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Density Measurements of Poly(Acrylic Acid) Sodium Salts

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Summary

Density measurements of poly(acrylic acid) sodium salts (PANa) with different degrees of neutralization and water contents are presented. The apparent partial molar volumes of polymer, V_2^*, and the partial molar volumes of water, V_1, were calculated from the densities. The values of V_2^* decreased with increasing water content and eventually leveled off. The values of V_1, which at low water contents were much smaller than that of free water increased with increasing water content and reached that of free water, showing consequently the appearance of free water. Before reaching the final value of free water, the data indicated the formation of primary and secondary hydration shells. The structure of primary hydration was suggested to be of octet coordination in which carboxyl oxygen atoms participate.

Introduction

The preceding papers in this series (HIRAOKA and YOKOYAMA 1980 a, b, and c) have discussed the dryimg process and equilibrium water uptake of poly(acrylic acid) (PAA), its sodium (PANa), potassium (PAK), and lithium salts (PALi). From the results it was considered that the vacant sites of metal atoms play an important role in the hydration of PAA salts. The state of hydrated water molecule was studied by pulsed n.m.r. technique for PALi, PANa and PAK (HIRAOKA and YOKOYAMA 1981).

The object of this work is to study the hydration of PAA and PANa in further detail through the measurement of partial molar volume. Though studies on partial molar volume of poly (acrylic acid) and its salts have been reported elsewhere (for example, TONDRE and ZANA 1972; ISE and OKUBO 1968), they have been confined to very dilute solutions. Contrary, this study was carried out for the states ranging from solid to highly concentrated solutions since the authors' interest was concerned with the appearence of free water by increasing content of water.

Experiment

Preparation of PANa with degrees of neutralization varying from 0 to 100 % were described in the preceding paper

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(HIRAOKA and YOKOYAMA 1980a). The degree of neutralization will be denoted by the numbers added to the abbreviated name as illustrated by PANa 60. The densities of the samples with different water contents were measured with a 25 cm^3 Harvard type pycnometer at 25°C. After preliminary examinations, p-xylene was chosen as the medium for density measurements because of its relatively low volatility and inactivity to samples. p-Xylene was distilled under reduced pressure.

Results

The densities of PANa with different water contents are shown in Fig. 1. The values of density decreased with increasing water content and increased with increasing degree of neutralization. In the following calculations, polymer mol refers to the repeat unit mol. Apparent partial molar volumes of PANa, V_2^*, were calculated from

$$\rho = \rho_1^0 + (1 - \rho_1^0 / \rho_2^*)\, c_2 \qquad (1)$$

$$V_2^* = M / \rho_2^* \qquad (2)$$

where ρ is the density of sample, ρ_1^0 density of the water at 25°C (0.99705 g/cm^3), c_2 polymer concentration in g per 1 cm^3 of solution, M the number average molecular weight of the repeat unit. The calculated values of V_2^* of PANa are plotted

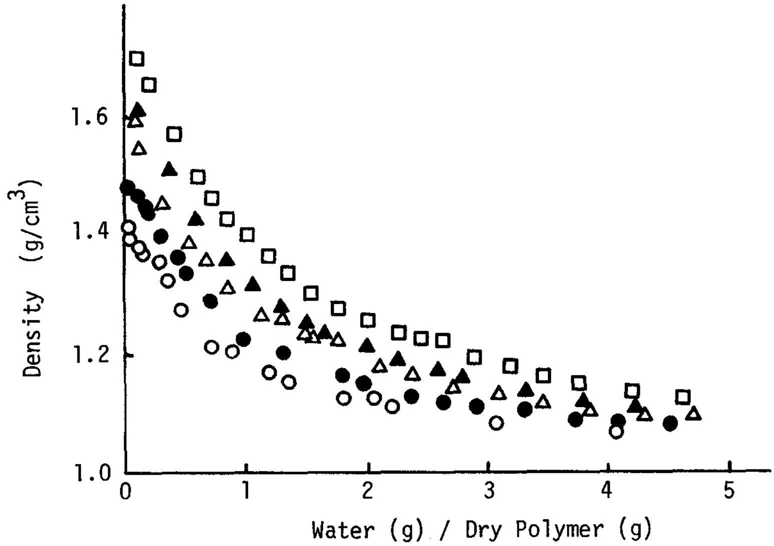

Fig. 1. Densities of poly(acrylic acid) sodium salts with degrees of neutralization from 0 to 100 % at 25°C; neutralization %, 100 % □ , 60 % ▲ , 45 % △ , 15 % ● , 0 % ○

as a function of water content in Fig. 2. The values of V_2^* decreased with increasing the degree of neutralization.

For the determination of the partial molar volumes of water and polymer, mean molar volume of the solution V_m are introduced, as defined by Eqs. (3) and (4),

$$V_m = V / (n_1 + n_2) \qquad (3)$$

$$V_m = X_2(dV_m / dX_2) + V_1 \qquad (4)$$

where V is the sample volume, n_1 and n_2 are the numbers of moles of water and polymer, respectively, and X_2 the mole fraction of polymer. Partial molar volumes of water and polymer, V_1, and V_2, can be determined from the intercepts of the tangent to the curve of V_m against X_2. The values of V_1 are summarized in Fig. 3. The values of V_2 were not determined because of the uncertainty of extrapolation to $X_2 = 1$, since the plots were limited to small values of X_2 owing to the large difference of molecular weights between water and polymer (repeat unit).

Discussion

The partial molar volume of water, V_1, finally reached the constant value of 18 cm³/mol which is the value of free water at 25°C (18.02 cm³/mol) in the region of low mole

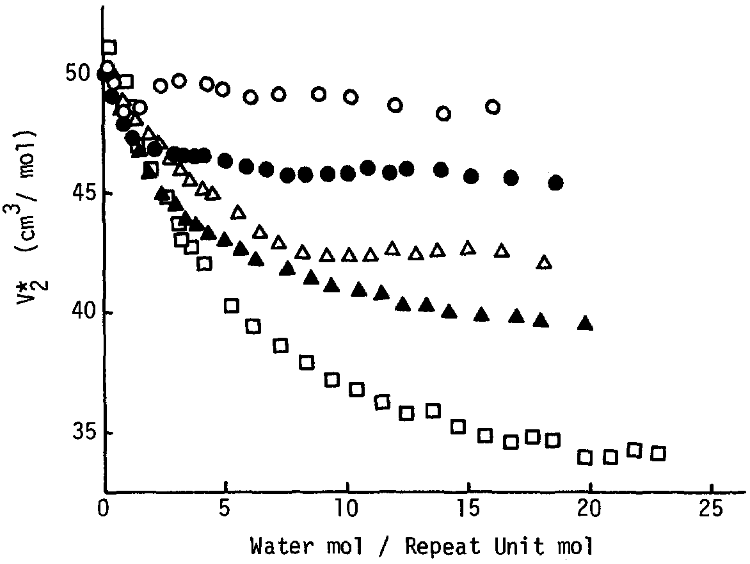

Fig. 2. Apparent molar volumes of poly(acrylic acid) sodium salts with degrees of neutralization from 0 to 100 % at 25°C; neutralization %, 100 % □ , 60 % ▲ , 45 % △ , 15 % ● , 0 % ○

fraction of polymer, that is, at high water contents. In this region, of course, apparent molar volumes of the polymer, V_2^*, have constant values, which should be almost equal to the partial molar volumes of polymer, V_2. As Fig. 2 shows, this value was 48.6 cm^3/repeat unit mol for PAA and decreased with increasing neutralization %. The value for PANa 100 was 34.8 cm^3/repeat unit mol. The both values are in good agreement with those reported by ISE and OKUBO, who obtained 47.8 and 33.0 cm^3/repeat unit mol for PAA and PANa 100, respectively, in the study of dilute solution (ISE and OKUBO 1968). The decrease in V_2 with neutralization is natural where solvation

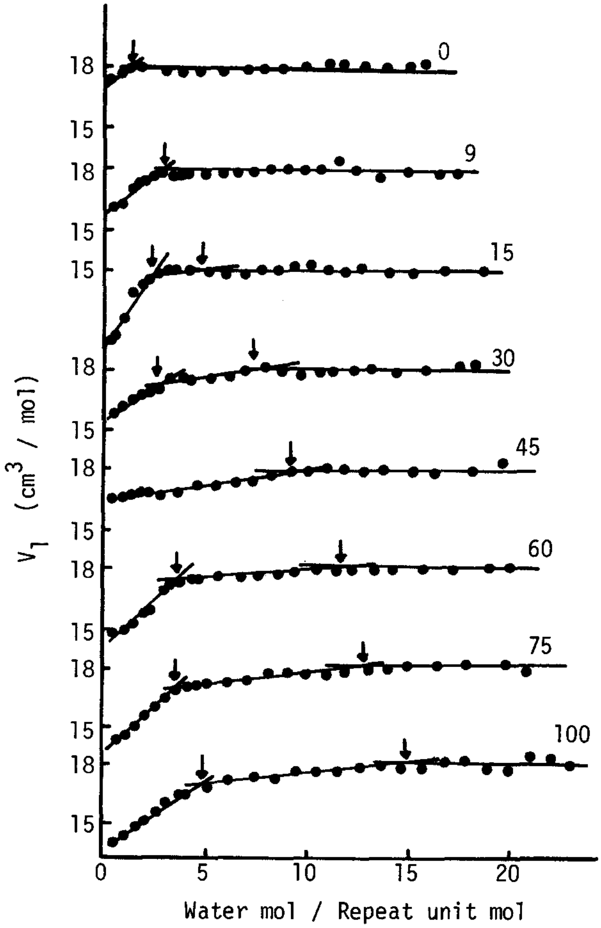

Fig. 3. Molar volumes of water coexisting with poly(acrylic acid) sodium salts at 25°C. Neutralization % are indicated in the figure

occurs in solution.

In Fig. 3, it is observed that before attaining the final value the partial molar volume of water increases as the water content increases, but a simple relationship dose not hold. Though there seems to be an almost linear increase for the samples with low neutralization %, distinct bendings of the plots appear as neutralization % increases. It is reasonable to consider that the hydration mechanism is different before and after these bendings. The first portion of the plot before bending is inferred to be the direct hydration to ion pairs. In this stage the carboxyl two oxygen atoms may be coordinated to a metal atom in octet coordination which was demonstrated in our previous study (HIRAOKA and YOKOYAMA 1980a). The structure is illustrated in Fig. 4. Such a chelation of carboxyl group is in line with the coordination structure of copper acetate monohydrate (MIPINERI and MEYER 1974). In the case of Na ion, though tetrahedral coordination has been verified for Na^+ ion, through the X-ray study on concentrated aqueous solution of NaOH (MAEDA and OHTAKI 1975), tetrahedral coordination is impossible where chelation of carboxyl occurs, since ionic radius of Na is much greater than that of the internal sphere of tetrahedron formed by chelation of carboxyl oxygen atoms. The vacant sites of coordination of metal atom will be occupied by oxygen atom of water molecules until the vacant sites diminished. The secondary hydration of water molecules to this primary hydration shell through coulomb interaction, and/or hydrogen bonding will continue hereafter. Further increase of water content leads to the appearance of free (bulk) water, which corresponds to the point where V_1 approaches 18.02. From the above consideration we can expect that the molar ratio of water to polymer where primary hydration sites are fulfilled is 4 for PANa 100. For partially neutralized samples, the molar ratio should be smaller than 4, depending upon the degree of neutralization.

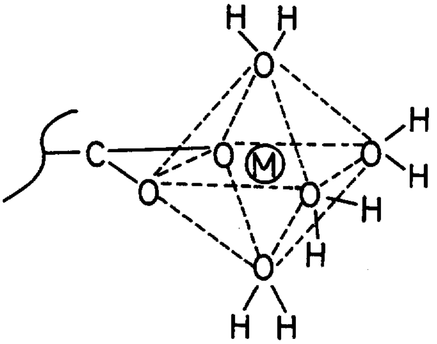

Fig. 4. A model for the octet coordination structure of metal atom

The lack of the indications of secondary hydration (bending of the plot) for PANas with low neutralization % may be attributed to indistinct changes of the slopes of the plots. As the degree of neutralization decreases, the amount of ion pair decreases. As a result, the both points where secondary hydration begins and free water appears should shift toward the smaller water content. At the same time the limiting value of V_1 at low water content should increase. In consequence, the change of the slopes due to the onset of secondary hydration will become indistinct. The situation is illustrated schematically in Fig. 5.

The molar ratio of water to polymer (repeat unit mol) where free water appears (where V_1 levels off to 18.02) increases with the increase of neutralization %. The ratio for completely neutralized PANa 100 is 15. As a simple calculation shows, the solution is still a fairly concentrated one. It is not expected that dissociation of ion pair occurs substantially in this solution. If we assume this situation, we may imagine the hydration shell of ion pair still exists at this stage. Further increase of water content should lead to the separation of ion pair and the appearance of hydration shell of cation (Na^+) and anion ($-COO^-$). The separation of both ions in this stage may not contribute to the partial molar volume of water because all ions are buried in hydration shell already.

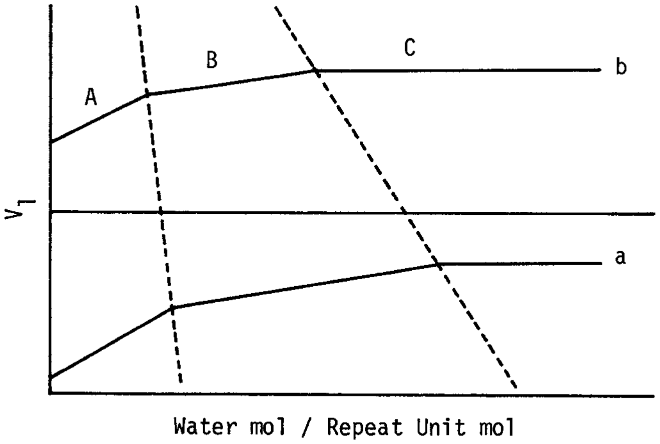

Fig. 5 . The schematically represented variation of the plot of V_1 as a function of water content and the degree of neutralization A, primary hydration range; B, secondary hydration rage; C, free water; a, high degree of neutralization; and b, low degree of neutralization

From the consideration described above it seems appropriate to regard the hydration number determined to be 15 as different from the hydration numbers in ordinary meaning. The latter values have been determined usually in dilute aqueous solutions where ions are in almost completely separated state. In addition, they vary according to the different characteristic of each measurement. Therefore it was avoided to compare the hydration number in this study with those for Na^+ ion reported in a variety of studies. However, it should be emphasized here that the results in this study clarified that (1) primary hydration is saturated at very low water content, (2) then, secondary hydration followed, (3) free water appears in fairly low content of water. These conclusions help to understand the complicated behavior of ionic polymers in solid state where a trace of water strongly influence the physical properties through shielding coulomb interactions.

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