

## 단신

### 폴리아크릴산/H<sub>2</sub>O 혼합물에서 H<sub>2</sub>O 열적 거동에 미치는 이온의 영향

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### The Effect of Ions on Thermal Behaviors of Water in Poly(acrylic acid)/Water Mixtures

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**Abstract:** Thermal behaviors of water in the poly(acrylic acid) (PAA)/water mixtures with 0.1 M NaCl, HCl, and NaOH were investigated by DSC. It showed that adding ions in the mixtures affected the crystallization of water evidently. Compared with the PAA/water mixtures, the  $T_m$  of freezable bound water in the mixtures with ions moved to lower values and varied with different cations and anions, due to the stabilization or destabilization of the hydrogen-bonding hydration between polymers and water molecules through ionic hydration. The content of non-freezable bound water in the non-crystalline phase of the PAA/water mixtures with ions was not constant, it increased with total water content gradually, owing to the more binding sites created by ions. The ions could change the distribution of different states of water in the polymer aqueous solutions evidently.

**Keywords:** bound water, poly(acrylic acid), differential scanning calorimetry, ions.

## Introduction

Hydrophilic polymer aqueous solutions have been applied in many areas during recent years.<sup>1</sup> The properties of water such as the melting point and crystallization temperature can be changed in the presence of a polymer, depending on the chemical or physical interactions with aqueous polymers. Based on the difference between the properties of water in

the polymer aqueous solutions and those of bulk water,<sup>2,3</sup> the classical view proposes that water molecules absorbed in polymer divide into three different states with distinctly various thermodynamical or dynamical properties: (i) free water, (ii) freezable bound water and (iii) non-freezable bound water.<sup>4,5</sup> The chemical structure of polymer repeating unit,<sup>6</sup> the degree of network in polymer hydrogels<sup>7</sup> and the composition of copolymers and temperature<sup>8</sup> were found to influence the distribution and amounts of different states of water in polymer aqueous solution.

It was reported that the adding ionic salts could change the distribution of bound and free water, creating more bound water through providing additional water binding sites,<sup>9,10</sup> due to the ionic hydration. In present work, poly(acrylic acid) (PAA) aqueous solutions with 0.1 M HCl, NaOH, NaCl aqueous solutions were used, and the melting curves and melting enthalpies were obtained by DSC to investigate the effect of ions on water crystallization in PAA/water mixtures.

## Experimental

**Materials.** Poly(acrylic acid) and water for HPLC (residue < 0.0003%) were purchased from Sigma-Aldrich. The NaCl, NaOH and HCl were obtained from Tianjin KeWei Company in China. The  $M_w$  of the polymer is  $1.25 \times 10^6$ . All the materials were used without purification.

All the four polymer materials were heated at 60 °C for about 1 h, then put them in the vacuum oven with phosphorus oxide powder (P<sub>2</sub>O<sub>5</sub>) at 80 °C for 24 h, in order to chemically react with the evaporated water molecules, which made it sure that there was no water left in materials. The dried PAA materials were obtained. The 0.1 M NaCl, NaOH and HCl aqueous solutions were also made.

**DSC Measurements.** A whole range of compositions of DSC samples (2–6 mg) were prepared by adding determined amounts of 0.1 M NaCl, NaOH and HCl aqueous solutions to dried PAA in aluminum sample pans directly, subsequently the samples were hermetically sealed in the aluminum pan quickly and were stored at room temperature for several days before analysis, in order to allow them to equilibrate and homogeneous mixtures were obtained. Sample weight was measured before and after calorimetric analysis to ensure the integrity of the hermetic seal. The water content ( $w_c$ ) was calculated from the following equation:

$$w_c = \frac{w_w}{w_w + w_p} \times 100 \text{ wt\%} \quad (1)$$

where  $w_w$  is the weight of added water,  $w_p$  is the weight of

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dried polymer. Calorimetric measurements were carried out with a Perkin–Elmer Diamond DSC equipped with a mechanical cooling system. High purity indium and Hg were used for temperature calibration and indium standard was used for calibration of heat flow. The samples were cooled down from 20 to  $-50\text{ }^{\circ}\text{C}$  at a  $10\text{ }^{\circ}\text{C min}^{-1}$  and reheated to  $20\text{ }^{\circ}\text{C}$  at the same rate. The melting temperatures ( $T_m$ ) were obtained as the onset values of the corresponding exothermic and endothermic peaks. The mass fraction of the freezable water including both free water and freezable bound water,  $w_f$ , was determined as:

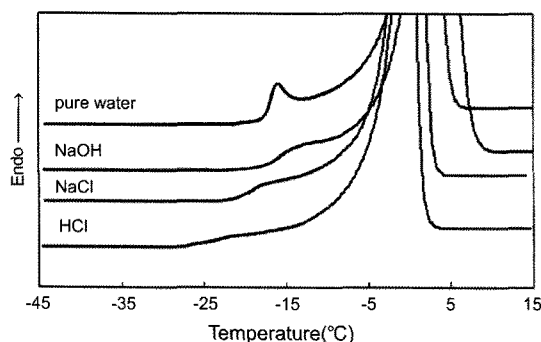
$$w_f = \frac{\Delta H_f}{\Delta H_m} \times 100 \text{ wt\%} \quad (2)$$

where  $\Delta H_f$  is the melting enthalpy of freezable water obtained by DSC measurement and  $\Delta H_m$  is the standard enthalpy of pure water as  $334\text{ Jg}^{-1}$ . The mass fraction of freezable water ( $w_f$ ) was subtracted from the total water content ( $w_c$ ) to calculate the mass fraction of non-freezable water ( $w_n$ ):

$$w_n = w_c - w_f \quad (3)$$

## Results and Discussion

Figure 1 displays the DSC curves of the PAA/water mixtures with different solvents. It displays that different solvents in the solutions change the DSC results evidently. As to the mixture with NaOH aqueous solution, the melting point ( $T_{m1}$ ) of ice crystals corresponding to the freezable bound water is nearly the same as that of PAA/pure water mixture. For the mixture with NaCl aqueous solution, the  $T_{m1}$  is a little smaller than that of water in the PAA/pure water mixtures. However, for the mixture with HCl aqueous solutions, the  $T_{m1}$  decreases evidently. DSC curves show that the ions in the



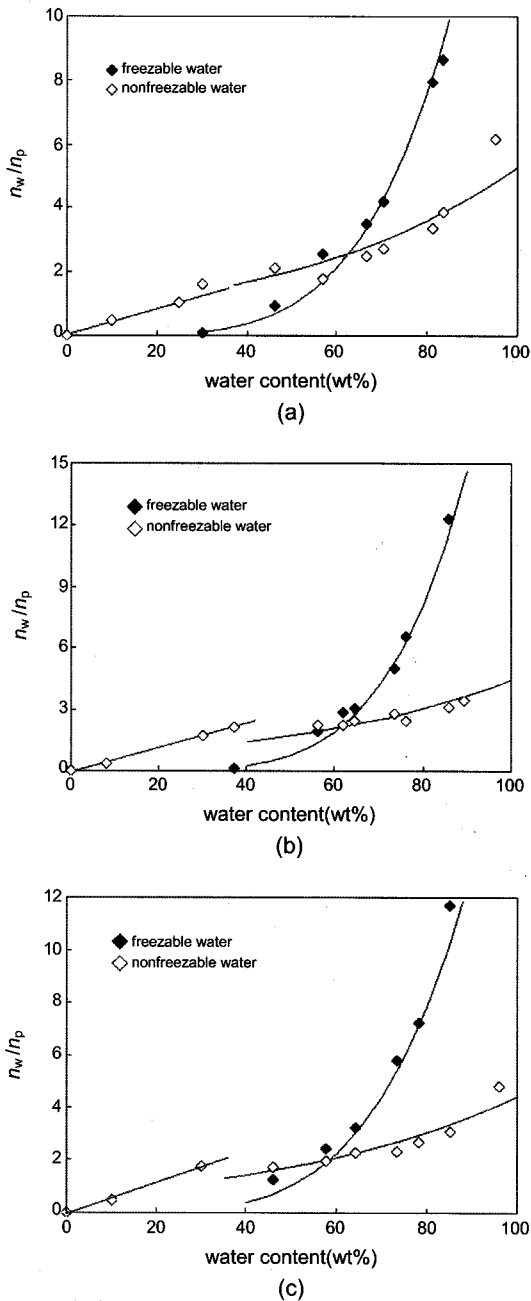
**Figure 1.** DSC curves of the PAA/water mixtures with different solvents.

solutions have an evident effect on the calorimetric behaviors of water in PAA/water mixtures. This behavior is interpreted by stabilization or destabilization of the hydrogen-bonding hydration through ionic hydration.<sup>11</sup> In the case of hydration to anions, positive charge on the water hydrogen decreases and negative charge on the water oxygen increases, which are corresponding to the decrease in the ability of electron-pair acceptance (EPA) and the increase in the ability of electron-pair donation (EPD) of water, respectively.<sup>12</sup> Because the hydrogen bonding interaction of PAA is from carboxyl oxygen, a decrease of EPA by anions can make a destabilization of the hydration, while an increased EPA by hydration to small cations would result in stabilization of the hydrogen bonding interaction. The cations specificity is much less significant than that of anions,<sup>13</sup> since the cations are repelled from the interface irrespective of ion sizes. When NaOH is in the solution, it reacts with the  $-\text{COOH}$  groups on the polymer chains of PAA. As the amount of NaOH is smaller than that of PAA, the pH value of the solution  $<7$  and the resultant solution is acidic. The  $\text{Na}^+$  stabilizes the hydration of PAA to water, so the  $T_{m1}$  is almost the same as that of PAA/water mixture. As to the mixture with NaCl,  $\text{Cl}^-$  destabilizes the hydration of PAA to water by decreasing EPA, the stabilization and destabilization occur at the same time. Due to the larger ion specificity, the destabilization is more significant than stabilization, the ions hydrate with water molecules and the structure of freezable bound water is broken, the  $T_{m1}$  becomes lower. For the mixture with HCl, there was only anions specificity in the solutions,  $\text{Cl}^-$  destabilizes the hydrogen bonding between PAA and water molecules, the anions form ion clusters with water molecules,<sup>14</sup> which influence the crystalline structure of the ice corresponding to the freezable bound water and result in the lowest  $T_m$  of freezable bound water.

Meanwhile, the width of melting peak of the crystals corresponding to the free water is various with different ions. It was found that the ion specificity could result in the swelling or deswelling in polymer hydrogels.<sup>11</sup> If the  $M_w$  of the polymer is high, the polymer/water mixtures could be considered as pseudo networks approximately,<sup>15</sup> thus the properties of the mixtures are close to those of the polymer gels. For the mixture with NaOH, the width of main melting peak is the largest, due to the swelling of the polymer/water mixtures by ion specificity. The swelling resulted in a larger water distribution which caused a wider melting peak. As to the NaCl and HCl, the destabilization is the main effect and the polymer aqueous solutions deswell due to the anions specificity. The resultant deswelling mixtures make a narrower free water distribution and the width of melting peak is smaller than that

of the mixture with NaOH. DSC traces of the PAA/water mixtures with different ions indicate that the ions have a big effect on the water crystallization in PAA/water mixtures, especially the crystallization of bound water. This is ascribed to the fact that the ions specificity affects the hydrogen bonding between water and polymer and the structure of freezable bound water is broken.

Figure 2 displays the molar ratio of non-freezable water and freezable water to polymers in PAA/water mixtures with



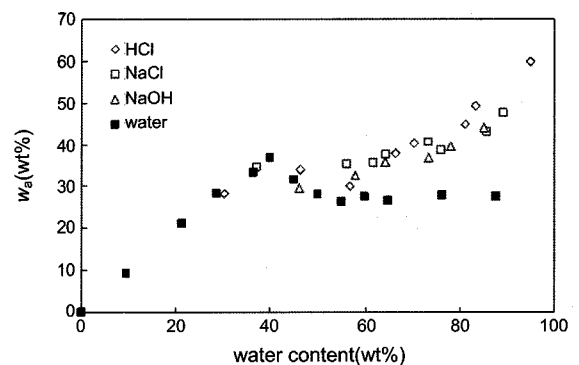
**Figure 2.** The molar ratio of non-freezable water and freezable water to polymer repeating units in PAA/water mixtures with different solvents. (a), (b), (c) are solutions with HCl, NaCl and NaOH, respectively.

different solvents. It is evident that the number of freezable water for each polymer repeating unit increases greatly with total water content in all mixtures with different solvents. At high water content, the molar ratio of freezable water to polymers is higher than 10. At the same time, the molar ratio of non-freezable bound water presents a different dependence on water concentration. The molar ratio of non-freezable bound water to polymer increases linearly with total water content at low water concentration. When the freezable water forms in the solutions, the molar ratio of non-freezable water to polymer increases with total water content in a nonlinear relation. This result is quite different from the one in the literature<sup>6</sup> that when the water content is higher than 40 wt%, the molar ratio of non-freezable water to polymer is constant, regardless of the total water content. The reason may be that the ions added in the solutions could arrest the crystallization of water in the PAA/water solutions. With increasing total water content, the amount of ions added in the PAA/water mixtures increases evidently, which cause more water molecules to bind with ions, thus more non-freezable water is created in the mixtures.

Figure 3 shows the mass fraction of non-freezable bound water in the non-crystalline phase of the PAA/water mixtures with different ions,  $w_a$ . The non-crystalline are composed of non-freezable bound water and PAA, which interact with each other through strong hydrogen bonds. The  $w_a$  was obtained by the following equation:

$$w_a = \frac{W_c - W_f}{1 - W_f} \times 100 \text{ wt\%} \quad (4)$$

It is clear that the ions in the PAA/water mixtures affect the content of non-freezable bound water in the mixtures greatly. For the ions-free mixtures, the  $w_a$  increases up to 40 wt% water content and then remain constant, irres-



**Figure 3.** The mass fraction of non-freezable bound water in non-crystalline phase of PAA/water mixtures with different solvents.

pective of the total water content when  $w_c \geq 50$  wt%, which have also been reported in other aqueous polymer solutions.<sup>6,16</sup>

The ions added in the mixtures create more bound water by providing additional water binding sites, and with the water content in the mixtures increases, the  $w_a$  increases gradually. The mixtures with HCl presents a larger  $w_a$  than the other systems at the same water content, revealing that compared with NaCl and NaOH aqueous solutions, the HCl created more non-freezable bound water, due to the ion-water clusters formed by ionic hydration. The result shows that adding ions in the polymer aqueous solutions may be a simple way to change the distribution and amounts of free water and bound water.

### Conclusions

Thermal behaviors of water in the PAA/water mixtures with 0.1 M NaCl, HCl and NaOH were investigated by DSC. The result indicated that the ions in the mixtures affected the crystallization of water evidently. The  $T_m$  of freezable bound water in the mixtures with ions moved to lower values and varied with different cations and anions compared with those of the PAA/water mixtures, due to the stabilization or destabilization of the hydrogen-bonding hydration between polymers and water molecules through ionic hydration. The content of non-freezable bound water in the non-crystalline phase of the PAA/water mixtures with ions was not constant, which was different from the mixtures without adding ions. It increased with total water content gradually, owing to the more binding sites created by ions. The ions could change the distribution and amounts of different states of water in the polymer aqueous solutions evidently.

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