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The Cooperative Binding Isotherms of Sodium Alkanesulfonates to Poly(1-methyl-4-vinylpyridinium chloride)

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Synopsis. Binding isotherms of nonane-, decane-, and undecane- sulfonate ions to poly (1-methyl-4-vinylpyridinium chloride) were determined by using nitrobenzene-membrane electrode. It was shown that an increase in alkyl chain length is accompanied not only by a rapid increase in the cooperativity parameter but by a regular decrease in an equilibrium surfactant concentration at half binding.

Recently, much attention has been paid to the potentiometric determination of the cooperative binding isotherms of the surfactant ion to polyions such as ionic polypeptide,[1,2] synthetic polyelectrolyte,[3–7] polysaccharide,[5–8] and DNA.[9] In all cases, the binding isotherm has been found to rise steeply in quite narrow range of the equilibrium surfactant concentration. It is now well recognized that the hydrophobic interaction among the bound surfactant molecules plays an important role in determining the nature of the cooperative binding isotherm. In order to make this point clear, we studied in this communication the effect of the surfactant chain length on the cooperative binding isotherm of sodium alkanesulfonate to poly (1-methyl-4-vinylpyridinium chloride) (PVMP) in the presence of added salt.

Experimental

Sodium alkanesulfonates (SAS) with carbon atoms (n) of 9, 10, and 11 were synthesized from the alkyl bromides purified by vacuum distillation.[10] The products were purified by the recrystallization from water, then from methanol and finally by extraction with petroleum ether for 20 h. PVMP was prepared by quaternization of poly (4-vinylpyridine) with methyl bromide.[11] The product was then converted to the chloride through dialysis against NaCl solution. An infrared spectrum showed that virtually all of the pyridine moiety was quaternized. The concentration (C_p) of PVMP in molarity of ionic groups was determined by titrating the corresponding polybase with HCl.

The binding isotherm of SAS to PVMP was determined potentiometrically at 25 °C by using the following cell. Reference electrode (Ag-AgCl)| NH_4NO_3 agar bridge| Reference solution (SAS, C_r)| Nitrobenzene (DTAAS, 1×10^{-4} mol dm^{-3})| Sample solution (PVMP, C_p; SAS, C; NaCl, C_s)| NH_4NO_3 agar bridge| Reference electrode (Ag-AgCl) where DTAAS denotes an ion exchanger, dodecyltrimethylammonium alkanesulfonate, and C_r and C the concentrations of SAS in reference and sample solutions, respectively. The concentrations of PVMP and NaCl were kept constant throughout whole experiments. The electromotive force (E) of the cell was measured with an Orion digital pH meter model 701 A with an accuracy of ±0.1 mV.

Results and Discussion

Prior to the measurements on PVMP solutions, the membrane electrode was calibrated with solutions of SAS. In the absence of PVMP, a plot of E *vs.* log C gave a straight line with a slope of 58.6 mV for n=9, 58.8 mV for n=10, and 59.7 mV for n=11, respectively. The linear relation was found to hold in the concentration range above 2×10^{-5} mol dm^{-3} for n=11 and 10, and 2×10^{-4} mol dm^{-3} for n=9. These calibration curves permit the determination of an equilibrium surfactant concentration (C_f) in solution of SAS with PVMP. The degree of binding of the surfactant ion by PVMP (β) can then be given by $\beta=(C-C_f)/C_p$.

The binding isotherms of SAS to PVMP thus determined are shown in Fig. 1. In conformity with the results obtained for a variety of surfactant ion-polyion systems,[1–9] the binding isotherm rises steeply in narrow range of C_f, reflecting the highly cooperative nature of the binding process of alkanesulfonate ion to PVMP. An important feature of Fig. 1 is the striking effect of the surfactant chain length on the critical range of C_f where the steep rise in binding isotherm occurs. Indeed, the successive decrease in n causes approximately four-fold increase of the value of C_f at β=0.5. Moreover, the steepness of the binding isotherm tends to decrease regularly with decreasing alkyl chain length. According to the theoretical treatment of the surfactant ion-polyion interactions, the surfactant ion is considered to cluster side by side onto the ionic groups of the polyion.[1] Hence, the regular dependence of the cooperativity on alkyl chain length may reasonably be ascribed to a change in hydrophobic interaction among the bound surfactant ions.

The cooperative binding isotherm in excess salt solution can well be described by the following expressions.[1]

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

$$KuC_f(\beta=0.5) = 1 \tag{2}$$

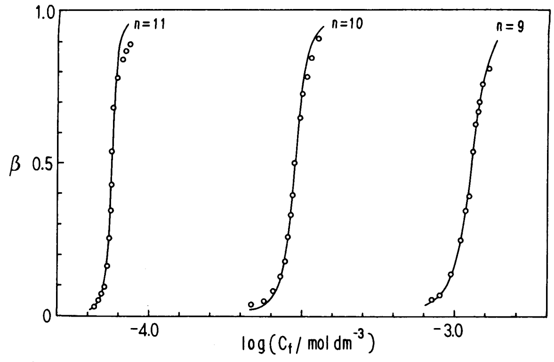

Fig. 1. The binding isotherms of alkanesulfonate ions to PVMP at 25 °C. $C_p=2.55\times10^{-4}$ mol dm^{-3}, $C_s=2.12\times10^{-2}$ mol dm^{-3}. ○, observed; solid line, calculated isotherm from Eq. 1 with u=220 for n=9, 480 for n=10, and 2000 for n=11, respectively.

Here, y refers to $C_f/[C_f(\beta=0.5)]$, K is the apparent binding constant of the surfactant ion to a site which has two unoccupied neighbors, and $K u$ is that to a site which has one or more occupied neighboring sites, respectively. Equation 1 can easily be rearranged to

$$2\beta - 1 = u^{1/2}(y-1)[\beta(1-\beta)/y]^{1/2}. \qquad (3)$$

This equation implies that the plot of β *vs.* $(y-1)[\beta(1-\beta)/y]^{1/2}$ gives a straight line with a slope of, $u^{1/2}/2$. As is shown in Fig. 2, such a plot gives in fact a straight line over a wide range of β. A least squares treatment leads to the most reliable value of the cooperativity parameter, u, of 220 for $n=9$, 480 for $n=10$, and 2000 for $n=11$, respectively. The calculated binding isotherms from Eq. 1 with the values of u so determined are shown in Fig. 1. In all cases, the agreement is satisfactory up to about $\beta=0.8$. As may be expected, the value of u increases rapidly with increasing alkyl chain length. This, in turn, suggests that the hydrophobic interaction among the bound surfactant ions is of primary importance in determining the cooperativity of the binding process of a homologous series of surfactant ions to a given polyion. An interesting comparison may be made here among the values of u for surfactant ions with the same alkyl chain length. For example with sodium decyl sulfate, the value of u was found to be 77 for helical poly(L-ornithine),[1] 161 for poly (D,L-ornithine),[1] and 26 for a copolymer of diallyldimethylammonium chloride and sulfur dioxide.[3] In the case of cationic surfactants, the value of u was estimated to be 40 for decylammonium chloride in a helical poly (L-glutamic acid) solution[2] and 200 for 1-decylpyridinium bromide in a sodium poly (vinyl sulfate) solution.[4] These observations indicate that the cooperativity parameter depends also on the polyion conformation as well as the hydrophobic character of the polyion residue.

According to Eq. 2, the logarithm of C_f ($\beta=0.5$) is anticipated to depend linearly on n, since an increment in $-RT \ln Ku$ per CH_2 group represents the free energy of transfer, w, of a methylene group from aqueous medium to the surfactant ion cluster on the polyion. Indeed, the plot of $\ln[C_f(\beta=0.5)/\text{mol dm}^{-3}]$ *vs.* n gives a straight line with a slope of -1.36 which corresponds to w of -3370 J mol^{-1} at 25 °C. The fact that the estimated value of w is comparable to that of -3700 J mol^{-1} from aqueous medium to liquid hydrocarbons[12] reflects well the hydrophobic character of the bound surfactant ion cluster on the polyion chain. In their study of the cooperative binding isotherms of dodecyl- and tetradecyltrimethylammonium ions to alginate, pectate, and carboxymethylcellulose, Hayakawa *et al.*[7] obtained the values of w of $-(3150—3330)$ J mol^{-1} at 30 °C. Thus, the local environment around the alkanesulfonate ions bound to PVMP is supposed to be similar in its hydrophobicity to those around the alkyltrimethylammonium ions bound to the ionic polysaccharides.

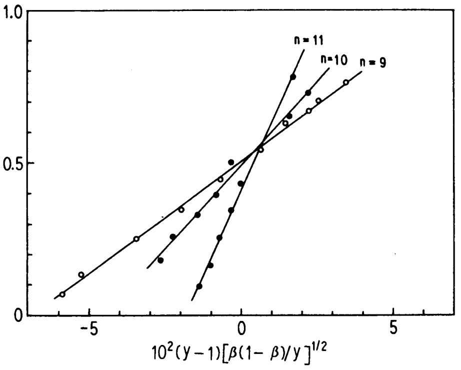

Fig. 2. Plots of β *vs.* $(y-1)[\beta(1-\beta)/y]^{1/2}$.

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