Binding of Sodium Dodecyl Sulfate to a Polyelectrolyte Based on Chitosan

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Received October 5, 1992; Revised Manuscript Received April 14, 1993

ABSTRACT: The binding behavior of sodium dodecyl sulfate (SDS) to cationic chitosan in free solution is described. Binding isotherms were determined potentiometrically. The results are rationalized by a cooperative binding model for a heterogeneous polyelectrolyte with ionic sequences and nonionic sequences. A theoretical expression for the binding isotherm of a random copolymer is obtained by using Lifson's sequence-generating function (SGF) method. The same binding constant K for chitosan with various degrees of N-acetylation (da) was estimated for the presented model calculation.

Introduction

Chitosan, partially deacetylated chitin, is a binary polysaccharide of 2-acetamido-2-deoxy-β-D-glucopyranose (GlcNAc) and 2-amino-2-deoxy-β-D-glucopyranose (GlcN) residues. At acidic pH values, the GlcN unit forms a cationic site, and chitosan may then be soluble in aqueous solution, depending on the degree of N-acetylation (da). The cationic polymer can then be considered as a heterogeneously structured polyelectrolyte. Chitosan is also a plentiful, highly versatile biopolymer, under consideration for a number of applications.[1]

It is well-known that the binding of ionic surfactant to a polyelectrolyte of opposite charge is highly cooperative. The nature of the binding and of the structural effects of the macromolecular chain as well as of the surfactant have been systematically studied for a number of systems.[2-5] Theoretical treatments of this subject generally follow the Zimm–Bragg theory, based on a simple Ising model.[6,7] Most applications have been directed to homogeneous polyelectrolytes with contiguous binding sites, where good agreement between experiment and theory is achieved. This model is derived on the assumption that cooperative interactions are confined to those of the nearest neighbors and that the lattice dimension is effectively infinite.[8] Therefore, in the case of a heterogeneous polyelectrolyte with nonionic sequences, this model is not appropriate since end effects are ignored.

In this work, we investigate the binding of an anionic surfactant, sodium dodecyl sulfate (SDS) to chitosan in free solution. The binding data were then analyzed with a cooperative model incorporating the end effects. The interaction between SDS and those polymers with various da allows us to study the influence of macromolecular chain structure on the binding process.

Experimental Section

Chitosan was obtained by the heterogeneous hydrolysis of chitin with 50% aqueous NaOH at 100 °C. Powdered crab shell chitin, from Sigma Chemical Co. and of the same lot as used previously,[9] was partially N-deacetylated by single and repeated 2-h treatments to prepare samples of different da. For high N-deacetylation, the partially N-deacetylated chitin was further treated homogeneously in solution.[10] Three samples, from each respective step, were used to prepare the chitosan hydrobromide salt by following the procedure of Domszy and Roberts.[11] The degree of N-acetylation was then determined by acid–base titration (da = 0.08, 0.16, 0.24). The da = 0.08 is the sample prepared by homogeneous N-deacetylation. The molecular weights and polydispersity of samples da = 0.16 and 0.24 are M_w = 4.0 and 1.9 and M_w/M_n = 1.3 and 2.1, respectively, as previously described.[9] The binding of surfactant by polyelectrolyte is essentially independent of the molecular weight of the polymer above a certain value.[12,13] The reagent-grade sodium dodecyl sulfate and dodecyltrimethylammonium bromide were obtained from Fluka Chemical Co. and used as received.

For the salt additive, a desired amount of NaBr was first dissolved in distilled water to prepare the stock solution. Dilute and unbuffered polymer solutions (about 10^{-4} mol/L (M) of the GlcN residue) were prepared by dissolving the chitosan hydrobromide in the NaBr aqueous solution. Stock solutions of surfactants of desired concentration were also prepared in the NaBr aqueous solution without buffer. Mixing was carried out by gradually adding a surfactant stock solution to a polymer solution. The final concentration of chitosan was about 5×10^{-5} M, with a pH of 4.2. The SDS concentration was always well below its critical micelle concentration (cmc = 8.2 mM at 25 °C[14]). The final mixed solutions were shaken at 25 °C for 1 week before measurement.

The binding isotherm of dodecyl sulfate anions to chitosan polycations in aqueous solution was determined potentiometrically at 25 °C by using the following cell:

reference electrode (Ag–AgCl)|3 M NH_4NO_3 agar bridge|test solution|PVC membrane|reference solution (5×10^{-4} M, SDS)|3 M NH_4NO_3 agar bridge|reference electrode (Ag–AgCl)

The electromotive force (emf) of the cell was measured with an Orion 701 A digital electrometer to an accuracy of 0.1 mV and monitored with a chart recorder. A surfactant selective electrode was constructed by using a poly(vinyl chloride) based membrane with a carrier complex prepared from sodium dodecyl sulfate and dodecyltrimethylammonium bromide.[15] The electrode shows Nernstian response for the dodecyl sulfate anion down to 2×10^{-5} M of SDS solution, as shown in Figure 1.

Results and Discussion

Binding Isotherms. Figure 2 shows the binding isotherms of surfactant, as the plot of the fractional binding saturation β versus the concentration of free surfactant, in dilute solutions of chitosans with different da. The binding was found to take place at very low concentrations of SDS. The steep rise reflects the highly cooperative nature of the binding process which is attributed to the contribution of hydrophobic interactions among bound surfactant.

We can express the fractional saturation β on the basis of the simple Ising model,[16] by the following relation

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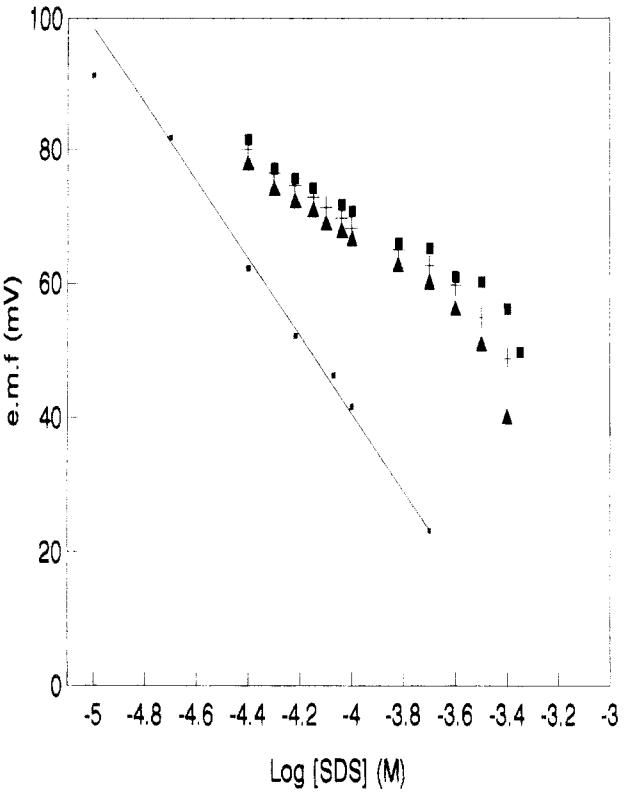

Figure 1. Response of the surfactant selective electrode to SDS at 25 °C. The solid line indicates the calibration in 20 mM aqueous NaBr solution without chitosan. Points ■, +, and ▲ refer respectively to chitosans with da = 0.08, 0.16, and 0.24. The concentration of chitosans is 0.1 g/L of chitosan hydrobromide in 20 mM of aqueous NaBr solution.

$$\beta = \{1 + (KwC_s - 1)/[(1 - KwC_s)^2 + 4KC_s]^{1/2}\}/2$$

$$(C_s)_{0.5} = (Kw)^{-1} \qquad (1)$$

$$(d\beta/d \ln C_s)_{0.5} = w^{1/2}/4$$

where $(C_s)_{0.5}$ is the concentration of free surfactant at the half-bound point ($\beta = 0.5$), K represents the equilibrium constant for the formation of the initial binding of surfactant with a cationic chitosan site, w is the extent of cooperativity, and Kw is the equilibrium constant for the binding to a site adjacent to an occupied site. By using K and w as two adjustable parameters, the theoretical curve was calculated and presented as the solid line in Figure 2. The binding equilibrium constant $Kw = 2.23 \times 10^4$ M^{-1} and the cooperativity parameter $w = 23$ are determined by the best fit for the data points of chitosan with da = 0.08. The experimental isotherms are in good agreement with that predicted for the region where $\beta < 0.2$. However, the agreement is unsatisfactory for the heterogeneously structural polyelectrolyte as the nonionic residue (GLcNAc) content increases. In the cases of da = 0.16 and da = 0.24, the isotherms indicate a considerable deviation of the theoretical predictions from the experimental data.

To study the ionic component of the polyelectrolyte–SDS interaction, we measured the binding of the polymers and SDS in NaBr solutions. The binding isotherms for chitosan of da = 0.08 at various NaBr concentrations are shown in Figure 3. Increasing the concentration of added salt results in a shift of the binding region to higher free surfactant concentrations because the polymer charge is screened by the counterion. The fact that the steepness of the isotherms does not change indicates that the cooperativity is independent of the added salt concentration.

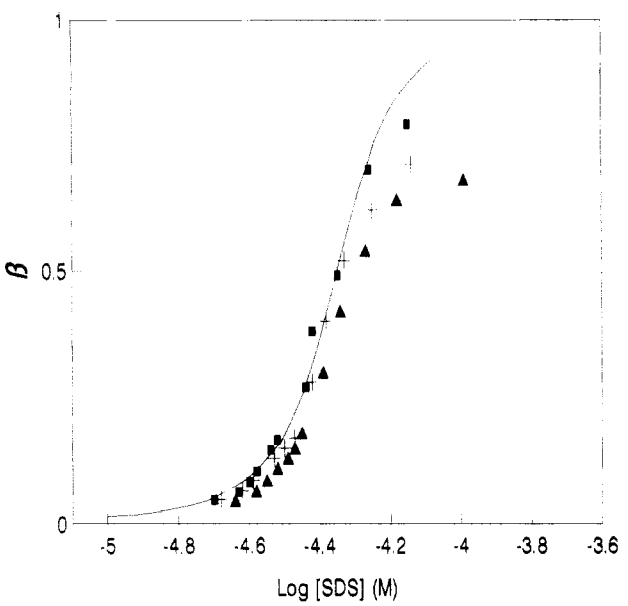

Figure 2. Binding isotherms of chitosans by SDS in the aqueous solutions of chitosan hydrobromide containing 2 mM NaBr: da = (■) 0.08, (+) 0.16, (▲) 0.24. Theoretical predictions are calculated from eq 1: solid curve, $Kw = 2.23 \times 10^4$ M^{-1}, $w = 23$. Kw and w are determined from the data of da = 0.08 by the least squares procedure in ref 17.

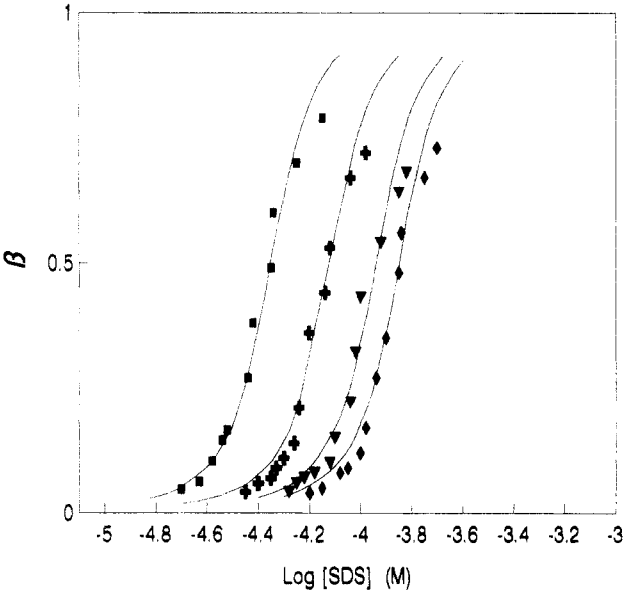

Figure 3. Binding isotherms of SDS to chitosan (da = 0.08) in aqueous NaBr solution and curves calculated from eq 1: [NaBr] = (■) 20, (+) 50, (▼) 100, (◆) 150 mM.

Cooperative Binding to a Random Copolymer. The matrix method is a standard technique for modeling macromolecular binding involving homopolymers. For many simple models, one can easily obtain analytic formulas to describe the thermodynamic behavior exactly.[18] The matrix method treatment of binding to copolymer, however, suffers from computational complexity since a large transfer matrix is required to account for the polymer sequence. The sequence generating function (SGF) method developed by Lifson[19] offers an alternative and provides a generally more applicable approach than the matrix method. There have been several extensions of the SGF method for theoretical treatments of complicated macromolecular binding systems.[20,21]

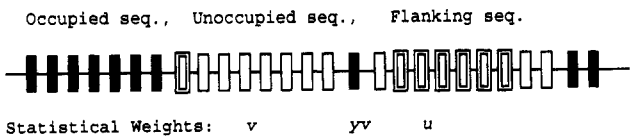

Figure 4. Schematic representation of the molecular chain of the heterogeneous polyelectrolyte. Statistical weights refer to the individual chain unit: v, unoccupied site; yv, occupied site; and u, flanking site.

The SGF approach involves constructing partition functions for a defined sequence and then combining these partition functions into a divergent generalized partition function for the system, by way of generating functions. The partition function represents a summing of all the microscopic states of binding with the polymer chain. To model the binding system of a surfactant on a heterogeneous polyelectrolyte, we consider here a copolymer composed of binding sequences and flanking sequences. In this model, the ligand cannot occupy the flanking sequence; the binding chain units exist either in an unoccupied state or in an occupied state. The polymer chain is taken as a linear array of occupied sequences, unoccupied sequences, and flanking sequences, as shown in Figure 4.

Let u be the statistical weight of the flanking sites. Because there are two states of binding chain units, we assign v as the statistical weight of the unoccupied sites, and the occupied states are weighted as yv, by introducing a factor y. Consequently, $y = KC_s$; here K and C_s are the same as those terms given in eq 1. Bound ligands on adjacent sites can interact cooperatively. Additionally, a statistical weight factor w is assigned to such arrangements. The SGFs for these three states of polymer chain sequences are then defined as

$$\mathbf{U}(x) = \sum_{i=1}^{\infty} u^i x^{-i} = u/(x-u) \qquad \text{(flanking sequences)}$$

$$\mathbf{V}(x) = \sum_{i=1}^{\infty} v^i x^{-i} = v/(x-v) \qquad \text{(unoccupied sequences)} \tag{2}$$

$$\mathbf{W}(x) = 1/w \sum_{i=1}^{\infty} (wyv)^i x^{-i} \qquad \text{(occupied sequences)}$$
$$= yv/(x-wyv)$$

Following the Lifson[19] approach, we array the SGFs in a matrix $\mathbf{M}$ to construct the overall partition function. The matrix $\mathbf{M}$ is

$$\mathbf{M} = \begin{bmatrix} \mathbf{O} & \mathbf{V} & \mathbf{W} \\ \mathbf{U} & \mathbf{O} & \mathbf{W} \\ \mathbf{U} & \mathbf{V} & \mathbf{O} \end{bmatrix} \tag{3}$$

which presents all possible alternations of different sequences $\mathbf{U}$, $\mathbf{V}$, and $\mathbf{W}$. By introducing eq 3 into the determinant equation $|\mathbf{I}-\mathbf{M}| = 0$ where $\mathbf{I}$ is the unit matrix, the secular equation for this system is given by

$$f(x) = x^2 - (u + v + yvw)x + yv(u+v)(w-1) = 0 \tag{4}$$

For a polymer chain having N units, the overall partition function of the binding system can be written as $Z = x_1^N$ when N approaches infinity. The quantity x_1 represents the contribution of each chain sequence to Z. Here, x_1 is the larger root of eq 4. The fractional binding saturation

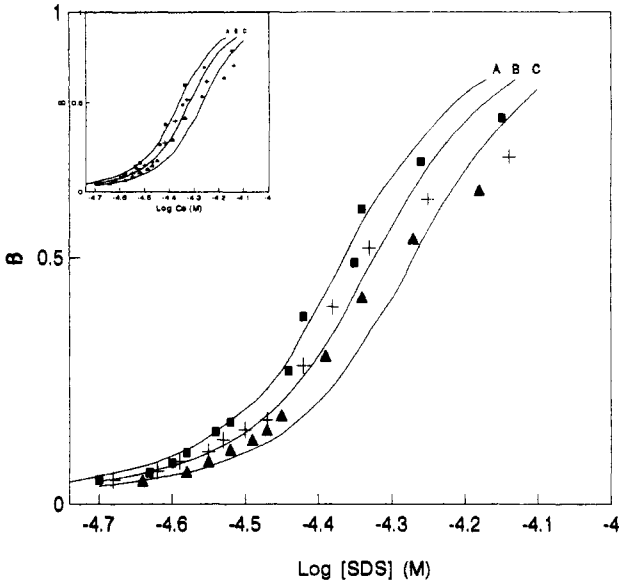

Figure 5. Binding isotherms of SDS to chitosans: data denoted as in Figure 2, with da = (■) 0.08, etc. The curves are calculated from eq 8: u_o = (A) 0.08, (B) 0.16, (C) 0.24. All calculated are for K = 1050 M^{-1} and w = 24.

β can be expressed as the derivative

$$\beta = (\partial \ln x/\partial \ln C_s)_{x=x_1} \tag{5}$$

Differentiating x in eq 4 with respect to C_s and introducing β give the binding equation

$$\beta = \frac{KC_s wvx_1 - KC_s v(u+v)(w-1)}{(u+v+KC_s wv)x_1 - 2KC_s v(u+v)(w-1)} \tag{6}$$

Solving eq 4 gives

$$x_1 = \{(u+v+KC_s vw) + [(u+v-KC_s vw)^2 + 4KC_s v(u+v)]^{1/2}\}/2 \tag{7}$$

where u is a constant and v is a function of C_s and K in this binding system. Setting $u = u_o$ and $v = v_o$ at the initial binding stage ($\beta = 0$) and then substituting $u = u_o$ and $v = v_o/(1 + KC_s)$ into eqs 6 and 7 yield

$$\beta = \frac{KC_s wv_o\rho - KC_s v_o(1+KC_s u_o)(w-1)}{(1+KC_s u_o + KC_s wv_o)\rho - 2KC_s v_o(1+KC_s u_o)(w-1)} \tag{8}$$

where

$$\rho = (1+KC_s)x_1$$
$$= \{(1+KC_s u_o + KC_s v_o w) + [(1+KC_s u_o - KC_s v_o w)^2 + 4KC_s v_o(1+KC_s u_o)]^{1/2}\}/2 \tag{9}$$

The statistical weights u_o and v_o account for the relative mole fractions of nonionic and ionic polymer chain units. When $u_o = 0$ and $v_o = 1$, eq 8 reduces to the binding equation for a homopolymer system, which is identical to eq 1 derived from the Zimm–Bragg theory.

Effect of da on the Binding Isotherms. For the binding system of SDS to partially N-acetylated chitosan polyelectrolyte, the uncharged GlcNAc residues are equivalent to flanking sequences and the degree of N-acetylation can be considered as the u_o value in eq 8. By introducing the da values determined by titration, we further examine the experimental data of this binding system, as shown in Figure 5. The theoretical curves in good agreement with the data points in the binding region of $\beta < 0.2$ are calculated according to eq 8, by using two parameters: K

= 1050 M^{-1} and $w = 24$. The same K and w values are used to approximate the experimental points for chitosans with da = 0.08, 0.16, 0.24. The binding degree β seems to be overestimated by eq 8 in the high binding region ($\beta > 0.5$). Satake and Yang[7] have pointed out that the binding constant K will be a function of the electrostatic potential at the polymer surface. As β approaches unity, the electrostatic potential can be reduced by the ion condensation and the assumption of a constant K in this model is no longer valid, which may explain the overestimation of β.

The end effect in the copolymer binding system can be identified by the comparison of these isotherms. As u_0 becomes larger, the slope of each isotherm curve decreases, suggesting that the end effect of flanking sequences results in less cooperative interaction. This model shows that the decrease in binding interaction with the increase in da mainly results from the less cooperative interaction caused by the end effects. The hydrophobic interaction is forbidden between the isolated GlcN residues separated by GlcNAc sequences.

The electrostatic interaction between the SDS anion and GlcN cation, which plays an important role in surfactant binding, has been demonstrated in Figure 3. The charge density of the polyelectrolyte is a determinant parameter when the influence of ionic interactions on the binding process is considered.[3] The same initial binding constant K, which was found for each of the systems, indicates that, in the case of the chitosans studied here, the contribution of the charge density variation may not be high enough to influence the effective potential at the polymer surface. However, we cannot further study this effect by using the potentiometric technique, because the highly N-acetylated chitosan salts are insoluble in water. Also these molecular chains are difficult to saturate, because saturation takes place at a concentration in excess of the experimentally determinable range. It should be noted that a phase separation occurs at approximately $\beta = 0.6$ and is being further investigated in this binding system.

In the cases of chitosans with da = 0.16 and da = 0.24, the upward deviation of data points below $\beta = 0.5$ in Figure 5 indicates that these binding systems are more highly cooperative than those predicted. This is possibly due to the slightly more blockwise distribution of GlcN residues than for a random copolymer since the theoretical curves are derived on the basis of a random copolymer. The reasonable fit found for the binding system of da = 0.08 indicates that the lowly N-acetylated chitosan prepared under homogeneous conditions is a random copolymer. This suggestion coincides with those of X-ray and NMR studies.[22,23]

Conclusion

A cooperative mode of binding is inferred for the aqueous system of cationic chitosan and anionic surfactant, sodium dodecyl sulfate. The cooperative binding occurs over the same concentration range of surfactant, for chitosans of da = 0.08, 0.16, and 0.24, but the cooperative nature decreases with increasing da. The lower cooperative interaction is due to the more nonionic GlcNAc sequences separating the neighboring ionic sites, which results in less hydrophobic interactions between bound surfactants. The binding behavior in the da = 0.08 system is consistent with the theoretical model based on a random copolymer, indicating the random structure of the lowest N-acetylated chitosan prepared under homogeneous conditions. In the cases for da = 0.16 and 0.24, the binding saturation is higher than the value calculated for the binding to random copolymer, which implies the blockwise distribution of ionic GlcN sequences in these chitosans prepared under heterogeneous conditions. The contribution of blocky structure and the stiffness of the chitosan molecular chain[24] to the local potential for electrostatic interaction may also explain why these bindings occur over the same surfactant concentration.

Acknowledgment. The support of the Ministry of Education, Republic of China, is gratefully acknowledged.

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