

Comparison of Dielectric Relaxations of Water Mixtures of Poly(vinylpyrrolidone) and 1-Vinyl-2-pyrrolidinone

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Microwave dielectric studies on the dynamics of water in poly(vinylpyrrolidone) (PVP)–water mixtures and 1-vinyl-2-pyrrolidinone (VP)–water mixtures were performed to compare the relaxation processes of water in polymer–water and monomeric compound–water mixtures. For the PVP–water mixtures, a relaxation peak for water was observed and the shape of the absorption curve was symmetrical about the logarithm of frequency, which the Cole–Cole equation describes well. In this case, the polymer behaves as a geometric constraint for rotational motion of water molecules, and a variation of the local structure of water yields the symmetrical relaxation curve. On the other hand, one relaxation peak due to the rotational motion of the dipoles of water and VP molecules was also observed for VP–water mixtures. However, the shape of the absorption curve is asymmetric and is described well by the KWW function. Cooperative motion of water and VP molecules resulted in a variation of local structure which is observed as an asymmetric relaxation curve.

Introduction

Despite the complexities of hydrogen-bonded liquids on the molecular level, the principal dielectric relaxation process of water and low molecular weight monohydroxyl alcohols nearly exhibits a practically Debye-type relaxation.^{1–3} This relaxation reflects the behavior of hydrogen-bonded clusters of molecules as large species.^{4–6} The reasonable explanation for this would be that the dielectric strength of water is carried by dipoles of correlated water clusters forming the hydrogen-bonded network patches, i.e., network clusters.

A relaxation process for water observed for the mixtures of water and a randomly coiled polymer shows a symmetric relaxation curve.^{7,8} The width of the relaxation curve and the relaxation time increase with increasing polymer concentration. In the polymer–water mixture, the rotational motion of the water cluster is hindered by the polymer chain. In the cases of PVP–water and poly(vinylmethyl ether) (PVME)–water mixtures, the lower frequency relaxation peak observed in the megahertz region could be assigned to the micro-Brownian motion of the polymer chain.^{9,10} Relaxation times obtained for the micro-Brownian motion are about 1000 times longer than that of pure water.

Kaatze et al. have carried out accurate measurements of aqueous solutions of polymer^{11,12} and small organic compound^{12,13} mixtures in the frequency range between 50 MHz and 70 GHz. They observed one relaxation peak, which was broader than that of pure water, for each aqueous solution and assumed two or more relaxation processes based on the model for the existence of relaxation processes of free water, hydration water, and solute. The complex permittivity of the aqueous solution of 5.53 mol/L of 1-ethyl-2-pyrrolidone was reported, and the relaxation curve was assumed to have the symmetric relaxation time distribution for comparison with the relaxation process of an aqueous solution of PVP.¹² On the other hand, previous dielectric measurements for various kinds of small organic compound–water mixtures^{13,14} rotational motion of

dipoles of water and solute molecules show an asymmetric relaxation curve. According to these experimental results, the dielectric relaxation curve concerned with the dipoles of water shows one relaxation peak, and the curve can be described by assuming one relaxation function. Furthermore, the asymmetric or symmetric relaxation time distribution function is determined by solute molecular size.^{7,8,13,14}

In this work, the difference of the dielectric relaxation process between PVP–water and 1-vinyl-2-pyrrolidinone (VP)–water mixtures is examined. The structure of VP is almost the same as that of the repeat unit of PVP. The concentration dependence of the shape of the relaxation curve and relaxation time of the VP–water mixture are compared with those of the PVP–water mixture in a wide concentration range of 0–85.15 wt % of PVP and 0–100 wt % of VP. The relaxation curves were treated assuming one relaxation process and their shapes will be discussed based on the cooperativity of water and solute molecules.

Experiment

1-vinyl-2-pyrrolidinone (VP) was purchased from Aldrich Chemical Co. Inc. Deionized and distilled water was obtained from Whittaker Bioproducts Inc. VP–water mixtures with the mole fraction of water, X_w , from 0 to 1 were prepared. Dielectric measurements over a frequency range from 100 MHz to 10 GHz were carried out by a time domain reflectometry (TDR) method.^{15–17} The detailed explanations of the apparatus¹⁴ and the procedures^{16,17} of the system have been previously reported. The digitizing sampling scope employed in this work was an HP54124T which involves a step pulse generator with a rise time of 38 ps and 200 mV height and covers a frequency range up to 10 GHz. The experimental error of our TDR measurements was less than 2–3% for the entire frequency range measured such that the complex permittivity measurements are reliable for discussing the shape of the relaxation curve.

The data for the PVP–water mixture were quoted from our previous measurements in refs 7 and 8.

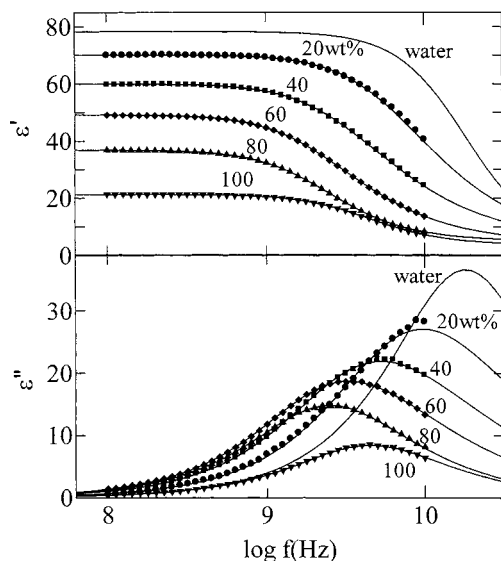


Figure 1. Dielectric dispersion and absorption curves for VP–water mixtures with various concentrations of VP at 25 °C. The solid lines were calculated using eq 1.

TABLE 1: Relaxation Parameters Determined by Eq 1 for VP–Water Mixtures at 25 °C

C_{VP} (wt %)	X_W	$\Delta\epsilon$	$\log \tau$ (s)	β_K	ϵ_∞
10.0	0.982	70.2	−10.96	0.882	4.6
20.0	0.961	65.5	−10.85	0.794	4.6
30.0	0.935	60.7	−10.71	0.766	4.5
40.0	0.903	55.0	−10.58	0.760	4.9
50.0	0.861	50.8	−10.49	0.764	3.6
60.0	0.804	45.0	−10.37	0.798	4.1
70.0	0.726	38.2	−10.27	0.866	5.1
80.0	0.607	31.9	−10.22	0.912	5.0
85.6	0.510	28.8	−10.24	0.932	4.5
90.0	0.407	25.4	−10.26	0.936	4.4
94.8	0.251	22.5	−10.34	0.945	4.1
98.4	0.090	19.6	−10.42	0.951	3.9
100	0.00	17.5	−10.47	0.949	3.7

Results

Figure 1 shows dielectric dispersion and absorption curves with various concentrations of VP–water mixtures at 25 °C. Only one relaxation process is observed clearly in the frequency range measured. The complex permittivity, $\epsilon^*(\omega)$, can be expressed by the Kohlrausch–Williams–Watts (KWW) function^{18,19} as

$$\epsilon^*(\omega) = \epsilon_\infty + \Delta\epsilon \int_0^\infty \left[-\frac{d\Phi(t)}{dt} \right] \exp(-j\omega t) dt \quad (1)$$

and

$$\Phi(t) = \exp\left\{-\left(\frac{t}{\tau}\right)^{\beta_K}\right\}, \quad 0 < \beta_K \leq 1$$

where $\Delta\epsilon$ is the dielectric relaxation strength, τ is the dielectric relaxation time, ϵ_∞ is the limiting high-frequency dielectric constant, and ω is the angular frequency. β_K is the shape parameter of the asymmetric relaxation curve given in the range $0 < \beta_K \leq 1$. $\beta_K = 1$ is the Debye-type relaxation, and a smaller β_K value yields a broader relaxation curve. These parameters, determined by the least-squares fitting procedure, are listed in Table 1. The plots shown in Figure 1 were obtained from the dielectric measurements, and the solid lines were calculated by eq 1 using the parameters listed in Table 1.

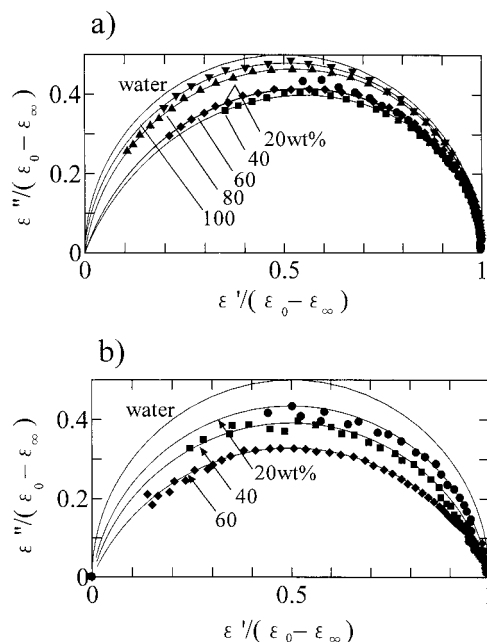


Figure 2. (a) Cole–Cole plots for the VP–water mixtures with various concentrations of VP at 25 °C. The solid lines were calculated using eq 1. (b) The Cole–Cole plots for PVP–water mixtures with various concentrations of PVP at 25 °C. Contribution of the lower frequency relaxation peak due to micro-Brownian motion of PVP chain^{7,8} is subtracted. The solid lines were calculated using eq 2.

In the PVP–water mixture, the higher frequency relaxation process of water is clearly distinguishable from the micro-Brownian motion of the PVP chain.⁹ Dielectric dispersion and absorption curves of water for PVP–water mixtures, $\epsilon_w^*(\omega)$, are described well by the Cole–Cole equation²⁰ given by

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (j\omega\tau)^{\beta_{CC}}} \quad (2)$$

where β_{CC} is the shape parameter of the symmetric relaxation curve in the range $0 < \beta_{CC} \leq 1$. $\beta_{CC} = 1$ indicates the Debye-type relaxation, and a smaller β_{CC} value yields a broader relaxation curve.

It was reported that the extrapolated value to a zero water content of $\Delta\epsilon$ in the PVP–water mixture is zero, and $\Delta\epsilon$ depends linearly on the concentration of PVP.^{7,8} Orientational motion of dipoles on the PVP chain contributes to the process observed at a lower frequency.⁹ Therefore, the relaxation process observed in a PVP–water mixture is due to the rotational motion of dipoles of water molecules. On the other hand, for mixtures with a lower VP concentration, the relaxation parameters approach those of pure water with increasing water content. Furthermore, the value of $\Delta\epsilon$ in pure VP is 17.5. It is reasonable to consider that the relaxation process observed for the VP–water mixture is due to the rotational motion of dipoles of both VP and water molecules. The dielectric relaxation process of rotational motion of dipoles of water molecules for the PVP–water mixture and that of water and VP molecules will be discussed.

The Cole–Cole plots normalized by the relaxation strength, $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$, for the VP–water and PVP–water mixtures are shown in Figure 2. The relaxation strengths were obtained by the fitting procedure. The plots for the VP–water and PVP–water mixtures clearly differ for the slopes at $\epsilon' / (\epsilon_0 - \epsilon_\infty) = 0$ and 1, i.e., the high- and low-frequency sides. The slope of the high-frequency side of both mixtures and low-frequency side

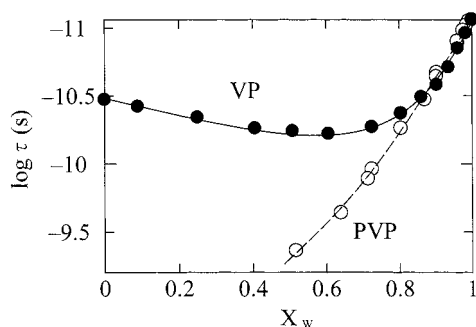


Figure 3. Plots of $\log \tau$ (s) against X_W for VP–water and PVP–water mixtures.

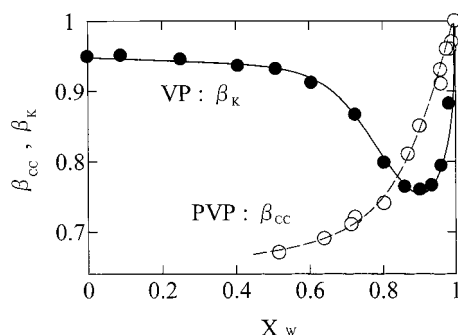


Figure 4. X_W dependence of the parameter for distribution of the relaxation curve. β_K , shown in eq 1, is used for VP–water mixtures and β_{CC} , shown in eq 2, is used for PVP–water mixtures.

of the PVP–water mixtures depend on the solute content. In addition, the PVP–water mixture exhibits symmetric curves. On the other hand, the low-frequency side for the VP–water mixture is not affected by the VP content and displays an asymmetric curve.

X_W dependencies of $\log \tau$ for VP–water and PVP–water mixtures are shown in Figure 3. The values of X_W for the PVP–water mixture are obtained from the mole fraction of water and those of the repeat unit of PVP. In the PVP–water mixture, $\log \tau$ increases with decreasing X_W . In the VP–water mixtures with $X_W > 0.9$, the plot is practically identical to that of the PVP–water mixture. The plots deviate from linear dependence of X_W for $X_W < 0.9$ and show a maximum value at $X_W = 0.6$. For $X_W < 0.6$, $\log \tau$ decreases linearly with decreasing X_W .

Figure 4 shows X_W dependence on the shape parameters of the relaxation curves. The errors for the values of β_{CC} and β_K were less than 0.02 for $0.96 < \beta_{CC}, \beta_K \leq 1$ and 0.01 for $\beta_{CC}, \beta_K < 0.96$. For the PVP–water mixture, β_{CC} decreases linearly with decreasing X_W . In contrast, the VP–water mixture β_K decreases quickly with decreasing X_W for $X_W > 0.9$, and a minimum point is observed at $X_W = 0.9$. β_K increases with decreasing X_W for $0.5 < X_W < 0.9$, and maintains approximately the same value with pure VP in $X_W < 0.5$.

Discussion

Despite the fact that the chemical structure of a VP molecule is almost the same as that of the repeat unit of PVP, the relaxation curve of the VP–water mixture is asymmetric and that for the PVP–water mixture is symmetric. It is reasonable to consider that the origin of the shapes of the relaxation curves of these two mixtures should be essentially different.

The asymmetric relaxation curve is generally observed in glass-forming liquids or local segmental motion of a polymer.²¹ Theoretical approaches for such a relaxation curve suggest that the distribution of the relaxation time originates from the

cooperative motion of moving units.^{22,23} The asymmetric relaxation curve is interpreted as a heterogeneous case such that each moving unit contributes a different value of τ .²² The ensemble average is obtained from the cooperative motion of moving units. The degree of cooperativity is characterized by defining the cooperative domain (CD) in which all dipoles must relax simultaneously. Stronger interaction among the moving units can yield larger CD, and a variation in CD size results in corresponding microscopic relaxation time; this ensemble of microscopic relaxation time exhibits the asymmetric relaxation curve.

The statistical model used to describe the dielectric behavior of binary solutions²⁴ is useful to discuss our experimental results of VP–water mixtures. According to the model, in the mixture with two liquids, three different types of microscopic dynamical environments coexist: the first includes molecules of liquid 1 only, the second includes molecules of liquid 2 only, while in the third one, molecules of both liquids coexist. A different type of short-range interaction (1–1, 2–2, 1–2) will be dominant in each environment.

We combine the above two theoretical approaches^{22,24} to interpret the dielectric behavior of the VP–water mixture. In the VP–water mixture, three kinds of CDs are present. CD_W includes water molecules only, CD_{VP} includes VP molecules only, and CD_{W-VP} includes molecules of both water and VP. The infrared measurement of the PVP–water mixture suggests that the water molecules at the nearest neighbor of the PVP chain can be bound to a carbonyl group or a CN site by a hydrogen bond.²⁵ Furthermore, computer simulations on molecular dynamics studies^{26,27} suggest that on adding hydrophobic molecules to the water system, the water molecules form a clathrate-like structure around the hydrophobic molecule, stabilizing the hydrogen bonds among these water molecules. Thus, it is reasonable to consider that water molecules around the hydrophobic parts of VP or PVP form a clathrate-like structure and the hydrogen bonds among the water molecules should be stabilized. These alterations in the water structure result in a larger relaxation time and a broader relaxation curve of the relaxation process of water in VP–water and PVP–water mixtures. In the VP–water mixture at a certain concentration, τ is larger than that of pure VP and pure water. It can be considered that water molecules form a clathrate structure around the VP molecules such that CD_{W-VP} is stable compared to the CD of pure substances. The concentration of the maximum relaxation time suggests the largest population of CD_{W-VP} .

A broader asymmetric relaxation curve should result from the heterogeneity of the local structure of the mixture. The maximum relaxation time is observed at about $X_W = 0.6$, but the broadest asymmetric relaxation curve is observed at $X_W = 0.9$. It can be interpreted that the population of CD_{W-VP} should be maximum at $X_W = 0.6$ and at $X_W = 0.9$; all VP molecules must interact with water molecules such that the mixture contains no CD_{VP} . Therefore, appropriate contents of CD_{W-VP} and CD_W result in the maximum variation of the local structure of the mixture. The mixture in a water-rich region, $X_W > 0.9$, shows a steep decrease in β_K from unity with decreasing X_W . This should arise from an increase in a fraction of CD_{W-VP} . These interpretations can be effective only when the molecular size of VP allows itself to move cooperatively with water molecules.

The dielectric relaxation curves of water observed for PVP–water mixtures show the Cole–Cole type of relaxation, which is symmetrical in $\log f$. The Cole–Cole equation is originally

introduced empirically to describe the dielectric relaxation curve, and it has a poor theoretical background with regard to the molecular aspect.²⁰ Recently, Monte Carlo simulations were performed on the basis of a random walk of a particle in the structure of fractal dimensions.²⁸ A random walk of a particle in space with geometrical constraint of the fractal structure shows a relaxation of the Cole–Cole type. The local variation of the fractal structure leads to the symmetrical distribution of relaxation time. This model is applicable to the dielectric relaxation of water in the PVP–water mixture, because the PVP chain is too large to move cooperatively with water molecules and the chain behaves as the geometrical constraint to the motion of water molecules. Therefore, local variation of the conformation of a randomly coiled polymer induces the variation of water structure analogous to the Monte Carlo simulation. Furthermore, dielectric relaxation measurements have been performed in order to investigate the effect of confinement on a glass-forming liquid inside a porous glass.^{29,30} Experimental results of these studies indicated that a geometrical restriction results in broadening of the primary relaxation process of the liquids. Therefore, the symmetric broadening of the relaxation curve of small molecules upon geometrical restriction is essential for the dielectric relaxation process for mixtures with large solute molecules.

If concentration dependence of τ and β for the relaxation process of water in the PVP–water mixture are compared to those of the VP–water mixture, a cooperative domain of water in the PVP–water mixture can be introduced. In the PVP–water mixture with lower PVP concentration, two types of microscopic dynamical water environments coexist: CD_W , which includes the water molecules that interact only with water molecules, and CD_{W-PVP} , which includes the water molecules which interact directly with PVP and water molecules which move cooperatively with the water molecules interact directly with PVP. CD_{W-PVP} does not include PVP because the PVP molecules are too large to move simultaneously with water molecules. The relaxation time of CD_{W-PVP} is larger than that of CD_W because of the restricted environment, and the variation in the structure of CD_{W-PVP} is larger than that of CD_W because of the effect of the variation of the local structure of the PVP chain. CD_W decreases and CD_{W-PVP} increases with increasing PVP concentration. In the higher PVP concentration range, CD_W disappears and the mixture contains only CD_{W-PVP} and PVP molecules. A further increase of PVP confines the CD_{W-PVP} . Therefore, relaxation time and distribution of relaxation time increase with increasing PVP because of the stronger restriction due to the PVP chain and the stronger effect of conformational variation of the PVP chain.

The symmetric absorption curve can also be obtained by assuming the Gaussian distribution of the activation-free energy.^{31,32} The curve is quite similar to that obtained using the Cole–Cole equation, and these two types of curves fit well

to the experimental results within the error limits. Generally, Gaussian distribution is observed in an assembly of noncorrelated events. If this idea is applied to the PVP–water mixtures, the relaxation process of water is considered to be due to the water clusters without correlation among surrounding water clusters but is hindered by the PVP chain.

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