Gel Shrinking Resulting from Uneven Distribution of Ionic Micelles Between the Inside and the Outside of the Polymer Gel Network

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ABSTRACT: The volume change of crosslinked nonionic poly (N-isopropylacrylamide) (NIPA) polymer gel immersed in tetradecyldimethylaminoxide (C14DMAO) surfactant solutions at $0.1M$ NaCl, were investigated to distinguish between binding and nonbinding polymer gel/ C14DMAO surfactants. Also, the aggregation behavior of C14DMAO surfactants the inside and the outside the polymer hydrogels has been studied through solubilization of Sudan III dye. For the C14DMAO surfactants at the degrees of ionization (α) of 0.5 and 1, they bind to the NIPA gel at low surfactant concentration (C_D) that enhance the gel swelling due mainly to the osmotic pressure contribution from the counter ions (regime I, $C_D < 10mM$). However, the deswelling behavior was observed as the surfactant concentration increases above 10 mM (regime II). The solubilization experiments indicated that the surfactant concentration inside the gel is lower than that outside the gel in the regime II, which may be due to the large micelle size that cannot accommodate the mesh size of the gel. It was suggested that the uneven distribution of the ionic micelles leads to the reduction of the net swelling osmotic pressure of the gel (i.e., the decrease of the gel volume). In the case of the nonionic C14DMAO at $\alpha = 0$, on the other hand, the deswelling behavior was not clearly observed and the surfactant concentration inside the gel and outside the gel was almost identical even at 30 mM. For the nonionic surfactant, it was also found that the gel volume increases with the surfactant concentration at low surfactant concentration less than 1mM. This may be attribute to the dipole-dipole repulsion of N-O headgroups. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2001–2006, 2004

Key words: tetradecyldimethylaminoxide; NIPA gel; degree of ionization; swelling

INTRODUCTION

The interaction of nonionic water-soluble polymers with surfactants is a subject of both theoretical and industrial interest. In particular, the polymer of N-isopropylacrylamide (NIPA) has received increasing attention because its aqueous solution exhibits a phase separation with lower critical solution temperature, LCST.[1] Since the earliest study by Eliassaf[2] on the binding of NIPA with sodium dodcylsulfate (SDS), various studies have been published which were summarized the behavior of association.[3–7] The association is best viewed as a micelle formation in the polymer at a critical association concentration (cac), which is lower than the critical micelle concentration (cmc) of the pure surfactant. The relative lowering of the cmc (i.e., the difference (cmc-cac)/cms) is a measure of the additional stabilization of the micelle that results from its binding to the polymer. Many classical methods, such as measurements of surface tension, electrical conductivity, have been used to detect cac's. Most of these methods rely on the observation of a significant lowering of the cmc in the presence of the polymer. However, in instances where the difference between the cmc and the cac is small, there may remain uncertainty as to whether a certain polymer-surfactant displays association or not.

Chemically crosslinked NIPA gel is well known as a thermoresponsive gel[8–9] and it shows a volume phase transition (i.e., a discontinuous volume change) at a transition temperature of 34°C, T_c.[10–14] The hydrophobicity of NIPA chains depends on the temperature due to the dehydration of NIPA chains.[15] The binding isotherm of a surfactant onto NIPA gel has been measured to understand the interaction between them,[4–6] which indicates that a conformational change of polymer chain was induced by the surfactants binds. The binding could also be clearly evidenced by a simple experiment of measuring the swelling behavior of the polymer gels. Recently, several studies on the aggregation behavior of surfactants in nonionic gels have been reported for the gel-surfactant systems.[16–17] The surfactant aggregation in the gel was affected by the

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gel network in the case of the surfactants that forms large cylindrical micelles in solutions.[16-17]

In the present study, simple experiment, based on the volume change (equilibrium swelling isotherm) of crosslinked nononic NIPA gel immersed in tetradecyldimethylaminoxide (C14DMAO) surfactant solutions at 0.1M NaCl were investigated. This work has been done for two purposes. One is to monitor the associative interaction of the surfactant to the gel by the swelling measurements. As the second purpose, the aggregation behavior of surfactant inside the gel was examined via the solublization of sudan-III by surfactant aggregates in the polymer gel network.

EXPERIMENTAL

Materials

Monomer and reaction accelerator for preparation of gel samples were N-isopropylacrylamide (Kohjin Co., Ltd), N, N-methylenebis (acrylamide) (a crosslinker; Nacalai tesque, Inc.), and N, N, N′, N′-tetramethylenediamine (an accelerator for polymerization reaction; Nacalai tesque, Inc.). Initiator used in gel preparation was ammonium persulfonate. Tetradecyldimethylamine oxide (C14DMAO) (nonionic surfactant; Fluka Chemie AG) was recrystallized three times from hot acetone. The nonionic C14DMAO sample was dissolved in water, and hydrochloric acid was added to protonate the amine oxide. The prepared solutions were freeze-dried and the solid samples of C14DMAO at different ionizations (α) were obtained.

Sample preparations

Poly (N-isopropylacrylamide) (NIPA) gel was prepared by radical polymerization at 5°C. A mixture of 3.96 g (700 mM) of NIPA monomer, 0.0655 g of N, N-methylene (acrylamide), and 120 μl of N, N, N′, N′-tetramethylethylenediamine was dissolved in pure water to make 50 mL of aqueous solution. For at least 30 min before polymerization, nitrogen gas was bubbled into above solution to purge oxygen. An aqueous solution of ammonium persulfate (4wt%) was bubbled by N_2 gas and a part of it (1 mL) was added to the above monomer solution. Polymerization reaction was performed under N_2 gas in a thin capillary of the diameter 3mm or in glass plates kept in refrigerator. The unreacted monomer and the residual impurities were leached out by immersing the gel samples in a large excess of deionized water followed by Millipore water for at least a week. Then the gel samples were dried at room temperature for another week. The cylinder gel of diameter 3mm was employed for the swelling. The bulk gel prepared between two flat glass plates was cut into cubes several centimetres in diameter. These cut gels were used for determination of

surfactant aggregate inside the gel via Sudan III solubilization. The equilibrium swelling of gels were determined by successive measurements of equilibrium swelling of gel samples at one week, three weeks, and one month. No equilibrium swelling change was observed between three weeks and one month

Gel swelling experiment

The dried gels of about 1 g were immersed in aqueous surfactant solutions of 10 mL at a given surfactant concentration. The surfactant concentrations of the solutions were 0, 0.05, 1, 5, 10, 20, and 30 mM. The swelling ratio was measured after immersing the gel in the solution for almost one month at different temperatures, 25, 30 and 40 ± 1°C.

The equilibrium swelling, W, was defined as

$$W = (W_{Wet}\text{-}W_{Dry})/W_{Dry}$$

where W_{Wet} and W_{Dry} are the weights of gels in the equilibrium swollen state and dried state, respectively.

Solubilization of Sudan III by surfactant aggregates

The cube gels of almost 1 g were equilibrated with surfactant solutions (10 mL) at a given surfactant concentration. Small amounts of solid Sudan III were added to the surfactant solutions containing the gel samples, and the solutions were allowed to be equilibrated for one month at 25°C. The gels were put in an injector and pressed. The pressure was high enough to squeeze out the solution inside the gel as a free micelles.[16] Squeezed solutions of about 0.5 mL were analyzed by UV at maximum absorption 500nm.

Reversibility of micelle formation

Cube gels of almost 1 g were immersed in C14DMAO surfactant solutions (10mM) at degrees of ionization, α = 0 and 0.5, at 25°C. A small amount of solid powder of sudan III was added to the surfactant solution containing the gel. The equilibrium of the solublization was confirmed after three weeks at 25°C. Then the degree of ionization of the solution, α = 0 was inverted to α = 0.5, and that of α = 0.5 to α = 0 by changing the pH. In both cases, the solutions inside the gel were squeezed out from the gel and the absorptions at 500 nm were determined by UV.

RESULTS AND DISCUSSION

Effects of ionization degree of C14DMAO surfactant on the swelling behavior of NIPA gel

Effects of degree of ionization of the surfactant (α) on the swelling behavior of NIPA gel were studied as a
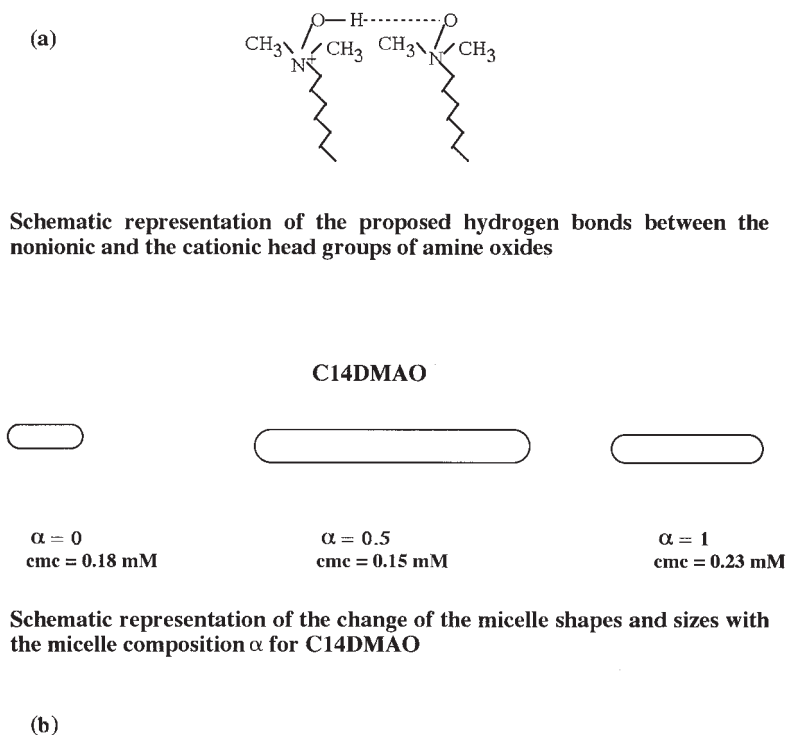
(a)

Schematic representation of the proposed hydrogen bonds between the nonionic and the cationic head groups of amine oxides

C14DMAO

$\alpha = 0$
cmc = 0.18 mM

$\alpha = 0.5$
cmc = 0.15 mM

$\alpha = 1$
cmc = 0.23 mM

Schematic representation of the change of the micelle shapes and sizes with the micelle composition α for **C14DMAO**

(b)

Figure 1 (a) Schematic representation of the proposed hydrogen bonds between the nonionic and the cationic head groups of amine oxides (b) Schematic representation of the change of the micelle shapes and sizes with the micelle composition α for C14DMAO

function of the surfactant concentration at different temperatures. Tetradecyldimethylamineoxide (C14DMAO) has been used mostly as nonionic surfactant, but it exist as either a nonionic or cationic (protonated form) species, depending on the pH of the aqueous solution.[18] The pH's of equilibrium solutions of C14DMAO were 8, 5 and 2 at $\alpha = 0$, $\alpha = 0.5$, and. $\alpha = 1$, respectively. The schematic representation of the change of the micelle sizes with the micelle composition of C14DMAO was shown in Figure 1(b). The maximum size of micelles observed at $\alpha = 0.5$ is explained in terms of the hydrogen bonding between the cationic and nonionic head groups-[Figure 1 (a)].[18–19] The cmc's of C14DMAO solutions were 0.18, 0.15, and 0.23 mM at $\alpha = 0$, $\alpha = 0.5$, and $\alpha = 1$, respectively.

Figure 2 shows the gel volume change (equilibrium swelling isotherm) of NIPA gels immersed in $0.1M$ NaCl solutions with increasing concentrations of the nonionic surfactants ($\alpha = 0$), at three different temperatures below and above the transition temperature, Tc of NIPA gel. The gel volume increases with surfactant concentration at low surfactant concentration, less than 1mM. The result shows that the nonionic C14DMAO surfactant binds to NIPA gel. At relatively high surfactant concentration region, above 10mM, the gel volumes were almost constant at 25 and 30°C below the Tc. The swelling may be attributed to the dipole-dipole repulsion among N-O head groups of

adsorbed C14DMAO. However, the measurements are performed in the presence of NaCl, the dipole-dipole repulsion is still enough to overcome the screen effect of the presence of NaCl. The repulsion enhances the swelling until it reaches the maximum followed by a steady level. It was reported that the increase of the volume of NIPA gel with nonionic surfactant concentration (without dipole groups) was very small,[6]
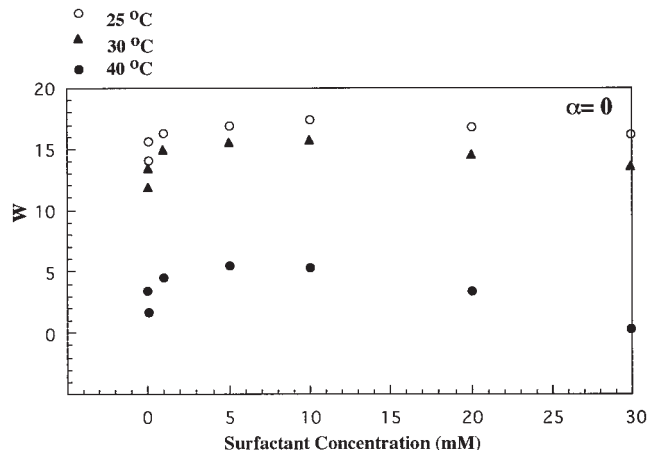
Figure 2 Volume swelling vs surfactant concentration of nonionic C14DMAO ($\alpha = 0$) at different temperatures below and above the Tc of NIPA polymer gel.
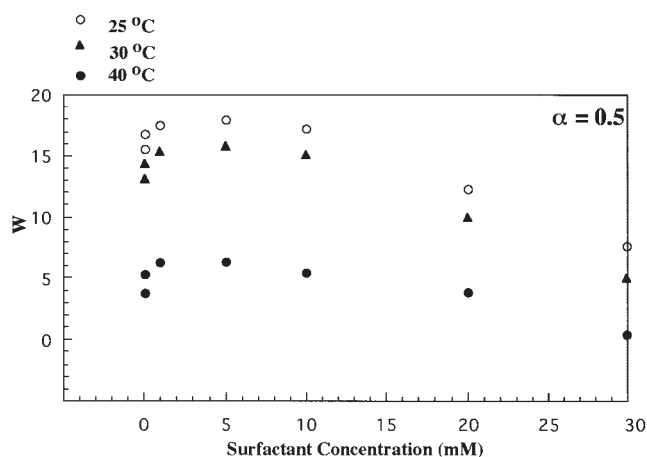
Figure 3 Volume swelling vs surfactant concentration of half-protonated C14DMAO (α = 0.5)

Figure 5 Volume swelling vs degree of ionization (α) in the range of 10, 20 and 30mM of C14DMAO surfactant concentration of 25°C.

which may be due to the absence of dipole-dipole effect that likely to be dominant in the nonionic C14DMAO surfactant case.

Figure 3 shows the variation of the gel volume (equilibrium swelling isotherm) of NIPA gel as a function of the concentration of half-protonated C14DMAO (α = 0.5) at three different temperatures below and above LCST of NIPA gel. These results show two regimes. An increase in the gel volume at low surfactant concentration was observed (regime I). Regime II commences from 10mM, where prominent decrease in the gel volume was clearly observed, in comparison with the case of the gel volume swelling at α = 0.

Figure 4 shows also the variation of the gel volume (equilibrium swelling isotherm) with surfactant concentration at α = 1 at three different temperatures below and above LCST. A similar trend was observed,
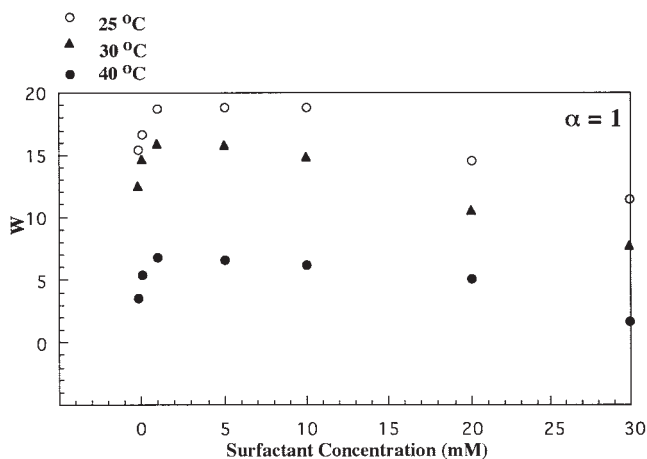
however the magnitude of gel volume was a bit higher than those obtained in the case of α = 0 and 0.5 in regime I. It can be concluded from the shape of the swelling curves, the C14DMAO surfactant at α = 1, binds to NIPA gel.

Figure 5 shows the gel volume dependence on the degree of ionization at 25°C, at three different surfactant concentrations of 10, 20, and 30 mM. The gel volume increases with the degree of ionization at 10 mM due to the increase of the osmotic pressure of counter ions of the adsorbed surfactant. In contrast, at 20mM, the gel volume decreases with the degree of ionization. The deswelling behavior was extensively observed at α = 0.5 in the surfactant concentration of 30mM. This revealed that the size of C14DMAO micelles plays an important role in the swelling behavior of NIPA gel.

Surfactant aggregates in the gel interior probed by the solubilization of Sudan III

To examine the aggregation behavior of nonionic and cationic surfactants inside the gel, the surfactant concentrations in the gel interior were monitored by the absorption of Sudan III. Figure 6 shows the difference in absorbance of surfactant solutions inside the gel interior and that of the bulk solution outside the gel, $\Delta_{Abs.} = A_{out} - A_{in}$. represented by UV absorption of Sudan III at 500 nm, plotted against the different degree of ionization in the range of 1, 10 and 30mM at 25°C. Where A_{in} and A_{out} are the absorbance of the surfactant solution inside the gel and the outside the gel, respectively. Different behaviors were observed for the gels at different α, depending upon the aggregation behavior of the micelles inside the gel. At α = 0, C14DMAO surfactant concentration inside the gel and outside the gel was almost identical and superimposed at 10 and 30mM of C14DMAO concentration.

Figure 4 Volume swelling vs surfactant concentration of full-protonated C14DMAO (α = 1) at different temperatures below and above the Tc of NIPA polymer gel.
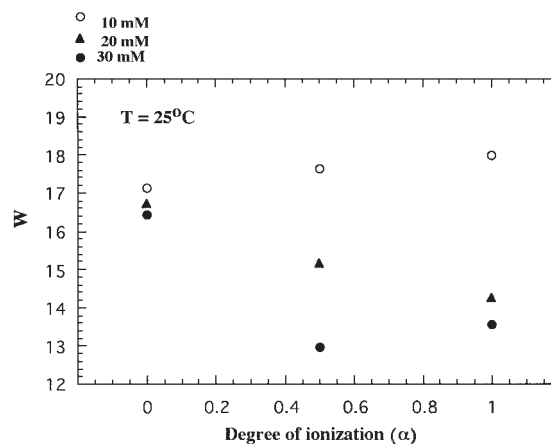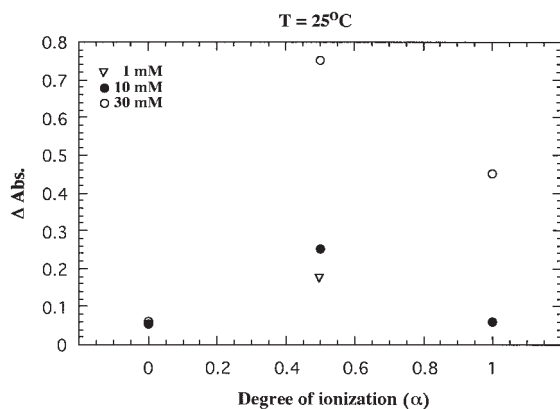
Figure 6 Difference in absorbance vs the degree of ionization (α) in the range of 1, 10 and 30 mM of C14DMAO surfactant concentration at 25°C.

This means that the micelles inside and outside the gel are formed in similar fashion. On the other hand, at α = 0.5 and 1, the difference of the surfactant concentration between the inside and the outside of the gel became more apparent with increasing surfactant bulk concentration from 1, 10mM to 30mM, in contrast with the case at α = 0. This indicates that the surfactant concentration (α = 0.5 and 1) inside the gel is lower than that outside the gel in the regime II. It is considered that the micelles at α = 0.5 and α = 1 inside the gel are less formed comparatively. The remarkable micelle growth with increasing surfactant concentration has been reported for the C14DMAO at α = 0.5 in the absence of gels.[20-21] From the dynamic light scattering measurement, the radii of the equivalent hydrodynamic sphere of the micelle were about 20 nm (α = 0.5) and about 8 nm (α = 1) at 30 mM, in the presence of 0.1M NaCl.[22] The decrease in surfactant concentration inside the gel may be interpreted in terms of the micelles size that cannot accommodate the mesh size of the gel. The gel network forbids the formation of large micelles due to the unfavorable surfactant-polymer steric repulsion.[16-17]

Another possible mechanism of the lower surfactant concentration inside the gel is the local binding of the surfactant to the gel surface.[23] It has been reported that sodium dodecylbenzensulfonate (NaDBS) surfactants are bound only to the regime in the vicinity of the gel surface and hence cannot penetrate into the gel interior.[23] Such local surfactant binding to the gel surface is expected to induce the decrease in surfactant concentration inside the gel.

To examine the effect of the local surfactant binding, the changes in the absorbance of Sudan III in the gel were measured by changing the pH of the solution. The absorbance of Sudan III in the gel decreased when α was inverted from 0 to 0.5, while it increased when α was inverted from 0.5 to 0, as shown in Figure 7. These results suggest that the decrease in surfactant

concentration of C14DMAO (α = 0.5) inside the gel may be attributed to a large micelle size that cannot accommodate the network of the gel.

Explanation and mechanism of swelling and deswelling behavior

The presence of the maximum of the swelling of NIPA gel in C14DMAO solutions observed at α = 0.5 and 1, in Figures 3 and 4 can be explained as follows. At low surfactant concentration (regime I) the C14DMAO surfactant adsorbs to the NIPA gel via hydrophobic interaction, leading to the swelling of the gel due mainly to the osmotic pressure contribution from the counterions of the adsorbed surfactants.[22]

To confirm the osmotic pressure effect, the swelling of NIPA gel at α = 0.5 in 0.4M NaCl was compared with that in 0.1 NaCl in Figure 8. It can be seen that the gel volumes were almost independent of the surfactant concentration at 0.4M NaCl. This means that the Donnan osmotic pressure effect was remarkably diminished at this high salt concentration.

In the higher surfactant concentration (regime II), we found that the gel starts to deswell in the case of α = 0.5 and 1. Such maximum swelling behavior has been reported for slightly hydrophobic nonionic polymers - ionic surfactant systems by L. Piculell.[7] According to this result,[7] at the cac, the gel volume increases sharply with increasing the surfactant concentration due to the swelling osmotic pressure of the counterion from the polymer-bound micelles. After a swelling maximum slightly above cmc, the gel starts to deswell
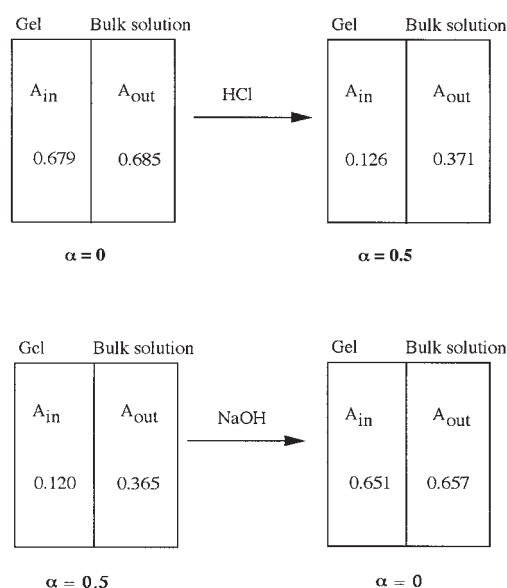

Figure 7 Schematic representation of the reversibility of the micelles formation between the degree of ionization, α = 0 and α = 0.5 by changing the pH of the C14DMAO solutions at 25°C.
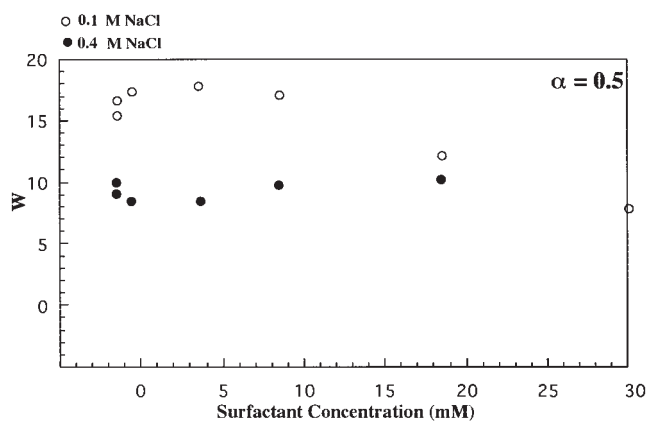
Figure 8 Volume swelling vs the different concentration of C14DMAO in the presence of different salt concentration at 25°C.

because the micelle formed outside the solution as well. The net osmotic pressure between the two compartments is thus reduced slightly above cmc, resulting in the deswelling of the gel. In the case of NIPA gel/C14DMAO surfactant system, this mechanism may not explain our result because the deswelling behavior was observed in the presence of 0.1M NaCl. It is considered that the deswelling behavior with increasing the surfactant concentration in the present study originates from that the surfactant concentration inside the gel is lower than that outside the gel in the regime II, as indicated by the solubilization experiments. This uneven distribution of the ionic micelles leads to the reduction of the swelling osmotic pressure of the gel (i.e., the decrease of the gel volume). In the case of $\alpha = 0$, on the other hand, the nonionic

C14DMAO surfactant concentration inside the gel and outside gel was almost identical at 10 and 30mM, as shown in Figure 6. As a result, the deswelling behavior was not clearly observed for $\alpha = 0$ below the Tc.

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