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Ion Specificity of Micelles Explained by Ionic Dispersion Forces

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We consider the origin of the ion specificity found for the physical properties of micelles. Ions in solution have a polarizability different from that of the surrounding water. The excess polarizability is different for different ions and gives rise to ion specific dispersion forces toward, or away from, interfaces. We show that ionic dispersion forces have important influences on self-consistent potentials, ion distributions, and surface adsorption excess per headgroup on micelles.

I. Introduction

Micelles and microemulsions have important industrial and household applications, and it is crucial to understand their underlying physical mechanisms. Indeed, a theory of dressed micelles has been developed during the past decades^{1–7} which has been found to be in reasonable agreement with experiment.⁸ Ion binding comes out in terms of physisorption excess. However, there does not yet exist a predictive theory which can explain the counterion specificity found for the change of headgroup area with added salt, curvature at surfactant–water interface, aggregate interactions, and phase changes.^{9,10} Micelle growth is often attributed to Coulombic screening of the headgroup repulsion by counterions permitting tighter headgroup packing, but size and shape dependence also depend on the counterion.

For example, the surfactant didodecyltrimethylammonium bromide is soluble in water up to 10^{-4} M, beyond which it forms a lamellar phase. If bromide counterions are replaced with hydroxide, it is soluble and forms a clear solution up to 1 M. The degree of micellar dissociation $\beta = 1 - q$, where q is the fraction of “bound” charge, is phenomenologically extracted from conductance data. The result using bromide as counterion is very different from using acetate, butyrate, or formate.⁹ Chemical trapping has also been used to explore the differences between using bromide and chloride as counterion.^{11–13}

Clearly some kind of forces which are specific to each ion need to be included in any predictive theory.^{14,15} The

purpose of this work is to demonstrate the importance of consistently including previously neglected ionic dispersion forces acting between ions and the micelle surface. We treat the micelle as a dielectric sphere with radius given by experiment and surface charge given by the number of headgroups. Since the ions have a different polarizability than the surrounding water, the micelle will experience a dispersion potential toward, or away from, the charged dielectric sphere.

Although we limit ourselves here to the problem of specific ion effects in micelles, these effects also occur in a large number of biological applications^{16,17} where they are often called Hofmeister effects. In fact, all of biology and colloid science is haunted by unexplained specific ion effects. Another example is the surface tension of electrolyte solutions. According to the Onsager–Samaras theory¹⁸ the surface tension change with added salt should be the same for all 1:1 salt solutions. This is not what is seen experimentally;¹⁹ e.g., the surface tension change with added KBr is much larger than with added CH₃COOK. We recently showed that when ionic dispersion potentials acting between ions and interface are included consistently in the theory, ion specific results emerge naturally.²⁰ The extension to two interfaces is straightforward, and we have shown that these ionic dispersion potentials have profound effects on the double layer force between charged interfaces.²¹ We are finally able to understand why forces between charged interfaces can vary by as much as a factor 50 when the counterion is changed from bromide to acetate.^{10,22} Br[−], which is a highly polarizable ion, experiences strong repulsive dispersion forces away from a water–air interface. This explains the larger surface tension change with added KBr. Near a mica–water interface the dispersion force becomes highly attractive and the bromide ions are effectively driven very

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close to the positively charged interface. This is consistent with the observation that Pashley et al.²² had to postulate that roughly 90% of the bromide ions were "bound" to the double layer to explain their measured double layer force. This "binding" is due to physisorption excesses in the same way as in the micelle theory.¹ One should note that the inclusion of ionic dispersion forces thus removes a very fundamental inconsistency between force measurements, where binding of the bromide ions had to be postulated, and the micelle picture. Acetate ions with approximately the same number of electrons as water are expected to have very little excess polarizability. Indeed, Pashley et al.²² found that they could readily explain the measured force without any assumptions of acetate counterions being "bound" to the surface.

The specific purpose of this work is to show how the previous work of Evans, Mitchell, and Ninham¹ can be extended to accommodate those specific ion effects that are related to ionic dispersion potentials. It is important to understand that it is inconsistent to neglect these dispersion potentials and that we can estimate their magnitude. In section II we first show how ionic dispersion potentials acting between an ion and the spherical micelle can be included consistently in the nonlinear Poisson–Boltzmann equation. We furthermore estimate the magnitude of these dispersion potentials. In section III we discuss how they influence ion distributions, surface adsorption excess/headgroup, and self-consistent potentials outside a cationic micelle. The surface adsorption excess per headgroup is found to be highly counterion specific and to a less extent co-ion specific. We also discuss the influence of number of headgroups, concentration, and magnitude of dispersion potentials on the ion specificity. Finally, in section IV we end with a brief summary and discussion of how ionic dispersion potentials will influence the general properties of micelles. This is a highly important issue that will be dealt with in more detail in the future.

We emphasize here that the dispersion potentials acting on ions are important, but they are not the full story. Other ion specific properties may also be important, such as ion size and the way ions affect the short-range structure of water.²³ We do not include these effects here, mainly because their effects are often not calculable with any certainty but also to demonstrate clearly how important the previously neglected dispersion potentials are.

II. Ion Specific Double Layer Theory Around a Spherical Micelle

We consider an aqueous solution of negatively charged anions and positively charged cations each with bulk concentration c and charge e outside a spherical cationic micelle. The self-consistent potential outside the charged sphere is found by solving numerically the nonlinear Poisson–Boltzmann equation,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) = -e(c_+ - c_-)/(\epsilon_w \epsilon_0) \quad (1)$$

with the ion concentrations given by

$$c_{\pm} = c \exp(-\beta[\pm e\phi + U_{\pm}(r)]) \quad (2)$$

Here $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, T is temperature, and ϵ_w is the dielectric constant of water (solution). Furthermore, ϕ is the self-consistent electrostatic potential experienced by the ions and $U_{\pm}(r)$ is the

interaction potential experienced by the ions. The purpose here is to demonstrate qualitative effects of including previously ignored ionic dispersion potentials between the ions and the interface (in general there will also be contributions from image potentials and, to a smaller degree, from ionic dispersion interactions between ions). Here we have included the dispersion potential that acts between an ion and the spherical interface. The boundary conditions follow from global charge neutrality. The first boundary condition is that the electric field vanishes at infinity faster than $1/r^2$. The second is that

$$(r_m + r_{\text{ion}})^2 \frac{d\phi}{dr_{r=r_m+r_{\text{ion}}}} = -Q_m/(4\pi\epsilon_0\epsilon_w) \quad (3)$$

Here we have made the plausible assumption that the ions cannot get any closer to the micelle surface than one ion radius (r_{ion}). Usually, the difference in ion size for similar ions is quite small, and to highlight the effects of dispersion potentials we take it to be the same for all ions (2 Å). The average area/headgroup, each taken to have a charge e , is equal to a . This means that the total charge on the micelle is equal to $Q_m = 4\pi\epsilon_r\epsilon_m^2/a$. The total number of headgroups N has been found to increase almost linearly above the critical micelle concentration with added monomers.²⁴ Typical values for a and r_m are given in Table 1 in ref 1. The fraction of "bound charge", which we take to be equal to surface adsorption excess near the spherical surface per headgroup, is

$$q = \frac{4\pi}{N} \int_{r_m+r_{\text{ion}}}^{\infty} dr r^2 (c_+ + c_- - 2c) \quad (4)$$

The nonretarded dispersion interaction between a point particle and a sphere can within the pair summation approximation (the Hamaker approach) be written

$$U_{\pm} = \frac{B_{\pm}}{(r - r_m)^3 [1 + (r - r_m)^3/(2r_m^3)]} \quad (5)$$

where the dispersion coefficient (B_{\pm}) will be different for different combinations of ion and spherical micelle. When retardation is neglected, we can calculate the dispersion coefficients (B_{\pm}) from the corresponding planar interface as a sum over imaginary frequencies ($i\omega_n = i2\pi k_B T n/\hbar$, where \hbar is Planck's constant)¹⁴

$$B_{\pm} = \sum_{n=0}^{\infty} \frac{(2 - \delta_{n,0})\alpha^{\pm}(i\omega_n)[\epsilon_w(i\omega_n) - \epsilon_{\text{oil}}(i\omega_n)]}{4\beta\epsilon_w(i\omega_n)[\epsilon_w(i\omega_n) + \epsilon_{\text{oil}}(i\omega_n)]} \quad (6)$$

We recently showed that the surface tension of different salts could be accommodated when ionic dispersion potentials were accounted for. For bromide and potassium we assumed that the values were $B_{\text{Br}^-} = 21 \times 10^{-50} \text{ N m}^3$ and $B_{\text{K}^+} = -5 \times 10^{-50} \text{ N m}^3$. Of course, the result was at high concentrations to some extent additive for the dispersion contributions, and it is not straightforward to obtain an unique set of dispersion coefficients. However, we keep these values for the purpose of demonstration. The increment of the refractive index of water when a salt solution is added is different for different salt solutions.²⁵ The refractive index of pure water is $n_w = 1.3333$; when 5 g/L of KBr is added, the refractive index increase is $\delta n = 6 \times 10^{-4}$. We know the mass of KBr (119.01 u) and can

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calculate the added concentration (c_{ion}). The sum of static excess polarizabilities for bromide and potassium can then be estimated from the following approximation

$$\epsilon(0) \approx \epsilon_w(0) + 4\pi c_{\text{ion}}(\alpha_+ + \alpha_-) \approx (n + \delta n)^2 \quad (7)$$

We find that the sum of static excess polarizability is $\approx 5 \text{ \AA}^{-3}$. We will for the sake of simplicity and demonstration here take the electron affinities (ionic resonance frequencies) to be the same for these ions (ω_0). We model the excess polarizability as

$$\alpha_{\pm}(i\omega_n) = \alpha_{\pm}(0)/(1 + \omega_n^2/\omega_0^2) \quad (8)$$

Obviously, within this approximation, and using the B values given above, the separation of the sum becomes trivial. We find that $\alpha_- = 6.6 \text{ \AA}^{-3}$ and $\alpha_+ = -1.6 \text{ \AA}^{-3}$. Using the experimental dielectric function for water²⁵ and solving the expression for B_{\pm} numerically at an air–water interface, we find that $\omega_0 = 2.23 \times 10^{16} \text{ rad/s}$. When we replace the air–water interface with “oil”–water (micelle in water), we need to estimate the optical properties of this “oil”. We will use a simple one oscillator model to describe this dielectric function,

$$\epsilon_{\text{oil}}(i\omega) \approx 1 + \frac{\epsilon_{\text{oil}}(0) - 1}{1 + \omega^2/\omega_{\text{oil}}^2} \quad (9)$$

where $\epsilon_{\text{oil}}(0)$ is the static dielectric function and ω_{oil} is a resonance frequency of the dielectric sphere. We take typical values of $\epsilon_{\text{oil}}(0)$ to range from 1.8 to 2.3 and typical values of ω_{oil} to range from 1×10^{16} to $3 \times 10^{16} \text{ rad/s}$. With these values we find that the dispersion coefficient for bromide varies from -10×10^{-50} to $10 \times 10^{-50} \text{ J m}^3$ and similar but smaller for potassium. Considering the many approximations used these values can obviously only give us an order of magnitude estimate. The point is that the dispersion coefficient at an “oil”–water interface has to be of the same order of magnitude as those near an air–water interface. Of course, this follows directly from Aveyard’s²⁶ measurements of the surface tension change of air–water ($\approx 1.36 \times 10^{-3} \text{ J m}^3 \text{ mol}^{-1} \text{ L}$ for KBr) and decane–water ($\approx 0.86 \times 10^{-3} \text{ J m}^3 \text{ mol}^{-1} \text{ L}$ for KBr) interfaces. The surface tensions changes with added salt of the “oil”–water interface is typically only slightly smaller in magnitude than the corresponding values for air–water interfaces (sometimes it even changes sign) reflecting the changes in dispersion forces that act on the ions.

III. Numerical Results for Adsorption Excess on Micelles

We solve the nonlinear Poisson–Boltzmann equation with the additional constraint that the system be overall charge neutral (with an accuracy better than 0.1%). The first example we consider is a micelle with radius $r_m = 21.7 \text{ \AA}$, 123 headgroups, and an average headgroup area of 48 \AA^2 . We choose 0.3 M which is a typical salt concentration in biological systems, and we consider three different cases: no ionic dispersion interaction (solid line); $B_+ = -5 \times 10^{-50} \text{ N m}^3$ and $B_- = 10 \times 10^{-50} \text{ N m}^3$ (dashed line); $B_+ = 5 \times 10^{-50} \text{ N m}^3$ and $B_- = -10 \times 10^{-50} \text{ N m}^3$ (dotted line). We can see in Figure 1 that there can easily be more than 40% ion specific changes in the self-consistent potential. There are similar large changes in the corre-

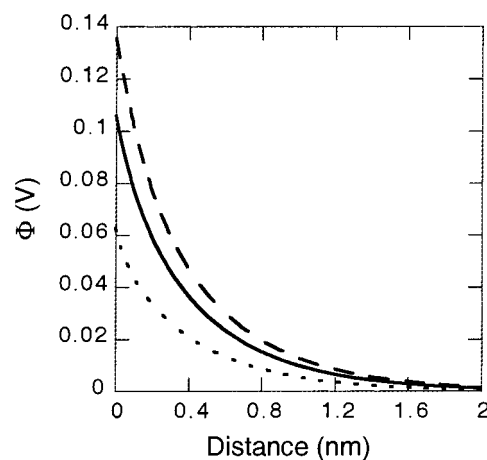


Figure 1. Ion specific self-consistent potentials (ϕ) versus distance from a micellar surface. Details are given in the text.

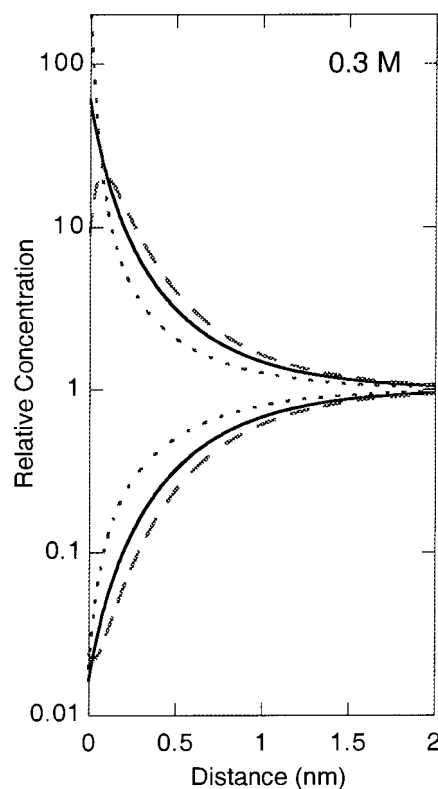


Figure 2. Ion specific self-consistent relative concentration profiles (c_{\pm}/c) as a function of distance from a micellar surface. Details are given in the text.

sponding relative concentration profiles (c_{\pm}/c) shown in Figure 2. The upper (lower) three curves are the counterion (co-ion) distributions. When the counterions for example experience an attractive dispersion interaction, there will be a large enhancement of the concentration close to the micellar surface and a corresponding depletion away from the surface. This offers an obvious explanation to the question why highly polarizable ions, such as bromide ions, sometimes behave as if they were “bound” to the surface. Hayter investigated micellar systems both experimentally and theoretically and found deviations from theory “for systems with a high concentration of added Br^- , for which polarizable effects such as specific adsorption (not included in the present theory) are expected to be important”.⁸ The same phenomena is found in surface force measurements,²² which could only be understood if bromide counterions were assumed to be “bound” to the

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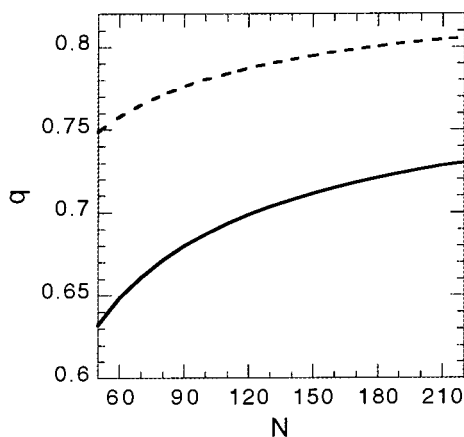


Figure 3. Ion specific surface adsorption excess/headgroup (q) on a micellar surface as a function of number of headgroups for fixed surface charge. Details are given in the text.

interface. Dubois et al.¹⁰ recently showed that the osmotic pressure and area/headgroup versus surfactant weight fraction are highly counterion specific. They found evidence that the bromide ions had to be considered to be “bound” to the “oil”–water interface by some “mechanism differing from electrostatics”. Indeed, they argued that the only possibility was by the “ionic strength dependent dispersion mechanisms”¹⁴ since “all other mechanisms would follow the mass action law and induce an increasing value of the area per polar head with dilution”.

In Figure 3 we consider the influence of ionic dispersion interaction on q , the adsorption excess/headgroup, for different sizes of the micelle for fixed surface charge. The area/headgroup is 50 Å, and we vary the number of headgroups from 50 to 220. The radius is given by $r_m = (Na/4\pi)^{1/2}$. We once again consider a 0.3 M salt solution and consider two cases: no ionic dispersion interaction (solid line); $B_+ = 5 \times 10^{-50}$ N m³ and $B_- = -10 \times 10^{-50}$ N m³ (dotted line). Regardless of the number of headgroups there is a large degree of ion specificity. Clearly, ionic dispersion potentials are important regardless of size. The influence of dispersion potentials will increase with decreasing surface charge. Outside a totally uncharged dielectric sphere a double layer is set up due to the unequal dispersion forces that act on cations and anions in exactly the same way as near an air–water interface.²⁰

It is experimentally well-known that the number of headgroups and area/headgroup changes with concentration, but for the sake of demonstration, and to highlight the underlying mechanisms, we here consider the hypothetical case when N and a are concentration independent. In Figure 4 we investigate q versus salt concentration for the same system that was used in Figures 1 and 2. At low concentrations electrostatics dominates, but there are still influences of ionic dispersion interactions. In the range from 1 mM to 0.3 M the effect of having attractive ionic dispersion potentials acting on the counterions is that q seemingly become less dependent on added salt. It is experimentally known that the value of q is fairly constant at low salt concentrations. However, at high salt concentrations the q values become very sensitive to changes in the dispersion potential that acts on the counterions. We see that q may even increase with added salt. Although we have here neglected differences in ion size and other sources of ion specificity, it is clear that there is a large degree of ion specificity due to ionic dispersion forces.

In Figure 5 we investigate how q depend on the magnitude of the ionic dispersion potentials, i.e., how q will change when we go from one pair of ions to another.

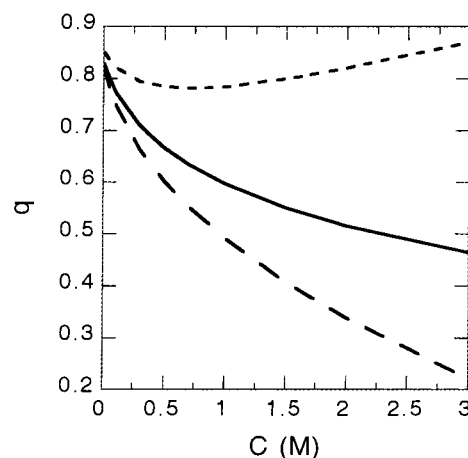


Figure 4. Ion specific surface adsorption excess/headgroup (q) on a micellar surface as a function of salt concentration. Details are given in the text.

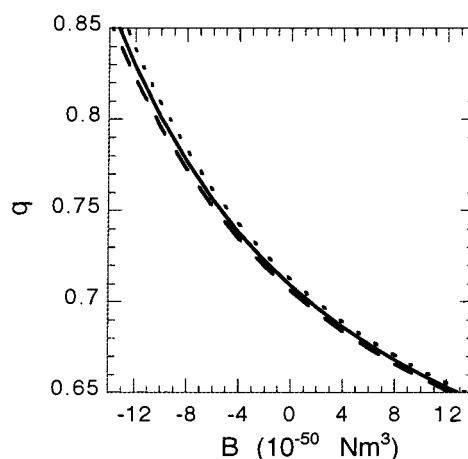


Figure 5. Ion specific surface adsorption excess/headgroup (q) on a micellar surface as a function of dispersion coefficient B_- (or dispersion potential) acting on the counterions. Details are given in the text.

We use the same data for the micelle as in Figure 1 and a salt concentration of 0.3 M. We consider three cases for the dispersion interaction that acts on the co-ions: no ionic dispersion interaction (solid line); $B_+ = 4 \times 10^{-50}$ N m³ (dashed line); $B_+ = -4 \times 10^{-50}$ N m³ (dotted line). An attractive force acting on the co-ions increase the value of q but to a much smaller degree than a corresponding force acting on the counterions. This of course is natural since there are so far fewer co-ions near the interface. The basic physics of cylindrical micelles and polyelectrolytes is the same as for spherical micelles and microemulsions. We can therefore use this figure also to understand why the osmotic pressure between polyelectrolytes is very counterion specific but quite insensitive to changes in co-ions.²⁷

IV. Conclusions

We have shown that ionic dispersion potentials have to be accounted for to obtain correct results for ion distributions outside micelles. When this is done properly, highly ion specific results are obtained, e.g., for surface adsorption excess/headgroup.

The meaning of ion binding to micelles is a physisorption excess, 80% for bromide and little for acetate. There need

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be no actual binding. Thus, force measurements where the fit to DLVO forces between cationic bilayers required more than 80% bound surface counterion for added KBr and no bound acetate in added CH₃COOK were fundamentally inconsistent. This inconsistency is removed when ionic dispersion potentials are included in the theory. Surface tension data at air–water and “oil”–water provide estimates of the dispersion coefficients, and consistency is required with measurements on micelles and forces between charged surfaces. In the earlier theory¹, which neglected specific ion effects, the optimal micelle (aggregation number) comes out from a balance between electrostatic energy against all other forces. The same is obviously still true after we have taken ionic dispersion potentials into account. This is something we will come back to. When the theory is done correctly, taking dispersion forces into account, we should finally be able to understand why for instance the optimal micelle size and critical micelle concentration depend on the supposedly irrelevant choice of counterion. This raises a very important point: measurements of ion binding to micelles

and for example Ca²⁺ to proteins, by for instance nuclear magnetic resonance experiments, use the phenomenological ion binding description. The interpretation assumes that the theory works; it does not and is going to be ion pair specific with background salt.

We finally note that detailed comparison with experiments can only be done if different ion sizes are accounted for. It is also important to consider dissolved gas²⁸ and the way dispersion forces are handled in the surface region. We have not presented the full picture here, but at the very least we have included important and previously neglected physics.

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