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Effects of Surfactants on the Phase Transition of Poly(*N*-isopropylacrylamide) Gel

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ABSTRACT: The swelling equilibrium of *N*-isopropylacrylamide (NIPA) gel was studied as a function of temperature in aqueous solutions of surfactants: sodium dodecyl sulfate (SDS, anionic), dodecyltrimethylammonium chloride (DTAC, cationic), and nonaoxyethylene dodecyl ether (NODE, nonionic). In pure water the gel showed a discontinuous volume phase transition at 33.6 °C with a volume change of $V_{\mathrm{swollen}}/V_{\mathrm{collapsed}} = 8$. With the addition of SDS, the transition temperature as well as the volume change at the transition increased. At 3.47×10^{-2} M of SDS concentration, the transition temperature became 88 °C and the volume ratio increased to $V_{\mathrm{swollen}}/V_{\mathrm{collapsed}} = 32$. A similar but less drastic change was observed when DTAC was used. In contrast, NODE induced little change in both the temperature and temperature phase transition for the concentration range studied ($<6.94 \times 10^{-2}$ M). In order to understand these effects of ionic surfactants, the association and dissociation of SDS with the gel or homopolymer of NIPA were investigated in an aqueous system. The amount of free SDS ions was measured at different temperatures by a conductometric method. An increase in the transition temperature was brought about by SDS binding to the gel or polymer whereupon the bound SDS was completely dissociated by cooling. The association and dissociation of SDS were reversible and, respectively, occurred in the temperature ranges above and below 30 °C. Thus, the ionic surfactant molecules convert the gel into an ionic gel due to binding through the hydrophobic interaction. The obtained experimental results have been qualitatively discussed in terms of the classical Flory–Huggins theory with modifications to account for the free energy of association of surfactant molecules with the gel network or polymer and surfactant self-association.

Introduction

Recently much attention has been focused upon phase transitions and critical phenomena in polymer gels.[1–3] Phase transitions accompanied by a reversible, discontinuous volume change as large as several hundred times the original volume, in response to infinitesimal changes in external conditions, have been universally observed in various gels made of synthetic and natural polymers.[1–11] Some of them are found to swell at low temperatures and collapse at high temperatures;[11,12] these are called thermosensitive or thermoshrinking gels.

The gel consisting of *N*-isopropylacrylamide (NIPA) is a well-known thermosensitive gel which shows a discontinuous volume phase transition in response to temperature changes. The thermally induced phase transition of NIPA gel has been extensively studied,[1,4,11] and several applications have been proposed in a variety of areas including transducers, sensors, drug-delivery devices, and actuators. In addition, the phase transition of NIPA gel is of interest as a model for understanding the folding and unfolding of biomolecuar systems, since the gel contains both hydrophilic amide groups and hydrophobic, hydrocarbon chains that play a vital role in determining the structures and functions of biopolymers.

Hydrophobic interactions are known to be essential for inducing the phase transition of NIPA gels. In general, the entropy of a system should increase linearly with a rise in temperature. In the case of NIPA gels, as the temperature is raised the polymer network shrinks to a compact state and its entropy decreases. The entropy decrease of the network should be compensated by an increase in the entropy of water molecules. That is, water molecules form a regular, ice-like structure when in contact with a hydrophobic polymer network, whereas they assume a random, liquid-like structure when expelled from the collapsed polymer network. As a result, the total entropy of a hydrophobic gel increases upon collapse. It is then natural to expect that a chemical compound having both hydrophilic and hydrophobic characters should influence significantly the phase transition properties of the gel. Studies of such effects would provide important information on the nature of polymer–solvent interactions within gel systems and help us to understand the structures and functions of biopolymers.

Surfactants are well suited for the present purpose because they are comprised of a hydrophilic, ionic or nonionic group bound to a nonpolar hydrophobic group. In the present study, the following three types of surfactants which have dodecyl groups as the hydrophobic chain have been used: the anionic surfactant $CH_3(CH_2)_{11}SO_4Na$ (sodium dodecyl sulfate, SDS), the cationic surfactant $CH_3(CH_2)_{11}N(CH_3)_3Cl$ (dodecyltrimethylammonium chloride, DTAC), and the nonionic surfactant $CH_3(CH_2)_{11}(CH_2CH_2O)_9H$ (nonaoxyethylene dodecyl ether, NODE). The effects of these surfactants on the swelling equilibrium and phase transition temperature of NIPA gels were studied in aqueous systems as a function of surfactant type and their respective concentrations. A rise in the phase transition temperature accompanied by an increase in the swelling ratio was observed when the anionic and cationic surfactants were used. The association of SDS ions with the NIPA chains in the gel or homopolymer was further investigated by conductometric measurements for aqueous solutions including both the surfactant and gel. The experimental results were analyzed semiquantitatively by a modified Flory–Huggins theory, where we assumed that the ionic surfactants bind with the network chains through hydrophobic interactions which then induce the observed effects via electrostatic interactions.

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Experimental Section

Materials. The gels were prepared by a free radical copolymerization. An aqueous monomer solution (100 mL) containing purified NIPA (Kodak, 7.8 g), *N,N'*-methylenebis(acrylamide) (cross-linker, Bio-Rad Lab., 0.133 g), and *N,N,N',N'*-tetramethylethylenediamine (accelerator, Bio-Rad Lab., 240 mL) was first prepared. NIPA was purified by recrystallization in toluene by adding petroleum ether. Cylindrical gels were prepared for swelling measurements by mixing 1 mL of the well-degassed monomer solution with 10 μL of an aqueous solution including ammonium persulfate (initiator, Mallinckrodt, 4% w/v), and quickly transferring it into a test tube in which capillaries (inner diameter, ca. 0.1 mm) were inserted in advance. Cubic gels for the study of SDS uptake of NIPA gels were also prepared by polymerizing 100 mL of the monomer solution in a glass container after the addition of an ammonium persulfate solution (4.0% w/v, 1 mL). In both cases the gelation took place at 0 °C in a nitrogen atmosphere. After the gelation was completed, all the sample gels were taken out of the containers, fully washed with a large amount of distilled water, and cut into suitable lengths.

A homopolymer of NIPA, poly(NIPA), was synthesized to study the association with SDS in aqueous solution. Polymerization was carried out by stirring a benzene solution (35 mL) containing the monomer and α,α'-azobis(isobutyronitrile) as an initiator at 75 °C for 20 min under nitrogen. The reaction mixture was slowly poured into *n*-hexane to precipitate the polymer, which was then separated by filtration, washed with *n*-hexane, and dried in vacuo. This process was repeated three times. Further purification was carried out by dialyzing aqueous polymer solution against distilled water for a week. The dialyzed solution was lyophilized and finally dried under reduced pressure at 50 °C for 3 days. The yield of NIPA was 6.62 g (75%). The number-average molecular weight is 80 000 as established by viscometric measurement in acetone.

SDS was commercially obtained from Aldrich Chemical Co. DTAC (Coatamine) and NODE (Emulgen) were supplied by Kao Corp., Tokyo, Japan. In all the experiments below distilled and deionized water was used.

Swelling Measurements. The cylindrical gels were inserted into a micropipet with an inner diameter of 1 mm. Aqueous surfactant solutions were then introduced into the micropipet, which was immediately sealed. Size and shape of the gel were monitored under a microscope with 200× magnification and analyzed using an AVEC image processor (Hamamatsu Photonics, C1966). Temperature was controlled within ±0.1 °C using a temperature control system with water circulating around the micropipet.

Conductivity Measurements. To study the hydrophobic interaction of SDS molecules with NIPA residues, the SDS uptake by the gel and the association of SDS with poly(NIPA) were examined in 0.347 mM (0.01% w/v) SDS solution at different temperatures. The concentration of free SDS ions in the solution was determined at different temperature from the conductivity measurements using a Radiometer conductivity meter (Model CDM83) equipped with a CDC 344 conductivity cell. Temperature was controlled within ±0.1 °C using a water-circulating system.

Results

Effects of Surfactants on Swelling Equilibria. The effect of each ionic surfactant on the reversible swelling or shrinking process of the NIPA gel was studied as a function of temperature and surfactant concentration. Figures 1a and 1b show the temperature dependence of the swelling ratio of NIPA gels obtained for the two different ionic surfactants used. In the absence of surfactants, NIPA gels were swollen at lower temperatures and underwent a discontinuous volume phase transition (collapse) at 33.6 °C with a volume change at this temperature defined by the ratio $V_{\mathrm{swollen}}/V_{\mathrm{collapsed}}$ (V/V_0) ~8. Here, V_0 is the volume of a collapsed gel at high temperatures, which is constant and the same for all the gels. In solutions containing ionic surfactants SDS (Figure 1a) and DTAC (Figure 1b), the volume phase transition was also discontinuous for all surfactant concentrations studied. Moreover, both the volume phase transition temperature (T_v) and the net volume change at the transition increased with increasing surfactant concentration. For example, at 34.7 mM concentration of SDS, T_v was found to be ~88 °C, which was accompanied by an increased volume ratio of V/V_0 ~30. In contrast, nonionic NODE did not exhibit any observable effects on either the volume phase transition temperature or the volume ratio of NIPA gels.

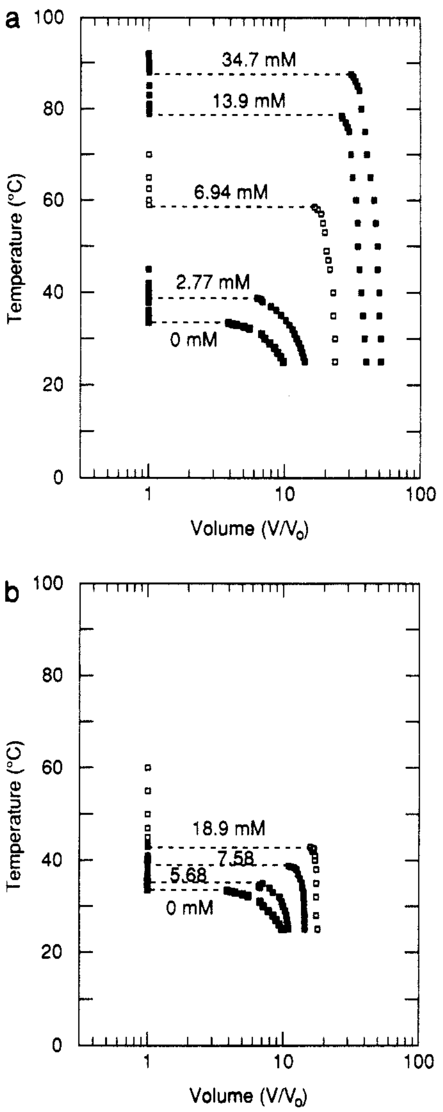

Figure 1. Typical temperature dependence of equilibrium volume for NIPA gel obtained from heating processes with SDS (a) and DTAC (b). Gel volumes (V) were normalized by the fully collapsed volume (V_0). All the curves determined at different concentrations (0–69.4 mM) of NODE were independent of the surfactant concentration and the same as the curves without the surfactants shown in (a) and (b). The surfactant concentrations in mM were shown in a and b.

The phase transition temperature T_v whereupon NIPA gels underwent a reversible volume change as a function of surfactant concentration is shown in Figure 2. Both SDS and DTAC surfactants brought about an initial increase in T_v up to a certain concentration; increasing further the concentration of these surfactants produced negligible effects on T_v (Figure 2) and could thus be considered as having reached a plateau beyond a characteristic concentration (~20 mM for SDS and ~16 mM for DTAC). The magnitude of the increase in T_v, however, was dependent on the type of surfactant used; i.e., the

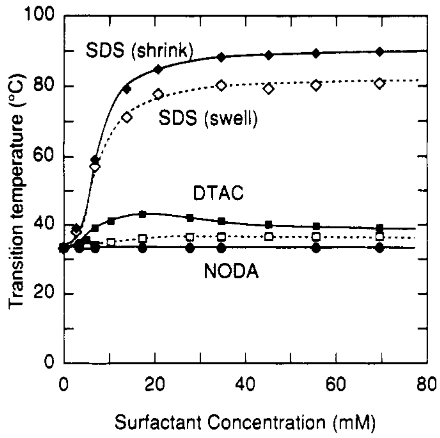

Figure 2. Transition temperatures for swelling (open symbols) and shrinking (solid symbols) processes as a function of the concentration of the surfactants SDS, DTAC, and NODE.

effect of SDS on the absolute values of T_v was much greater than DTAC for the range of concentration studied. It is also interesting to note that at SDS concentrations (>34.7 mM) beyond its characteristic concentration (~20 mM), the gel swelling or collapse was different from position to position within the cylindrical gel; for example, both ends underwent volume collapse at a temperature higher than that of the central portion. Such a position dependence was not observed at lower SDS concentrations nor in any of the concentration ranges of the other surfactants.

The magnitude of increase in T_v and its plateau, as well as the increase in the ratio V/V_0, can be quantified theoretically if hydrophobic binding of the surfactant molecules to the NIPA gel network is considered (see Discussion).

SDS Uptake by NIPA Gel. The interaction between NIPA gel and SDS was further studied by monitoring SDS uptake by gel. Conductivity measurements were used to determine the concentration of SDS in the aqueous supernatant in the presence and absence of gels. The gel should absorb a portion of the SDS molecules and the conductivity is proportional to the amount of free SDS molecules. To avoid experimental error due to dilution by diffusion of water out of the gel, the samples were thoroughly equilibrated in an SDS solution prior to conducting experiments. In addition, preliminary experiments have shown that an SDS concentration of about 0.01% w/v was most suitable for performing conductivity measurements, because at this concentration range nonlinear effects on conductivity with respect to temperature variation were not observed. Hence all conductivity measurements in this study were performed using a 0.01% w/v SDS solution.

Figure 3 shows the temperature dependence of the conductivity in the absence and presence of the gel cubes in the SDS solution. The conductivity of the solution without gel increases linearly with temperature. In the presence of NIPA gels, the conductivity was also linearly dependent with respect to temperature variation for the temperature range investigated, except in the vicinity of 33 °C, where a significant decrease in the slope of the curve was observed. [Note: this temperature can be thus referred to as the binding temperature.] There was no marked difference in the conductivity curves between the heating and cooling processes, indicating no hysteresis in the conductivity. From these results, it can be said that at a temperature higher than the binding temperature a strong uptake of SDS molecules by the gel occurs via primarily due to hydrophobic interaction.

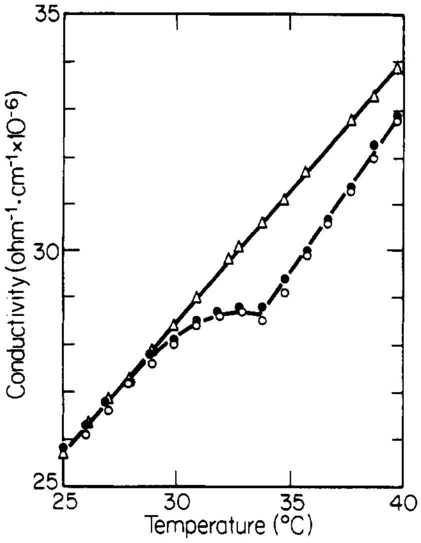

Figure 3. Temperature dependence of conductivity of 0.347 mM (0.01% w/v) SDS solution in the presence and absence of the NIPA gel. The conductivity without gel is represented by triangles, while those in the presence of gel are given by open circles for the heating process and solid circles for the cooling process. The measurements were made using 20 mL of the SDS solution and 2.1 mL of the cubic gels at 20 °C.

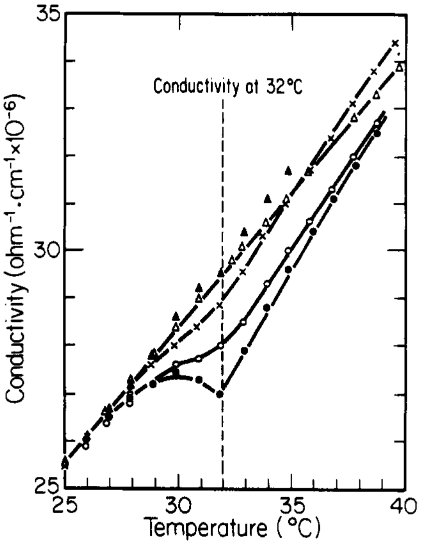

Figure 4. Temperature dependence of the conductivity of 3.47 mM (0.01% w/v) SDS solution containing different amounts of poly(NIPA). The polymer concentrations are 0 (▲), 0.063 (△), 0.773 (×), 1.24 (○), and 2.32% (w/v) (●), respectively.

Association of SDS with Poly(NIPA). There are common factors between the volume phase transition of NIPA gel and the phase separation of poly(NIPA) solution;[11] for example, the interaction parameter should be common to both systems. Thus, a comparison of SDS/poly(NIPA) association with SDS uptake by the gel would be helpful to understand the hydrophobic interaction in the gel system. Figure 4 shows the temperature dependence of the conductivity of 0.01% (w/v) SDS solutions containing different amounts of poly(NIPA). A decrease in the conductivity caused by the SDS/polymer association was observed in a narrow temperature range from 28 to 32 °C. The magnitude of the decrease in the free SDS concentration, indicated by the decrease in conductivity, was found to increase with the polymer concentration. To clarify this relationship, differences in the conductivities (ΔC) at 32 °C between each polymer solution and the polymer-free SDS solution were plotted as a function of

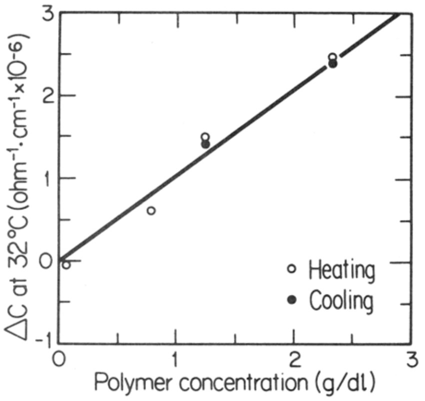

Figure 5. Polymer-concentration dependence of difference in the conductivity, ΔC, between polymer-containing and polymer-free 0.347 mM (0.01% w/v) SDS solutions. The data were determined from Figure 4.

the polymer concentration (Figure 5). As shown, this value increases linearly with increasing polymer concentration. The cloud points of the SDS solutions containing poly(NIPA) were determined visually during the conductivity measurements. The obtained values (30.5 ± 0.3 °C) were independent of the polymer concentration. By comparing this result with that in Figure 4, it is clear that the association of SDS with the polymer became stronger in the vicinity of the cloud point. It has been reported that the endothermic or exothermic peak on a DSC thermogram for poly(NIPA)/water system was observed only in the temperature range near the cloud points.[11] Also, the transition heat at the cloud point was very close to the heat of the collapse of the NIPA gel.

Discussion

The observed effects of the ionic surfactants on NIPA gels can be readily understood by assuming that the gel is ionized upon binding of the surfactant molecules to the polymer network: It is reasonable to consider that both SDS and DTAC bind to the polymer network within the gel phase through hydrophobic interactions, subsequently converting an otherwise neutral NIPA gel into a polyelectrolyte gel. These acquired network charges and counterions associated to the charges exert an extra osmotic pressure on the network. As a result, both the transition temperature T_v and volume change at the transition V/V_0 were increased, in direct analogy with previously reported data on the phase transitions of polyelectrolyte copolymer gels composed of NIPA and sodium acrylate.[13-15] However, nonionic NODE did not induce a significant change in the phase transition of NIPA gel. As will be discussed in more detail later, this is due to the absence of electrostatic interactions between surfactant molecules bound to the network.

The above hypothesis can also explain the observation that the transition temperature T_v became almost constant at a certain concentration of SDS or DTAC. That is, for aqueous surfactant systems it is well-known that a critical micelle concentration (C_{cmc}) exists such that above this concentration the amount of the "free" surfactant in the system remains unaltered even if further surfactant is added. The observed position-dependent gel swelling or collapse at high concentrations of SDS lends support to this assumption, because the result can be related to a heterogeneous distribution of the surfactant molecules within the gel phase. Conversely, one could also argue that all of the possible sites within the gel network to which the surfactants may bind are occupied, thereby obtaining a saturation value for T_v. At surfactant concentrations beyond this characteristic concentration, the excess "free" surfactant is in a dual equilibria with micelle formation and binding to the gel matrix. As will be discussed in greater detail later, both cases would result in a saturation value for the amount of surfactant bound to the gel matrix.

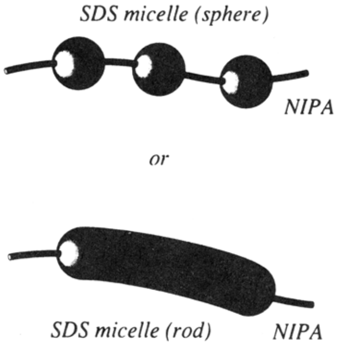

Figure 6. Schematic illustration for the system of a hydrophobic gel in a surfactant solution.

Another important characteristic of surfactant effects on the volume phase transition of NIPA gels is the large differences in the values for T_v and V/V_0 ratio observed between SDS and DTAC (see Figure 2). Several factors should be considered capable of inducing these results, i.e., (a) a difference in the counterions, (b) a difference in the ionizable groups, (c) a difference in the binding amounts, and so on. At the present stage, however, we cannot say which is the main factor. Therefore, the curve of the transition temperature appears to level off at the concentration characteristic of surfactants, 20 mM for SDS and 16 mM for DTAC. These results are close to the C_{cmc} values of SDS (8-9 mM) and DTAC (16 mM). A slight difference observed in SDS may be due to the fact that the phase transition of NIPA gel in the SDS solution takes place at very high temperature (see Figure 2).

Theoretical Considerations

This section provides a simple theoretical formulation to describe the effect of surfactant on the phase transition of gels and the conductivity of the supernatant surfactant solution. The model on which the theoretical calculation will be made is schematically shown in Figure 6. As stated previously, the primary assumption is that the surfactant solutions consist of free surfactant molecules and, at higher surfactant concentrations, micelles consisting of M monomers. Some of the free surfactant molecules are bound to the polymer network, thereby effectively making the gel ionic. The ionization is considered to be the main factor to induce the drastic changes in the phase transition properties of the neutral NIPA gel by ionic surfactants.

Binding of Surfactant to the Polymer Network. The equilibrium volume of an ionic gel is given by the zero osmotic pressure condition:[8,12,16]

$$\frac{\pi}{k_B T} = \frac{v\nu_e}{N_A}\left\{(2f+1)\left(\frac{\phi}{\phi_0}\right) - 2\left(\frac{\phi}{\phi_0}\right)^{1/3}\right\} - 2\phi - 2\ln(1-\phi) + \frac{\Delta F}{kT}\phi^2 = 0 \quad (1)$$

where T is the absolute temperature, ΔF (=$\Delta H - T\Delta S$) is the free energy for polymer-polymer contact, ΔS and ΔH are their entropy and enthalpy, respectively, k_B is the Boltzmann constant, N_A is the Avogadro number, v is the molar volume of water, ν_e is the total number of the effective polymer chains in the gel, ϕ is the polymer network density, ϕ_0 is the density at the Θ temperature, and f is the number of counterions per chain. For NIPA gels the interaction parameters ΔS and ΔH are both negative. It is well established that the transition temperature of NIPA gel rises and the volume change at the transition increases as the gel becomes more ionized. It will be shown that the ionization f indeed increases for the case when ionic surfactants are added to the gel network.

The ionization f is zero in the absence of ionic or presence of nonionic surfactants. In the presence of ionic surfactants, the f value becomes finite due to the binding of ionized surfactant molecules via hydrophobic interactions with the polymer network. That is

$$f = |z|\frac{N_B}{\nu_e} \tag{2}$$

where N_B denotes the amount of the surfactant molecules bound to the polymer network. z is the valency of the surfactant; i.e., $z = -1$ for anionic, 0 for neutral, and +1 for cationic surfactant.

The interaction free energy is also expected to change with the binding of surfactant in proportion to N_B:

$$\Delta H = \Delta H_0 + \Delta h\frac{N_B}{S_0}$$

$$\Delta S = \Delta S_0 + \Delta s\frac{N_B}{S_0} \tag{3}$$

where S_0 is the total number of available binding sites for surfactant, ΔH_0 and ΔS_0 are the contact enthalpy and entropy without the binding of surfactant, and Δh and Δs indicate their changes when all the sites are covered by surfactant. The changes in ΔH and ΔS seem to be much smaller than the effect of ionization. This is because the experiments on the neutral surfactant showed no influence on the phase transition. We, therefore, neglect this alteration in the following discussion.

Let us now derive N_B. We assume that the gel volume is much smaller than the surfactant solution in which the gel is immersed. The proportion of the sites occupied by surfactant molecules should be described by Langmuir's adsorption formula:

$$\frac{N_B}{S_0} = \frac{C_F}{C_F + C^* \exp(-\beta\Delta F_B)} \tag{4}$$

where C_F is the number concentration of free surfactant in the solution and is given by $C_F = N_F/V$, β is the effective binding constant, and C^* is the total concentration of bound and free surfactant molecules, which is constant for a given system. The binding free energy ΔF_B is given by

$$\Delta F_B = \Delta H_B - T\Delta S_B - a\frac{N_B}{S_0} \tag{5}$$

Table I
References for Surfactants

sodium dodecyl sulfate (SDS) (or lauryl sulfate sodium salt)
Fw = 288.38
cmc = 8.1–8.3 mM
mol/L (or *M*) = 0.03468 × (*W* %)
dodecyltrimethylammonium bromide (DTABr)
Fw = 308.35
cmc = 14 mM
(Sigma Catalog, 1990, p 1500)
dodecyltrimethylammonium chloride (DTAC)
Fw = 263.90
mol/L (or *M*) = 0.03789 × (*W* %)
nonaoxyethylene dodecyl ether
OHV = 96.26 (calcd), 98.7 (obsd)
cmc (or $n = 8$) 8.7×10^{-5} M

where the last term represents the mean field interaction between the bound surfactant and other bound surfactant molecules surrounding that particular molecule, which is assumed to be proportional to the average concentration of surfactant. The parameter a is constant whose sign defines the nature of interaction between occupied sites. These terms are essential to be able to explain the change in the phase transition temperature due to addition of surfactant molecules to gels. The combination of eqs 4 and 5 gives a self-consistent expression

$$\frac{N_B}{S_0} = \frac{C_F}{C_F + C^* \exp\left\{\beta\left(\Delta H_B - T\Delta S_B - a\frac{N_B}{S_0}\right)\right\}} \tag{6}$$

Defining

$$x \equiv N_B/S_0 \tag{7}$$

eq 6 becomes

$$x = \frac{C_F}{C_F + C^* \exp\left(\frac{\Delta S_B}{k}\right) \exp\left\{\beta a\left(x - \frac{\Delta H_B}{k}\right)\right\}} \equiv g(x) \tag{8}$$

Equation 8 shows a variety of phase equilibria for the state of absorbed surfactants depending on the values of the parameters appearing in the equation. Figure 6 shows how the solution for x is obtained as intercepts of equations $y = x$ and $y = g(x)$. Ionic surfactant molecules repel each other and the coefficient a is positive. The parameter a may be negative for neutral surfactants, whose head groups are hydrophilic.

The equilibrium states of surfactant binding are classified as shown in Table I. It is important to note that for attractive interaction $a < 0$, there are three different solutions for the absorption portion, two corresponding to the free energy minimum and the other corresponding to a maximum. In that case there will be a first-order phase transition in the adsorption. It is interesting to observe that the high-temperature limit corresponding to the maximum adsorption does not reach 1 for our experimental conditions with repulsive interaction, but only the maximum value defined as

$$x_{\max} = \frac{C_F}{C_F + C^* \exp\left(\frac{\Delta S_B}{k}\right)} \equiv x_0 \tag{9}$$

We now calculate C_F, the concentration of the free surfactant in the solution, from which N_B will be known and thus the ionization coefficient f. The calculation of C_F will cover the concentration region where micelle can be formed out of M surfactant molecules. The equilibrium distribution of surfactant molecules among three states, micellar, free, and bound, can be obtained by the condition of equal chemical potentials for these states:

$$\mu_M = \mu_F = \mu_B \tag{10}$$

We have used the latter half of the equation to derive the amount of bound surfactant when the concentration of free surfactant is given. Denote the average number concentration of micelles by $C_M = N_M/V$ (N_M = number of micelles in solution of volume V) and the total number concentration of surfactant by $C_0 = N_0/V$ (N_0 = initial number of surfactant molecules added to the system of volume V). Since the gel volume is much smaller than the total volume of the solution, the equilibrium between free and micellar states is determined independently of the presence of the gel. Thus

$$C_F + MC_M = C_0 \tag{11}$$

From the first equality of eq 4

$$C_M/(C_F)^M = K \tag{12}$$

where K is the binding constant. Since $M \gg 1$

$$C_F = C_0 \qquad \text{for } C_F < C_{cmc} \tag{13}$$

$$C_F = C_{cmc} \qquad \text{for } C_0 > C_{cmc} \tag{14}$$

where C_{cmc} is the critical micellar concentration defined as

$$C_{cmc} \equiv (KM)^{1/(M-1)} \tag{15}$$

The combination of eqs 1, 2, 6, 7, 13, and 14 gives the solution for swelling curve, i.e., the relation between T and the network density ϕ. The equation is in general too complicated to be solved in an explicit analytic form. However, since the transition temperature is higher than the binding temperature (~30 °C) and since the binding transition is quite sharp, it may be a good approximation to use the higher temperature limit for f:

$$\frac{N_B}{S_0} = \frac{C_F}{C^*}\exp\left(\frac{\Delta S_B}{k}\right) \tag{16}$$

Therefore

$$f = |z|\frac{C_0}{C^*}\frac{S_0}{\nu_e}\exp\left(\frac{\Delta S_B}{k}\right) \qquad \text{for } C_0 < C_{cmc} \tag{17}$$

$$f = |z|\frac{C_{cmc}}{C^*}\frac{S_0}{\nu_e}\exp\left(\frac{\Delta S_B}{k}\right) \qquad \text{for } C_0 > C_{cmc} \tag{18}$$

Using f in eqs 17 and 18, we can express the swelling curve by

$$\frac{1}{T} = \frac{\Delta S}{\Delta H} + \frac{k}{\Delta H}\left[\frac{v_1\nu_e}{N\phi^2}\left\{(2f+1)\left(\frac{\phi}{\phi_0}\right) - 2\left(\frac{\phi}{\phi_0}\right)^{1/3}\right\} - \frac{2}{\phi} - \frac{2\ln(1-\phi)}{\phi^2}\right] \equiv g_{gel}(\phi) \tag{19}$$

The expression for f shows that the ionization of the gel is proportional to C_0 under the condition $C_0 < C_{cmc}$, while it is constant and only proportional to C_{cmc} when C_0 exceeds C_{cmc}. In the case of nonionic surfactant with $z = 0$ the changes in the equilibrium swelling curves are only due to a change in interaction free energy. Indeed the surfactant effects on the phase transition were large for anionic and cationic surfactants but negligible for the nonionic one. Thus, the change of interaction free energy caused by binding of NODE seems to be very small. The experiments on the phase transition of copolymer gels of hydrophilic acrylamide and hydrophobic NIPA showed that the phase transition temperature rises by 10 °C when 5% of a total 32 mM of NIPA monomers in the system are replaced by acrylamide molecules. Only in 3–4 mM of SDS solution, however, the transition temperature of NIPA gel increased by 10 °C. This indicates the preferential uptake of SDS to the network in the gel.

Conclusion

Addition of a small amount of ionic surfactant to a solution where a NIPA gel is immersed brings about a significant rise in the transition temperature and an increase in the volume change at the transition of the gel. This is interpreted in terms of preferential uptake and binding of surfactant ions onto the polymer network as schematically shown in Figure 6. The surfactant molecule consists of a long aliphatic hydrocarbon chain with a sulfate group at the other end. On the other hand, NIPA polymers in the gel network have hydrophobic isopropyl groups $CH_2(CH_3)_2$ in its side residues and CH_2CHR in the chain backbone. When surfactant molecules diffuse into the gel network of NIPA, strong association takes place through the hydrophobic interaction. The polymer network is coated by surfactant which converts it into a hydrophilic network. When the hydrophilic groups are ionic, the large increase in the transition temperature and volume change at transition is brought about by the excess osmotic pressure due to ionization.

The large change in both the phase transition temperature and gel volume at the transition in response to a small amount of SDS indicates that the system behaves as a molecular sensor. The present study shows that the hydrophobic gel–detergent–water system can be a macroscopic model for better understanding of the structure of proteins within a membrane. It will also model the protein unfolding in SDS column chromatography. Such a system may be used to purify water from detergent contamination for a better environment.

It is clear that our study here is by no means complete. In particular, it will be interesting to vary the molecular structures of hydrophilic and hydrophobic groups of surfactants and study how they affect the phase transition. There are some questions yet to be solved. For example, we have no obvious explanations as to (1) the large difference between T_{shrink} and T_{swell} for ionic surfactants, (2) the decrease of T_{shrink} and T_{swell} above 0.5% for cationic surfactants, and inhomogeneous shrinking of the gel in ionic surfactants above approximately cmc. They were not observed in low $C_{surfactant}$.

The fact that both the transition temperature and the volume change at the transition are dependent on the type of the surfactants can be regarded as a model for molecular sensing. Molecular sensing would be ideal if a system directly recognizes a kind of molecule and converts an interaction between the molecule and the system into an observable change in the system. The present results seem to be a significant step toward such a goal, since the gel has functional abilities to bind a small amount of surfactant molecules and then to amplify its stimulation into the large changes in both the transition temperature and the volume change at the transition. In addition, such abilities vary depending on the types of surfactant molecules, at least on the three kinds used here.

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