

IMPACT OF NONUNIFORM COUNTERION CONDENSATION ON THE GROWTH OF LINEAR CHARGED MICELLES

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At low ionic strength counterions cluster nonuniformly around a linear, highly charged micelle. The micelle is regarded as a finite line charge with relatively fewer counterions condensing on the two ends. The end contribution to the electrostatic free energy is positive, so that the micelles shorten upon addition of simple salt to the solution.

It is reasonable to approximate a linear charged micelle by a finite line charge when the ionic strength is low so the Debye screening length exceeds the micellar diameter. For a line considerably longer than the Debye length the electric double layer is virtually homogeneous along its midsection. The electrostatic potential exerted by the line charge weakens close to the ends, the regions of nonuniformity being about a Debye length long. As has recently been pointed out [1], this end effect implies that a linear micelle should grow as we add salt to the solution. The electrostatic interaction between micelles also displays an end contribution that has been elaborated in ref. [2].

The reasoning above is unequivocal for a micelle of low charge density when the Debye–Hückel approximation is legitimate. On the other hand, if the charge density is high, counterions are expected to cluster around the micelle. I erroneously argued that one need then merely renormalize the charge density in the end effect [1, 2]. In this note I reexamine the problem pointing out that counterion condensation may be inhomogeneous enough to change the sign of the end effect. Instead of growing, highly charged micelles should shorten upon increasing the salt concentration.

Ideally, one would like to investigate the potential exerted by a finite line charge with the help of the nonlinear Poisson–Boltzmann equation or a similar continuum approximation. Analytical calculations on short rods do exist [3] but none on the electric inhomogeneity of finite rods much longer than the Debye

radius. In the work by Safran et al. on polyions without salt [4], each charged rod is viewed as consisting of three independent and separate entities namely a cylinder without end effects and two hemispherical caps. In our view this is a severe approximation to an inherently nonlinear problem. In a globally correct analysis Ramanathan and Woodbury showed that counterions condense on a rod a Debye length long, to about the same extent as on an infinite line charge of similar charge density [3]. Nevertheless, the counterion distribution may be nonuniform. This effect is here investigated for finite long lines. Counterions are postulated to be condensed inhomogeneously onto the finite line charge while the effective or renormalized electrostatic interactions are treated in the Debye-Hückel approximation. Although not exact, our results should be close to lead terms within a Poisson-Boltzmann theory at low ionic strength.

The micellar solution has a permittivity D and a temperature T . A relevant electric scale is the Bjerrum length $Q = q^2/Dk_B T$ in terms of the elementary charge q . A 1-1 electrolyte of concentration c is added to the solution in excess so that the Debye screening length λ equals $(8\pi Qc)^{-1/2}$. Whether or not counterions cluster around a (finite) line is determined by the charge density parameter $\bar{\xi}$, which is the linear charge density ν of the micelle scaled by Q . If the length L of the line charge is much larger than the Debye length counterions should condense [5, 6] on its midsection when $\bar{\xi} > 1$. Near the two ends the counterion distribution is nonuniform, so we introduce the renormalized or effective charge density $\xi(s) \equiv Q\nu_{\text{eff}}(s)$, which is a function of s the micellar contour distance from one end. In the midsection we set $\xi(s) = 1$ in accordance with the usual theory of counterion condensation [5, 6]. By balancing the electrostatic forces against the decrease in entropy arising from the nonuniform distribution we can ascertain $\xi(s)$ close to the ends of the micelle.

Let point P be at a distance ρ from the line charge with s being the projection of P onto the line. The electrostatic potential $\psi(\rho, s)$ at P is given by

$$\frac{q|\psi(\rho, s)|}{k_B T} = \int_0^L dt \frac{\xi(t) \exp\{ -[(t-s)^2 + \rho^2]^{1/2}/\lambda \}}{[(t-s)^2 + \rho^2]^{1/2}}. \quad (1)$$

This is a superposition of Debye-Hückel potentials exerted by the renormalized charge distribution. In reality the micelle has a nonzero radius a , so it makes sense to adopt the line charge approximation only when $\lambda \gg a$. The fraction of condensed counterions is proportional to $\bar{\xi} - \xi(s)$, which gives rise to an ideal mixing entropy. We may write for the chemical potential of a condensed counterion situated on the micellar surface

$$\mu_i = \mu_0 + k_B T \log[\bar{\xi} - \xi(s)] - q|\psi(a, s)| = \text{constant}, \quad (2)$$

where μ_0 is an unimportant constant. Since the system is in equilibrium, the

chemical potential is independent of s . Eq. (2) expresses a Boltzmann distribution. It must conform to the following boundary condition: if $L \gg \lambda \gg a$ at low ionic strength, $\xi(s)$ is unity and $q|\psi|/k_B T \approx 2 \log(\lambda/a)$ along the midsection defined by $\lambda \leq s \leq L - \lambda$. In effect the midsection has the electric properties of an infinite line charge [5, 6].

In order to assess eq. (2) analytically I shall focus on the limit of very high charge density ($\bar{\xi} \gg 1$). Although the regime $1 \leq \bar{\xi} \leq 2$ is of particular interest, it is outside the scope of this note. We want to solve the integral equation (2) to leading order regarding the quantity $w \equiv \log(\lambda/a)$ as a large parameter. Eq. (1) is then rewritten as

$$\frac{q|\psi(a, s)|}{k_B T} \approx \begin{cases} [w + \log(s/a)]\xi(s) + \int_a^{s+\lambda} dt \frac{\xi(t) - \xi(s)}{|t-s|} & \text{for } a \leq s < \lambda, \\ 2w\xi(s) + \int_{s-\lambda+a}^{s+\lambda} dt \frac{\xi(t) - \xi(s)}{|t-s|} & \text{for } \lambda \leq s \leq \frac{1}{2}L. \end{cases} \quad (3a)$$

$$(3b)$$

A zero-order solution to eqs. (2) and (3) is derived by setting the integrals in eq. (3) equal to zero. Then for $s \geq \lambda$, $\xi(s)$ must be equal to unity because of the boundary condition mentioned above. Next, eqs. (2) and (3a) show that $\xi(s)$ remains of the order of unity along the entire contour. Hence we may set $\log[\bar{\xi} - \xi(s)] \approx \log \bar{\xi} - \xi(s)/\bar{\xi}$ in eq. (2) so that the ideal mixing term is negligible compared with the potential because $w \gg 1$. Accordingly, the zero-order effective potential is virtually constant along the micellar length. The zero-order solution to eq. (2) is simply

$$\xi_0(s) = \begin{cases} \frac{2w}{w + \log(s/a)}, & a \leq s \leq \lambda, \\ 1, & \lambda \leq s \leq \frac{1}{2}L, \end{cases} \quad (4)$$

with $\xi_0(s) = \xi_0(L - s)$ for $a \leq s \leq L - a$.

It is now possible to prove that the integrals in eq. (3) may be disregarded in the calculation of the micellar end effect. For instance, let us focus on the case $a \leq s \leq \lambda$. The function $\xi_0(s)$ is monotone decreasing or constant in the interval $a \leq s \leq \frac{1}{2}L$, which permits us to establish the following bounds:

$$0 \leq \int_a^s dt \frac{\xi_0(t) - \xi_0(s)}{s-t} \leq \int_a^s dt \frac{\xi_0(a) - \xi_0(s)}{s-a} = \xi_0(a) - \xi_0(s) \leq 1,$$

$$\begin{aligned}
0 &> \int_s^{2s} dt \frac{\xi_0(t) - \xi_0(s)}{t-s} > \int_s^{2s} dt \xi_0'(s) = -\frac{\xi_0^2(s)}{2w}, \\
0 &\geq \int_{2s}^{s+\lambda} dt \frac{\xi_0(t) - \xi_0(s)}{t-s} \\
&> 2w \int_0^{\log(\lambda/s)} d\mu \{ [w + \mu + \log(2s/a)]^{-1} - [w + \log(s/a)]^{-1} \} \\
&= -\mathcal{O}(w^{-1} \log^2(\lambda/s)).
\end{aligned}$$

The last inequality is obtained via the substitutions $t = s(1+x)$ and $\mu = \log x$ and the fact that $\log(1+x) \leq \log(2x)$ for $x \geq 1$. Hence in eq. (3a) the absolute magnitude of the integral is smaller than the zero-order term by a factor ranging from about $w^{-2} \log^2(\lambda/s)$ to w^{-1} . In other words, in a large section of the interval $a \leq s \leq \lambda$, eq. (4) represents the leading solution to our integral equation. As s tends to a , eq. (4) is not very accurate but the relative effect of this region diminishes as w increases. Therefore, the integrals calculated below should be estimates correct to the leading order. A similar error analysis applies to eq. (3b).

In order to establish the impact on growth, we need to calculate the electrostatic free energy of the micelle (the entropy from the nonuniform counterion distribution is a higher order term). Within the limitations outlined above, it is given by

$$\begin{aligned}
\frac{f}{k_B T} &= \frac{1}{2} Q^{-1} \int_0^L \int_0^L ds dt \frac{\xi(s) \xi(t) \exp(-|s-t|/\lambda)}{[(s-t)^2 + a^2]^{1/2}} \\
&\approx \frac{1}{2} Q^{-1} \int_a^{L-a} ds \xi_0(s) \frac{q|\psi(a,s)|_0}{k_B T} \approx w Q^{-1} \int_a^{L-a} ds \xi_0(s). \quad (5)
\end{aligned}$$

This consists of an extensive part proportional to L and a positive end effect, which can be expressed as

$$\frac{f_{\text{end}}}{k_B T} \approx 2w Q^{-1} \int_a^\lambda ds [\xi_0(s) - 1] \approx \frac{\lambda}{Q} \quad (6)$$

to leading order. The integral is evaluated by the substitution $s = a \exp(w-x)$ and an asymptotic expansion for large w . Note that eq. (6) bears a minus sign [1] when the micelle has a low charge density ($\bar{\xi} < 1$).

Eq. (6) implies a “growth” law [1]

$$n \log L = \text{constant} + \frac{\lambda}{Q}, \quad (7)$$

where n is a constant related to the degrees of freedom the amphiphiles lose on micellization. This expression states that a very highly charged micelle decreases in length as salt is added to the solution. This is caused by counterions clustering nonuniformly around the micelle: relatively fewer counterions condense on the ends than on the midsection. Our arguments should be valid when the ionic strength is low enough. We require that the two dimensionless parameters $\bar{\xi}$ and $w = \log(\lambda/a)$ be substantially greater than unity although this regime may not be easily accessible in experiments. Sometimes micelles do shorten with increasing ionic strength [7] but under conditions that do not seem to correspond to the requirements posed here.

One premise in our simplified analysis is that the form of the entropy of the sheath of condensed counterions is ideal (see eq. (2)). This is actually quite plausible from a physical point of view. The external field exerted by the bare, highly charged line is so high that it induces a dense clustering of counterions. In this limit, density fluctuations are very small, so that the entropy reduces to a functional of the single particle density. At low ionic strength the removal of even one counterion from one of the ends entails an increase in the free energy many times $k_B T$. On a more formal level Fixman [8] in an exhaustive analysis has concluded that the Poisson–Boltzmann equation is accurate at low salt concentration. Hence, within our context, a Boltzmann ansatz like eq. (2) is reasonable.

Of course, it remains to be seen how well the simple theory based on eq. (2) can stand up to a more exacting, nonlinear analysis. Furthermore, it is of great interest to discover under what conditions the end effect (eq. (6)) changes sign. This probably happens when the charge parameter $\bar{\xi}$ is in between unity and two.

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