Kinetic Study of Surfactant Binding into Polymer Gel−Experimental and Theoretical Analyses

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Kinetic studies of the cationic surfactant uptake into an anionic polymer network have been made using surfactants with various alkyl chain lengths changing ionic strength. The rate of the surfactant uptake is strongly dependent on the surfactant alkyl size and ionic strength, and it was explained in terms of two factors: surfactant diffusion process and binding process. A mathematical model for the surfactant diffusion was developed, taking into account the surfactant binding process by numerically solving diffusion equations. The obtained results were compared with those of experiments.

1. Introduction

Extensive studies of polyelectrolyte gel−surfactant binding have been made from equilibrium and structural viewpoints, where the contribution of both electrostatic and hydrophobic interactions have been emphasized for the cooperative binding.[1,2] The binding of the surfactants onto the charged networks often results in volume collapses of the gels as well as aggregations with ordered supramolecular structures.[3,4] Three categories of surfactant binding, i.e., (1) cooperative and stoichiometric, (2) cooperative and nonstoichiometric, and (3) noncooperative and stoichiometric processes, have been proposed.[5,6] The existence of the frontal heterogeneous reaction which results in the formation of a polycomplex between the cross-linked polyelectrolyte and surfactant has been proposed.[7] However, so far as the authors know, no systematic kinetic studies of the surfactant uptake through the charged gels have been made.

In the previous paper,[8] we have made a kinetic study of the cationic surfactant *N*-alkylpyridinium chloride (C_nPyCl; $n = 4$, 8, 10, 12, or 16) uptake into weakly cross-linked poly(sodium 2-acrylamido-2-methylpropane sulfonate) (PNaAMPS). We have found that despite the substantial increase in network density due to the collapse of the gel, the flux of the surfactant uptake was remarkably enhanced, and the phenomenon was explained in terms of increased electrostatic interaction. This means that an increase in the network density did not cause any steric interference for the surfactant permeation but enhanced the electrostatic attraction between the surfactant and the oppositely charged network and accelerated the surfactant uptake. This was experimentally confirmed by investigating the effects of charge density using PNaAMPS gel with various network densities. The flux increased with an increase in the volume fraction of the gel, i.e., the larger the swelling of the gel, the smaller the flux.

One should note that the process of the surfactant uptake is governed by two factors. One is the surfactant diffusion driven by the concentration gradient of the surfactant between inside and outside of the gel. The other is the stoichiometric binding process in the charged network. If no binding takes place, Fick's law mainly governs the process of the surfactant uptake. However, if there is strong binding to a given complex, the free surfactant molecules that penetrated through the gel surface should be quickly trapped in the electrostatic potential well of the network, and an extremely low free surfactant concentration is sustained in the gel. Thus, the high concentration gradient of the free surfactant inside and outside of the gel always facilitates the subsequent surfactant diffusion into the charged network to prolong the surfactant uptake.

In this paper, we have studied the effects of ionic strength on the rate of the surfactant uptake. An increased ionic strength affects the diffusion velocity of charged surfactant into the network not only by the screening of the charges but also by inducing a shifting of the binding equilibrium[1] and the size contraction of the gel through which the surfactant penetrates. We also report here a theoretical modeling of surfactant diffusion based on the enhanced velocity of the surfactant uptake due to the binding which explained the diffusion process well.

2. Experimental Section

Materials. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) (Tokyo Kasei Co., Ltd.) was used as received. Its sodium salt (NaAMPS) was obtained by neutralization of AMPS with sodium hydroxide (Junsei Chemical Co., Ltd.). *N*,*N*′-Methylenebisacrylamide (MBAA) (Tokyo Kasei Co., Ltd.) used as a cross-linking agent was recrystallized from ethanol. Potassium persulfite (Tokyo Kasei Co., Ltd.) which was used as a radical initiator was recrystallized from water. *N*-Alkylpyridinium chlorides (C_nPyCl) with $n = 4$, 12, or 16 (Tokyo Kasei Co., Ltd.) were used as received, and C_nPyCl with $n = 8$, 10, or 14 were synthesized according to the literature.[9]

Gel Preparation. A weakly cross-linked poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS gel) and its sodium salt (PNaAMPS gel) were prepared by radical polymerization of a 1.0 mol/L aqueous solution of AMPS (or NaAMPS) monomer in the presence of a calculated amount of *N*,*N*′-methylenebisacrylamide and 0.001 mol/L potassium persulfite. The polymerization was carried out at 60 °C for 12 h under a nitrogen atmosphere in a test tube (10 mm in diameter and 100 mm long). The detailed procedure of the polymerization was described elsewhere.[1]

Measurement. *Surfactant Uptake.* To measure the penetration profiles of the surfactants, a piece of gel ($1 \times 1 \times 0.08$ cm^3, degree of swelling: 133) was immersed in 40 mL of aqueous C_nPyCl ($n = 4$, 8, 10, 12, or 16) solution (4×10^{-4}

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mol/L) at 25 °C. In order to monitor the concentration change by measuring the UV absorption at 259 nm, the solution was circulated by a micropump with a pumping rate of 3×10^{-2} mL/s. The change in length of the gel was followed using a cathetometer at 25 °C with time. Assuming isotropic gel contraction, relative volume change of the gel is defined as the cube of the relative length change. Surfactant flux (mol cm^{-2} s^{-1}) is defined as the uptake rate (mol s^{-1}) per unit surface area of the gel, where the uptake rate is calculated from the slope of the time course of uptake amount and the surface area from the square of the gel length.

To examine the uptake behavior in increased ionic strength, we immersed water-swollen PNaAMPS gels ($1 \times 1 \times 0.08$ cm^3, degree of swelling: 133) in NaCl solutions of various concentrations, which resulted in shrinkage of the gel volume. Then the gel was put into the surfactant solution containing NaCl to follow the time course of the uptake and volume change with the same method as described above.

Concentration Dependence. Dependence of the initial surfactant concentration on the uptake rate was also studied. A piece of PAMPS gel ($1 \times 1 \times 0.4$ cm^3, degree of swelling: 170) was immersed in 5−40 mL of a C_nPyCl ($n = 4$, 12, 14, or 16) solution at a concentration range of 5×10^{-5} to 5×10^{-2} mol/L. When the concentration was higher than 5×10^{-3} mol/L, the solution was repeatedly sampled to measure the absorbance.

3. Results and Discussion

I. Experimental Analysis. Effects of Salt. The effects of increased ionic strength on the surfactant uptake were studied in the presence of 0.01 mol/L NaCl and compared with the results in water. Figure 1a shows time profiles of degree of binding (β) of $C_{10}PyCl$ and $C_{12}PyCl$ in the presence and absence of 0.01 mol/L NaCl. β is defined as the molar ratio of surfactant uptake to the anionic charge on the polymer network. In the absence of NaCl, both $C_{10}PyCl$ and $C_{12}PyCl$ showed almost the same uptake rate in the initial stage and then leveled off (at about $\beta = 0.75$). In NaCl solution, however, these surfactants showed different behaviors. $C_{10}PyCl$ uptake was totally suppressed, while that of $C_{12}PyCl$ reached $\beta = 0.7$ in 3 h, which was slower than that in water. The uptakes of surfactants with shorter alkyl tails, i.e., C_4PyCl and C_8PyCl, were also totally suppressed in NaCl, while they showed almost the same uptake velocity as those of $C_{10}PyCl$ and $C_{12}PyCl$ in water, as reported in the previous paper.[8] Figure 1b shows time profiles of the volume changes of the PNaAMPS gel caused by the surfactant uptake ($C_{10}PyCl$ and $C_{12}PyCl$). Note that the initial equilibrium volumr in NaCl solution were reduced to 60% compared with that in water, due to the suppression of repulsive force in the gel. $C_{10}PyCl$ in NaCl solution induced no shrinkage because of less surfactant uptake, but $C_{12}PyCl$ caused a collapse at 2 h after the experiment started. This is in good contrast to that in water because uptakes of $C_{10}PyCl$ and $C_{12}PyCl$ in water induced the gel collapse at 1 h and was finally reduced to 5% of the initial volume. Here the interesting feature is the relationship between β and V. If V/V_0 is plotted against β (Figure 2), one can notice that the volume collapse started at $\beta \approx 0.5$ and completed at $\beta \approx 0.7$, regardless of the size of the alkyl chain of the surfactants ($C_{10}PyCl$, $C_{12}PyCl$, and $C_{16}PyCl$) and regardless of the salt. Since the larger the hydrophobic tails of the surfactant, the larger their binding constants as reported before,[1] the β values at which the gel collapse occurred should be expected to change as a function of the tail size. We have previously reported[3] that the surfactants form a supramolecular

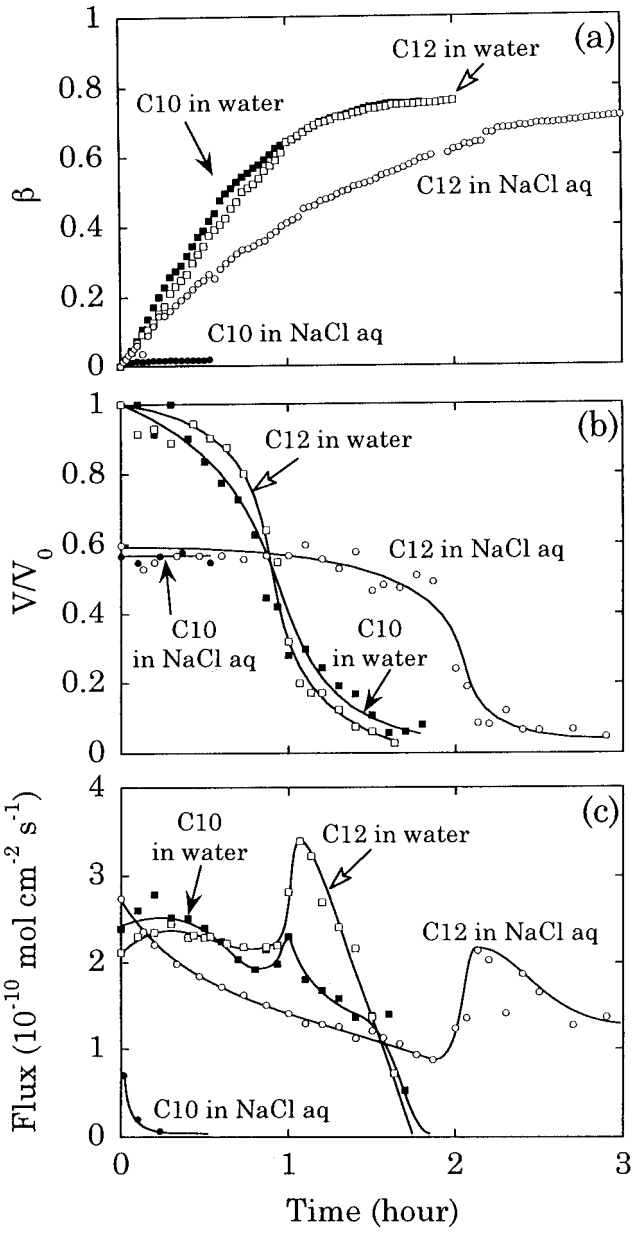

Figure 1. Time profiles of (a) the degree of binding (β) of the surfactants ($C_{10}PyCl$ and $C_{12}PyCl$) with PNaAMPS gel, (b) the relative volume change of the PNaAMPS gel by uptake of surfactants, and (c) surfactant flux: (■) $C_{10}PyCl$ in water; (□) $C_{12}PyCl$ in water; (●) $C_{10}PyCl$ in 0.01 M NaCl; (○) $C_{12}PyCl$ in 0.01 M NaCl. Initial gel size V_0 was $1 \times 1 \times 0.08$ cm^3, initial surfactant concentration was 4×10^{-4} mol/L, total volume of the system was 40 mL, and temperature was 25 °C.

ordered structure in the PAMPS gel. This ordered structure could be formed only when β exceeds 0.6. Consequently, the volume collapse of the given system might be associated with the formation of the supramolecular structure in the charged network. But this should be left for further study.

Figure 1c shows time profiles of surfactant flux calculated using the data in parts a and b of Figure 1. $C_{12}PyCl$ showed an enhanced flux in water after the collapse of the gel because of the enhanced electrostatic interaction as reported previously.[8] Similar to this case, the flux of $C_{12}PyCl$ in NaCl showed a sudden increase at the moment when the gel collapsed, although the electrostatic interaction is suppressed at increased ionic strength.

As described above, the kinetic nature of the surfactant uptake might be governed by the diffusion process and/or binding

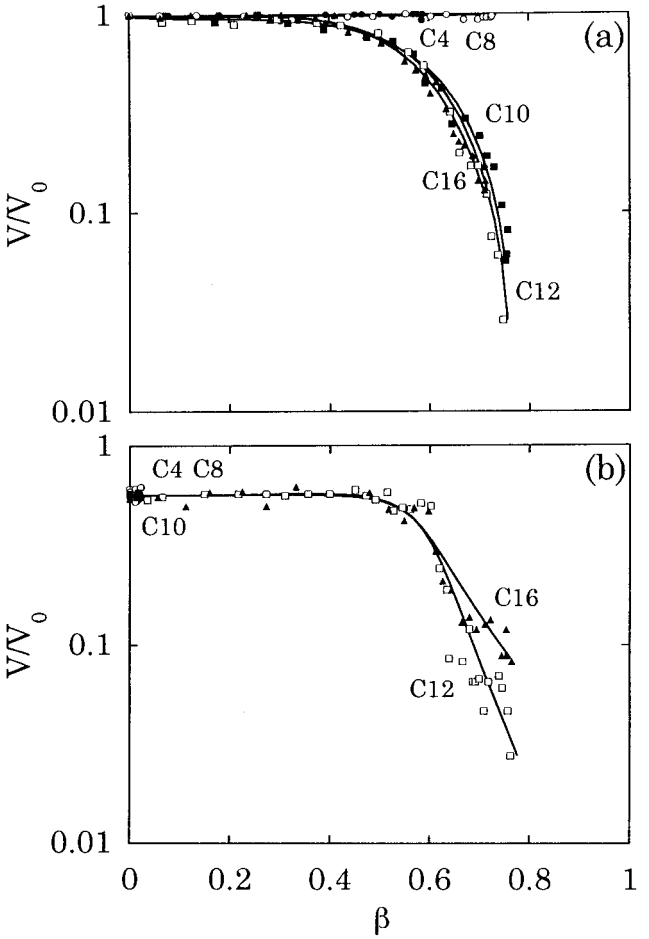

Figure 2. Relative volume changes of the PNaAMPS gel as a function of degree of binding (β) (a) in water and (b) in 0.01 M NaCl: (●) C_4PyCl; (○) C_8PyCl; (■) C_{10}PyCl; (□) C_{12}PyCl; (▲) C_{16}PyCl. Initial gel size V_0 was $1 \times 1 \times 0.08$ cm^3, initial surfactant concentration was 4×10^{-4} mol/L, total volume of the system was 40 mL, and temperature was 25 °C.

equilibrium. Figure 3 shows the binding isotherms of the gel with C_{10}PyCl and C_{12}PyCl. β and C_s are the equilibrated amount of surfactant uptake and surfactant concentration of the solution, respectively. The figure indicates that both surfactants started binding in water below 1×10^{-5} mol/L and continued through a wide concentration range, while in NaCl solution C_{12}-PyCl binding was practically prevented at a concentration lower than 10^{-4} mol/L due to decreased electrostatic interaction. C_{10}-PyCl started binding at 4×10^{-4} mol/L. The presence of NaCl, instead, resulted in an alkyl size dependence of the concentration at which the binding started and an increased steepness of the curves, i.e., increased cooperativity of the binding due to hydrophobic interaction.[1]

The different uptake behaviors of C_{10}PyCl and C_{12}PyCl in the presence and absence of NaCl as shown in Figure 1 correspond well with the difference in binding equilibrium presented in Figure 3. The shifting by NaCl addition was so substantial that no uptake occurred for C_{10}PyCl under the given experimental conditions as shown in Figure 1a. The gel collapse resulted in an increased network density which favored hydrophobic interaction though the electrostatic interaction was suppressed in the presence of the salt. Thus, C_{12}PyCl flux was enhanced in NaCl solution as shown in Figure 1c.

Figure 4 shows the flux of surfactant uptake as a function of the number of carbon atoms of the alkyl chain of the surfactant in various ionic strengths. One can clearly see that the fluxes

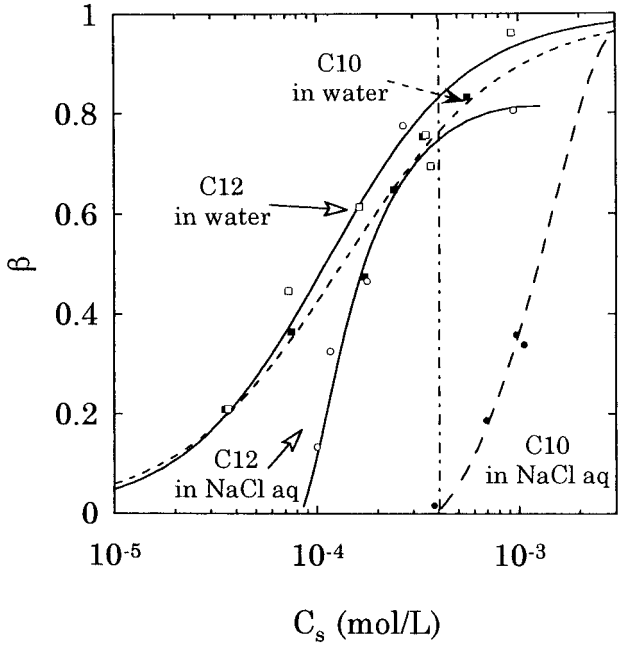

Figure 3. Binding isotherms of surfactants (C_{10}PyCl and C_{12}PyCl) with PNaAMPS gel: (■) C_{10}PyCl in water; (□) C_{12}PyCl in water; (●) C_{10}PyCl in 0.01 M NaCl; (○) C_{12}PyCl in 0.01 M NaCl. Initial gel size V_0 was $1 \times 1 \times 0.08$ cm^3, total volume of the system was 40 mL, equilibration time was 1 day, and temperature was 25 °C.

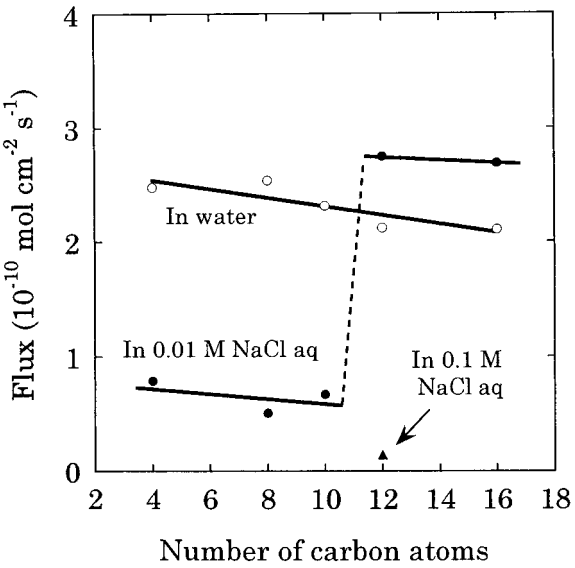

Figure 4. Changes in surfactant flux as a function of alkyl size of surfactant: (○) in water; (●) in 0.01 M NaCl; (▲) in 0.1 M NaCl. The flux data were averages over the first 8 min of the experiment. Initial gel size was $1 \times 1 \times 0.08$ cm^3, initial surfactant concentration was 4×10^{-4} mol/L, total volume of the system was 40 mL, and temperature was 25 °C.

in the presence of NaCl are classified by two regimes: a low flux regime observed for the surfactants with shorter alkyl tails and a high flux regime for the surfactants with longer alkyl tails. Fluxes in water always showed a high flux regime for every surfactant. The increased fluxes of C_{12}PyCl and C_{16}PyCl in 0.01 mol/L NaCl compared with those in aqueous solution suggest the increased cooperative hydrophobic binding despite the shielded electrostatic interactions.

Effects of Surfactant Concentration. Another interesting subject to be studied is whether the surfactant diffuses in a monomeric form or as an aggregate or a micelle. Since surfactants form micelles above critical micelle concentration

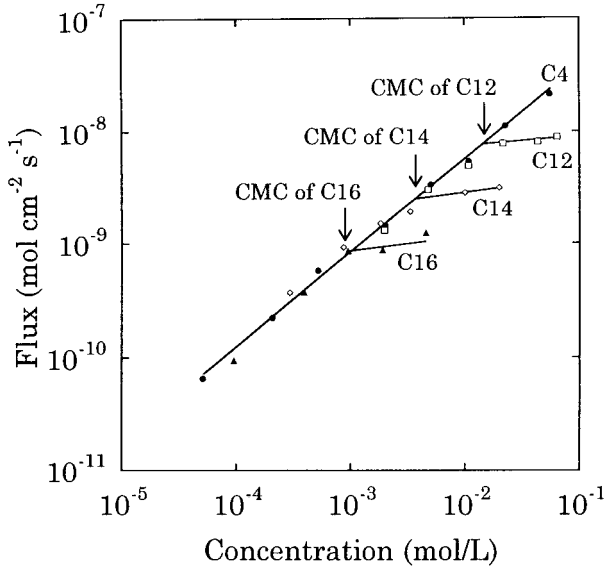

Figure 5. Dependences of the flux on the surfactant concentration: (●) C_4PyCl; (□) C_{12}PyCl (cmc, 1.5×10^{-2} mol/L); (◇) C_{14}PyCl (cmc, 3.6×10^{-3} mol/L); (▲) C_{16}PyCl (cmc, 9.0×10^{-4} mol/L). Initial gel size V_0 was $10 \times 10 \times 4$ mm^3 and temperature was 25 °C.

(cmc), this might be a critical factor for the diffusion because of their increased size as well as their charge states. Thus, we have studied the effect of micelle formation on the rate of surfactant uptake by changing the surfactant concentration below and above the cmc. The results are shown in Figure 5. As shown in Figure 5, the logarithmic plot of concentration vs flux gave straight lines with slopes of 0.8 regardless of the surfactant size. However, when the concentration exceeded each cmc[10] (C_{12}PyCl: 1.5×10^{-2} mol/L, C_{14}PyCl: 3.6×10^{-3} mol/L and C_{16}PyCl: 9.0×10^{-4} mol/L), only a negligibly small increase in the flux was observed. On the other hand, the flux of C_4PyCl which does not form micelle structure increased monotonously in the concentration range studied. These results demonstrate that a micelle which forms in the solution is not able to bind with the charged network in that form and only surfactant molecules in a monomeric state are able to penetrate through the network to give binding. Because micelles have high surface charge density, they attract counterions; thus, diffusivity of micelles is much smaller than that of monomeric surfactants.[11] Therefore, the surfactant uptake is mostly due to the monomeric surfactants. Since there exists an equilibrium between the micellar and the monomeric states, the micelles behave as a reserevoir of the monomers, and this reservoir supplies the monomeric surfactant according to the decrease of the monomer concentration due to uptake.

II. Theoretical Analysis. The experimental results described in the previous section suggest that the kinetics of surfactant uptake can well be expressed in terms of diffusion and binding processes. Immobilization of one substance due to adsorption or to some other chemical reaction by the medium through which it diffuses has been theoretically investigated by some researchers. Crank has presented several examples of solutions to the partial differential equation describing simultaneous diffusion and chemical reaction.[12] We followed the modeling of Vieth et al.[13] used for gas sorption onto glassy polymers. Grimshaw et al. has studied the kinetics of ion diffusion concomitant with the volume change of poly(methacrylic acid) gel in terms of proton binding onto the carboxylates on the gel.[14] Since the diffusion process was extremely complicated as they showed, for the simplification of equations, the following assumptions have been made in the present case:

(1) The surfactant binding with the gel proceeds very rapidly compared with the diffusion, so that a local equilibrium always exists between the free and bound surfactant anywhere in the gel.

(2) The diffusion is one-dimensional and the diffusion coefficient D is a constant which does not vary with the concentration or time.

(3) The volume change and ionic properties of the surfactant including counter ions are ignored.

Volume change accompanied by diffusion is important because it must strongly affect the diffusion. In this case we did not take into account the volume change because boundary conditions and network density change with time, which makes the diffusion equation extremely difficult to solve. However, this assumption is valid for the diffusion of C_4PyCl and C_8PyCl since they do not induce any volume change.[8] Ionic properties of the surfactant might affect the surfactant uptake, since it is essentially an ion-exchange reaction. However, in this paper we left these effects for further study.

From the continuity condition we have an equation as follows:

$$D\frac{\partial^2 C_f}{\partial x^2} = \frac{\partial C_f}{\partial t} + \frac{\partial C_b}{\partial t} \tag{1}$$

where C_f is the free surfactant concentration in the gel and C_b is that bound to the polymer chain. If there is no binding, we have $C_b = 0$ and eq 1 reduces to Fick's second law of diffusion.

Assuming the local equilibrium C_b is expressed as a function of C_f via binding isotherm. We have proposed a theoretical binding isotherm in which C_b is described as a complicated function of electrostatic and hydrophobic interactions and C_f.[15] In order to avoid introducing the complicated function to eq 1, we use the following equation which well describes the binding phenomenonogically

$$C_b = C_{p^0}\frac{C_f^{\sqrt{u}}}{C_f^{\sqrt{u}} + C_{f^0}^{\sqrt{u}}} \tag{2}$$

where C_{p^0} is the initial concentration of anionic charge on the polymer and u the cooperative parameter of the binding which has been defined in the previous papers.[1,15] C_{f^0} is the free surfactant concentration at half of the saturated binding. The difference in affinities such as hydrophobic interaction is expressed by the difference in u and C_{f^0}. When $u = 1$, the curve gives Langmuir's isotherm. Thus, one can say eq 2 is an expanded Langmuir's isotherm which can express the cooperative binding. Note that we do not consider the driving forces of the binding, or only the relationship between the free and bound surfactants is considered for the simplification. Using eq 1 and eq 2 to eliminate C_b, we have

$$D\frac{\partial^2 C_f}{\partial x^2} = \left[1 + C_{p^0}\frac{\sqrt{u}\, C_{f^0}^{\sqrt{u}}\, C_f^{\sqrt{u}-1}}{(C_f^{\sqrt{u}} + C_{f^0}^{\sqrt{u}})^2}\right]\frac{\partial C_f}{\partial t} \tag{3}$$

The following coordinates were used in order to apply this equation to the experimental results: the polymer gel of thickness $2L$ is assumed to occupy the space $-L \le x \le L$. The boundary conditions on eq 3 are

$$C_f(x,0) = 0 \qquad (-L < x < L) \tag{4}$$

$$C_f(\pm L,t) = C_{s^0} - \frac{LS}{V}\int_{-L}^{L}\left(\frac{C_f + C_b}{L}\right) dx \qquad (t \geq 0) \quad (5)$$

$$\frac{\partial C_f(0,t)}{\partial x} = 0 \qquad (t \geq 0) \quad (6)$$

where S is the surface area of the gel and V is the total volume of the system. Equation 5 is associated with the concentration of the surfactant outside the gel which decreases from the initial value C_{s^0} with time due to the uptake by the gel. Equation 6 is associated with the symmetry condition at $x = 0$. For the dimensionless equation, five variable substitutions were performed:

$$T = \frac{D}{L^2}t \quad \text{and} \quad X = \frac{x}{L}$$

$$C_n = \frac{C_f}{C_{p^0}}, \quad C_{n^0} = \frac{C_{f^0}}{C_{p^0}}, \quad \text{and} \quad C_{sp} = \frac{C_{s^0}}{C_{p^0}}$$

The dimensionless final equation and the boundary conditions are summarized below:

$$\frac{\partial^2 C_n}{\partial X^2} = \left[1 + \frac{\sqrt{u}\, C_{n^0}{}^{\sqrt{u}}\, C_n{}^{\sqrt{u}-1}}{(C_n{}^{\sqrt{u}} + C_{n^0}{}^{\sqrt{u}})^2}\right]\frac{\partial C_n}{\partial T} \quad (7)$$

$$C_n(X,0) = 0 \qquad (-1 < X < 1) \quad (8)$$

$$C_n(\pm 1,T) = C_{sp} - \frac{LS}{V}\int_{-1}^{1}\left(C_n + \frac{C_b}{C_{p^0}}\right) dX \qquad (T \geq 0) \quad (9)$$

$$\frac{\partial C_n(0,T)}{\partial X} = 0 \qquad (T \geq 0) \quad (10)$$

By the following summation we have β at dimensionless time T.

$$\beta(T) = \int_{-1}^{1}\left(C_n + \frac{C_b}{C_{p^0}}\right) dX = \int_{-1}^{1}\left(C_n + \frac{C_n{}^{\sqrt{u}}}{C_n{}^{\sqrt{u}} + C_{n0}{}^{\sqrt{u}}}\right) dX \quad (11)$$

Many attempts to solve eq 7 have been made, but no successful method has been found because of the difficulties which arise from the nonlinear form and the transient boundary condition. In this study, we have used the same numerical method to obtain the solution as Vieth et al. developed.[13] Equation 7 with boundary conditions was programmed to be solved numerically on a digital computer.

The parameters for the binding curves are determined experimentally by fitting eq 2 with the experimental data. The binding data of the surfactants (C_4PyCl and C_{12}PyCl) with the PNaAMPS gel were plotted in Figure 6. The solid lines are given by eq 2 using the following parameters:

	C_{n^0} (mol/L)	u	C_{f^0} (mol/L)
C_4PyCl	3.3×10^{-2}	0.482	2.0×10^{-4}
C_{12}PyCl	3.3×10^{-2}	1.51	1.1×10^{-4}

Other parameters determined by the experimental condition of the system are as follows: $C_{s^0} = 4.0 \times 10^{-4}$ mol/L, $LS/V = 2.0 \times 10^{-3}$.

By numerical calculations of eq 7 with the above determined parameters, we obtain dimensionless free surfactant concentrations C_f as a function of dimensionless time T and distance X. The free surfactant concentration calculated for C_4PyCl uptake is plotted against the distance X at various times T (Figure 7a). To see the effects of the binding process incorporated in the

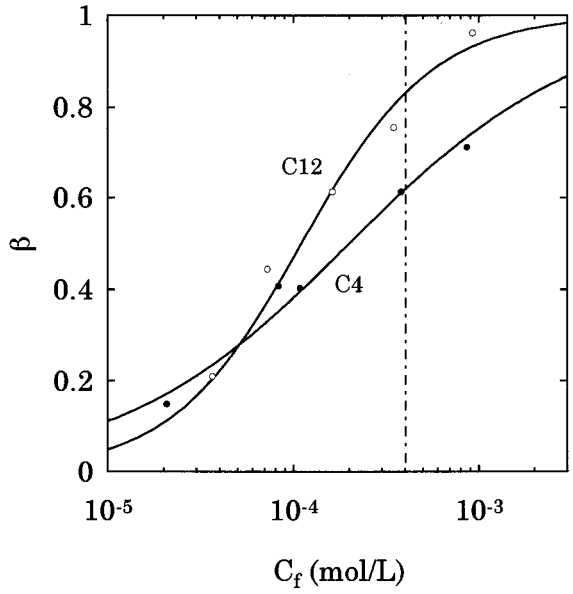

Figure 6. Binding isotherms of surfactants (C_4PyCl and C_{12}PyCl) with PNaAMPS gel: solid lines, theoretical curves defined by eq 2; (●) C_4PyCl; (○) C_{12}PyCl. Initial gel volume V_0 was $1 \times 1 \times 0.08$ cm^3, total volume of the system was 40 mL, equilibrating time was 1 day, and temperature was 25 °C.

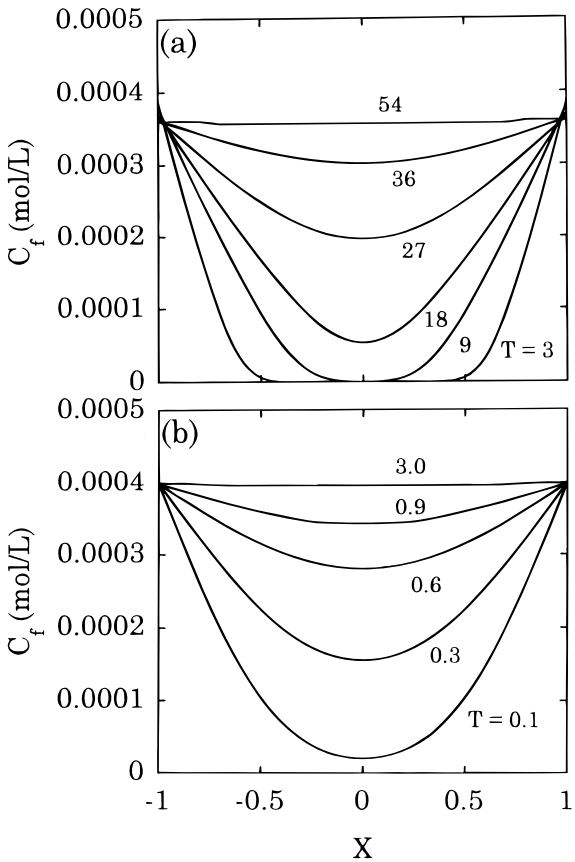

Figure 7. Free surfactant distribution in the gel at various dimensionless times T obtained by numerical calculation: (a) with binding, (b) without binding. Curves in (a) were calculated using parameters determined by the experimental binding isotherm of C_4PyCl shown in Figure 6.

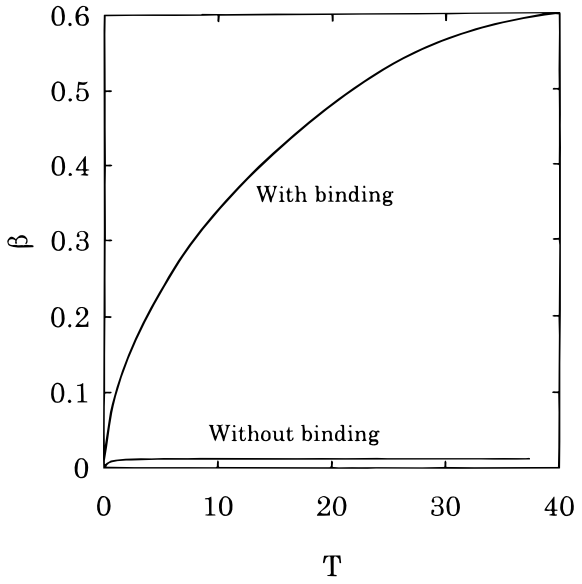

Figure 8. Time profiles of surfactant uptake with and without binding.

equation, a calculation which excluded the binding is also shown in Figure 7(b). The surfactant penetrates from the surfaces to the center of the gel with time, and the system reaches equilibrium at $T = 3$ if the binding process is excluded (Figure 7b). On the other hand, when the binding process is taken into account, the equilibration time is longer than 54 (in Figure 7a). At $T = 3$ the surfactant does not diffuse deeply enough into the gel and the concentration gradient is still kept high. Thus, introduction of the binding process keeps the free surfactant concentration low through a prolonged period of time.

Time profiles of β are shown in Figure 8. The calculated curve with the binding process reaches a value of $\beta = 0.6$, while it levels off at $\beta = 0.01$ if the binding is not taken into account. These results coincide well with those observed for C_4PyCl in water and C_{10}PyCl in NaCl solution as shown in Figure 1. Thus, it is theoretically confirmed that the surfactant molecules diffuse into the gel by the concentration gradient and then bind with the network, keeping the free surfactant concentration low.

Time profiles of β of calculated solutions (solid lines) are compared with experimental data (dots) for C_4PyCl and C_{12}PyCl, and the results are shown in Figure 9. T is substituted into t (h) using various diffusion coefficients D cm^2 s^{-1} and $L = 0.04$ cm, and increasing D results in fast uptake. The curve for C_4PyCl, which induced no shrinkage of the gel, was calculated using $D = 10 \times 10^{-6}$ cm^2 s^{-1}. As shown in the figure both theoretical and experimental curves fit well. The value of the D is quite reasonable if we compare it with the diffusion coefficient of C_4PyCl in water, which is 12.6×10^{-6} cm^2 s^{-1}. Thus, the essential feature of the theory is quite reasonable. However, the calculated curves for C_{12}PyCl, which brought about a drastic gel collapse, did not satisfactorily fit, presumably because changes in the gel size, diffusion coefficient, or binding affinity were not taken into account in this study. As the experimental results suggest, the uptake of surfactant is linear in time in contrast to the theoretical curves for both C_4PyCl and C_{12}PyCl. This discrepancy may be due to a boundary layer effect which should become less important with increasing time.

We calculated that the bound surfactant did not distribute uniformly and was concentrated close to the boundary (Figure 10). We also observed that an increase in the cooperativity parameter u resulted in high nonuniformity. Thus, we can

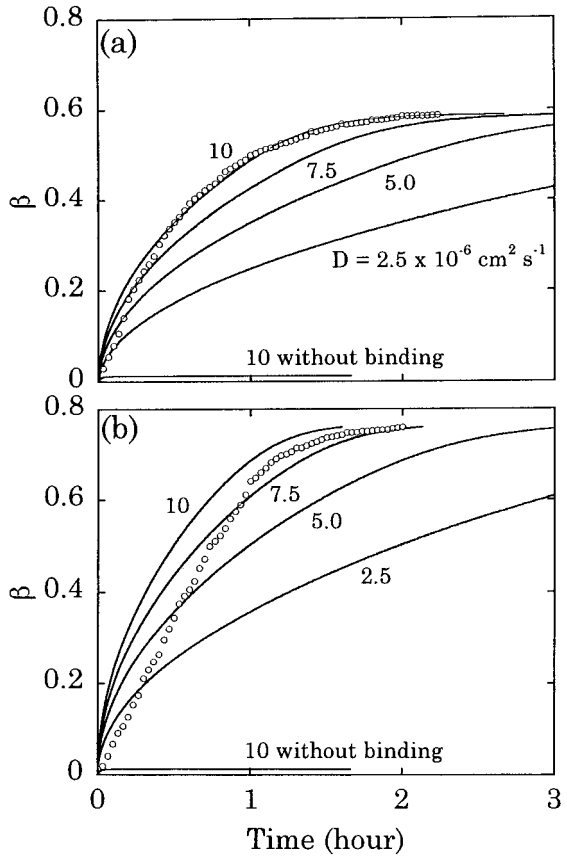

Figure 9. Theoretical (solid lines) and experimental results (dots) of surfactant uptake: (a) C_4PyCl; (b) C_{12}PyCl. Numbers in the figure denote diffusion coefficient D (10^{-6} cm^2 s^{-1}).

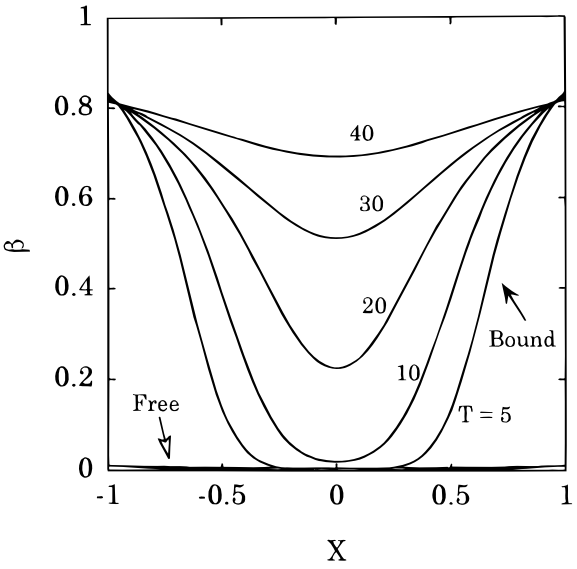

Figure 10. Free and bound surfactant distribution in the gel at various dimensionless times T. Curves were calculated using parameters determined by the experimental binding isotherm of C_{12}PyCl shown in Figure 6.

predict that if the bound surfactant induces the gel collapse, a dense outer layer which progresses from the surface toward the center of the gel will be formed as Kabanov et al. experimentally observed a in poly(sodium acrylate) gel−quaternary ammonium salt system.[7] In fact, Kabanov et al. made experiments in the presence of salt, and the surfactant binding was highly cooperative.

Conclusion

The driving force of surfactant diffusion into the gel is the concentration gradient of the surfactant. The binding of surfactant with the polymer network sustains a high concentration gradient, which facilitates the subsequent surfactant diffusion. Mathematical modeling of the surfactant diffusion process accompanied by the binding onto the polymer network was developed which explained the fact that the binding enhances the velocity of surfactant uptake.

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