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Surfactant Binding of Polycations Carrying Charges on the Chain Backbone: Cooperativity, Stoichiometry and Crystallinity

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ABSTRACT: Studies on the interaction between polycations carrying charges on the chain backbone [*x*,*y*-ionene bromides ($x = 3, 6, 12$; $y = 3, 4, 6, 12$)] and anionic surfactants (sodium alkyl sulfates and sodium alkanesulfonates) have been made in water. It was found that there are two categories of surfactant binding: one is the formation of insoluble complex with one-to-one composition and the other is that of soluble complex with nonstoichiometric composition. Some of these complexes have ordered structure on a molecular and a supramolecular level, wherein the charge density and the alkyl size separating the charges on the chain backbone play an important role. The mechanism and process of the complex formation have been discussed.

Introduction

Studies of surfactant binding with polyelectrolyte and polyelectrolyte gels have been extensively made in recent years.[1−7] Among them, many investigations have focused on the binding isotherm and its thermodynamic analysis. The binding of ionic surfactants with oppositely charged polyelectrolytes has been reported to be cooperative,[2] whereupon the side by side hydrophobic interactions between bound surfactants is most often attributed. Shirahama et al.[4] reported that the binding of sodium decyl sulfate onto a cationic poly(dimethyldiallylammonium chloride) is completed in a very narrow range of equilibrium concentration, indicating the strong cooperative nature of the binding process. The characteristic concentration at which binding starts was about 2 orders of magnitude smaller than the critical micelle concentration (cmc) of the surfactant. It has also been shown that the interaction between polyions and ionic micelles leads to an associative phase behavior analogous to that of polyanion−polycation systems.[5] In these cases, the surfactant undergoes one-to-one stoichiometric binding with respect to their complementary charges. The binding process of the surfactant onto the charged network was studied and was found that the presence of cross-linkage significantly enhances the initiation process but strongly suppresses the cooperativity of the binding.[6] This was interpreted in terms of osmotic pressure of the gel which results from the conformational shrinkage caused by the surfactant binding.[7]

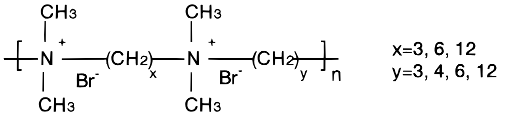
Recently, we have reported that a two-step surfactant binding to give soluble complexes occurs for various types of amphiphilic polymers.[8] The formation of the soluble complex was associated with the excess amount of surfactant binding occurring mainly by the hydrophobic interaction with the one-to-one complex.

In this paper, we report on the systematic study of the binding of anionic surfactants: sodium alkyl sulfates ($n = 6, 12$) and sodium alkanesulfonates ($n = 8, 10$), with the synthetic polycations carrying charges on the chain backbone: *x*,*y*-ionene bromides ($x = 3, 6, 12$; $y = 3, 4, 6, 12$). We have found that ionene polymers, depending on their structure, undergo two-step binding: first, they form stoichiometric one-to-one insoluble complexes and then nonstoichiometric soluble complexes. The formation of soluble complex was closely associated with the chemical structure of the ionenes. There existed a critical charge density and alkyl size length to give the two-step binding, below which only the conventional one-to-one stoichiometric binding formed. Roles of electrostatic and hydrophibic interactions on the process of the complex formation have been described. X-ray diffraction analyses of the complexes showed different molecular and supermolecular structures depending on the different binding behaviors.

Experimental Section

Materials. 1,4-Dibromobutane, 1,6-dibromohexane, and sodium dodecyl sulfate (C_{12}) were purchased from Wako Pure Chemical Industries, Ltd., 1,12-dibromododecane, *N*,*N*,*N*′,*N*′-tetramethyl-1,3-diaminopropane, sodium methyl sulfate (SMS), and sodium octanesulfonate (C_8) were from Tokyo Kasei Co., Ltd., 1,3-dibromopropane, sodium hexyl sulfate (C_6), *N*,*N*,*N*′,*N*′-tetramethyl-1,6-diaminohexane, and *N*,*N*-dimethylformamide (DMF) were from Kanto Chemical Co., Ltd., and sodium decanesulfonate (C_{10}) was from Acros Organics, and they were all used as received. *N*,*N*,*N*′,*N*′-Tetramethyl-1,12-diaminododecane was synthesized according to Leuckart's reaction.[9]

Preparation of polycation polymers *x*,*y*-ionene ($x = 3, 6, 12$; $y = 3, 4, 6, 12$) bromide polymers with the following molecular structure were synthesized through the successive Menschutkin reaction of *N*,*N*,*N*′,*N*′-tetramethyl-1,*x*-diaminoalkane and 1,y-dibromoalkane in DMF.[10] The structures of *x*,*y*-ionene bromides were confirmed by NMR and FT-IR. The intrinsic viscosities of 6,4-, 6,6- and 6,12-ionene bromides in 0.4 mol/L KBr aqueous solution at 25 °C are 0.12, 0.19 (corresponding to a weight-average molecular weight of 19 000, calculated from the equation obtained by Noguchi et al.[10]), and 0.22, respectively.



$$\left[\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{+}{N}}}\,Br^- \!-\!(CH_2)_x\!-\! \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{+}{N}}}\,Br^- \!-\!(CH_2)_y\! \right]_n \qquad x=3, 6, 12 \quad y=3, 4, 6, 12$$

x,y-ionene bromide polymer

Formation of the Complexes. The complex formation was carried out at room temperature by mixing a relatively concentrated aqueous solution of surfactant (16 mol/L) and *x*,*y*-

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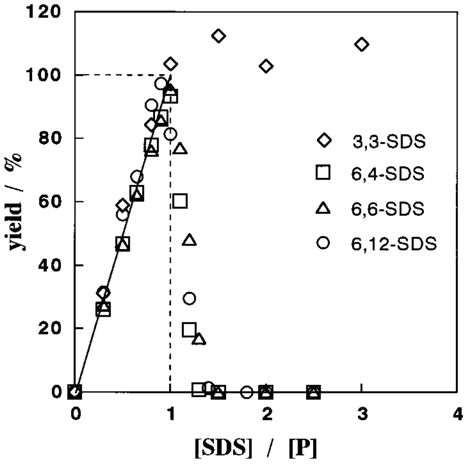


Figure 1. Relationships between the yield of complex formation and the mixing ratio [S]/[P] for various ionene−SDS systems. [S] = [P] = 0.16 mol/L.

ionene polymer ([polycation] = 0.16 mol/L) at different ratios. The precipitates were collected by centrifugation (3000 rpm).

Elementary Analysis. The samples were dried in vacuo at 40 °C overnight, and elementary analyses were carried out.

Viscosity. Viscosities of the complex solutions at different concentrations were measured with an Ubbelohde viscometer at 25.0 ± 0.1 °C.

Transmittance. The transmittance of the aqueous solutions was determined at 600 nm by a Hitachi U-3000 spectrophotometer at room temperature.

Binding Isotherm. The binding isotherm of surfactant with *x*,*y*-ionene polymers was established by measuring free surfactant concentration in the polymer solution ([polycation] = 2×10^{-4} mol/L, [NaBr] = 0.02 mol/L) using a surfactant-selective membrane electrode prepared from SDS and dodecyl trimethylammonium chloride (Tokyo Kasei) in poly(vinyl chloride) film.[4] The detailed procedure was described elsewhere.[6]

X-ray Diffraction. The structures of the complexes were analyzed by using both a small-angle X-ray diffractometer (SAXD, 40 kV, 30 mA; Shimazu XD-610, SAG-6A) and an X-ray image diffractometer (WAXD, 40 kV, 200 mA; RINT-2000, Rigaku Co. Ltd.). Ni-filtered Cu Kα radiation was used.

Results and Discussion

1. Formation of Soluble Complexes. When a relatively concentrated (0.16 mol/L) aqueous solution of C_{12} (SDS) is added dropwise to the solution of *x*,*y*-ionene bromides ([polycation] = 0.16 mol/L, *x* = 3, 6, 12; *y* = 3, 4, 6, 12), a white cotton-like precipitate appears and the amount of precipitate increases with an increase in the amount of surfactant until the molar ratio of surfactant to polymer charge unit ([S]/[P]) is 1. However, when [S]/[P] exceeds 1.0, the amount of precipitate decreases dramatically and all of the precipitate disappears at a certain mixing ratio except for 3,3-ionene polymer. The dissolved complexes are transparent and highly viscous and sometimes show gel-like behaviors.

Figure 1 shows the amount of precipitate as a function of [S]/[P]. The “yield” of the complex is defined as a ratio in percent of the weight of precipitate formed to that of the calculated amount supposing an equimolar complex formation. One can see that there are two regions of the complex formation. In the first region, the precipitate is formed in proportion to the molar mixing ratio, and the precipitate reaches theoretically evaluated values at [S]/[P] = 1, suggesting that the one-to-one stoichiometric complex is formed for each ionene polymer. In fact, elementary analyses of the 6,4-SDS complex with the feed ratios of [S]/[P] = 0.7, 1.0, and 1.1 show an equimolar composition and confirm the stoichiometric complex formation (Table 1). The stoichiometric complexes are insoluble in water, apparently because of the increase in the hydrophobic nature due to the neutralization of the charges.

Table 1. Elementary Analyses of 6,4-SDS Complexes Prepared at Various Mixing Ratios

	[S]/[P]	% C	% H	% N	% S
calcd	1.0	60.12	10.89	3.69	8.45
found	0.7[a]	57.36	9.72	3.51	8.22
	1.0[a]	58.89	10.83	3.45	8.34
	1.1[a]	57.76	10.76	3.46	8.35
	2.0[b]	59.03	10.65	3.69	8.30

[a] Precipitate obtained at the concentration of 0.16 mol/L, i.e., [polymer] = 3.1 g/dL, [SDS] = 4.6 g/dL. [b] Precipitate obtained after dilution of the complex solution of [S]/[P] = 2.0, i.e., [cation] = 2.6×10^{-4} mol/L, [SDS] = 5.2×10^{-4} mol/L. Refer to the arrow in Figure 2.

In the second region, the amount of the precipitate decreases quickly when an excess amount of SDS is introduced into the one-to-one complexes and all of the complexes completely dissolve at the [S]/[P] of 1.3−1.5 except for 3,3-ionene polymer. There are two possibilities why the dissolution of the polymer−surfactant complexes takes place in the second region. One is that the stoichiometric complexes dissolved due to increased ionic strength by the presence of excessive surfactant. The other is the formation of nonstoichiometric complexes with negative charges. To confirm the possibility of the former case, the same amount of sodium methyl sulfate was added, instead of SDS, to the solution containing the one-to-one complex. However, no dissolution occurred at all, indicating that the dissolution of the complex is not associated with the increased ionic strength.

If the complex dissolution occurs by the binding of excessive surfactant, the following equilibria should exist in the solution:

$$P_n(x,y\text{-ionene bromide}) + nS\ (\text{surfactant}) \overset{K_1}{\rightleftharpoons} P_nS_n \qquad (1)$$

$$P_nS_n + mS \overset{K_2}{\rightleftharpoons} P_nS_{n+m} \qquad (2)$$

where *n* is the number of positive charges of the ionene or negative charges of the surfactant, *m* is the number of negative charges of the excessive surfactant. Equation 1 corresponds to the formation of equimolar (per charge) insoluble complex, and eq 2, to the formation of nonequimolar soluble complex. Therefore, we might expect the dissociation of surfactant if the total concentration is diluted, keeping [S]/[P] constant. Thus, we tried to dilute the 6,4-SDS complex solution prepared at a ratio of [S]/[P] = 2 ([polycation] = [SDS] = 0.16 mol/L) by adding water. As we expected, the solution became hazy when it was diluted to a concentration of 1.6×10^{-3} mol/L or 5×10^{-3} g dL^{-1}, as shown in Figure 2, and the precipitate is formed. Further addition of water made the solution transparent again. The elementary analysis of the precipitate appearing at this concentration showed the same composition as that of the precipitate of equimolar complex obtained at higher concentration ([polycation] = [SDS] = 0.08 mol/L) (Table 1). A similar but less distinctive change in transmittance is also observed when 6,6-SDS is diluted, although

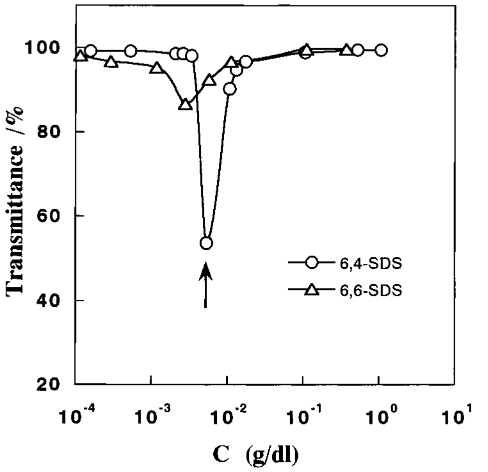


Figure 2. Concentration dependences of the transmittance of complex solutions observed at 600 nm. [S]/[P] = 2, temp. 25.0 ± 0.1 °C.

the minimum of the transmittance shifted to a lower concentration (Figure 2). However, no change in transmittance was observed in the cases of 6,12-SDS and 12,12-SDS, indicating irreversible stable complex formation. As will be described later, the 6,4-SDS and 6,6-SDS complexes were amorphous while those of 6,12-SDS and 12,12-SDS were crystalline. The molecular and supramolecular structure should certainly be related to the equilibrium states in eqs 1 and 2.

To characterize the change in the hydrodynamic properties of the complex occurring by dilution, the viscosity of the complex solution at various concentrations was measured by keeping [SDS] (or [SMS])/[polycation] = 2.0 and compared with that of 6,4-SMS solution. As shown in Figure 3, the reduced viscosity of 6,4-SMS increased exponentially with a decrease in the concentration, showing a typical behavior as a polyelectrolyte solution. Contrastly, the viscosity of 6,4-SDS showed a slight decrease with the dilution and then abruptly increased below a concentration of 10^{-3} g/dL. The minimum viscosity observed around 10^{-3}–10^{-2} g/dL is in accordance with results from the turbidity measurement. Similar changes of hydrodynamic properties were obtained for 6,6-SMS;6,6-SDS and 6,12-SMS;6,12-SDS systems, as shown in Figure 3b,c. Note that the 6,12-SDS complex solution of 10° g/dL was gel-like and showed a very large viscosity. This will be described later.

These experimental results demonstrate that the soluble complexes ([S]/[P] = 2.0) of 6,4-SDS and 6,6-SDS are dissociated to give one-to-one insoluble complexes and free surfactant according to the equilibrium (2) by dilution. Additional dilution makes the equilibrium shift to the left side in eq 1 and the one-to-one complexes are further dissociated to each component. This leads to an abrupt increase of reduced viscosity in Figure 3 and the decrease in transmittance in Figure 2.

2. Effects of Charge Density and Hydrophobicity on the Complexation. The results in Figures 2 and 3 indicate an important contribution of hydrophobic nature of the ionene chain backbone and of the surfactant. Therefore, we investigated the effects of alkyl size of the surfactant, e.g., C_6, C_8, C_{10}, and C_{12} on the complex formation of 3,3- and 12,12-ionenes. Experiments of the complex formation of 3,3-ionene with C_6~C_{12} were made varing [S]/[P] from 0.1 to 10. As shown in Figure 1, 3,3-ionene formed only a stoichiometric insoluble complex with every surfactant and no dissolution occurs at any mixing ratios. Figure 4 shows the results of the complex formation of 12,12-ionene with C_6, C_8, C_{10}, and C_{12}. It is seen that C_6 forms only a one-to-one insoluble complex. However, C_8, C_{10}, and C_{12} form one-to-one complexes first and then soluble complexes at certain molar mixing ratios, the value of which decreased with increasing chain length of the surfactants. The different profiles of the complex formation described here clearly show the important contribution of the hydrophobic interaction on the complexation.

Thus, a systematic study of complex formation using various kinds of ionenes and surfactants has been made, and the results are summarized in Table 2. Complexation of 6,4-ionene and 6,6-ionene were similar: they do not form any insoluble complex with C_6 surfactant, but only with C_8 or larger. No dissolution occurred with C_8 but occurred with C_{10} and C_{12}. 6,12-Ionene and 12,12-ionene formed both insoluble and soluble complex with any surfactants except for the soluble complex with C_6.

These results confirm the importance of the hydrophobic nature of the chain backbone and of the surfactant: if the charge density of the ionene is high (3,3-ionene), only a one-to-one insoluble complex is formed, and if it is lower (6,4- and 6,6-ionenes), the complexation occurs only with the surfactant with sufficiently longer alkyl groups. If the positive charges on the chain backbone are separated by the long methylene units, they again form stable complexes. The short distance between two adjacent surfactants bound on the 3,3-ionene polymer brings about the strong side-by-side hydrophobic interaction to form lamellar-like packing.[11] This lamellar-like complex might prevent the additional binding of the extra amount of surfactant and stay in

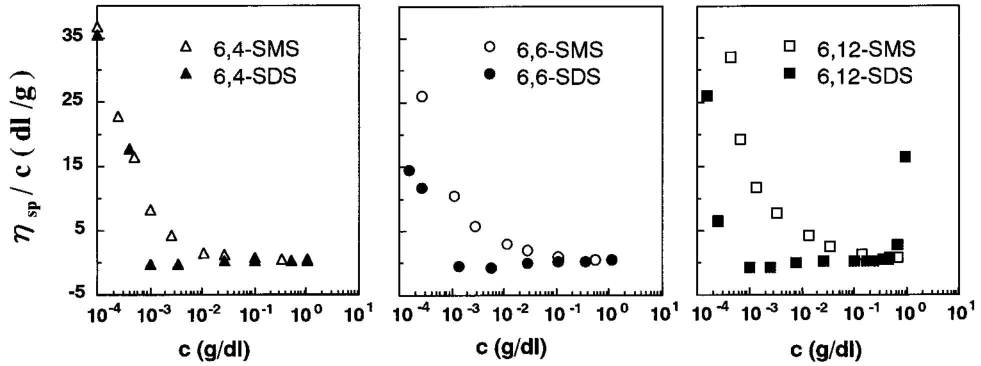


Figure 3. Concentration dependences of the viscosities of 6,*y*-SDS and 6,*y*-SMS complex solutions. [S]/[P] = 2, temp. 25.0 ± 0.1 °C.

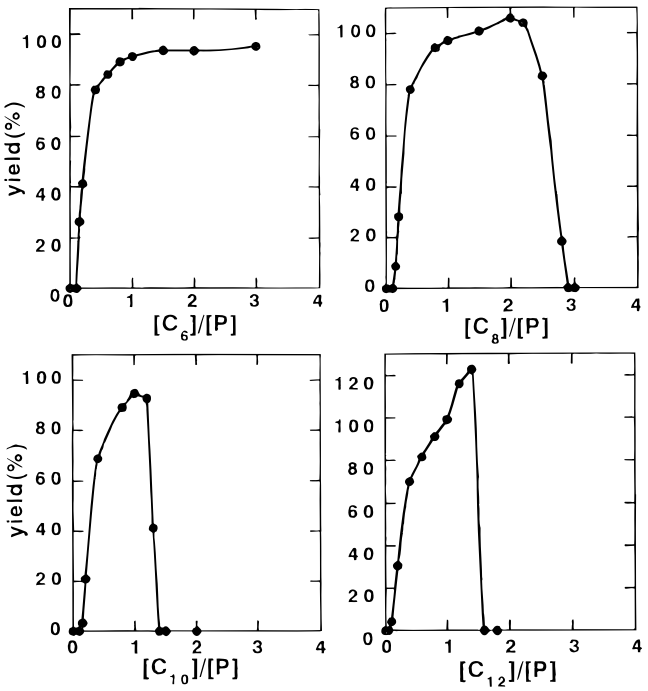


Figure 4. Relationship between the yield of complex formation and the mixing ratio [S]/[P] for various 12,12-ionene surfactants. [S] = [P] = 0.16 mol/L.

Table 2. Formation of Insoluble and Soluble Complexes[a]

	polymer									
	3,3		6,4		6,6		6,12		12,12	
surfactant	A	B	A	B	A	B	A	B	A	B
C_6	○	×	×	×	×	×	○	×	○	×
C_8	○	×	○	×	○	×	○	○	○	○
C_{10}	○	×	○	○	○	○	○	○	○	○
C_{12}	○	×	○	○	○	○	○	○	○	○

[a] A: insoluble and one-to-one stoichiometric complex formation. B: soluble and nonstoichiometric complex formation. ○: yes. ×: no.

water as an insoluble one-to-one complex. In the case of other *x*,*y*-ionenes with lower charge densities, the long distance between two adjacent binding sites would make it difficult to form an adjacent organization among the bound surfactants but able to align in parallel with the main chain backbone through their hydrophobic interaction. This allows subsequently binding of additional surfactants to give the complex solubility due to charges of the surfactant.

Another important reason the dissolution occurs is the fact that the SDS concentration at which the dissolution occurs is lower than the cmc of SDS. (The cmcs of SDS are 8.1 × 10^{-3} and 3.2 × 10^{-3} mol/L in the absence and presence of salt,[12] respectively.) This causes SDS to bind preferentially with the neutralized insoluble complex rather than to form micells. An extensive increase in the reduced viscosity of 6,12-SDS solution at 1.0 g/dL in Figure 3c suggests that an intermacromolecular interaction is introduced by extra SDS binding.

3. Binding Isotherms. To quantitatively characterize the dissolution process, we have attempted to establish the binding isotherms of *x*,*y*-ionene–SDS systems, and the results are shown in Figure 5. The degree of binding (β) in Figure 5 is defined as a molar ratio of bound surfactants to total cationic groups on polymer, and C_s is the free surfactant concentration at equilibrium. As is well established,[6,7,13,14] the overall stability constant K is expressed as follows:

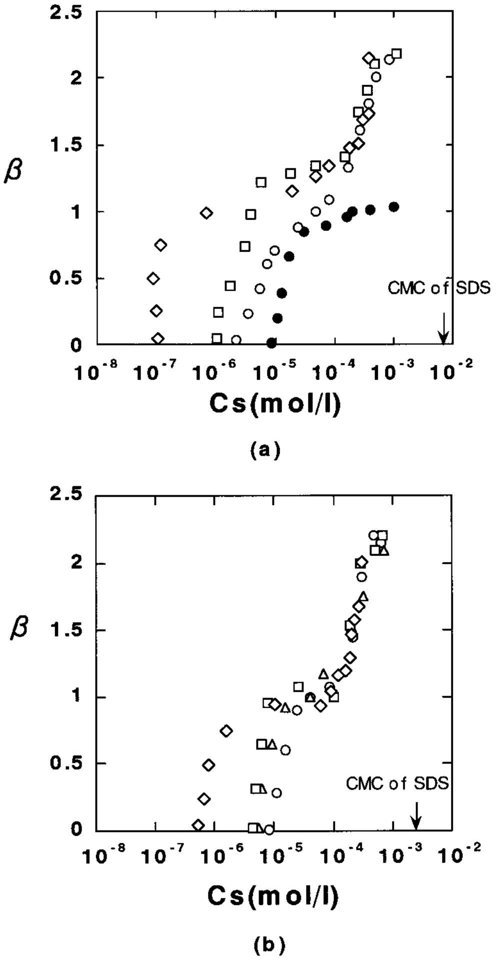


Figure 5. Binding isotherms of SDS with *x*,*y*-ionene polymers in the absence (a) and presence of NaBr (b): (●) 3,3-SDS; (○) 6,4-SDS; (△) 6,6-SDS; (□) 6,12-SDS; (◇) 12,12-SDS. [Ionene] = 2 × 10^{-4} mol/L, [NaBr] = 0.02 mol/L, temp. 25 °C.

$$K = K_0 u = 1/(C_f)_{0.5}$$

where K_0 is the binding constant of a surfactant molecule bound to an isolated binding site on a polymer and u is a cooperativity parameter characterizing the advantage of adjacent surfactant binding and is determined from the slope of the binding isotherm at the half-bound point:

$$(d\beta/d \ln C_f)_{0.5} = \sqrt{u}/4$$

As shown in Figure 5a, β for 3,3-ionene abruptly increases at an SDS concentration of 10^{-5} M and then saturates at $\beta = 1.0$. Further addition of the surfactant brings about practically no increase in β. This is the typical binding isotherm observed in many polyelectrolyte–surfactant systems.[6,15,16] Contrastly, SDS bindings of 6,4-, 6,12-, and 12,12-ionenes consist of two steps: first, an abrupt increase in β occurs in a narrow surfactant concentration range, which then levels off near $\beta = 1.0$. The solution becomes hazy due to the insoluble complex formation. This is similar to the process observed for 3,3-ionene. Note that the minimum surfactant concentration at which the binding starts decreases as much as 2 orders of magnitude when the distance of alkyl chain between charges on the chain

Table 3. Interaction Parameters of SDS with *x,y*-Ionenes[a]

	step 1		step 2	
polymer	10^{-4} K_1 (L mol^{-1})	u_1	10^{-4} K_2 (L mol^{-1})	u_2
3,3	6.3	9		
6,4	17 (7.6)	6 (32)	0.4 (0.5)	21 (35)
6,6	(14)	(26)	(0.5)	(7)
6,12	53 (20)	5 (79)	0.4 (0.5)	23 (21)
12,12	909 (130)	7 (66)	0.4 (0.5)	10 (25)

[a] Numbers in parentheses are values the presence of 0.02 mol/L NaBr.

backbone increases. K and u calculated from Figure 5a are summarized in Table 3. The data show that the overall stability constant in the first step (K_1) increases with an increasing in the alkyl size of the ionenes. This quantitatively comfirms that the surfactant binding of the first step is associated not only with the electrostatic interaction but also with the hydrophobicity of the chain backbone. The second binding step takes place at a free surfactant concentration of 10^{-4} mol/L regardless of the ionene species and tends to increase above $\beta = 2.1-2.2$. Since the solution becomes clear again in this area, the dissolution of the complex can be attributed to an extra amount of sufactant binding of the second binding step.

The binding isotherms in the presence of sodium bromide (0.02 mol/L) were also established, and the results are shown in Figure 5b. K and u are also summarized in Table 3. It is seen from Figure 5b that the presence of the salt leads to the decreased K_1 and increased u_1. The enhanced cooperativity (u_1) in the presence of the salt was also observed for the poly(2-(acrylamido)-2-methylpropanesulfonic acid) (PAMPS)−laurylpyridinium chloride (C_{12}PyCl) system and attributed to the effective shielding of the electrostatic repulsion among surfactant. The stability constant (K_2) and the cooperativity parameter (u_2) of the second step did not vary with the difference of ionene structure and the ionic strength.

Accordingly, the binding isotherms composed of two-step binding well confirmed the equilibria given by eqs 1 and 2.

4. Molecular and Supramolecular Structures of the Complexes. Molecular structures of the ionene polymers are strongly dependent on the alkyl size between ammonium cations on the chain backbone. 3,3-, 6,4-, 6,6-Ionenes are crystalline but 6,12- and 12,12-ionenes are amorphous. According to SAXD measurement, neither of them showed long-range ordering. Surfactant powders showed both short-range (d_1) and long-range (d_2) periodicity.

Table 4[a]

(a) *d* Spacings of *x,y*-Ionene Polymers

3,3		6,4		6,6		6,12		12,12	
d_1	d_2	d_1	d_2	d_1	d_2	d_1	d_2	d_1	d_2
0.43 (w) 0.36 (w)	×	0.62 (s) 0.51 (s) 0.42 (s) 0.37 (s) 0.32 (s)	×	0.75 (s) 0.55 (s) 0.51 (s) 0.40 (s) 0.37 (s) 0.35 (s) 0.34 (s)	×	×	×	×	×

(b) *d* Spacings of C_n Surfactants

C_6		C_8		C_{10}		C_{12}	
d_1	d_2	d_1	d_2	d_1	d_2	d_1	d_2
0.59 (m) 0.52 (m) 0.46 (m) 0.43 (s) 0.40 (m)	1.9 (w) 1.1 (w)	0.44 (s)	2.5 (m) 1.2 (w)	0.44 (s) 0.42 (s) 0.41 (s)	3.4 (m) 1.6 (w)	0.78 (s) 0.49 (s) 0.45 (m) 0.42 (m)	2.0 (m) 1.4 (m)

(c) *d* Spacings of *x,y*-Ionene−Surfactant Complexes[b]

	3,3		6,4		6,6		6,12		12,12	
	d_1	d_2	d_1	d_2	d_1	d_2	d_1	d_2	d_1	d_2
C_6	0.44 (w) 0.41 (s) 0.39 (m)	1.40 (w) 0.68 (m)					0.42 (w)	1.84 (m) 0.91 (w) 0.62 (w)	0.45 (m) 0.41 (s)	1.42 (w)
C_8	0.44 (s) 0.41 (m) 0.38 (m) 0.32 (w)	1.90 (w) 0.64 (w)	×	2.38 (m)	×	2.35 (w)	0.40 (s) 0.33 (s) 0.29 (s)	2.16 (w)	0.39 (s)	1.50 (w)
C_{10}	0.42 (s) 0.38 (w)	2.93 (w) 0.61 (w) 2.09 (m) 1.01 (w) 0.71 (w) 0.51 (w)	×	2.85 (w)	×	2.53 (w) 1.76 (w)	0.39 (s)	2.82 (m)	0.44 (m) 0.40 (s)	2.72 (w)
C_{12}	0.41 (s) 0.38 (m)	3.68 (w) 2.02 (m) 1.02 (w) 0.71 (w)	×	3.50 (m)	×	3.20 (m)	×	2.50 (m)	0.44 (s)	3.91 (w) 1.76 (m)

[a] Peak intensity: s, strong; m, middle; w, weak. [b] Underlined values are *d* spacings that constitute consecutive orders.

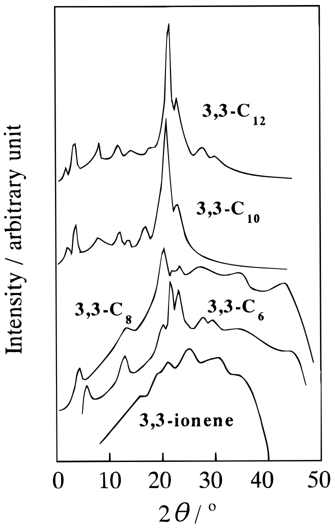


Figure 6. X-ray profiles of 3,3-ionene complexes with C_6, C_8, C_{10}, and C_{12}.

The spacing sizes of *x*,*y*-ionenes and their one-to-one complexes with C_6, C_8, C_{10}, and C_{12} obtained by X-ray diffractometer are summarized in Table 4a–c. We can roughly classify the complex structure into three categories. They are indicated by bold frames in Table 4c.

3,3-Ionene shows very weak WAXD peaks without any long-range ordering, but the insoluble complexes formed with C_6, C_8, C_{10}, and C_{12} show strong WAXD peaks with a d_1 spacing of 0.41–0.44 nm and the peak intensities and the peak sharpness increase with an increase of alkyl size of the surfactant (Figure 6). The d_1 spacings around 0.4 nm correspond to the side-by-side packing of alkyl chains of the surfactant. Note that the 3,3-C_6 complex shows a clear X-ray pattern even though C_6 has a short alkyl chain. Increases in peak intensity and peak sharpness with an increase in the surfactant alkyl size suggest the enhanced stability and ordering with increased alkyl size. The X-ray also shows clear small-angle reflections corresponding to periodicities (d_2) of 1.40 and 0.68 nm for C_6, 1.90 and 0.64 nm for C_8, 2.93, 2.09, 1.01, 0.71, 0.61, and 0.51 nm for C_{10}, and 3.68, 2.02, 1.02, and 0.71 nm for C_{12}. By comparison of these lattice spacings, except that the periodicities 2.93 and 0.61 nm of C_{10} and 3.68 nm of C_{12} have no correlation with other spacing values, the inverse values of other spacings have ratios of 1:2 for C_6, 1:3 for C_8, 1:2:3:4 for C_{10}, and 1:2:3 for C_{12}. These relations suggest the presence of layered structures with periodicities $d_2 = 1.40$, 1.90, 2.09, and 2.02 nm for C_6, C_8, C_{10}, and C_{12}, respectively. These periodicities are approximately equal to the lengths of surfactant (L), as evaluated from standard bond lengths and angles under the assumption of all-trans conformation ($L = 1.29$, 1.54, 1.80, and 2.05 nm for C_6, C_8, C_{10}, and C_{12}, respectively). Combining with the WAXD results that indicate the side-by-side alkyl chain packing, it is reasonable to speculate the arrangement of a monolayer lamellar-like structure, as schematically shown in Figure 7a. In the case of the PAMPS–CnPyCl complexation, a critical alkyl chain length to form the ordered structure was 10.^{6} The distinct structure formed even in 3,3-C_6 complex indicates that the three methylene groups on the main chain of 3,3-ionene play an important role to form the molecular-ordered structure.

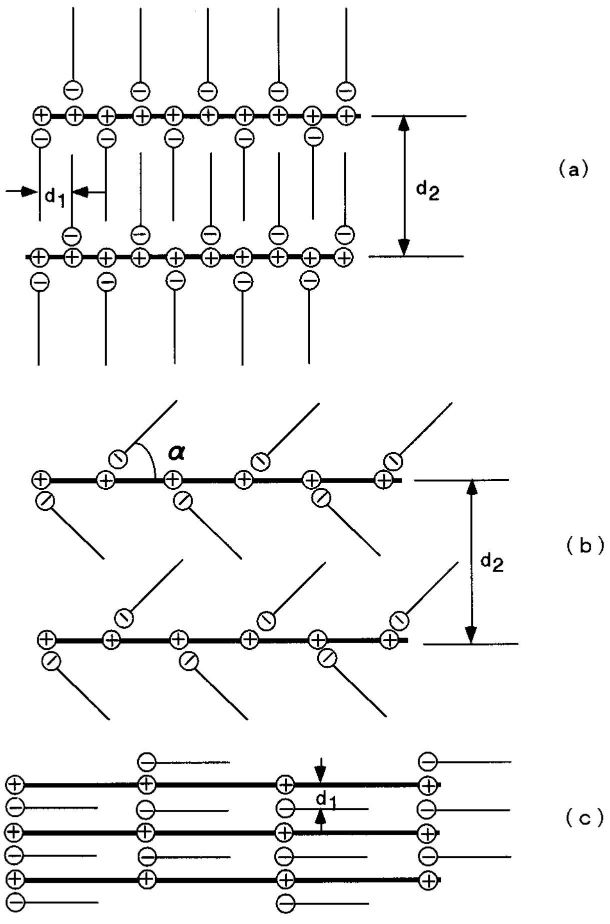
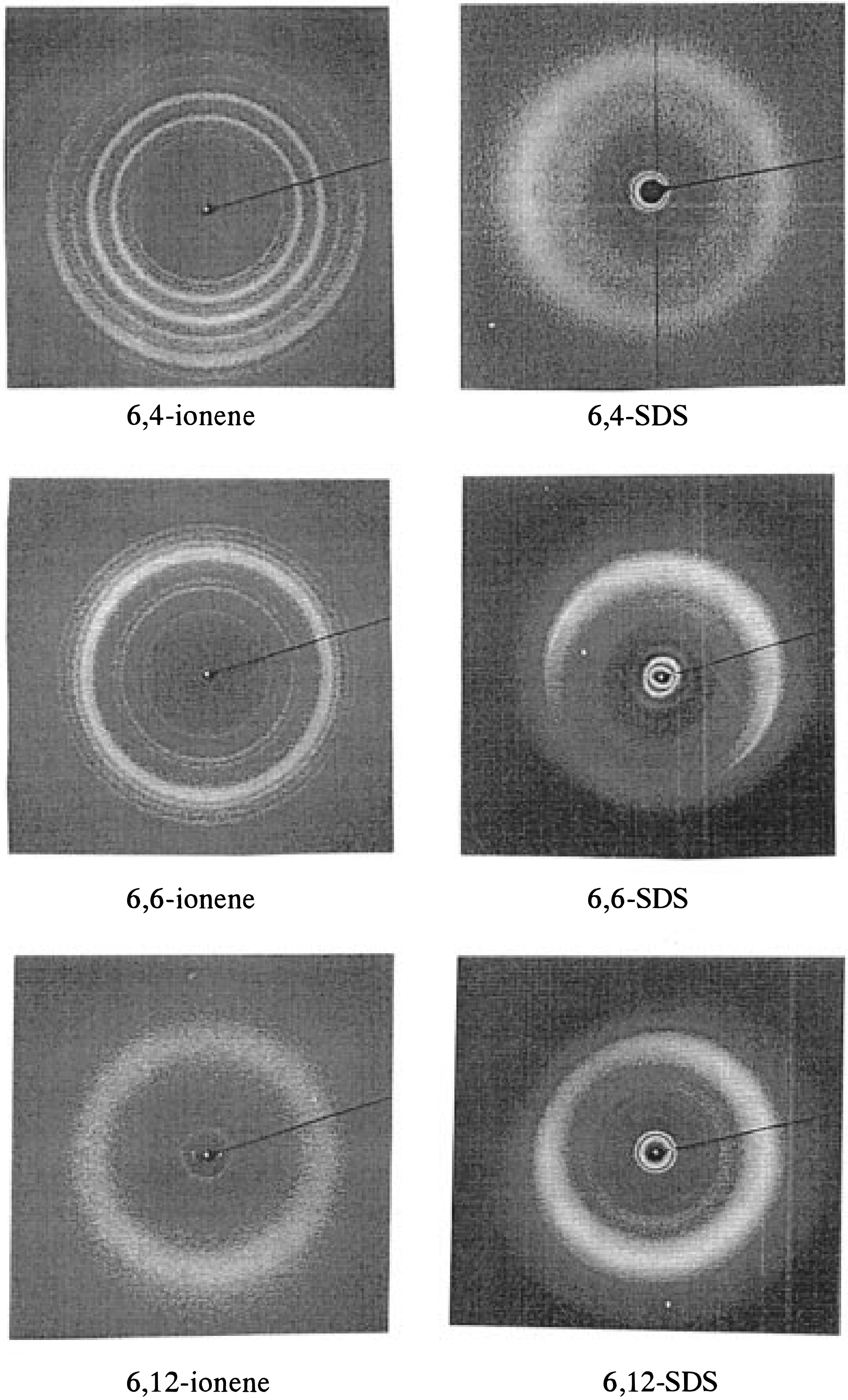


Figure 7. Schematic illustration of structures of one-to-one complexes for various ionene polymers. (a) 3,3-ionene with C_6–C_{12}; (b) 6,4- and 6,6-ionenes with C_6–C_{12}, 6,12-ionene with C_{12}; (c) 6,12-ionene with C_6–C_{10}, 12,12-ionene with C_6–C_{12}. Details are described in the text.

Complex formations of 6,4- and 6,6-ionenes are unique (note 6,4- and 6,6-ionenes are not able to form any insoluble complex with C_6). These ionene polymers are crystalline, showing clear crystalline peaks in a range of 0.3–0.7 nm, but their insoluble (one-to-one) complexes formed with C_8, C_{10}, and C_{12} have shown only very diffuse WAXD diffractions around $d = 0.4$ nm, indicating they cannot form a crystalline structure at a molecular level (Figure 8). No distinct supra-molecular structure was formed for the 6,4 and 6,6 complexes with C_8 and C_{10}. However 6,*y*-C_{12} complexes show long-range ordering with a d_2 spacing of 3.5 and 3.2 nm for 6,4-C_{12} and 6,6-C_{12}, respectively (Figure 9). 6,12-C_{12} also showed no structure in WAXD, but a clear peak in SAXD. As shown in Figure 9 the peak shifts to a lower d spacing when the alkyl chain length on the chain backbone increases and the ordering becomes more pronounced, suggesting the enhanced supra-molecular organization with increased hydrophobicity of the polymer chain. Figure 7b shows a speculated structure for the one-to-one complexes of 6,4-C_{12}, 6,6-C_{12}, and 6,12-C_{12}. C_{12} molecules might make an arrangement with the main chain of ionene polymers with a tilting of a certain angle α which in turn reflects how strong the hydrophobic interaction is: the higher the hydrophobicity of the polymer chain, the smaller the value of α, therefore, the smaller the d_2 spacing. Interestingly, these complexes in the wet state show no WAXD peak but intensive and oriented SAXD peaks.

The 12,12-ionene is amorphous in nature, but its one-to-one complexes with C_6, C_8, C_{10}, and C_{12} show a strong



6,4-ionene

6,4-SDS

6,6-ionene

6,6-SDS

6,12-ionene

6,12-SDS

Figure 8. X-ray diffraction images of ionene polymers and their complexes.

WAXD peak near 0.4 nm and SAXD peaks near 1.4−4.0 nm depending on the surfactant size, whereupon the peak intensity gradually increases with an increase in the alkyl size of the surfactant (Figure 10).

The appearance of short-range ordering of a $d_1 = 0.4$ nm spacing observed in 6,12 and 12,12 complexes suggests a molecular arrangement aligned parallel between the surfactant tail and the polymer main chain,

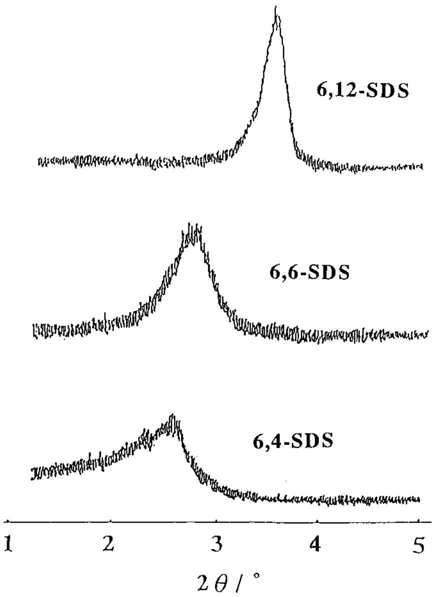


Figure 9. Small-angle X-ray diffraction profiles of 6,*y*-SDS one-to-one complexes.

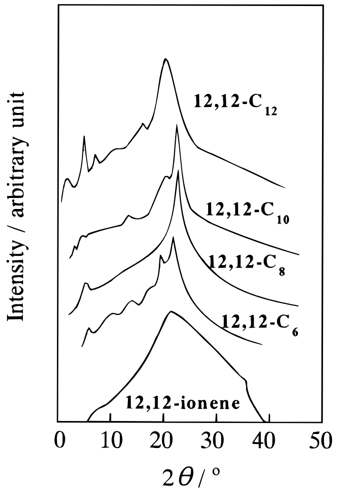


Figure 10. X-ray profiles of 12,12-ionene complexes with C_6, C_8, C_{10}, and C_{12}.

as schematically illustrated in Figure 7c. The increased stability constants K_1 (Table 3) of 6,12- and 12,12-ionenes in comparison with that of 3,3-ionene also support this structure formation. Although we do not have enough data to explain the formation of the long-range ordering observed in 6,12 and 12,12 complexes at present, it might correspond to the bundle-like formation in a direction along the main chain.

As described before, soluble 6,12-SDS complexes are formed when the in feed ratio [S]/[P] = 1.4 ([SDS] = [polycation] = 0.4 mol/L) and exhibit very high viscosities due to the intermolecular association. Expecting the formation of ordered structures of the soluble complexes, WAXD and SAXD have been measured after drying these samples. Many strong WAXD peaks appeared in a range of 0.3−1.0 nm and strong oriented SAXD peaks appeared at 2.0 and 4.4 nm for 6,4-C_{12} and 6,6-C_{12} complexes, respectively, suggesting the formation of well-organized structure of the solubilized complexes.

The models illustrated in Figure 7 involve some speculation. Further studies with methods such as microscopy are necessary to corroborate the proposed structures.

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