February, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **54**, *375—377 (1981)* 375

Binding of Sodium Decyl Sulfate to a Cationic Polymer

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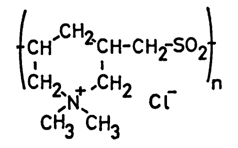
(Received May 26, 1980)

Interaction between sodium decyl sulfate and a cationic copolymer of dimethyldiallylammonium chloride and sulfur dioxide was studied by a potentiometric method utilizing a surfactant-selective electrode. Binding occurs suddenly and is completed in a very narrow range of equilibrium concentration, indicating the strongly cooperative nature of the binding process. The characteristic concentration at which binding starts is about two orders of magnitude smaller than the critical micelle concentration. The cooperativeness parameters as estimated by a nearest neighbor interaction model remains almost constant on increasing sodium chloride concentration, affinity for an isolated binding site decreasing.

Surfactants are bound not only to two-dimentional interfaces, but also to linear polymers, *viz.*, synthetic nonelectrolytes such as poly(*N*-vinylpyrrolidone),[1] and poly(ethylene oxide),[2,3] and biological polyelectrolytes such as polypeptides,[4,5] and nucleic acid.[6] The binding process is characterized on a binding isotherm by remarkable cooperativeness: sudden occurrence and completion of binding in a very narrow range of equilibrium concentration.

The present study deals with the binding of an anionic surfactant, sodium decyl sulfate (SDeS), to a synthetic polycation as measured by potentiometry. The polyelectrolyte used is a copolymer of dimethyldiallylammonium chloride and sulfur dioxide with the following structure.[7] The polymer has proportionate hydrophobic character in addition to positive charge, being very stable around neutral pH. This polycation is considered to be a good model compound for examining the effect of electric charge and hydrophobicity in surfactant-polymer interactions. A surfactant-selective electrode was used for potentiometry.[5,8,9]



The results obtained were analyzed in the framework of one-dimentional nearest neighbor interaction model.[4,10]

Experimental

Materials. The polycation (Nittō Bōseki Co., Ltd., PAS-250, degree of polymerization≒800) was purified by dialysis against water for 3 days, the concentration being determined by colloid titration using poly(vinyl potassium sulfate) as a titrant and Toluidine Blue as an indicator.[11] Sodium decyl sulfate was synthesized by esterification of fractionally distilled 1-decanol with concentrated sulfuric acid followed by neutralization with sodium hydroxide. The crude surfactant was recrystallized once from acetone and twice from ethanol. The recrystallized sample was extracted with diethyl ether in a Soxhlet extractor for 40 h in order to remove trace of residual decanol. The critical micelle concentration (cmc) determined by an electric conductivity method was 32 mol m^{-3} in water at 25 °C.[12]

Potentiometry. The carrier used in the surfactant-selective electrode was prepared by suspending equivalent amounts of SDeS and dioctadecyldimethylammonium chloride (Kaō Soap Co., Ltd.,) in water. The resulting white precipitate (dioctadecyldimethylammonium decyl sulfate) was collected by centrifugation (3000 rpm for 30 min) and resuspended in distilled water. Decantation was repeated three times followed by recrystallization from acetone. A mixture of poly (vinyl chloride) (0.6 g) and tritolyl phosphate (2.4 g) was added to a tetrahydrofuran solution (15 cm^3) containing an appropriate amount of the carrier (0.25 mmol kg^{-1} membrane). The resulting mixture was heated (80 °C) to give a clear viscous solution which was then cast on a flat glass plate. The solvent was gradually evaporated in a desiccator for 2 d. The poly(vinyl chloride) gel membrane, *ca.* 0.3 mm thick, was put on one end of a poly(vinyl chloride) tube (i.d. 9 mm, length 11 cm), tetrahydrofuran being found to be a good adhesive. The electrode was annealed in a vacuum at 40 °C for 2 d. The electrode forms a concentration cell,

$$\text{Calomel}\left|\begin{array}{l}1\ \text{mol dm}^{-3}\\ \text{NH}_4\text{NO}_3\end{array}\right|\begin{array}{l}0.5\ \text{mol m}^{-3}\ \text{SDeS}\\ 20\ \text{mol m}^{-3}\ \text{NaCl}\end{array}\left|\begin{array}{l}\text{PVC gel}\\ \text{membrane}\end{array}\right|$$

$$\left|\begin{array}{l}C_s\ \text{SDeS}\\ C_a\ \text{NaCl}\end{array}\right|1\text{mol dm}^{-3}\ \text{NH}_4\text{NO}_3\left|\ \text{Calomel}\right.$$

The electrode was treated in 1 mol m^{-3} SDeS solution for *ca.* 30 min before each run. Potentiometric titration was carried out in a small cocylindrical cell (25 cm^3) thermostated at 25 °C. The electromotive force was measured with an electrometer (Takeda Riken TR-8651) equipped with a paper recorder.

Results and Discussion

The surfactant-selective electrode shows the Nernstian response above 0.2 mol m^{-3} SDeS, slightly deviating from it at lower concentration. The reproducibility is so good that an emf *vs.* log C_s (C_s: SDeS concentration) plot can be used as a calibration curve. A potentiometric curve deviates from the calibration curve when the polymer exists in a solution (Fig. 1) where ΔC is the amount of SDeS bound to the polymer, C_f the corresponding equilibrium concentration. The binding isotherms thus constructed in three NaCl concentrations at 25 °C are shown in Fig. 2, where X (number of bound SDeS/number of cationic groups on polymer) is the degree of binding. The tendency that X becomes unity with increase in equilibrium concentration indicates that binding sites are primarily the cationic groups. Binding occurs all of sudden and concludes within a narrow range of C_f indicating cooperative effect. The isotherm shifts to a higher C_f with increase in the added

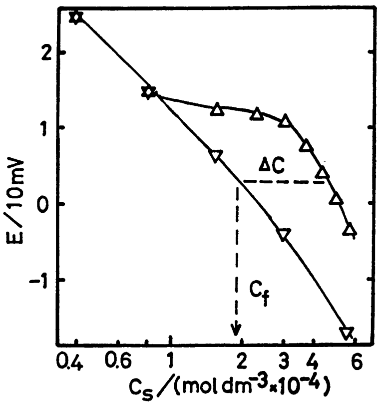


Fig. 1. Emf. *vs.* SDeS concentration plot.
NaCl concentration: 20 mmol dm^{-3}, the polymer concentration: 0.3 mmol dm^{-3} as cationic groups, temperature: 25 °C.

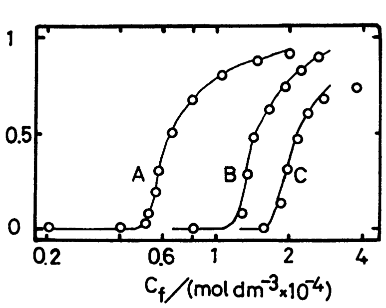


Fig. 2. Binding isotherms of SDeS–PAS systems at 25 °C.
X: degree of binding, C_f: free SDeS concentration, NaCl concentration: A; 20, B; 50, C; 100 mmol dm^{-3}.

electrolyte, C_a, the surfactant becomes less affinitive. This can be analyzed in terms of the Ising model with the nearest neighbor interaction.[4,10]

Let us consider a system where a polymer molecule binding surfactant molecules is in equilibrium with the surfactant whose equilibrium concentration is C_f. The partition function Z, for the system is

$$Z = (1,1)\begin{pmatrix}1 & 1\\ s/u & s\end{pmatrix}^n \begin{pmatrix}1\\ 0\end{pmatrix}, \tag{1}$$

where s ($=KuC_f$) is a sort of binding "*pressure*," K being a binding constant of a surfactant molecule bound to an isolated binding site on a polymer molecule, u a parameter of interaction between adjacently bound surfactants, or a cooperativeness parameter, and n the number of binding sites on a polymer molecule.[10] Equation 1 furnishes various useful quantities such as[4]

$$K = 1/[uC_f(0.5)], \tag{2}$$

and

$$(\mathrm{d}X/\mathrm{dln}C_f)_{X=0.5} = \sqrt{u}/4. \tag{3}$$

In Eq. 2, $C_f(0.5)$ is an equilibrium concentration at X=0.5. The parameters derived from Eqs. 2 and 3 are given in Table 1.

TABLE 1. BINDING PARAMETERS

C_a/mol dm^{-3}	0.02	0.05	0.10
u	25.6	26.3	26.1
K/mol^{-1} dm^3	601	271	180
K'/mol^{-2} dm^6 × 10^3	30.1	5.42	1.80

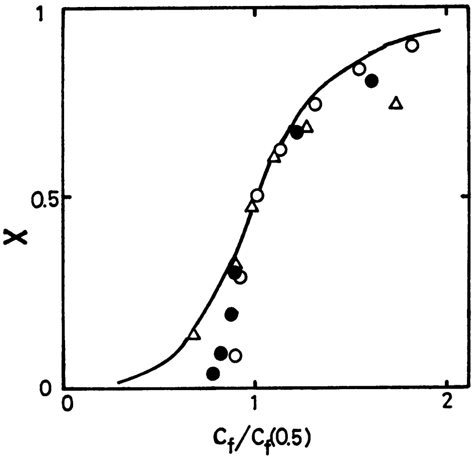


Fig. 3. X *vs.* C_f/C_f (0.5) plot.
NaCl concentration: ○ 20, ● 50, △ 100 mmol dm^{-3}, u=26.

We see how the parameters fit the experimental data in Fig. 3, where X is plotted against $C_f/C_f(0.5)$ (*cf.* Eq. 15 in Ref. 4). The value of K decreases with increase in sodium chloride concentration, u remaining nearly constant. The decrease in the binding affinity should be even steeper, since contribution from the counterions should be taken into account in the binding process of an electrolyte. Ionic product C_fC_a in place of C_f in $s=KuC_f$ and therefore in Eq. 2 should be used. A new equilibrium constant is defined by $K'=K/C_a$ (Table 1). The steeper decrease in K' than K reflects a substantial shielding effect of electrostatic potential of the polymer which overwhelms the effect by the increase in sodium chloride concentration. It is enlightening to compare the characteristic concentration, C_t, at which binding starts, of a nonelectrolytic polymer, poly(ethylene oxide)–SDeS system with that of the present system. C_t was deduced to be about 13 mol m^{-3} for the former[3] and 0.16 mol m^{-3} for the latter, both in 0.1 mol dm^{-3} NaCl. By consideration of free energy we find that the polycation binds SDeS more strongly than poly(ethylene oxide) does by $\Delta G_e = -kT\ln(13/0.16) = -4.4\,kT$. If the free energy is entirely ascribed to an electrostatic term, we have $\Delta G_e = ze\phi$ with ϕ=133 mV. This potential difference might be high, but not unrealistic for ordinary polyelectrolytes.[13] Hydrophobic interaction should be included since the hydrophobicity of the polycation is larger than that of poly(ethylene oxide).

The parameter u changes little in contrast with the drastic change in K'. Once bound onto the polycation, surfactants are scarcely influenced by electrostatic potential, and interact one another through short-range interaction. The parameter u is defined by

$$u = (11)(00)/(01)(01), \tag{4}$$

where (01) denotes the number of bound surfactants on isolated binding sites, (11) that of surfactants bound side by side, and (00) the number of unoccupied sites (*cf.* Eq. 10 in Ref. 4). u is an equilibrium constant for an aggregation process of surfactants on the polymer. The corresponding free energy is

$$\Delta G^\circ = -kT\ln(u) = -3.3\,kT. \tag{5}$$

ΔG° is divided by the free energy of transfer of a methylene group ($1.32\,kT$),[14] to give m=3.3/1.32=2.5. It is presumed that the strong cooperativeness is brought about by mutual contact of certain 2—3 methylene groups of adjacently bound surfactants. Takagishi *et al.* reported that anionic dye, Methyl Orange and its homologs are bound to the same polycation in such a way as to give Klotz plots which are quite straight.[15] This indicates that there is no interaction amoung bound dye molecules. Shorter and stiff molecular structures of these dyes are not susceptible to mutual contact on the polycation, longer and flexible decyl chain being ready to interact.

In conclusion, electrostatic force enhances binding and surfactans are anckored on charged groups on the polycation with subsequent interaction between alkyl chains giving rise to marked cooperativeness.

The samples were kindly supplied by Nittō Bōseki Co. Ltd., and Kaō Soap Co., Ltd.

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