A Method for Direct Determination of the Prevailing Counterion Distribution at a Charged Surface

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The surface charge of an anionic or cationic monolayer at the air–water interface is compensated by the oppositely charged counterions that are either located within the diffuse layer or directly bound to the interface. In this paper we demonstrate that ellipsometric measurements allow a direct determination of the prevailing ion distribution. A simple analytical expression is derived, which can be used to retrieve the number of ions within the compact layer. This formalism is applied to the experimental data gained on aqueous alkyl pyridinium bromide solutions. The analysis of the experimental ellipsometric isotherm provides evidence for the existence of an ion condensation just before the cmc. The derived formalism relates ellipsometric signal with the surface charge and should be of utmost importance to discard or proove the recently introduced concept of fluctuation driven ion condensation at a charged surface.

1. Introduction

Electrostatic interactions are a central theme in colloidal and interface science.[1] The preferential adsorption of ionic amphiphiles at the air–water interface produces a surface charge that is compensated by the oppositely charged counterions. Their distribution is governed by two competing interactions: The electrostatic interaction leads to a condensation of counterions at the surface whereas the thermal motion favors a randomization of the ions.

The classical way to treat this problem is based on an analysis of the nonlinear Poisson–Boltzmann (PB) equation.[2–4] The amphiphilic monolayer is treated as a planar interface with a homogeneous charge density. The PB equation relates the surface charge density and the electric potential and yields the corresponding ion distribution. The PB theory is a mean field approach and describes successfully many experimental facts. However, close to the interface unrealistic results are predicted, a consequence of the assumption of point charges and the neglect of the discreteness of charges. A reasonable way to overcome this difficulty is the introduction of a compact layer of directly bound ions close to the interface, the so-called Stern layer.[5] The remaining crux is then an estimation of the amount of ions entering the compact layer, as most experimental techniques are unable to discriminate between directly bound and diffuse layer of ions.[6]

Recently, we could demonstrate that ellipsometry is sensitive to the prevailing ion distribution.[7] Ellipsometry is a well-established optical reflection technique that analyzes changes in the state of polarization upon reflection of light on a film covered surface.[8] These changes are expressed by the so-called ellipsometric angles that are in turn related to the overall reflectivity coefficient parallel and perpendicular to the surface. A good review reporting on recent development in this field with a special focus on colloidal science can be found in ref 9. Our experimental arrangement leads to certain peculiarities that are analyzed in this contribution. The major accomplishment is a derivation of a handy analytical formula relating the surface charge density and number of condensed counterions to the measured ellipsometric signal. This formula does not contain a free parameter and is tested on a set of experimental data that we recently published.

The results are of particular importance to experimentally proove or discard various new theories dealing with effects not captured on a mean field level. Lau et al. predict a fluctuation driven counterion condensation.[10,11] For a system consisting of a single charged surface and its oppositely charged counterions, Netz and Orland showed that a perturbative expansion about the mean-field PB solution breaks down if the surface charge is sufficiently high.[12] Thus, in this limit, fluctuation and correlation corrections are important and the mean-field picture must be modified.[13] To overcome this difficulty, a two-fluid model was proposed in ref 10, in which the counterions are divided into a free and a condensed fraction. The free counterions have the usual three-dimensional mean-field spatial distribution, whereas the condensed counterions are confined to move only on the charged surface and thus effectively reduce its surface charge density. The number of condensed counterions is determined self-consistently, by minimizing the total free energy, which includes fluctuation contributions. This theory predicts that if the surface charge density of the plate is sufficiently high, a large fraction of counterions is condensed. The result resembles features of a phase transition similar to the liquid–gas transitions.

The assessment of these theories requires reliable experimental data. These can be obtained by performing ellipsometric measurement on ionic soluble surfactants. The formula derived in this paper can be directly used to retrieve the number density of ions in the diffuse Stern layer from an experimental ellipsometric isotherm. The analysis is put in a simple mathematical framework. Hence, our contribution should be of great value for the experimentalist.

2. Background

2.1. Distribution of Counterions for Insoluble Ionic Surfactants. Consider a flat charged interface between air and an

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aqueous solution with a surface charge density σ. This situation can be obtained by nonsoluble adsorption layers of ionic surfactants. At temperature $T = 0$ all ions are condensed at the interface as a consequence of the electrostatic bindings. At room temperature the electrochemical potential μ_i of the ith ion is defined as $\mu_i = eZ\psi + k_BT \ln(n_i)$, where the first term is the electrostatic contribution (e = electronic unit charge, Z = valence, ψ = electric potential) and the second one (k_BT = thermal energy, n = number density) comes from the (ideal) entropy of the ions in the weak solution limit. In thermal equilibrium μ_i remains constant throughout the system. Consequently, each sort of ion i obeys a Boltzmann distribution in the solution. Recall that the combination of the Boltzmann distribution with the Poisson equation leads to a nonlinear second-order differential equation for the electric potential ψ:

$$\frac{\partial^2 \psi(z)}{\partial z^2} = -\frac{4\pi e}{\epsilon_w} Z \exp\left(\frac{-eZ\psi(z)}{k_BT}\right) \tag{1}$$

where ϵ_w is the dielectric constant of the aqueous solution and z is the distance to the interface.

The solution of eq 1 reveals the number density of the counterions as a function of the distance to the interface:

$$n(z) = \frac{1}{2\pi Z^2 l_B} \frac{1}{(z+b)^2} \tag{2}$$

The number density decays to zero algebraically with the characteristic Gouy–Chapman (GC) length $b = e/2\pi|\sigma|l = \epsilon_w k_BT/2\pi e|\sigma|$, where $l_B = e^2/\epsilon_w k_BT \approx 7$ Å is the Bjerrum length in water at room temperature. The GC length defines a sheath near the charged surface whithin most of the counterions are confined. The physical meaning of the Gouy–Chapman length becomes obvious by the integrated amount of counterions (per unit area) attracted to the surface from $z = 0$ to $z = b$, which is $-\sigma/2$. Namely, it balances half of the surface charge. Typically it is on the order of a few angstroms for $\sigma = e/100$ Å^{-2}. Note that the GC length is only a function of the surface charge density σ at room temperature.

2.2. Adsorption Layers Formed by Soluble Ionic Surfactants. Consider that the flat charged surface consists of an adsorbed layer of soluble ionic surfactants. The profile of the counterion distribution in the solution is decreasing with increasing depth until it reaches the concentration of the bulk. The situation is described by the Poisson–Boltzmann (PB) equation for a symmetric electrolyte solution:

$$\frac{\partial^2 \psi(z)}{\partial z^2} = -\frac{4\pi e n_0}{\epsilon_w} Z\left(\exp\left(\frac{eZ\psi(z)}{k_BT}\right) - \exp\left(\frac{-eZ\psi(z)}{k_BT}\right)\right)$$

$$= -\frac{8\pi e n_0}{\epsilon_w} Z \sinh\left(\frac{eZ\psi(\vec{r})}{k_BT}\right) \tag{3}$$

where n_0 is the bulk concentration. In the following derivation we insert explicitly $Z = 1$ for monovalent ions. Divalent ions have important consequences for example on the electrostatics of membranes. Most of those consequences go beyond the continuum approach of the PB theory and are discussed in refs 14 and 15.

For surface potentials less than 25 mV at room-temperature we can expand the right side of eq 3 to the first order in ψ:

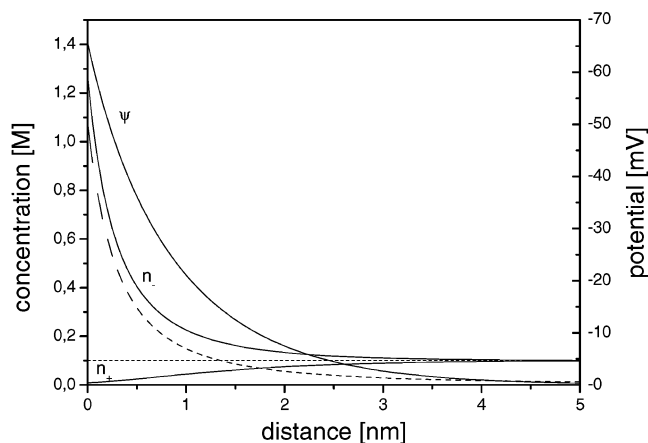$$\nabla^2 \psi(\vec{r}) = \lambda_D^{-2} \psi(\vec{r}) \tag{4}$$

Figure 1. Surface potential and concentration as a function of the distance to the air–water interface. A surface charge density of $\sigma = 0.385$ e/nm^2 and a bulk concentration of 100 mM was used for the calculations. The dashed line displays the distribution of the counterions under the assumption that there are no co-ions in the solution. In this concentration regime an influence of the co-ions on the prevailing distribution of the counterions is observed.

with

$$\lambda_D^{-2} = \sqrt{\frac{8\pi e n_0}{\epsilon_w k_BT}} \tag{5}$$

λ_D is the so-called Debye–Hückel screening length. The electrostatic interactions are exponentially screened and can be effectively neglected for lengths larger than the Debye–Hückel screening length. λ_D is at room temperature a function of the bulk concentration and on the order of a few nanometers for millimolar solutions.

A solution of the PB eq 3 for the potential ψ under the boundary condition of a flat charged membrane with a surface charge density σ at $z = 0$ and vanishing potential at $n(\infty) = n_0$ is[16]

$$\psi(z) = \frac{2k_BT}{e} \ln\left(\frac{1 + \gamma e^{-z/\lambda_D}}{1 - \gamma e^{-z/\lambda_D}}\right) = \frac{4k_BT}{e} \text{arctanh}(\gamma e^{-z/\lambda_D}) \tag{6}$$

where the parameter γ is the positive root of the quadratic equation

$$\gamma^2 + \frac{2b}{\lambda_D}\gamma - 1 = 0 \tag{7}$$

Hence γ depends on the relation between the Gouy–Chapman and the Debye–Hückel screening length and is consequently a function of the surface charge density σ and the bulk concentration n_0. The parameter γ adopts values between 0 and 1.

The situation is plotted in Figure 1 for a value of $\gamma = 0.56$, which corresponds to a surface charge density of $\sigma = 0.385$ e/nm^2 and a bulk concentration of $n_0 = 0.1$ M. There is a distinct difference in the distribution of the counterions with or without co-ions in the solution. At a similar surface charge density but an essentially lower bulk concentration of $n_0 = 0.3$ mM the parameter γ is 0.9. The result of the calculations are shown in Figure 2. In this case the counterion distribution is not influenced by the presence of the co-ions. For values of $\gamma > 0.8$ the distribution of the counterions can be described in the same fashion for Gibbs and Langmuir layer. It is therefore justified to use eq 2 for the number density as a function to the distance to the surface.
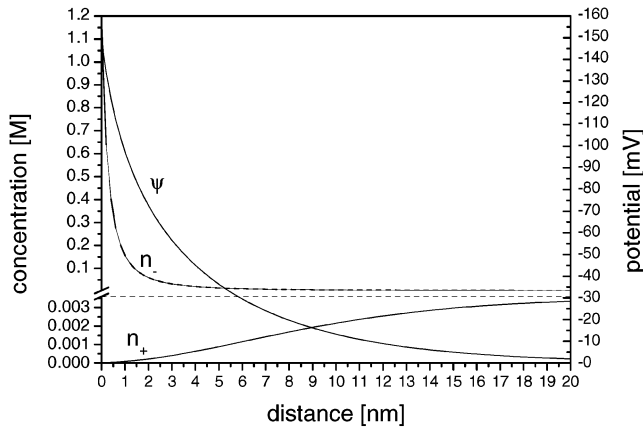
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Figure 2. Surface potential and concentration as function of the distance to the air−water interface. A surface charge density of $\sigma = 0.385$ e/nm^2 and a bulk concentration of $n_0 = 3$ mM was used for the calculations. The dashed line displays the distribution of the counterions under the assumption that there are no co-ions in the solution. In this concentration regime the presence of co-ions do not influence the prevailing distribution of the counterions.

2.3. Stern Layer. Several features such as the physical dimensions of the ions are not accounted for in the Gouy−Chapman model; hence it fails in the direct vicinity of the interface. Stern addressed this by a division of the interfacial region in two distinct regions, a layer of directly bound ions and a diffuse layer. The directly bound counterions effectively reduce the surface charge density σ_0:

$$\sigma = \sigma_0 - en_c \qquad (8)$$

where n_c is the number density of the condensed counterions. The reduced surface potential σ changes the counterion distribution in the diffuse layer.

The challenging task is the direct measurement to which extent the counterions condense in the Stern layer. Potential measurements or electrochemical sensors are inappropriate because the new interfaces influence the system. Optical reflection techniques such as ellipsometry may provide insight into the prevailing ion distribution. Ellipsometry probes the profile of the dielectric function that is directly given by the concentration profile of the counterions. In this paper we derive a functional relation between the ellipsometric signal and the distribution of the counterions of ionic Gibbs and Langmuir monolayers. Moreover we define under which conditions it is possible to measure directly the isotherm of the Stern layer in an ellipsometric measurement.

2.4. Ellipsometry Used for the Investigation of Adsorption Layers of Soluble Surfactants. Ellipsometry is a classical optical reflection technique. Light with a well-defined state of polarization is incident on the sample. Upon reflection the state of polarization is changed. These changes can be expressed by two measurable quantities, Ψ and Δ, which are related to the ratio of the complex reflectivity coefficients for $\hat{s}$ and $\hat{p}$ polarization by the basic equation of ellipsometry:[8]

$$\tan\Psi e^{i\Delta} = \frac{r_p}{r_s} \qquad (9)$$

This equation outlines the strategy for ellipsometric data analysis. The task requires the translation of the interfacial architecture in the corresponding refractive index profile. The reflectivity can then be calculated by a numerical Fresnel algorithm, as outlined in ref 17. The correct treatment of charged interfaces requires the explicit consideration of the counterion distribution and their corresponding refractive index profile.

In the thin film limit ellipsometry measures only a single parameter that is proportional to the following integral of the dielectric function ϵ across the interfacial region[9]

$$\eta = \int \frac{(\epsilon - \epsilon_0)(\epsilon - \epsilon_2)}{\epsilon} \, dx \qquad (10)$$

and

$$\Delta \approx \frac{4\sqrt{\epsilon_0}\epsilon_2\pi \cos\varphi \sin^2\varphi}{(\epsilon_0 - \epsilon_2)((\epsilon_0 + \epsilon_2)\cos^2\varphi - \epsilon_0)} \cdot \frac{1}{\lambda} \cdot \eta \qquad (11)$$

where ϵ_0 and ϵ_2 are the dielectric constants of the adjacent bulk phases, in our case air and water, respectively, φ is the angle of incidence, and λ is the wavelength of light. This equation is used for a further analytical simplification as outlined in the next section.

3. Theory

3.1. Impact of the Diffuse Layer on the Ellipsometric Angle Δ. The condensed counterions in the Stern layer reduce the surface charge density and influence the counterion distribution in the diffuse layer. The distribution of the counterions is only a function of the effective surface charge density σ as soon as the parameter γ (section 2.2) exceeds a value of 0.8. The relation is then described by eq 2. Because of the linear relation between the dielectric function and the concentration in the diffuse layer we can translate the ion distribution in a refractive index profile:

$$\epsilon(z) = \epsilon_2 + c(z)\frac{d\epsilon}{dc} = \epsilon_2 + \frac{1}{2\pi l_B N_A (z + b)^2}\frac{d\epsilon}{dc} \qquad (12)$$

where N_A is Avogadro's constant. To quantify the impact of the counterion distribution in the diffuse layer on the ellipsometric angle Δ, we separate the integral over the interface in eq 10:

$$\eta = \int_0^d \frac{(\epsilon - \epsilon_0)(\epsilon - \epsilon_2)}{\epsilon} \, dz + \int_d^a \frac{(\epsilon - \epsilon_0)(\epsilon - \epsilon_2)}{\epsilon} \, dz$$
$$= \eta_{SL} + \eta_{DL} \qquad (13)$$

where the second term η_{DL} describes the influence of the counterions in the diffuse layer. The length d is the thickness of the stern layer. Ellipsometry probes the system off-resonant at optical frequencies (10^{15} Hz). If the adsorption process does not form new species with new electronic signatures, the polarizability at optical frequencies remains unchanged. Hence η_{SL} is dominated by the adsorbed surfactants and not significantly changed upon ion condensation. Note that the dielectric constant of the layer consisting of the surfactants is typically about 2.2. Inserting eq 12 in the integral η_{DL} and transforming the variable $\epsilon(z) \rightarrow \epsilon(z-d)$ leads to

$$\eta_{DL} = \int_0^{a-d} \frac{\left(\epsilon_2 - \epsilon_0 + \dfrac{\frac{d\epsilon}{dc}}{2\pi l_B N_A (z + b)^2}\right)\left(\dfrac{\frac{d\epsilon}{dc}}{2\pi l_B N_A (z + b)^2}\right)}{\epsilon_2 + \dfrac{\frac{d\epsilon}{dc}}{2\pi l_B N_A (z + b)^2}} \, dz \qquad (14)$$

with further simplifications:

$$\eta_{DL} = \int_0^{a-d} \frac{\frac{d\epsilon}{dc}\left(\epsilon_2 - \epsilon_0 + \frac{\frac{d\epsilon}{dc}}{2\pi l_B N_A (z+b)^2}\right)}{2\pi l_B N_A (z+b)^2\left(\epsilon_2 + \frac{\frac{d\epsilon}{dc}}{2\pi l_B N_A (z+b)^2}\right)} dz \quad (15)$$

$$= \int_0^{a-d} \frac{\frac{d\epsilon}{dc}\left(\frac{d\epsilon}{dc} - (\epsilon_0 - \epsilon_2)2\pi l_B N_A (z+b)^2\right)}{2\pi l_B N_A (z+b)^2\left(\frac{d\epsilon}{dc} + \epsilon_2 2\pi l_B N_A (z+b)^2\right)} dz \quad (16)$$

The ellipsometric signal is sensitive to changes in the dielectric function. Therefore the upper bound $(a - d)$ must resemble the distance r in the solution, where the dielectric function reaches the value of ϵ_2. Because the integration of η_{DL} to higher distances r does not change the value of η_{DL}, we just have to choose a sufficient length r. With this deliberations we found the following solution of eq 16:

$$\eta_{DL} = \frac{\frac{d\epsilon}{dc}(b - r)}{2\pi l_B N_A b \cdot r} + k\epsilon_0 \cdot \left(\arctan\left(\frac{r}{k}\right) - \arctan\left(\frac{b}{k}\right)\right) \quad (17)$$

with

$$k = \sqrt{\frac{\frac{d\epsilon}{dc}}{2\pi l_B N_A \epsilon_2}} \quad (18)$$

The limiting value of the ellipsometric moment η reads

$$\eta_{DL} = \lim_{r \to \infty} \eta_{DL} = -\frac{\frac{d\epsilon}{dc}}{2\pi l_B N_A \cdot b} + k\epsilon_0\left(\frac{\pi}{2} - \arctan\left(\frac{b}{k}\right)\right) \quad (19)$$

With the relation $b = e/(2\pi\sigma l)$ we derive the following expression describing the influence of the diffuse layer on the ellipsometric angle Δ:

$$\eta_{DL} = -\frac{d\epsilon}{dc} \cdot \frac{\sigma}{eN_A} + k\epsilon_0\left(\frac{\pi}{2} - \arctan\left(\frac{e}{\sigma}\sqrt{\frac{\epsilon_2 N_A}{2\pi l_B \frac{d\epsilon}{dc}}}\right)\right) \quad (20)$$

This equation in combination with the prefactor of eq 11 describes the ellipsometric response of the distribution of the counterions within the diffuse layer. It can be used to retrieve the effective surface charge density σ and contains only direct measurable quantities. The experimentalist can use this formula for a straightforward interpretation of measured ellipsometric isotherms for ionic surfactants at the air−water interface. The relation is plotted in Figure 3.

The impact of the compact layer η_{SL} on the ellipsometric angle Δ is dominated by the amphiphiles and scales linearly with the surface coverage. Therefore any deviation from linearity can be attributed to changes in the distribution of the counterions. All other effects such as changes in the orientation or conformation of the amphiphiles are only fine corrections and insufficient to account for the experimental observation discussed in the next chapter.
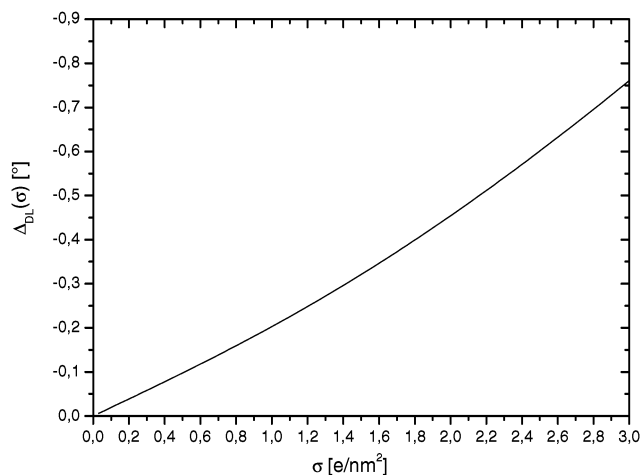

Figure 3. Impact of the counterions in the diffuse layer on the ellipsometric angle Δ with dependence on the prevailing surface charge density of the compact layer. The dielectric constant increment of Potassium bromide was used ($d\epsilon/dc = 3.453 \times 10^{-5}$ m^3/mol) for the calculations, the angle of incidence is $\varphi = 56°$, and the dielectric constant of air $\epsilon_0 = 1.0$ and water $\epsilon_2 = 1.77$, respectively.

The procedure for the determination of the ion distribution on the basis of eq 20 can be reduced to a simple recipe: (1) Determine the surface coverage Γ by an independent technique. It is, for instance, given by the derivative of the surface tension isotherm. There is a linear relation between the surface coverage and ellipsometric angle Δ provided that all counterions are located in the diffuse layer. (2) Measure the ellipsometric isotherm. Deviations from the linearity $\Delta(\Gamma)$ can be attributed to changes in the counterion distribution. A comparison of the deviations with Figure 3 yields directly the effective charge density of the surface layer, which can alternatively expressed as the number of condensed counterions. This strategy gives the very same result as more complex data evaluation schemes. We tested this by an explicit calculation of the coverage dependent refractive index by using the ellipsometric isotherm of a chemically closely related nonionic amphiphile for the estimation of η_{SL} as shown in the next chapter.

4. Experimental Section

The derived formalism is tested on published experimental data. To improve the readability of the manuscript, we summarize here the relevant experimental key facts. Synthesis and surface characterization of the components are described in ref 19, investigation on the factor in Gibbs equation and surface purification are in ref 18, and the SHG and ellipsometric isotherm are discussed in ref 7.

The soluble cationic amphiphile 1-dodecyl-4-dimethylaminopyridinium bromide, C12-DMP 4 bromide possesses a surface tension isotherm shown in Figure 4, which resembles all features of classical soluble surfactants including a critical micelle concentration cmc. The model system possesses a headgroup with a sufficiently high hyperpolarizibility to enable investigations with surface second harmonic generation, SHG. SHG is a nonlinear optical technique[20] that probes, in our case, only the headgroup of the surfactants. It allows an independent and direct determination of the surface excess as well the orientation of the headgroup.[21] The SHG data prove that the surface excess increases in a monotonic fashion with the bulk concentration until the cmc is established.[7] The filled circles in Figure 5 show the number density of the adsorbed amphiphile retrieved by calibrated SHG measurements.

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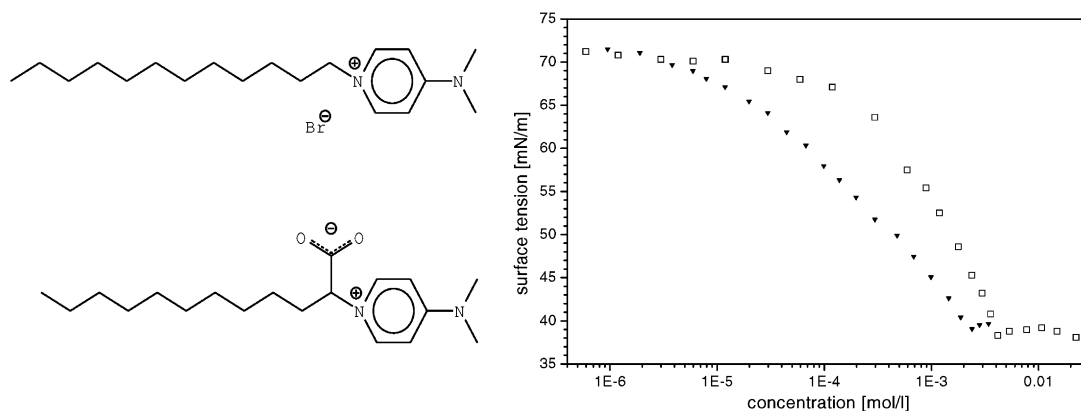*J. Phys. Chem. B, Vol. 108, No. 48, 2004* **18663**

Figure 4. Chemical structures of the cationic amphiphile 1-dodecyl-4-(dimethylamino)pyridinium bromide, C12-DMP bromide, and the closely related nonionic 2-(4'-(dimethylamino)pyridinio)dodecanoate, C12-DMP betaine. The equilibrium surface tension σ_e of a purified aqueous solution of the ionic C12-DMP bromide (squares) and the nonionic C12-DMP betaine (triangles) as a function of the bulk concentration c_o.
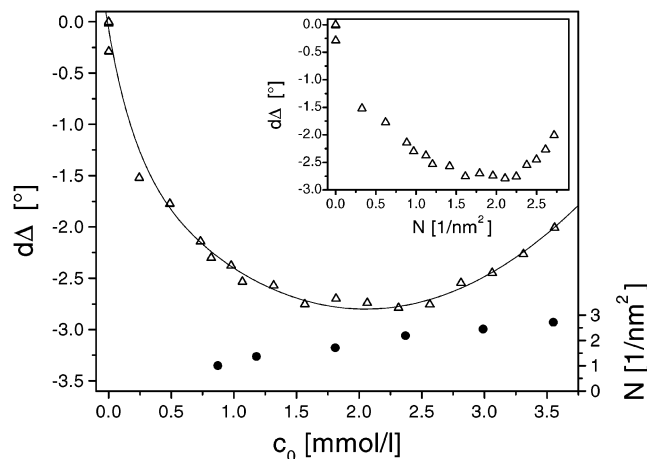

Figure 5. Characterization of the equilibrium properties of the cationic amphiphile C12-DMP bromide by ellipsometry and Surface second harmonic generation, SHG. The SHG-signal $\sqrt{I^{2\omega}(P=45,A=90)}$ (circles) is proportional to the surface coverage and increases monotonously with the bulk concentration. The ellipsometric quantity $d\Delta = \Delta - \Delta_0$ (triangles) shows an extremum at an intermediate concentration far below the cmc. The inset cleary shows the nonmonotonic dependency of dD on the adsorbed amount.

The corresponding ellipsometric isotherm $\Delta - \Delta_{H_2O}$ shows a unusual and unexpected behavior. The data as displayed by the triangles in Figure 5 increase in a nonmonotonic fashion with the bulk concentration and have a pronounced extremum at concentrations below the cmc. This implies that the surface layer at low coverage possesses an identical optical reflectivity r_p/r_s to the fully covered layer established just before the cmc. This surprising finding can be clearly attributed to changes in the ion distribution with increasing bulk concentration. It is not observed with the closely related betaine one analyzes, the C-12-DMP betaine shown in Figure 4. In the betaine the positive and negative charges are fixed onto the same headgroup and there cannot be any effects attributed to ions. The ellipsometric isotherm of aqueous solutions shows a monotonic behavior. A direct proportionality between surface excess as defined by the derivative of the surface tension isotherm and the ellipsometric angle $\Delta - \Delta_0$ could be established.

Hence the cationic amphiphile C12-DMP bromide is ideally suited to apply and test our formalism. Our formalism requires knowledge of the dielectric constant increment $d\epsilon/dc$. This quantity can be accurately determined using the interferometric techniques described in ref 22. The experimental dependence of the dielectric constant ϵ as a function of the bulk concentra-
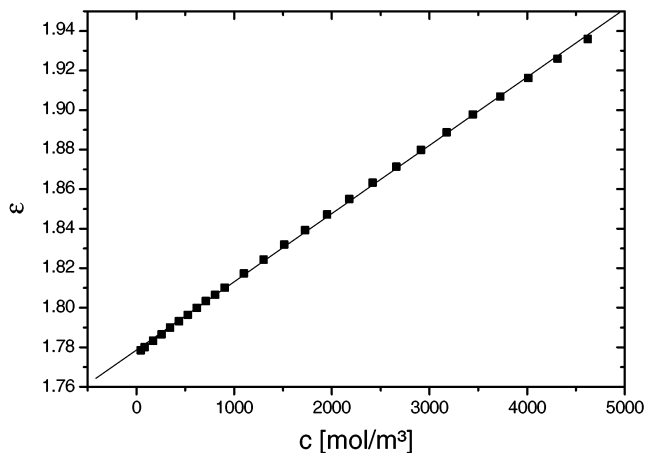

Figure 6. Dielectric constant of potassium bromide as a function of the concentration c. The slope leads the desired constant $d\epsilon/dc = 3.453 \times 10^{-5}$ m³/mol required for the data analysis.
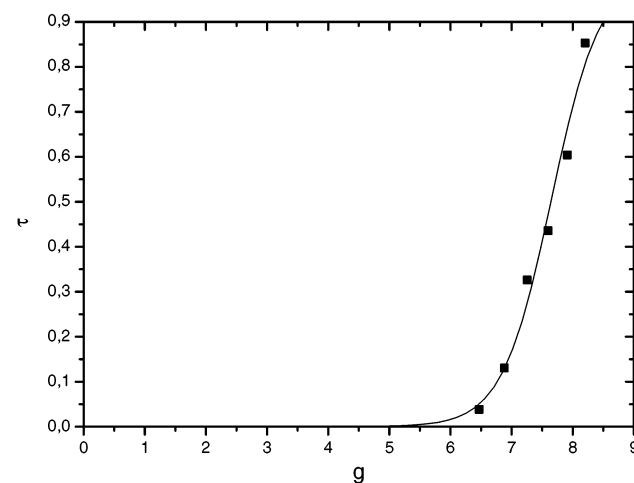

Figure 7. Parameter τ describes the fraction of condensed ions $\tau = Zen_c/\sigma_0$. All ions are condensed if $\tau = 1$ and $\tau = 0$ refers to a state where all ions are in the diffuse layer. The experimental isotherm of C12-DMP bromid has been analyzed using eq 20 and τ is plotted as a function of the order parameter $g = Z^2 l_B/b$. The solid line is a fit of the experimental data to the theory presented in ref 10.

tions is shown in Figure 6. The relation can be approximated by a straight line and the desired increment is given by the slope: $d\epsilon/dc = 3.453 \times 10^{-5}$ m³/mol.

Equation 20 can be used to determine directly the effective surface charge density. It is desirable to plot the isotherm of

the compact layer using the order parameter $g = Z^2 l/b$ and τ introduced in ref 10. The quantity Z characterizes the valence of our ions and is in our case $Z = 1$, l is the Bjerrum length, and b is the Gouy–Chapman length, which is effectively a function of the surface charge density measured with SHG. The parameter $\tau = Zen_c/\sigma_0$ describes the fraction of the condensed ions. If $\tau = 1$ all ions are condensed at the interface.

The interpretation of the experimental data is shown in Figure 7. Obviously there is a sharp transition favoring the condensed state at higher surface concentrations just below the cmc. The data are in semiquantitative agreement with the prediction of the two fluid model derived in ref 10. In this paper a condensation phenomenon in an overall neutral system, consisting of a single charged plate and its oppositely charged counterions is predicted. The counterions are divided into a free and a condensed fraction. On the basis of a minimization of the free energy it is shown that fluctuations can lead to a phase transition in which a large fraction of counterions is condensed. Even though the data are in semiquantitative agreement, further experiments are required to rule out effects such as a specific ion interaction.

5. Conclusion

Ellipsometry is an optical technique with a high sensitivity to thin films. It can also be successfully applied to determine the ion distribution of counterions at a charged interface. The analysis of ellipsometric data is based on Fresnel theory. The crucial part is the translation of the interfacial architecture in the corresponding refractive index profile. By combining the solution of the nonlinear Poisson–Boltzmann equation with the Fresnel theory we were able to derive a simple analytical formula that relates the effective surface charge density and ellipsometric signal. This formula has no free parameter and significantly simplifies the analysis of ellipsometric isotherms. The result is the fraction of condensed counterions as a function of the bulk concentration. This concept has been applied to an ellipsometric isotherm of aqueous solutions of an alkylpyridinium bromide. At low concentration the ions are spread out in the diffuse layer but with increasing bulk concentration a sharp transition toward a condensed state occurs. The derived isotherm of the condensed ions follows in a semiquantitative

fashion the prediction of the two fluid model introduced in ref 10. Furthermore, we interpreted the parameter γ, which describes the impact of the co-ions on the counterion distribution. Below a critical value of γ the influence of the co-ions on the distribution of the counterions can be effectively neglected. Our results are valuable for the experimentalist because the interpretation of the data is straightforward.

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