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SHORT COMMUNICATION

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Swelling of poly(ethylene oxide) gel in aqueous solutions of sodium dodecyl sulfate with added sodium chloride

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Abstract The swelling behavior of poly(ethylene oxide) (PEO) gels in aqueous solutions of sodium dodecyl sulfate (SDS) with and without NaCl was investigated. In the absence of NaCl, PEO gels with different degrees of cross-linking began to swell from a concentration lower than the critical micelle concentration (cmc) of SDS, then showed sigmoidal enhancements of swelling in a higher SDS concentration region until the degrees of swelling reached maximum values. The SDS concentration at which the swelling began to appear was in reasonable agreement with the critical aggregation concentration (cac) value reported for the aqueous PEO system. For the cases where NaCl was present, the swelling behavior of PEO gel was different from that when NaCl was absent in the following way. The concentrations where the swelling begins to appear, and hence those where the degree of swelling rises steeply, decreased with an increase in NaCl concentration. The ultimate degrees of swelling at higher concentration regions also decreased with an increase in the NaCl concentration. The lowering of the SDS concentrations at which the PEO gel began to swell is in line with the decreases in the cmc of SDS solutions containing NaCl and also with the decreases in the cac of PEO solution.

Keywords Poly(ethylene oxide) · Gel · Sodium dodecyl sulfate · Salt effect · Micelle

Introduction

Recently, from the viewpoint of fundamental research and application to various fields, the behavior of polymer gel swelling responding to the changes in the condition of external solutions has been widely studied. Particularly, swelling of gels by interactions with surfactants has been extensively investigated [1, 2, 3, 4, 5, 6].

The present work reports the swelling behavior of poly(ethylene oxide) (PEO) gels in the presence of sodium dodecyl sulfate (SDS) with added NaCl. The interaction between PEO and surfactants in aqueous solutions has been thoroughly studied with various experimental techniques, for example, surface tension, viscosity, NMR, conductivity, and so on [7, 8, 9, 10]. This interaction is characterized by two critical concentrations, i.e., the critical aggregation concentration (cac), at which polymer and surfactant begin to aggregate, and the polymer saturation point, at which the aggregation of the surfactant on the polymer is saturated [11]. For a gel system, however, there are few studies on the interaction between PEO gel and SDS. For the swelling behavior of polyacrylamide (PAAm) gel with PEO side chains, Rosén et al. [12] reported the interaction of SDS with the side chain in some detail.

In this study, the PEO gel was prepared by γ-ray irradiation of aqueous solution of PEO. This gel preparation method has the advantage of obtaining a homopolymer gel without any cross-linker. The present work reports the swelling of PEO gels with different degrees of cross-linking by the interaction with SDS. The study was extended to NaCl-containing systems with reference to the critical micelle concentrations (cmc) of SDS in the presence of the salt.

Experimental

Gel preparation

PEO ($M_w = 5 \times 10^5$) was purchased from Wako Pure Chemical Industries and was used without further purification. PEO (8 wt%) was dissolved under heating in deionized and afterward distilled water with stirring for 24 h; this was followed by degassing to remove air bubbles in the solution. The gels were prepared by irradiating the solution with γ-ray of ^{60}Co. The PEO solution was filled in glass capillaries of 0.2-mm inner diameter and 32-mm length. The irradiation dose was 50–300 kGy. Four kinds of transparent, colorless, cylindrical gels with different degrees of cross-linking were obtained.

Water content of the gel

The water contents of the gel were determined from the weight differences between the swollen and the dried gels. The gel sample equilibrated with distilled water was weighed after blotting the water on the surface of the gel. The gel was dried at 50 °C for 5 h and was then dried in vacuo at 50 °C for 24 h. After drying, the gel was weighed again. The water content was defined as the weight fraction of the water in the swollen gel.

Measurement of the degree of swelling

The gels were taken out of the capillaries, cut into specimens about 5–10-mm long, and immersed in distilled water completely to desalt and equilibrate. Then, the gels were immersed in NaCl solutions of appropriate concentrations for 24 h. The diameter, d_s, of the gels in the respective NaCl solutions was measured with a microscope. Then, the gel was immersed in SDS solutions containing NaCl and the diameter of the gel was measured under the swelling equilibrium. The degree of swelling of the gel was defined as the ratio, d/d_s, of the diameter in SDS/NaCl solution to that in the respective NaCl solution. The NaCl concentrations in SDS solutions were 0, 5, 10 and 20 mM. All the measurements were carried out at 20.0 ± 0.1 °C.

Surface tension of SDS/NaCl solution

Prior to use, SDS (99%, Sigma) was dried in vacuo at 90 °C for 5 h. Analytical grade NaCl (Kanto Chemical) was dried at 120 °C for 5 h. The surface tensions of the solutions of SDS/NaCl were measured with an electro surface balance(Kyowa Scientific) by the platinum-plate method. The concentrations of added NaCl were 0–20 mM. The measurements were carried out at 20.0 ± 0.1 °C and 65% relative humidity.

Results and discussion

Plots of the water content of PEO gels in water against the irradiation dose are shown in Fig. 1. It is found that the water content decreases linearly with the increase in the irradiation dose. This relation shows that the higher irradiation dose generates more polymer radicals, resulting in the more cross-linking points.

Plots of d/d_w, where d_w is the diameter of the gel in water, of PEO gels of different degrees of cross-linking against the SDS concentration of the immersing solution are shown in Fig. 2. The general feature of the swelling behavior is that the gel begins to swell nearly at 5 mM SDS, which is followed by a steep increase in the swelling at 5–10 mM until the degree of swelling reaches a maximum value, about 1.5–1.8, at an SDS concentration higher than 10 mM. This swelling behavior is the same for all the gels; the difference in irradiation dose and hence in the degrees of cross-linking have no influence on the critical swelling features of the gels. The gels prepared in the present study should have relatively low degrees of cross-linking and chains of high molecular weight between the cross-links. As expected, the d/d_w value at SDS concentrations higher than 25 mM decreases with an increase in the irradiation dose. Rosén et al. [12] reported qualitatively similar swelling curves for PAAm gel with pendant PEO chains immersed in SDS solution. When PAAm and PEO homopolymers are mixed in an aqueous solution, they are separated in different phases. This incompatibility gives an additive swelling property to the copolymer gel. Since PAAm does not show any interaction with SDS, the swelling was caused solely by the interaction between the pendant PEO chain and SDS. The swelling of PEO gel observed at SDS concentration higher than 5 mM is caused by the aggregative binding of dodecyl sulfate (DS) anions to the PEO chain. This gives rise to the temporal fixation of the anions on the PEO chain. As a result, the gel

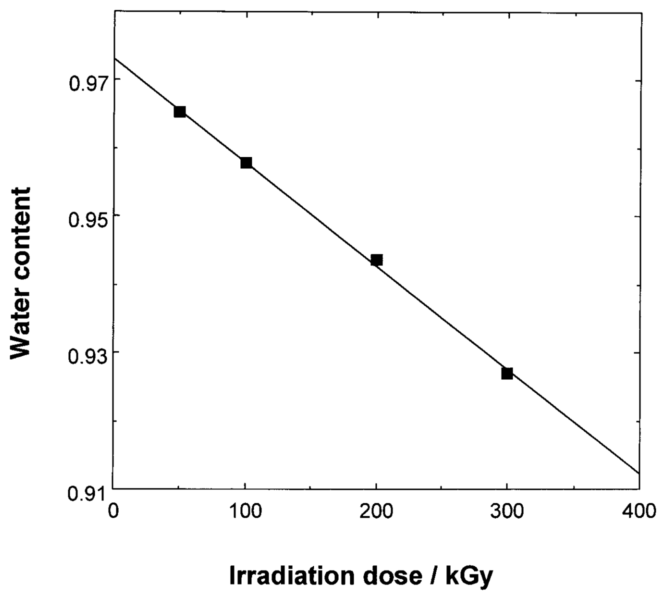

Fig. 1 Plots of water content of poly(ethylene oxide) (*PEO*) gels against irradiation dose

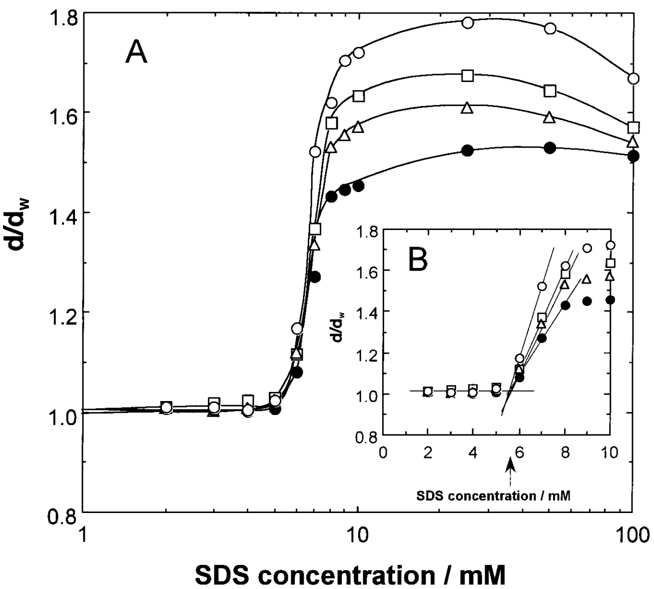

Fig. 2 Plots of the degree of swelling for PEO gels against the external sodium dodecyl sulfate (*SDS*) concentration. Irradiation doses: 50 kGy (*open circles*), 100 kGy (*squares*), 200 kGy (*triangles*), and 300 kGy (*filled circles*). In the *inset*, the concentration at the beginning of the gel swelling is indicated by the *arrow*

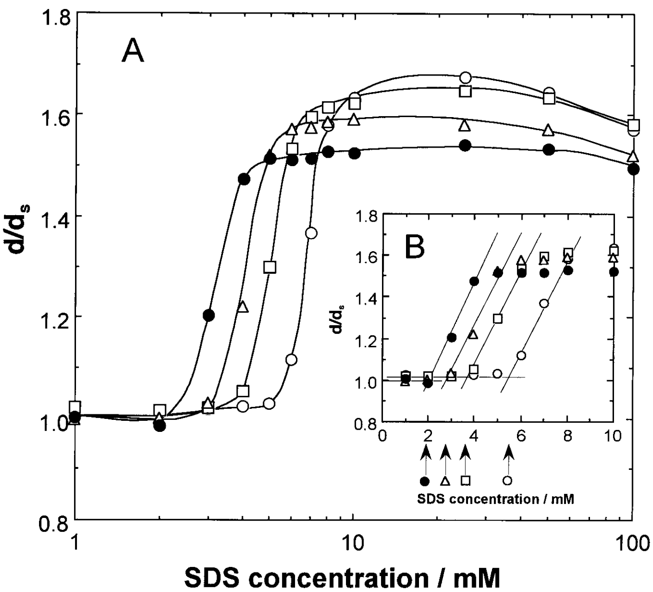

Fig. 3 Plots of the degree of swelling for PEO gel prepared by 100-kGy irradiation against the external SDS concentration. Concentration of added NaCl: 0 mM (*open circles*), 5 mM (*squares*), 10 mM (*triangles*) and 20 mM (*filled circles*). In the *inset*, the evaluated concentrations, c_g, at the beginning of the gel swelling are indicated by the *arrows*

becomes charged with the increase in the mobile counterion concentration in the gel, which leads to the enhancement of the osmotic pressure inside the gel. The electrostatic interaction and the osmotic pressure work for the enhancement of the swelling of the gel. Above 10 mM, the degrees of swelling were almost indifferent to SDS concentration, implying that the amount of cooperatively bound SDS does not increase above that concentration. The binding of SDS is counteracted by the elastic energy of the gel. Above 40 mM SDS, the gels with relatively higher degrees of swelling show the maximum values followed by decreases of the swelling with increasing SDS concentration. However, for the gel irradiated with 300 kGy, the degree of swelling increases moderately and reaches a maximum at a SDS concentration higher than that for the other gels, and is followed by little deswelling. With the increased degree of cross-linking, the charge density of the gel becomes high because of the confined volume of the gel and hence the influence of a high SDS concentration is relatively low.

Plots of d/d_s of a PEO gel prepared by irradiation of 100 kGy against SDS concentration for NaCl-containing solutions are shown in Fig. 3. Comparison of the swelling curves with the corresponding one for no NaCl present shows clearly that the SDS concentration, c_g, at the beginning of the PEO gel swelling, i.e., PEO and SDS begin to interact, is lowered with the increase in the concentration of added NaCl. The *cg* values were determined from the intersections of the lines as shown in the inset of Fig. 3. To find the relationship between the cmc of SDS and c_g, the surface tensions of SDS solutions with different NaCl concentrations were measured. Salt addition to SDS solutions lowered the cmc as indicated in Fig. 4, in which the surface tension is plotted against SDS concentration for different concentrations of added NaCl. The cmc values were estimated from the breakpoints indicated by the arrows in the inset of Fig. 4. The cmc and c_g are shown against the concentration of added NaCl in Fig. 5. In this figure, the curves calculated by the equations obtained by Minatti and Zanette [10] are also shown:

$$\log(\mathrm{cmc}) = -0.71\log(\mathrm{cmc} + c_s) - 3.51, \quad (1)$$

$$\log(\mathrm{cac}) = -0.57\log(\mathrm{cac} + c_s) - 3.55, \quad (2)$$

where c_s is the concentration of the added salt. They investigated the salt effect on the cmc and the cac for PEO/SDS solutions conductometrically, and the equations were evaluated from the linear fitting to the data. Both the cmc estimated from the surface tension and c_g decrease with the increase in the concentration of added NaCl. At each NaCl concentration, the values of c_g are lower than the cmcs. As found for aqueous system with added NaCl, the gel also begins to interact with SDS below the cmc. The cmc values measured by us are considerably lower than those of Minatti and Zanette. Such a discrepancy is quite common among the cmcs evaluated by the different methods. On the other hand, the dependence on the concentration of added NaCl of

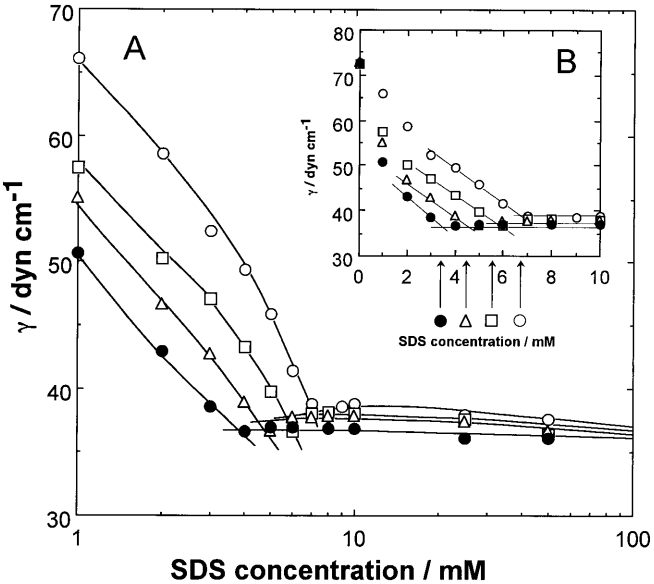

Fig. 4 Surface tension of SDS solution against the logarithm of SDS concentration. Concentration of added NaCl: 0 mM (*open circles*), 5 mM (*squares*), 10 mM (*triangles*) and 20 mM (*filled circles*). In the *inset*, the evaluated critical micelle concentration (*cmc*) values are indicated by the *arrows*

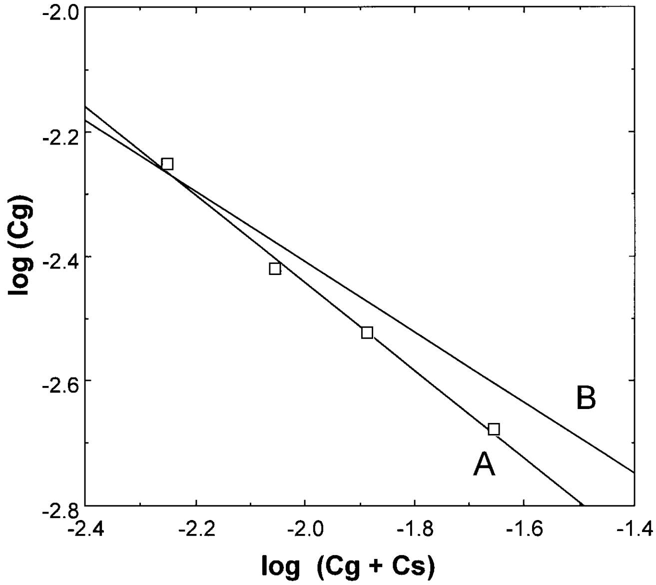

Fig. 6 Plots of $\log c_g$ against $\log(c_g + c_s)$ for the gel prepared by 100-kGy irradiation. *Line A* was obtained by regression for the plots. *Line B* was calculated by the equation of Minatti and Zanette for the cac (Eq. 2)

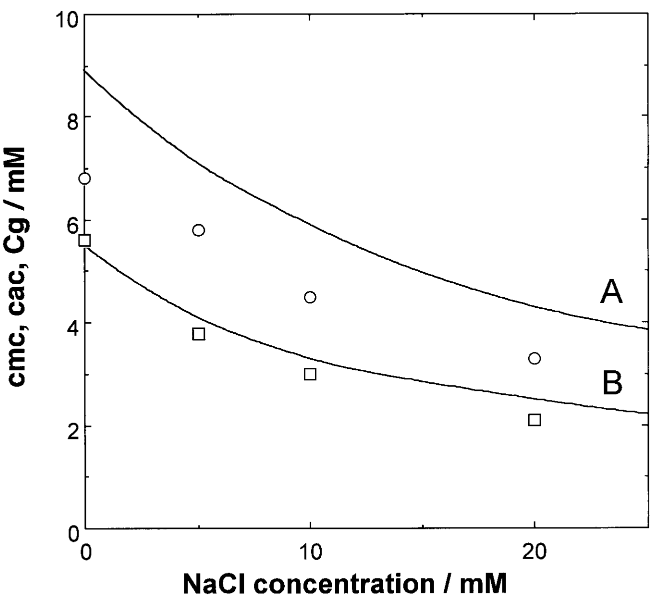

Fig. 5 Plots of the cmc, the critical aggregation concentration (*cac*) and the concentration, c_g, at the beginning of the gel swelling against NaCl salt concentration: cmc observed (*circles*); c_g observed (*squares*). *Lines A* and *B* represent the cmc and the cac, respectively, calculated by the equations of Minatti and Zanette

c_g is well correlated with the dependence reproduced by Eq. (2). It is clear that the swelling of the gels starts near the cac for each salt concentration. An equation of the type of Eqs. (1) and (2) is used for the evaluation of the degree of ionization, α, of the micelles [13]. For PEO/SDS complex, the slope of the plots of log(cac) against $\log(\text{cac} + c_s)$ is $(1–\alpha)$ [10, 13]. This plot was applied for c_g, as shown in Fig. 6. The value of α evaluated was 0.29, which is somewhat lower than 0.43 for the cac of PEO/SDS solution. It seems that the electronegative field around the SDS aggregates inside the gel is higher than that around the linear polymer. This may be either due to the overall field or to the local field, for example, the lowering of α is induced by the structural alteration of the DS micelle.

Next, we deal with the swelling behavior of the gel at SDS concentrations above 10 mM. Close inspection of the curves in Fig. 3 indicates that the leveling off of d/d_s is roughly classified into two groups; that under 0–5 mM NaCl and that under 10–20 mM. This may be correlated with the cmc values of SDS, about 3–7 mM. When the concentration of added NaCl is lower than this value, the cmc concentration of SDS is operative as the ionic strength of the solution. When the concentration exceeds the cmc of SDS, the concentration of NaCl becomes operative as the ionic strength in the solution. Therefore, it seems that the ionic strength acting in the solution determines the leveling off values of the gel swelling. In the higher-concentration region, the leveling-off value of d/d_s after the steep rise of the swelling is lowered with an increase in NaCl concentration. This observation may be explained by the increase in ionic concentration outside the gel reducing the difference in the osmotic pressures of the inside and the outside of the gel, and also repulsion between DS ions bound to PEO chains is suppressed sufficiently to contribute little to the swelling.

In the present study, we investigated the swelling of PEO gels in SDS solutions in the absence and in the presence of NaCl. The results show the gel interacts with SDS principally in the same way as the corresponding linear polymer: the micelle formation is induced by the PEO chain. The swelling of the gel takes place upon the micelle formation, and reaches the maximum within twice the SDS concentration at the beginning of the swelling. The degree of dissociation of SDS aggregates in the gel estimated from the variation of the cac with salt concentration showed a slightly lower degree of dissociation than that of PEO-bound SDS micelles. It was also found that the maximum degree of swelling at higher SDS concentrations depends on the relative values of the cmc of SDS and the salt concentration.

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