

## Effect of Neutralization of Poly(acrylic acid) on the Structure of Water Examined by Raman Spectroscopy

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The structure and property of water in aqueous solutions and cross-linked gels of poly(acrylic acid) (PAA) were investigated by using Raman spectroscopy. Relative intensity of the polarized O–H stretching band (*C*) due to an in-phase collective stretching of O–H oscillators within hydrogen-bonded water clusters was used to estimate degree of water–water hydrogen bonding. The *C* values vs degree of neutralization ( $\alpha$ ) plots showed a maximum at around  $\alpha = 0.3$  in the solutions of PAA with relatively high molecular weight ( $M_w = 50\,000, 500\,000$ ), whereas the *C* value of PAA with relatively low molecular weight ( $M_w = 2000, 5000$ ) decreased linearly with an increase in  $\alpha$ . Defects of water–water hydrogen bonds within the interstitial water surrounded by the polymer chains were suggested in the solutions of PAA with high molecular weight and low degree of neutralization. The network of polymer chain supported by entanglement and hydrogen bonds between carboxyl groups on the polymer chain was destroyed, and concomitant release of interstitial water to bulk induced an increase in the *C* value with an increase of  $\alpha$  at  $\alpha < 0.3$ . Further neutralization brought about the perturbation of water structure because of increase in the concentrations of carboxylate ion and  $\text{Na}^+$ .

### Introduction

The micro- and macroscopic properties of solutions of synthetic and biological polyelectrolytes are determined by the electrostatic interaction between macroions and surrounding small ions including their counterions, intramolecular interaction between ionic groups on a polymer chain, and intermolecular interaction of the macroions. Moreover, interaction between macroions and water has significant effects on the properties of aqueous solutions. Many investigations have been done to reveal the relationship among those intra- and intermolecular interactions, conformation of macroions, and properties of the solutions.<sup>1,2</sup>

Polyelectrolytes are usually classified as anionic and cationic and further subdivided into strong and weak electrolytes in analogy to strong and weak acids and bases of simple electrolytes. A strong electrolyte such as sodium poly(styrenesulfonate) is dissociated into macroion and counterions in aqueous solutions in the whole pH range, whereas a weak polyelectrolyte is ionized only in a limited pH range. Since poly(acrylic acid) (PAA) is a weak polyacid, unneutralized PAA is scarcely ionized in water. However, neutralized carboxyl groups on PAA are almost completely ionized, and therefore, the density of charge on the polymer chain can be tuned by neutralization. Many studies on the properties of aqueous solutions of PAA showed their characteristic dependence on the degree of neutralization ( $\alpha$ ); that is, these properties change discontinuously at  $\alpha = 0.2$ – $0.3$ . For example, there is a maximum or a minimum around  $\alpha = 0.3$  in reduced viscosity<sup>3</sup> and ultrasonic relaxation frequency<sup>4</sup> vs  $\alpha$  curves for PAA solution neutralized with NaOH. These phenomena are interpreted by conformational changes of the macroion and concomitant structural change of hydration water. Though the structural change of the macroions has been revealed by many studies, discussion about the structure of hydration water has been done with few direct observations of water structure in the system. Taking the present situation into consideration, analysis on the structure of water in aqueous PAA solution is highly worthwhile.

Recently, we demonstrated that analysis of the O–H stretching Raman spectrum of water can yield important information on the structure of water in aqueous polymer systems.<sup>5</sup> We proposed a hypothesis that insists that water in both aqueous polymer solutions and gels can be divided into three parts: (1) hydration water, (2) water in spaces surrounded by polymer chains (so-called *interstitial water*), and (3) bulk water. When the size of the interstitial water surrounded by the polymer network is smaller than some critical value, its structure changes to have a relatively lower probability of water–water hydrogen bonding than bulk water.<sup>5</sup> Existence of the interstitial water was also suggested in semidilute solutions of polymers with relatively large molecular weight, in which polymer chains entangled each other and made a pseudonetwork.<sup>6</sup>

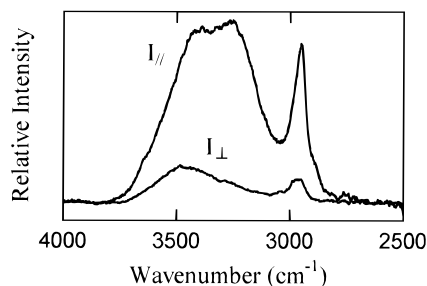
In the present report, the effects of molecular weight of PAA and ionization of carboxyl groups (degree of neutralization,  $\alpha$ ) on the structure of water in aqueous PAA solutions and gels were investigated in detail by using Raman spectroscopy.

### Experimental Section

**Materials.** Poly(acrylic acid)s (PAAs) were purified by ultrafiltration ( $M_w = 2000$  (abbreviation, PAA-2k) (Aldrich, Milwaukee, WI); Amicon Model 8200; membrane, Amicon Diaflo YC05 (exclusion limit  $M_w = 500$ )) or repeated precipitations in water–methanol ( $M_w = 2500, 5000$  (abbreviations, PAA-2.5k and PAA-5k) (Polysciences Inc., Warrington, PA)) or dialysis ( $M_w = 5 \times 10^4, 5 \times 10^5$  (abbreviations, PAA-50k and PAA-500k) (Polysciences); seamless cellulose tubing from Viskase Sales Co.). To prepare a PAA gel, acrylic acid (700 mM) and *N,N'*-methylenebis(acrylamide) (BIS, 7.05–95.45 mM) were polymerized with potassium peroxydisulfate (60 mM) and *N,N,N',N'*-tetramethylethylenediamine (535 mM) in water.  $f_{\text{BIS}}$ , which means molar fraction of BIS ( $f_{\text{BIS}} = [\text{BIS}]/([\text{BIS}] + [\text{acrylic acid (AA)}])$ ), in the reaction mixture was 0.01–0.12. The reaction mixtures were incubated overnight at room temperature, and polymer gels obtained were dialyzed against water for a week. The PAA and PAA gels were subsequently treated with an ion-exchange resin, Amberlite IR-120B ( $\text{H}^+$  type), and finally lyophilized. By the addition of a calculated amount of solution of sodium hydroxide to PAA solutions or

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**Figure 1.** O—H stretching Raman spectra of water in aqueous solutions of PAA at parallel and perpendicular positions.

PAA gels and subsequent lyophilization, PAA (gel) of various degrees of neutralization was obtained.

Propionic acid (Nacalai Tesque, Kyoto, Japan) was purified by vacuum distillation. Sodium propionate (Nacalai Tesque) was recrystallized from methanol. By mixing propionic acid and sodium propionate solutions, propionic acid solution of various degrees of neutralization was obtained. A Milli-Q grade water was used for sample preparation.

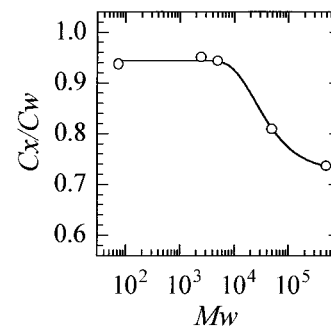
#### Raman Spectroscopic Measurements and Data Analysis.

The Raman spectra were recorded on a NR-1100 (Japan Spectroscopic Co., Tokyo, Japan; light source, argon laser 488.0 nm) with a band resolution of 5 cm<sup>-1</sup>. The relative intensities of collective bands (C) were evaluated from O—H stretching spectra measured at parallel and perpendicular positions to the linearly polarized incident laser beam as described previously.<sup>5</sup>

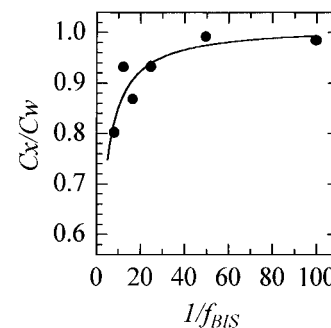
### Results and Discussion

**The Effect of  $\alpha$  on the  $C$  Value of PAA Solutions.** The O—H stretching band of liquid water was observed between 2800 and 3800 cm<sup>-1</sup>. A component centered at about 3200 cm<sup>-1</sup> was highly polarized and diminished in the spectra at the perpendicular position (Figure 1). The polarized O—H stretching band was attributed to the *in-phase* collective stretching of O—H oscillators (*collective band*), which are hydrogen bonded with water molecules nearby in water clusters.<sup>7</sup> The relative intensities of the collective bands (C) are known to be reduced by the decoupling of O—H oscillators. Decoupling of the oscillation occurs (1) when a stretching frequency of an O—H oscillator is largely different from that of the O—H oscillator that is combined by hydrogen bond with the former one and (2) when the hydrogen bond between coupled O—H oscillators is broken by translational or rotational rearrangement of water molecules.<sup>8</sup> In the case of pure water, values of  $C$  are reduced linearly with an increase of temperature by intrinsic hydrogen bond defects.<sup>7a</sup> Since water molecules are restricted in their positions and orientations in hydration shells around solutes, the intensities of the collective band are reduced by the latter mechanism. The smaller ratios of  $C$  values of aqueous solutions ( $C_x$ ) to that of pure water at the same temperature ( $C_w$ ) than unity indicates the break of water—water hydrogen bonds, and  $C_x/C_w > 1$  means enhancement of the hydrogen-bonding structure of water by the solutes.

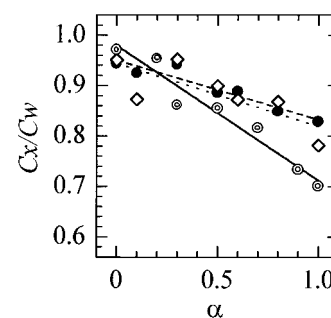
Dependence of  $C_x/C_w$  values of PAA solutions on the molecular weight of the polymers is shown in Figure 2. Those of PAA gels as a function of the reciprocal of the molar fraction of BIS in the gels ( $1/f_{BIS}$ , proportional to the distance between cross-linking points) are plotted in Figure 3. The  $C_x/C_w$  values of PAA solutions ( $\alpha = 0$ ) are almost constant for polymers with relatively low molecular weight and decreased with an increase of molecular weight at the higher molecular weight region (PAA-2.5k = PAA-5k > PAA-50k > PAA-500k). Similar dependence was also observed in  $C_x/C_w$  vs  $1/f_{BIS}$  curve; that is, the values are almost constant for gels with relatively low density of cross-linkage and decreased with an decrease of



**Figure 2.** Effect of molecular weight of PAA on the  $C_x/C_w$  values of PAA solutions. (molar fraction of monomeric residue,  $p_x = 0.05$ ).



**Figure 3.** Effect of densities of cross-linkage of PAA gels on the  $C_x/C_w$  values of the gels (5 wt %). The  $1/f_{BIS}$  is the reciprocal of the molar fraction of BIS in the gels.

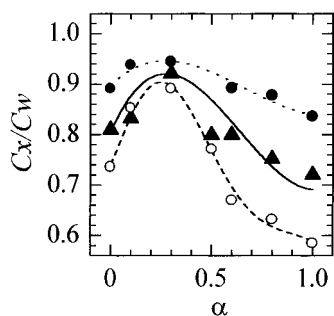


**Figure 4.** Effect of  $\alpha$  on the  $C_x/C_w$  value of aqueous solutions of PAA ( $M_w = 2500, 5000$ ) and propionic acid at  $p_x = 0.05$  and 25 °C:  $\diamond$ , PAA-2.5k;  $\bullet$ , PAA-5k;  $\circ$ , propionic acid.

$1/f_{BIS}$  above critical density. Since the concentration of the monomer unit was constant for all of the solutions and gels, probability of the defects in the hydrogen-bonding network of water in the vicinity of the polymer chains might be similar. Existence of the second kind of perturbed water, the *interstitial water*, is strongly suggested in the solutions and gels of PAA with relatively high molecular weight or high density of cross-linkage.

Figure 4 shows the effect of the degree of neutralization ( $\alpha$ ) on the  $C_x/C_w$  values of aqueous solutions of PAA ( $M_w = 2500$  and 5000), in which the *interstitial water* does not exist. The  $C_x/C_w$  values of solutions of propionic acid, which is analogous to the monomer unit of PAA, are also plotted for comparison. The  $C_x/C_w$  values of those solutions monotonously decreased with an increase in  $\alpha$ . Since the concentration of PAA or propionic acid is constant in the solutions, the monotonous decrease in the  $C_x/C_w$  value might be due to the perturbation of water structure caused by Na<sup>+</sup> and carboxylate ions, quantities of which increase with  $\alpha$ .

Dependence of  $C_x/C_w$  values of the solutions of PAA with high molecular weight ( $M_w = 5 \times 10^4, 5 \times 10^5$ ) on  $\alpha$  was different from that of low molecular weight PAA solutions (Figure 5). With the increase in  $\alpha$ , the  $C_x/C_w$  values of the solutions of PAA-50k and PAA-500k increased correspondingly

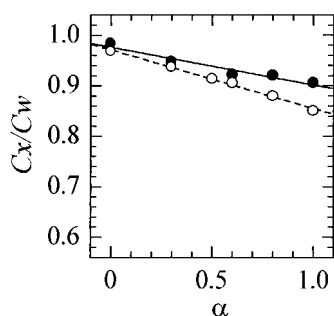


**Figure 5.** Effect of  $\alpha$  on the  $C_x/C_w$  value of aqueous solutions of PAA ( $M_w = 5 \times 10^4$ ,  $5 \times 10^5$ ) at 25 °C: ●, PAA-50k ( $p_x = 0.02$ ); ▲, PAA-50k ( $p_x = 0.05$ ); ○, PAA-500k ( $p_x = 0.05$ ).

**TABLE 1:  $C_x/C_w$  Values of Solutions of PAA Neutralized with Alkali Metal Ions and Those of Alkali Chloride Solutions**

anion/cation	$C_x/C_w$			
	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Cs}^+$
PAA-50k <sup>a</sup>	0.83	0.72	0.66	
$\text{Cl}^-$ <sup>a</sup>	0.60	0.68	0.70	0.81

<sup>a</sup> Measured with  $p_x = 0.05$  solutions at 25 °C.



**Figure 6.** Effect of  $\alpha$  on the  $C_x/C_w$  value of aqueous PAA gels ( $f_{\text{BIS}} = 0.01$ ) at 25 °C: ●, 5 wt %; ○, 20 wt %.

below  $\alpha = 0.3$  and decreased above  $\alpha = 0.3$ . These phenomena indicate that perturbation of the water structure was once reduced by the presence of a small amount of carboxylate ions and  $\text{Na}^+$ . Further increase in  $\alpha$  brought about the destruction of hydrogen bonds in the network structure of water in PAA solutions. Figure 5 also shows that the maximization of the  $C_x/C_w$  values around  $\alpha = 0.3$  was observed in the solutions of PAA-50k at low concentration (molar fraction,  $p_x = 0.02$ ) and that changes in  $C_x/C_w$  values were less significant than those at  $p_x = 0.05$ .

The  $C_x/C_w$  values of PAA completely neutralized with LiOH, NaOH, or KOH decreased with an increase in the radius of the alkali metal ions as shown in Table 1 ( $\text{LiPAA} > \text{NaPAA} > \text{KPAA}$ ). The result was contrary to the dependence of the  $C_x/C_w$  value of alkali chloride solutions on the radius ( $\text{LiCl} < \text{NaCl} < \text{KCl} < \text{CsCl}$ ). As will be discussed later, the differences in the strength of electrostatic interaction between carboxylates on the polymer chains and alkali metal cations and in the extent of accumulation of the cations around macroions may be the most responsible factors for the apparently opposite behavior of the polyelectrolyte solutions to that of simple electrolyte solutions.

The  $C_x/C_w$  value of PAA gel cross-linked with  $f_{\text{BIS}} = 0.01$  continuously decreased with an increase in  $\alpha$  in a similar manner with the solutions of PAA-5k and PAA-2k (Figure 6).

**Dependence of Conformation of PAA Chains and Water Structure on  $\alpha$ .** Characteristic dependence of the  $C$  values of PAA solutions on  $\alpha$  can be rationalized by a structural change in the polymer chain at around  $\alpha = 0.3$ . The slightly neutralized polymer chains are considered to be more extended than unneutralized ones because of electrostatic repulsion between

negative charges on the polymer. In the high  $\alpha$  region, oppositely charged counterions may be strongly attracted by the charged polymer chain due to a high charge density on PAA chain. A recent neutron and X-ray scattering experiment on poly(methacrylate) solutions showed a hydration layer between the charged backbone and condensed counterions.<sup>8</sup> Distribution of counterions around polyelectrolytes can be described by various models, for example, the Oosawa-Manning model.<sup>9</sup> The linear charge density on the polyion is described by the charge density,  $\xi$ , which is the ratio of the electrostatic energy between neighboring charges on the chain to the thermal energy.

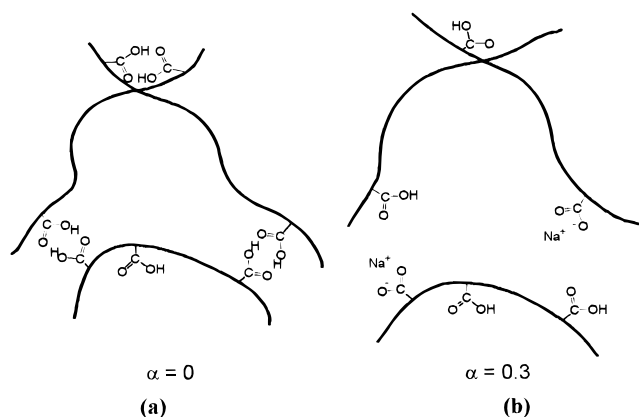
$$\xi = e^2/4\pi\epsilon_0\epsilon A kT = \lambda_B/A \quad (1)$$

$A$  denotes the distance between neighboring charged beads on the chain and  $\lambda_B$  is the Bjerrum length, the value of which in water at 25 °C is about 7.2 Å. For  $A < 7.2$  or  $\xi > 1$  a certain fraction of counterions is clustered around the polyion. With an assumption that the length of each vinyl unit is as long as 2.54 Å (all-trans conformation),  $A$  becomes smaller than  $\lambda_B$  when a carboxylate anion exists every 2.83 units along PAA chain. The condition is satisfied at  $\alpha > 0.35$ .<sup>10</sup> The model indicates that neutralization above  $\alpha > 0.35$  causes an accumulation of counterions around the macroion, which prevents increase in effective charge on the macroion.

Actually, many studies showed that PAA underwent a conformational change driven by electrostatic interaction at  $\alpha = 0.2$ – $0.3$ . Sakamoto et al. showed that there was a maximum around  $\alpha = 0.3$  in reduced viscosity vs the  $\alpha$  curve for PAA solutions neutralized with NaOH.<sup>3</sup> Ikegami showed that the slope of refractivities of PAA solutions vs the  $\alpha$  curve became steeper above  $\alpha = 0.3$  than that at  $\alpha < 0.3$  and suggested a structural change of hydration water around the polyion.<sup>11</sup> Mathieson and McLaren showed that there are two different conformations denoted PAA(a) and PAA(b) and that PAA(a) is intact up to  $\alpha = 0.22$  and is completely converted into PAA(b) above  $\alpha = 0.75$ .<sup>12</sup> Kato et al. showed that there was a shallow minimum at  $\alpha = 0.2$ – $0.3$  in the plot of ultrasonic relaxation frequencies vs  $\alpha$ .<sup>4</sup> In the early studies these phenomena were interpreted to show that chain stiffness increases with ionization, and it has been suggested that in the extreme case the chain becomes fully stretched out like a rod. Recent studies by Walczak et al. on polarized Raman spectra of the C–H stretching region of PAA, however, showed that the change in chain stiffness is not rather significant and the macroion is not fully stretched out even at  $\alpha = 1$ .<sup>13</sup> By the very careful viscometric measurements Yamanaka et al. also concluded that sodium poly(styrenesulfonate), a strong polyelectrolyte, is not fully stretched even at infinite dilution.<sup>14</sup>

If we assume that accumulation of counterions and conformational change in PAA chains by themselves have significant effect on the structure of water around them, the maximization of the  $C_x/C_w$  value near  $\alpha = 0.3$  has to be observed even in the solutions of PAA with low molecular weight. It is contrary to the experimental results shown in Figure 4. Consequently, the molecular weight dependence of  $C_x/C_w$  vs  $\alpha$  curve could be accounted for by the presence or absence of the *interstitial water* in a similar manner as we reported previously.<sup>5,6</sup>

As is well-known, each polymer chain is isolated from others in dilute solutions, but when the concentration of the polymer is higher than some crossover value ( $c^*$ ), polymer chains entangle each other and make a pseudonetwork.<sup>15</sup> The value of  $c^*$  decreases with an increase in molecular weight. Moreover, two protonated carboxyl groups on PAA chain are able to form an inter- or intrachain hydrogen bond and act as a temporal cross-linkage.<sup>16</sup>



**Figure 7.** Schematic structure of PAA in aqueous solution at (a)  $\alpha = 0$  and (b)  $\alpha = 0.3$ .

PAA chains might be isolated from others in the solutions of PAA-2k and PAA-5k at  $p_x = 0.05$ , and so the interstitial water does not exist even at  $\alpha = 0$ . Structurally perturbed water, therefore, could be considered to locate principally in the hydration shell around the polymer chains and counterions. The monotonous decrease of the  $C_x/C_w$  value, therefore, can be simply attributed to the hydrogen bond defects, which are proportional to the concentrations of counterion and carboxylate anion.

Solutions of PAA-50k and PAA-500k were semidilute solutions at  $p_x = 0.05$ , and PAA chains form a pseudonetwork structure due to entanglement of the polymer chains. In addition, parts of protonated carboxyl groups on PAA dissolved in water form hydrogen bonds with one another at low  $\alpha$  (Figure 7a).<sup>19</sup> The structure of water surrounded by the polymer network may be disturbed at low  $\alpha$ . However, the extension of polymer chains caused by the neutralization induces the destruction of inter- and intramolecular hydrogen bonds between carboxyl groups (Figure 7b), and the interstices are diminished. Consequently, the interstitial water turns to bulk water, and the enhancement of long-range coupling of hydrogen bonds between water molecules induces the increase of the  $C_x/C_w$  value. When the concentration of counterion increases further, however, both hydration water around the counterions and the extended anionic polymer molecules destroy the water structure, resulting in the decrease in the  $C_x/C_w$  values. Monotonous decrease in  $C_x/C_w$  of PAA gel, in which polymer chains are fixed by cross-linkage, also supports the hypothesis.

**Influence of Properties of Counterions.** Influence of properties of counterions on the structure of water in aqueous polyelectrolytes, in general, can be divided into (1) a direct interaction between the counterions and water molecule and (2) a change in the interaction between the polyelectrolyte and counterions, causing a change in conformation of the polymer chains or association state of polymer chains, which may affect the structure of water (indirect influence).

As for the interaction between water and alkali metal ions as counterions,  $\text{Li}^+$  and  $\text{Na}^+$  are known to be positively hydrated, whereas alkali metal ions larger than  $\text{Na}^+$  ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) are negatively hydrated.<sup>17</sup> It was previously reported that viscosities of aqueous sodium salt solutions are higher than that of pure water, whereas those of potassium are lower.<sup>18</sup> These facts indicate that the interaction of smaller alkali metal ions with water molecules is stronger than that of larger ions in aqueous solutions. Lower  $C_x/C_w$  values of smaller alkali metal ions than those of larger ions indicate that the smaller ions interact with water more strongly and disturb the structure of water more significantly than the larger ions.

As for the interaction between polyelectrolytes and counterions, it is well-known that smaller alkali metal ions interact

more strongly with macroions than larger alkali metal ions.<sup>10,19</sup> Tondre and Zana measured molal volumes of alkali metal salts of polyelectrolytes and pointed out that the fraction of counterions bound to PAA or poly(maleic acid-co-methyl vinyl ether) increased with a decrease in the size of the metal ions.<sup>20</sup> Eisenberg et al. reported that the glass transition temperature of NaPAA (251 °C) is higher than that of KPAA (194 °C).<sup>21</sup> Van der Maarel et al. showed that the nuclear magnetic relaxation rates of water ( $1/T_1$ ) in PAA solutions with various counterions increase with decreasing size of cation ( $\text{Li}^+ > \text{Na}^+ > \text{K}^+ = \text{Rb}^+$ ).<sup>10</sup> They interpreted the result as an increase in local water density around macroions induced by accumulation of counterions. Electric field intensity of smaller counterions on the surface is higher than that of larger ones and the counterion accumulates closer to the charged polymer chain than the larger one. As a result, induced increase in local water density close to the macroion is more significant for the smaller ion. A reduction of the reorientational mobility of the electrostricted water molecules to a large extent causes an increase in relaxation rates. On the other hand, accumulation of the ions may induce overlap of hydration shells of ions, which reduces effective volume of the shell per ion, in which the degree of water–water hydrogen bonding is smaller than that in pure water. This is one of possible explanations for the experimental result that the  $C_x/C_w$  values for PAA salts were in the opposite order to those for alkali metal chlorides.

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