Role and Effect of Cross-Linkage on the Polyelectrolyte−Surfactant Interactions

Hidenori Okuzaki and Yoshihito Osada*

Division of Biological Sciences, Graduate School of Science, Hokkaido University, Sapporo 060, Japan

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ABSTRACT: Study of binding of the cationic surfactant molecule—*N*-dodecylpyridinium chloride (C_{12}PyCl)—onto the anionic polyelectrolyte network—poly[2-(acrylamido)-2-methylpropanesulfonic acid] (PAMPS) gel—with different cross-linking densities was made and compared with that with linear PAMPS. The experimental results showed that the presence of cross-linkage significantly enhances the initiation process but strongly suppresses the cooperativity of the binding. The binding process of the surfactant onto the charged network was interpreted in terms of osmotic pressure of the gel which results from the conformational shrinkage caused by the surfactant binding.

Introduction

In the previous papers, we have made thermodynamic and kinetic studies of the surfactant (*N*-alkylpyridinium chloride: C_nPyCl, n = 4, 8, 10, 12, 16, 18) binding onto the anionic polymer network (poly[2-(acrylamido)-2-methylpropanesulfonic acid]: PAMPS) over a wide range of concentrations as well as ionic strengths, and the binding constant K and the cooperativity parameter u have been evaluated.[1,2] Both K and u increased with increasing alkyl chain length, indicating that the binding is cooperative in nature and is dominated by a hydrophobic interaction. The role of electrostatic and hydrophobic interactions on the processes of initiation and propagation in the polymer network has been discussed. The electrostatic potential and the ionic transportation in the polyelectrolyte network have been theoretically evaluated using the one-dimensional capillary model.[3] We have also found that surfactant molecules with an alkyl chain size larger than C_{10} can form micelle-like aggregates to give a crystalline structure of a primitive lattice in the linear as well as the cross-linked PAMPS.[4] This surfactant binding reaction allowed us to establish a chemomechanical system which exhibited biomimetic motility under an electric field.[5−7]

A number of studies regarding the surfactant−polyelectrolyte interaction have been conducted.[8−11] Recently, Khokhlov et al. have investigated the interaction of cetylpyridinium bromide with cross-linked PMAA gel and theoretical consideration of the structure of the gel−surfactant aggregate has been made.[12] The effects of charge density, mobility, ionic strength, and network topology on the complex formation have been emphasized. However, no comparative study of surfactant binding with solubilized polymer and cross-linked network has been done.

This paper concerns the effect and role of the cross-linkage on the surfactant−network interaction. We have found that the presence of cross-linkage significantly enhances the initiation process while it suppresses the cooperative process of the binding. This experimental result was explained in terms of the presence of deep electrostatic potential around the charged network and the large osmotic pressure of the gel which tends to expand the network.

* To whom correspondence should be addressed.
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Experimental Section

Materials. 2-(Acrylamido)-2-methylpropanesulfonic acid (AMPS) (Nitto Chemical Co., Ltd.), *N,N'*-methylenebis(acrylamide) (MBAA) (Tokyo Kasei Co., Ltd.), and potassium persulfate (Tokyo Kasei Co., Ltd.) were purified in the same manner as described in the previous paper.[4] *N*-Dodecylpyridinium chloride (C_{12}PyCl) (Tokyo Kasei Co., Ltd.) was used without further purification.

Preparation of the PAMPS Gel and Linear Polymer. A series of PAMPS gels with different cross-linking densities was prepared by radical polymerization of AMPS in water by changing the amount of cross-linking agent: MBAA.[1] After polymerization, the gel was immersed in a large amount of water to remove unreacted monomer and initiator until it reached equilibrated size. The percent of cross-linkage (DCL) was simply calculated as a molar ratio of cross-linking agent (MBAA) to AMPS monomer (DCL = 100[MBAA]/[AMPS]). The degree of swelling of the gel (q) was determined as a weight ratio of water swollen gel to its dry state. Linear PAMPS (L-PAMPS) was obtained in the same manner, but without cross-linking agent, and precipitated twice from ethyl acetate.

Measurement. The process of the surfactant binding onto PAMPS gel was followed by measuring a change in the UV absorption of the surrounding surfactant solution at 259 nm (molar extinction coefficient of C_{12}PyCl: ϵ = 4070) in the presence of a prescribed amount of cylindrical PAMPS gel (dry weight 6 mg). The polymer gel was immersed in the surfactant solution and left to stand for at least 2 weeks in order to establish an equilibrium state. The surfactant binding with L-PAMPS was followed by measuring the free surfactant concentration in the polymer solution (the concentration of AMPS by repeat unit is 3×10^{-3} mol L^{-1}, dry weight 6 mg) using a surfactant-selective membrane electrode. The binding was made by mixing solutions of C_{12}PyCl and linear PAMPS (3×10^{-3} mol L^{-1}). To reach equilibrium, the solutions were left to stand under thermostatic conditions for more than 1 week. The surfactant-selective membrane electrode was prepared from an α-cyclodextrin (Tokyo Kasei Co., Ltd.) esterified with propionic anhydride in poly(vinyl chloride) film.[8]

Results and Discussion

The binding process of the surfactant onto an oppositely charged polyelectrolyte is characterized by two processes.[1] One is an electrostatic salt formation of the surfactant molecules with oppositely charged sulfonates in the gel (*initiation process*). The other is a hydrophobic interaction between adjacently bound surfactant molecules, which stabilizes the aggregate (*propagation process*). The latter is called a "cooperative process".

When the surfactant molecule undergoes a stoichiometric binding, the overall stability constant (K) can be

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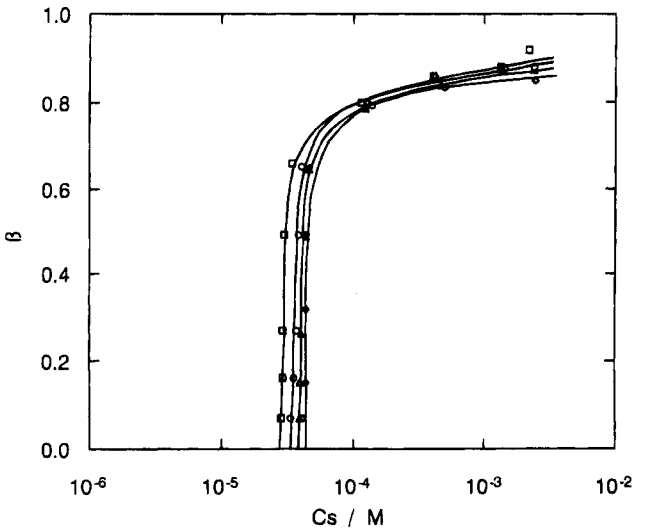

Figure 1. Binding isotherms of $C_{12}PyCl$ with L-PAMPS under various temperatures: (◇) 5 °C; (△) 15 °C; (○) 25 °C; (□) 35 °C. Polymer concentration: 3×10^{-3} mol L^{-1}.

calculated as[9]

$$K = K_0 u = 1/(C_s)_{0.5} \quad (1)$$

where $(C_s)_{0.5}$ is the equilibrium free surfactant concentration at $\beta = 0.5$ and K_0 is the binding constant of a surfactant molecule bound to an isolated binding site on a polymer chain (initiation process). Here, the degree of binding (β) is defined as a molar ratio of bound surfactant to total sulfonate group in PAMPS gel or solution. The value of u is a cooperativity parameter characterizing the interaction between adjacently bound surfactants (propagation process) which is calculated from the slope of the binding isotherm at the half-bound point:[8]

$$(d\beta/d \ln C_s)_{0.5} = \sqrt{u}/4 \quad (2)$$

Figure 1 shows the binding isotherms of $C_{12}PyCl$ made for L-PAMPS solution under various temperatures. One can see an abrupt increase in β in a very narrow range of surfactant concentration, which later leveled off near $\beta = 0.8$. The presence of such a "critical" surfactant concentration for the surfactant binding can be explained in terms of the cooperative nature of complexation. An increase in temperature brought about a shift of the binding curve slightly toward the higher surfactant concentration, while the slope of the curve remained unchanged.

In order to clarify the effect of the cross-linkage on the surfactant binding, the binding isotherm of the $C_{12}PyCl$ with the PAMPS gel was made under various temperatures. As shown in Figure 2, the binding of surfactant starts at such low concentrations as 10^{-6} mol L^{-1} and continues up to 10^{-3} mol L^{-1}, showing a sigmoidal dependence with the surfactant concentration. Similarly to L-PAMPS, an increase in temperature shifted the binding curve toward lower surfactant concentrations; i.e., an increase in temperature favored the binding. An increase in temperature brought about a slight decrease in the slope of the curve and suggested a decrease in the cooperativity. Thus, the cross-linking of PAMPS favored the initiation process while it suppressed the propagation and decreased the cooperativity.

Figure 3 shows the binding isotherms of $C_{12}PyCl$ onto

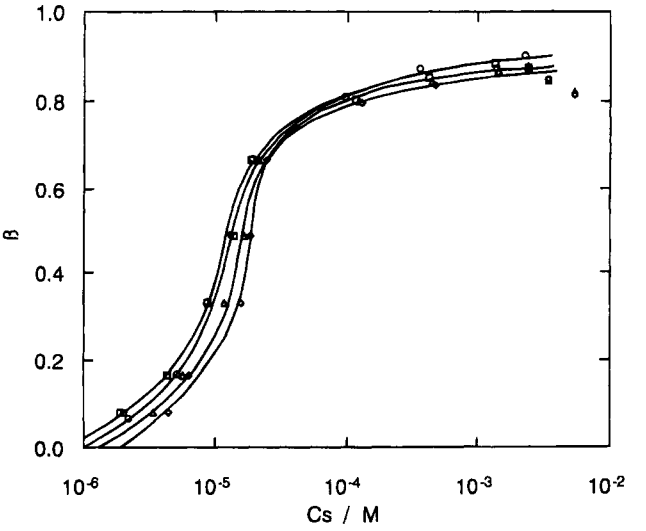

Figure 2. Binding isotherms of $C_{12}PyCl$ with PAMPS gel under various temperatures: (◇) 5 °C; (△) 15 °C; (○) 25 °C; (□) 35 °C. DCL of the PAMPS gel = 4.5%, $q = 50$.

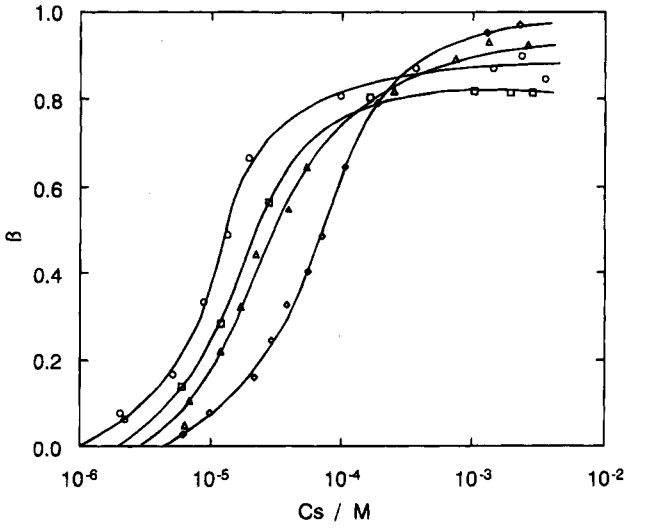

Figure 3. Binding isotherms of $C_{12}PyCl$ with PAMPS gel of various DCL: (○) DCL = 4.5%, $q = 50$; (□) DCL = 2.0%, $q = 350$; (△) DCL = 1.2%, $q = 490$; (◇) DCL = 1.1%, $q = 790$. Temperature: 25 °C. The amount of sulfonate group in the gel was kept constant at 3×10^{-5} mol for all samples.

PAMPS gels with different degrees of cross-linkage (DCLs). It is seen that an increase in DCL decreases the minimum surfactant concentration at which the binding starts, but increases the maximum β value, approaching nearly 1.0. If the overall stability constant of the complex formation is calculated for various gels using data in Figures 1 and 3 and eq 1, one can get Figure 4 which shows a rapid increase of K with an increase in DCL or a reciprocal dependence K on the degree of swelling (Figure 4, inserted). Thus, a cross-linkage of PAMPS favors the surfactant binding, and the larger the cross-linking density, the larger the overall stability constant. It should be noted that K for L-PAMPS is strongly deviated from the curve made for the gels. This suggests that the process of binding of the network should be essentially distinct from that of L-PAMPS.

Enthalpy and entropy changes of the binding were calculated from the temperature dependence of the stability constant, and the results were summarized in Table 1. Values of ΔH and ΔS for the gel (DCL 4.5%) and for L-PAMPS were almost the same with positive

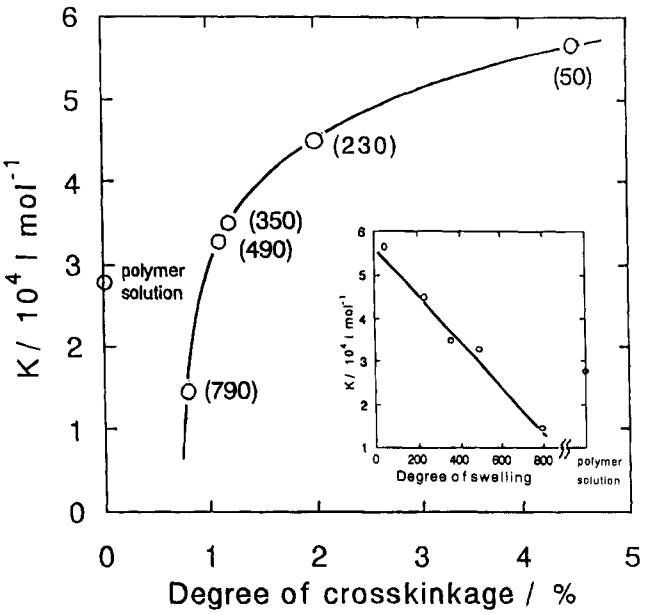

Figure 4. Dependence of the stability constant (K) on the degree of cross-linkage or degree of swelling (inserted). Temperature: 25 °C. Numbers in the figure denote q.

Table 1. Interaction Parameters of C12PyCl with PAMPS of Various DCL

DCL/%	q	$10^{-3}K$/ mol^{-1}	u	$10^{-3}K_0$/ mol^{-1}	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$\Delta S°$/ J mol^{-1} K^{-1}
0	1600[a]	28	630	0.044	−26	9.2	120
0.8	790	15	1.8	8.3	−24		
1.1	490	33	2.3	14	−26		
1.2	350	35	1.7	21	−26		
2.0	230	45	1.9	24	−26		
4.5	50	57	1.3	44	−27	9.7	120

[a] Corresponds to polymer dilution.

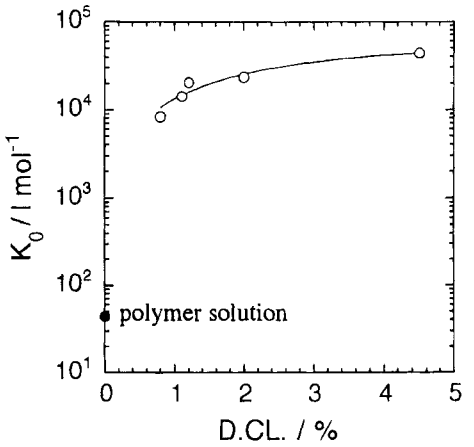

Figure 5. Dependence of the stability constant of the initiation process (K_0) on the degree of cross-linkage. Temperature: 25 °C.

sign and indicated the contribution of the hydrophobic interaction. As we know,[10] the hydrophobic interaction is well characterized as the large and positive entropy change while a nearly zero or small positive enthalpy change.

The stability constant of the initiation process (K_0) and the cooperativity parameter (u) of the binding were calculated using the data in Figure 4 and eq 2 for the various gels, and the results are shown in Figure 5 and Table 1. As seen in Figure 5, K_0 increases slightly with an increase in DCL and the K_0 for L-PAMPS is 2 orders of magnitude smaller than that of the gel. The obtained experimental result should be explained in terms of the increased charge density of the network. One can easily calculate that the charge density of the sulfonate in the gel with a DCL of 4.5% (q = 50) is 98 × 10^{-3} mol L^{-1}, while that of the corresponding polymer solution is 3 × 10^{-3} mol L^{-1}. In the previous paper,[1] we have demonstrated that the initiation process of the binding is largely dominated by the long-range interaction of electrostatic force between positive surfactant and negative polyelectrolyte. With regard to this, an evaluation of the electrostatic potential distribution of cross-linked polyelectrolyte gels has also been made by using the one-dimensional capillary model[3] and three-dimensional lattice model.[13] The simulation result revealed that there exists deep electrostatic potential wells at every cross-linking point, and the electrostatic field was as high as 10^8 V/m at the cross-linking points. The high electrostatic potential of the gel results in an increased local concentration of the surfactant in the network domain due to the Donnan equilibrium and shifts toward the enhanced binding at the given surfactant concentration. Thus, there should be equilibria of three types, the surfactant dispersed in the solution, locally concentrated in the network domain, and bound with the network. Therefore, it is reasonable that K_0 increases with an increase in the cross-linking density.

On the other hand, the cooperativity parameter u of the gel was more than 2 orders of magnitude smaller than that of the polymer solution (Table 1) and the values were almost independent of the cross-linking density. The decreased cooperativity could be associated with the large osmotic pressure of the charged network which is balanced with the rubber-like elasticity.

As well established, the polyelectrolyte chains are in an extended conformation due to their strong electrostatic repulsion between charges. The cross-linkage of the chain results in a strong suppression of the segmental motion of the network and produces a large osmotic pressure which is, in turn, balanced with the rubber elasticity of the network. Therefore, if a water-swollen PAMPS gel is immersed in the C_{12}PyCl solution, the surfactant molecules quickly penetrate into the polymer network and cause a contraction in volume.[1,2] However, this conformational shrinkage should be balanced with the osmotic pressure which tends to expand the network dimension and consequently decreases the cooperativity.

In other words, the surfactant binding on the charged network requires extra work of the network contraction and the value is the same as that of osmotic pressure per unit volume.

It is now understandable why the increase in the ionic strength greatly decreases K_0 but enhances the cooperativity of the gel, as reported in the previous paper.[6] The decrease in K_0 should be explained in terms of the reduction of electrostatic repulsion between the charged network (screening effect) and surfactant. And an enhanced cooperativity by the salt could be associated with the decrease in the osmotic pressure of gel.

In order to characterize the cooperative process, the cluster size of the bound surfactants was estimated according to further treatment by the Zimm–Bragg theory,[11] and the average number of bound surfactant molecules forming a micellar cluster on the polymer chain (m) was calculated using the following equation:

$$m = 2\beta(u-1)/[\{4\beta(1-\beta)(u-1)+1\}^{1/2}-1] \quad (3)$$

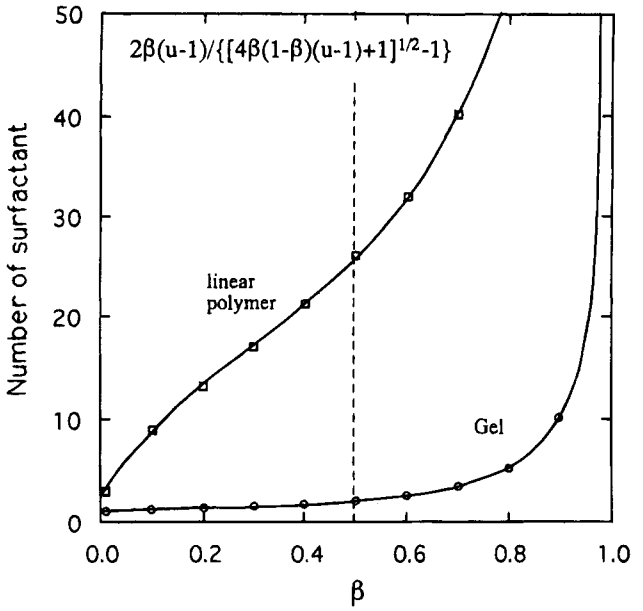

Figure 6. Average number (m) of the surfactant in a cluster for PAMPS gel or L-PAMPS.

m for the gel (DCL = 4.5%, q = 50) and L-PAMPS are shown in Figure 6. One can easily see that the value of m for the gel is very small until β = 0.8 and later diverges. This indicates that the surfactant molecules make randomly-dispersed binding on a wide area of the polymer network and are unable to form a long continuous sequence until β becomes 0.9. On the contrary, m of L-PAMPS increases with an increase in β and indicated the formation of a micellar-like cluster with a continuous sequence on the PAMPS chain. The average sequence number of the surfactant aggregate on the L-PAMPS was calculated as 26 at β = 0.5 while that of the gel was only 2. This well coincides with the formation of ordered aggregate.

As reported earlier,[4] the surfactant molecules with an alkyl chain size larger than C_{10} formed crystalline aggregates of a primitive lattice; L-PAMPS formed them at β = 0.67 while the PAMPS gel could not.[4] The continuous sequences on L-PAMPS should favor the crystallization of the polyelectrolyte–surfactant aggregates. Theoretical modeling of the binding for the polyelectrolyte network on the basis of a nearest neighbor interaction is now under progress.

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References and Notes

(1) Okuzaki, H.; Osada, Y. *Macromolecules* **1994**, *27*, 502.
(2) Okuzaki, H.; Eguchi, Y.; Osada, Y. *Chem. Mater.* **1994**, *6* (10), 1651.
(3) Gong, J. P.; Nitta, T.; Osada, Y. *J. Phys. Chem.* **1994**, *98*, 9583.
(4) Okuzaki, H.; Osada, Y. *Macromolecules* **1995**, *28*, 380.
(5) Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992**, *355*, 242.
(6) Osada, Y.; Ross-Murphy, S. B. *Sci. Am.* **1993**, *268* (5), 82.
(7) Okuzaki, H.; Osada, Y. *J. Biomater. Sci. Polym. Ed.* **1994**, *5* (5), 485.
(8) Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1983**, *87*, 506.
(9) Hayakawa, K.; Santerre, J. P.; Kwak, J. C. T. *Macromolecules* **1983**, *16*, 1642.
(10) Khokholov, A. R.; Kramarenko, E. Yu.; Makhaeva, E. E.; Strarodubtzev, S. G. *Macromolecules* **1992**, *25*, 4779.
(11) Khokholov, A. R.; Kramarenko, E. Yu.; Makhaeva, E. E.; Strarodubtzev, S. G. *Macromol. Chem., Theory Simul.* **1992**, *1*, 105.
(12) Tanford, C. *The Hydrophobic Effect*; John Wiley & Sons: New York, 1073.
(13) Gong, J. P.; Osada, Y. *Chem. Lett.*, in press.
(14) Zimm, B. H.; Bragg, J. K. *J. Chem. Phys.* **1959**, *31*, 526.

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