# Effect of Charge Density on the Cooperative Binding Isotherm of Surfactant Ion to Polyelectrolyte

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**Synopsis.** The binding isotherm of dodecyltrimethylammonium ion to partially hydrolyzed poly(potassium vinyl sulfate) was determined potentiometrically as a function of the average separation ($d$) between neighboring ionic groups. The cooperativity in binding process was found to decrease rapidly to about $d \approx 0.44$ nm and eventually disappear at $d \approx 3.7$ nm.

Recently, extensive studies have been carried out on the cooperative bindings of surfactant ions to a variety of polyions of both synthetic and biological origins.[1] A highly cooperative character of such bindings is well-demonstrated by the binding isotherm which rises steeply in quite narrow range of equilibrium surfactant concentration.[1] At constant salt concentration, the cooperativity in binding process increases regularly with increasing hydrophobicity of the surfactant ion.[2–5] The increase in salt concentration causes the increase in the surfactant concentration at which the steep rise in binding isotherm occurs.[2,3,6–8] In addition, the cooperativity parameter which characterizes the steepness of the binding isotherm is found to depend markedly on the local structure of polyions even for a given surfactant ion.[4,9] So far as we know, however, the study on the charge density dependence of the binding cooperativity is limited only to anionic polysaccharide systems.[4] These observations prompted us to study further the effect of polyion charge density on the cooperative binding of surfactant ion to a simple synthetic polyelectrolyte. In this paper is described the potentiometric determination of the binding isotherms of dodecyltrimethylammonium ion (DTA$^+$) to partially hydrolyzed poly(potassium vinyl sulfate) (PVS).

## Experimental

Polyions of varying charge density were prepared by hydrolyzing PVS (Wako Pure Chemical Industries Ltd. Degree of esterification 0.969) in 0.2 mol dm$^{-3}$ HCl for several hours at 80 °C. After cooling, the reaction mixture was titrated with NaOH in order to estimate the degree of hydrolysis ($\theta$). The resulting solution was dialized against water and passed through a cation-exchange resin in the H$^+$ state. The polyion concentration ($C_p$) expressed in molarity of ionic groups was determined by titrating the polyacid with KOH. Dodecyltrimethylammonium bromide (purity> 99%, Tokyo Kasei Kogyo Co., Ltd.) was used without further purifications. The binding isotherms of DTA$^+$ to polyions were determined potentiometrically at 25 °C by using the following poly(vinyl chloride)(PVC) membrane electrode.

Ag–AgCl| 1 mol dm$^{-3}$ $NH_4NO_3$ Agar bridge| Reference solution (1 mmol dm$^{-3}$ DTABr)| PVC membrane| Sample solution (PVS, $C_p$: DTABr, $C$: KCl, $C_s$)| 1 mol dm$^{-3}$ $NH_4NO_3$ Agar bridge| Ag–AgCl

The preparation of PVC membrane electrode is described elsewhere.[10] The electromotive force ($E$) of the cell was measured with a Takeda Riken vibrating reed electrometer TRB 411 to a precision of 0.1 mV. All measurements were conducted at 25 °C under the conditions of constant $C_p$ and $C_s$.

## Results and Discussion

In the absence of polyion, the semilogarithmic plot of $E$ vs. $\log C$ gave a straight line with a slope of 58.3 mV down to $1 \times 10^{-5}$ mol dm$^{-3}$ DTABr. This calibration curve permits the estimation of an equilibrium surfactant ion concentration ($C_f$) which leads immediately to the binding degree of the surfactant ion defined by $\beta = (C - C_f)/C_p$. In Fig. 1 is shown the binding isotherm of DTA$^+$ to PVS of varying charge density. At lower values of $\theta$, the binding isotherm is seen to rise steeply in narrow range of $C_f$ as low as $10^{-4}$ mol dm$^{-3}$. This characteristic behavior which is common to all surfactant ion-polyion systems[1] reflects the strong cooperativity in binding process arising from the hydrophobic interaction among bound surfactant ions. This in turn suggests that the average distance ($d$) between neighboring ionic groups of the polyion is small enough to permit the overlapping of the hydrocarbon chains of the bound surfactant ions. As would be expected, however, the slope of the binding isotherm decreases successively with increasing value of $\theta$, suggesting the rapid decrease in the binding cooperativity. In Fig. 1 is also shown the calculated binding isotherm based on the following equations.[11]

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

$$y = C_f/(C_f)_{0.5} \tag{2}$$

where, $(C_f)_{0.5}$ refers to the value of $C_f$ at half binding and $u^{-1}$ to a cooperativity parameter which is defined as an equilibrium constant for the following process.[11]

$$(00) + (11) \rightleftharpoons 2(01) \tag{3}$$

Here, (00) and (11) represent the neighboring unbound ionic site pair and bound site pair, respectively. The estimation of $u$ can easily be attained by using a curve fitting method except for $\theta = 0.93$ where the experimental value of $(C_f)_{0.5}$ is unavailable. In this case, however, the binding process becomes virtually statistical, i.e., $u = 1$. The theoretical isotherm for $\theta = 0.93$ in Fig. 1 is based on the statistical binding model with the intrinsic binding constant ($K$) of 500 mol$^{-1}$ dm$^3$. As is clearly shown in Fig. 1, the calculated isotherm reproduces well the experimental curves at higher

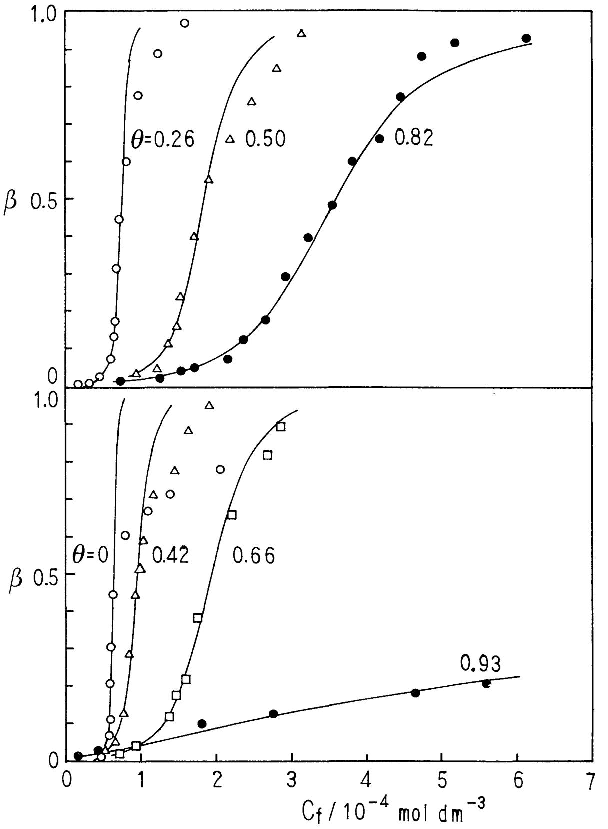

Fig. 1. The binding isotherms of $DTA^+$ to partially hydrolyzed PVS with varying values of $\theta$ at 25 °C. $C_p=2.00\times10^{-4}$ mol dm$^{-3}$. $C_s=1.00\times10^{-2}$ mol dm$^{-3}$. Solid lines show the calculated isotherms from Eq. 1 with the values of $u$ given in Table 1.

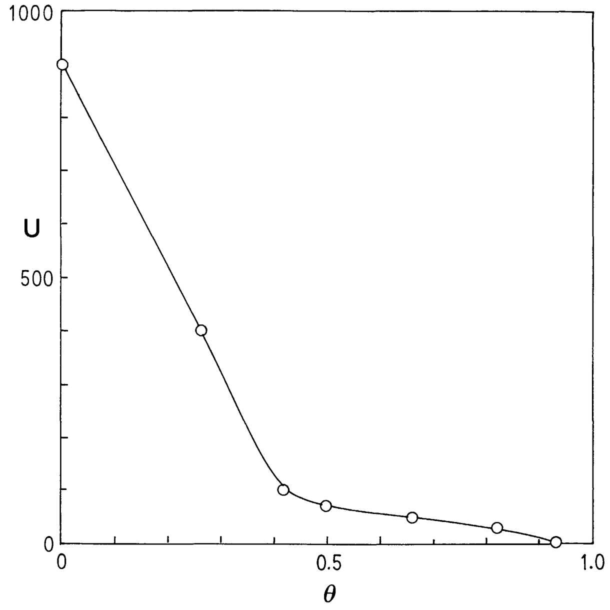

Fig. 2. A plot of $u$ against $\theta$.

Table 1. The Estimated Values of $u$ at Varying Values of $\theta$

| $\theta$ | $d$/nm | $u$ |
|---|---|---|
| 0 | 0.26 | 900 |
| 0.26 | 0.35 | 400 |
| 0.42 | 0.45 | 100 |
| 0.50 | 0.52 | 70 |
| 0.66 | 0.77 | 50 |
| 0.82 | 1.45 | 30 |
| 0.93 | 3.73 | 1 |

values of $\theta$ than 0.6. However, the agreement is limited to about $\beta$=0.5 at lower values of $\theta$. In this connection, it is worth to remember that Eq. 1 is based on an one-dimensional lattice model in which the nearest neighbor interaction at a constant surface potential is taken into account. Therefore, the observed deviations between theoretical and experimental binding isotherms at lower values of $\theta$ are supposed to arise partly from the contraction of the polymer chain which leads to the deviation from linearity, since an increase in $\beta$ is necessarily accompanied by an increase in overall hydrophobicity of polymer molecule. It should be noted that an increase in $\theta$ causes a regular increase in the fraction of hydrophilic OH groups on the polymer chain. At higher values of $\theta$, therefore, it is highly probable that the polymer chain takes comparatively extended conformation even at higher values of $\beta$. The decrease in the surface potential arising from the increase in $\theta$ may also be responsible for this phenomenon. Figure 2 shows the plot of $u$ vs. $\theta$. The numerical values of $u$ are summarized in Table 1 together with the average separation between neighboring ionic groups for a fully extended chain. It can immediately be seen that the value of $u$ decreases rapidly to about $\theta$=0.4 and goes gradually to unity at $\theta$=0.93. The values of $\theta$=0 and 0.4 correspond to $d$ of 0.26 and 0.44 nm respectively. This in turn suggests that the value of $d$ less than 0.44 nm is essential for the appearance of the strong hydrophobic interaction between neighboring bound surfactant ions. In fact, the slope of $u$ vs. $d$ curve in this range is as large as $-4000$ nm$^{-1}$. Another interesting feature of Fig. 2 is the gradual decrease in $u$ above 0.4. It should be noted that the small but appreciable cooperativity is still observed even at $\theta$=0.82 ($d$=1.45 nm). We must keep in mind that $d$ defined here represents an average distance between neighboring ionic groups based on the assumption of uniform distribution of ionic groups on the polymer chain. In fact, the probability of persisting the ionic site pair with an initial separation of 0.26 nm at $\theta$=0 is given by $(1-\theta)^2$ provided that the hydrolysis reaction proceeds in a random fashion. Thus the observed cooperativity at higher values of $\theta$ will reasonably be attributed partly to the presence of ionic sites which locate closely with each other and take part in effective hydrophobic interaction. The critical distance $d$=3.73 nm ($\theta$=0.93) at which the surfactant ion binding becomes statistical is comparable with twice the chain length of a fully extended dodecyl chain (ca. 1.8 nm).

The present result demonstrates well the importance of the charge density or the separation between neighboring ionic groups in determining the cooperativity of the surfactant ion binding to polyions. A similar result was obtained by Malovikova et al.[4] for the bindings of *N*-tetradecylpyridinium ion to pectate and pectinate of varying charge density. They estimated the values of $u$ of 250, 26, 12, and 12 at $d$=0.44, 0.56, 0.82, and 1.49 nm in 0.01 mol dm$^{-3}$ NaCl solutions, respectively. This trend is just the same as what is found for the present experiment, though the magnitude of $u$ is somewhat different from that given above because of the difference in the hydrophobicity of the surfactant ion. It their study of the cooperative bindings of dodecyl- and tetradecyltrimethylammonium (DTA$^+$ and TTA$^+$) ions to carboxylic polyelectrolytes, Hayakawa et al.[9] obtained the values of $u$ of 600 for TTA$^+$–polyacrylate ($d$=0.25 nm), 30 for TTA$^+$–carboxymethylcellulose ($d$=0.54 nm), 500 for DTA$^+$–polyacrylate, and 650 for DTA$^+$–dextran sulfate ($d$=0.26 nm) in 0.01 mol dm$^{-3}$ NaCl solutions, respectively. These results are also in accord with the prediction based on the charge density consideration. As is pointed out by them, however, additional factors such as chain flexibility and hydrophobic character of repeating unit should be taken into account for the clear understanding of the cooperative interaction between surfactant ion and polyion.

## References

1) E. D. Goddard, *Colloids Surfaces,* **19**, 301 (1986).
2) K. Hayakawa, J. P. Santerre, and J. C. T. Kwak, *Biophys. Chem.,* **17**, 175 (1983).
3) A. Malovikova, K. Hayakawa, and J. C. T. Kwak, *J. Phys. Chem.,* **88**, 1930 (1984).
4) A. Malovikova, K. Hayakawa, and J. C. T. Kwak, ACS Symp. Ser. No. 253, 225 (1984).
5) I. Satake, K. Hayakawa, M. Komaki, and T. Maeda, *Bull. Chem. Soc. Jpn.,* **57**, 2995 (1984).
6) K. Hayakawa and J. C. T. Kwak, *J. Phys. Chem.,* **86**, 3866 (1982).
7) K. Hayakawa and J. C. T. Kwak, *J. Phys. Chem.,* **87**, 506 (1983).
8) K. Shirahama, H. Yuasa, and S. Sugimoto, *Bull. Chem. Soc. Jpn.,* **54**, 375 (1981).
9) K. Hayakawa, J. P. Santerre, and J. C. T. Kwak, *Macromolecules,* **16**, 1642 (1983).
10) T. Maeda, M. Ikeda, M. Shibahara, T. Haruta, and I. Satake, *Bull. Chem. Soc. Jpn.,* **54**, 94 (1981).
11) I. Satake and J. T. Yang, *Biopolymers,* **15**, 2263 (1976).