Effects of Counterions and Co-Ions on the Surfactant Binding Process in the Charged Polymer Network

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Received: February 1, 1999; In Final Form: May 1, 1999

Kinetic studies of cationic surfactant uptake in an anionic polymer network have been performed, varying the species of co-ions of the surfactant and counterions of the charged network. It was found that the rate of surfactant uptake is distinctly dependent on both the counterions and co-ions which could be explained in terms of the ion pair diffusion mechanism associated with their mobilities in the network. A simple linear relation between the surfactant flux and the harmonic mean of the molar mobilities of the surfactant ion, its co-ion, and the network counterion has been established experimentally.

Introduction

Thermodynamic studies of polymer−surfactant and gel−surfactant binding have been performed, and the contributions of both electrostatic and hydrophobic interactions to cooperative binding have been emphasized.[1−10] The role of the ionic network on surfactant binding has been studied in comparison with linear polyelectrolytes, and it has been found that a polymer network exhibits much less cooperativity than the corresponding linear polymer as a result of osmotic pressure.[11−13] The composition and chemical structure of surfactant−polymer aggregates have been studied in various systems. Many of them form precipitates at low surfactant/polymer mixing ratio, while viscous solutions or gels are formed at high mixing ratio because of nonstoichiometric binding of the surfactant.[5,14] The supramolecular structures of the obtained aggregates have also been studied. The aggregates feature ordered micelle-like structures, whose spacing increases with increase in the surfactant alkyl chain length.[15−17]

Although Grimshaw et al.[18] both experimentally and theoretically studied the swelling kinetics of polymethacylic acid gels and the diffusion and binding process of protons in buffer solution, there have been a few kinetic studies of surfactant binding. Kabanov et al.[19] have shown that the transport of the cationic surfactant dodecylpyridinium chloride in poly(acrylic acid) gel is performed by the individual surfactant diffusion and not by the diffusion of micelles. Philippova et al.[20] have measured the velocity of diffusion of sodium dodecyl sulfonate into poly(diallyldimethylammonium bromide) gel without taking account of any specific interactions between the surfactant and polymer network.

In the previous papers,[21,22] we have reported a systematic kinetic study on the uptake of cationic surfactants *N*-alkylpyridinium chloride (C*n*PyCl; $n = 4, 8, 10, 12, 16$) into weakly cross-linked poly(sodium 2-acrylamido-2-methylpropane sulfonate) (PNaAMPS) gels and experimentally demonstrated that the process of the surfactant uptake can be associated with two processes: surfactant diffusion driven by the concentration gradient of the surfactant between inside and outside of the gel and stoichiometric binding in the charged network. It was found that the surfactant uptake is largely dominated by the binding process, since the free surfactant molecules penetrating through the gel surface are quickly trapped in the electrostatic potential well of the network,[23] thereby sustaining an extremely low free surfactant concentration in the gel through the whole process. Thus, a high concentration gradient of the free surfactant inside and outside of the gel is always maintained which facilitates the subsequent surfactant diffusion into the charged network. This binding accelerated diffusion process has also been confirmed theoretically.[22]

Though the electrostatic interaction between the ionic surfactant and the charged network has been emphasized owing to the fully ionized nature of the species, the effects and roles of the co-ions of the surfactants and the counterions of the network on the rate of surfactant uptake cannot simply be excluded. The surfactant diffusion process might be affected by these mobile ions because the surfactant binding is essentially an ion-exchange reaction preceded by the diffusion of these mobile ions which cannot diffuse independently because of a requirement of electroneutrality at the macroscopic level. Despite these circumstances, the authors are unaware of any kinetic study of surfactant diffusion and binding which takes into account the effects of co-ion and counterion.

In this paper, we experimentally demonstrate the effects of the co-ions and counterions on the kinetics of surfactant uptake in the charged network. We have found that the rate of the surfactant uptake into the gel is distinctly dependent on the mobilities of the co-ions of the surfactant and counterions of the charged network. The surfactant flux was well explained in terms of a mutual diffusion process of ions through the charged network which is dependent on the harmonic mean of the mobilities of these mobile ions.

Experimental Section

Materials. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) (Tokyo Kasei Co., Ltd.) was used as received. Its alkali metal salts (MAMPS: $M = Li^+$, Na^+, or K^+) were obtained by neutralization of 0.1 M AMPS ethanol solution with 0.03 M ethanol solution of hydroxides of the corresponding metals (Junsei Chemical Co., Ltd.). Then ethanol was removed by evaporation and precipitated MAMPS powder was dried in vacuo. *N*,*N*′-Methylenebisacrylamide (MBAA) (Tokyo Kasei Co., Ltd.) used as a cross-linking agent was recrystallized from ethanol. Potassium persulfate (Tokyo Kasei Co., Ltd.) which was used as a radical initiator was recrystallized from water.

10.1021/jp990358l CCC: $18.00
Published on Web 07/13/1999

N-Dodecylpyridinium chloride (C12PyCl) (Tokyo Kasei Co., Ltd.) was used as received. *N*-Dodecylpyridinium bromide (C12PyBr) was synthesized according to the literature.[24] Surfactants with various co-ions *N*-dodecylpyridinium iodide (C12PyI), *N*-dodecylpyridinium acetate (C12PyAce), *N*-dodecylpyridinium salicylate (C12PySal) were obtained by ion exchange reaction of C12PyCl with KI, potassium acetate, and sodium salicylate, respectively, in acetone or ethanol. C12PyCl was added in saturated KI (or potassium acetate or sodium salicylate) acetone (or ethanol) solution, and chloride salts of alkali metal were precipitated because of their very low solubility in organic solvent. The solvent was evaporated to obtain C12PyI (or C12PyAce or C12PySal).

Gel Preparation. Weakly cross-linked poly(2−acrylamido−2−methylpropanesulfonate) with various counterions (H^+, Li^+, Na^+, or K^+) (PMAMPS gels) was prepared by radical polymerization of a 1.0 mol/L aqueous solution of MAMPS in the presence of calculated amounts of MBAA and 0.001 mol/L potassium persulfate. 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.[6]

Measurement. *Surfactant Uptake.* In order to establish the time profiles of surfactant uptake, a piece of PMAMPS gel (M= H^+, Li^+, Na^+, or K^+, $1 \times 1 \times 0.4$ cm^3) was immersed in 40 mL aqueous C12PyX (X = Cl^-, Br^-, I^-, Ace^-, or Sal^-) solution (1×10^{-3} mol/L) at 25 °C, and the change in surfactant concentration was monitored by UV absorption at 259 nm. The $C12Py^+$ uptake was calculated from the assumption that the uptake amount corresponded to the concentration decrease in the solution phase. The solution was circulated by pumping at 3×10^{-2} mL/sec. The concentration change of salicylate ion was also followed by the same method at 296 nm. Surfactant flux (mol cm^{-2} sec^{-1}) at the initial stage of binding was defined as the uptake rate (mol sec^{-1}) per unit surface area of the gel, neglecting the change in the gel volume.

Ion Mobilities. In order to measure the mobility of $C12Py^+$ and Sal^-, equivalent conductance of the ions λ (S cm^2 mol^{-1}) was measured according to the literature.[25] Mobilities of other ions were referenced from the literature.[26] The molar mobility ω (mol cm^2 J^{-1} s^{-1}) of the ions was calculated from the following equation:

$$\omega = \frac{\lambda}{F^2}$$

where F is the Faraday constant.[27]

Results and Discussion

The effect of co-ions on the rate of surfactant uptake by PNaAMPS gel was studied using $C12Py^+$ with various co-ions (Cl^-, Br^-, I^-, Ace^-, or Sal^-). As shown in Figure 1, the rate of surfactant uptake varies with the co-ion species. The surfactants with inorganic co-ions, Cl^-, Br^-, or I^-, diffused into the gel faster than those with organic ions such as Ace^- or Sal^-. Surfactant uptake was completed after about 1 h, and the gel volume change was observed simultaneously. Different species of co-ion did not affect the behavior of the collapse because the gel volume contraction was induced mainly by hydrophobic interaction of the surfactant.[22] The effects of the gel volume contraction on the surfactant uptake were discussed previously in detail.[21,22] The surfactant concentration change in the external solution and size change of the gel should be influential to the total process of the surfactant uptake; however, in the beginning

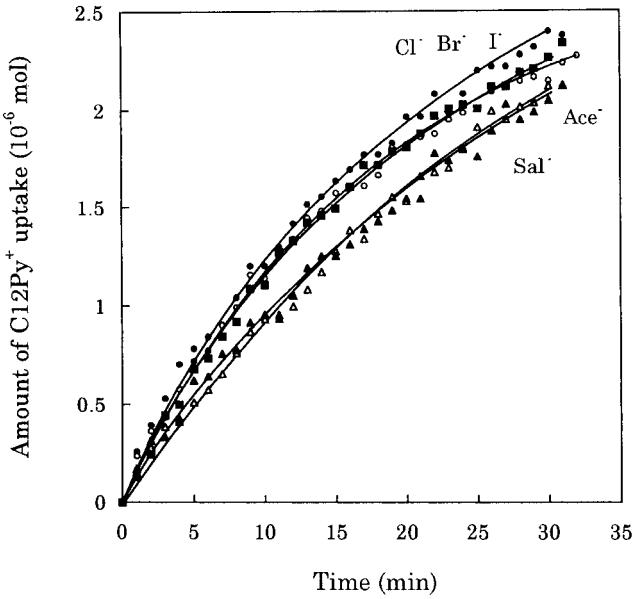

Figure 1. Time profiles of the amount of $C12Py^+$ uptake with various co-ions in PNaAMPS gel. (●)Cl^-; (○)Br^-; (■)I^-; (△)Ace^-; (▲)Sal^-. Initial gel size V_0: $1 \times 1 \times 0.4$ cm^3; degree of swelling of the gel: 119; initial surfactant concentration: 1×10^{-3} mol/L; total volume of the system: 40 mL; temperature: 25 °C.

of the process, the concentration change of the solution phase and the volume change of the gel were negligibly small (concentration decrease was less than 8% for the initial 10 min). Therefore, the values of the initial 10 min were taken to discuss the effect of species of the co-ion on the surfactant uptake rate.

In the previous works, [21,22] reproducibility of the results was intensively studied with Cl^- as a co-ion, changing the concentration of both the surfactant and the network or alkyl chain length of the surfactant, and experimental error was found to be less than 11%. In the present work we have followed the same methodology, therefore we think the obtained results were reasonably reproducible.

Figure 2 shows the initial rate of the surfactant uptake calculated as the average over the first 10 min. The amount of $C12Py^+$ uptake in this region was almost proportional to time as shown in Figure 1. One can see that the rates of $C12Py^+$ uptake with inorganic co-ions were almost the same, while those of organic co-ions were lower. As Figure 2 shows, $C12Py^+$ flux for every co-ion increased with decrease in the degree of swelling (q) of the gel. This is apparently due to the enhanced electrostatic interaction between the surfactant cation and the anionic gels as described in the preceding paper.[21]

As we previously reported,[22] the surfactant uptake is described by two processes; one is the diffusion process, which is driven by the surfactant concentration gradient, and the other is the binding process, which is due to the salt-forming ability between the surfactant and the network. Supposing the counterions of the ionic network are fully ionized and the binding affinity of the surfactant is not strongly influenced by the species of co-ions, the difference in the rate of uptake observed here should be attributed not to the binding process but to the diffusion process. In other words, the rate of the surfactant uptake can be associated with the mobilities of the surfactant ion as well as its co-ions. If the molar mobility ω of the co-ions in water (which is almost the same as that in hydrogel of low polymer concentration) is plotted against species of co-ion, Ace^- and Sal^- ions showed lower mobilities than those of the halides as shown in Figure 2, which well coincides with the experimental results of the surfactant flux. This result indicates that the

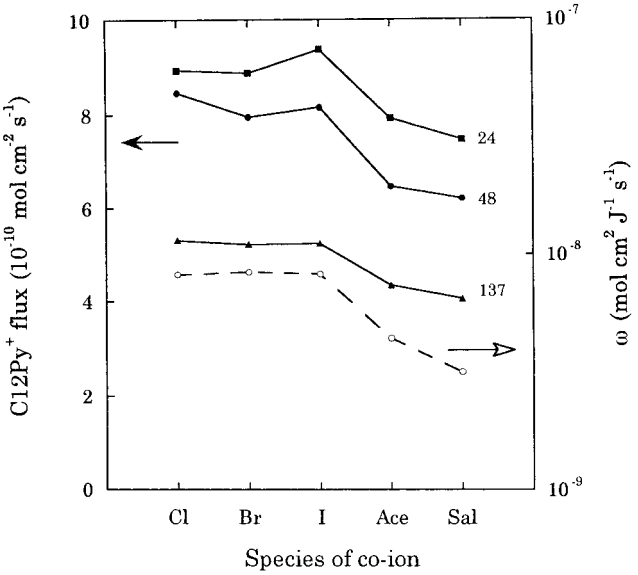

Figure 2. Flux of $C12Py^+$ with various co-ions into PNaAMPS gel with various degrees of swelling (left ordinate) and molar mobility of the co-ion (right ordinate). Numbers in the figure denote the degree of swelling. Initial gel size V_0: $1 \times 1 \times 0.4$ cm^3; total volume of the system: 40 mL; temperature: 25 °C.

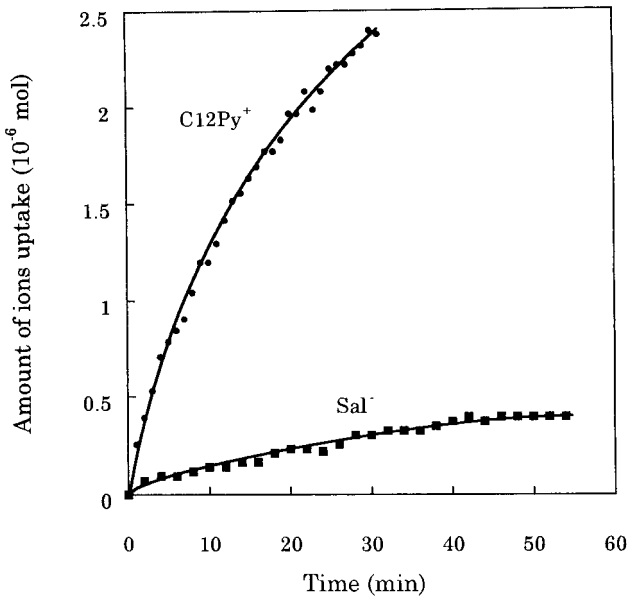

Figure 3. Time profiles of the amounts of $C12Py^+$ and Sal^- uptake by PNaAMPS gel. (●) $C12Py^+$; (■) Sal^-. Initial gel size V_0: $1 \times 1 \times 0.4$ cm^3; degree of swelling of the gel: 119; initial surfactant concentration: 1×10^{-3} mol/L; total volume of the system: 40 mL; temperature: 25 °C.

surfactant ion diffuses into the charged network accompanied by the corresponding co-ion and then binds with the oppositely charged network.

We have further monitored the time profile of the amount of co-ion uptake in PNaAMPS gel. For this experiment, C12PySal was used and change in Sal^- ion concentration can be easily monitored by UV adsorption change. As shown in Figure 3, the amount of $C12Py^+$ uptake in the gel attained 2×10^{-6} mol in the initial 30 min, while that of the corresponding co-ion (Sal^-) was very low (0.4×10^{-6} mol). Since the co-ion concentrations inside and outside the gel were found to be the same after reaching the equilibrium, one can speculate that $C12Py^+$ diffuses into the charged network accompanied by its co-ions. $C12Py^+$ binds with the charged network, thus eliminating the electrostatic attractions not only between the surfactant and its co-ions but also between the charged network, and its counterions allow the co-ion and the counterion to form a new ion pair and diffuse out of the gel according to their concentration gradient.

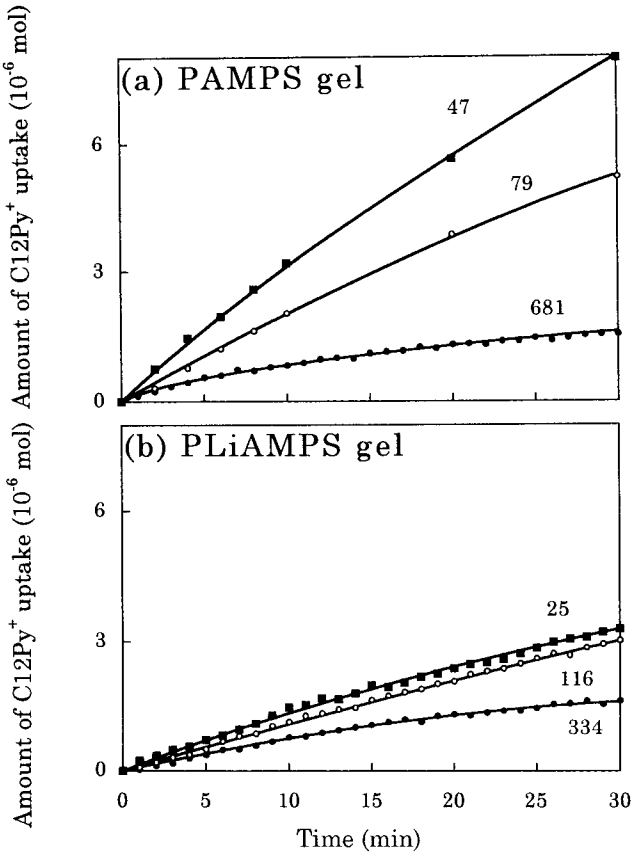

Figure 4. Time profiles of the amount of $C12Py^+$ uptake by PAMPS gel (a) and PLiAMPS gel (b) of various degrees of swelling. Numbers in the figure denote the degree of swelling. Initial gel size V_0: $1 \times 1 \times 0.4$ cm^3; initial surfactant concentration: 1×10^{-3} mol/L; total volume of the system: 40 mL; temperature: 25 °C.

Thus, the mobility of the gel counterion becomes an important factor to determine the velocity of $C12Py^+$ uptake, since the concentration gradient of the newly formed co-ion−counterion pair has an effect on the surfactant−co-ion pair diffusion. Thus, the rate of $C12Py^+$ uptake was studied using the gels with various counterions. In the course of this study we have found that the gels exhibit slightly different degrees of swelling, q, when the counterions are varied although they have the same degree of chemical cross-linking, presumably due to the different hydration power of the counterions. Therefore, we studied the effects of counterions on the kinetics of $C12Py^+$ uptake, systematically changing the degrees of swelling of the gel. Figure 4 shows an example of time profiles of $C12Py^+$ uptake when PAMPS gels (a) or PLiAMPS gels (b) with various degrees of swelling are used. Here again,[21] the lower the degree of swelling, the faster $C12Py^+$ uptake as a result of the enhanced charge density of the gel. Similar kinetic curves were obtained for Na^+ and K^+ salts of the anionic gels, and the average fluxes for the first 10 min were calculated and plotted as a function of the gel volume fraction ϕ ($\approx 1/q$) (Figure 5). One can clearly see that the rate of $C12Py^+$ uptake increases with the increase of the volume fraction ϕ, the rate of $C12Py^+$ uptake varied with the species of counterions, and the fastest uptake was observed for H^+, followed by K^+, Na^+, and Li^+.

If the flux at $\phi = 8.4 \times 10^{-3}$ ($q = 119$) is calculated from

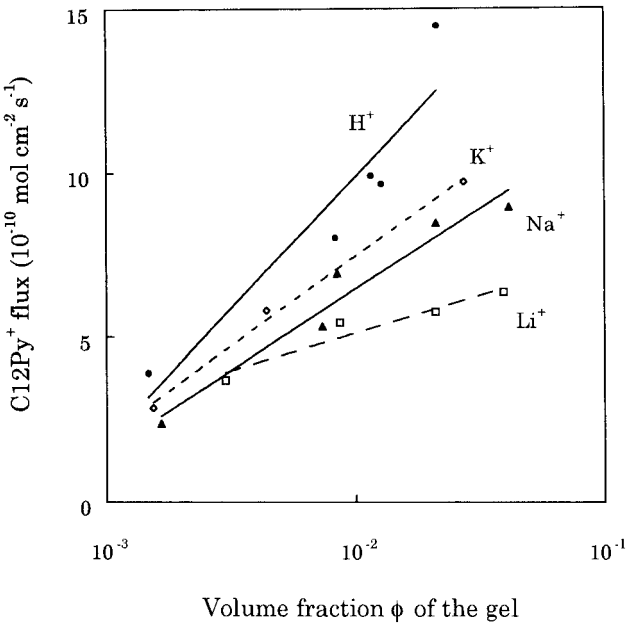

Figure 5. Surfactant flux as a function of the volume fraction of the gels with various counterions. (●) H^+; (□) Li^+; (▲) Na^+; (◇) K^+. Initial gel size V_0: $1 \times 1 \times 0.4$ cm^3; temperature: 25 °C.

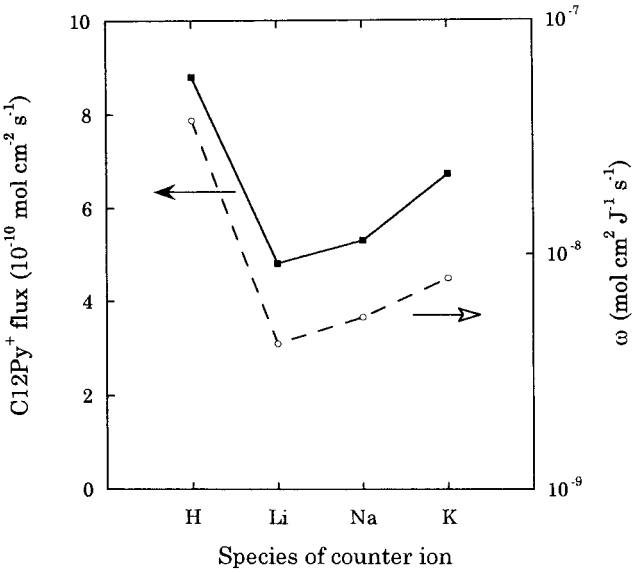

Figure 6. Flux of $C12Py^+$ into PMAMPS gel with various counterions (left ordinate) and molar mobility of the counterion (right ordinate). The flux at $q = 119$ was calculated from fitting curves in Figure 5. (■) $C12Py^+$ flux; (○) molar mobility. Initial gel size V_0: $1 \times 1 \times 0.4$ cm^3; total volume of the system: 40 mL; temperature: 25 °C.

the fitted lines and plotted for various ionic species, a good coincidence with the molar mobility of the counterions in water is seen as shown in Figure 6. The large mobility of H^+ in water is apparently associated with the specific transport mechanism of the proton jump, and low mobility of Li^+ is due to the large Stoke's radius. This result in Figure 6 experimentally demonstrates that the velocity of $C12Py^+$ uptake is strongly affected by the mobilities of counterions of the gel.

As described before, kinetics of the total surfactant uptake is associated with two processes: one is the surfactant diffusion and the other is surfactant binding. Although the binding process dominates the total process, this experimental result indicates that the diffusion process of the co-ion and counterion is nevertheless influential to the total uptake rate in the following way. When ions diffuse in water by chemical potential gradient, macroscopically, electric neutrality must always be satisfied, and this should be true in the present case. The surfactant ion diffuses in the gel accompanied by its co-ion until it reaches the place where an ion-exchange (binding) occurs. The rate of the surfactant uptake increases with increasing the mobility of the co-ion. As soon as the surfactant binding is complete, the co-ions (of the surfactant) and counterions (of the network) form a new pair of ions and diffuse out of the gel, maintaining electroneutrality. The diffusion rate of this pair of ions is also associated with the mobilities of the co-ion and counterion. The ion pair diffusion reduces the concentration of co-ion inside the gel, which in turn, accelerates the co-ion and surfactant uptake.

In the previous paper,[22] we have proposed a kinetic theoretical modeling of the ionic surfactant binding in the oppositely charged network, whereupon the effect of counterions and co-ions was excluded for simplification. Now taking account of the effects of the counterion and co-ion, the flux, J, of each monovalent ion (surfactant, counterion and co-ion) can be obtained following the Nernst and Planck equation:

$$J_{\pm} = -\omega RT\left(\frac{\partial C_{\pm}}{\partial x} \pm C_{\pm}\frac{F}{RT}\frac{\partial \psi}{\partial x}\right) \tag{1}$$

where ω is the molar mobility of the ions (mol cm^2 J^{-1} s^{-1}), C is the concentration (mol/L), R is the gas constant (J mol^{-1} K^{-1}), T is the temperature (K), F is the Faraday constant (C mol^{-1}), ψ is the electric potential (J C^{-1}), respectively. The electrostatic interactions among ions are expressed by the second term of the equation.

A full analysis of eq 1 incorporating diffusion and binding parameters is too difficult to do at present because of the transient electrostatic interaction and effects of volume change of the network. Several studies showed that the interdiffusion coefficient was a function of mobilities of individual ions weighed by their local concentration.[27,28] However, in the present system, the concentration change in immobilized charges in the gel as a result of neutralization by the surfactant binding was not negligible. Therefore, we propose a simple empirical formula.

The harmonic mean among the molar mobilities of surfactant (w_{s+}), co-ion (w_-), and counterion (w_+) is

$$\omega = \frac{3}{1/\omega_{s+} + 1/\omega_{+} + 1/\omega_{-}} \tag{2}$$

and we plotted the experimental results of $C12Py^+$ flux J_{s+} against ω, calculated from molar mobilities of the ions in water. A linear relation was observed between J_{s+} and ω as shown in Figure 7 for various combinations of co-ions and counterions. This indicates that the process can be roughly expressed by eq 3 at the initial stage of interaction.

$$J_{s+} \propto \frac{3}{1/\omega_{s+} + 1/\omega_{+} + 1/\omega_{-}} \tag{3}$$

Equation 3 means that the total kinetics of surfactant uptake consists of each elementary diffusion process of mobile ions affecting each other according to the electrostatic interaction. This simple empirical relation would be very helpful in estimating the effect of co-ion and counterion on the kinetics of the surfactant binding.

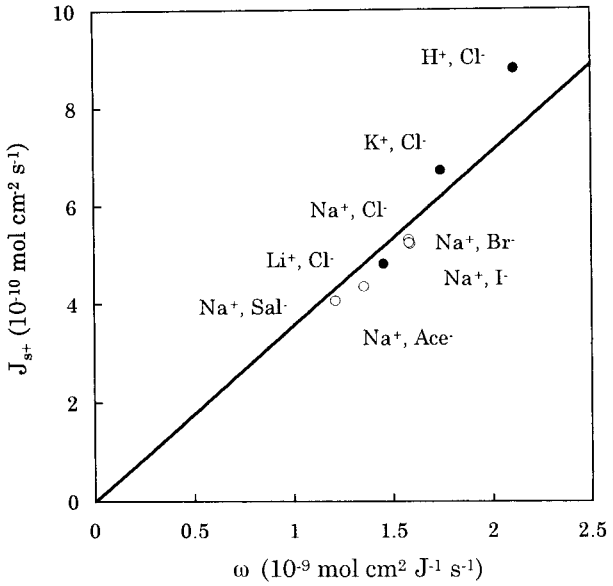

Figure 7. Relationship between initial flux J_{s+} of C12Py$^+$ and the mobility ω defined by eq 2 for various co-ions and counterions.

Acknowledgment. This work was supported by a Grant-in-Aid for the Specially Promoted Research Project "Construction of Biomimetic Moving System Using Polymer Gels" from the Ministry of Education, Science and Culture, Japan. We were also indebted to the support of the Proposal-Based Advanced Industrial Technology R&D Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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