

Properties of Amphoteric Surfactants Studied by ζ -Potential Measurements with Latex Particles

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Received August 25, 1997. In Final Form: January 15, 1998

To study the electric properties of adsorption monolayers of an amphoteric surfactant, in our case lauryl dimethyl amine oxide (LDAO), we measured the ζ -potential of latex particles covered with this surfactant. Its adsorption on the latex particles is estimated by dynamic surface tension measurements coupled with light scattering experiments. The influence of pH, ionic strength, and surfactant concentration on the electric properties of the adsorption monolayer has been examined. We propose a theoretical model which describes the dependence of ζ -potential on both pH and the ionic strength. The model accounts for the adsorption of H^+ , Na^+ , and Cl^- ions on the amphoteric surfactant headgroups. Very good agreement between theory and experiment is achieved. The ζ -potential measurements, coupled with the theoretical model, can be considered as a method for quantitative characterization of the ionization properties of amphoteric surfactants in adsorption layers. The latter properties are, in general, different from the surfactant ionization properties in the bulk of solution. We hope this approach can find application for characterizing various formulations used in the house hold and personal-care detergency, foaming, emulsification, etc.

1. Introduction

In the last years there has been a growing interest in the properties of amphoteric surfactants in relation to their applications in personal-care and house hold detergency.¹ An important property of the amphoteric is the ionization state of their molecules, which is dependent on the pH of the solution. One way to determine the ionization state is to experimentally obtain the neutralization (titration) curves for the amphoteric surfactant solution.¹ Other methods described in the literature^{1,2} are infrared (IR) and proton magnetic resonance (PMR) spectrometry; in particular, the IR spectra exhibit absorption bands due to COO^- and N^+H_2 groups. All these methods give information about the ionization state of the surfactant molecules in the *bulk* of solution, which could be markedly different from the ionization state of the same molecule when it is incorporated into an *adsorption monolayer*.

Our aim in the present study is to examine the ionization state of adsorption monolayers from the amphoteric surfactant lauryl dimethyl amine oxide, $CH_3(CH_2)_{11}(CH_3)_2N^+O^-$, which will be referred to in the text as LDAO. With that end in view we measure the ζ -potential of polystyrene latex particles covered with an adsorption monolayer of LDAO. Then the data are interpreted by means of an appropriate theoretical model, which allows one to determine the state of the surfactant ionizable groups.

The earlier works on the ζ -potential measurements with colloid particles covered by adsorption layers are reviewed in the book by Hunter.³ More recently, Zhao and Brown⁴ investigated the adsorption of the cationic surfactant DTAB on latex particles as a function of surfactant concentration by dynamic light scattering. The same system was studied by electrophoretic mobility (ζ -potential) measurements by Xu and Smart.⁵ An electrophoretic study of fluorinated particles covered by a mixed adsorption layer of ionic and nonionic surfactants has been conducted by Bellini et al.⁶ Electrophoretic studies have been carried out also with oil droplets (instead of solid spheres) covered by anionic⁷ and nonionic⁸ surfactants. It should be mentioned that electrophoretic measurements have been applied to study the properties of adsorption layers from polyelectrolytes,^{9–11} polymers,^{12–14} proteins, and/or phospholipids.^{15–17}

In the present work we study amphoteric (LDAO) adsorption monolayers on polystyrene latex particles. We

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(1) Lomax, E. G. *Amphoteric Surfactants*; Marcel Dekker: New York, 1996.

(2) Okumura, T.; Tajima, K.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1067.

(3) Hunter, R. J. *Zeta Potential in Colloid Science*; Academic Press: New York, 1981; Chapter 8.

(4) Zhao, J.; Brown, W. *Langmuir* **1996**, *12*, 1141.

(5) Xu, R.; Smart, G. *Langmuir* **1996**, *12*, 4125.

(6) Bellini, T.; Degiorgio, V.; Mantegazza, F.; Marsan, F. A.; Scarnechia, C. *J. Chem. Phys.* **1995**, *103*, 8228.

(7) Barchini, R.; Saville, D. A. *Langmuir* **1996**, *12*, 1442.

(8) Marinova, K. G.; Alargova, R. G.; Denkov, N. D.; Velez, O. D.; Petsev, D. N.; Ivanov, I. B.; Borwankar, R. P. *Langmuir* **1996**, *12*, 2045.

(9) Hermans, J. J. *J. Polym. Sci.* **1955**, *18*, 527.

(10) Overbeek, J. Th. G.; Stigter, D. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 543.

(11) Imai, N.; Iwasa, K. *Isr. J. Chem.* **1973**, *11*, 223.

(12) Koopal, L. K.; Lyklema, J. *J. Electroanal. Chem.* **1979**, *100*, 895.

(13) Furusawa, K.; Chen, Q.; Tabori, N. *J. Colloid Interface Sci.* **1990**, *137*, 456.

(14) Churayev, N. V.; Nikologorskaja, S. *Colloids Surf.* **1991**, *59*, 71.

(15) Garvey, M. J.; Tadros, Th. F.; Vincent, B. J. *J. Colloid Interface Sci.* **1976**, *44*, 440.

(16) Johner, A.; Joanny, J. F. *Macromolecules* **1990**, *23*, 5299.

(17) Ho, C. C.; Kondo, T.; Muramatsu, Oshima, H. *J. Colloid Interface Sci.* **1996**, *178*, 442.

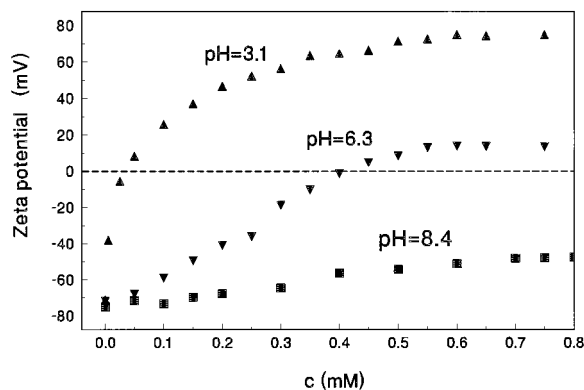


Figure 1. Measured ζ -potential of latex spheres vs the LDAO concentration, c . The three curves correspond to solutions of different pH, all of them containing 0.01 M NaCl.

first measure the dependencies of the ζ -potential on the surfactant concentration, pH, and ionic strength of the solution. The density of the adsorption monolayer is estimated from the decrease of the dynamic surface tension of the solution due to the adsorption of surfactant on the latex particles. To compare the ionization state of the amphoteric surfactant on the surface and in the bulk, we measure also the titration curve of the surfactant solution. To interpret the ζ -potential data, we develop a theoretical model, based on the classical electrokinetic theory,¹⁸ which takes into account the competitive adsorption of H^+ , Na^+ , and Cl^- ions on the surfactant ionizable groups. The comparison between theory and experiment yields the respective adsorption constants, which can be utilized to calculate the ionization state of adsorption monolayer at various values of the pH and ionic strength. Thus, the combination of the ζ -potential measurement with the theoretical model can be considered as a method for determining the ionization state of the adsorbed LDAO molecules, which can be applied also to other amphoteric surfactants.

2. Experimental Section

2.1. Materials, Sample Preparation, and Experimental Methods. As mentioned, in our experiments we used the amphoteric surfactant lauryl dimethyl amine oxide (LDAO), $CH_3(CH_2)_{11}(CH_3)_2N^+O^-$. A suspension of polystyrene latex spheres (Dow Chemicals, sulfate latex spheres, 170 ± 3 nm in diameter, polydispersity 3–5%, mass density 1.05 g/cm³) was used for the ζ -potential measurements. The concentration of the latex particles in the original suspension is 47 wt %. In the ζ -potential measurements we used the suspension after a considerable dilution: the working concentration of the latex particles was 0.094 g/L.

The pH of the solutions was varied by addition of hydrochloric acid or sodium hydroxide, both of analytical grade. The ionic strength was controlled by addition of NaCl (KCl in some experiments). All solutions were prepared with deionized water (Milli-Q, Organex grade). The temperature was maintained at 25 °C.

The effective hydrodynamic radius of the latex particles was determined by dynamic light scattering system 4700C (Malvern, U.K.). The ζ -potential measurements were performed by means of Zetasizer IIC (Malvern, U.K.). The maximum bubble pressure (MBP) method was used to measure the dynamic surface tension of the LDAO solutions.

2.2. ζ -Potential Measurements. Figure 1 presents our experimental results for the ζ -potential as a function of the LDAO concentration, c , for three values of the pH of the solution. To

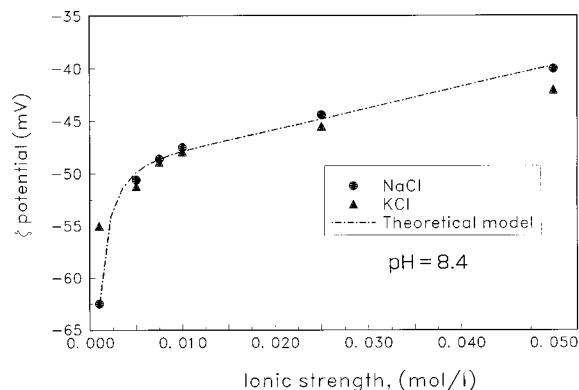


Figure 2. ζ -Potential of latex particles covered by LDAO adsorption monolayer vs the ionic strength due to NaCl or KCl at pH = 8.4 and concentration of LDAO $c = 0.7$ mM. The dashed curve represents the best fit of the data with NaCl by means of the theoretical model from section 3.

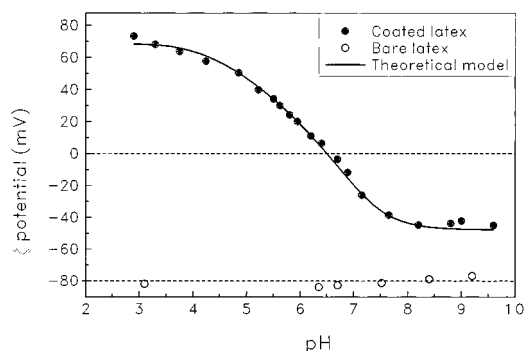


Figure 3. ζ -Potential of latex spheres vs pH, which was varied by HCl or NaOH in the presence of 0.01 M NaCl and concentration of LDAO $c = 0.7$ mM. The empty circles (○) and the solid circles (●) represent data for bare and LDAO-coated latex particles, respectively. The solid curve is the best fit by means of the theoretical model from section 3.

obtain an experimental point, we have measured the ζ -potential 10 min, 2 h, and 24 h after the preparation of the solution. The measured values of ζ turned out to be independent of time; i.e., the adsorption of LDAO on the latex particles is a relatively fast process. As seen in Figure 1, for $c = 0$ (no surfactant in the solution) the measured ζ -potential is -80 mV. This means that the “bare” latex particles have negative surface charge, which is most probably due to the ionization of the sulfate groups on their surfaces. When increasing the concentration of LDAO at fixed pH, the ζ -potential also increases and levels off for $c > 6 \times 10^{-4}$ M for each of the experimental curves (Figure 1). The existence of a plateau indicates saturation of the LDAO adsorption layer on the latex particle surface for the higher surfactant concentrations. Since LDAO has a relatively low cmc (3×10^{-5} M), the addition of more surfactant will only result in the formation of more micelles, once the adsorption layer on the latex particles has been saturated.

To study the dependence of the ζ -potential on the ionic strength, I , and pH at fixed surfactant concentration c (see Figures 2 and 3 below), we choose the working concentration to be $c = 0.7$ mM, because this concentration belongs to the plateau region for each of the curves in Figure 1; i.e., for $c = 0.7$ mM one can expect that the LDAO adsorption layer on the latex particles is saturated.

In addition, one sees in Figure 1 that the measured ζ -potential of the latex particles coated by a LDAO adsorption layer depends strongly on the pH of the solution: ζ increases with a decrease of pH. This evidences that the positive charge of the surfactant headgroups increases with a decrease of pH. At the highest pH (8.4), the ζ -potential is close to that of the bare latex spheres (-80 mV), which indicates that the LDAO headgroups are preferentially electroneutral (zwitterionic) at that pH. As the region of the plateau of the curves in Figure 1 ($c \geq 0.6$ – 0.7 mM) is not too sensitive to the value of pH, one could conclude that

(18) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: Cambridge, U.K., 1989.

(in a first approximation) the adsorption of LDAO on the latex particle is not related to the ionization state of the amphoteric headgroups; most probably the LDAO hydrophobic tails attach to the hydrophobic regions at the surface of the latex particles.

Figure 2 presents data for the ζ -potential vs the ionic strength of the solution, I , at fixed surfactant concentration, $c = 0.7$ mM, and at fixed pH = 8.4. The ionic strength has been varied by the addition of NaCl or KCl. As seen in Figure 2, the absolute value of ζ decreases with an increase of I , as could be expected because of suppression of the electric double layer by the added electrolyte. Moreover, the values of ζ measured with NaCl or KCl at the same I coincide (except the point at the lowest I). This indicates that the adsorption of Na^+ and K^+ ions on the surfactant headgroups is not specific and probably has a purely electrostatic origin.

In Figure 3 we plot data for ζ vs pH at fixed ionic strength $I = 0.01$ M and fixed surfactant (LDAO) concentration, $c = 0.7$ mM. One sees that at the lowest pH ζ is about +70 mV, then ζ decreases with an increase of pH, and finally ζ levels off at pH > 7.5, reaching a value of about -47 mV. In particular, $\zeta = 0$ at pH ≈ 6.5 . The open circles in Figure 3 denote the values of ζ measured for bare latex particles (in the absence of surfactant in the solution). One sees that ζ of the bare particles is practically constant, $\zeta = -80 \pm 5$ mV for $3 < \text{pH} < 9.5$, which is in agreement with the value of ζ for $c = 0$ in Figure 1. The fact that ζ of the bare latex particles is independent of pH can be attributed to the constancy of the ionic strength, $I = 0.01$ M, in these experiments.

The shape of the curve ζ vs pH for the LDAO-coated latex particles (Figure 3) could be anticipated keeping in mind the chemical structure of this amphoteric surfactant. Indeed, in solution LDAO can exist in cationic or zwitterionic form. Then one can expect that the cationic form is predominant at the lower pH, whereas the dipolar zwitterionic form is predominant at the higher pH. One sees that at the higher pH (for pH > 7.5, for which LDAO is expected to be in zwitterionic form) ζ levels off, but still there is a difference of about 30 mV between the ζ -potential of the coated and bare latex. A quantitative interpretation of this difference, as well as those of the whole plots of ζ vs pH and ζ vs I , can be achieved by taking into account the binding of H^+ , Na^+ , and Cl^- ions to the headgroups of the adsorbed LDAO molecules. For that purpose a theoretical model is developed in section 3.

2.3. Adsorption of LDAO on the Latex Particles. As was already mentioned, the curves in Figure 1 indicate saturation of the LDAO adsorption monolayer for $c > 0.6$ mM. To be sure that one adsorption monolayer is really formed and to estimate its surface density, we carried out independent surface tension measurements. We measured the surface tension, σ , of solutions of LDAO with and without latex particles. As the latex spheres adsorb part of the surfactant (LDAO) and thus decrease its bulk concentration, their addition in the solution leads to an increase of its surface tension. It is worth noting that the latter effect can be detected only by *dynamic* surface tension measurements, because in our case the surfactant concentrations are above the critical micellization concentration (cmc) and, consequently, the *static* surface tension is not sensitive to the variation of the total surfactant concentration in the solution.

We used the MBP method for dynamic surface tension measurement; see, e.g., refs 19–21. We carried out measurements with three samples containing 0.5, 0.7, and 1.0 mM LDAO and 10 mM NaCl. The first sample was used without latex, as well as mixed with 3 and 5 g/L latex particles. The data for the dynamic surface tension σ vs time are plotted in Figure 4 for the 5 investigated solutions. One sees that the values of σ coincide for the solutions of 1.0 mM LDAO + 5 g/L latex and 0.5 mM LDAO without latex; the same is true for the solutions of 1.0 mM LDAO + 3 g/L latex and 0.7 mM LDAO without latex. Assuming that the bulk surfactant concentration is the same for the solutions with equal dynamic surface tension, one can calculate

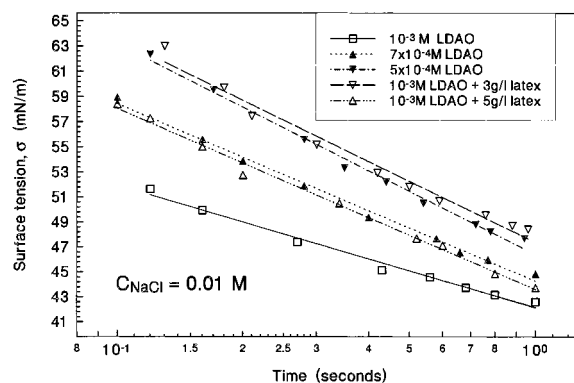


Figure 4. Surface tension σ vs time measured by means of the MBP method for LDAO solutions with and without added latex spheres. All samples contain 0.01 M NaCl; pH = 6.5.

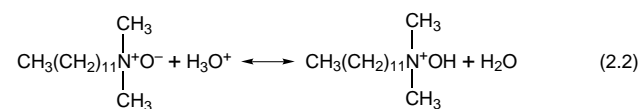
the adsorption, Γ , of surfactant (LDAO) on the surface of the latex spheres:

$$\Gamma = \frac{R\rho_1 N_A \Delta c}{3\eta_1} = 1.79 \times 10^{18} \frac{\Delta c}{\eta_1} \quad (\text{cm}^{-2}) \quad (2.1)$$

where R ($=85 \pm 1.5$ nm) is the radius of the latex spheres, ρ_1 ($=1.05$ g/cm³) is their mass density, N_A is Avogadro's number, Δc (mol/L) is the difference between the surfactant concentrations in the two solutions of coinciding σ , and η_1 (g/L) is the concentration of the latex spheres. Keeping in mind that the experimental error of the MBP method is ± 0.4 mN/m, we obtain the area per adsorbed LDAO molecule on the latex surface to be $1/\Gamma = 56 \pm 5$ Å² for *both* couples of solutions with coinciding σ (Figure 4). Hence, one can conclude that LDAO covers the latex particles with a dense monolayer.

We carried out also dynamic *light-scattering* experiments in order to determine the change in the hydrodynamic diameter of the latex spheres due to adsorption of LDAO. This could allow us to independently estimate how many adsorption layers of LDAO are formed on the surface of the latex particles. The hydrodynamic diameter of bare latex particles is measured to be $d_h = 170 \pm 3$ nm, while in the presence of 0.7 mM LDAO the coated latex spheres have diameter $d_h = 175 \pm 3$ nm. This is an indication that one layer of LDAO is adsorbed on the latex surface. Indeed, from the structure of the LDAO molecule one can estimate that the thickness of a closely packed monolayer of LDAO should be about 3 nm. However, the experimental error of d_h is comparable with the monolayer thickness, and it turns out that in our case the dynamic light-scattering method is not accurate enough to give the coverage of the latex particles by adsorbed LDAO, as the MBP method does. Hence, we should rely on the value $1/\Gamma = 56 \pm 5$ Å² determined by the MBP method; see above.

2.4. Titration Curves for LDAO. The variation of the charge of the latex particles coated by LDAO layer is (at least partially) due to the association of H^+ ions at low pH:



With a decrease of the pH the equilibrium in eq 2.2 is shifted to the right, and at pH = 3 the LDAO molecules are preferentially cations. We determined the respective equilibrium constant from the titration curve (Figure 5) of a 0.01 M LDAO solution. The titration curve presents a plot of the measured pH vs the volume of the added HCl, V_{HCl} . Since LDAO is a weak base, the titration curve for LDAO was compared with that for an empty sample of NaOH. The final result for the basic constant is

$$K_b = \frac{[\text{AOH}^+][\text{OH}^-]}{[\text{AO}]} = \frac{[\text{AOH}^+]K_w}{[\text{AO}][\text{H}^+]} = 1.21 \times 10^{-10} \text{ M}, \quad \text{p}K_b = 9.91 \quad (2.3)$$

(19) Mysels, K. J. *Colloids Surf.* **1990**, *43*, 241.

(20) Fainerman, V. B.; Miller, R.; Joos, P. *Colloid Polym. Sci.* **1994**, *272*, 731.

(21) Horozov, T. S.; Dushkin, C. D.; Danov, K. D.; Arnaudov, L. N.; Velev, O. D.; Mehreteab, A.; Broze, G. *Colloids Surf. A* **1996**, *113*, 117.

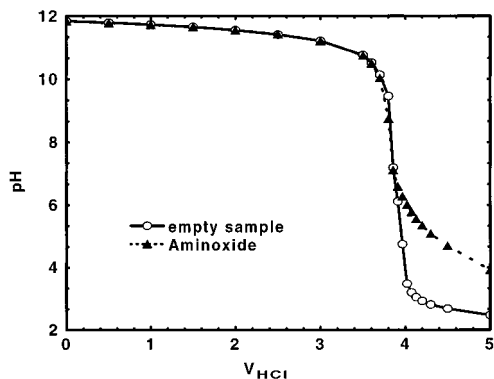


Figure 5. Titration curve of pH vs V_{HCl} (in cm^3) for LDAO. The empty circles correspond to the empty sample of 25 mL of H_2O + 5 mL of 0.1 M NaOH (no LDAO in the solution). The triangles correspond to the titration curve of 25 mL of 0.01 M LDAO + 5 mL of 0.1 M NaOH.

where K_w is the dissociation constant of water. The basic constant, K_b , of LDAO in the bulk is simply related with the respective association constant

$$\bar{K}_1 = 1000K_b/(K_wN_A) = 2.0 \times 10^{-17} \text{ cm}^3 \quad (2.4)$$

of the H^+ ions. \bar{K}_1 is a bulk analogue of the association constant K_1 of the H^+ ions to the LDAO molecules adsorbed at the latex surface. More precisely, at $c = 0.01$ M the surfactant in solution is present predominantly in micellar form; hence, \bar{K}_1 is related to the association of H^+ ions with the micelle surfaces. Below we will compare the value of \bar{K}_1 in eq 2.4 with the result for K_1 obtained by interpretation of the data from the ζ -potential measurements.

3. Theoretical Model

3.1. Basic Assumptions. Below we propose a theoretical model describing the behavior of the ζ -potential of latex particles covered by a monolayer of amphoteric surfactant. We should note that we tried many models (about 20) of the ionic adsorption on the surface of the LDAO-coated latex particles. Only one of them could successfully interpret the dependence of the ζ -potential on *both* ionic strength (Figure 2) and pH (Figure 3). We present this model below. Its basic assumptions are the following:

(i) The surfactant (LDAO) molecules are adsorbed with their hydrocarbon tails at the hydrophobic parts of the latex surface. We assume that the adsorption energy is high enough and the adsorption of LDAO at the latex is not sensitive to the pH and ionic strength of the solution. We discuss this assumption in section 4.2.

(ii) Since our latex particles are large enough (diameter 170 nm) compared to the thickness of the electric double layer, $\kappa^{-1} = 3$ nm (cf. eq 3.11), the influence of the particle curvature on the structure of the electric double layers is negligible. We accept that the shear plane coincides with the plane of the surfactant headgroups ($x = \delta$); i.e., the ζ -potential is equal to the electric potential there, $\zeta = \psi(\delta) = \psi\delta$.

(iii) Hydrogen (H^+) and sodium (Na^+) ions from the background electrolyte can competitively adsorb on the anionic ionizable groups of the surfactant molecules, see

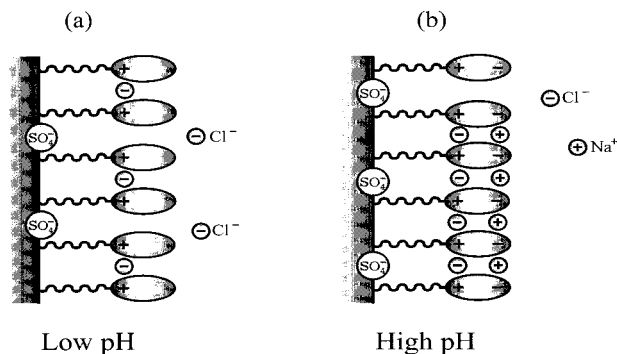


Figure 6. Sketch of the electric double layer of a latex particle coated by a LDAO monolayer: (a) at low pH; (b) at high pH.

eq 2.2. In our model we assume that their adsorptions Γ_{H^+} and Γ_{Na^+} satisfy the Stern adsorption isotherm²²⁻²⁴

$$\Gamma_{\text{H}^+} = \frac{\Gamma K_1 n_{\text{H}^+}^s}{1 + K_1 n_{\text{H}^+}^s + K_2 n_{\text{Na}^+}^s}, \quad \Gamma_{\text{Na}^+} = \frac{\Gamma K_2 n_{\text{Na}^+}^s}{1 + K_1 n_{\text{H}^+}^s + K_2 n_{\text{Na}^+}^s} \quad (3.1)$$

Here $n_{\text{H}^+}^s$ and $n_{\text{Na}^+}^s$ are the subsurface concentrations of hydrogen and sodium ions and, as before, Γ is the total surfactant adsorption on the latex surface.

(iv) Since the quaternary ammonium of the LDAO molecule is always positively charged, we assume adsorption of Cl^- ions at the headgroups of the LDAO monolayer. (Note that Cl^- is always available in solution because of the dissolved NaCl.) Moreover, it is natural to assume that Cl^- adsorbs only when the LDAO headgroup is positively charged. In terms of eq 3.1 this means that a precondition for the adsorption of Cl^- at a given headgroup is its negative charge ($-\text{O}^-$; see eq 2.1) to be neutralized by the adsorption of H^+ or Na^+ . Therefore, with account for this precondition one can write

$$\Gamma_{\text{Cl}^-} = \frac{\Gamma_{\text{H}^+} K_3 n_{\text{Cl}^-}^s}{1 + K_3 n_{\text{Cl}^-}^s} + \frac{\Gamma_{\text{Na}^+} K_4 n_{\text{Cl}^-}^s}{1 + K_4 n_{\text{Cl}^-}^s} \quad (3.2)$$

Note that the concentration of OH^- ions in our experiments ($\text{pH} \leq 9.5$) is always much smaller than that of Cl^- ; for that reason in our model we neglect the adsorption of OH^- ions on the LDAO headgroups.

The adsorption constants in eqs 3.1 and 3.2 are simply related to the adsorption energies, Φ_j , of the respective species²⁵

$$K_j = a d_j \exp(\Phi_j/kT) \quad (j = 1, \dots, 4) \quad (3.3)$$

where $a = 1/\Gamma = 0.56 \text{ nm}^2$ is the area per LDAO headgroup in the adsorption monolayer and d_j is the diameter of the respective (hydrated) ion. We use the values $d_{\text{H}^+} = 0.56$ nm, $d_{\text{Na}^+} = 0.72$ nm, $d_{\text{Cl}^-} = 0.66$ nm, taken from ref 26.

In Figure 6 we present our expectations about the

(22) Hunter, R. J. *Foundation of Colloid Science*; Clarendon Press: Oxford, U.K., 1987; Vol. I.

(23) Adamson, A. W. *Physical Chemistry of Surfaces*; Wiley: New York, 1976.

(24) Derjaguin, B. V. *Theory of Stability of Colloids and Thin Liquid Films*; Plenum Press: New York, 1989.

(25) Shchukin, E. D.; Pertsov, A. V.; Amelina, E. A. *Colloid Chemistry*; Moscow University Press: Moscow, 1982 (in Russian).

(26) Israelachvili, J. N. *Intermolecular & Surface Forces*; Academic Press: London, 1992.

structure of the adsorption layer at low and high pH. The headgroups (depicted elliptical) are zwitterions at *high* pH, whereas their negative charge is neutralized by the adsorption of H^+ at *low* pH. (In fact, the adsorption of H^+ at the LDAO headgroups can be termed "chemisorption" insofar as a covalent bond is formed.) Thus, at low pH the headgroups of LDAO are positively charged and, consequently, intercalation of Cl^- between them could be expected (Figure 6a). On the other hand, at high pH the negative charges of the LDAO headgroups are ionized; then adsorption of Na^+ could also be expected (Figure 6b).

Below we couple the electric double layer theory with the model adsorption equations (3.1) and (3.2), which determine the surface charge density.

3.2. Model of the Double Layer. For the sake of simplicity we consider two regions around the latex particle: region I of the adsorbed surfactant monolayer, $0 \leq x < \delta$, including the LDAO hydrocarbon tails and headgroups, and region II of the diffuse part of the electric double layers, $\delta \leq x < \infty$. This is a modified version of the Stern model of the electric double layer. The electrical potential, ψ , in these two regions around the latex particle satisfies the Poisson equation

$$\frac{d^2\psi^I}{dx^2} = 0, \quad 0 \leq x < \delta \quad (3.4a)$$

$$\frac{d^2\psi^{II}}{dx^2} = -\frac{4\pi}{\epsilon}\rho(x), \quad \delta \leq x < \infty \quad (3.4b)$$

where ϵ is the bulk dielectric permittivity of the solution. The bulk charge density in region I is zero, and in region II it is

$$\rho(x) = \sum_k Z_k e n_k(x) = \sum_k Z_k e n_k^0 \exp\left[-\frac{e\psi(x)}{kT}\right], \quad \delta \leq x < \infty \quad (3.5)$$

where the summation is carried out over all ionic species; Z_k and n_k^0 denote their valence and bulk concentration. In eq 3.4a we have assumed that there is no penetration of electrolyte among the hydrocarbon tails of the adsorbed LDAO molecules. The boundary conditions for eq 3.4a,b are

$$\left.\frac{d\psi^I}{dx}\right|_{x=0} = -\frac{4\pi\sigma_0}{\epsilon_0}, \quad \psi^I(\delta) = \psi^{II}(\delta) = \zeta \quad (3.6)$$

$$\epsilon_0 \left.\frac{d\psi^I}{dx}\right|_{x=\delta} - \epsilon \left.\frac{d\psi^{II}}{dx}\right|_{x=\delta} = 4\pi\sigma_\delta, \quad \lim_{x \rightarrow \infty} \psi^{II}(x) = 0 \quad (3.7)$$

Here ϵ_0 is the dielectric constant in region I, σ_0 is the surface charge density at the original latex surface (at $x = 0$) and σ_δ is the surface charge density in the plane of the surfactant headgroups. In eq 3.6 we have assumed that the intensity of the electric field into the latex particle is zero. The solution of eq 3.4a together with eq 3.6 is

$$\psi^I(x) = -\frac{4\pi\sigma_0}{\epsilon_0}(x - \delta) + \zeta \quad (0 \leq x \leq \delta) \quad (3.8)$$

By means of eq 3.8, the boundary conditions, eq 3.7, can be transformed to read

$$\left.\frac{d\psi^{II}}{dx}\right|_{x=\delta} = -\frac{4\pi}{\epsilon}(\sigma_0 + \sigma_\delta) \quad (3.9)$$

For monovalent symmetrical electrolytes, eq 3.4b takes the form

$$\varphi''(x) = \kappa^2 \sinh \varphi(x), \quad \varphi(x) \equiv \frac{e\psi^{II}(x)}{kT} \quad (3.10)$$

with

$$\kappa^{-1} \equiv \left[\frac{4\pi e^2}{\epsilon kT} (n_{Na^+}^0 + n_{H^+}^0 + n_{Cl^-}^0 + n_{OH^-}^0) \right]^{-1/2} \quad (3.11)$$

being the Debye screening length. Here $n_{Na^+}^0$, $n_{H^+}^0$, $n_{Cl^-}^0$, and $n_{OH^-}^0$ are the bulk concentrations of sodium, hydrogen, chlorine, and hydroxyl ions. Taking the first integral of eq 3.10 and using the boundary condition, eq 3.9, we obtain the connection between surface potential and surface charge in the form

$$2\kappa \sinh \frac{y}{2} = \frac{4\pi e}{\epsilon kT} (\sigma_0 + \sigma_\delta), \quad y \equiv \varphi(\delta) = \frac{e\zeta}{kT} \quad (3.12)$$

It is important to note that the parameter δ does not enter eq 3.12; therefore, our results below, based on eq 3.12, will not depend on the exact position of the shear plane. Fortunately, the unknown dielectric constant of region I, ϵ_0 , also does not appear in eq 3.12. The surface charge density of the original latex surface, $\sigma_0 = -e/A_0$ (A_0 is area per charge on the bare latex surface), can be determined from the ζ -potential of the bare latex; see below. The net surface charge density in the headgroup region (at $x = \delta$) is a result of the adsorption of various ions, described by eqs 3.1 and 3.2:

$$\sigma_\delta = e(\Gamma_{H^+} + \Gamma_{Na^+} - \Gamma_{Cl^-}) \quad (3.13)$$

Introducing the notation

$$Y \equiv \left(\frac{1}{A_0} + \frac{\epsilon k T \kappa}{2\pi e^2} \sinh \frac{y}{2} \right) / \Gamma \quad (3.14)$$

from eqs 3.1, 3.2, 3.12, and 3.13 we obtain

$$(e^y + K_1 n_{H^+}^0 + K_2 n_{Na^+}^0) Y = \frac{K_1 n_{H^+}^0}{1 + K_3 n_{Cl^-}^0 e^{-y}} + \frac{K_2 n_{Na^+}^0}{1 + K_4 n_{Cl^-}^0 e^{-y}} \quad (3.15)$$

Equation 3.15 is to be solved numerically to determine y , which is the dimensionless ζ -potential; see eq 3.12.

4. Comparison between Theory and Experiment.

4.1. Numerical Procedure. From the measured ζ -potential of the bare latex particles, $\zeta_0 = -80$ mV (at $C_{el} = 0.01$ M; see Figure 3), we can estimate the respective surface charge density, σ_0 . Substituting $\delta = 0$ and $\sigma_\delta = 0$ into eq 3.12, we obtain

$$A_0 = \frac{2\pi e^2}{\epsilon k T \kappa_0} \left(\sinh \frac{e\zeta_0}{2kT} \right)^{-1} = 603 \text{ \AA}^2 \quad (\sigma_0 \equiv -e/A_0) \quad (4.1)$$

In other words, the density of the ionizable SO_4 groups on the latex surface (603 \AA^2 per charge) is low compared with the density of the LDAO adsorption monolayer ($1/\Gamma = 56 \text{ \AA}^2$). It seems that the ionizable groups on the latex surface are separated with large hydrophobic domains, where the attachment of the surfactant hydrocarbon tails takes place. This finding is consonant with assumption i of our model; see section 3.1.

To determine some of the parameters of our model, we use the data for ζ vs I in Figure 2 for latex particles coated by LDAO at pH = 8.4. At this value of pH the terms with $n_{\text{H}^+}^0$ and Γ_{H^+} are negligible and eq 3.15 reduces to

$$(e^y + K_2 n_{\text{Na}^+}^0)(1 + K_4 n_{\text{Cl}^-}^0 e^y) Y = K_2 n_{\text{Na}^+}^0 \quad (4.2)$$

where Y is defined by eq 3.14. We determine the adsorption constants K_2 and K_4 from the best fit of the data in Figure 2 with eq 4.2 by means of the least-squares method. For that purpose we minimize the function

$$Q(K_2, K_4) = \sum_i [\zeta_i - \zeta(n_{\text{NaCl}}^0, K_2, K_4)]^2 \quad (4.3)$$

where the summation is carried out over all experimental points, ζ_i vs n_{NaCl}^0 , and the theoretical ζ -potential, $\zeta(n_{\text{NaCl}}^0, K_2, K_4)$, is determined by solving numerically eq 4.2 for y , along with eq 3.14, at given values of K_2 , and K_4 . The best fit of the data for NaCl yields $K_2 = 1.62 \times 10^{-20} \text{ cm}^3$ and $K_4 = 7.60 \times 10^{-18} \text{ cm}^3$. Using these values, we plotted the theoretical curve in Figure 2. One sees that the agreement between the theory and experiment is very good in the whole range of ionic strengths. From eq 3.3 one can easily estimate the adsorption energies of the sodium and chlorine ions: $\Phi_2 = 14.8kT$ and $\Phi_4 = 9.9kT$; see eq 3.3.

The other two parameters of the model, K_1 and K_3 , will be determined from the experimental data in Figure 3 for the dependence of the ζ -potential on pH. We obtain an explicit expression for the constant K_3 in the following way. Let us use the experimental value of the H^+ concentration, $n_{\text{H}^+}^*$, corresponding to $\zeta = 0$ (pH = 6.5). From eqs 3.12 and 3.14 we obtain the respective value of Y : $Y^* \equiv 1/A_0\Gamma$ and

$$K_3 = \frac{K_1 n_{\text{H}^+}^* (1/n_{\text{Cl}^-}^0 + K_4)}{(1 + K_1 n_{\text{H}^+}^* + K_2 n_{\text{Na}^+}^0)(1 + K_4 n_{\text{Cl}^-}^0) Y^* - K_2 n_{\text{Na}^+}^0} - \frac{1}{n_{\text{Cl}^-}^0} \quad (4.4)$$

Since the constants K_2 and K_4 have been already determined from the fit in Figure 2, eq 4.4 expresses K_3 as a function of K_1 . Further, K_1 (and K_3) is obtained by fitting the data points ζ_i vs (pH) $_i$ in Figure 3 by means of the least-squares method. We numerically minimize the function

$$Q_1(K_1) = \sum_i [\zeta_i - \zeta(K_1, (\text{pH})_i)]^2 \quad (4.5)$$

where the summation is carried out over all experimental points, and the theoretical ζ -potential, $\zeta(K_1, (\text{pH})_i)$, is determined by solving numerically eq 3.15 along with eqs 3.14 and 4.4. The best fit gives the value $K_1 = 8.05 \times 10^{-16} \text{ cm}^3$; then from eq 4.4 we calculate $K_3 = 5.70 \times 10^{-20} \text{ cm}^3$. The curve corresponding to the best fit is shown in Figure 3. One sees that there is a very good agreement between the theoretical model and the experimental data. The values of the determined equilibrium constants and adsorption energies (calculated from eq 3.3) are summarized in Table 1.

4.2. Discussion. It is instructive to see what is the adsorption of different ionic species on the LDAO head-

Table 1. Parameters of the Adsorption Isotherms Determined from the Fits of the Data

adsorbed ion	adsorption constant (cm ³)	adsorption energy
H ⁺ on LDAO (eq 3.1)	$K_1 = 8.05 \times 10^{-16}$	$\Phi_1 = 14.8kT$
Na ⁺ on LDAO (eq 3.1)	$K_2 = 1.62 \times 10^{-20}$	$\Phi_2 = 3.7kT$
Cl ⁻ on LDAO + H ⁺ (eq 3.2)	$K_3 = 5.70 \times 10^{-20}$	$\Phi_3 = 5.0kT$
Cl ⁻ on LDAO + Na ⁺ (eq 3.2)	$K_4 = 7.60 \times 10^{-18}$	$\Phi_4 = 9.9kT$

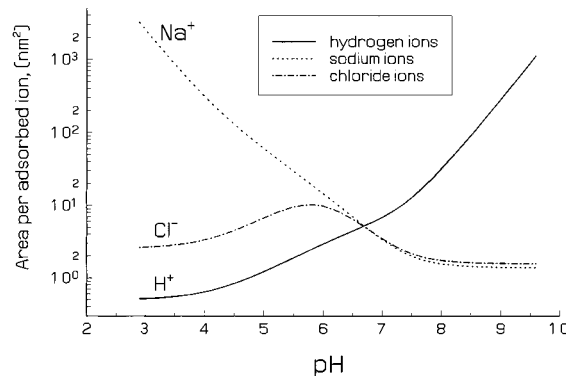


Figure 7. Area per ion (H^+ , Na^+ , or Cl^-) adsorbed on a LDAO monolayer vs pH of the solution.

groups at various pH of the solution. Having determined the four adsorption constants, K_1, \dots, K_4 , we can calculate the adsorption of H^+ , Na^+ , and Cl^- ions on the LDAO headgroups from eqs 3.1 and 3.2. The calculated areas per adsorbed ion are plotted vs pH in Figure 7. One sees that for $\text{pH} < 4$ saturation of the LDAO headgroups with H^+ takes place ($\Gamma_{\text{H}^+}^1 \approx 0.56 \text{ nm}^2$). The adsorption energy of the H^+ ions on LDAO, $\Phi_1 = 14.8kT$ (Table 1), is relatively high, which is not surprising insofar as we deal with the formation of a covalent bond; see eq 2.1. As could be expected, the adsorption of H^+ ions decreases (the area per adsorbed H^+ ion increases) with an increase of pH (Figure 7).

Na^+ ions are present in the solution for all pH because of the added 0.01 M NaCl. However, Na^+ ions can adsorb on the LDAO headgroups only when the latter are not occupied by covalently bonded H^+ ions. Indeed, the adsorption energy Φ_2 is markedly smaller than Φ_1 (Table 1), which is not surprising, because the Na^+ ion is not expected to form a covalent bond with the LDAO headgroups. Therefore, the adsorption of Na^+ ions becomes significant for $\text{pH} > 6.5$; see Figure 7.

In contrast with the H^+ and Na^+ ions, the Cl^- ions are present in the adsorption layer for all pH; see Figure 7. One may hypothesize that the Cl^- ions are attracted in the LDAO adsorption monolayer by the positive charge of the quaternary ammonium of the LDAO headgroup (see eq 2.2 and Figure 6). It turns out that Φ_4 is about 2 times larger than Φ_3 (see Table 1) as a consequence the adsorption of the Cl^- ions is greater at the higher values of pH (Figure 7). One possible explanation is that the configuration of charges in the headgroup region is energetically more advantageous for the higher pH (Figure 6b; note the antiparallel dipoles) than for the lower pH (Figure 6a). Note also that the adsorptions of Cl^- and Na^+ ions are equal for $\text{pH} > 6.5$ (Figure 7), which is consonant with the ionic configuration depicted in Figure 6b.

As mentioned above, from the data in Figure 5 we determined the protonization constant of the LDAO molecules in the *bulk* of the solution, $\bar{K}_1 = 2.0 \times 10^{-17} \text{ cm}^3$. The constant K_1 in eq 3.1 has the meaning of the protonization constant of the LDAO molecules in the

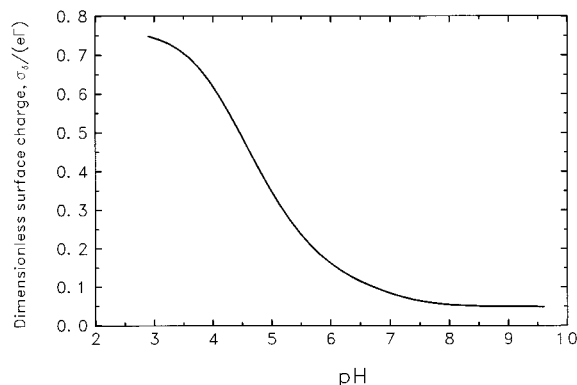


Figure 8. Plot of the calculated dimensionless net surface charge of the surfactant headgroups, $\tilde{\sigma}_\delta \equiv \sigma_\delta/e\Gamma$, vs pH of the solution for the data from Figure 3; see eq 3.13.

surface adsorption monolayer. The ratio of these two constants is

$$\frac{K_1}{\bar{K}_1} = \frac{8.05 \times 10^{-16}}{2.0 \times 10^{-17}} \approx 40 \quad (4.6)$$

One sees that the surface protonization constant of LDAO is greater than the bulk one. This could be attributed to some collective effects; for example, the charge of a binded H^+ ion could be effectively distributed among several neighboring LDAO molecules in the adsorption monolayer. We recall that \bar{K}_1 reflects the protonization of the headgroups of LDAO molecules, incorporated into surfactant micelles, which (due to curvature effects) typically exhibit 2–3 times larger area per headgroup than that in a planar adsorption layer.

In Figure 8 we plot the calculated dimensionless net surface charge of the surfactant headgroups, $\tilde{\sigma}_\delta \equiv \sigma_\delta/e\Gamma$, vs pH of the solution. Note that $\tilde{\sigma}_\delta$ would be equal to +1 (or –1) if every surfactant headgroup bears a positive (or negative) elementary charge. One sees in the figure that, for $pH > 6.5$, $\tilde{\sigma}_\delta \ll 1$, which means that for the higher pH the surface charge density is much smaller than the surface density of the surfactant headgroups. On the other hand, $\tilde{\sigma}_\delta$ raises up to 0.75 for the lower pH because of the neutralization of the negative surface charge groups by adsorbed H^+ ions.

One can estimate the energy of adsorption of a Na^+ ion, Φ_2 ; supposedly, it is determined by the electrostatic interactions. In general, Φ_2 presents the work carried out to bring one Na^+ ion from the subsurface to the surface. Points A–C and A'–C' in Figure 9 denote respectively the positions of the first and second neighboring surfactant headgroups at the surface of the coated latex; D denotes the position of a Na^+ ion in the subsurface and P is the position of this ion when it is intercalated among the headgroups. Then we use the Coulomb law to estimate the work carried out to bring the Na^+ ion from point D to point P; thus, we obtain

$$\Phi_2 \approx \frac{3e^2}{\epsilon_h} \left(\frac{1}{r_a} - \frac{1}{\sqrt{r_a^2 + \delta^2}} \right), \quad r_a = \sqrt{\frac{2}{\Gamma\sqrt{27}}} \quad (4.7)$$

Here δ is the distance between points D and P and r_a is estimated assuming hexagonal packing of the surfactant headgroups (see Figure 9); ϵ_h is the dielectric constant in the headgroup region, which is expected to be smaller than the dielectric constant of the bulk water because of the water molecules belonging to the hydration shells around the ions.^{22,23} In our case $1/\Gamma = 56 \text{ \AA}^2$ and then one

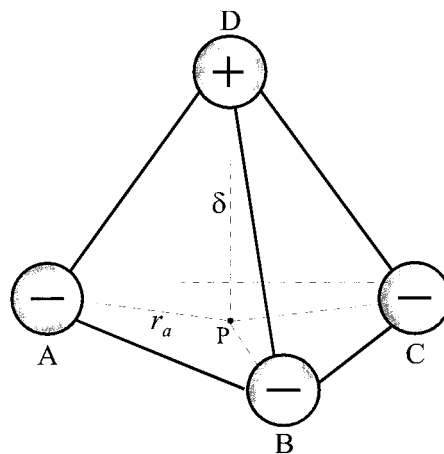


Figure 9. To the derivation of eq 4.7. A, B, and C denote the positions of first three neighboring surfactant headgroups; D and P denote the positions of a Na^+ ion in the subsurface and among the headgroups, respectively.

calculates $\rho_a = 4.6 \text{ \AA}$. Then taking the value $\Phi_2 = 3.7kT$ from Table 1 and setting $\epsilon_h = 32$ (see ref 23) by means of eq 4.7, one calculates $\delta = 5.1 \text{ \AA}$ for the adsorption of Na^+ ions; see Figure 6b. The latter value of δ is comparable to the diameter of the hydrated sodium ion, $d_{Na} = 7.2 \text{ \AA}$.

Changing the signs of the charges in Figure 9 to the opposite ones, one obtains the situation at low pH. Then taking the value $\Phi_3 = 5.0kT$ from Table 1 by means of eq 4.7, one calculates $\delta = 7.0 \text{ \AA}$ for the adsorption of Cl^- ions; see Figure 6a. The calculated values of δ seem reasonable as magnitude, and moreover, δ is expected to be larger for the Cl^- ions as compared to the Na^+ ones; cf. Figures 6 and 9. Of course, the above estimates of the δ 's are approximate insofar as the interaction of the adsorbing ion with the second neighbors, as well as the Debye screening of the electrostatic interaction, are neglected.

The fact that Φ_4 is larger than Φ_2 and Φ_3 can be attributed to collective effects due to the formation of an interfacial two-dimensional array of dipoles of mutually antiparallel orientation; see Figure 6b.

Finally, let us discuss the assumption of our model that the energy of adsorption of a LDAO molecule on the latex surface is not sensitive to the pH and ionic strength of the solution. This assumption will be true if the following condition is satisfied:

$$\exp(|u_{hph}|/kT) \gg \exp(|u_{el}|/kT) \quad (4.8)$$

Here u_{hph} is the contribution of the hydrophobic energy to the adsorption energy per LDAO molecule; u_{el} is the energy of the electrostatic repulsion between an adsorbed LDAO molecule and its neighbors. u_{el} could be larger for low pH (larger surface charge; see Figure 8) and for low ionic strength (weak Debye screening of the surface charges), and then eq 4.8 could be violated. Let us now check whether eq 4.8 is satisfied for our data in Figures 2 and 3.

One can estimate u_{hph} by means of the expression $u_{hph} = u_{chem} + 2u_{CH_3}$, where u_{chem} denotes the free energy gained when the hydrocarbon tail of LDAO is brought from the aqueous into the hydrophobic environment (see Figure 6); $2u_{CH_3}$ is the free energy of interaction of the two CH_3 groups of a LDAO molecule (those attached to the nitrogen atom; see eq 2.2), with their counterparts belonging to the neighboring molecules in the adsorption layer. One estimates $u_{chem} \approx \alpha_p l \approx 5.0 \times 10^{-20} \text{ J} \approx 12.2kT$, where l

= 1.67 nm is the length of a dodecyl chain²⁷ and $\alpha_p = 3 \times 10^{-11}$ J/m is a parameter related to the hydrophobic interaction.²⁸ In addition, u_{CH_3} can be estimated as the energy of hydrophobic attachment of two methane molecules in water, i.e., $u_{\text{CH}_3} \approx 8.5$ kJ/mol $\approx 3.44kT$; see, e.g., ref 26. Thus, finally one obtains $|u_{\text{hph}}| \approx 19.1kT$.

On the other hand, assuming hexagonal packing in the adsorption layer, one can estimate the electrostatic energy for the lower pH (all adsorbed LDAO molecules positively charged) by means of the expression

$$u_{\text{el}} \approx \frac{6e^2}{\epsilon_{\text{h}} r_{\text{a}}} \exp(-\kappa_{\text{s}} r_{\text{a}}) \quad (4.9)$$

where κ_{s} is a Debye screening parameter related to the concentration of the Cl^- ions, which are situated among the LDAO headgroups in the adsorption layer. Taking the value $\tilde{\sigma}_{\text{d}} \approx 0.75$ for pH = 3 (see Figure 8), one can estimate $\kappa_{\text{s}}^{-1} \approx 1.83$ Å, and then from eq 4.9 with $\epsilon_{\text{h}} = 32$ and $r_{\text{a}} = 4.6$ Å, one calculates $u_{\text{el}} \approx 1.9kT$. Consequently, it turns out that for the data in Figure 3 (pH ≥ 3 , $I = 0.01$ M) eq 4.8 is satisfied.

In addition, for our data in Figure 2 we have pH = 8.4 and hence the surface charge $\tilde{\sigma}_{\text{s}}$ is very small (see Figure 8). Therefore, for this practically electroneutral surface u_{el} should be much smaller than that for pH = 3, and eq 4.8 should be satisfied again, irrespective of the values of the ionic strength.

5. Summary and Concluding Remarks

In this work we investigate the properties of adsorption monolayers of an amphoteric surfactant, lauryldimethylamine oxide (called for brevity LDAO) by measuring the ζ -potential of latex particles covered with adsorbed surfactant molecules. In particular, we study the dissociation of the surfactant ionizable groups, as well as the association of ions from the solution to the ionizable groups of the amphoteric adsorption layer.

(27) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; Wiley: New York, 1980

(28) Israelachvili, J. N.; Wennerström, H. *J. Phys. Chem.* **1992**, *96*, 520.

First, we measured the ζ -potential vs the LDAO concentration (Figure 1). The results imply that for LDAO concentrations above 6×10^{-4} M the adsorption of LDAO on the latex particles exhibits saturation. This is confirmed also by independent determination of the amount of LDAO adsorbed on the particles by means of dynamic surface tension measurement (see Figure 4), which gives $1/\Gamma = 56$ Å² for the area per LDAO headgroup. The latter value corresponds to a dense adsorption layer.

Next, we measured the dependencies of ζ on the ionic strength and the pH of the solution; see Figures 3 and 4. These two experimental curves, coupled with the theoretical model for data interpretation (section 3), can be considered as a quantitative method for determination of the ionization state of the surfactant headgroups in the adsorption layer. We determine the equilibrium constants of association of H^+ , Na^+ , and Cl^- ions with the amphoteric surfactant headgroups. This enables one to predict the surfactant ionization state at various ionic strengths for $2.5 < \text{pH} < 9.5$; see eqs 3.1 and 3.2 and Table 1.

It is worth noting that the ionization state of the amphoteric surfactant turns out to be markedly different when the molecule is in the bulk of the solution and when it is incorporated in an adsorption monolayer; see eq 4.6 and the related text. In this aspect the method applied in this paper (based on the experimental curves from Figures 2 and 3 and the theoretical model from section 3), which gives the ionization state of the *adsorbed* molecules, brings additional information as compared with the *bulk* methods, such as the titration methods described in ref 1.

We hope that the method proposed in this study can be successfully applied also to other amphoteric surfactants and that it could be further extended to mixtures of amphoteric and anionic surfactants, which find application in household and personal-care detergency, emulsification, foaming, etc.

Acknowledgment. This work was supported by Colgate–Palmolive Co. and by the Bulgarian National Science Fund. The authors are indebted to Mr. Nikolai Dimov for obtaining the titration curves.

LA970958G