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Interaction of Cationic Surfactant with Arabate and Chondroitin Sulfate¹⁾

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Interactions of cationic surfactants with a branched polymer, arabate (Ar), and a linear polymer, chondroitin sulfate (Chs), were investigated by the potentiometric technique using surfactant ion-selective electrodes. The results indicated a highly cooperative nature in the binding process of *n*-dodecyltrimethylammonium ion (DOTMA⁺) with Chs, but not Ar, in spite of the similarity of the charge density parameter, ξ , between the two polymers. The cooperativity parameter, u , was estimated from the Zimm-Brag theory in the present experimental system to be 3.5 for Ar and 200 for Chs, each of which was independent of the concentration of added salt. The binding constant, K , in the case of the Chs-DOTMA⁺ system was considerably larger than that of the Ar-DOTMA⁺ system. This difference of binding behavior of DOTMA⁺ to Ar and to Chs was considered to be mainly due to the structural difference between the two polymers.

Keywords—arabic acid; chondroitin sulfate; cationic surfactant; binding isotherm

Gum arabic is an important material in drug processing as an emulsifying agent, suspending agent, binding agent and raw materials for preparing microcapsules.²⁾ The main component of gum arabic is arabic acid, which is a branched heteropolysaccharide containing one glucuronic acid for every seven glycosides.³⁾

In the previous papers,^{3,4)} in order to clarify the fundamental properties of arabic acid as a polyelectrolyte, the osmotic coefficient, ϕ ,³⁾ counterion activity coefficient, γ_+ ,³⁾ and transport parameter, f ,⁴⁾ of arabate solution were measured. The results suggested that the interaction of arabic acid with counterions is due to electrostatic force alone, and further that Manning's theory for cylindrical polyelectrolytes could be applicable to the branched polysaccharide, if the interchange distance, b , can be assumed to be a parameter reflecting a spatial interchange distance.

In the present work, the interaction of arabate with cationic surfactants was investigated as a model system to examine the effect of the structural properties of arabate, having low charge density and branching, on the binding behavior with large-molecular ionic substances. For this purpose, binding isotherms of cationic surfactants to arabate were measured by using a surfactant ion-selective electrode as reported previously.^{5,6)}

Materials and Methods

Materials—Sodium arabate (Ar) was purified from acacia senegal gums as reported previously.³⁾ Sodium chondroitin sulfate (Chs) of the c type was purchased from Seikagaku Kogyo Co., Ltd. and used without further purification. Cationic surfactants such as *n*-octyltrimethylammonium bromide (OTMABr), *n*-decyltrimethylammonium bromide (DETMABr) and *n*-dodecyltrimethylammonium bromide (DOTMABr) were purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by recrystallization from acetone. All the other chemicals used in this work were of reagent grade and were used without further purification.

Measurements of Free Surfactant Concentration—Surfactant-selective electrodes developed recently were

applied to determine the free surfactant concentration. Alkyltrimethylammonium cation-selective membrane, or a solid state-membrane made of poly(vinyl chloride) (PVC), was prepared by the following method.^{5,6)} A mixture of 0.2 g of PVC, 0.79 g of bis(2-ethylhexyl) phthalate, and 10 mg of the carrier described below was dissolved in an aliquot of 6 ml of tetrahydrofuran by heating. The obtained clear viscous solution was poured into a Petri dish of 10 cm in diameter. The solvent, tetrahydrofuran, was allowed to evaporate off gradually overnight at room temperature, and a thin membrane was obtained. The carrier used for preparing the membrane was propionyl- α -cyclodextrin, which was prepared by the esterification of α -cyclodextrin.⁵⁾ The electrode membrane was annealed at 40–50 °C under reduced pressure for 4 h, and cut to a suitable size. A piece of the PVC membrane was glued onto the bottom of a PVC tube by using a tetrahydrofuran solution of PVC as an adhesive.

The membrane potential was measured with the following cell: | calomel electrode | agar, 1 M NH_4Cl | test solution | PVC membrane | reference solution | agar, 1 M NH_4Cl | calomel electrode |. The electromotive force (EMF) of the cell was measured with a Metrohm 654 potentiometer. The EMF value reached a constant within a few minutes under the present experimental conditions and the values at various concentrations of surfactants were reproducible with accuracy of within ± 0.1 mV over 2 months. With regard to the PVC membrane, its selectivity was confirmed not to be interfered with by any of the wide range of inorganic ions used in the experiments. All the measurements in the present experiments were carried out at 25 °C.

Measurements of Sodium Ion Activity Coefficients—Activity coefficients of sodium ion, γ_{Na^+} , were determined at 25 °C by using an Orion combination electrode, model 97—12, in the usual way.³⁾

Results

Precipitation of Polyanions by Surfactants

Interactions between polyanions and cationic surfactants were investigated in terms of the turbidity change measured as the optical density at 400 nm. In these experiments, we used sodium Ar and sodium Chs as polyanions and OTMABr, DETMABr and DOTMABr as cationic surfactants.

In the case of OTMABr, no precipitation and no turbidity change in the polyelectrolyte solutions occurred at any concentration of the surfactant added. On the other hand, in the case of the other two surfactants, both polyanions showed a turbidity change following precipitation in a certain concentration range as shown in Fig. 1.

In the Ar–DETMA⁺ system, the turbidity increases in the concentration range above the critical micelle concentration (cmc) of DETMABr (0.065 M), while in the Ar–DOTMA⁺ system, the turbidity increases at concentrations below the cmc of DOTMABr (0.016 M). Figure 1 also showed that the concentration of surfactants needed to cause the turbidity change or precipitation was dependent on the concentration of Ar.

Fig. 1. Changes in the Absorbance at 400 nm of 0.01 eq/dm³ Chs and Ar with Various Concentrations of DETMAr (A) or DOTMAr (B)

Chs: ○, Ar (eq/dm³): ●, 0.00125; ◊, 0.0025; ⊕, 0.05; ⊖, 0.01; ●, 0.02; ●, 0.03.

In the case of Chs, the Chs-DETMA⁺ and Chs-DOTMA⁺ systems both showed similar behavior to that found in Fig. 1, but in each system, the turbidity change of the Chs solution started at a very low concentration of the added surfactant compared to the case of Ar solution. These results indicated that the interaction of polyanions with cationic surfactants depends on the characteristics of the polyions and on the carbon number of the side chain in the surfactant molecule, which is similar to the results reported on anionic surfactants.⁷⁾

Binding Isotherms of Cationic Surfactants to Polysaccharides

The amounts of three cationic surfactants bound to Ar and Chs were determined by using the cationic surfactant-selective electrode, and the results obtained are shown in Figs. 2–4. In Fig. 2A, EMF, the response of the PVC membrane electrode to OTMA⁺, is plotted against the concentration of surfactant, $\log m_D$, where the solid line indicates the calibration curve for OTMA⁺Br. It is clear from Fig. 2A that the electrode response curves in the presence of Ar and Chs were identical with each other and that the observed values of EMF deviated from the calibration curve. The deviation is considered to reflect the binding degree of surfactants to the polyanion at the corresponding equilibrium molar concentration of surfactant, m_D^f , as illustrated by the dotted line in Fig. 2A. From the data, the binding degree, β , was calculated as a function of free surfactant concentration, m_D^f , where β equals the fraction of ionic sites on the polyanion occupied by the bound surfactants: $\beta = (m_D - m_D^f)/c_p$, where c_p indicates the polyanion concentration, which was kept constant at 1×10^{-2} eq/dm³ in this experiment. The calculated results are presented in Fig. 2B. In the case of OTMA⁺, binding isotherms for Ar and Chs were identical with each other and the values of β increased gradually with increasing m_D^f . From the standpoint of the counterion, or Na, a slow dissociation of Na from the polyions was observed with increase of m_D^f , as is also clear from Fig. 2B.

In the Ar-DETMA⁺ and Ar-DOTMA⁺ systems shown in Figs. 3 and 4, the electrode response curves were similar to that of the Ar-OTMA⁺ system, except that the deviations from the corresponding calibration curves were larger than that of the Ar-OTMA⁺ system in the order of Ar-OTMA⁺ < Ar-DETMA⁺ < Ar-DOTMA⁺, as is reflected in the behavior

Fig. 2. (A) Response Curves of the Surfactant-Selective Electrode to OTMA⁺Br in the Presence of 0.01 eq/dm³ Ar and/or 0.01 eq/dm³ Chs

The solid line indicates the calibration curve.

(B) Binding Isotherms of OTMA⁺ for Ar and Chs, and the Corresponding Sodium Ion Activity Coefficients

Ar: (Δ , $\blacktriangle$). Chs: ($\circ$, $\bullet$).

Fig. 3. (A) Response Curves of the Surfactant-Selective Electrode to DETMAr in the Presence of 0.01 eq/dm³ Ar and/or 0.01 eq/dm³ Chs

The solid line indicates the calibration curve.

(B) Binding Isotherms of DETMA⁺ for Ar and Chs, and the Corresponding Sodium Ion Activity Coefficients

Ar: (Δ , $\blacktriangle$). Chs: ($\circ$, $\bullet$).

Fig. 4. (A) Response Curves of the Surfactant-Selective Electrode to DOTMAr in the Presence of 0.01 eq/dm³ Ar and/or 0.01 eq/dm³ Chs

The solid line indicates the calibration curve.

(B) Binding Isotherms of DOTMA⁺ for Ar and Chs, and the Corresponding Sodium Ion Activity Coefficients

Ar: (Δ , $\blacktriangle$). Chs: ($\circ$, $\bullet$).

of the β - m_D^f curve. In other words, the slope of the β - m_D^f curve becomes steeper with the increase of the carbon number of surfactants, as shown in Figs. 2B–4B.

On the other hand, the Chs-DETMA⁺ and Chs-DOTMA⁺ systems showed different behavior. As is clear from the electrode response curves in Figs. 3A and 4A, the deviation of

the observed values from the calibration curve is larger at a certain concentration of surfactant, that is, 0.01 M in the case of DETMA⁺ and 0.001 M in the case of DOTMA⁺. These phenomena were represented as a steeper rise of β in the binding isotherms, (Figs. 3B and 4B), which is thought to be due to the cooperative binding of surfactants to the polymer, as discussed elsewhere.⁵⁻¹² As for the $\gamma_{\text{Na}^+} - m_{\text{D}}^f$ curve, the increase of the value of γ_{Na^+} was observed to start parallel with that of the β , as shown in Figs. 3B and 4B.

Effect of Added Salt on the Binding Isotherms

In order to elucidate how the electrostatic or hydrophobic forces contribute to the binding of surfactant ions to polyanions, the interactions between cationic surfactants, DETMA⁺ or DOTMA⁺, and the polyanions, Ar or Chs, were investigated in the presence of NaCl. In these experiments, polyanion concentration was kept constant at 1×10^{-3} eq/dm³, since this concentration was low enough not to produce precipitation even at $\beta = 1$. The results obtained were represented as binding isotherms, plotted as the degree of binding, β , against the free surfactant concentration, m_{D}^f , in Figs. 5—8.

In the Ar-DETMA⁺ (Fig. 5), the binding curves increased monotonously to reach a plateau region near $\beta = 1$ under the experimental conditions tested, and the initial slope increases with increasing concentration of NaCl. In the Chs-DETMA⁺ system (Fig. 6), the binding behavior was similar to that of the Ar-DETMA⁺ system except that the plateau region appears near $\beta = 0.7$. The behavior in the Chs-DETMA⁺ system (Fig. 6) is fairly different from the result at higher concentrations of Chs (Fig. 3B), which suggested that the interaction of Chs with DETMA⁺ was distinctly affected by the concentration of Chs.

With DOTMA⁺ as a surfactant ion, the binding isotherms for Ar were apparently different from those for Chs, as is clear from comparing the results in Figs. 7 and 8. The binding isotherms for Ar gave gentle slopes, and adding NaCl resulted in a shift of the binding isotherms to higher concentrations of free surfactant. The slopes increased with increasing concentration of NaCl.

In contrast, the binding isotherms for the Chs-DOTMA⁺ system began to level off near $\beta \approx 0.6$ in the absence of NaCl and the presence of NaCl caused a shift in the binding

Fig. 5. Binding Isotherms of DETMA⁺ to Ar (0.001 eq/dm³) in the Absence and Presence of NaCl

NaCl (M): ●, 0; ○, 0.0025; ◐, 0.01; ○, 0.1.

Fig. 6. Binding Isotherms of DETMA⁺ to Chs (0.001 eq/dm³) in the Absence and Presence of NaCl

NaCl (M): ○, 0; ◐, 0.01; ○, 0.1.

Fig. 7. Binding Isotherms of DOTMA⁺ to Ar (0.001 eq/dm³) in the Absence and Presence of NaCl

NaCl (M): ●, 0; ○, 0.001; ⊙, 0.0025; △, 0.01; ⊖, 0.1.

Fig. 8. Binding Isotherms of DOTMA⁺ to Chs (0.001 eq/dm³) in the Absence and Presence of NaCl

NaCl (M): ○, 0; ⊖, 0.001; ⊙, 0.005; △, 0.01; ⊓, 0.05; ●, 0.1.

isotherms for the Chs–DOTMA⁺ system to higher free surfactant concentrations, following the changes in the slopes of the isotherms. Above 0.01 M added NaCl, the degree of binding, β , went up to and over unity.

As can be seen in Figs. 5–8, every binding isotherm increased over unity, where the surface charges of the polymer should be saturated with cationic surfactants. This is presumably because additional surfactant could be bound to the surfactant–polymer complex by hydrophobic interaction.

Discussion

In the previous reports,^{3,4)} we investigated the various colligative properties of Ar and determined the values of b , a parameter reflecting a spatial interchange distance, and the charge density parameter, ξ , according to Manning's theory to be 6.64 Å and 1.19, respectively for Ar. These values are similar to those of Chs ($b=6.3$ Å, $\xi=1.13$). Hayakawa and Kwak⁸⁾ suggested that the charge density parameters ξ is the dominant factor in the binding isotherms for polyion–surfactant systems. However, the binding isotherms for the Ar–DOTMA⁺ and Chs–DOTMA⁺ systems were unexpectedly not similar in the presence and absence of added salts, as shown in Figs. 7 and 8. In order to clarify the reasons for this, the binding isotherms for the polyion–surfactant ion systems were investigated semi-quantitatively according to the theories reported by Hayakawa and Kwak,^{6,8)} and Satake and Yang,¹³⁾ as described below.

As for the cooperative binding of small ions to polyions, a convenient form based on the nearest-neighbor interaction model provided by Zimm and Bragg¹⁴⁾ can be expressed as follows: $(OO) + A \xrightleftharpoons{K} (OA)$, $(OA) + A \xrightleftharpoons{K_u} (AA)$, where O represents a binding site on the polyion, A the surfactant ion, K the binding constant between the surfactant and an isolated

TABLE I. Binding Constants and Cooperativity Parameters

Sodium Ar			Sodium Chs		
NaCl (M)	log Ku	u	NaCl (M)	log Ku	u
0	2.99	1.5	0	3.60	45
0.001	2.78	2.9	0.001	3.48	60
0.0025	2.70	3.6	0.005	3.24	200
0.01	2.52	3.5	0.01	3.19	200
0.1	2.52	3.5	0.05	2.92	200
			0.1	2.80	200

binding site on the polyion, and u the cooperativity parameter. As Ku can be seen as the binding constant between a surfactant and a site adjacent to the site already occupied by a surfactant ion, $kT \ln Ku$ corresponds to the free energy which can transfer the surfactant ions from the bulk solution to the polymer-surfactant complex. When u is larger than unity, the proposed model means that the first surfactant bound will help the second surfactant to bind to a site adjacent to the site already occupied by the first surfactant ion. With reference to the cooperative binding process described above, the following relations for the degree of binding, β , were derived by Satake and Yang¹³⁾

$$\beta = \frac{1}{2} \{1 + (s-1)/((1-s)^2 + 4s/u)^{1/2}\} \quad (1)$$

$$(m_D^f)_{0.5} = (Ku)^{-1} \quad (2)$$

$$(d\beta/d \ln m_D^f)_{0.5} = u^{1/2}/4 \quad (3)$$

where s equals Kum_D^f , and $(m_D^f)_{0.5}$ is the concentration of free surfactant at the half-bound point ($\beta=0.5$). In these equations applied to the simple model, the electrostatic potential of the polymer is considered to be kept constant during the binding process of surfactant ions to the polymer, and therefore complicated phenomena such as conformational change of the polymer and the formation of hydrophobic regions within the polymer are not taken into account. Best fitting values of Ku and u for the binding isotherms in the Ar-DOTMA⁺ or Chs-DOTMA⁺ systems were estimated from the β -log m_D^f curves and are given in Table I. The predicted binding isotherms, calculated from Eq. 1 by using the observed values of Ku and u listed in Table I, are represented by the broken lines in Figs. 7 and 8.

In the case of the Ar-DOTMA⁺ system (Fig. 7), Eq. 1 gave an excellent fit to the data for the degree of binding, β , below $\beta \simeq 0.6$ in the presence of NaCl as well as in the absence of NaCl, and above $\beta \simeq 0.6$ the observed values increased sharply above the broken line. On the other hand, in the case of the Chs-DOTMA⁺ system, there was some difference from the results on Ar. Although below $\beta \simeq 0.6$ the observed binding isotherms agree well with the expected curves in the regions below 0.001 M NaCl, above $\beta \simeq 0.6$ the observed curve deviates from the expected values. At NaCl concentrations above 0.05 M, there was poor agreement between the two curves. This discrepancy between the Ar and Chs systems can be explained as follows. The binding constant K is expected to be a function of the electrostatic potential on the polyion surface. According to Manning's condensation theory for polyelectrolyte solution,¹⁵⁾ a constant fraction of counterion will be trapped in the close vicinity of the polymer, reducing the polymer's effective charge density parameter ξ to unity for monovalent counterions. Thus, in the case of Chs the bound surfactant counterions would not affect the effective linear charge density parameter until β reaches 0.6, because of its charge density parameter $\xi=1.13$. On the basis of this theory, K should be constant up to $\beta=0.6$ and

Fig. 9. NaCl-Concentration Dependence of the Binding Constant K_u for DOTMA⁺

○: Chs. ●: Ar. △: data from ref. 10 for pectinate-tetradecylpyridium⁺ systems, 1, $\xi = 1.61$; 2, $\xi = 1.28$; 3, $\xi = 0.87$; 4, $\xi = 0.48$.

decrease at higher degrees of binding. In fact, the observed isotherms for Chs, at NaCl concentrations below 0.005 M were in very reasonable agreement with this predicted behavior, while those of Ar did not agree in spite of the similar value of ξ to Chs. This discrepancy between Ar and Chs may be due to the difference of structure (linear or branching). This point is further discussed below.

The phenomena described above can be considered in terms of the parameters, u and K_u . As presented in Table I, the relationship between the concentration of added salt and the values of K_u and u in both the Ar-DOTMA⁺ and Chs-DOTMA⁺ systems was similar to the reported results⁶⁾ for dextran sulfate and polystyrene sulfate. That is, the values of $\log K_u$ for Ar systems are much smaller than those of the Chs systems, and $\log K_u$ for each system decreased with increasing concentration of added NaCl, which may be due to the diminished electrostatic potential on the polymer surface resulting from compression of the electric double layer. With respect to u , in both cases (Ar and Chs), the values of u are independent of the concentration of added salt in the concentration range of NaCl above 0.005 M and the value of u was constant at about 3.5 for the Ar system and about 200 for Chs. This may indicate that the cooperative effect in the binding of DOTMA⁺ to Ar or Chs is due to the hydrophobic mutual interaction among surfactant ions bound to the polyion backbone and not due to the electrostatic interaction between them, although the cooperative effect in the binding of DOTMA⁺ by Ar seemed considerably smaller than that of Chs.

We now turn our attention to the ionic strength dependence of the binding constant K_u , since the values of charge density parameter ξ for both polyions are very similar to each other. The values of $\log K_u$ were plotted against $\log m_s$ and the results obtained are shown in Fig. 9, where m_s indicates the molar concentration of added salt. Figure 9 also shows literature values on the pectinate-tetradecylpyridium⁺ system¹⁰⁾ for comparison. In this system, four kinds of pectinate with differently esterified carboxyl groups were used in order to investigate the effect of ξ , and the results demonstrated that the added salt concentration dependence of K_u became smaller with decreasing charge density of the polyion. Considering that the slope for Ar-DOTMA⁺ was comparable with that for Chs-DOTMA⁺, the spatial charge density, or intercharge distance, b , of Ar seems to be similar to the value of b for Chs even in the binding process of DOTMA⁺ to the polyions. In the present work, we showed that the binding behaviors of Ar and Chs to cationic surfactant ions are obviously different although both polyions show very similar binding behavior with inorganic cations. In other words, this suggests that the charge density parameter ξ may not always be dominant in the process of binding described here.

Several rod-like molecules, carboxy methyl cellulose (CMC), alginate and pectinate,⁸⁾

have similar values of ξ in the 1.32–1.61 range. The values of Ku for the binding isotherms of DOTMA⁺ were similar, but the cooperativity parameter, u , of CMC was only about one-eighteenth of that of the other two polyions. In the cases of dextran-sulfate (Dxs) and polystyrene sulfonate (PS),⁶⁾ both polyions have the same value of $\xi = 2.80$ but the binding constant, Ku , for the Dxs–DOTMA⁺ system was smaller than that of the PS–DOTMA⁺ system in the presence of 0.01 M NaCl and the value of the cooperativity parameter, u , for the Dxs–DOTMA⁺ was 3 times larger than that of the PS–DOTMA⁺ system. This may be because both polymers, CMC and PS, have a hydrophobic polymer backbone based on the carboxymethyl group and styrene group, respectively. In addition, these reported results strongly suggest that the detailed structural properties as well as the charge density of the polymer play an important role in the polymer–surfactant binding process. We may now consider the observed binding difference with surfactants between Ar and Chs as follows. Both polymers have a similar hydrophilic backbone, but Chs is a linear polysaccharide and Ar is a branched heteropolysaccharide. Considering that the surfactant has a long hydrophobic chain and a fairly large molecular size, it is suggested that the interaction between Ar and surfactant will be affected by steric hindrance arising from the branching, resulting in lower values of Ku and u for Ar compared to those for Chs.

In the above discussion on the binding behavior of cationic surfactants with polysaccharides, the difference of binding behavior between Ar and Chs was suggested to be caused by the structural difference. This structural difference may also account for the difference of visually detected phenomena, precipitation and gelation, after mixing of the polyions and cationic surfactants, DETMA⁺ and DOTMA⁺. As shown in Fig. 1, surfactant was added to each polysaccharide solution up to $\beta = 1$ in the test tube and the mixture was left overnight at room temperature. Ar formed a gel on the bottom of the test tube, but in the case of Chs the gel was observed to lie flat on the wall of the tube. In addition, the Ar–surfactant gel could be easily dispersed simply by light shaking by hand and the suspension returned again to the gel phase on standing. Further the gel was water-soluble. On the other hand, the gel of Chs–surfactant could not be dispersed by shaking and did not dissolve even in a large amount of water. Such characteristics may be due to the structural difference of the polyanions as discussed above. In the case of the linear polymer Chs, surfactant molecules bound to the polymer can easily interact hydrophobically with other surfactant molecules bound to another polymer molecule because of the linear backbone. In the case of the branched polymer Ar, however, hydrophobic interaction among surfactant molecules bound to different polymer molecules does not seem to occur easily because of the steric hindrance due to the side chains or branches of Ar, which may prevent close mutual contact of the polymers molecules. Therefore the gel formed by the interaction between Chs and surfactant may be more stable than that in the case of Ar.

References

- 1) This work was presented at the 106th Annual Meeting of the Pharmaceutical Society of Japan, Chiba, 1986.
- 2) R. L. Whistler, "Industrial Gums," 2nd ed., Academic Press Inc., New York, 1973, pp. 197–263.
- 3) C. Yomota, S. Okada, K. Mochida, and M. Nakagaki, *Chem. Pharm. Bull.*, **32**, 3793 (1984).
- 4) C. Yomota, S. Okada, and M. Nakagaki, *Yakugaku Zasshi*, **106**, 653 (1986).
- 5) K. Shirahama and M. Tashiro, *Bull. Chem. Soc. Jpn.*, **57**, 377 (1984).
- 6) K. Hayakawa and J. C. T. Kwak, *J. Phys. Chem.*, **86**, 3866 (1982).
- 7) K. Shirahama and N. Ide, *J. Colloid Interface Sci.*, **54**, 450 (1976).
- 8) K. Hayakawa and J. C. T. Kwak, *J. Phys. Chem.*, **87**, 506 (1983).
- 9) K. Hayakawa, J. P. Santer, and J. C. T. Kwak, *Macromolecules*, **16**, 1642 (1983).
- 10) A. Malovikova, K. Hayakawa, and J. C. T. Kwak, "Structure/Performance, Relationships in Surfactants," ed. by M. J. Rosen, Academic Press Inc., New York, 1984, p. 225.

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- 11) J. P. Santerre, K. Hayakawa, and J. C. T. Kwak, *Colloids and Surfaces*, **13**, 35 (1985).
 - 12) K. Shirahama, H. Yuasa, and S. Sugimoto, *Bull. Chem. Soc. Jpn.*, **54**, 375 (1981).
 - 13) I. Satake and J. T. Yang, *Biopolymers*, **15**, 2263 (1976).
 - 14) B. H. Zimm and J. K. Bragg, *J. Chem. Phys.*, **31**, 526 (1959).
 - 15) G. S. Manning, *Q. Rev. Biophys.*, **2**, 179 (1978).