $K_c=0$. The values of K_b for curves (A), (B),.., (H) are 0, 0.5, 1.0, 2.0, 4.0, 8.0, 15.0, and 30.0, respectively. The experimental data are for the 1-propanol solutions at 25 °C which are diluted with the following solvents.[5,6,8]

▲: Benzene, ◎: chlorobenzene, ●: water, ◐: camphor, ◑: cyclohexanone, △: pyridine, ○: 3-pentanone, ◉: acetone, ⦶: dioxane.

shown by solid curves in Fig. 1. Into this figure we add also the result of calculation for the case when K_b is equal to zero. This theoretical curve (*i.e.*, (A)), which decreases linearly with the increase in x_B, compares well with the data of the principal relaxation time observed for the 1-propanol/benzene mixtures. Our previous papers[5–8] have shown that, when solutions are diluted with solvents having a hydrogen-bond capacity, the principal relaxation times of the solutions change in quite different manners from those in which the relaxation times of alcohol solutions change as they are diluted with inert solvents. As the results summerized in Fig. 1 show, the principal relaxation times of mixtures of 1-propanol and solvents with a hydrogen-bond capacity do not exibit a linear decrease with dilution, and this decrease is more pronounced than that observed for the 1-propanol/benzene system. The results of calculation for the K_b in the range from 4 to 15 correspond very well to the abovementioned observation.

Conclusion

Our mechanism, which was originally proposed to explain the anomalous dielectric relaxation behavior of pure primary alcohols, has now been extended to an examination of the effect of dilution upon the principal dielectric relaxation of 1-propanol using both inert and hydrogen-bonding solvents. The results obtained so far are in fair agreement with the experiments, confirming that our theory is valid for the dielectric relaxation of the liquid primary alcohols.

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22) A maximum in τ_p *vs.* x_B curves was observed by Sagal[23] and Komooka[24] for alcohol–cyclohexane solutions. This suggests that the nature of benzene as a solvent is different from that of inert solvents, such as cyclohexane and hexane.[25] We can suspect that the properties of a solvent cause the dependency of τ_H in Eq. 12 upon the atmosphere surrounding alcohol molecules or, rather, surrounding the end OH group of the molecule. In this case, we can tentatively put $\tau_H = \tau_H(A)x_A + \tau_H(B)x_H$, where $\tau_H(A)$ is associated with the hydrogen-bonded chain in pure alcohols, and $\tau_H(B)$, with that isolated from each other with solvent molecules. On the basis of this assumption, we calculated τ_p *vs.* x_B while varying the $\tau_H(B)/\tau_H(A)$ ratio. The result of calculation shows a maximum in fair agreement with the observations of Sagal and Komooka.

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