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Binding of 1-Decylpyridinium Bromide to Poly(vinyl sulfate)

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Binding of 1-decylpyridinium bromide onto poly(vinyl sulfate) in aqueous solution is measured by using a potentiometric titration method which employs propionyl-α-cyclodextrin as a neutral carrier in a 1-decylpyridinium selective electrode. Binding is highly cooperative and biphasic. The first step binding is reduced, while the second one increased on increasing added NaBr concentration. Temperaure dependence is very small giving an enthalpy of binding equal to -1.4 kJ mol^{-1}

Surfactants, a group of molecules possessing a large hydrophobic group as well as a strong hydrophilic group, show remarkable characters:[1,2] adsorption onto surfaces and aggregation into micelles. Furthermore surfactants are bound onto macromolecules, both natural and synthetic.[3,4] Recently relevant studies are being accumulated.[5-11] We also have reported binding isotherms for such systems as poly(ethylene oxide)-alkyl sulfates,[12,13] dodecyl sulfate-denatured proteins,[14] decyl sulfate-synthetic cationic polymer,[15] and DNA-1-dodecylpyridinium salt.[16] All the systems mentioned above are characterized by very marked cooperative binding: a sudden occurrence and completion of binding in a very narrow range of equilibrium concentration.

There are several methods in order to study surfactant–polymer interactions. We prefer a binding isotherm method which provides with a direct evidence of interaction and allows for thermodynamic interpretation by the aid of statistical mechanics. This kind of study can afford fundamental knowledges about interactions of various sorts of biomedical materials with biomacromolecules such as proteins and nucleic acids.

In the present study, binding of 1-decylpyridinium bromide (DePBr) to poly(vinyl sulfate) (PVS) was measured by a potentiometric titration method which employs a DeP-sensitive electrode to seek for a further understanding of the phenomena. A potentiometric method is superior to an equilibrium dialysis method in constructing a binding isotherm, because the former measures a thermodynamic activity directly and promptly, while the latter takes a very long time to reach an equilibrium followed by tedious analytical procedures, especially when a surfactant is used as a dialysate. A DeP-selective electrode prepared by using a hydrophobic cyclodextrin derivative dissolved in poly(vinyl chloride) (PVC) membrane was successfully used.[16]

Experimental

Materials. 1-Decylpyridinium bromide was synthesized by treating a fractionally distilled 1-bromodecane with dried pyridine and recrystallized from acetone three times followed by decolorization with active charcoal in a methanol solution. The critical micelle concentration as measured by an electric conductivity method is 51.6 mM† at 25 °C. Potassium poly(vinyl sulfate) (Wako Chemicals Co.) was converted into the sodium salt by dialysis in a concentrated sodium bromide solution (1 M) and then in pure water for days. The polymer solution was slightly acidic (pH 6). The sulfate content of the polymer solution was determined by a colloid titration method.[17]

Electrode. α-Cyclodextrin (Tokyo Kasei) was esterified with propionic anhydride in dried pyridine at room temperature for 1 d. Purification by precipitation with water followed by dissolution in acetone was repeated three times. The obtained white material is propionyl-α-cyclodextrin (prop-α-CD) working as a neutral carrier of the surfactant. Poly(vinyl chloride) (0.6 g), bis(2-ethylhexyl) phthalate (2.37 g), and the neutral carrier (0.03 g) are mixed well. Into the slurry mixture, 6 ml of tetrahydrofuran is added. The whole mixture is heated at 60 °C until it becomes a clear and viscous solution, which is then cast on a flat glass plate. After gradual evaporation of the solvent, the gel membrane (about 0.2 mm thick) is cut out and put on one end of a PVC tube (9 mm inner diameter and 11 cm long), where a 10% PVC tetrahydrofuran solution is a good adhesive. The electrode membrane is "annealed" at 40—50 °C under reduced pressure. A concentration cell is formed as follows:

$$\text{Calomel}\left|\begin{matrix}\text{1 M KCl}\\ \text{agar bridge}\end{matrix}\right|\begin{matrix}C_o\text{mM DePBr}\\ C_a\text{mM NaBr}\end{matrix}\Bigg|\mathbf{M}\Bigg|\begin{matrix}C_s\text{mM DePBr}\\ C_a\text{mM NaBr}\end{matrix}\left|\begin{matrix}\text{1 M KCl}\\ \text{agar bridge}\end{matrix}\right|\text{Calomel},$$

where **M** is the surfactant-selective membrane, C_S and C_O are the outer and inner surfactant concentrations respectively, and C_a is the added NaBr concentration. The polyelectrolyte concentation is usually about 1 mM residue. The potentiometric titration is carried out in a thermostated cocylindrical cell. The electromotive force (EMF) is measured with a digital voltmeter (Takeda Riken TR-6843). Asymmetric potential is usually less than ±2 mV and is not corrected for.

Results and Discussion

Figure 1 shows a relation between the EMF and logarithm of surfactant concentration. The electrode is excellently responsive from the cmc down to *ca.* 2×10^{-6} M with a slope of 58 mV per decade concentration difference at 20 °C. In the presence of 1 mM residue PVS, however, a deviation from the linearity is found suggesting that a part of surfactant is bound onto the polymer. Amount of binding, $\Delta C=C_s-C_f$ at an equilibrium concentration, C_f, is obtained by following the arrows shown. A degree of binding, X, is defined as ΔC/(total concentration of sulfate groups on polymer). A binding isotherm is constructed by plotting X against $\log C_f$.

† 1 M=1 mol dm^{-3}.

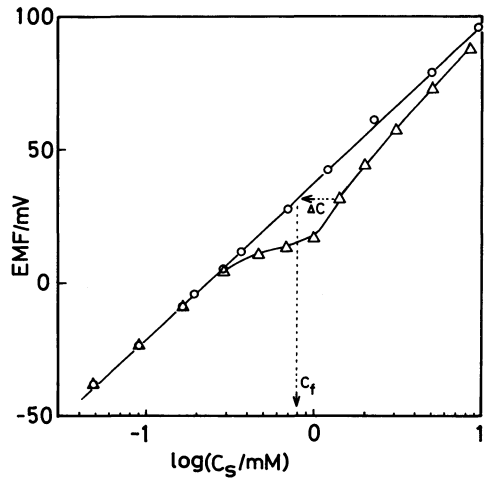

Fig. 1. Potentiogram of DePBr in 20 mM NaBr at 20°C.
○: Without polymer, △: with 1 mM PVS.

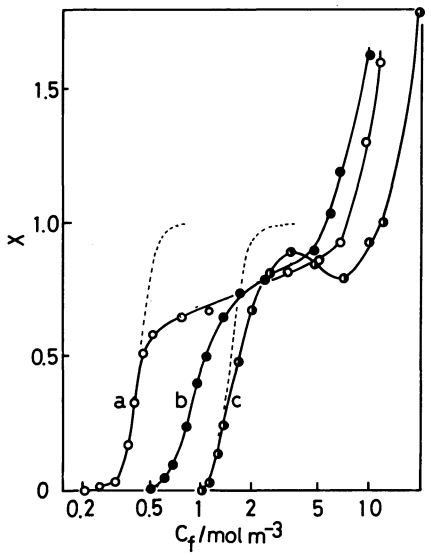

Fig. 2. Effect of added NaBr on binding isotherms at 20°C.
NaBr concentration in mM: a; 20, b; 50, and c; 100.

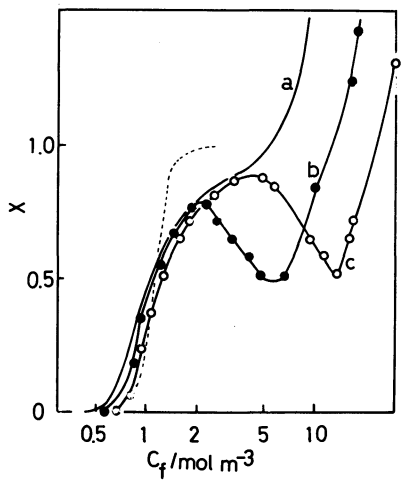

Fig. 3. Effect of temperature on binding isotherms in 50 mM NaBr.
Temperature in °C: a; 20, b; 40, and c; 50.

In Fig. 2, there are three binding isotherms in different NaBr concentrations at 20 °C. It is seen on an isotherm that there are two-step bindings: one occurring suddenly and sharply increasing until a shoulder around $X=1$, followed by another step binding. Titrated solution sometimes became turbid near $X=1$ due to neutralization of charges on the polymer and subsequent precipitation. The turbidity, however, soon disappears on further addition of surfactant. The hydrophobic precipitate is redispersed on further binding surfactants with their polar groups exposed to the bulk water phase, while their alkyl chains are in contact with the hydrophobic surfactant-polymer complex.

Now our analysis is mainly limited within the first step binding, since the second one is less reproducible probably because of the precipitation. The binding isotherm shifts right along the equilibrium concentration axis with increase in the added electrolyte concentration. This is the same tendency as we observed previously in the sodium decyl sulfate-cationic polymer system.[15] Added counterions suppress the electrostatic potential on a polyelectrolyte and reduce an affinity potential. It is a cooperative nature that the binding occurs suddenly and concludes within a very narrow range of equilibrium concentration: an already bound surfactant helps later coming surfactants bound through hydrophobic interaction between alkyl chains.

In Fig. 3, binding isotherms at three temperatures in the presence of 50 mM NaBr are shown. It is noted that isotherms slightly shift right on increasing temperature. Maxima and minima found at 40 and 50 °C: should be ascribed to precipitation mentioned above, which is apt to occur at higher temperature.

The following features are extracted from the binding isotherms semiquantitatively in accordance with the above discussion. According to the Ising's nearest neighbor interaction theory,[18] PVS may be viewed as one dimensional array of binding sites where surfactants are bound with mutual interaction. A partition function for such a system is explicitly expressed and yields a lot of important relations,[18] two of which are especially useful for the present purpose:

$$[\mathrm{d}X/\mathrm{d}\ln C_f]_{X=0.5} = \sqrt{u}/4, \tag{1}$$

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

where $C_f(0.5)$ is an equilibrium concentration corresponding to half binding ($X=0.5$), u the cooperative parameter, or an equilibrium constant for an aggregation process among bound surfactants, and K means a binding constant for a process that a surfactant ion is transferred from an aqueous solution phase onto an isolated binding site on a polyelectrolyte molecule. These thermodynamic parameters are obtained by fitting the lower half of the binding isotherms (actually $X<0.4$) to the theoretical formula (3), which is also derived from the original partition function.[15,18]

$$X = \frac{1}{2}\left[1 - \frac{1-s}{\sqrt{(1-s)^2+4s/u}}\right], \tag{3}$$

where $s=uKC_f$, or a kind of binding "pressure". Curve-fitting was carried out starting with an observed $C_f(0.5)$ and an assumed u, readjusting the two parameters until the best fit on a CRT display of a microprocessor was obtained. A small variation in the parameters (*ca.* 20% in u or 5% in K) results in appreciable deviation from the experimental points. Use of lower half of binding isotherm may be justified because the electrostatic potential of the polymer remains nearly constant there by the ion-condensaion effect as depicted by Manning.[19] So the Ising's theory may be applied. The calculated isotherms are plotted with dashed lines in Figs. 2 and 3. Deviation from the theoretical values at $X>0.5$ indicates a break down of the ion-condensation effect due to decreased ionization of the polyelectrolyte below a critical value predicted by the Manning's theory as a result of surfactant-binding. Electrostatic potential now is so much reduced on binding surfactants that a sort of negative cooperativity decreases actual binidng less than a theoretical one. The values of K and u are summarized in Table 1. It is a remarkable feature that u is insensitive to changes in added salt concentration as well as in temperature, albeit u contains substantial amount of uncertainty (some 30%). The insensitivity of u to added salt may be expected because a surfactant ion is discharged on binding and aggregation on polymer should be little influenced by changes in ionic atmosphere.[15] The aggregation is mainly promoted by hydrophobic interaction which usually accompanies very little thermal changes leading to a very small temperature-dependence of u values. If u is assumed to be constant then the observed variation in the binding isotherms is solely ascribed to the changes of K. The decrease in K with increasing C_a is evidently due to a diminished electrostatic potential at the polymer surface that is brought about by compression of electric double layer. Binding tendency is inversed, however, above $X=1$ where electric charges are accumulated on binding surfactant, while electric charges are reduced in the course of the first step binding. So the effect of added electrolyte on the second step binding is in the same direction as that for ordinary micelle formation in which electric charge is accumulated.

Table 1. Thermodynamic parameters

(1) Effect of added NaBr at 20 °C.

C_a/mM	20	50	100
u	200	150	150
K/M^{-1}	12	7.4	4.4

(2) Effect of temperature in 50 mM NaBr.

t/°C	20	40	50
u	150	150	150
K/M^{-1}	7.4	6.7	6.3

The values of K were calculated by using u and C_h instead of $C_f(0.5)$, where u and C_h are determined so that they give the best fit. C_h is usually about 10% smaller than $C_f(0.5)$.

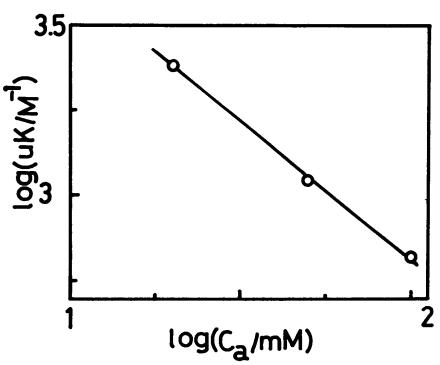

Fig. 4. Effect of added NaBr on binding affinity.

Temperature dependence of K is very small. van't Hoff plot gives an enthalpy change of the corresponding process -1.4 kJ mol^{-1} which may be a difference between exothermic discharging and endothermic rearrangement of hydration. The slightly negative enthalpy change suggests that some entropic effect also should contribute to promote the binding process.

Reciprocal of $K(K^{-1}=0.15$ M) is an equilibrium concentration that would be required to ensure a half-binding if the cooperativity were absent. In this context, it is easily understood why no binding is observed at such low C_f, *e.g.*, 0.1 mM. So it is stressed that the cooperativity is important for the binding process to appear in such a low equilibrium concentration.

A free energy of aggregation, or cooperativity, $\Delta G_u=-kT\ln(u)=-5kT$ is divided by a free energy of aggregation per methylene group, $\Delta\Delta G_u=-0.52$ kT/CH_2 which is half a difference of ΔG_u's between tetradecyltrimethylammonium and dodecyltrimethylammonium in their binding to DNA,[8] to result in $5/0.52=9.6$. It is interpreted that almost all methylene groups are in action to gain cooperativity.

In Fig. 4, a $\ln(uK)$ *vs.* $\ln(C_a)$ plot shows a good linearity with a slope$=-0.81$, which is roughly interpreted as a fraction of released counterions (Na^+) having been condensed around charged sites on polyelectrolyte, when a surfactant cation is bound there. The condensed counterions are replaced with bound surfactant thus maintaining nearly constant electrostatic potential until the critical linear charge density is attained.[7,19]

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