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Dielectric dispersion of primary alcohols in polymer complex

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Dielectric measurements using a frequency region 10^6 – 10^{10} Hz were performed on methanol and ethanol-polyvinyl pyrrolidone systems by a time domain reflectometry. Two relaxation peaks were observed for each system. The high frequency process is the primary process of the alcohols. Relaxation time varies little with the polymer concentration. In the case of the ethanol system, its extrapolated value for pure polymer is 280 ps and does not differ much from the value of 130 ps for pure alcohol. For the methanol system, it changes from 280 to 55 ps. It is suggested that the process is due to reorientation of two hydroxyl groups in the alcohol chain, which involves breakage and remaking of a hydrogen bond and the low frequency process, of which relaxation time is about 10 ns, is due to reorientation of alcohol molecules bonded to the polymer.

I. INTRODUCTION

Dielectric properties of aqueous solution of deionized polymer such as polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) were investigated recently in the frequency range 10^6 – 10^{10} Hz.¹ Only a relaxation process due to rotational diffusion of water clusters was observed in the PEG–water system. The relaxation time depends greatly on the polymer concentration. The dependence is explained quite satisfactorily by an equation derived from the free-volume theory. On the other hand, two relaxation processes were discovered in the PVP–water system. The high frequency process could be attributed to the same mechanism as that of the PEG–water system. The low frequency process, of which relaxation time shows no definite dependence on the concentration, was indicated to be due to reorientation of water molecules hydrogen bonded to the polymer.

The existence of ring-like clusters consisting of five and six water molecules has been referred from x-ray analyses.² Rotational motions of the clusters as diffusive with a frictional resistance from the viscous environment can yield relaxation times strongly dependent on the polymer concentration.

PVP is soluble not only in water but also in low molecular weight alcohols such as methanol and ethanol. These alcohols have a primary relaxation process of Debye type, of which relaxation times are 55 ps for methanol and 125 ps for ethanol, respectively, at 25 °C.³ If the process is caused by the rotational diffusion of alcohol clusters like that of water, influence of the polymer concentration on the diffusion should be as great as for the water system.¹ On the other hand, if it is attributed to localized orientations in the cluster, the relaxation time will not depend on the concentration. In liquid ethanol and methanol, it was reported that a value of $\tau T/\eta$, where τ is the relaxation time, T is the absolute temperature, and η is the viscosity, varies with temperature.³ This suggests that the process is not due to apparent diffusive motion of alcohol clusters.

In this work dielectric measurements were performed over the frequency range 10^6 – 10^{10} Hz on PVP–methanol

and ethanol systems with changing concentration of PVP in order to see the influence of polymer concentration on the primary process. The measurements were made by a time domain reflectometry method (TDR)^{1,4} and the PVP sample was the same as that used for the previous study of the PVP–water system.¹

II. RESULTS AND DISCUSSION

Two relaxation peaks were clearly observed both in methanol and ethanol systems if contribution of dc conductivity σ was subtracted from the absorption curve as shown in Fig. 1. The dispersion and absorption curves are described satisfactorily by the following equation:

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon_h}{1 + (i\omega\tau_h)^{\beta_h}} + \frac{\Delta\epsilon_l}{(1 + i\omega\tau_l)^{\alpha_l}} \quad (1)$$

The parameters in Eq. (1) determined by a least-square fitting procedure are listed in Table I, where values of determined σ are also given.

Relaxation time τ_h of the high frequency process for the ethanol system varies only slightly with the polymer concentration c as shown in Fig. 2. It has an extrapolated value of 280 ps for pure polymer, which is only two times greater than that of pure ethanol.⁵ For the methanol system, it also has the extrapolated value of 280 ps for pure polymer, five times greater than that for pure methanol. It is noted that these two extrapolated values agree with each other. The variations in τ_h for these alcohol systems are negligibly small compared with that of the water system, where the extrapolated value to pure polymer is 4 ns which is 500 times greater than that for pure water.¹

The high frequency process for the ethanol system is undoubtedly attributed to the primary process of alcohol. The relaxation time τ_h observed agrees with that of pure alcohol. The relaxation strength $\Delta\epsilon_h$ decreases linearly with c and vanishes at $c = 100$ wt. %.

In the methanol–PVP system, the relaxation time τ_h depends on c slightly more than in the ethanol system as shown in Fig. 2. However the dependence is not as strong as expected for rotational diffusion of methanol clusters. In

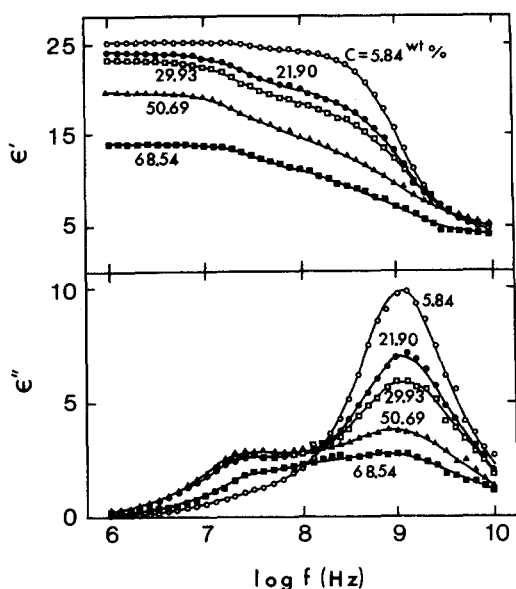


FIG. 1. Dielectric dispersions and absorptions for ethanol-PVP system at 25°C.

this case too, the relaxation time of the high frequency process agrees with that of the primary process of methanol as the PVP concentration approaches zero.

Alcohols of low molecular weights are believed to have a linear chain, resulting from hydrogen-bonded linkage. If such a chain has a molecule, of which oxygen is hydrogen bonded by two adjacent protons as shown in Fig. 3, orientation of this molecule can take place through rotations of two protons around O-C bonds accompanied with breakage and remaking of a hydrogen bond. It is not affected by the frictional resistance from the environment. Activation energies observed for methanol and ethanol by dielectric measurements³ are quite reasonable for this orientation.

The change shown is definitely active in dielectric relaxation. If a tetrahedral angle is assumed as the bond angle alcohol chain, displacement of dipole moment $\Delta\mu$ caused by the change along the chain is estimated as

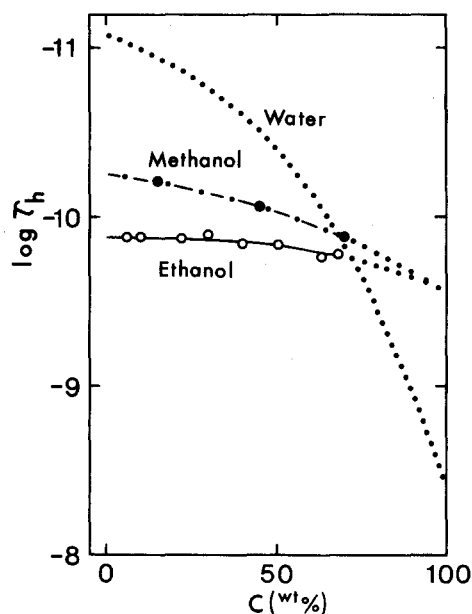


FIG. 2. Variation of relaxation time τ_h with polymer concentration c for PVP-ethanol and methanol systems at 25°C.

$$\Delta\mu = 2\mu_{\text{OH}} \sin \frac{109^\circ}{2} = 1.6\mu_{\text{OH}}.$$

When this configurational change propagates along the chain, it will induce a displacement large enough to give the primary process of alcohol.⁶

If the stretching vibrational frequency ν_0 of neighboring oxygens in the chain is known, the relaxation time for the process can be estimated by

$$\tau = \nu_0^{-1} \exp \left(\frac{\Delta H_A}{kT} \right), \quad (2)$$

where ΔH_A is apparent activation energy. As examples of one-dimensional hydrogen bond linkage, values of ν_0 were reported to be 6.3×10^{12} Hz for ice and 5.7×10^{12} Hz for

TABLE I. Relaxation parameters for PVP-ethanol and methanol systems at 25°C.

c (wt. %)	Low frequency process			High frequency process			ϵ_∞	σ ($\Omega^{-1} \text{ m}^{-1} \times 10^{-2}$)	$\langle \Delta \epsilon_1 \rangle_{\text{red}}$ ($\times 10^{-2}$)
	$\Delta \epsilon_1$	$\log \tau_1$ (s)	α_1	$\Delta \epsilon_h$	$\log \tau_h$ (s)	β_h			
Ethanol									
5.84	1.54	− 8.24	1.00	20.00	− 9.88	0.99	4.33	1.07	3.80
9.98	2.56	− 8.12	0.70	18.79	− 9.88	0.96	4.55	1.48	3.99
21.90	5.18	− 8.07	0.70	14.91	− 9.87	0.93	4.26	1.98	5.28
29.93	6.22	− 8.01	0.60	12.99	− 9.90	0.90	4.26	1.77	5.61
40.16	7.03	− 8.01	0.53	11.80	− 9.84	0.88	4.21	1.39	5.40
50.69	6.92	− 8.01	0.48	8.24	− 9.84	0.83	4.63	0.82	6.17
63.31	6.26	− 7.98	0.44	6.66	− 9.77	0.81	4.04	0.41	6.13
68.54	4.80	− 8.12	0.41	6.19	− 9.78	0.77	3.24	0.00	5.36
Methanol									
15.06	7.81	− 8.21	0.53	22.51	− 10.22	0.98	4.51	6.44	6.16
44.94	11.62	− 8.01	0.53	14.86	− 10.06	0.92	4.72	5.01	5.55
70.28	6.97	− 8.10	0.47	8.49	− 9.87	0.83	4.42	0.79	4.46

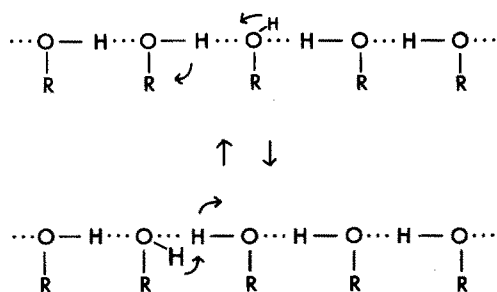


FIG. 3. Schematic representation of orientation of two hydroxyl groups in alcohol chain.

formic acid.^{7,8} If a value of 6×10^{12} Hz is employed tentatively for ν_0 and 17 kJ/mol for ΔH_A which is obtained for ethanol around room temperature,³ a value of 0.17 ns is obtained for τ from Eq. (2). This value is quite reasonable in comparison with that observed for the ethanol-PVP system, which is 0.13–0.28 ns.

In the case of methanol, if 18 kJ/mol is employed for ΔH_A , a value of 0.28 ns is obtained for τ . This value is certainly bigger than that of pure methanol, which is 55 ps. However the relaxation time for the methanol system varies slightly with the polymer concentration. The value extrapolated to zero alcohol concentration is 0.28 ns and in good agreement with that calculated. In this case, the orientation may be supplemented by the mobility of the methyl group of the alcohol. The mobility is suppressed by its surrounding polymer. Therefore, it is reasonable that the relaxation time extrapolated to $c = 100$ wt. %, where the mobility is greatly suppressed, agrees with that calculated. The ethyl group is bigger than the methyl group and its movement may be slower. Therefore effect of the concentration is less than that of the methyl group.

The relaxation time τ_1 for the low frequency process does not depend on the polymer concentration c or on the kind of alcohol. At nearly the same frequency, a relaxation peak due to bound water was already found in the PVP-water system. In this case, if the relaxation strength is normalized by the Debye internal field and the polymer

concentration, it gives almost a constant value over the whole range of polymer concentration examined. The relaxation strength normalized is

$$\langle \Delta \epsilon_1 \rangle_{\text{red}} = \frac{100 \Delta \epsilon_1}{c(\Delta \epsilon_h + \epsilon_\infty + 2)^2}. \quad (3)$$

Values of the normalized strength thus obtained for the ethanol and methanol systems are listed in Table I. They are considerably bigger than that for the water system, which is around 2×10^{-2} .¹ Therefore the low frequency process cannot be attributed to the residual water molecules bonded to PVP. Alcohol molecules are possibly hydrogen bonded to nitrogens of PVP. Orientation of such molecules in an applied field occurs in a different manner from that in the alcohol chain. Hydrophobic attraction between the polymer is another origin of the bound alcohol. Orientation of the hydroxyl group in the bound alcohol may occur after a breakage of the hydrogen bond. Namely, it depends entirely on the rate of the breakage. If alcohol molecules are firmly bound to PVP, the rate will be small and the relaxation time will be long. Micro-Brownian motion of PVP is slow and its dielectric relaxation peak locates at a frequency far lower than the frequency region concerned here.¹ This may give an explanation of the stable bound alcohols.

Alcohol molecules may not have the regular chain structure in the neighborhood of the randomly coiled polymer and the irregularity of the alcohol structure may account for the distribution of relaxation times. This is consistent with the experimental result that β_h decreases with the polymer concentration.

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