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Volumetric and Thermal Behaviors of Water Uptaken in Superabsorbent Polymer

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For the water uptaken in a superabsorbent polymer gel (Sumikagel) bearing polar groups (–COONa and –OH), the partial molar volume, heat of fusion, and melting point, have been determined over a wide region of water content, from water-free to a saturated state. The results indicate that the region can be classified into three characteristic parts. In the lowest water content region, the –COONa forms a monohydrate in the solid state. In the next region, the primary hydration of both groups and the dissociation of –COONa occur. In both regions the water is antifreezing. In the highest content region, secondary and higher hydration occurs; the hydrated water is freezing, and the so-called free water appears.

It is known that the water uptaken in hydrophilic polymers can be generally classified into bonded water and free water. The interaction of water with a polymer is, however, complex. It has been reported that a more detailed classification of these waters is possible.[1–3]

Superabsorbent polymers are characteristic polymers which can uptake and keep a few hundred times more water than the polymer's weight. The polymer is therefore an interesting sample for studying the states of hydration. This study attempted to elucidate the hydration mechanism for a superabsorbent polymer called Sumikagel on the basis of the volumetric properties and thermal properties of water over a wide region of the water content, from the water-free to the saturated state.

Volumetric quantity provides useful information concerning hydration.[1,4] A novel dilatometric method was used here in order to determine the partial molar volume of water uptaken in the polymer gel.

Experimental

Materials. As the sample gel, Sumigagel S-50[5] (particle size: 200—280 μm) produced by Sumitomo Chemical Co., Ltd. was used. The polymer is a sodium salt of the block copolymer of vinyl alcohol with acrylic acid, with the molecular structure, $-(CH_2CHCOONa)_4-(CH_2CHOH)_6-$. Before use, the gel was dried in vacuo at 50 °C for 30 d until its weight attained constancy. The drying was substantially completed during the first 15 d (weight decrement: 3.0%). Dodecane and deionized water were fractionally distilled for use. Commercially available benzophenone (Tokyo Kasei, GR grade) was used without any further purification.

Dilatometry. Measurements of the partial molar volume of water uptaken in the gel were carried out using a novel dilatometer. Its structure was illustrated in a previous paper.[6] The glass dilatometer comprises a capillary (inner diameter 1.5 mm and 20 cm long), and a bulb (about 15—30 cm^3) with a metal fitting for fixing a silicone rubber seal. In order to restrain the silicone rubber from being swollen with dodecane, thin fluorinated rubber was sandwiched between the glass injection hole and the selicone rubber. A magnetic stirring bar coated with Teflon® was placed in the bulb. A given weight of gel was measured into the bulb. The inside of the bulb was filled with dodecane which was chosen as the medium for volume measurements because of its relatively low volatility and inactivity to the sample. After the bulb contents were degassed, the capillary with a cap was fixed in the bulb and the prepared dilatometer was set in a water bath; the temperature was controlled at $25\pm1/1000$ °C. Water (40—50 mg) was successively added into the dilatometer by weight with a microsyringe. After each addition, the level of dodecane in the capillary was measured with a cathetometer to 1/100 mm. The volume increment (ΔV) and the mole number of added water (Δn) give the partial molar volume of the water ($\overline{V}$), defined as $\Delta V/\Delta n$.

Thermometry. The heat of fusion (ΔH_f) and the melting point (T_m) of water uptaken in the gel were determined on a DSC meter (Seiko Densi: SSC-544 type). Given amounts of water and gel were weighed into an aluminum capsule; the sealed capsule was allowed to stand for one day in order to attain sample equilibration. The sample placed in the DSC meter was cooled to −30 °C with a dry ice-methanol coolant. Measurements were made at a heating rate of 100 s/°C.

Results and Discussion

For the dilatometric measurements, dodecane was used as an inert filler, sice it is considered to be a poor solvent to such a hydrophilic polymer. However, a very slow, but steady, increase in volume was detected for the water-free system (gel+dodecane). The time dependence of the volume is shown in Fig. 1. The increase may be due to a swelling of the gel in dodecane. The volume increase indicates that the partial molar volume of dodecane absorbed in the gel is greater than the molar volume of pure liquid dodecane. If we apply a model of unsteady-state diffusion to the swollen system, Fick's second law for diffusion in a semiinfinite medium gives the total amount of dodecane (M_t) diffusing during the time (t) according to the following expression.[7]

$$M_t = 2C_0(Dt/\pi)^{1/2}. \qquad (1)$$

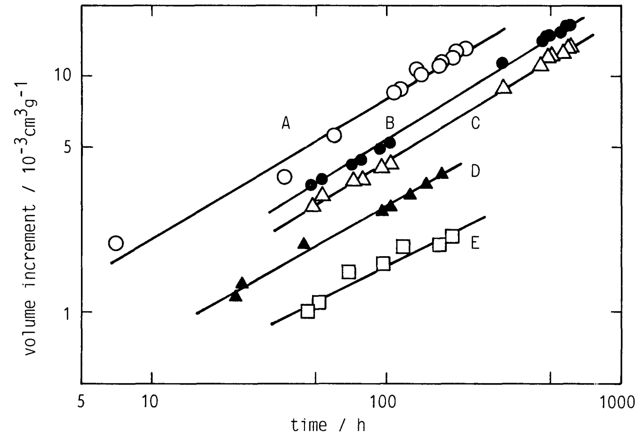

Fig. 1. Time dependence of the volume increment per weight of gel by swelling in dodecane at 25 °C. Water-free system (cm^3(dodecane)/g(gel)): A (13.5/1.454), B (17.0/1.308), C (31.0/4.808). Water-containing system (cm^3(dodecane)/R): D (16.0/0.0868), E (17.0/0.0558).

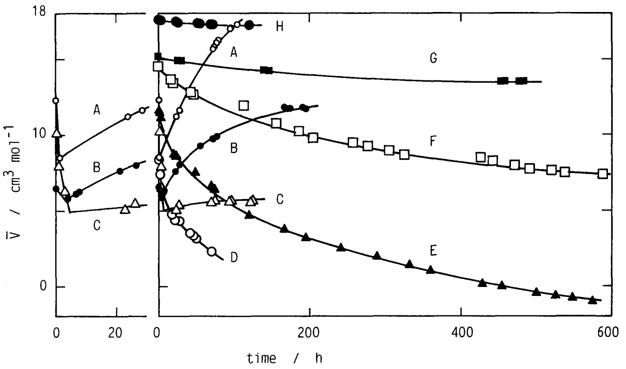

Fig. 2. Time dependence of the partial molar volume ($\overline{V}$) of water uptaken in gel immersed in dodecane at 25 °C. System (4.449 g(gel)/33.0 cm^3(dodecane): R: 0.0226 (A), 0.0406 (B), 0.0765 (C), 0.0855 (D), 0.0943 (E), 0.110 (F), 0.132 (G). System (1.454 g(gel)/13.5 cm^3(dodecane)): R: 0.619 (H).

Here, C_0 and D refer to the concentration of dodecane on the surface of the gel and the diffusion coefficient of dodecane in the gel medium, respectively; both are assumed to be constant. This relation represents a logarithmic linear relationship between ΔV and t, with a slope of 0.5, since ΔV is regarded as being proportional to M_t. The straight lines in Fig. 1 have a common slope of about 0.6; which can be taken to be in agreement with 0.5 in Eq. 1. The linear relationship suggests that dodecane penetrates into the gel by a diffusion mechanism.

Since it was supposed to take a long time before completing the swelling, about one month later than the preparation of gel+dodecane, we started to measure $\overline{V}$. The dependence of the determined $\overline{V}$ on t is represented in Fig. 2. The water content is expressed here as R (the weight ratio of water to gel). Upon some initial additions (up to about 0.08 of R, denoted by Region A), $\overline{V}$ decreased rapidly down to a minimum, and then slowly increased. Before the volume increase had come to completion in each run, the next addition of water was made for the same reason mentioned above regarding the water-free system. The increasing tendency after the minimum becomes less remarkable with increasing water content. For comparing the time dependence of the increase after the minimum with that in the water-free system, the volume increment only after the minimum in each curve in Fig. 2 is also plotted in Fig. 1. The plots also show a linear relation with almost the same slope (0.50—0.55) as that in the water-free systems. This result suggests that the swelling due to the diffusion mechanism holds even after the addition of small amounts of water.

At only a slightly higher water contents $\overline{V}$ decreases down to even negative values, and no increasing tendency follows, as can be seen in Fig. 2. Considering that the partial molar volume of dodecane in the gel is larger than that in its pure liquid, as mentioned before, and that water has a greater affinity to the polar gel than dodecane does, the obstinate decrease in $\overline{V}$ can be explained by an exchange of uptaken dodecane with water in the gel. The water content region in which $\overline{V}$ continues to decrease for a long time is very narrow (R=about 0.08—0.1: denoted by Region B). Upon the further addition of water (R>0.1, Region C), $\overline{V}$ starts to decrease at a higher value than in Regions A and B, and attains constancy in a short time through a slight decrease.

The equilibrium values of $\overline{V}$ are determined from the time dependence in Fig. 2, and they are plotted in Fig. 3 as a function of R; the values obtained in different 18 experimental runs are shown together. The consistency of the data given in Fig. 3 implies that the period of time for determining each value is sufficiently long for the added water to attain a uniform distribution in the gel. In Region A, the value of $\overline{V}$ at the minimum of each curve in Fig. 2 is taken, since the water uptake is considered to promptly reach its equilibrium state, being still followed by the dodecane absorption. In Regions B and C, the final value in each run is taken, where some values in Region B are not for the equilibrium condition. In Fig. 3, $\overline{V}$ in Region A can be regarded to be constant, while ignoring the scatter in the plots. In Region B, the volumetric effect of dodecane on $\overline{V}$ is so remarkable that $\overline{V}$ does not reflect the property of water itself. In Region C, $\overline{V}$ increases asymptotically to the molar volume of liquid water (18.02 cm^3 mol^{-1},[8]) expressed as V_0) with an increase in R. It seems to be reasonable that a discontinuous increase in $\overline{V}$ occurs between two regions, at R=0.11 (denotes by R_s), ignoring values in Region B.

The heating DSC curve gives a single peak which broadens with increasing R. In order to calibrate ΔH_f and T_m, benzophenone[9]) and water[8]) were used. The determined values of ΔH_f and T_m are also plotted in Fig. 3 against R. The respective values tend to increase asymptotically toward the values of pure water, 80 cal

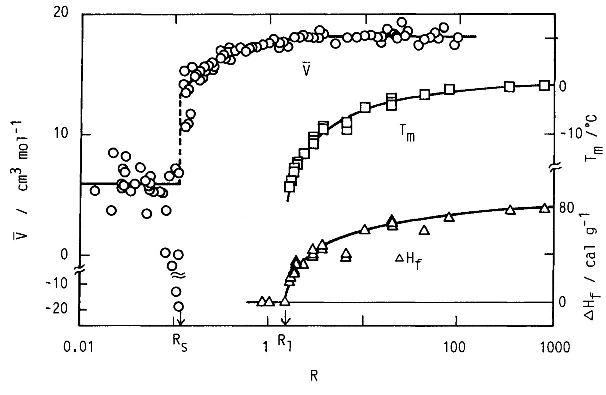

Fig. 3. Water content (R) dependence of $\overline{V}$ (equilibrium value at 25 °C), T_m, and ΔH_f of the water uptaken in the gel . Regarding R_s and R_l, see in text.

g^{-1} and 0 °C.[8] Some data points obtained by repeating measurements for a given sample show good reproducibility, as can be seen for each curve. This reflects the fact that the standing time, one day, is enough for attaining the equilibrium state. Below R=1.5 (denoted by R_l) no peak was detected in the heating curve. In Fig. 3, the rapid increase just above R_l in the curves (notice the curves being semilogarithmic) suggests that the water uptaken in the gel below R_l is unfreezing. Even if freezing, T_m must be far lower than −30 °C.

Against the increasing tendency of ΔH_f and T_m, $\overline{V}$ changes only slightly above R_l. The discrepancy can be explained as follows. The partial molar volume of water is thermodynamically a differential molar quantity, which reflects the property of the water, itself, just at a certain R; in contrast, ΔH_f is an apparent molar quantity which expresses the overall property of all the water in the gel. Therefore, the constancy of $\overline{V}$ close to V_0 indicates the existence of free water like ordinary water.

The curves given in Fig. 3 allow us to divide the water content region into a freezing region ($R>R_l$) and an antifreezing one ($R<R_l$); further, the latter can be divided into two regions at R_s. For a gradual increase in $\overline{V}$ above R_s, the following two explanations seem to be possible. One is that the interaction between the hydrophilic groups and the nonfreezingly hydrated water becomes weaker with increasing R: There exists not a single type, but rather, various types of water with continuously different characteristics of interaction. The other is that the ion, -COO$^-$ or Na$^+$, dissociated by the hydrated water acts repulsively to each other, resulting in an expansion of the polymer network. This explanation indicates the existence of a single type of water (hydration to the ions); the amount of the type of hydrated water increases with R.

In a previous study[10] the partial molar volume of hydrating water to some salts was determined by the same dilatometric method. For a salt such as LiCl or $C_2H_5SO_4Na$ which forms monohydrate crystals, $\overline{V}$ depends on R in the following way. Until the monohydrate compound forms, $\overline{V}$ remains constant (about 13 cm³ mol^{-1} for both salts). As the equimolar water content, $\overline{V}$ suddenly increases; it is then followed by higher constant values, as long as the solution is saturated. Once the water content attains the solubility of the salts, $\overline{V}$ suddenly decrease and then increases asymptotically towards V_0 with dilution.

The volumetric behavior for hydrate salts well-compares with the present behavior. It is apparent that the constancy of $\overline{V}$ below R_s is consistent with that for monohydrate salts. If we consider the hydration of only -COONa, though there exist -OH in the polymer, such hydration as the solid hydrate is supposed to occur below R_s. The constant $\overline{V}$ (6 cm³ mol^{-1}) in the gel is appreciably lower than that for the solid hydrates (13 cm³ mol^{-1}).[10] The lower value can be attributed to the interestitial hydration of the water which is located in the cavity of the polymer network. Once hydration has been completed at R_s, more added water would dissociate -COONa into -COO$^-$ and Na$^+$ ions, where they would coexist with the undissociated -COONa.

Such ionization was confirmed by the conductivity of the gel+water system. An amount of water was successively added (once a day) to a given amount of the gel (0.9 and 1.3 g) placed in a test tube. Two electrodes were immersed in the gel for measuring the conductivity at room temperature by a conductivity meter (TOA, CM-30ET type). The obtained relation between the conductivity and R is as follows (the data are not given here). The conductivity was undetectable below R=0.5, above which it increased sharply and then decreased slightly via a maximum around R=3. The conductivity tendency is in line with that obtained in some natural polymer gel-water systems.[11] Taking into account a retardation of equilibrium achievement, the respective values of R are regarded as corresponding to R_s and R_l. The zero conductivity and the increasing tendency are consistent with the formation of solid hydrate and the dissociation of -COONa, respectively. The slight decrease may be due to dilution of the dissociated ions with free water.

The value of each characteristic R, i.e., R_s and R_l, allows us to estimate the hydration number to each group, -COONa and -OH, provided that the molecular structure of the polymer is as shown above and that the gel is free from any contamination, the present sample being a manufactural product. R_s(=0.11) corresponds to a 3.9H_2O/average base unit: a tentative assignment is possible that a single water molecule hydrates to a -COONa group while the -OH group is water-free. This assignment suggests that the monohydrate, -COONa(H_2O), is in an undissociated ion pair in the solid state, on the basis of well known ordinary hydrated solid salts. The facts concerning the nondetectable conductivity and antifreezing mentioned above support the assignment as being reasonable. For $R_l(=1.5)$, the water (53.3H_2O/average base unit) may be tentatively assiged to each group (9H_2O to -COONa and 3H_2O to -OH) upon assuming an integral number of water molecules hydrating to each group. Concerning the hydration number at R_l, the number of water molecules coordinated with -OH and -COOH in a gelatin-water gel were estimated to be 4 and 4—5, respectively, by Sponsler et al.[12] Further, the hydration number for Na^+ ion in an aqueous solution of its halide was estimated to be 4.6.[13] Therefore, the assigned hydration numbers at R_l are reasonable: The hydrated water is located in the inner hydration layer of the dissociated ions as well as the -OH group. Namely, these water molecules result in antifreezing because of their strong interaction with each ion and -OH group. With an increase in the water content above R_s, the concentration of dissociated and mobile Na^+ ions coexisting with undissociated ion pairs leads to an increase in the conductivity of the gel, up to R_l.

This consideration provides an explanation that the gradual increase in $\overline{V}$ in Region B is due to an expansion of the polymer network caused by the electrostatic repulsion, not due to the existence of various states of hydration, as mentioned above. Above R_l, secondary and higher hydration in the outer layers occur. As can be seen in Fig. 3, the water is capable of freezing. The weaker is the interaction between water and the hydrophilic group or ion, the easier does the freezing of water become, with increasing R. In this region $\overline{V}$ is constant and close to V_0, in contrast to the well-known fact that $\overline{V}$ for a concentrated solution of ordinary salts markedly depends on the composition. The discrepancy can be ascribed to the characteristics of the polymer electrolytes. For the polymer, the hydrophilic group is fixed on the network chain and isolated from each other. The isolation predicts that the state of hydration at even a low water content is similar to that at high dilution of an ordinary salt solution. Hence, a constant $\overline{V}$ appears above R_l.

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