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Formation of Soluble Complexes by Two-Step Surfactant Bindings

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Introduction. Ionic surfactant bindings to oppositely charged macromolecules are generally highly cooperative due to strong electrostatic and hydrophobic interactions and, as a result, often form micelle-like organized structures even at concentrations nearly 1 order of magnitude lower than that in the absence of polyelectrolytes.[1−3] It is also known that the surfactant binding induces a volume contraction of polyelectrolyte gel and forms ordered supermolecular structures.[1,4,5] The charged network strongly depresses the cooperativity of binding due to osmotic pressure in the network.[1,6] In all these cases, the surfactant is assumed to undergo one-to-one stoichiometric binding with respect to their complementary charges. However, we have found that amphiphilic polymers, i.e., ionene polymers, and copolymers of acrylate with long alkyl side groups or bulky hydrophobic groups exhibiting a lower critical solution temperature (LCST) undergo two-step binding to give soluble complexes. The mechanism of such binding is here briefly described.

Experimental Section. Preparation of Polymers. Molecular structures of amphiphilic polymers used in this work are shown in Figure 1. *x*,*y*-Ionene (*x* = 6, 12; *y* = 4, 6, 12) bromide polymers were synthesized through the successive Menschutkin reaction of *N*,*N*,*N*′,*N*′-tetramethyl-1,*x*-diaminoalkane and *y*,*ω*-dibromoalkane in DMF.[7] The structure of *x*,*y*-ionene bromide was confirmed by NMR and FT-IR.

The copolymer and its corresponding gel of *N*-isopropylacrylamide (IPAAm) and 2-(acrylamide)-2-methylpropanesulfonic acid (AMPS) were synthesized by radical polymerization of IPAAm and AMPS in the absence or presence of *N*,*N*′-methylenebis(acrylamide) (MBAA) as a cross-linker in DMF at 70 °C for 2 h.

A copolymer of 12-acryloydodecanoic acid (ADA) and acrylic acid (AA) [poly(ADA-*co*-AA)] was prepared as described in a previous paper.[8]

Complex Formation. The complex formations of ionene polymers with sodium dodecyl sulfate (SDS) were carried out by mixing 0.16 M aqueous solution of SDS to 0.16 M aqueous solution of *x*,*y*-ionene bromides in different ratios at room temperature. The precipitates were collected by centrifugation and dried under vacuum. The complex formations of poly(IPAAm-*co*-AMPS) and poly(ADA-*co*-AA) with dodecyl pyridinium chloride (C_{12}-PyCl) were made in the same way as the ionene−SDS system.

Binding Isotherm. The binding isotherms of SDS with *x*,*y*-ionene polymers were determined by measuring free surfactant concentration in the polymer solutions using a surfactant-selective membrane electrode.[9] The binding isotherm of poly(IPAAm-*co*-AMPS) gel with C_{12}-PyCl was established spectrophotometrically, i.e., by measuring the change in UV absorption of C_{12}PyCl at 259 nm as described previously.[1]

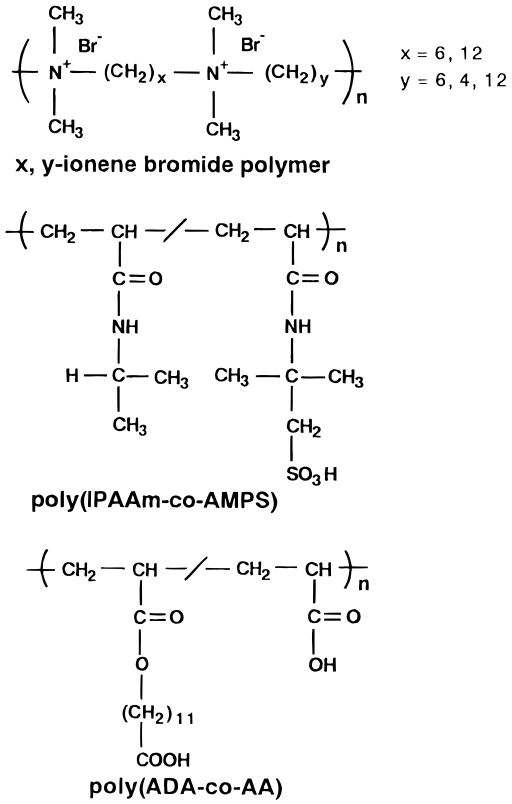

Figure 1. Molecular structures of amphiphilic polymers used in this work.

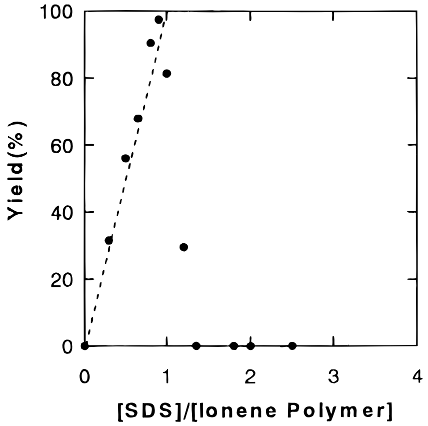

Figure 2. Relationships between the amount of precipitates and the molar mixing ratio of SDS to 6,12-ionene polymer. The theoretical yield (dotted line) was calculated on the assumption of the formation of a one-to-one complex. Concentration of the mixing SDS and ionene polymer solution are 0.16 M.

Results and Discussion. When a concentrated aqueous solution of SDS was added to the solution of *x*,*y*-ionene polymers with different charge densities (*x* = 6, 12; *y* = 4, 6, 12), at different mixing ratios, insoluble complexes were formed and the amount of precipitate was proportional to the mixing ratio, suggesting that SDS formed a one-to-one stoichiometric complex with each ionene polymer. The elemental analysis of the complexes also confirmed the formation of a one-to-one complex. However, when SDS was further added and the molar mixing ratio of [SDS]/[cation] exceeded 1.0, the precipitate started to disappear and completely dissolved at the [SDS]/[cation] mixing ratio of 1.3−1.5, depending on *x* and *y*. The dissolved complexes were transparent and highly viscous, sometimes gel-like. Figure 2 shows the dependence of precipitation on the molar mixing ratio of SDS and the 6,12-ionene polymer.

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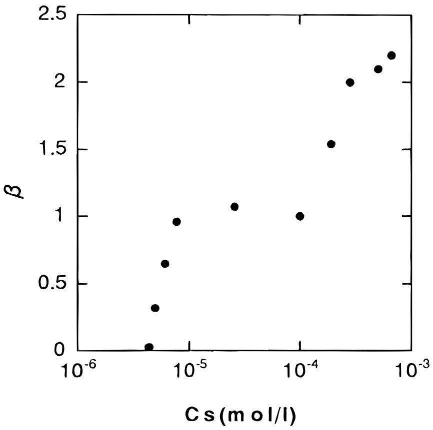

Figure 3. Binding isotherm of SDS with 6,12-ionene polymer at 25 °C. The degree of binding β is defined as the molar ratio of bound surfactants to cationic groups on the polymer. [ionene polymer] = 2×10^{-4} M, [NaBr] = 0.02 M.

If, instead of a solvated ionene polymer, a chemically cross-linked ionene gel[10] was mixed with SDS, the gel showed first a strong contraction, but later reswelled, corresponding to the behavior of linear ionenes. Since the addition of sodium methyl sulfate (SMS) did not bring about any dissolution of ionenes and reswelling of ionene gels, the described phenomena are not associated with an effect of ionic strength but with the binding of an excess of SDS to the ionenes and their gels.

Experiments to establish the binding isotherm for ionene−SDS systems were carried out using an ion selective electrode at SDS concentrations below the critical micelle concentration and the result for 6,12-ionene is shown in Figure 3, which clearly demonstrates the two-step binding of SDS. Let us define β as the molar ratio of bound surfactant to total cationic groups of polymer. In the first step, an abrupt increase of β starts at the surfactant concentration of 10^{-6} M, which later levels off at $\beta = 1$ when the surfactant is 10^{-5} M. In these processes, the solution became hazy due to the complex formation. This is the typical binding isotherm observed in many polyelectrolyte−surfactant systems.[1−13] However, interestingly, the second binding takes place at a free surfactant concentration near 10^{-4} M and the solution became clear again, indicating the dissolution of the complex. The value of β increases to as high as 2.2 and tends to increase further (further experiments were not possible because of the range of the electrode). Therefore, the dissolution of the stoichiometric complex should be associated with the excess amount of bound of SDS. Since the one-to-one complex has no electrical charge, the second binding presumably takes place through the hydrophobic interaction between SDS and the stoichiometric complex. Binding of excess SDS produces a negatively charged complex and leads to solubilization.

Such a two-step equilibrium was further confirmed by diluting the solubilized complex with water. For example, when the transparent complex solution of 10^{-2} g/dL was diluted to 5×10^{-3} g/dL, it became hazy, and a precipitate was formed, indicating the appearence of the insoluble one-to-one complex. The resolubilization of the stoichiometric complex can be observed for every x,y-ionene polymer ($x = 6, 12$; $y = 4, 6, 12$) with the SDS system. This kind of two-step binding behavior of SDS cannot be observed with polyelectrolytes carrying cationic charges in their side groups, and these complexes does not dissolve again.[2]

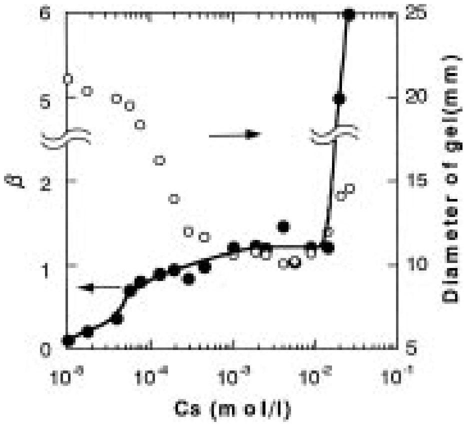

Figure 4. Binding isotherm of C_{12}PyCl with poly(IPAAm-*co*-AMPS) gel (●) and the change in the diameter of the gel (○). Copolymer contains 10 mol % AMPS unit. Equilibrium was established by allowing the gel-containing solution to stand for 3 weeks at 25 °C.

It is not completely understood why the two-step binding occurs for the ionene−SDS system. However, in the case of x,y-ionenes, the charge density of which is rather lower than that of common vinyl-type cationic polymers, the long distance between two adjacent binding sites makes it difficult for the two neighbor-bound surfactant molecules to align adjacently, producing cooperativity. Instead, the surfactant might bind along the main chain through their hydrophobic interaction. This explains why the first step of binding is not as cooperative as in the PAMPS−C_{12}PyCl system. The cooperativity parameter, u, for 6,12-ionene−SDS was 68 and that of PAMPS−C_{12}PyCl was 610.[1] The second step of binding presumably occurs by adsorbing additional surfactant molecules through hydrophobic interactions between the alkyl chains to acquire extra charges.

In order to confirm this, an attempt was made to observe the interactions between C_{12}PyCl and poly(IPAAm-*co*-AMPS) (molar fraction of AMPS: 0.1). When an aqueous solution of C_{12}PyCl was added to that of poly(IPAAm-*co*-AMPS) to form a one-to-one complex with AMPS units, an insoluble complex was formed. However, when an excess of C_{12}PyCl was added with respect to the AMPS units, the complex dissolved again.

When a chemically cross-linked poly(IPAAm-*co*-AMPS) gel was mixed with C_{12}PyCl, instead of using a linear copolymer, the gel showed considerable shrinkage and reswelling according to the surfactant concentration (Figure 4). The binding isotherm of C_{12}PyCl to the copolymer gel (Figure 4) shows that the binding starts at a free C_{12}PyCl concentration of 10^{-5} M with a steep increase in β and then levels off at a concentration of 10^{-4} M with $\beta = 1$. When the free surfactant concentration exceeds 10^{-2} M, the second step of binding starts and quickly attains $\beta = 6.0$, which corresponds to the reswelling of the gel (Figure 4). It should be noted here that the β value of C_{12}PyCl for the PAMPS gel never exceeded 1.0 and the gel remained contracted without reswelling. No precipitate was formed when C_{12}PyCl was mixed with the IPAAm homopolymer.

These results strongly suggest that AMPS units in the copolymer are able to form first a one-to-one complex and then bind excess C_{12}PyCl to produce a soluble positively charged complex. Since IPAAm units themselves have no interactions with C_{12}PyCl, the excess surfactant binding should occur at the surface of the complex through the hydrophobic interaction.

Similar solubilization phenomena were also observed for the interaction between poly(ADA-*co*-AA) and C_{12}-PyCl at pH 12. When the molar fraction of ADA in the copolymer is larger than 0.5, the polymer first formed a complex with C_{12}PyCl to produce an insoluble complex, but later dissolved, while no soluble complex was formed by the homopolymer PAA or poly(ADA-*co*-AA) with the molar fraction of ADA less than 0.5.

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