Influence of Shear Stress on Cationic Surfactant Uptake by Anionic Gels

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Kinetic studies of cationic surfactant uptake by anionic polymer gel membrane under various shear flow have been performed, varying the alkyl chain length of surfactant, the ionic strength of surfactant solution, and the charge density of gel. By exposing the gel surface to a shear flow of ca. 1 Pa, the rate of surfactant uptake is distinctly enhanced, while the maximum binding ratio to the gel is not influenced. A linear relationship between the surfactant initial flux and shear stress has been established. At a high ionic strength, the effect of shear stress is suppressed, suggesting that the enhancement of surfactant uptake under shear flow is caused by a decrease in the surface electrostatic potential of the negatively charged polyelectrolyte gel, which favors the uptake of the positively charged surfactant. From the Nernst and Planck equation, a relationship between the surfactant uptake kinetics and the electrostatic field is derived that allows us to estimate the shear stress dependence of the change in the electrostatic field on the gel surface. The origin of the shear-induced surface electrostatic field change is discussed.

1. Introduction

Blood flow through a vessel generates a frictional drag due to the movement of the fluid phase, creating a shear stress on the vascular wall surface. The endothelial cell lining on the surface of the blood vessel is exposed to a wide range of haemodynamically generated shear stress through the vascular system. The average level of shear stresses in the arterial system ranges from 1 to 2 Pa, independent of blood flow rate, size, location, and species, significantly higher than those in the venous system ranging from 0.1 to 0.6 Pa.[1] The endothelial cells of the blood vessel are known to change their morphology and biological function in response to shear stress. The enhanced wall shear stress on the endothelial cell transmits the mechanical stimulus from the cell surface to the cytoplasm,[2,3] resulting in a series of physiological effects such as an increase in endothelial cell density,[4] adaptive regulation of vascular tonus,[5] prostacylin production,[6] tissue plasminogen activator production,[7] uptake of low-density lipoproteins,[8] and protein permeability across the endothelial layer at the arterial wall,[9] as well as the onset of vascular diseases such as atherosclerosis.[10]

It is well-known that the surface membrane of the endothelial cell is covered with a high density of polyanionic macromolecules, proteoglycans and acid glycoproteins that have sulfated, carboxylated, or sialic containing resides. Therefore, the endothelial cell surface is negatively charged with an electrostatic potential about −30 to −40 mV.

We consider that the change in the strength of the blood stream could also cause a surface electrostatic potential change of the endothelial cell because the diffuse electric double layer of the polyelectrolyte might be disturbed by the blood stream, and this would initiate a series of subsequent physiological reactions. However, it is quite difficult to experimentally measure the surface potential change of the endothelial cell under a shear flow.

As an intuitive physical-chemical model, we study the influence of shear flow on the surface potential change of a polyelectrolyte gel membrane by using oppositely charged surfactants as probe molecules, based on the idea that a change in the surface potential of a gel would influence the kinetics of the ionic surfactant diffusion into the gel.

Charged groups of a strong polyelectrolyte gel are fully ionized in water. Counterions stay close to the groups of compensating fixed charges on the macromolecular chains with a large concentration gradient. In a previous study, the electrostatic potential distribution and the counterion distribution have been numerically calculated from the Poisson−Boltzmann equation supposing that the polymer network consists of stacking of 2-dimensional lattices.[11,12] It has been predicted that deep potential energy wells of every cross-linking point and valley along the polymer chain in the polyelectrolyte gels exist. On the surface of the polyelectrolyte gel, a diffused electric double layer is formed that produces a negative surface potential, for example, of an anionic gel.

The objective of this work is to investigate whether the diffusion of cationic surfactant, *n*-alkylpyridium chloride (C_n-PyCl), to anionic hydrogel, poly[2-(acrylamido)-2-methylpropanesulfonic acid] (PAMPS), is aided by surface shear flow of the gel, and accordingly to elucidate the surface electrostatic potential change under the shear flow.

2. Experiment Section

Materials. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) (Tokyo Kasei Co., Ltd), as a monomer, was used as received. *N*,*N*′-Methylenebisacrylamide (MBAA) (Tokyo Kasei Co., Ltd), as a cross-linking agent, was recrystallized twice from pure ethanol before use. Benzophenone (Kanto Chem. Co., Inc.), as a radical initiator, was used as received. Vinyl acetate polymer, as an adhesive agent, was used as received. *N*-Alkylpyridium chlorides (C_nPyCl, *n* = 4, 12, 16) (Tokyo Kasei Co., Ltd) were used as received. Low-density polyethylene plate (LDPE), used as a gel membrane supporting plate, was immersed in acetone stirring for 1 h to remove impurities at 50 °C before use.

Gel Preparation. PAMPS gels were prepared as follows. Benzophenone (0.3 wt %) and vinyl acetate polymer (1 wt %)

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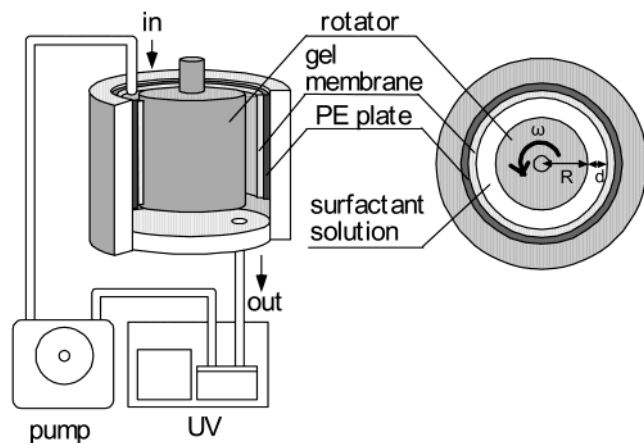
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Figure 1. Schematic diagram of the apparatus for studying the kinetics of surfactant uptake by gel under shear flow.

were dissolved in acetone used as initiator solution. LDPE plates were immersed in the initiator solution for 10 min, and then were dried in a desiccator to remove acetone. AMPS (1.0 M) and MBAA (1 mol %) were dissolved in purified water and bubbled with nitrogen for 30 min and then the solution was injected into a cell that consists of a glass plate and a LDPE plate separated by a Teflon gasket 1.0 mm in thickness. The cell was irradiated with an UV lamp (400 W) 60 cm from the LDPE plate side for 2 h to polymerize the AMPS. After the polymerization, the glass plate was removed and the PAMPS gel membrane adhered on the LDPE plate was immersed in a large amount of purified water for at least one week to remove all unreacted compounds and used until the equilibrium swelling state was reached. The degree of swelling (q) of the gel was 56.6: q = (weight of swollen gel)/(weight of dry gel). The PAMPS gel membrane used for measurement was 11.1 cm in length, 3.5 cm in width, and 0.05 cm in thickness. The average dry weight of one piece of gel membrane was 37.6 mg, or 1.73 $\times$ 10^{-4} mol repeating unit. The standard error of the molar weight of gel membranes on the LDPE plates was 0.38%.

Measurement. *Apparatus Used To Generate Shear Flow.* The apparatus is schematically shown in Figure 1. The shear flow generator consists of a cylindrical container and a coaxially fixed rotator. Both the container and the rotator were made of stainless steel with a dimension of 2.0 cm in radius and 5.0 cm in height for the container and 1.5 cm in radius and 3.0 cm in height for the rotator. The gel membrane fixed on the flexible LDPE plate was fixed on the inner wall of the container and the distance between the surface of gel and the wall of the rotator was adjusted to ca. 1.5 mm by using a silicone sheet. An aqueous solution of 55 mL (7×10^{-4} M) of surfactant was injected into the cylindrical container. The rotational velocity was changed in a range of 0–600 rpm.

According to the theory on the Taylor–Couette problem,[13,14] the flow stability of a coaxial system is characterized by the following several parameters: $Re^{\delta} = \Omega_1 R_1 D/\nu$ (Reynolds number), $\eta = R_1/R_2$, and $\mu = \Omega_2/\Omega_1$. Here R_1 and R_2 are the inner and out radius of the coaxial cylinder, respectively, $D = R_2 - R_1$, and ν is the kinematic viscosity of the liquid. Ω_1 and Ω_2 are the angular velocity of the inner and outer cylinder, respectively. Re^{δ} should be smaller than a critical value $Re^{\delta}_{cr}(\eta)$ to maintain a stable Couette flow. In our system, $D = 0.15$ cm, $R_1 = 1.5$ cm, $R_2 = 1.5 + 0.15 = 1.65$ cm, $\Omega_1 = 0$–600 rpm, $\Omega_2 = 0$, and $\nu = 10^{-2}$ cm^2/s. So, $\eta = 0.91$, $\mu = 0$, and $Re^{\delta} = 0$–1350. No exact value of $Re^{\delta}_{cr}(\eta)$ is found in the literature and it seems to lie around a value of 200 for a system with $\eta = 0.91$ and $\mu = 0$.[13,14] Therefore, some of our experiments might

be performed in the non-Couette flow region. However, all of these theoretical calculations are made for hard wall systems, supposing a nonslippery boundary condition at the cylinder surfaces. Hard wall theory might be not be valid in a system that consists of a viscoelastic surface such as a gel. It is difficult to experimentally check if the Taylor–Couette instability occurs in the experimental range of our study. As a reference, we have performed a similar experiment in a water–glycerol mixing solution that has a viscosity 4.7 times higher than that of pure water with Reynolds number of 0–120 and found similar results with those in water.

Even if an unstable flow occurs in the present study, the surfactant uptake is only influenced by shear force exerted on the gel surface, and any force exerted on the axial direction does not make a remarkable contribution, since the centrifugal force has a negligible effect on the surfactant flux. According to the Taylor–Couette instability theory, the true shear stress exerted on the cylindrical wall in the non-Couette flow region is higher than the value supposing a laminar flow that is given by

$$f = \eta_{vis} \frac{R_1 \Omega_1}{D} \tag{1}$$

where f is the shear stress (Pa) generated on the gel surface, and η_{vis} is the viscosity of the solution (N s/m^2). In addition, a non-Couette flow may also lead to enhanced mass transfer, due to mixing within the roll cells and convection. Therefore, we use the term "apparent shear stress" in the text and also indicate the value of the Reynolds number (Re^{δ}) in the figures.

Surfactant Flux. 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 the slope of the time course of uptake amount (mol)

$$J = \frac{1}{A} \frac{dM}{dt} \tag{2}$$

where J is the flux (mol cm^{-2} s^{-1}), M is the molar quantity of surfactant uptake by the gel, and A is the surface area of the gel (cm^2). C$_n$PyCl aqueous solutions have absorption at 258.5 nm with a molar extinction coefficient of 4400, 4070, and 4230 mol^{-1} dm^3 cm^{-1} for C$_4$PyCl, C$_{12}$PyCl, and C$_{16}$PyCl, respectively. The uptake kinetics of surfactant molecules to gel was investigated by monitoring the surfactant concentration change with UV spectroscopy. The surfactant solution was circulated by a micropump with a pumping rate of 500 mL/h, so the solution can be completely circulated in 7 min. The shear stress induced by circulation can be neglected in comparing with the shear stress applied by the rotation. The initial flux of surfactant was calculated from data within 1000 s. The solution in the cylinder was completely circulated two times within 1000 s. The experimental error was less then 7%.

The amount of surfactant diffused into the gel was also expressed in terms of β, which is the molar ratio of the surfactant ions uptake by the gel to the sulfonate groups of the gel. According to our previous study, volume collapse of PNaAMPS gel started at $\beta \approx 0.5$ and completed at $\beta \approx 0.7$, regardless of the size of the alkyl chain of surfactants and the concentration of salt.[15] To avoid contraction of the gel upon surfactant binding, the experiment was carried out at an initial surfactant concentration where the equilibrium degree of binding (β_{eq}) is lower than 0.25. Because the gel was fixed on a low-density polyethylene plate (LDPE), deformation is more difficult in the lateral

direction, so the shrinkage of the gel that might influence the total process of the surfactant uptake is negligible.

To examine the uptake behavior with increased ionic strength, water-swollen PAMPS gels were immersed in NaCl solutions of various concentrations before use, which resulted in shrinkage of the gel thickness on the LDPE plate. After equilibration in salt solution, the gel membrane thickness changed from 0.05 cm to 0.035 cm, and the lateral size of the gel did not change due to fixation on the LDPE plate. Then the gel was put into the surfactant solution containing NaCl to follow the time course of the uptake under various shear stresses. All the measurements were carried out at 25 °C.

3. Results and Discussion

The effects of shear stress on C_nPy^+ ($n = 4, 12, 16$) uptake by PAMPS gel in aqueous solution without simple salt were studied first. Gel membranes were exposed to steady shear stress in a range from 0 to 0.6 Pa for 1.5 to 5 h. Figure 2 shows the time profiles of the surfactants uptake by gels in terms of the molar quantity (mol) and the degree of binding (β) under various shear stresses. All of these kinetic phenomena were well reproducible.

One can clearly see that an application of shear stress increases the rate of surfactant uptake at the initial stage, before 1 h, and an increase in the shear stress increases the rate of surfactant uptake. The uptake rates decrease with time and then level off nearly at the same β, regardless of the strength of the shear stress. For example, $C_{12}Py^+$ (Figure 2b) achieves an equilibrium degree of binding (β_{eq}) at about 40 min under a shear stress of 0.6 Pa, which is about 2 times quicker than that of 0.3 Pa (70 min).

Figure 3 shows the equilibrium degree of binding (β_{eq}) as a function of shear stresses obtained from the results of Figure 2. β_{eq} is not dependent on the shear stress and it follows an order of $C_{12}Py^+ > C_{16}Py^+ > C_4Py^+$. The values of β_{eq} coincide with our previous results on the effect of alkyl chain length of the surfactants uptake without shear stress.[16] The complexation between the surfactant and polymer gel has been emphasized by two processes: In the first process surfactants adsorb due to electrostatic attraction, at this process electrostatic salt was formed between the surfactant ions and the oppositely charged moieties of the gel, this process is called initiation process. With increasing adsorption density the charged sites of the polymer chain become occupied, then hydrophobic interaction of the nonpolar chain group of surfactant is the driving force for formation of aggregates; this process is called propagation process.[17,18] The result that β_{eq} of $C_{16}Py^+$ is lower than that of $C_{12}Py^+$ might be attributed to its long alkyl tail that occupies more space although $C_{16}Py^+$ has the strongest propagate ability in the polymer network. On the other hand, C_4Py^+ has the weakest hydrophobic nature, which is less favorable for the propagating process in the gel network. The result shows an important fact that although shear stress can accelerate the rate of surfactant uptake, it cannot affect β_{eq}, whcih is determined by the equilibrium interaction energy between the surfactant and the bulk gel. This confirms that the shear stress alters the surface nature of the gel and does not cause any change in the bulk properties of the gel, such as a bulk deformation of the gel.

At the beginning of the uptake process, the amount of surfactant uptake is almost proportional to time. Figure 4 shows the initial flux of surfactant of different alkyl chain lengths calculated as the average over the first 1000 s from the data in Figure 2. One can see that the surfactant flux of different
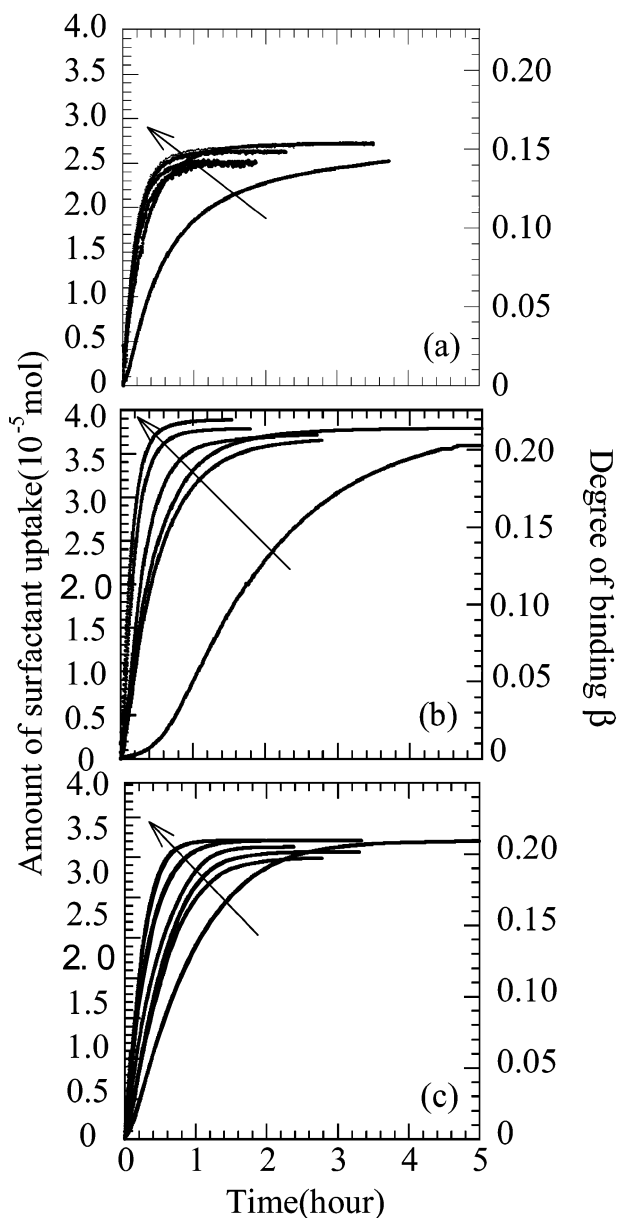

Figure 2. Time profiles of the amount of C_nPy^+ uptake by PAMPS gel under various apparent shear stresses in water: (a) C_4Py^+, (b) $C_{12}Py^+$, and (c) $C_{16}Py^+$. Arrows indicate the increase of apparent shear stress from 0, 0.1, 0.2, 0.3, 0.45, to 0.6 Pa. The right vertical axes are the degree of binding (β), which is the molar ratio of the surfactant ions uptake by the gel to the sulfonate groups of the gel.

hydrophobic alkyl chain lengths increases with increasing shear stress. It is shown that the effect of shear stress to C_4Py^+ and $C_{16}Py^+$ is less distinct than that of $C_{12}Py^+$ for all shear stresses. The phenomenon is in agreement with the foregoing study that $C_{12}Py^+$ showed the largest initial flux in the absent of shear stress.[16]

To confirm if this flow-enhanced surfactant flux is due to a surface shear stress exerted on the gel surface, not due to the effect by a possible non-Couette flow, we further performed the experiment in water solution with 45 wt % glycerol, which has a viscosity 4.7 times higher than that of pure water. In this case, the experiment was performed in $Re^\delta = 0-120$, smaller than the critical Re^δ_{cr} of 200. We also found a very nice linear dependence of the surfactant flux on the shear stress. The similar tendency of flow-induced surfactant uptake suggests that this flow-enhanced surfactant uptake phenomena is intrinsically induced by shear flow and not due to the instability of the flow.
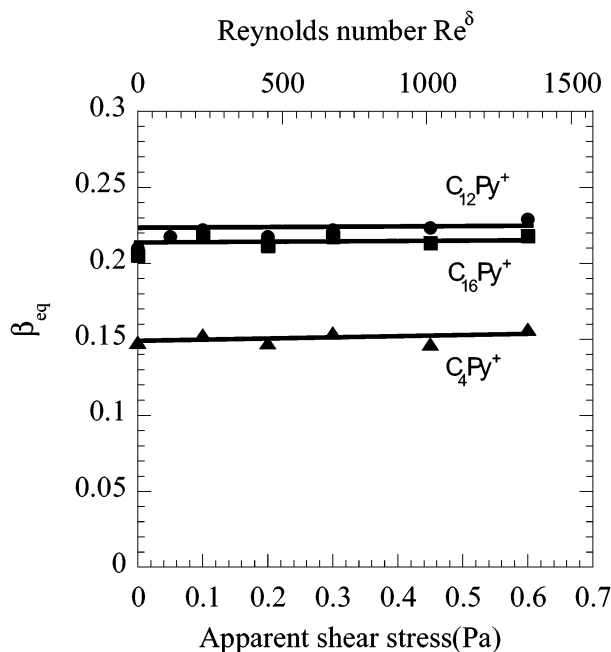
Figure 3. Dependence of the equilibrium degree of binding (β_{eq}) on the Reynolds number and apparent shear stress of the flow: (▲) C_4Py^+, (●) $C_{12}Py^+$, and (■) $C_{16}Py^+$.
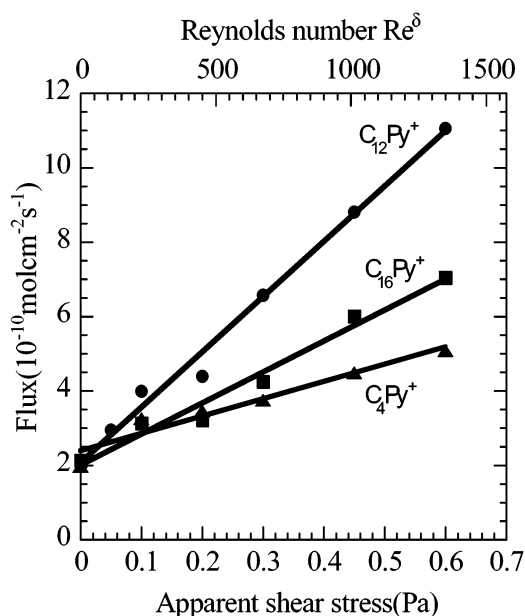

Figure 4. Initial surfactant flux as a function of the Reynolds number and apparent shear stress of the flow: (▲) C_4Py^+, (●) $C_{12}Py^+$, and (■) $C_{16}Py^+$.

As discussed in our previous works,[16] the kinetics of surfactant uptake is controlled 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. When a positively charged surfactant encounters a negatively charged gel, the diffusion of the surfactant into the gel will be accelerated by the surface negative electrostatic potential. Taking account of the electrostatic interaction, the flux J of positively charged ions diffusing into a polyelectrolyte gel membrane is determined by the Nernst and Planck equation[19]

$$J(z,t) = -D\frac{\partial C(z,t)}{\partial z} + \frac{DFC(z,t)}{RT}E(z,t) \quad (3)$$

where D and C are the diffusion constant and the molar concentration of free surfactant ions, respectively, F is the Faraday constant, R is the gas constant, T is the absolute temperature, z is the position axis normal to the gel membrane surface, $E(z,t) = -\partial\psi(z,t)/\partial z$ is the electric field, and $\psi(z,t)$ is the electrostatic potential.

We can write the same equation as eq 3 for the case when a shear flow is applied by denoting the quantities $J(z,t)$, $C(z,t)$, and $E(z,t)$ with a superscript s. Accordingly, the change in the flux induced by the shear stress can be expressed as

$$\Delta J(z,t) = -D\left(\frac{\partial C^s(z,t)}{\partial z} - \frac{\partial C(z,t)}{\partial z}\right) +$$
$$\frac{DF}{RT}[C^s(z,t)\, E^s(z,t) - C(z,t)\, E(z,t)] \quad (4)$$

Equation 4 indicates that an increase in the electric field on the gel surface enhances the flux of the surfactant. It is easy to analyze that there is a coupling between the first term and the second term in eq 4, that is, the acceleration of the diffusion due to an increase in the surface electric field will in turn enhance the concentration gradient $-\partial C(z,t)/\partial z$, therefore, we have $(\partial C^s(z,t)/\partial z) \geq (\partial C(z,t)/\partial z)$. This coupling prevents us from accurately estimating the electric field increase by the shear flow from the flux change. However, the magnitude of the first term would not be larger than the second term, as the first approximation, and we can evaluate the electric field change at the initial stage of diffusion supposing $\partial C(z,t)/\partial z|_{z=0,t=0} \approx \partial^s C(z,t)/\partial z|_{z=0,t=0}$ and $C(0,0) \approx C^s(0,0) \approx C_0$. Here, C_0 is the initial surfactant concentration. So we have

$$\Delta J(0,0) \approx \frac{DFC_0}{RT}[E_z^s(0,0) - E_z(0,0)] \equiv \frac{DFC_0}{RT}\Delta E \quad (5)$$

The above equation indicates that the change in the electrostatic field by the shear stress causes a change in the flux. Using the diffusion coefficient $D = 1.0 \times 10^{-9}$ m²/s for C_4Py^+ obtained in our previous work[16] and $C_0 = 7 \times 10^{-4}$ M $= 7 \times 10^{-1}$ mol/m³, we calculated the semiquantitative values of the electric field increase ΔE at various shear stresses, as shown in Figure 5. We could not estimate ΔE from other two-surfactant probes due to the unknown diffusion coefficients. In principle, ΔE should not be affected by the surfactant probes used. Thus, we can in turn estimate the diffusion coefficient of $C_{12}Py^+$ and $C_{16}Py^+$ from ΔE, which are 3.65×10^{-9} and 2.17×10^{-9} m²/s, respectively. As shown in Figure 5, the perturbation of the electric field by the shear stress is in an order of 10^1-10^2 V/m, this value is very small in comparison with the electric field of the diffuse layer within a thickness of the Debye length, which will be discussed later in detail.

Since the Debye length and the diffuse electric double layer decreases with an increase in ionic strength, we further studied the kinetic process of the $C_{12}Py^+$ uptake in the presence of 0.01 M NaCl and 0.1 M NaCl, respectively.

Figure 6 shows the β_{eq} as a function of shear stress in various ionic strengths. Although β_{eq} of $C_{12}Py^+$ decreases with the increase in ionic strength, coinciding with the results in aqueous solution, β_{eq} in NaCl solution does not change with shear stress. Note that the average β_{eq} of $C_{12}Py^+$ in 0.01 M NaCl solution is reduced from 0.22 to 0.19, and the average β_{eq} of $C_{12}Py^+$ in 0.1 M NaCl solution is reduced to 0.0856, comparing with that in aqueous solution. This is because the electrostatic interaction between $C_{12}Py^+$ and sulfonate anions on the polymer network is screened by the increased ionic strength.
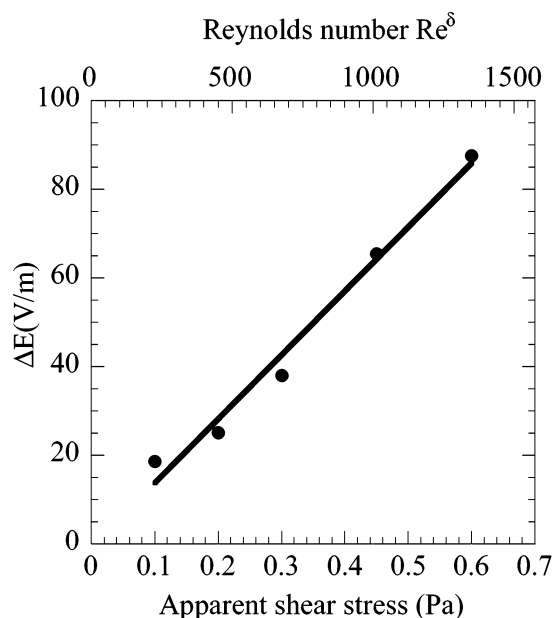
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Figure 5. Changes in the electric field on the surface of PAMPS gel under the flow of various Reynolds number and apparent shear stress as estimated from the flux of C_4Py^+ in Figure 4.
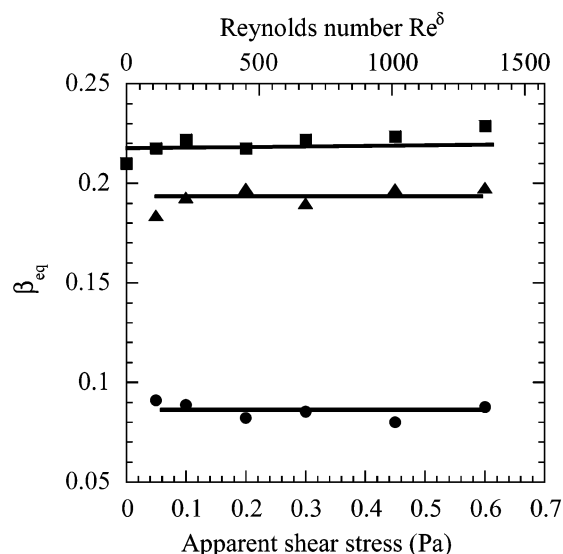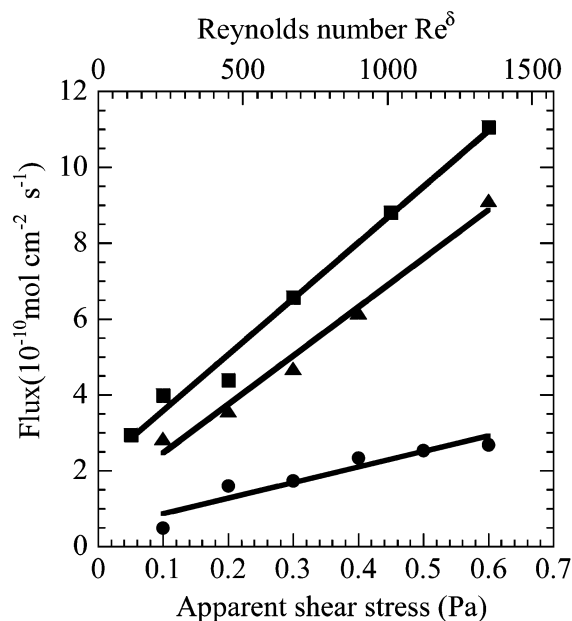

Figure 7. Dependence of the initial flux of $C_{12}Py^+$ on the Reynolds number and apparent shear stress of the flow in various ionic strengths: (■) 0 M NaCl; (▲) 0.01 M NaCl; and (●) 0.1 M NaCl.

Figure 6. Dependence of the equilibrium degree of binding (β_{eq}) of $C_{12}Py^+$ on the Reynolds number and apparent shear stress of the flow in various ionic strengths: (■) 0 M NaCl; (▲) 0.01 M NaCl; and (●) 0.1 M NaCl.

Figure 7 shows the initial flux of $C_{12}Py^+$ as a function of shear stress in various ionic strengths. One can clearly see that the initial flux of $C_{12}Py^+$ increases linearly with increasing shear stress, and the slopes of the linear lines decrease with an increase in NaCl concentration. Two factors should be accounted for by the suppressed effect of shear stress on the flux at a high ionic strength. One is due to a decrease in the ability of complex formation between surfactant and the gel, as indicated by the equilibrium degree of binding in Figure 6. The other is due to the screening of the surface potential distribution. At an increased ionic strength, the effective electric double layer becomes thin and thus reduced the shear effect.

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.[16] Although the binding process dominates the total processes, the experimental result

on the effect of surfactant co-ions and counterions of the polyelectrolyte gel indicated that the diffusion processes of the co-ions and counterions are nevertheless influential to the total uptake rate.[20] When ions diffuse in water by chemical potential gradient, electric neutrality must always macroscopically be satisfied, and this should be true in the present case. The surfactant ion diffuses into the gel accompanied by its co-ion until it reaches the place where an ion-exchange (binding) takes place. Our previous study showed that the rate of the surfactant uptake increases with increasing the mobility of the co-ion.[14] As soon as the surfactant binding completes, 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 mobility of co-ion and counterion. The ion-pair diffusion out of the gel reduces the concentration of co-ion inside the gel, which in turn accelerates the surfactant uptake. It has been found that at the initial stage of diffusion, the $C12Py^+$ flux is proportional to the harmonic mean of the individual diffusion constants of surfactants, co-ions, and counterions.[18] Since a harmonic mean would be dominated by the smallest component, the diffusion constant of the surfactants, though affected by co-ions and counterions, plays a rate-determining role. This explains why we observe a net enhancement of surfactant uptake under a shear flow regardless of its hindrance effect on the co-ions and counterions.

Why does shear stress induce a change in the surface electric field? As has been discussed in the previous section, for an ideal flat surface that is homogeneously and continuously charged, a shear flow should not disturb the diffuse electric double layer since the counterion distribution does not vary along the lateral direction. However, when the gel surface has an inhomogeneous charge distribution or has a finite surface roughness, the shear flow would disturb the counterion distribution in the electric double layer and in turn induce a change in the surface electric potential.

To elucidate which of the two origins should be accounted for, we first compare the average mesh size of the gel network with the distance from the gel surface where the electric field is effectively perturbed by the shear flow.

According to Gouy−Chapmann theory,[21] the electrostatic potential distribution $\psi(z)$ in the diffuse electric double layer is expressed as follows for a homogeneously and continuously charged surface immersed in monovalent salt solution,

$$\psi(z) = \frac{2kT}{e} \log\frac{1 + \gamma \exp(-\kappa z)}{1 - \gamma \exp(-\kappa z)} \qquad (6)$$

where

$$\gamma = \tanh\left(\frac{e\psi_0}{4kT}\right) \qquad (7)$$

the Debye length

$$\kappa^{-1} = \sqrt{\frac{kT\epsilon_r\epsilon_0}{2e^2C_s^\infty}} \qquad (8)$$

and the potential on the gel surface

$$\psi_0 = \frac{2kT}{e} \sinh^{-1}\left(\frac{\sigma}{\sqrt{8\epsilon_r\epsilon_0 kTC_s^\infty}}\right) \qquad (9)$$

Here, z is the distance to the gel surface with its origin on the gel surface, σ is the surface charge density, C_s^∞ is the ionic concentration at infinite bulk, k is the Boltzmann constant, e is the elementary electric charge, ϵ_r is the relative dielectric constant of water, and ϵ_0 is the dielectric constant in a vacuum. The surface charge density σ (C m^{-2}) can be related to the bulk charge density of the gel ρ_e (m^{-3}) by $\sigma = e(\rho_e)^{2/3}$, where

$$\rho_e = \frac{10^6 N_A}{q M_w} \qquad (10)$$

Here, N_A is the Avogadro's number, and M_w is the molecular weight of repeating unit of the polymer. The bulk number charge density of the PAMPS gel is $\rho_e = 2.90q^{-1}$ nm^{-3} ($M_w = 207.25$). So the electric field is

$$E_z = -\frac{\partial\psi(z,t)}{\partial z} = \frac{4kT}{e}\frac{\gamma\kappa\exp(-\kappa z)}{1 - \gamma^2\exp(-2\kappa z)} \qquad (11)$$

In pure water, the ionic strength is determined by the surfactant concentration, that is, $C_s^\infty = C_0 = 7 \times 10^{-4}$ M. When $q = 56.6$, we have $\sigma = e(\rho_e)^{2/3} = 2.2 \times 10^{-2}$ C/m^2. At 25 °C, $\psi_0 = 136.724$ mV, $\gamma \approx 0.86925$, $\kappa^{-1} = 11.5$ nm, and

$$E_z(\text{V/m}) = 7.78 \times 10^6 \frac{\exp(-z/11.5)}{1 - 0.7556\exp(-z/5.75)} \qquad (12)$$

Here, z is in nm. This indicates that at a distance of Debye length $z = 1/\kappa = 11.5$ nm from the gel surface, the electric field is as strong as 3.2×10^6 V/m.

As shown in Figure 5, the perturbation of the electric field by the shear stress is in an order of 10^1-10^2 V/m; this value is very small in comparison with the electric field of the diffuse layer within a thickness of the Debye length. This means that only the counterions far from the gel surface (several times the Debye length) are disturbed by the shear flow where the electrostatic interaction with the polyions is very weak. For example, at a distance 10 times that of the Debye length $z = 10/\kappa = 115$ nm, the electric field of the double layer $E_z = 350$ V/m. Therefore, when the electric field change is $\Delta E = 100$ V/m under the shear flow, the relative change of the electric field $\Delta E/E_z = (100/350) = 22.85\%$. This indicates that the

electric field at a distance ca. 100 nm from the gel surface is effectively perturbed by the shear flow. This is easy to understand since the shear force is very weak.

Next, we estimate the network mesh size of the gel. The polymer chains of a strong polyelectrolyte gel are fully extended at equilibrium swelling in pure water, and the mesh size of the gel is approximately equal to the contour length of the polymer chain between next neighboring cross-linking points.[20] Supposing that the polymer gel composed of cubic lattice meshes, the mesh size, ξ, can be estimated from the number charge density of the gel by the following relation

$$\xi = \sqrt{\frac{3}{b\rho_e}} \qquad (13)$$

Here, b is the spacing between charged groups taken along the axis of the polyion chain. For PAMPS gel, $b = 0.255$ nm and $\rho_e = 2.90q^{-1}$ nm^{-3}. When $q = 56.6$, we have $\xi = 2.01q^{1/2} = 15.1$ nm.

Since the shear effect occurs at ca. 100 nm, a distance much larger than the mesh size ($\xi = 15.1$ nm), the inhomogeneous charge distribution in a mesh size level seems unimportant in bringing about the shear effect in the present case.

It has long been well-known that, different from the corresponding polymer solutions, polymer gels contain spatial inhomogeneities in addition to the thermal fluctuations.[23] These inhomogeneities are built in during the gelation process and/or the cross-linking process.[24] Light- and neutro-scattering studies have shown that the inhomogeneities in the gel have various sizes ranging from a few nanometers to submillimeters with a hierarchical structure.[25−27] Spatial inhomogeneities of charged polymers with a scale larger than a few decade nanometers might be the origin of this surface shear effect.

It is difficult to characterize the surface roughness of a polyelectrolyte gel in pure water. A neutral gel, polyacrylamide (PAAm), prepared on the same glass plate as that of PAMPS was found to have the root-mean-square average of surface roughness, R_q, of 55 nm in water by using atomic force microscopy (AFM). We consider that the polyelectrolyte gel might have a slightly rougher surface than the neutral gel due to its higher swelling ability after synthesis. This would also induce the surface shear effect observed in the present study. A systematic study on the surface roughness effect should be carried out in the future.

Finally, we should point out that the polymer chain elongation along the shear flow could be negligibly small in the present study. Shear force f exertion on one polymer chain is in the order $F = f\xi^2$ and the work done by the shear flow is $W = F\xi = f\xi^3$. Using $f = 1$ Pa and $\xi = 15$ nm, $W = (3.4 \times 10^{-24})J \ll kT$. So the shear flow is too weak to cause a deformation of the polymer network.

4. Conclusions

This work indicates that flux of the ionic surfactant to the oppositely charged gel is enhanced by surface shear stress. A linear relationship between the initial flux of surfactant uptake by oppositely charged polymer gel and shear stress is observed. Surface shear stress distorts the counterion distribution at the surface of a polyelectrolyte gel, which decreases the surface electrostatic potential and promotes the ion exchange between counterion in the gel network and its surrounding surfactant ions. It is considered that the distortion of the diffuse electric double layer under the shear flow is due to the inhomogeneous surface charge distribution and/or morphology, not due to the

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discrete network charging. The results suggest that the response of the blood vessel to haemodynamicity might also be through the change of the membrane potential in the same mechanism as a polyelectrolyte gel under shear stress. The results of this work are primarily useful in understanding the ion transmit and interaction in the blood vessel system under shear stress.

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