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Binding of Sodium Dodecyl Sulfate to a Cationic Polymer of High Charge Density

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An investigation was made into the binding of sodium dodecyl sulfate (SDS) to a cationic polymer of high charge density, the homopolymer of diallyldimethylammonium chloride (PDADMAC), in 1 mM (1 M = 1 mol dm^{-3}) NaCl solution using a potentiometric titration method utilizing a surfactant-selective electrode at 15, 20, 25, 30, 35, and 45 °C. The concentrations of PDADMAC examined were 100, 200, and 400 ppm. SDS ions bound very cooperatively to the PDADMAC polymer. Variation of the polymer concentration had almost no effect on the binding parameters at the same temperature, while increasing the temperature had a large effect on the binding system at the same polymer concentration. The intrinsic binding constant (K) and the critical aggregation concentration (cac) decreased and then increased with increasing temperature, having minimum values of 17.9×10^{-2} mM^{-1} and 0.19×10^{-2} mM at 25 °C, respectively. However, the cooperativity parameter (u) and the binding affinity (uK) had a maximum value of 20.0×10^2 and 357 at the same temperature, respectively. The polymer-concentration-independence of the binding parameters for the anionic surfactant (SDS) to the cationic polymer (PDADMAC) corresponds to the binding of a cationic surfactant to an anionic polymer, and the maximum in the binding affinity at 25 °C is quite similar to the binding of a cationic surfactant to an anionic polymer, and also to the micellization of ionic surfactants having a minimum cmc value at 25 °C.

In almost all cosmetic and household products surfactants and polymers are formulated together, and this co-formulation brings about advanced functions or new functions that surfactants alone cannot achieve. Therefore, studies of binding of surfactants to polymers are intriguing academically and very important in cosmetic and household products.

The binding phenomena of anionic surfactants to cationic polymers have been studied thoroughly by Goddard and coworkers,[1–3] where the systems were at relatively high polymer or surfactant concentration. They found a relatively strong interaction between surfactant and polymer that lead to a hydrophobic complex formation, which made the solution turbid or phase-separated. Also, they revealed that the turbidity reached a maximum at electrical neutrality of a polymer and that the complex formed at that condition gave rise to a liquid crystal or vesicles at the same time.

Binding isotherms of anionic surfactants to cationic polymers, on the other hand, have scarcely been studied[4,5] compared with those of cationic surfactants to anionic polymers,[6–10] in which case the polymers of interest were generally biopolymers such as proteins or DNA, both negatively charged. This is because an anionic surfactant-selective membrane in the solid state is not easy to prepare.[11]

In the present study, we investigated the binding isotherm of sodium dodecyl sulfate to PDADMAC by a potentiometric titration method using a surfactant-selective electrode in the solid state, and then evaluated the binding parameters at various temperatures and at three different polymer concentrations.

Experimental

The cationic polymer examined in this study is a homopolymer of diallyldimethylammonium chloride (PDADMAC) (McINTIRE), as shown in Chart 1. It has a relatively high cationic charge density (5.2 meq/g), and has been used as a hair or skin conditioning agent in cleansing products based on anionic surfactants. The amount of cationic charge of this linear polymer was determined by a colloidal titration method using Toluidine Blue solution (0.1 w/v %) as an indicator and 1/400 M potassium polyvinyl sulfate solution as a titrant.

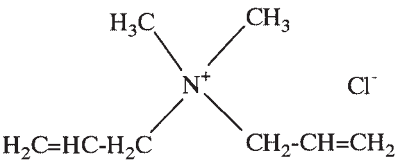

Chart 1. DADMAC.

Sodium dodecyl sulfate (Nacalai Tesque, 99%), as a binding anionic surfactant to a cationic polymer, was used without further purification.

A surfactant anion-selective cationic PVC membrane has been developed by the group of Shirahama.[12] We synthesized the membrane, following this method. First, partially cationic poly(vinyl chloride) (PVC) was synthesized as the functional membrane responsible for surfactant anions by copolymerization of vinyl chloride and *N*-3-(dimethylamino)propylacrylamide followed by quaternization with methyl iodide. In order to prepare a membrane film, Elvaroy 742 (Du Pont) was selected as a polymeric plasticizer. The partly cationic PVC and Elvaroy 742 were dissolved in THF, and then the mixture was cast onto a flat glass plate and covered. This plate was left overnight to allow the THF to evaporate slowly at room temperature. The membrane was cut out and pasted on one end of PVC tubing, using THF as an adhe-

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sive.

The potentiometric measurements were conducted using a digital volt-meter (Advantest R6441B) with an accuracy of ±0.5 mV. The potentiometric titration apparatus is the same as described previously.[13] In all experiments the temperature was controlled within ±0.003 K and the sample solution was continuously stirred using a magnetic stirrer. The cell system is as follows:

Ag|AgCl||reference solution|cationic PVC membrane|sample solution||AgCl|Ag.

Concentration of the test sample solution was changed stepwise by adding a certain volume of stock solution to the sample solution using a microsyringe, after which about 10 min were allowed to pass until the potential ΔE stabilized.

The experiments were carried out at 15, 20, 25, 30, 35, and, 45 °C, and at 100, 200, and 400 ppm PDADMAC solution in the presence of 1 mM NaCl. In all conditions of the present experiments, the solutions became turbid in the course of titration due to the neutralization of the polymer charges and subsequent aggregation by hydrophobic interaction. Therefore, the experiments were usually stopped before the system became turbid, since the data thereafter became less reproducible and the precipitation was unfavorable for the membrane electrode.

All the solutions in the experiments were freshly prepared and the experiments were sufficiently reproducible. The concentrations of surfactant solution were expressed in mM (mmol dm^{-3}).

Results and Discussion

By using a surfactant ion-sensitive membrane electrode, the emf between the reference solution and the sample solution was measured by titrating the sample solution with surfactant solution in the absence and in the presence of polymer. A linear calibration line with Nernstian slope was observed in the polymer-free solutions at each temperature. In the presence of PDADMAC, however, a certain amount of surfactant was bound to the polymer even after the first drop of the surfactant solution, which caused the deviations from the calibration line, as shown in Fig. 1. The difference between the calibration line and the experimental points at the lowest two concentrations seems relatively large in Fig. 1, but the difference due to the binding is expressed on a logarithmic scale, and the amount of bound SDS is very small, as shown below (Fig. 2). The emf values were almost constant at low concentrations of surfactant and then quickly dropped, which indicates the saturation of surfactant binding. As a matter of course, the saturation concentrations of the system were shifted to the right of the abscissa as the polymer concentration became higher. In cases where highly charged colloidal particles like exchange resins and clay articles are present in a system, a diffusion potential at a bride junction should exist.[14,15] However, the diffusion potential becomes negligible in the present system due to the low concentrations used which are 40 to 10 times smaller than 0.1 molar.[14]

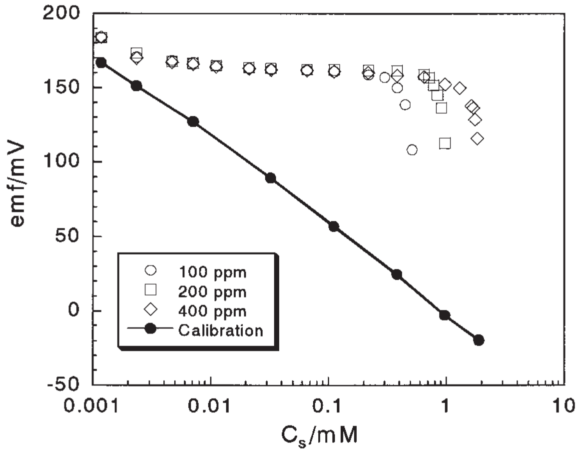

Fig. 1. EMF versus surfactant concentrations of SDS in the absence (●) and in the presence of PDADMAC (◇, □, and ○) at 308.15 K.

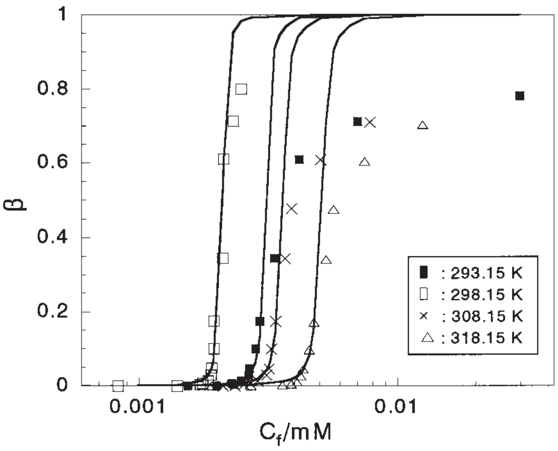

Fig. 2. Binding isotherms of DS$^-$ to PDADMAC at PDADMAC concentration of 100 ppm in 1 mM NaCl solution. Solid lines are simulated by the Satake–Yang equation.

From the amount of free surfactant ions obtained by using the calibration line, the degree of binding (β) can be calculated from the following equation:

$$\beta = C_b/C_p = (C_s - C_f)/C_p, \tag{1}$$

where C_b is the concentration of bound surfactant, C_s is the total surfactant concentration, C_f is the free surfactant concentration at equilibrium, and C_p is the mono-molal concentration of charged groups (binding sites) of the polyion. β equals the fraction of occupied binding-sites and approaches unity when binding becomes complete. The binding isotherms are analyzed by fitting the evaluated data to the Satake–Yang equation.[16]

$$\beta = \frac{1}{2}\left[1 - (1-s)/\sqrt{(1-s)^2 + 4s/u}\right], \tag{2}$$

where $s = C_f/C_f(\beta = 0.5)$, a reduced concentration, and $u = 1/KC_f$ $(\beta = 0.5)$, a cooperativity parameter. K is the intrinsic binding constant. The parameters were obtained by fitting the lower part of binding isotherms, typically, $\beta < 0.3$ where the electrostatic potential around the polyelectrolyte is kept relatively constant because of counter-ion condensation.

The binding isotherms of SDS to PDADMAC at four different temperatures are shown in Fig. 2. With increasing temperature, cooperative binding took place at the lower free SDS concentration up to 25 °C, and then increased above it. The critical aggregation concentrations could be estimated from the plot of β against free SDS concentration (not a logarithmic scale but an ordinary scale), and are summarized in Table 1. The cac was also examined by the change of I_1/I_3 value of pyr-

Table 1. The Binding Parameters of DS^- to PDADMAC at 100 ppm PDADMAC Concentration in 1 mM NaCl Solution

Temperature/K	288.15	293.15	298.15	303.15	308.15	318.15
uK	286	333	357	323	263	179
$u \times 10^{-2}$ (±10%)	15.0	17.5	20.0	18.0	10.0	6.0
$K/10^{-2}$ mM^{-1} (±10%)	19.0	19.0	17.9	17.9	26.3	29.8
cac/10^{-2} mM	0.30	0.26	0.19	0.28	0.31	0.41
ΔH^0/kJ mol^{-1}		12.9			−26.0	

Table 2. The Binding Parameters of DS^- to PDADMAC at 308.15 K in 1 mM NaCl Solution

Cationic polymer concentration/ppm	100	200	400
uK	263	278	256
$u \times 10^{-2}$ (±10%)	10.0	13.0	9.3
$K/10^{-2}$ mM^{-1} (±10%)	26.3	21.4	27.6
cac/10^{-2} mM	0.30	0.31	0.31

ene fluorescence intensities with SDS concentration.[17] The concentrations obtained by the two methods agreed well within experimental error. The binding affinity uK, the cooperativity value u, and other binding parameters are also summarized in Tables 1 and 2.

In Table 1, as the temperature went up at a constant concentration of PDADMAC (100 ppm), the binding affinity uK increased up to 25 °C, and then decreased. That is, it had a maximum value at this temperature. The cooperativity value u also had a maximum at the same temperature. On the contrary, the intrinsic binding constant K and critical aggregation concentration (cac) had the minimum value at that temperature. The uK values were precisely determined, but the values of both u and K could not be precisely evaluated by curve fitting of the binding data. The precision of these values is given in Table 1. Table 2 gives the binding parameters at 35 °C for the three different polymer concentrations. The four parameters did not show any tendency against the polymer concentration and remained almost the same.

Figure 3 shows the variation of the overall binding constant uK with temperature at the same polymer concentration. It is very interesting that the binding affinity uK for SDS binding to PDADMAC had a maximum value at ca. 25 °C, which is quite similar to the case of the binding of a cationic surfactant to an anionic polymer.[18] This is also similar to the micelle formation of a surfactant. For example, sodium dodecyl sulfate shows a pronounced minimum for the CMC around 25 °C.[19] The maximum for uK, of course, leads to a reversal in the enthalpy change of binding ΔH_b^0, from endothermic at lower temperatures to exothermic at higher temperatures (Table 1), where the enthalpy change is defined by the Gibbs–Helmholtz equation[18]

$$\Delta H_b^0 = RT^2(\partial \ln uK/\partial T)_P. \tag{3}$$

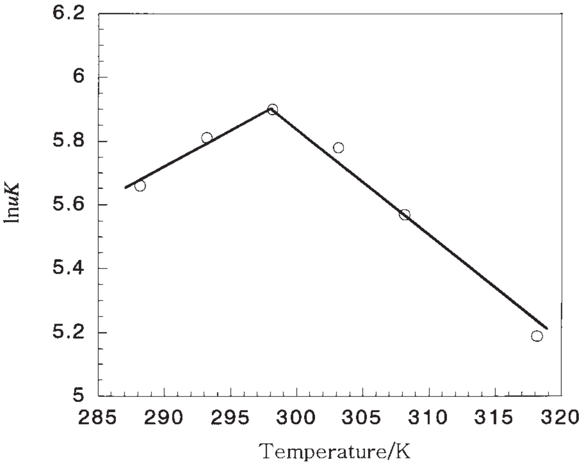

Fig. 3. Variation of overall-binding constant uK with temperature at PDADMAC concentration of 100 ppm in 1 mM NaCl solution.

Table 1 shows the estimated enthalpies at 20 °C and 35 °C. The average value of ΔH_b^0 below 25 °C was about 3 times higher than that of micelle formation for SDS and about 5 times lower than that above 25 °C.[20] That means that the process of surfactant binding to the cationic polymer is more affected by the temperature than that of micelle formation. The presence of a cationic polymer enables anionic surfactants to aggregate much easier, with the aggregate surface covered by the polymer. This is the reason why aggregation starts at a concentration much lower than the original cmc of SDS, 8.3 mM at 298.2 K. In other words, the aggregation of SDS is compressed into a small concentration range by the actions of the polymer. The original cmc of SDS decreases and then increases with increasing temperature, with its minimum at 298.2 K. At temperatures up to 298.2 K, the micellization is driven by a positive entropy change or a positive enthalpy change, while at temperatures above 298.2 K the micellization is driven by a negative entropy change or a negative enthalpy change. The changes of these thermodynamic parameters are closely related to the melting of structured water molecules around a long alkyl chain of SDS. This is also the case for the temperature dependence of cac, which is represented by the sharp change in slope with temperature in Fig. 2. In other words, the temperature dependence of cac seems to be exaggerated by the high charge density of the polymer. The rate of decrease of the binding affinity uK at temperatures above 25 °C was larger in magnitude than its rate of increase at temperatures below 25 °C.

The variation of polymer concentration brings about almost no change in the binding parameters at the same temperature, as can be seen from Table 2. This means that the polymer chains are sufficiently separated from each other. Figure 4 shows the variation of the overall binding constant uK with the polymer concentration at three different temperatures. For the same temperature, the binding constants uK were almost the same for different polymer concentrations. So, it can be concluded that the binding parameters do not depend on the polymer

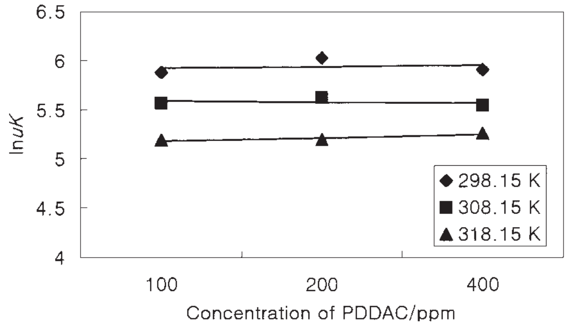

Fig. 4. Relationship between ln *uK* and the concentration of PDADMAC.

concentration. The present results obtained for the binding of anionic surfactant to cationic polymers are also quite similar to those for the binding of cationic surfactants to anionic polymers.[8]

Conclusion

The binding isotherm of sodium dodecyl sulfate to PDADMAC was investigated. The SDS ions were found to bind very cooperatively to PDADMAC, and the variation in polymer concentration showed almost no effect on the binding parameters at the same temperature. On the contrary, the change in temperature had a lot of effect on the binding system at the same polymer concentration.

The intrinsic binding constant (K) and the critical aggregation concentration (cac) had a minimum at 25 °C when plotted against temperature, while the cooperativity value u and the binding affinity uK had a maximum at the same temperature. This means that the enthalpy change of the binding is endothermic at temperatures below 25 °C and exothermic above it.

The polymer-concentration-independence of the binding parameters of the anionic surfactant (SDS) to the cationic polymer (PDADMAC) corresponds to the binding of the cationic surfactants to anionic polymers. The maximum of the binding affinity at 25 °C is similar to that of the binding of cationic surfactants to anionic polymers, and also to the micellization of ionic surfactants having a minimum cmc value at 25 °C.

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