Heterogeneous Solvent Dielectric Relaxation in Polymer Solutions of Water and Alcohols

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The dynamics of polymer solutions are heterogeneous. The different molecule sizes and structures cause different mobilities of polymers and solvents. Recently, regarding the heterogeneity of water, two dielectric relaxation processes of water were argued in several supercooled polymer–water mixtures. To investigate whether this is unique to water, we performed broadband dielectric spectroscopy measurements of poly(vinylpyrrolidone)–water (PVP–water), PVP–propylene glycol, PVP–ethylene glycol, and PVP–propanol mixtures with 65 wt% PVP in a temperature range of 123–298 K. For the PVP–water mixture, $\alpha$-relaxation of PVP and two distinct relaxation processes appeared simultaneously: one was the primary relaxation process of water (fast water process) and the other was the relatively small relaxation process (slow process), at a frequency between that of the $\alpha$-process of PVP and the fast water process. The strength ratio of the large fast water and small slow processes remained nearly constant in all the temperatures measured. For the PVP–alcohol mixtures, in addition to the $\alpha$-process of PVP, two or three relaxation processes of alcohol appeared. The primary relaxation process of alcohol above 240 K changed to the small fast secondary process. The small slow processes, which can be recognized below 240 K (the glass transition temperature of the $\alpha$-process of PVP, $T_{g,PVP}$) appears at intermediate frequency between that of the PVP $\alpha$-process and the primary process of alcohol. The small slow process changed to the primary larger process. The properties of the multiple relaxation processes of solvents below $T_{g,PVP}$ in PVP–alcohol mixtures are completely different from those in PVP–water mixture.

Keywords: water, alcohol, polymer, solution, dielectric relaxation, glass transition

INTRODUCTION

Water is the most abundant liquid on Earth and exhibits numerous peculiar properties. The supercooled state and the glassy state of water have been studied extensively [1]. Unfortunately, pure water is easily crystallized; hence, it is impossible to obtain water in a liquid state between 150 and 234 K (the so-called “no man’s land”) [2]. To understand the phenomena in the no man’s land, various types of systems that include water have been examined. The crystallization of water can be avoided by dissolving guest molecules in water [3–23]. Impregnating porous materials with water [24–35] can also prevent water’s crystallization. These systems have been called soft and hard
confinements, respectively. The physics of such systems involves not only the water but also the interaction between water and the guest molecules or the surface of the porous material.

One of the most intriguing and controversial aspects of the dynamics of water from its liquid state to its glassy state is the non-Arrhenius-Arrhenius (non-A-A) crossover [35–37]. This crossover has been discussed based on the observations of water dynamics over an extremely wide range of relaxation times and viscosities. The non-A-A crossover of water dynamics has been observed in various types of aqueous systems, such as aqueous solutions of alcohols, ethylene glycol (EG) oligomers, sugars, polymers, and protein and porous systems that contain water [3, 5–11, 35]. The temperature dependence of the relaxation process of water in these systems changes at a certain temperature, which is called the crossover temperature, \( T_c \), in this paper. \( T_c \) has been observed in the temperature range of 160–260 K, depending on the kind of solute and water content. Below \( T_c \), the relaxation process involves a temperature-independent apparent activation energy classified as the strong glass. Conversely, above \( T_c \), the relaxation time, or viscosity shows a non-Arrhenius temperature dependence. The temperature dependence of the relaxation time of water increases with decreasing temperature; it shows Vogel–Fulcher–Tammann (VFT) temperature dependence [38–40]. In this case, the apparent activation energy of the relaxation process increases with decreasing temperature, which leads to the conclusion that the relaxation process is cooperative, and that the cooperativity of the molecular motion increases with decreasing temperature. The glass-forming materials whose apparent activation energy increases with decreasing temperature are called the fragile glasses [41]. For this reason, the non-A-A crossover of water dynamics has also been called the fragile–strong transition of water.

The non-A-A crossover has been generally observed for the Johari–Goldstein (JG) secondary \( \beta \) relaxation in glass-forming materials at \( T_g \) of the \( \alpha \)-relaxation and also for the \( \alpha \)-relaxation of faster components in dynamically asymmetric binary systems [42–44]. The dynamic crossover of the transport properties of glass-forming liquids has been actively discussed [45]. That study suggested the importance of the dynamic crossover temperature instead of the glass transition on single component glass-forming liquids. In this study, we discuss the role of the glass transition in the dynamic crossover of binary mixtures of a polymer and hydrogen-bonding solvents. In order to discuss the non-A-A crossover of water dynamics in a polymer matrix, in addition to the previous works, we performed broadband dielectric spectroscopy measurements of poly(vinylpyrrolidone)–water (PVP–water), PVP–propylene glycol (PG), PVP–EG, and PVP–1-propanol (PrOH) mixtures with 65 wt% of PVP in a wide frequency over a temperature range of 123–318 K. For the PVP–water mixture, three relaxation processes were observed simultaneously: the slowest process originated from the segmental chain motion of PVP (called the \( \alpha \)-relaxation of PVP), the fastest process originated from the primary relaxation process of water (called the \( \nu \)-process) [3], the relatively small relaxation process at a frequency between those of the \( \alpha \)-relaxation of PVP and the \( \nu \)-process. The temperature dependence of the relaxation time of the \( \nu \)-process exhibits a non-A-A crossover at the glass transition temperature \( T_{g,PVP} \) of the \( \alpha \)-relaxation of PVP. Conversely, the crossover of the relaxation process of alcohol at \( T_{g,PVP} \) in alcohol–PVP mixtures differs completely from that observed in the PVP–water mixture.

**EXPERIMENTAL**

The PVP used in this study was purchased from Sigma Aldrich and had a weight-averaged molecular weight \( M_w = 10,000 \) g/mol. The PG, EG, and PrOH were purchased from Wako Pure Chemical Industries, Ltd. The purities of the solvents (guaranteed reagent grade) were better than 99 % in those mass. Before use, the PVP was purified using an ion-transfer resin and then freeze-dried in a vacuum before being mixed with water or alcohols to reduce dc conductivity and electrode polarization (EP). The aqueous PVP solution was prepared with a PVP concentration \( C_{PVP} = 65 \) wt% in pure water with a conductivity of 18.2 MΩ cm (Milli-Q water) to avoid the crystallization of water. PVP solutions with PG, EG, and PrOH were also prepared with \( C_{PVP} = 65 \) wt%.

Dielectric measurements were carried out in the frequency range from 10 mHz to 3 GHz using an Alpha-A analyzer (Novocontrol, 10 mHz to 10 MHz), a precision impedance analyzer (IA; Agilent Technologies 4294A, 1 MHz to 1.8 GHz, and Agilent Technologies E4991A, 1 MHz to 3 GHz). For the IA and IMA measurements, the temperature was controlled using a Kleemenko Cooler (Bio120; MMR Technologies) and a laboratory-made cooling system with liquid nitrogen, which allowed cooling from 153 to 298 K in steps of 5 K with an accuracy of ±0.1 K. For the Alpha-A analyzer measurement, the temperature was controlled using a Quatro cryosystem (Novocontrol) from 123 to 298 K in steps of 5 K with an accuracy of ±0.01 K. A coaxial cylindrical-cell-type electrode with an outer conductor with an inner diameter of 3.5 mm and an inner conductor with a diameter of 2.0 mm and a length of 2.0 mm (geometrical capacitance: 0.23 pF) was used for the IA and IMA measurements. A coaxial cylindrical-cell-type electrode with an outer conductor with an inner diameter of 24.0 mm and an inner conductor with a diameter of 19.0 mm (geometrical capacitance: 1.11 pF), an interdigitated electrode with 15 µm spacing between the electrodes (geometrical capacitance: 0.9 pF), and a parallel plates electrode with 0.1 mm spacing (geometrical capacitance: 28 pF) were used for the Alpha-A analyzer measurement. To determine \( T_g \), differential scanning calorimetry (DSC) measurements were also carried out over a temperature range from 108 to 298 K, at a rate of 20 K/min using a DSC 7 (PerkinElmer).

**RESULTS**

Figure 1 shows the real and imaginary parts of the complex permittivity of the 65 wt% PVP–PG mixture as a function of frequency. At 298 K, two relaxation steps appear clearly in the real part \( \varepsilon' \): one around 100 Hz and the second around 100 MHz. A loss peak near 100 MHz appears in the imaginary part
As shown in Figure 1, the \( \alpha_{\text{PVP}} \)- and \( h_1 \)-processes shift to lower frequencies with decreasing temperature. Below 260 K, the \( \alpha_{\text{PVP}} \)-process shifts to below our lowest detectable frequency; hence, only the \( h_1 \)-process can be observed for temperatures below 260 K. On further decreasing the temperature, another relaxation process, which is not visible at higher temperatures, appears on the low-frequency side of the \( h_1 \)-process. At 238 K and lower in the imaginary parts, two peaks are clearly visible, both of which originate from the solvent because the sum of their strengths is consistent with the strength of the single relaxation process of the solvent observed at higher temperatures, as shown in the real parts in Figure 1.

Figure 2 shows the dielectric losses at temperatures between 238 and 128 K, in which the additional processes of the solvents can be identified in the mixtures. At 238 K, the \( h_1 \)-process appears in the MHz range. Above 238 K, the single relaxation process, \( h_1 \), of the solvents is visible in all PVP–alcohol mixtures. In addition to the \( h_1 \)-process, one or two processes can be identified at lower temperatures in PVP–alcohol mixtures. We call the solvent processes at higher, medium, and lower frequencies \( h_1 \), \( h_2 \), and \( h_3 \)-processes, respectively. For the PVP–water mixture, the loss peak of the \( \nu \)-process retains its strength and simply shifts to lower frequency with decreasing temperature. In Figure 2, the dotted black curves with arrows show how the peaks shift as the temperature changes. The \( h_1 \)- and \( h_2 \)-processes appear for the PG solution, whereas the \( h_1 \)-, \( h_2 \)-, and \( h_3 \)-processes appear for the PrOH solution.

Although a loss peak was concealed by the large contribution of EP and dc conductivity, the real parts of dielectric permittivity of the PVP–water mixture show a small step that can be observed at a frequency range between the \( \alpha_{\text{PVP}} \)-process and \( \nu \)-process. To clearly illustrate this small step, Figure 3 shows frequency dependences of the real part of permittivity at various temperatures and frequency derivatives of the real part at 218 K. The frequency derivative of the real part has been known to correspond to the same profiles of dielectric loss. The small peak can be seen at the lower frequency side of the prominent peak of the \( \nu \)-process of water at 218 K.

To characterize each process, we fit the data by the following equation:

\[
\varepsilon^\prime (\omega) = \varepsilon_\infty + \sum_{i=1}^{3} \frac{\Delta \varepsilon_{h_i}}{1 + (j\omega \tau_{h_i})^\beta_{h_i}} + \frac{\varepsilon_{\text{EP}}}{1 + (j\omega \tau_{\text{EP}})^\beta_{\text{EP}}} - j \sigma \int_0^{\infty} \frac{d\varphi}{dt} \exp \left( -j\omega t \right) dt
\]

with

\[
\varphi = \exp \left[ -t \left( \frac{t}{\tau_{\text{KWW,\nu}}} \right)^\beta_{\text{KWW,\nu}} \right].
\]

Here \( \omega \) is the angular frequency, \( j \) is the imaginary unit defined by \( j^2 = -1 \), \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_\infty \) is the high-frequency dielectric constant, \( \sigma \) is the dc conductivity, and \( \beta \) and
$\beta_{KWW}$ ($0 < \beta, \beta_{KWW} \leq 1$) are the parameters indicating the broadness of the symmetric and asymmetric relaxation curves, respectively. The subscripts $i = 1$, 2, and 3 refer to $h_1$, $h_2$, and $h_3$ processes, respectively, whereas $\alpha$ denotes the $\alpha$-relaxation process of PVP. This equation includes Cole–Cole relaxation functions [51] for the solvent-processes and EP contribution, one Kohlrausch–Williams–Watts relaxation function [52, 53] for the $\alpha_{PVP}$-process, and a dc conductivity term. Although the $\alpha$-process of the pure PG [54], EG [55], and PrOH [56] has an asymmetric peak shape, we used a symmetric Cole-Cole relaxation function to fit them. It is because that the loss peak of the solvent processes, especially that of the $h_1$-process, cannot be seen clearly to determine whether the loss peak is asymmetry or symmetry. Figure 4 shows the examples of relaxation processes determined using the curve fitting procedures of PVP-PG mixture at 283, 284, and 213 K.

Figure 5 shows the relaxation time, $\tau$, as a function of reciprocal temperature for PVP-water, -PG, -EG, and -PrOH mixtures. In this figure, red and blue symbols indicate $\alpha_{PVP}$- and solvent ($h_1$-, $h_2$-, and $h_3$-) processes. Error bars indicate uncertainty of the fitting procedure as the maximum and minimum values of $\tau$. The plots without error bars indicate that the uncertainty is smaller than the plot size. For comparison, $\tau$ of the pure solvents are plotted as gray solid symbols [56–58]. $\tau$ of $\alpha_{PVP}$- and solvent ($h_1$-, $h_2$-, and $h_3$-) processes are fitted by the Vogel-Fulcher-Tammann (VFT) equation [38–40] and the Arrhenius equation, respectively. The VFT equation is $\tau = \tau_{VF\infty}\exp(A/(T-T_0))$, where $\tau_{VF\infty}$, $A$, and $T_0$ are empirical VFT parameters. The Arrhenius equation is $\tau = \tau_{Arr\infty}\exp(\Delta E/(RT))$, where $\tau_{Arr\infty}$ is the preexponential factor, $\Delta E$ is the apparent molar activation energy, and $R$ is the gas constant. The temperature at which the dielectric relaxation time $\tau$ reaches 100–1000 s can be defined as the glass-transition temperature $T_g$. In terms of a general treatment, we considered defining $T_g$ here as the temperature at which $\tau = 100$ s. The vertical dotted lines in Figure 5 show $T_g$ for the $\alpha$-relaxation process ($T_g,PVP$) for each solution. Moreover, the vertical dashed lines show $T_g$ both $h_2$- and $h_3$-processes in each solution. Note that Figure 5 shows the results of DSC thermograms with the gray bands indicating possible $T_g$ ranges. Moreover, for the PVP–PG and PVP–EG mixtures, DSC thermograms show two steps, at high-$T$ and low-$T$ sides, whereas PVP-water and PrOH mixtures show a single step that corresponds to the high-$T$ side glass transition temperature in other mixtures. The results clearly show that $T_g$ of the $\alpha_{PVP}$-process obtained by BDS falls into the range of the high-$T$ side $T_g$ obtained by DSC, whereas for the PVP–PG and –EG mixtures, $T_g$ of the slowest solvent process falls into the range of the low-$T$ side $T_g$. Note that DSC measurements cannot detect the low-$T$ side $T_g$ for the PVP–water and PrOH mixtures. Steps in the DSC thermograms on the high-$T$ side are placed at almost the same temperature range as that for all mixtures. The $\alpha_{PVP}$-processes observed for all the mixtures are originated from the segmental motion of PVP, and this structural relaxation is related to the glass transition at the high-$T$ side. On the other hand, the slowest process of solvent is related to the glass transition at the low-$T$ side, which indicates that the slowest process of solvent can be interpreted to be the structural relaxation of the solvent.

Although $\Delta \varepsilon$ of the $\alpha_{PVP}$-process monotonically increased with decreasing temperature, $\Delta \varepsilon$ of the solvent processes...
DISCUSSION

In the PVP-PG mixture, the $h_1$-process can be observed at a temperature above $T_{g,PVP}$. Above $T_{g,PVP}$, $\tau_{h1}$ closes to the relaxation time of pure PG. Below $T_{g,PVP}$, the loss peak of the $h_2$-process can be visible. Moreover, the temperature dependence of $\tau_{h1}$ does not undergo a non-A-A crossover at $T_{g,PVP}$. However, at $T_g$ for the $h_2$-process ($T_{g,h2}$), the temperature dependence of $\tau_{h1}$ exhibits a crossover. It is well known that the main relaxation process of pure PG exhibits an asymmetric loss peak with an excess wing at the high-frequency shoulder [54]. For an aged pure PG below its $T_g$, the excess wing has been confirmed to originate from the JG relaxation [54]. For PVP-PG mixtures with up to 50 wt% of PVP, the main PG process corresponds to the $\alpha$-relaxation of PG. The relaxation time for the $\alpha$-relaxation of PG increases with PVP concentration. Another secondary relaxation process has been recognized on the high-frequency side of the $\alpha$-relaxation [50]. On the basis of a comparison between the relaxation times and the strength of the $h_1$- and $h_2$-process in the 65 wt% PVP-PG mixture and the $\alpha$-relaxation of PG in PVP-PG mixtures with 50 wt% of PVP or less, the $h_1$-process above $T_{g,PVP}$ mimics the $\alpha$-relaxation of PG, whereas below $T_{g,PVP}$ the $h_2$-process in the 65 wt% PVP mixture corresponds to the $\alpha$-relaxation of PG. It is also consistent with the glass transition observed by DSC. For the 65 wt% PVP-PG mixture, the $h_1$-process at high temperatures does not continue to the $\alpha$-relaxation, and the loss peak of the $h_2$-process (i.e., the $\alpha$-relaxation of PG) can be clearly identified at a temperature below $T_{g,PVP}$. On the basis of a comparison between the $h_1$-process in the 65 wt% PVP-PG mixture below $T_{g,PVP}$ and the secondary process on the high-frequency side of the $\alpha$-relaxation of PG in PVP-PG mixtures with up to 50 wt% of PVP, the $h_1$-process below $T_{g,PVP}$ corresponds to the secondary process of PG. This interpretation is consistent with the reciprocal temperature dependence of the ratio of the $\Delta \varepsilon$ that is shown in Figure 6B, i.e., the ratio of the $\Delta \varepsilon$ of the $h_1$-$h_2$ process decreases (increases) with decreasing temperature.

For the PVP-EG mixture, in addition to the $\alpha$-relaxation of PVP, only the $h_1$-process can be recognized at temperatures above $T_{g,PVP}$. Below $T_{g,PVP}$, the loss peaks of the $h_2$- and $h_3$-processes can be observed. Moreover, the temperature dependence of $\tau_{h1}$ exhibits no crossover at $T_{g,PVP}$. However, at $T_{g,h3}$, the temperature dependence of $\tau_{h1}$ exhibits a crossover. The $T_{g,h3}$ has uncertainty caused by the relaxation time obtained from broad spectra of the $h_2$-process and the determination by the assumption of a linear extrapolation of the temperature dependence of $\tau_{h3}$. Therefore, we regard the crossover of $T_{g,h3}$ at $T_{g,h3}$ as a crossover at $T_{g,h3}$. The temperature dependence of $\tau_{h1}$ seems to show another weak crossover at $T_{g,h2}$, at which the slope below $T_{g,h2}$ is larger than that above $T_{g,h2}$. The change of the temperature dependence of $\tau_{h1}$ at $T_{g,h2}$ is opposite compared to that at $T_{g,h3}$. This trend also appears $T_{h1}$ for PVP-PG mixture below $T_{g,h2}$. Below $T_{g,h2}$ for PVP-PG mixture and at around $T_{g,h2}$ for PVP-EG mixture, the extremely broad spectra of the $h_1$-processes and the presence of the contributions of high frequency wing of the relaxation processes at lower frequency...
side seem to give rise to this crossover. These results imply that the \( h_1 \)-process and \( h_3 \)-processes correspond to the JG \( \beta \) relaxation and \( \alpha \)-relaxation of EG. This is consistent with the reciprocal temperature dependence of the ratio of the \( \Delta \varepsilon \) of the solvent processes that is shown in Figure 6B as having the same manner as those of the \( h_1 \) - and \( h_2 \)-processes in PVP–PG mixture. The existence of \( h_2 \)-process in the PVP–EG mixture is somewhat peculiar and seems to be due to the mixture's dynamic heterogeneity. Details will be discussed in future works of the concentration dependence study. The \( h_1 \)-process corresponds well with the main process of pure EG [46, 58] at temperatures above \( T_{g,PVP} \).

For the PVP–PrOH mixture, in addition to the \( h_1 \)-process, the loss peaks of the \( h_2 \)- and \( h_3 \)-processes can be observed below \( T_{g,PVP} \). Above \( T_{g,PVP} \), \( \tau_{h_1} \) agrees with the relaxation time of pure PrOH. In contrast to the PVP–PG and EG mixtures, no crossover of \( \tau_{h_1} \) appears in the PVP–PrOH mixture at \( T_{g,h_2} \) and \( T_{g,h_3} \). Even the reciprocal temperature dependence of \( \tau_{h_1} \) of the PrOH–PVP mixture differs from that of the other PVP–alcohol mixtures. The reciprocal temperature dependence of the \( \Delta \varepsilon \) of the \( h_1 \)-process of the PVP–PrOH mixture shows similar behavior to that of other mixtures. Generally, the dielectric response of pure PrOH shows the so-called Debye process, which is attributed to the dynamics of a chain-like supermolecular structure composed of mono-alcohol molecules [59]. The \( h_1 \)-process of the PVP–PrOH mixture at temperatures above \( T_{g,PVP} \) thus relates to the Debye process. According to our previous work that focused on the dielectric relaxation of the PVP-normal alcohol mixtures [47], the Debye process of pure PrOH smoothly connects to the \( h_1 \)-process (in the previous study, it has been denoted as the \( h \)-process). Therefore, we considered that the \( h_1 \)-process at temperatures above \( T_{g,PVP} \) seems to be related to the "modified" supermolecular structure of PrOH. A detailed discussion of the origin of the solvent processes in the PVP–PrOH mixture cannot be given because of the different origins of the \( h_1 \) processes in PVP–PrOH mixture and in the other PVP–alcohol mixtures. This point should be studied further in future investigations.

For the PVP–water mixture, Figure 5A clearly shows that the non-A-A crossover of the \( \nu \)-process occurs at \( T_{g,PVP} \), which is consistent with the results reported in Sasaki et al. [3] and also the results of Cerveny et al. [5]. The non-A-A crossover of the \( \nu \)-process is mostly observed in various systems containing water. The activation energy \( E_a \) of water relaxation in the low-\( T \) Arrhenius region is nearly 50 kJ/mol, which is the universal value for supercooled water in aqueous mixtures [7, 35]. It is true that the PVP–water mixture shows an additional process (slow process) between the \( \alpha_{PVP} \)-process and the primary process of the solvent (the \( \nu \)-process) that can be found in the PVP–PG, PVP–EG, and PVP–PrOH mixtures, i.e., the \( h_2 \) - and/or \( h_3 \)-processes. However, the role of the slow process in the PVP–water mixture is much different from those of \( h_2 \) - and/or \( h_3 \)-processes in the PVP–alcohol mixtures, because the reciprocal temperature dependence of \( \tau_{h_1} \) shows crossover at \( T_{g} \) of \( h_2 \) - and/or \( h_3 \)-processes, and \( \tau_{\nu} \) does not show crossover at the glass transition temperature of the slow process. In addition, the ratios of the \( \Delta \varepsilon \) of the \( \nu \)-process and the slow process are very different from those of the solvent processes in other mixtures. In addition, whereas the DSC thermograms for PVP–PG and -EG mixtures
FIGURE 5 | The corresponding DSC thermograms are also shown above each panel, with the gray ranges indicating the possible glass transition temperatures. Gray plots indicate the relaxation time of pure solvents [56–58]. Error bars indicate uncertainty of the fitting procedures. Plots without error bars have errors within the plot size. Multiple plots for the PVP–water mixture indicate measurements with different electrodes to characterize the additional small process.

FIGURE 6 | The reciprocal temperature dependence of (A) the relaxation strength of the solvent processes and (B) the ratio of the relaxation strength of the solvent processes divided by the summation of the relaxation strength of all solvent processes for each mixture. Black, green, red, and blue plots indicate the data for PVP–water, PVP–PG, PVP–EG, and PVP–PrOH mixtures, respectively. Vertical dashed lines indicate $T_g$ of the slowest solvent process for each mixture. The error bars indicate errors of the fitting procedure.

show two steps that correspond to the glass transition of the $\alpha_{PVP}$- and $h_2$- or $h_3$-process, the DSC thermogram of PVP–water mixture shows a single step that corresponds to the $\alpha_{PVP}$-process. This result suggests that the characteristic properties of the slow process are somewhat different from those of the structural relaxation of water. One possibility of the origin of the slow process is the JG $\beta$-process of PVP because $\tau$ of the slow process shows crossover at $T_g \text{,PVP}$. The origin of the slow process may yet be discovered with further investigation.

One major interpretation of the non-A-A crossover in water-containing systems is the freezing of the solute matrix at $T_g \text{,PVP}$. Above $T_g$, the solute molecules are mobile,
and the relaxation time follows a VFT temperature dependence. The activation energy of solute relaxation, which is related to the cooperativity of the motion of solute molecules, increases with decreasing temperature. The change in the mobility of the solute matrix affects the mobility of confined water; hence, the relaxation time of water also exhibits a VFT temperature dependence. Below \( T_g \), the matrix freezes, then the water environment no longer changes and the relaxation time of water exhibits an Arrhenius temperature dependence [35]. Below \( T_g \), the fluctuation of solute molecules freezes not only for the PVP–water mixture but also for PVP–alcohol mixtures. If the freezing of the solute matrix is the origin of the non-A-A crossover of the solvent, then this must also appear in PVP–alcohol mixtures. Otherwise, the influence of the frozen matrix would differ between water and alcohols. In any case, the solute matrix freezes below \( T_g \) in all mixtures. Note that the freezing of the solute matrix does not always cause a non-A-A crossover.

In addition, the confinement effect by the polymer chains should also exist even above \( T_g \). Because of the relaxation time of the \( \alpha \)-process of PVP is always several decades larger than those of alcohols and water, and the \( \alpha \)-process is essentially frozen matrix even both above and below \( T_g \). Therefore, the freezing of the solute matrix cannot be considered the origin of the non-A-A crossover.

Alternatively, even the non-A-A crossover may be interpreted by invoking the "finite size effect" for spatially confined molecular liquids [35]. Following the Adam–Gibbs theory [61], the size of the cooperative rearranging region (CRR) of the liquid increases with decreasing temperature. On decreasing the temperature, the CRR eventually reaches the size defined as the finite size, at which point the dynamic property of the liquid changes to an Arrhenius temperature dependence. This interpretation is based on the idea that the CRR size cannot exceed the given finite size. For the case of PVP solutions, according to this "finite size effect," the finite size is determined by the freezing of the \( \alpha_{PVP} \)-process. If this is true, then the \( h_1 \)-process in the PVP–EG and PVP–PG solutions should exhibit a crossover at \( T_g \). However, the \( h_1 \)-processes in PVP–EG and PVP–PG solutions do not exhibit a non-A-A crossover at \( T_g \), but rather at \( T_g \) of the \( h_1 \) and/or \( h_2 \)-processes, indicating that the frozen matrix of the \( \alpha_{PVP} \)-process does not serve as a template of confinement for the solvent processes. In addition, even if the \( \tau_{h_1} \) crosses over at \( T_{g,h_2} \) instead of at \( T_g \), the finite size effect cannot describe the discontinuity in the first derivative of the temperature dependence of \( \tau_{h_1} \). When the CRR size reaches the given finite size, \( E_g \) should become fixed, which means that the first derivative of \( \tau \) with respect to temperature related to the confined molecules should be continuous. However, this is not the case. For these reasons, the non-A-A crossover of the solvent dynamics in the mixtures cannot be described by the finite size effect.

One interpretation of the effect of matrix freezing is captured by the Coupling Model (CM). In general, glassy materials show two distinct relaxation processes: the structural \( \alpha \)- and secondary \( \beta \)-processes. Currently, the origin of the \( \alpha \)-process is understood to be a cooperative structural relaxation related to the glass transition. The secondary \( \beta \)-process has been characterized and classified [62]. The dynamics of molecules in glass formers of rigid molecules were investigated in the 1970s by Johari and Goldstein [63, 64]. The secondary relaxation found in rigid molecules with no internal degrees of freedom falls into the category of the JG \( \beta \)-process. The JG \( \beta \)-process cannot be assigned to any relaxation process involving the motion of an isolated part of a molecule. The temperature dependence of the relaxation time for the JG \( \beta \)-process, \( \tau_{JG} \), follows an Arrhenius temperature dependence at temperatures below the glass transition temperature, \( T_g \), where the relaxation time of the \( \alpha \)-process is \( 100–1,000 \) s. The Arrhenius temperature dependence of \( \tau_{JG} \) does not continue at temperatures above \( T_g \) but changes to a VFT temperature dependence. The crossover of \( \tau_{JG} \) can be understood as crossing a boundary of the system from equilibrium to nonequilibrium. CM has also been successfully applied to interpreting the relationship between the relaxation process of water and the \( \alpha \)-relaxation observed in aqueous solutions [7]. According to CM description, it has been suggested that the JG \( \beta \)-process is the precursor of the cooperative \( \alpha \)-process in analogy to the primitive relaxation of the CM. At temperatures far above \( T_g \), a single relaxation process is observed in aqueous solutions of glycerol, EG oligomers, and fructose. At lower temperatures, the single relaxation process separates into two processes. The relaxation process with the smaller (larger) relaxation time originates from the local motion of water molecules (from the cooperative \( \alpha \)-relaxation of solute and water molecules). In this case, the \( \alpha \)-relaxation of water, and that of the solute do not appear individually. The relationship between water relaxation and \( \alpha \)-relaxation mimics that of the JG \( \beta \)-process and the \( \alpha \)-relaxation of various types of conventional glass formers. In other words, the relaxation process of water behaves like the JG \( \beta \)-process, which means that the water molecules in the mixtures move cooperatively with the solute molecules at low temperatures around \( T_g \). For the PVP–water mixture, the relaxation time of (\( \nu \)-process) behaves like the JG \( \beta \)-process because water molecules can move cooperatively with PVP, which is the origin of the \( \alpha \)-relaxation. As a result, the structure, which fluctuates globally as the \( \alpha \)-relaxation, behaves like a matrix for the local fluctuation of water.

In contrast, for the PVP–alcohol mixtures, the relaxation process of alcohol, which follows the \( h_1 \)-process, does not exhibit a non-A-A crossover at \( T_g \). The relaxation processes of the solvent are separated into a local motion (the \( h_1 \)-process for the PVP–PG and PVP–EG mixtures and the \( h_2 \)-process for the PVP–PrOH mixture) and an \( \alpha \)-relaxation (the \( h_2 \)-process for the PVP–PG mixture, the \( h_2 \) and \( h_3 \)-processes for the PVP–EG mixture, and the \( h_3 \)-process for the PVP–PrOH mixture) due to the presence of PVP. In this case, the \( \alpha \)-relaxations originating from PVP and alcohol coexist. For PVP–PG and PVP–EG mixtures, the temperature dependence of \( \tau_{h_1} \) changes at \( T_{g,h_2} \) and/or \( T_{g,h_3} \), which is lower than \( T_g \). This indicates that the \( h_2 \) and/or \( h_3 \)-process corresponds to the fluctuation of the matrix, and the freezing of the matrix affects the local \( h_1 \)-process. Therefore, the temperature dependence of \( \tau_{h_1} \) changes at \( T_{g,h_2} \) or \( T_{g,h_3} \). These results indicate that the \( h_1 \)- and other solvent processes seem to correspond to the JG \( \beta \)-process and the structural \( \alpha \)-relaxation of the solvent, respectively. For the relaxation process of water in...
the PVP–water mixture, the h₁-process in PVP–alcohol mixtures, and the JG β-process in conventional glass formers, the non-A-A crossover of the relaxation time of local motion initiated by the freezing of the matrix is universal.

Based on these results, the peculiarity of water is that the relaxation time of the cooperative motion of water is the same as that of the local chain motion of PVP, implying that water molecules cooperatively move with the PVP chains. For the PVP–alcohol mixtures, the α-relaxation of PVP and that of alcohol appear individually, which means that even alcohol molecules move cooperatively, and this appears as the α-relaxation of alcohol (i.e., an h₂ or h₃-process), although alcohol cannot move cooperatively with PVP chains. The separation of solvent relaxation in binary systems has not been generally observed, although it seems to be brought about by high polymer concentration, which is rarely measured. As seen for the PVP–PG mixtures with 50 wt% PVP and lower, the h₂-process does not appear on the low-frequency side of the h₁-process [50]. Two α-relaxations of PG h₂- and PVP- processes at temperatures far above T₉ are observed continuously down to T₉, and both the PG h₂- and PVP- processes exhibit α-relaxation time with a VFT temperature dependence. In addition to the two α-relaxations, a secondary process can be observed on the high-frequency side of the α-relaxation of PG that corresponds to the h₁-process in the 65 wt% PVP–PG mixture.

CONCLUSION

This paper reports the dielectric relaxation processes observed in PVP mixtures with water and three types of alcohol. The results clearly show the uniqueness of water’s relaxation process. We focused on comparing the relaxation processes of water with those of PG, because PG is a well-known glass former with a simple relaxation map and no crystallization. The presence of the single primary relaxation process of the solvent above T₉,PVP is common to all the solutions measured in this work. At T₉,PVP, the relaxation process of water exhibits a non-A-A crossover, whereas the observation of the multiple relaxation processes of the solvent is common to the three PVP–alcohol mixtures measured. From this point of view, the peculiarity of water is that the relaxation time of the cooperative motion of water is the same as that of the local chain motion of PVP, which means that water molecules move cooperatively with PVP chains. For the PVP–alcohol mixtures, the α-relaxations of PVP and that of alcohol appear individually. The multiple relaxation processes of alcohols remain veiled, and a better understanding of these mechanisms will require more detailed studies on the concentration dependence of the relaxation processes in alcohol–polymer mixtures.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

KS and NS conceived and designed the research and wrote the manuscript. KS, KB, MaT, and MF performed the experiments. KS, KB, MaT, MF, and NS analyzed the data. MiT and HK contributed to designing of the interdigitated electrode. All the others (RK and SY) have contributed to its evolution to the final form.

FUNDING

This study was partly supported by JSPS KAKENHI Grant Numbers 16K05522, 19K14679, 19J02028, and 17K06005 and by the MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2014–2018.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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