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Hydration of Poly(Acrylic Acid) Potassium Salts

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Summary

Drying and water uptake of poly(acrylic acid) potassium salts with different degrees of neutralization were studied. The slowing down of drying speed in solid state was not due to Tg but due to the difficulty of the release of water molecule bound to two metal carboxylates or carboxyls. The equilibrium water uptake decreased below 25 % neutralization, whereas it increased linearly with neutralization beyond 25 %. The bending in the plot of equilibrium water uptake was explained by the appearance of vacant sites in body-centered cubic coordination. The initial decrease was attributable to the sum of the two opposite effect, that is, the decrease of free carboxyl groups and the increase in dielectric nature. The results were discussed in connection with those for sodium salts described in the preceding paper.

Introduction

In the previous paper (HIRAOKA and YOKOYAMA 1980), hydration of poly(acrylic acid) sodium salts (PANa) was studied and attention has been drawn to the unusual behavior of equilibrium water uptake as a function of the extent of neutralization. The present study was undertaken to see the effect of potassium ion whose ionic radius is larger than that of sodium. Emphasis will be placed on the differences in hydration behaviors between potassium and sodium salts.

Experimental

Poly(acrylic acid) potassium salts (PAK) with degrees of neutralization varying from 0 % to 100 % were prepared from poly(acrylic acid) (PAA, MW=100,000) according to the procedure described before (HIRAOKA and YOKOYAMA 1980).

The drying process of PAK salts at 100°C under atmospheric pressure was followed by weighing them at

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appropriate time intervals.

Water uptake of PAK salts at 25 °C in an atmosphere of 73 % relative humidity was followed by weighing them at appropriate time intervals. A sensitive spring balance made of thin phosphor bronze wire was used. The method and the apparatus used here were virtually identical with those described for PANa (HIRAOKA and YOKOYAMA 1980).

Results and Discussion

Drying process

Drying process of PAK is shown in Fig. 1. In the course of drying the state of samples changes from aqueous solution to solid. At the stage of the second curvatures in drying curves, all samples were in solid state already. The rate of drying in solution state

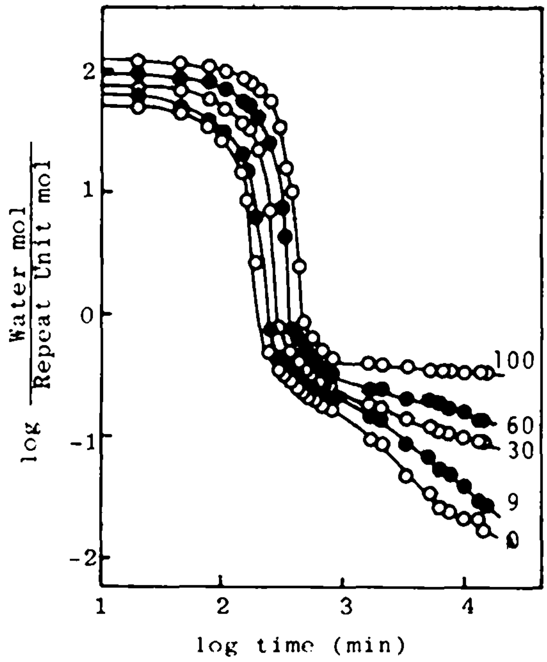

Fig. 1: Drying process curves at 100°C and 1 atm for poly(acrylic acid) potassium salts with degrees of neutralization from 0 to 100 percent, as indicated.

was not affected by the extent of neutralization, indicating that the evaporation of free water is not influenced by the existence of ion. In contrast, the rate of drying in solid state decreased remarkably with increasing neutralization %. It is also noticed that the second curvature becomes indistinct with decreasing neutralization %. These behaviors are quite similar with those of PANa except that PAK has smaller final drying speed and consequently more distinct second curvature and somewhat higher residual water level. This is an interesting observation because potassium ion has much smaller charge density due to larger ionic radius in comparison with sodium ion, which may result in the easier elimination of water molecules in the vicinity of potassium ion. The result may be explained by the steric difficulty of diffusion of water molecules in solid PAK caused by the existence of large potassium ions.

Fig. 2 illustrates the drying curves of PAK 60 and PAK 15 (The numbers added refers to neutralization %). The arrow on each curve indicates the water content which yields Tg of 100°C (drying temperature). Although the slowing down of drying appears to occur when Tg reached drying tempeature for high level of neutralization, this relation does not hold for low level of neutralization. This observation is identical with that encountered for PANa salts and leads to the same conclusion that drying process of PAK in solid state is not governed by Tg.

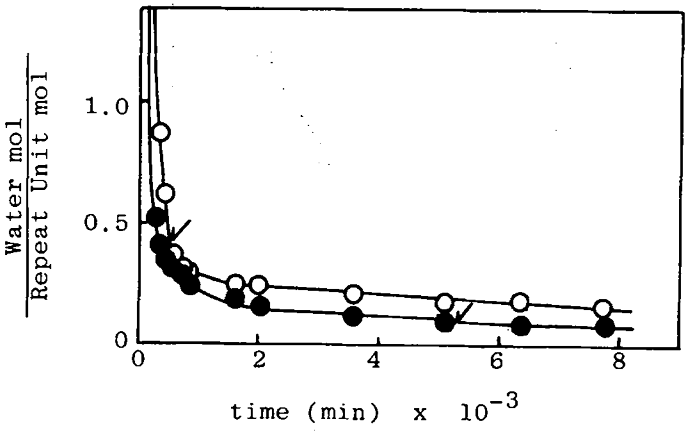

Fig. 2: Drying process curves at 100°C and 1 atm for poly(acrylic acid) potassium salts. 60 % neutralization ○ ; 15 % neutralization ● . The arrows indicate the points where Tg reaches drying temperature.

The level of water content where slowing down occurs is nearly 0.5 of H_2O mol/repeat unit mol as in the case of PANa. The value of 0.5 means that dehydration of water molecule which is bound to two carboxylates or carboxyls by means of two electron pairs is difficult. The situation of water molecules and the possible structure have been discussed already (HIRAOKA and YOKOYAMA 1980). Also, the explanation of the trend that the slowing down of drying speed becomes indistinct with decreasing neutralization % has been given for PANa in our previous paper (HIRAOKA and YOKOYAMA 1980) and it can be applied for PAK.

Thus it is concluded that the drying process of PAK is not governed by Tg (diffusion-controlled), but is governed by the release from hydrated state (dehydration-controlled).

Water uptake

Water uptake proceeds very rapidly in the initial stage, but becomes slow and reaches absorption equilibrium. Fig. 3 shows the equilibrium water uptake as a function of the degree of neutralization. It is observed that equilibrium water content decreases up

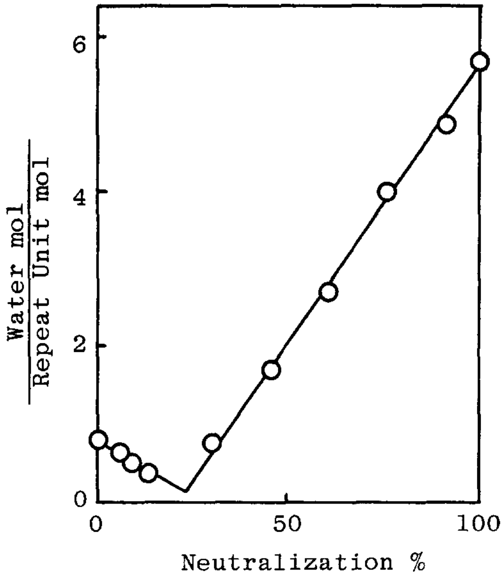

Fig. 3: Equilibrium water uptake at 25°C and 73 % relative humidity for poly(acrylic acid) potassium salts with different degrees of neutralization.

to about 25 % neutralization. Then it increases linearly with neutralization. In the case of PANa, the bending of the plot appeared at 33 % neutralization. This was reasonably explained by assuming the octet coordination structure of sodium ion. In the case of potassium ion, it is considered that the octet coordination is difficult because its ionic radius is larger than that of sodium. This is ascertained by simple geometry using the reported value of ionic radius. More probable structure is body-centered cubic (BCC) coordination as illustrated in Fig. 4. If the coordination sites are occupied by carboxyl oxygen atoms, one metal ion for 8 oxygen atoms, that is 4 carboxyl groups, therefore 1/4 neutralization corresponds to equimolar situation. Hence carboxyl oxygen atoms are in excess when the degree of neutralization is less than 25 %. Conversely, when neutralization is higher than 25 %, vacant sites appear which may be available for coordination of oxygen atoms of water molecules. Thus we can understand the linear increase in equilibrium water uptake above 25 % neutralization differing from 33 % neutralization for PANa.

On the other hand, the number of water molecules per repeat unit for PAK 100 is 6 as seen in Fig. 3. At a glance this number seems to agree with the foregoing discussion because the number of vacant sites per metal atom of PAK 100 is 6. However there remains some question.

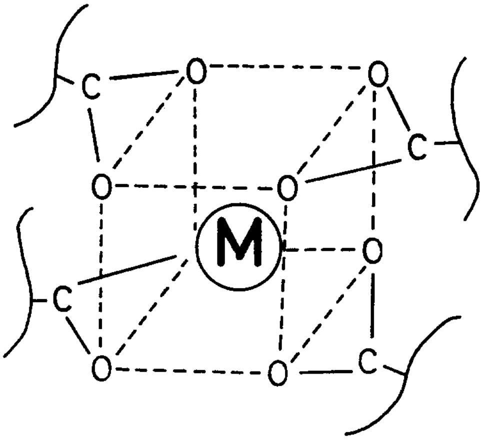

Fig. 4: A model for the body-centered cubic coordination structure of metal atom. (the state of 1/4 neutralization is illustrated)

According to Brady (BRADY and KRAUSE 1957), the radial distribution function of X-ray diffraction for concentrated KOH solution indicated that the hydration number of potassium ion is 4. The difference in hydration number between the reported value and that in this study may be explained as follows. In Brady's work much more water exists in the system compared with the system in this study. For such a situation K^+ which is close in size to the H_2O molecule enters substitutionally into the pseudostructure of H_2O without disturbing the structure to any marked extent as Brady suggested. In the present situation, however, the quantity of the H_2O molecules at equilibrium water uptake corresponds to the situation that the H_2O molecules merely fill up the vacant sites of coordination of potassium ion, though the sample reaches solution state in the final stage of experiment.

Another interesting observation is the decrease in equilibrium water content with increasing neutralization % below 25 % neutralization. This is contrary to the usual expectation because the dielectric constant of the system should increase by neutralization. In the case of PANa the slope of the plot in problem was undoutedly positive. The unsual result for PAK may be explained by the decrease of the free carboxyl groups which can hydrate with H_2O through hydrogen bonding. Though metal carboxylate groups increase in content, they are not available for hydration because coordination sites are occupied by carboxyl oxygen atoms below 25 % neutralization. The actual extent of water uptake may be the result of the two opposite contributions, that is, the increase in dielectric constant and the decrease in free carboxyls. The positive and negative slopes of the plots of equilibrium water uptake in the region of low neutralization % for PANa and PAK respectively can be accounted for in this manner. For PAK the smaller charge density of K^+ due to larger atomic size will weaken the hygroscopic property through decreased dielectric nature, resulting in the negative slope of the plot. The foregoing consideration leads to the expectation that the slope in problem become larger if Li^+ is introduced as counter ion. This is verified and will be reported in our succeeding paper.

References

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