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ORIGINAL CONTRIBUTION

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Two-step surfactant binding of solvated and cross-linked poly(*N*-isopropylacrylamide-co-(2-acrylamido-2-methyl propane sulfonic acid))

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Abstract A solvated and cross-linked copolymer of *N*-isopropylacrylamide (IPAAm) and 2-(acrylamido)-2-methyl propane sulfonic acid (AMPS) was synthesized and its interaction with cationic surfactant lauryl-pyridinium chloride (C_{12}PyCl) was investigated. The solvated copolymer exhibited a lower critical solution temperature (LCST) in water, which was extensively shifted to a higher temperature due to the increase of hydrophilicity introduced by AMPS. In C_{12}PyCl solution, LCST of the copolymer was dramatically decreased due to the binding of C_{12}PyCl to AMPS unit, forming a stoichiometric complex. However, in the concentrated C_{12}PyCl solution, its LCST increased due to the non-stoichiometric complex formation. This phenomenon was further examined in the cross-linked copolymer, analyzed by binding isotherms. Two-step binding of surfactant was demonstrated followed by gel shrinking and re-swelling. This binding mechanism was further discussed regarding the effect of charge density and the hydrophobicity of the main-chain backbone in terms of electrostatic and hydrophobic interactions.

Key words Poly(*N*-isopropyl-acrylamide) – poly(2-acrylamido-2-methyl propane sulfonic acid) – surfactant – one-to-one complex – two-step binding

Introduction

We have systematically investigated the interactions between solubilized and the cross-linked poly[2-(acrylamido)-2-methylpropane sulfonic acid] (PAMPS) and cationic surfactants (*N*-alkylpyridinium chloride: C_nPyCl, $n = 4, 8, 10, 12, 16, 18$) over a wide range of concentrations and ionic strengths [1–4]. In these cases, the surfactant undergoes one-to-one stoichiometric binding with the polymer in regard to their complementary charges to give an ion complex. The binding of C_nPyCl is cooperative in water to give a supramolecular-organized structure through side-by-side molecular interaction of surfactant tails [5], whereupon the cooperativity increases with an increase in the alkyl chain length due to an increase in the hydrophobicity.

In this paper we report on the effect of poly(*N*-isopropylacrylamide) (PIPAAm) incorporated with PAMPS on the surfactant binding. PIPAAm has a similar structure to that of AMPS but being without the sulfonic group, at the same time having totally different properties. It is well-known water-soluble polymer, showing reversible hydration–dehydration changes in response to small temperature changes manifested as a lower critical solution temperature (LCST) at 32 °C [6]. Since surfactant binding is closely associated with the hydrophobic nature of the polymers, the IPAAm unit in the copolymer which

sensitively changes its hydration property with temperature might totally change the surfactant-binding process. Decreased charge density of the chain backbone might also change the binding process, since it may affect the side-by-side interaction of surfactant molecules. The interaction of poly(IPAAm-co-AMPS) with laurylpyridinium chloride (C_{12}PyCl) was investigated by the change in LCST and the volume contraction–re-swelling phenomena, together with the binding isotherms. As a result, we found that the copolymer and its cross-linked gel undergo non-cooperative and non-stoichiometric binding with the surfactant. We discuss this binding mechanism, regarding the effect of charge density and the hydrophobicity of the main-chain backbone in terms of electrostatic and hydrophobic interactions.

Experimental

Materials

N-Isopropylacrylamide (IPAAm) was provided by Kojin (Tokyo, Japan) and was purified by recrystallization from toluene/petroleum ether. 2-(Acrylamido)-2-methyl propane sulfonic acid (AMPS) was obtained from Kanto Chemicals (Tokyo, Japan) and used as received. *N*,*N*′-Azobisisobutyronitrile (AIBN), *N*,*N*-dimethylformamide (DMF) were obtained from Wako Pure Chemicals and purified by conventional methods. *N*-alkylpyridinium chloride (C_nPyCl, $n = 4, 12, 16$) were purchased from Tokyo Kasei (Tokyo, Japan) and used as received.

Polymerization

Copolymer of IPAAm and AMPS (poly(IPAAm-co-AMPS), IA copolymer) was prepared by radical polymerization of IPAAm with AMPS in DMF, by varying the mole fraction of AMPS by the same method described previously, using AIBN as an initiator [7]. The reaction was performed at $70 \pm 1\,^{\circ}C$ for 2 h. IA copolymer yielded a white powder with a yield of ca. 40%. The copolymers were coded as IAX, where X stands for the mole fraction of AMPS, which was determined by titration with $0.1\ mol\,l^{-1}$ NaOH aq. at room temperature. Monomer reactivity ratios were determined by a conventional method and calculated by Kelen–Tudos method [8].

Copolymer gel which contains 10 mol% of sodium salt of AMPS (NaAMPS) was prepared as follows. IPAAm (1.8 M), NaAMPS (0.2 M), *N*,*N*′-methylenebisacrylamide (40 mM) as a cross-linker and tetramethylethylenediamine (48 μl) as an accelerator were dissolved in distilled water and bubbled with nitrogen for 15 min. Ammonium persulfate (7.3 mg, initiator) was added, and then the solution was injected between glass plates separated by a Teflon gasket (1.0 mm). It was polymerized at 20 °C for 24 h and the membrane obtained was immersed in distilled water for one week to remove all unreacted compounds. The gel was transparent and had a swelling ratio of 27.7 at 25 °C. The swollen gel membrane (1.56 mm in thickness) was cut into disks (20 mm diameter) using a cork borer. Homo-PIPAAm and PAMPS gels were also prepared under the same conditions and their swelling ratios at 25 °C were 12.8 and 30.9, respectively.

Measurements of solution properties

The temperature dependence of the solubility of the linear copolymers in water as well as in C_{12}PyCl aqueous solution was characterized by measuring the optical transmittance of IA copolymer solution ($10\ mg\,ml^{-1}$, 2 ml) at 500 nm using a spectrophotometer (Shimazdu 160 A, Tokyo, Japan). The sample cell was thermostated by a temperature controller and the temperature was changed from 20 °C to 100 °C. Transmittance of solutions was measured three times with a 10 min interval at the temperature examined to confirm the equilibrium state. The LCST was determined as the temperature of half-change in transmittance.

Binding isotherms of C_{12}PyCl with IA10 copolymers were obtained by measuring free-surfactant concentrations in the mixed solution using a surfactant-selective membrane electrode [9]. The complex formed was collected by centrifugation and dried *in vacuo*.

Adsorption of surfactant to the gel and swelling measurement

In order to obtain the binding isotherm of the surfactant with the copolymer gel, the disk-shaped gel was immersed in the surfactant solution at least for two weeks to establish an equilibrium state. The process of the surfactant binding with IA10 copolymer gel was followed by measuring a change in UV absorption of the surrounding surfactant solution at 259 nm directly or diluted below cmc (molar extinction coefficient: ε (C_4PyCl) = $4400\ mol^{-1}\,dm^3\,cm^{-1}$, ε (C_{12}PyCl) = $4070\ mol^{-1}\,dm^3\,cm^{-1}$, ε (C_{16}PyCl) = $4230\ mol^{-1}\,dm^3\,cm^{-1}$. β, the degree of binding, is defined as the ratio of the molar number of surfactants penetrated into the gel to the total monomeric units of the sulfonic group in the copolymer gel. D, the diameter of the gel was measured and D/D_0 is used to characterize the volume change, where D_0 is the initial diameter swollen in pure water.

Results and discussion

Solution properties of IA copolymers

Change in LCST

We have found that when a small amount of AMPS was incorporated with IPAAm, the LCST of the polymer can extensively be changed. Figure 1 shows the transmittance change of IA copolymers with various AMPS contents. An introduction of AMPS as low as 10 mol% shifted LCST from 32 °C to 79 °C. When 50 mol% of AMPS was incorporated, the phase separation was diminished. The dramatic elevation of the LCST of the copolymer should apparently be attributed to the strong hydration ability of ionized AMPS.

Change in LCST of PIPAAm has been widely studied by changing the ionic strength, solvent composition and copolymer composition [10–13]. Copolymerizing IPAAm with hydrophilic and/or hydrophobic comonomers, such as acrylic acid, dimethylacrylamide and butylmethacrylate, modulated the LCST of PIPAAm within the range of several degrees centigrade. For example, 10 mol% of ionized acrylic acid shifted LCST to 40 °C [13]. This suggests that the hydrophilicity of a sulfonic ion is much stronger than that of an ionized carboxyl group. We do not have a definite answer why the sulfonate has a larger hydration ability than the carboxylate, however, one can associate it with the difference in the structure of water bound to these ions. Ikada et al. reported that chondroitin sulfate A possesses more non-freezing water than other mucopolysaccharides without sulfonic groups such as hyaluronic acid sodium salt [14]. Our results made by DSC also showed that PAMPS gel possesses eight non-freezing water per monomer unit [15], while poly(acrylic acid) gel possesses two per monomer unit. The reason why sulfonic group can attract such an amount of water should be left for further studies.

As shown in Fig. 1, the transmittance change of IA copolymers was not as sharp as that of homo-PIPAAm, especially when the AMPS content was increased, meaning that the phase separation became less cooperative. Since the transition behavior might be associated not only with the composition of AMPS but also with its sequential distribution, we attempted to calculate the average number of successive sequences of IPAAm $\langle l_1 \rangle$ and that of AMPS $\langle l_2 \rangle$ upon reaction conversion. According to Markov chain theory, we have the following relations [16]:

$$C_{1,0} = M_{1,0} C_{\mathrm{tot},0} \,, \tag{1}$$

$$m_{1,q}/(1 - m_{1,q}) = [M_{1,q}(r_1 M_{1,q} + M_{2,q})] / [M_{2,q}(r_2 M_{2,q} + M_{1,q})] \,, \tag{2}$$

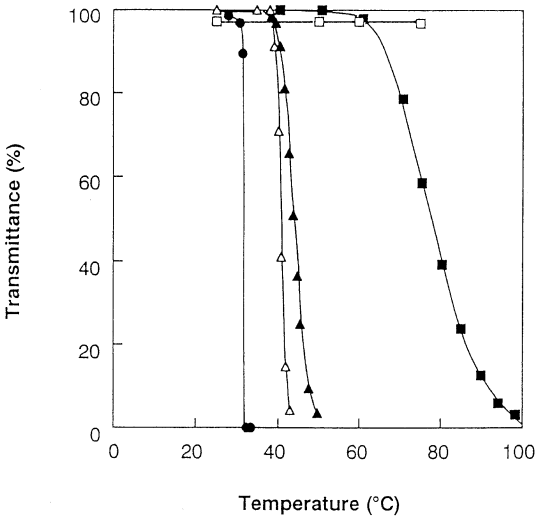

Fig. 1 Temperature dependence of transmittance for aqueous solutions of various IA copolymers (●; PIPAAm, △; IA3, ▲; IA5, ■; IA10, □; IA50)

$$C_{1,q} = C_{1,q-1} - m_{1,q-1} \delta_q C_{\mathrm{tot},0} \,, \tag{3}$$

$$C_{\mathrm{tot},q} = C_{1,q} + C_{2,q} \,, \tag{4}$$

$$M_{1,q} = C_{1,q}/C_{\mathrm{tot},q} \,, \tag{5}$$

$$\langle l_{1,q} \rangle = \frac{r_1 M_{1,q} + M_{2,q}}{M_{2,q}} \,, \tag{6}$$

$$\langle l_{2,q} \rangle = \frac{r_2 M_{2,q} + M_{1,q}}{M_{1,q}} \,, \tag{7}$$

where $C_{i,q}$ ($i = 1, 2$; $q = 0$–1) and $M_{i,q}$ are the concentration and the composition of monomer i in the solution at a conversion of q, respectively. $m_{i,q}$ is the copolymerized composition of monomer i at a conversion of q. δq is the conversion step. $C_{\mathrm{tot},q}$ is the total monomer concentration at a conversion of q. $q = 0$ denotes the initial (in feed) value. $\langle l_{i,q} \rangle$ is the average number of successive sequence of monomer i at conversion q. r_i is the monomer reactivity ratio of monomer i.

The monomer reactivity ratios were determined by titration and calculated as $r_1 = 0.96$ (IPAAm), $r_2 = 0.06$ (AMPS). Using $\delta q = 0.01$, we calculated $\langle l_{1,q} \rangle$ and $\langle l_{2,q} \rangle$ by computer simulation and the results are shown in Fig. 2. $\langle l_{1,q} \rangle$ and $\langle l_{2,q} \rangle$ did not vary prominently with the conversion q, if the composition of AMPS was less than 0.1 ($M_{2,0} < 0.1$). This indicates that IPAAm and AMPS are homogeneously distributed in the chain backbone, meaning that AMPS appears after every 10 IPAAm monomer units in IA10 copolymer. Thus, an increase of LCST and the transition width with an increase of AMPS content

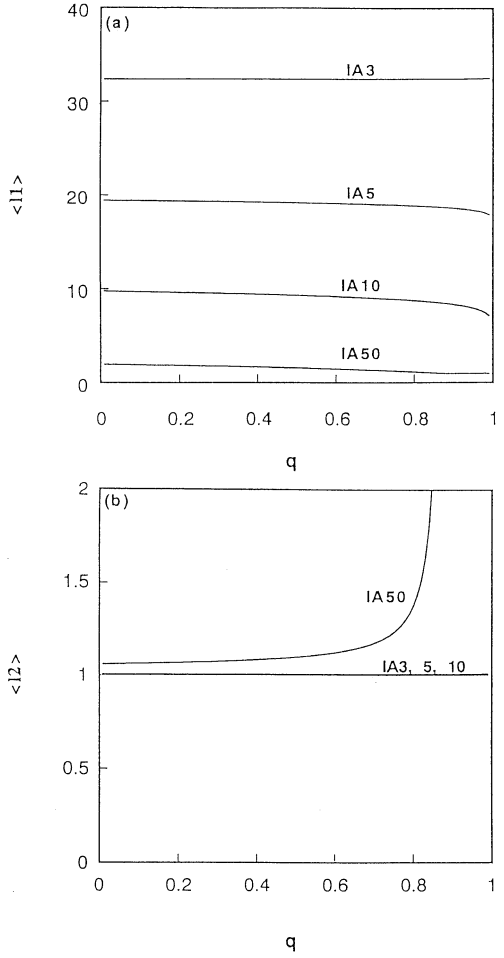

Fig. 2 Dependence of the successive sequence of IPAAm unit $\langle l_1 \rangle$ (a) and that of AMPS unit $\langle l_2 \rangle$ (b) on the conversion of the reaction q for IA copolymers with various compositions

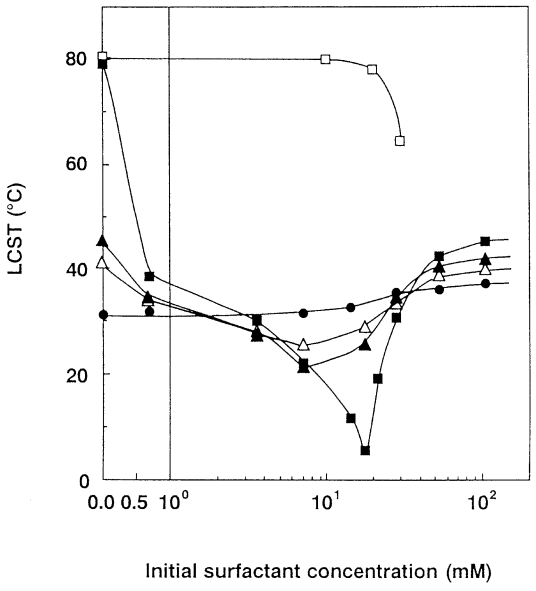

Fig. 3 LCST of IA copolymers as a function of surfactant concentration (●; PIPAAm, △; IA3, ▲; IA5, ■; IA10, □; IA10 in NaCl aqueous solution)

should be attributed to the decrease in the number of successive sequences of IPAAm units to undergo cooperative dehydration, and not to its inhomogenity in the copolymer chain.

Binding of surfactant

We have made detailed studies of the binding process of C_nPyCl to PAMPS homo-polymer and found that the surfactant undergoes one-to-one stoichiometric binding initiated by electrostatic force. Therefore, it is of interests to know how the surfactant binds to IA copolymer and how the binding affects the LCST. Surfactant binding to IA copolymer was made in various concentrations of $C_{12}PyCl$ and its LCST was measured (Fig. 3). LCST of all IA copolymers first decreased with the increase of the surfactant concentration, and then, increased above a certain surfactant concentration. Among them change in LCST of IA10 was the most significant. The LCST of IA10 was 79 °C in water, but in 18 mM of $C_{12}PyCl$ solution it reached a minimum at as low as 4 °C, which was much lower than that of homo-PIPAAm. Since PAMPS forms a one-to-one ion complex with the cationic surfactant, AMPS unit in IA copolymer should also make a complex with surfactants and the charges should be annihilated. The drastic decrease of LCST was obviously due to the surfactant, since the effect of sodium chloride on the LCST of IA10 was much less significant. Alkyl chains of the surfactant molecules introduced extra hydrophobicity and shifted the LCST even lower than that of homo-PIPAAm.

Supposing that all of the surfactants in the solution were bound to the AMPS units in the copolymer, one can roughly illustrate the relationship between LCST and the free AMPS content in the copolymer (Fig. 4). Curve A shows the LCSTs of IA copolymers in water and curve B in the LCST of IA10 equilibrated in dilute $C_{12}PyCl$ solution. The LCST of IA10 drastically decreased from 79 °C to 38 °C by addition of the surfactant, while further addition of the surfactant modestly decreased the LCST. One should note here that the IA10–$C_{12}PyCl$ complex showed a much lower LCST than that of the copolymer corresponding to the same charge content in pure water. For example, IA10 (1.6×10^{-5} mol of AMPS unit), equilibrated in 0.7 mM $C_{12}PyCl$ (1.4×10^{-6} mol of $C_{12}PyCl$) contains 9 mol% free AMPS in the copolymer solution, showed LCST at 38 °C, while LCST of copolymer in

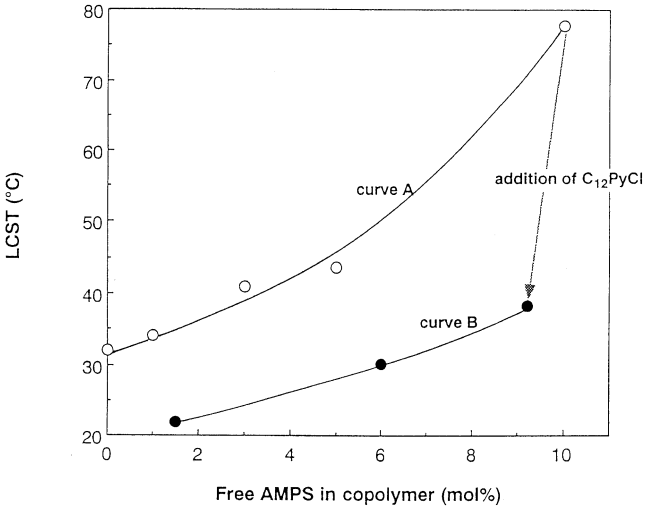

Fig. 4 LCST of IA copolymers in water (○) and that of IA10 equilibrated in surfactant solution (●) as a function of free AMPS content in the copolymer, supposing all the surfactants in solution were bound to AMPS units

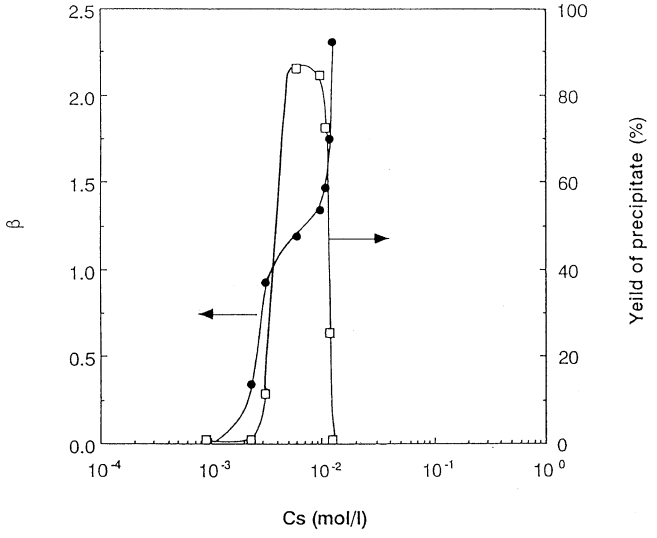

Fig. 5 Binding isotherm of C_{12}PyCl with IA10 copolymer (●) and the amount of complex precipitate (□) at 25 °C. The yield of precipitate was calculated on the assumtion of a one-to-one complex formation

water, as suggested from curve A was 70 °C. This large difference in the LCST cannot be explained only by the introduction of surfactant alkyl chains. As described at the beginning of this section, the copolymer has a homogeneous sequence distribution and an AMPS unit appears after every 10 IPAAm units for IA10, and every 20 IPAAm units for IA5. If one surfactant molecule binds to an AMPS unit of IA10, the number of successive sequences of IPAAm units in that part of the chain will be 20, which is equivalent to that of IA5, whose LCST is 44 °C. Since the phase transition has a cooperative nature, this large IPAAm sequence initiates the phase separation to give an LCST much lower than that of the copolymer with the same charge density in a homogeneous sequence distribution. This result suggests that formation of long hydrophobic domains through surfactant binding plays an important role in initiating the phase-separation process.

We discussed the solubility of IA copolymer bound with C_{12}PyCl, however, the binding of C_{12}PyCl should depend on temperature. In order to study this complex-formation process more precisely, a binding isotherm was made at a fixed temperature (25 °C). By using an ion-selective electrode one can analyze the free-surfactant concentration in the polymer–surfactant mixture, so as to determine the amount of surfactant bound to the polymer. The result is plotted in Fig. 5. The binding started at a C_{12}PyCl concentration as low as 10^{-3} M and the degree of binding (β), which is defined as the molar ratio of bound surfactant to total sulfonate groups in the copolymer, increased quickly. With the increase of surfactant concentration, the insoluble complex appeared at a certain mixing ratio. The maximum of insoluble complex yield coincided with $\beta = 1$ and additionally indicates the formation of the one-to-one complex.

We have characterized the binding process of surfactant onto PAMPS by two processes [1]. One is an electrostatic salt formation (initiation process) and the other is a hydrophobic interaction between adjacently bound surfactant molecules (propagation process), which is called a "cooperative process". The overall binding constant (K) for the complexation can be calculated as follows:

$$\text{polymer} + \text{surfactant} \overset{K}{\leftrightarrows} \text{complex} . \tag{8}$$

From the binding isotherm curve we can characterize the K value as well as the other interaction parameters by the following equation [4, 17, 18]:

$$K = K_0 u = 1/(C_S)_{0.5} , \tag{9}$$

where K_0 is the binding constant of the surfactant bound to an isolated binding site on the polymer and u is the cooperativity parameter which tells the interaction between adjacently bound surfactant molecules. u can be determined from the slope of the binding isotherm at the half-bound point [4, 17, 18].

$$(\mathrm{d}\beta/\mathrm{d}\ln C_S)_{0.5} = \sqrt{u}/4 . \tag{10}$$

Since in PAMPS linear polymer charges are accumulated along the polymer chain, once the surfactant binds by electrostatic force, the binding is enhanced cooperatively by hydrophobic interaction. In fact, the increase of ionic

Colloid & Polymer Science, Vol. 276, No. 1 (1998)

strength, which arises from electrostatic shielding, decreases the K_0 value (initiation process) and increases the cooperativity (hydrophobic interaction) [1]. With the same method, we characterized the interaction parameters of C_{12}PyCl with IA10 copolymer at 25 °C and the results are summarized in Table 1. By comparing them with data for PAMPS-C_{12}PyCl system one can easily see that IPAAm units strongly interfere with the cooperativity of binding. K_0 value is almost the same as that of PAMPS, while cooperativity parameter of IA10 is much smaller. This indicates that the dispersed distribution of AMPS does not affect the initial binding, but it strongly affects the side-by-side hydrophobic interaction.

Another specific feature of the surfactant binding with IA10 is the fact that β increased to more than 1. Interestingly, the precipitate formed quickly dissolved accompanying the increase of β. This is completely different from that of PAMPS, where a quantitative amount of insoluble one-to-one complex is formed and no re-dissolution occurs.

We have recently reported that some amphiphilic polymers, i.e., ionene polymers, copolymers of 12-acryloyldodecanoic acid and acrylic acid bind with oppositely charged surfactants in two steps [19]: The first step is one-to-one stoichiometric insoluble complex formation through electrostatic and hydrophobic interactions. The second step is mainly promoted by the hydrophobic interaction to give soluble non-stoichiometric complexes. Magny et al. reported the poly(sodium acrylate) with a few mol% of alkyl side groups bind the cationic surfactant and forms a cluster containing surfactant molecules and alkyl side groups of the polymer [20]. All these polymers have charges distributed along the polymer chains separated by some hydrophobic segments in between. This might explain well for the IA copolymer system. After all of the AMPS units are bound by C_{12}PyCl, additional surfactants bind to the polymer through hydrophobic interaction, which in turn gives positive charges and, thus, increases the hydrophilicity and forms soluble complex (increases LCST). Here we come to a question where this excess amount of surfactant binds. It is reported that the LCST of PIPAAm increases in highly concentrated anionic surfactant solution [21], however, under our experimental surfactant concentration, LCST of PIPAAm practically did not change (Fig. 4). Besides, the LCST of IA copolymers saturated in concentrated surfactant solutions. Among them saturated LCST of IA10 was higher than those of others; the second step of binding was apparently enhanced in the IA copolymer with high AMPS content. This suggests that the surfactant subsequently binds to the hydrophobic domain formed by the surfactant already bound to AMPS. It should also be noted that the concentration where solubilization of the complex occurred coincided with the cmc of C_{12}PyCl.

Table 1 Interaction parameters of C_{12}PyCl with IA10 copolymer and PAMPS linear polymer at 25 °C

	K ($l\,mol^{-1}$)	K_0 ($l\,mol^{-1}$)	u
IA10	390	35	11
PAMPS[a)]	28000	44	630

[a)] Data from ref. [3].

Surfactant binding with IA10 gel

As the LCST change of the copolymer composed of IPAAm and sodium salt of AMPS (NaAMPS) was practically the same as that of AMPS, chemically cross-linked IA copolymer gel containing 10 mol% of NaAMPS was prepared to prevent hydrolysis of the cross-linking agent, and the effects of surfactant binding was studied. The binding isotherms of C_{12}PyCl were made at 5 °C, 25 °C and 45 °C, and the size change immersed in the surfactant were also measured. As shown in Fig. 6a, the binding isotherm with IA10 gel at 25 °C consisted of two processes. The first step of binding started at a free C_{12}PyCl concentration of 10^{-5} M, which was one order of magnitude higher than that of PAMPS gel, as shown in the same figure. β increased with increase of the concentration and then leveled off around $\beta = 1$, at a concentration of $10^{-4} - 10^{-3}$ M. However, β increased sharply above a free-surfactant concentration of 10^{-2} M, attaining $\beta = 6$, suggesting that IA10 gel adsorbed an excess amount of surfactant. This was in contrast to the case of PAMPS gel. Its β value saturated at 1.0, and further addition of surfactant brought about no increase in β. PIPAAm gel did not bind C_{12}PyCl at the concentration examined either below (25 °C) or above (45 °C) its LCST. The first step of binding of IA10 gel was extensively promoted at an elevated temperature, which suggests the contribution of hydrophobic interaction. This was again in contrast to that of PAMPS gel, in which the binding is quite insensitive to the temperature [3].

In order to study the effect of IPAAm units in IA10 gel, K_0 and u were calculated and the results are summarized in Table 2. K_0 as well as the u value of IA10 gel was smaller than that of PAMPS gel, which, however, increased with temperature. These results suggest that the hydrophobic environment of the IPAAm main chain also plays an active role in both the initial binding process and the cooperative propagation process. One should note that both K and K_0 of IA10 gel at 25 °C are nearly two orders of magnitude larger than those of solvated IA10, while u was smaller. We have reported that in the case of PAMPS the initiation process of the binding is largely dominated by the electrostatic attractive force between

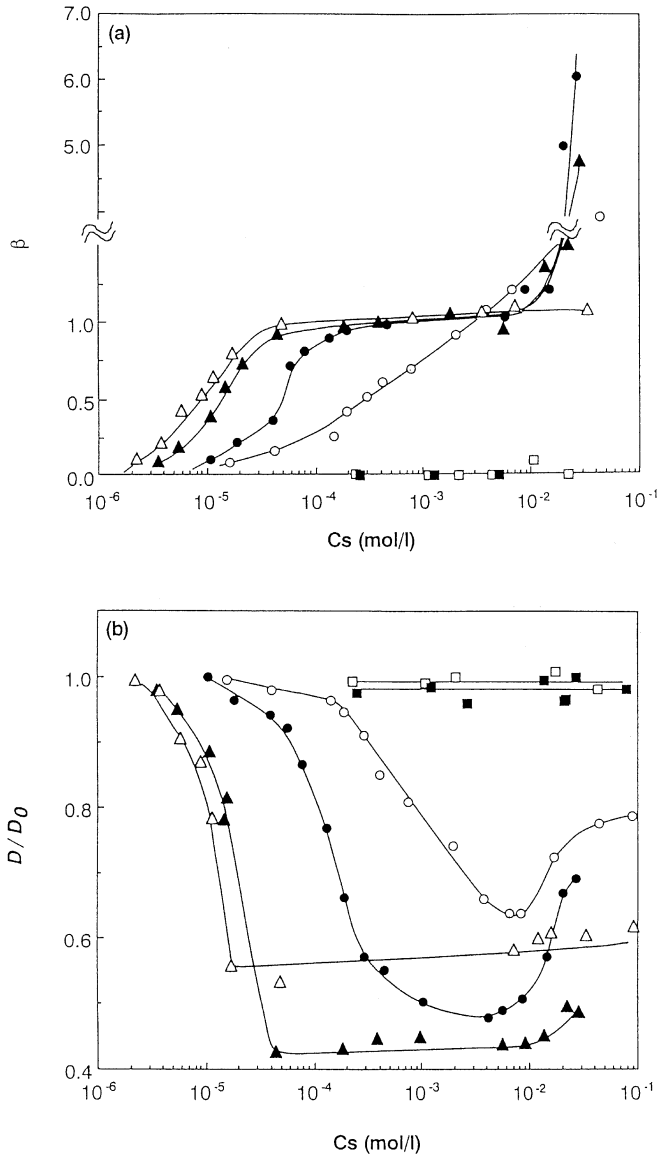

Fig. 6 Binding isotherm of C_{12}PyCl with A10 gel at various temperatures (a) and its size change (b) (○; 5 °C, ●; 25 °C, ▲; 45 °C, □; PIPAAm gel at 25 °C, ■; PIPAAm gel at 45 °C, △; PAMPS gel at 25 °C)

macroions and surfactant cations, whereupon charge density of the macroions affects the value of K_0. The cross-linkage brings about the increase of charge density and results in larger K_0 and less cooperativity [3].

Enthalpy and entropy changes were calculated from the temperature dependence of the stability constant and the results are summarized also in Table 2. ΔH and ΔS for both IA10 and PAMPS gels are positive, which proves that the complex formation is due to the hydrophobic interaction. Note that both ΔH and ΔS for IA10 gel were larger than that of PAMPS, indicating the hydrophobic interaction was enhanced due to the presence of IPAAm on the chain backbone. Corresponding to the binding, the IA10 gel considerably shrank and attained a constant after β reached 1 (Fig. 6b). However, it re-swelled at the surfactant's cmc, at which β jumped up sharply, indicating that re-swelling occurred due to a second step of binding.

In order to study the role of the cmc on the second step of binding, a contraction experiment of the IA10 gel was made using surfactants with different alkyl tails (Fig. 7). The gels contracted when the surfactants were added, but the ones that equilibrated in C_{12}PyCl and C_{16}PyCl solutions re-swelled at around their cmc. No re-swelling occurred for the gel immersed in the C_4PyCl solution which has no cmc.

Two-step binding mechanism

The main reason for the different behavior of the excessive surfactant binding of IA10 is considered to be the distribution of ionized groups separated by hydrophobic chain backbones. In the case of the PAMPS–surfactant interaction, the strong hydrophobic interaction between the long hydrocarbon tails of adjacently bound surfactants forms a supra-ordered organization with a long sequence [2]. Here the hydrophobic tails of the surfactant are kept inside to avoid any contact with water, to give a tightly coiled conformation to the PAMPS polymer or to bring about a volume collapse in the gel. This prevents subsequent surfactant interaction; surfactants stay freely in water or form micelles of their own, leaving the one-to-one complex

Table 2 Interaction parameters of C_{12}PyCl with IA10 copolymer gel at various temperatures

Temperature [°C]		K [10^{-4} l mol^{-1}]	K_0 [10^{-4} l mol^{-1}]	u	ΔH [kJ mol^{-1}]	ΔS [J K^{-1} mol^{-1}]
IA10	5	0.3	0.5	0.62		
	25	2.4	1.0	2.47	28	170
	45	8.1	2.4	3.39		
IA50	25	7.5	2.8	2.67		
PAMPS	25	13.3	5.5	2.42	9.6	117

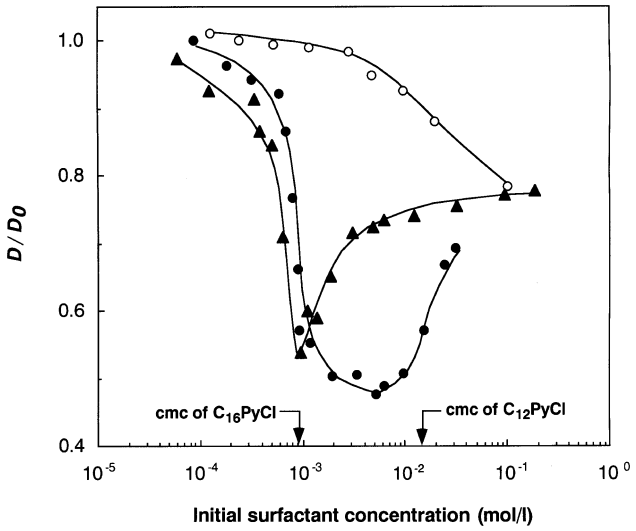

Fig. 7 Effect of surfactant concentration on the size of IA10 gel at 25 °C (○; C_4PyCl, ●; C_{12}PyCl, ▲; C_{16}PyCl)

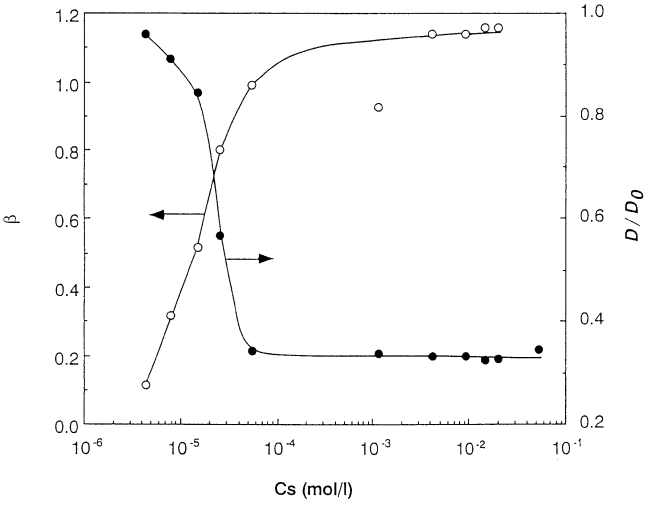

Fig. 8 Binding isotherm of C_{12}PyCl with IA50 gel and its size change at 25 °C

insoluble. On the other hand, in IA copolymer, in which two adjacent ionic sites are separated by long hydrophobic units, adjacent surfactant molecules are unable to pack together. Instead, the bound surfactant would associate with the main chain randomly through their hydrophobic interaction. As seen from Fig. 6, the interaction between the surfactants and PIPAAm was weak even at a high temperature. Therefore, near the surfactant's cmc, the alkyl tails of the bound surfactant would preferentially interact with the free surfactant. As a result, a mixed micelle is formed, containing the polymer main chain as a component and the polymer complex is solubilized.

The above discussion suggests that if the AMPS content in the copolymer is increased so as to make a relatively long successive sequence, the second step of binding should be suppressed. As shown in Fig. 8 IA50 gel, in which successive sequence of IPAAm and AMPS are calculated to be 2 and 1, respectively, showed neither two-step binding nor solubilization.

Wide-angle X-ray studies of dry IA10 gel–surfactant complex were made, but no distinctive diffraction pattern was observed, suggesting the solubilized complex has no ordered structure.

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