

## Letters

### Formation of Polyelectrolyte-Micelle Complexes

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Polyelectrolytes may bind to oppositely charged micelles to form soluble complexes. The onset of complexation is known to obey an empirical rule connecting the surface charge densities of the polyion and the micelle with the ionic strength. We argue that this restricts severely the types of viable statistical theories of complexation. A scaling analysis rationalizes the empirical law and shows which dimensionless groups are unimportant at the onset of complexation.

Polyelectrolytes are known to form soluble complexes with oppositely charged micelles (both spherical and rodlike<sup>1-5</sup>). Under a wide variety of conditions, the onset of complexation conforms to a simple empirical law discovered by Dubin et al.<sup>1-5</sup>

$$\sigma\nu/I^{1/2} = \text{constant} \quad (1)$$

This expression relates the charge density  $\sigma$  of the micellar surface (or number of elementary charges per unit area) to the ionic strength  $I$  of the solution and the linear charge density  $\nu$  of the polyion (the number of elementary charges per unit length viewed along the polyion axis). In the experimental plots<sup>1-5</sup> of  $\sigma$  versus  $I^{1/2}$  and  $\nu$  versus  $I^{1/2}$ , the intercepts at zero ionic strength are not always precisely zero, but this complication will be disregarded here. In this Letter I point out the theoretical implications of eq 1 by using a scaling analysis in which I leave the precise mechanism of the complexation unspecified.

In refs 1-5 the curvature radii of the micellar surface are generally much larger than the Debye radius  $\kappa^{-1}$ , so we consider them irrelevant variables. Hence, the micellar surface is effectively planar. If it is uniformly (and positively) charged, its electric potential  $\phi$  is connected to

the surface charge density  $\sigma$  via Gauss' law

$$\left. \frac{d\psi}{dX} \right|_{\text{surface}} = -4\pi Q\sigma\kappa^{-1} \quad (2)$$

Here, we have introduced the dimensionless variables  $\psi \equiv q\phi/k_B T$  and  $X \equiv \kappa x$  with  $q$  the elementary charge,  $T$  the temperature, and  $x$  the distance from the surface. The right-hand side of eq 2 expresses a dimensionless charge density: the Bjerrum length  $Q \equiv q^2/Dk_B T$  is a basic electrostatic scale for the solvent of permittivity  $D$ . If the solution contains an excess of monovalent electrolyte, the Debye length  $\kappa^{-1}$  is given by  $\kappa^2 = 8\pi QI$ , where  $I$  denotes the ionic strength.

If we furthermore suppose that the Debye length is the sole scale relevant to the decay of the electrostatic interactions, then eq 2 shows that the potential must have the general form

$$\psi = \psi(X, Q\sigma\kappa^{-1}) \quad (3)$$

Note that the boundary condition at infinity ( $\psi = 0$ ) does not introduce a dependence of  $\psi$  on an additional dimensionless quantity.

A flexible polyanion is attracted by the micellar surface. The potential energy of one of its Kuhn segments of length  $A$  is simply  $-\nu A\psi$ . If the attraction is strong enough, the micelle and the polyanion will form a complex. This may be viewed as a case of polymer adsorption in which the micellar surface induces a polymeric bound state. For a polyion consisting of very many links ( $N$ ), a dimensionless and unnormalized probability  $P$  of the chain starting at  $X$  and ending at  $X'$  will have the form<sup>6</sup>

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(3) Dubin, P. L.; Thé, S. S.; McQuigg, D. W.; Chew, C. H.; Gan, L. M. *Langmuir* **1989**, *5*, 89.

(4) Dubin, P. L.; Chew, C. H.; Gan, L. M. *J. Colloid Interface Sci.* **1989**, *128*, 566.

(5) Dubin, P. L.; Curran, M. E.; Hua, J. *Langmuir* **1990**, *6*, 707.

$$P(X, X'; N) = e^{\mu N} \eta(X) \eta(X') \quad (4)$$

depending on the eigenvalue  $\mu$ . In a bound state the two ends of a very long chain are statistically independent so that the probability factorizes. In addition, an integration of  $P$  over  $X$  and  $X'$  yields the partition function  $Z(N)$  to within a constant. For a long chain the free energy equal to  $-k_B T \log Z$  must be extensive, i.e. proportional to  $N$ .

As usual the square of the eigenfunction  $\eta(X)$  is proportional to the segment density<sup>6</sup> so it is a functional of the energy of interaction of a Kuhn segment

$$\eta = \eta(X; A\kappa; \mu; \nu A\psi(X, Q\sigma\kappa^{-1})) \quad (5)$$

Note that we expect  $\eta$  to depend on  $A\kappa$  also, since the Kuhn length<sup>9</sup> is the relevant scale pertaining to the statistics of the chain.

A complex, that is an adsorbed state, exists<sup>6</sup> whenever the eigenvalue  $\mu$  is larger than zero. This possibility is investigated by solving the eigenvalue equation for  $\eta$  which satisfies the boundary conditions  $\eta = 0$  at  $X = 0$  and  $X = \infty$ . Our interest centers on the onset of adsorption which corresponds to the limit  $\mu \rightarrow 0$ . Furthermore, by analogy with our WKB treatment,<sup>8</sup> we expect that  $\eta$  must obey a global condition involving an integration over  $X$ . Applying these arguments to eq 5, we get a general relation valid at

the onset of complexation

$$F[A\kappa, \nu A G(Q\sigma\kappa^{-1})] = 0 \quad (6)$$

in terms of two unspecified functions  $F$  and  $G$ .

The empirical eq 1 now imposes a drastic simplification of eq 6:

(I)  $G(z) = z$ ; in other words the potential  $\psi$  is proportional to the charge density  $\sigma$ . This implies that the Debye-Hückel approximation must be valid.

(II) The variable  $A\kappa$  does not play a role and must be considered irrelevant. This means the chain statistics do not determine the onset of complexation, at least to a first approximation.

(III) Because eq 1 imposes  $\sigma \sim \kappa$ , any other dimensionless group depending on the ionic strength is irrelevant, e.g., one containing the excluded volume between two segments if we take this possibility into consideration.

In previous theories<sup>7,8</sup> various assumptions have led to explicit expressions for the functions  $F$  and  $G$ . One premise is that the diffusion limit of the general recursion relation<sup>6</sup> for the probability function  $P$  is applicable. This is legitimate for external fields that are weak. Actually the micellar surface attracts a segment of the polyanion quite strongly, so this assumption may be the source of an artificial dependence of  $F$  on  $A\kappa$ , ultimately causing refs 7 and 8 to conflict with eq 1. Granting the validity of eq 1, a much more complete theory will have to account for the conclusions reached in this work.

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(9) In our simplified picture we assume the Kuhn length  $A$  is independent of the ionic strength; this is reasonable at high salt concentrations.<sup>1-5</sup>