Effects of Hydrophobic Interaction on the Cooperative Binding of a Surfactant to a Polymer Network

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ABSTRACT: Thermodynamic and kinetic studies of the binding of cationic surfactant molecules (*N*-alkylpyridinium chloride: C_nPyCl, $n = 4, 8, 10, 12, 16, 18$) to an anionic polymer network (poly(2-(acrylamido)-2-methylpropanesulfonic acid): PAMPS) over a wide range of concentrations and ionic strengths have been made, and the binding constant K and the cooperativity parameter u are calculated. These parameters increase with increasing alkyl chain length, indicating the binding is cooperative in nature and dominated by a hydrophobic interaction. The role of electrostatic and hydrophobic interactions in the initiating and propagating binding processes in the polymer network are discussed. The chemomechanical contractile profiles of PAMPS gel could be explained in terms of these binding parameters and diffusion parameters in the polymer network.

Introduction

A polymer gel consists of a cross-linked elastic network filled with solvent. Its shape and volumes varies in response to changes of temperature,[1,2] solvent composition,[3] pH,[4] and electric field.[5,6] A polymer gel often undergoes discontinuous volume phase transition between the swollen and collapsed states.[7-9] This has stimulated interest in "intelligent gels"[10] with considerable work on "stimuli-responsive polymer gels" including specific adsorbents, soft actuators,[11] drug delivery systems[12,13] (DDS), and chemical valves.[14]

Polymer gels swollen in water[6,15,16] as well as in organic solvent[17-20] undergo intensive contraction under a dc electric field. However, these phenomena have not been satisfactorily interpreted. An attempt has been made to associate the phenomena with the electrophoretic and electroosmotic transport of highly solvated macro- and microcounterions, and the behavior was explained in terms of electrokinetic processes.[6,16]

Recently, we have developed a new type of electrically-driven chemomechanical system which shows quick responses with motility.[21] The principle of this movement is based on an electrokinetic *molecular assembly reaction* of solvated cationic surfactants, *N*-dodecylpyridinium chloride ($C_{12}PyCl$), onto the cross-linked polymer gel made from poly(2-(acrylamido)-2-methylpropanesulfonic acid) (PAMPS). The shrinkage was attributed to the neutralization of negative sulfonates of the gel due to complex formation (binding) with surfactant cations through electrostatic interaction which leads to a decrease in the osmotic pressure difference between the interior of the gel and the surrounding solution.[22] Here, the electric field drives and controls the direction of the equilibrium to give anisotropic binding. When the dc voltage is turned on, the surfactant molecules move by electrophoresis toward the cathode and bind with the gel, preferentially on the side of the PAMPS gel strip facing the anode. This causes an anisotropic contraction of the gel and bending toward the anode. By changing the polarity of the electric field the polymer gel stretches. Thus, by an alternative application of electric field the gel moved forward stretching and bending along the ratchet bar suspended in the surfactant solution.

The present paper deals with thermodynamic and kinetic studies of binding of cationic surfactants *N*-alkylpyridinium chloride (C_nPy) with different alkyl chain sizes ($n = 4, 8, 10, 12, 16, 18$) to the PAMPS network. Experiments have been carried out over a wide range of surfactant concentrations and ionic strengths. This system is of interest not only in suggesting molecular designs for improved chemomechanical behavior but also for the physico-chemical understanding of the diffusion of charged molecules through oppositely charged polymer networks.

Experimental Section

Materials. 2-(Acrylamido)-2-methylpropanesulfonic acid (AMPS) (Nitto Chem. Co., Ltd.) was purified by repeated recrystallization. *N,N'*-Methylenebis(acrylamide) (MBAA) (Tokyo Kasei Co., Ltd.) used as a cross-linking agent was recrystallized twice from pure ethanol. Potassium persulfite (Tokyo Kasei Co., Ltd.) which was used as a radical initiator was recrystallized from pure water. *N*-Alkylpyridinium chlorides (C_nPyCl) with $n = 4, 12, 16$ (Tokyo Kasei Co., Ltd.) were used as received, and those with $n = 8, 10, 18$ were synthesized according to the literature.[23]

Preparation of the Gel. A weakly cross-linked PAMPS gel was prepared by radical polymerization of a 1.0 M solution of the AMPS monomer in the presence of 0.05 M MBAA and 0.001 M $K_2S_2O_8$. The polymerization was carried out in the ampule at 333 K for 12 h under a nitrogen atmosphere. After polymerization, the gel was immersed in a large amount of pure water until it reached its equilibrated size (degree of swelling: a factor of 50 unless stated otherwise) and unreacted monomer and initiator has been removed.

Measurement. The complexation of surfactants with the PAMPS gel was followed spectrophotometrically at 25 °C, i.e., by following the change in UV absorption of the 0.01 M surfactant solution containing a piece of cylindrical PAMPS gel (12.8 mm in diameter, 2 mm thick, and 5.6 mg dry weight or 3×10^{-5} mol per repeated unit) at 259 nm. The contraction of the gel was followed using a cathetometer at 25 °C.

Results and Discussion

Cooperativity of the Surfactant Binding in the Polymer Network. When a water swollen PAMPS gel is immersed in a C_nPyCl solution, the gel shrinks with time. In order to study the effects of concentration and alkyl chain length of the surfactant molecules on the contraction of the polymer gel, a piece of the cross-linked polyelectrolyte gel was placed in 10 mL of water containing a calculated amount of C_4PyCl, $C_{12}PyCl$, or $C_{16}PyCl$ and

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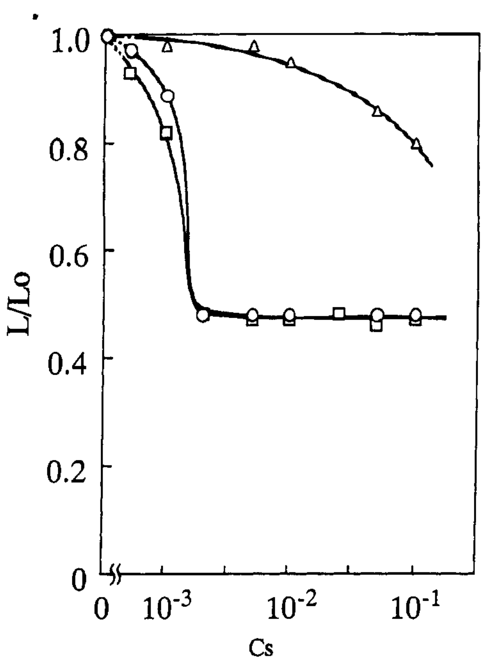

Figure 1. Contraction of the PAMPS gel by addition of surfactants with different alkyl chain lengths: (△) C_4PyCl; (○) C_{12}PyCl; (□) C_{16}PyCl. Temperature: 25 °C.

left standing for several days until the gel reached a constant size.

Figure 1 shows the contraction of PAMPS gels, obtained nearly 10 days after immersing in the surfactant solutions. It is seen that C_4PyCl induces only monotonic and insignificant shrinkage of the gel, while C_{12}PyCl and C_{16}PyCl can result in drastic shrinkages at the specific surfactant concentration near 0.001 M. No notable contraction of the gel occurs above this concentration. The presence of such a "critical" concentration to induce a sudden shrinkage of the gel suggests that the surfactant–gel complexation is cooperative, leading to a micelle-like aggregate in the gel network. In fact, if yellow OB—a pigment soluble only in the micelle domain in water—is allowed to mix with water containing the surfactant-treated gel and stirred for a while, the pigment migrates into the gel which becomes colored.

When the shrunken gel is immersed in pure water or concentrated salt solution, a part of the bound surfactant is released, indicating that the complexation of the cationic surfactant with the oppositely charged polymer network is reversible. The binding isotherm was determined by plotting the degree of binding (β), defined as the molar ratio of bound surfactant to total sulfonate group in the gel, vs the free surfactant concentration. The binding of the surfactant onto polymer gel is a reversible and stoichiometric ion exchange reaction, and therefore, taking account of the volume change, one can observe a stoichiometric release of hydrochloric acid on surfactant binding. Comparing pH measurements of the surrounding solution with the spectral observation of absorbed surfactants, we found that the amount of proton released is equivalent to the surfactant molecules absorbed in the concentration range 10^{-4}–10^{-2} M. This indicates that every surfactant absorbed is electrostatically bound to the polymer network. Figure 2 shows equilibrated binding isotherms of surfactants of various alkyl chains (C_4, C_8, C_{10}, C_{12}, C_{16}, and C_{18}) onto PAMPS gel. In general, the equlibrium of the surfactant binding is obtained slowly and the results in Figure 2 were obtained after 1 month. The results show that every surfactant except for C_4PyCl exhibits a sigmoidal dependence of β in the surfactant concentration range. This indicates that the surfactant molecules can penetrate through the water swollen network and bind at any site of the gel. It should be noted that an increase in chain length of the surfactant not only shifts the "minimum" surfactant concentration at which the binding starts toward a lower concentration but also increases the sharpness of the sigmoidal binding curve.

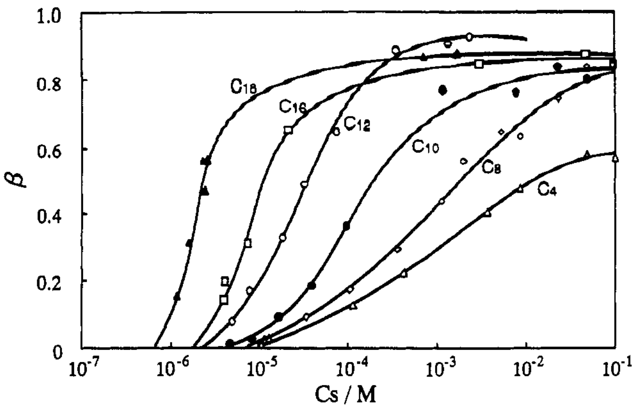

Figure 2. Binding isotherms of surfactant molecules with PAMPS gel at 25 °C: (△) C_4PyCl; (◇) C_8PyCl; (●) C_{10}PyCl; (○) C_{12}PyCl; (□) C_{16}PyCl; (▲) C_{18}PyCl. Equilibration time: 30 days. The degree of binding (β) is defined as the molar ratio of bound surfactant to total sulfonate group in the gel.

As well established the overall stability constant (K) for the complexation can be calculated as follows[24] when the surfactant undergoes a stoichiometric reaction with the gel in a concentration range of 10^{-4}–10^{-2} M,

$$\text{polymer gel} + \text{surfactant} \overset{K}{\rightleftharpoons} \text{complex}$$

$$K = (C_{s0} - C_s)/\{C_p - (C_{s0} - C_s)\}C_s \qquad (1)$$

where C_p is the exchanged molar concentration defined as the amount of sulfonic acid group in the total volume of the solution, C_{s0} is an initial concentration of the surfactant, and C_s is the surfactant concentration surrounding the polymer gel at equilibrium.

On the basis of the Zimm–Bragg theory for helix–coil transition,[25] Satake and Yang[26] derived the following expression for the cooperative binding:

$$K = K_0 u = 1/(C_s)_{0.5} \qquad (2)$$

where K_0 is a binding constant of a surfactant molecule bound to an isolated binding site on a polymer and u is a cooperativity parameter characterizing the interaction between adjacently bound surfactants. Thus, K can be calculated as the value of the reciprocal of the equilibrium free surfactant concentration (C_s) at $\beta = 0.5$.

In the Satake–Yang treatments the cooperative parameter, u, expresses an equilibrium constant for the aggregation of bound surfactant molecules, i.e., for a process

$$2\mathrm{OD} \rightleftharpoons \mathrm{OO} + \mathrm{DD} \qquad u = (\mathrm{OO})(\mathrm{DD})/(\mathrm{OD})^2 \qquad (3)$$

where OO presents two neighboring free surfactant sites and D an occupied site. u is determined from the slope of the binding isotherm at the half-bound point:[26]

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

Thus, the chain length dependence of the stability constant (K) should also be reflected in the difference in u.

A clear indication of the importance of the alkyl chain for the surfactant–gel interaction is demonstrated in Figure 3. Figure 3 shows that the stability constant (K) significantly increases with increasing alkyl chain length. Thus, the K of C_{18}PyCl is more than 4 orders of magnitudes

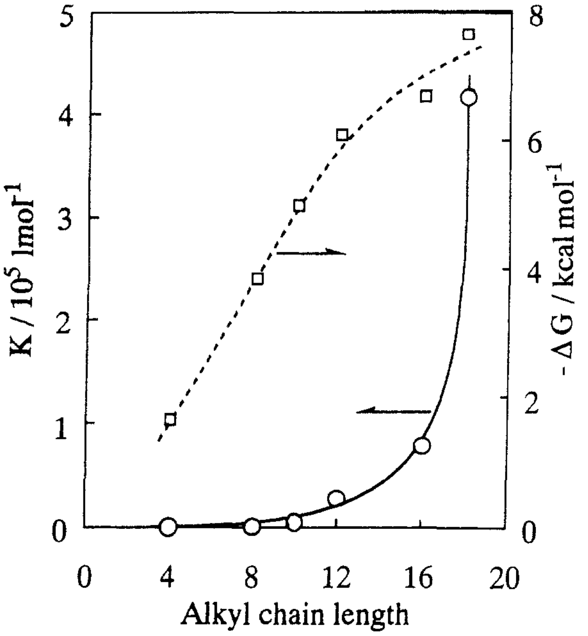

Figure 3. Dependences of the stability constant (K) and free energy change ($\Delta G°$) of binding on the alkyl chain length of the surfactant. Temperature: 25 °C.

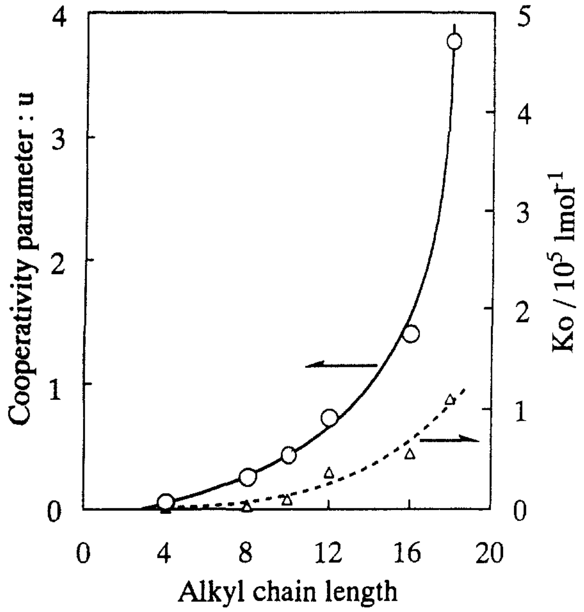

Figure 4. Dependences of the cooperativity parameter (u) and stability constant of the initiating process of binding (K_o) on the alkyl chain length. Temperature: 25 °C.

larger than that of C_4PyCl. This is clear evidence of the cooperativity, and an increase in $\ln(K)$ (or $\Delta G°$) for each CH_2 group attached to the surfactant can roughly be calculated as 0.88 kT/CH_2 group when expressed as $kT \ln(K)$. The value is smaller compared with micelle formation in the absence of polyelectrolyte, or with those processes involving the transfer of an alkyl chain from an aqueous to a hydrocarbon environment, calculated as $1.29kT$.[23]

Using these data of K and eq 4, one can calculate the cooperativity parameter (u) and the binding constant of the initiation process parameter (K_o), and their dependences on alkyl chain length are shown in Figure 4. A significant increase in the cooperativity parameter with increasing alkyl chain length is obviously due to the hydrophobic interaction of bound surfactants, i.e., the complex formation with a sulfonate through electrostatic salt formation, is followed by micelle formation in the gel. The hydrophobic interaction is dominated by an increase in entropy and stabilizes the complex.[27]

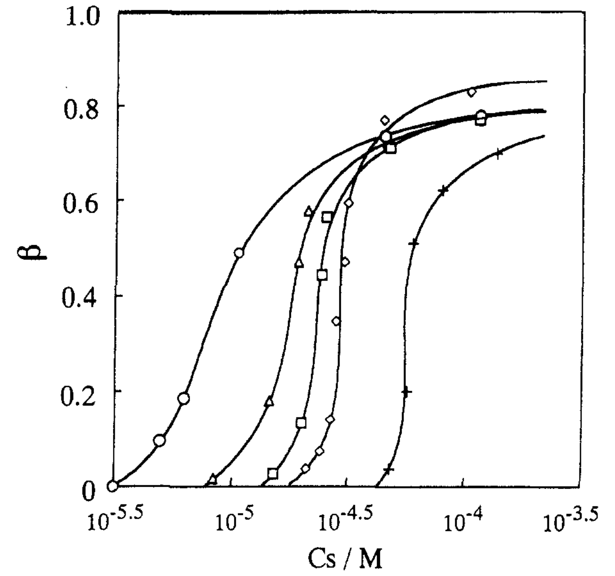

Figure 5. Binding isotherms of $C_{12}PyCl$ with PAMPS gel at various sodium sulfate concentrations at 25 °C: (○) no salt; (△) 1×10^{-3} M; (□) 3×10^{-3} M; (◇) 5×10^{-3} M; (+) 1×10^{-2} M. Equilibration time: 14 days. Degree of swelling of PAMPS gel: 98, 3 mg dry weight.

Table 1. Interaction Parameters of Surfactant with Polymer Gel for Various Salt Concentrations

$[Na_2SO_4]$/mol L^{-1}	$10^{-3}K$/L mol^{-1}	K_o/L mol^{-1}	cooperativity param: u
0	2.9	530	5.5
1×10^{-3}	1.6	68	24
3×10^{-3}	1.5	11	130
5×10^{-3}	1.3	2.8	470
10×10^{-3}	0.53	0.74	710

In order to clarify the roles of electrostatic binding and hydrophobic interaction in the course of binding, the effect of ionic strength on the binding isotherm was studied using $C_{12}PyCl$ at various sodium sulfate concentrations, and the result is shown in Figure 5. An introduction of the salt results in an extensive shift of the "minimum" surfactant concentration at which the binding starts toward a higher concentration and brings about an increase of the steepness of the binding isotherm, i.e., enhances the cooperative process. The "negative" effect of the salt which required increased surfactant concentration is obviously due to electrostatic shielding of the oppositely charged ions of the gel and surfactant, and the "positive" effect on the cooperativity parameter should be associated with the suppression of the repulsive force between adjacent surfactant molecules in the network. An increase in ionic strength results in a decrease in the critical micelle concentration (cmc)[27] and favors larger micelles as compared to salt-free solutions. Thus, an increase in ionic concentration in our case brings about the dramatic increase of u and a decrease of K_o, as summarized in Table 1. These results demonstrate that an electrostatic interaction plays a predominant role for the "initiation" step of the binding. Thus, addition of the salt enhances the continuous binding of surfactant molecules to the polyanion gel with minimized defect due to cooperativity.

Kinetics of Surfactant Binding and the Contraction of the Gel. The contractile behavior of the gel should also reflect the kinetics of the surfactant binding. Figures 6 and 7 show the time profiles of the degree of binding β and the contraction of the gel when a piece of cylindrical gel (13 mm in diameter, 2 mm thick, and 5.6 mg dry weight)

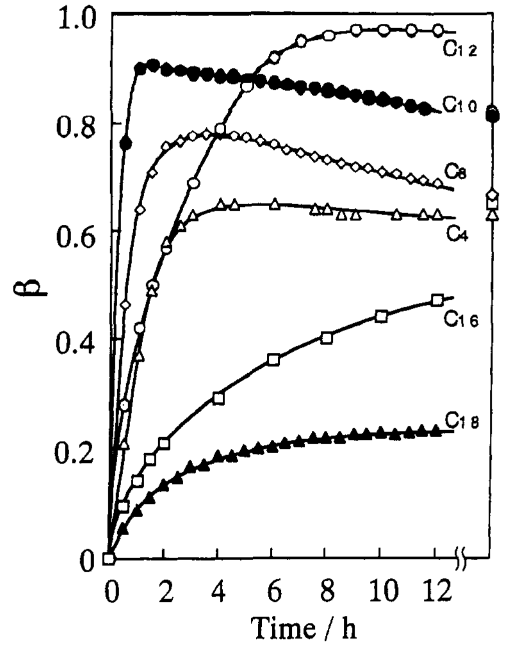

Figure 6. Time profiles of the degree of binding (β) of surfactants with various alkyl chain lengths: (△) C_4PyCl; (◇) C_8PyCl; (●) $C_{10}PyCl$; (○) $C_{12}PyCl$; (□) $C_{16}PyCl$; (▲) $C_{18}PyCl$. Surfactant concentration: 0.01 M, 10 mL. Temperature: 25 °C.

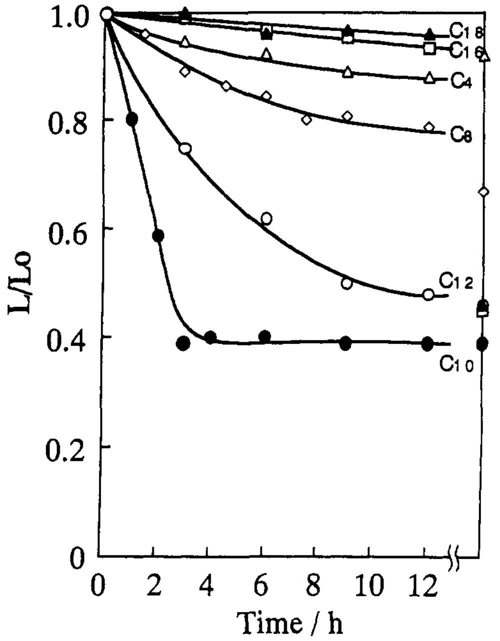

Figure 7. Time profiles of contraction of the gel on addition of surfactants with various alkyl chain lengths: (△) C_4PyCl; (◇) C_8PyCl; (●) $C_{10}PyCl$; (○) $C_{12}PyCl$; (□) $C_{16}PyCl$; (▲) $C_{18}PyCl$. Surfactant concentration: 0.01 M, 10 mL. Temperature: 25 °C.

is immersed in the surfactant solution (0.01 M, 10 mL). It is seen from Figure 6 that the surfactant molecules with a short alkyl chain such as C_4PyCl and C_8PyCl bind rapidly to the gel, attaining β 0.6 or 0.8 within 3 h, while no significant contraction of the gel was observed. $C_{16}PyCl$ and $C_{18}PyCl$, on the other hand, bind extremely slowly, with the gel contraction again negligibly slow. For instance, $C_{18}PyCl$ took 2 weeks to reach equilibrium binding with a β of 0.8, and 1 month to reach equilibrium contraction reaching only 10% of the initial size. Among the surfactants used, $C_{10}PyCl$ showed the largest rate of binding with the largest contraction.

If the diffusion process of the surfactant is Fickian, assuming an instantaneous proton exchange with the cationic surfactant in the gel, an apparent diffusion

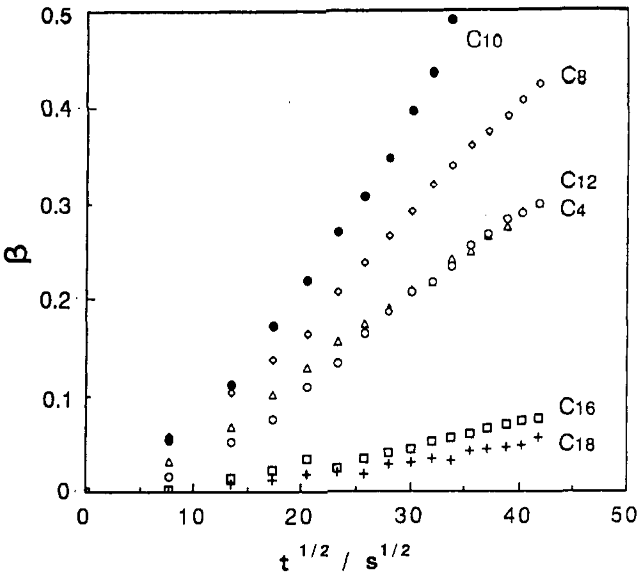

Figure 8. Plot of degree of binding (β) against the square root of time for the surfactants with various alkyl chain lengths: (tuo) C_4PyCl; (◇) C_8PyCl; (●) $C_{10}PyCl$; (○) $C_{12}PyCl$; (□) $C_{16}PyCl$; (+) $C_{18}PyCl$. Surfactant concentration: 0.01 M, 10 mL. Temperature: 25 °C.

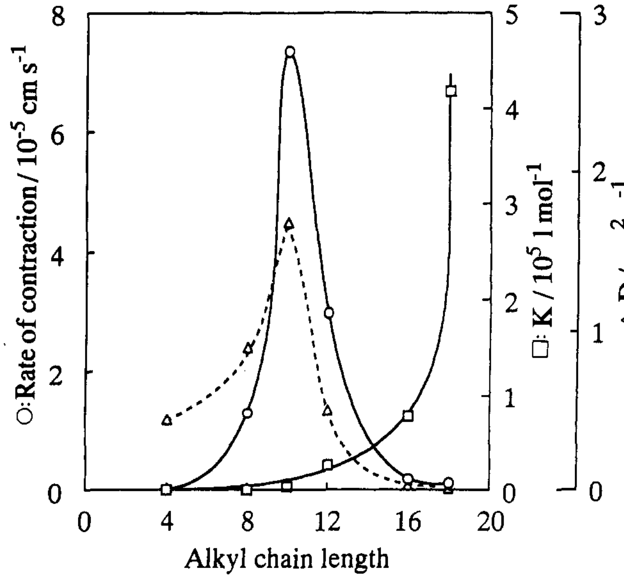

Figure 9. Dependences of alkyl chain length of the surfactant on the rate of contraction *R* (○), diffusion coefficient *D* (△), and stability constant *K* (□). Temperature: 25 °C.

coefficient *D* of each surfactant in the 2-mm-thick gel can empirically be estimated using for the β values[28]

$$\beta = 4D^{1/2}t^{1/2}/\pi^{1/2}h \qquad (5)$$

where *h* is the thickness of the gel. Figure 8 shows that β is approximately linear to the square root of time in the beginning of the experiment, and the diffusion coefficient can thus be estimated from the slope of this plot. The results are shown in Figure 9 for various C_nPyCl and show a maximum diffusion rate at $C_{10}PyCl$. If the rate of contraction of the gel is calculated from Figure 7 and plotted against the alkyl chain length, one obtains an excellent correlation between them. Diffusion occurs simultaneously with the extensive deformation of the network. The condition used for the kinetic measurements is 0.01 M surfactant solution (salt-free) which is below the cmc for C_4PyCl–$C_{12}PyCl$ (cmc of $C_{12}PyCl$: 1.5×10^{-2} M), but well above those for $C_{16}PyCl$ and $C_{18}PyCl$ (cmc of $C_{16}PyCl$: 0.9×10^{-3} M). Therefore, all or nearly all of C_4PyCl–$C_{12}PyCl$ are monomeric in this solution, so that they can penetrate through the polymer network with high diffusion coefficients. On the other hand, $C_{16}PyCl$ and $C_{18}PyCl$ possibly penetrate quite slowly because almost all of the surfactant forms micelles in the solution. Nevertheless, it is remarkable that the diffusion rate of the surfactants increases with an increase of their alkyl chain length.

Thus, the profiles of the contraction of the gel should be interpreted in terms of the thermodynamics and kinetics of binding. An attempt to express an apparent rate of contraction of the gel R (cm s^{-1}) as a function of the stability constant K (L mol^{-1}) and diffusion coefficient D (cm^2 s^{-1}) has been made by assuming that R is a simple combination of them,

$$R = A(K)^a(D)^b \tag{6}$$

where A is an empirical constant and a and b are the parameters indicating the relative weights of K and D toward contraction. Using six combinations of values of R, K, and D in Figure 9, one can calculate A, a, and b values by solving six simultaneous equations to give minimum errors: $a = 0.44$, $b = 1.42$, and $A = 283$ cm s^{-1}, i.e., $R = 283(K)^{0.44}(D)^{1.42}$ (cm s^{-1}). The experimental results suggests that a certain length of alkyl chain is necessary for the surfactant binding, but the diffusion process contributes more strongly to the effective contraction of the gel.

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