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The Binding Characteristics of Sodium Decyl Sulfate to Poly(L-ornithine) with 1-Alkanesulfonate Counter Ions

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Synopsis. The study was made of the binding isotherms of decyl sulfate ion to poly(L-ornithine) with 1-alkanesulfonate counter ions of the chain length (*n*) from 3 to 7. The coil to helix transitions of polypeptide chain in these systems were also studied. Although the binding cooperativity decreased rapidly with increasing *n*, the conformational change was insensitive to *n*.

Surfactant ions are known to bind cooperatively to a variety of polyions of opposite sign in a quite low concentration range to give rise to the micelle like clusters on the polymer chain.1) In the case of ionic polypeptides, the resulting clusters induce conformational transitions from coil to ordered structures.1—12) It is inferred from binding isotherm studies that an increase in the hydrophobicity of the surfactant ion causes an increase in the binding cooperativity,10,13—16) while an increase in salt concentration is accompanied by an increase in the concentration range where the cooperative binding of surfactant ion occurs.13,14,17—19) The charge density15,20) and the local structure of the polyion15,21) also play important roles in surfactant ion-polyion interactions. However, little is known about the effect of organic counter ions on the binding characteristics of the surfactant ion to polyion.

In a previous paper, we studied the coil-helix transition of poly (L-ornithine) (PO) with 1-alkanesulfonate counter ions of varying chain length (*n*) in salt free solution of sodium 1-decanesulfonate.11) It was found that the helix content vs. total surfactant concentration curves are virtually independent of *n*.11) In this paper we studied the binding isotherms of decyl sulfate ion to PO with 1-alkanesulfonate counter ions of *n* from 3 to 7 with an attention to the effect of counter ion chain length on the binding cooperativity and the related conformational change of PO chain.

Experimental

Sodium decyl sulfate (SDeS) was synthesized by the esterification of 1-decanol (Guaranteed grade, Tokyo Kasei Kogyo Co., Ltd.) purified by vacuum distillation. The product was purified by repeated recrystallization from ethanol. Hydrochloride of PO (PO·Cl) was prepared by dialyzing the hydrobromide of PO (Sigma, MW=32000) against 0.1 mol dm^{-3} HCl and then against distilled water. The concentration (C_p) of PO·Cl in molarity of ionic groups was determined by colloid titration with poly(potassium vinyl sulfate) (Wako Pure Chemical Industries Ltd.). Sodium 1-alkanesulfonates of n=3—7 (n=3,6,7 from Tokyo Kasei Kogyo Co., Ltd., n=4 from Aldrich Chem. Co., and n=5 from Wako Pure Chemical Industries Ltd.) were used without further purifications.

The binding isotherms of DeS$^-$ to PO were determined potentiometrically by using the cell based on nitrobenzene membrane electrode containing 0.1 mmol dm^{-3} dodecyltrimethylammonium decyl sulfate as an ion exchanger. The construction of the cell was described elsewhere.16) The measurements were conducted at constant C_p of 0.20 mmol dm^{-3} and sodium 1-alkanesulfonate concentrations of 20 mmol dm^{-3} at 25 °C. In the absence of PO, this electrode responds selectively to DeS$^-$ ion down to 0.1 mmol dm^{-3} with a slope of 58.4 mV per decade change in SDeS concentration.

Circular dichroism (CD) spectra were recorded on JASCO spectropolarimeter J-20A under the same experimental conditions as for binding isotherms.

Results and Discussion

In polyelectrolyte solutions, the counter ions are known to condense onto polymer chain and reduce an apparent degree of dissociation to $1/\xi$ even at infinite dilution.22,23) Here, ξ refers to a dimensionless structural parameter defined in terms of the average axial charge spacing (d) in nm as ξ=0.714/d in water at 25 °C.22,23) In the case of PO, the value of $1/\xi$ is of the order of 0.5. In the presence of homologous series counter ions, therefore, an increase in the chain length of the counter ion is anticipated to cause a regular decrease in the binding cooperativity of the surfactant ion as a result of the counter ion condensation phenomenon which leads to a regular increase in the average hydrophobicity of the local environment around poly-

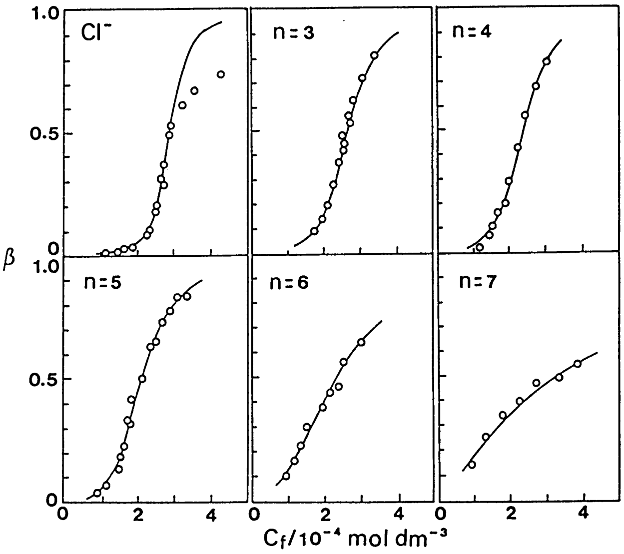

Fig. 1. The binding isotherms of DeS$^-$ to PO with 1-alkanesulfonate counter ions of varying chain length (n). C_f (β=0.5)/mmol dm^{-3}: 0.30 (Cl$^-$), 0.27 (n=3), 0.24 (n=4), 0.22 (n=5), 0.23 (n=6), 0.33 (n=7). Solid lines show the calculated isotherms from Eq. 1 with the values of u given in the text.

mer chain. This is in fact the case for the present systems. Figure 1 shows the change in the binding degree (β) of DeS$^-$ to PO with the equilibrium concentration (C_f) of DeS$^-$. As would be expected, the slope of the binding isotherm which reflects directly the binding cooperativity[24] decreases successively with increasing n. The solid lines in Fig. 1 show the calculated isotherms from the following expression based on one-dimensional lattice model.[24]

$$2\beta-1=(y-1)/[(1-y)^2+4yu^{-1}]^{1/2} \qquad (1)$$

Here, y refers to $C_f/C_f(\beta=0.5)$ and u to a cooperativity parameter which becomes unity in the case of statistical binding. The values of u estimated by curve fitting method are 120 for Cl$^-$, 40 for n=3, 35 for n=4, 20 for n=5, 6 for n=6, and 1.7 for n=7, respectively. As is clearly shown in Fig. 1, the agreements between calculated and experimental isotherms are satisfactory for all of n, except for Cl$^-$ at higher values of β. It should be noted that the binding cooperativity decreases rapidly as n increases and virtually disappears at n=7.

According to the theoretical consideration of the surfactant induced coil-helix transition of polypeptide, the fraction (δ) of the helical conformation depends strongly on u in such a way that the δ vs. β curve not only shifts to higher values of β but becomes steep with decreasing value of u.[8] In this connection, we studied the binding degree dependences of the helix content for the present systems. In the absence of DeS$^-$ ion, the CD spectrum of PO shows the characteristics of a random coil regardless of n. This in turn suggests that the hydrophobic environment around PO chain produced by the counter ion condensation phenomenon is insufficient to induce a conformational change even at n=7. In all cases, however, the CD spectrum varies progressively with increasing β and tends eventually to a characteristic spectrum for helical conformation with a double minimum at 208—209 and 226—227 nm. It has been found that the CD spectrum of PO in surfactant solution shows the marked time dependence over a period of days.[10,11] This is also the case for the present systems. At lower values of β, the mean residue ellipticity at 227 nm, $[\theta]_{227}$, decreases monotonically with time and becomes eventually constant. At higher values of β, it goes through a minimum or increases rapidly with time, since the aggregation of the hydrophobic PO-surfactant complex proceeds at the same time. With these in mind, we adopted the minimum value of $[\theta]_{227}$ as a measure of helix content at a given value of β. Regardless of n, the value of $[\theta]_{227}$ so determined decreases as the total concentration of SDeS increases and converges to -16000 deg cm^2 dmol^{-1} at higher concentrations where β becomes virtually unity.

Figure 2 shows the binding degree dependence of $[\theta]_{227}$. In all cases studied, the helix content of PO is seen to increase monotonically with increasing β. Taking into account an inherent error in the determination of $[\theta]_{227}$ especially at higher values of β, the effect of counter ion chain length on the transition curve is supposed to be considerably small. According to the foregoing treatment of the surfactant induced coil-helix transition of polypeptide, the decrease in u is accompanied by the decrease in the helix content through the decrease in the average cluster size of the bound surfactant ions.[8] This may also be true for the present systems, i.e., an increase in n at a given value of β is considered to cause the regular decrease in the helix inducing effect of the bound surfactant ion clusters. In the present systems, however, we must take into consideration an additional helix promoting effect arising from the counter ion condensation phenomenon, since an overall hydrophobicity around PO chain is expected to increase regularly with increasing n even if β remains constant. Apart from the detailed mechanistic consideration of the transition curves, it seems probable that these two factors are compensated roughly each other.

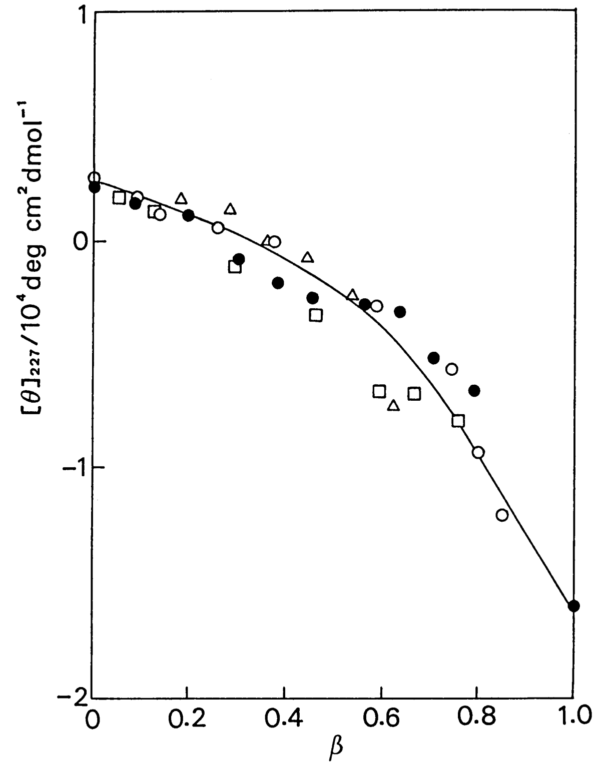

Fig. 2. The binding degree dependence of $[\theta]_{227}$. □, Cl$^-$; ●, n=3; ○, n=5; △, n=6.

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