Titration of Fatty Acids Solubilized in Cationic and Anionic Micelles. Calorimetry and Thermodynamic Modeling

Olle Söderman,* Bengt Jönsson, and Gerd Olofsson

Physical Chemistry 1, P.O. Box 124, S-221 00 Lund, Sweden

Received: November 25, 2005; In Final Form: January 4, 2006

The electrostatic properties of charged surfactant micelles are investigated through titrations of fatty acid probes solubilized in the micelles. The titration process is followed by means of calorimetric measurements and by determining the pH values as a function of added base. This approach yields a complete thermodynamic description of the titration process. In particular, we find that the process is endothermic at 298 K. This is contrary to the titration of carboxylic acids in water, where ΔH is approximately 0. To identify the main effect underlying the difference in ΔH between titration in a micelle and water, a thermodynamic model has been developed which focuses on the transfer properties of charged and uncharged species from bulk water to the surface of a micelle and which incorporates a dielectric discontinuity at the micellar surface. The model relies on the use of the Poisson−Boltzmann equation which is solved using a finite element method. Experimental results and the model calculations imply that the dielectric discontinuity at (or near) the micellar surface plays a major role and hence must be included when analyzing the titration behavior of an acid functionality at the surface of a charged micelle.

Introduction

The electrostatic properties of ionic micelles continue to attract attention. One central issue is concerned with the polarizability of the interior and surface region of a micelle. After all, the interior of the micelle is expected to have a substantially lower value of the static permittivity than the surrounding water/counterion solution. This problem has been addressed in a recent publication,[1] in which it was argued that the presence of a dielectric interface in surfactant micelles gives rise to large energies for charges located very close to the interface; this is the so-called "image charge effect". This is contrary to some investigations of proteins, where the pK_a values of the amino acids at the surface of the proteins are predicted from Monte Carlo simulations using the dielectric continuum model without the need to include a dielectric discontinuity.[2,3]

Following the classical works of Mukerjee and Banerjee,[4] Fernandez and Fromherz,[5] and later Drummond et al.,[6] a typical experimental approach in the study of the electrostatic properties of the micellar surface has been to employ dye-based pH indicators with properties such that they are located at the micellar interface. Often these indicators are quite bulky, and it is unclear whether they really report on the properties of an unperturbed micelle.

In the present work, we investigate the electrostatic properties of ionic micelles by performing calorimetric experiments on the neutralization of dodecanoic acid solubilized in cationic and anionic C12-surfactant micelles. Dodecanoic acid is chosen as a probe, since it has 11 carbons in the chain, and is thus expected to minimally perturb the C12 micelles and can be expected to solubilize with the acid group at or close to the micellar charged headgroups. The experiments are carried out with on the average one acid probe per micelle, so as to minimize the perturbation of the micelles. By determining the heat evolved and the pH change as the acid is neutralized with NaOH, one can obtain

the acidity constant of the solubilized dodecanoic acid, $pK_{a,m}^{obsd}$ (in the quantities and equations presented here, we will use the index "m" to indicate micelles, whereas no index relates to conditions of bulk water) as well as the $\Delta H_{HA(m)\rightarrow A^-(m)+H^+}^{\circ}$ value for the reaction. This means that, by virtue of eq 1, both the $\Delta G_{HA(m)\rightarrow A^-(m)+H^+}^{\circ}$ and $\Delta S_{HA(m)\rightarrow A^-(m)+H^+}^{\circ}$ values for the dissociation of a fatty acid solubilized in a micelle are obtained in the experiments:

$$pK_{a,m}^{obsd} = \frac{\Delta G_{HA(m)\rightarrow A^-(m)+H^+}^{\circ}}{RT \ln 10} = \frac{\Delta H_{HA(m)\rightarrow A^-(m)+H^+}^{\circ} - T\Delta S_{HA(m)\rightarrow A^-(m)+H^+}^{\circ}}{RT \ln 10} \quad (1)$$

By comparing the $\Delta H_{HA(m)\rightarrow A^-(m)+H^+}^{\circ}$, $\Delta S_{HA(m)\rightarrow A^-(m)+H^+}^{\circ}$, and $\Delta G_{HA(m)\rightarrow A^-(m)+H^+}^{\circ}$ values with corresponding values for the dissociation of a fatty acid in an aqueous solution without the presence of other surfactant molecules, the difference in thermodynamics for the transfer of a charged dodecanoate species and an uncharged fatty acid from a bulk solution to the surface of an ionic micelle can be determined:

$$\Delta H_{transfer}^{\circ} = \Delta H_{HA(m)\rightarrow A^-(m)+H^+}^{\circ} - \Delta H_{HA\rightarrow A^-+H^+}^{\circ} = \Delta H_{A^-\rightarrow A^-(m)}^{\circ} - \Delta H_{HA\rightarrow HA(m)}^{\circ} \quad (2a)$$

$$\Delta S_{transfer}^{\circ} = \Delta S_{HA(m)\rightarrow A^-(m)+H^+}^{\circ} - \Delta S_{HA\rightarrow A^-+H^+}^{\circ} = \Delta S_{A^-\rightarrow A^-(m)}^{\circ} - \Delta S_{HA\rightarrow HA(m)}^{\circ} \quad (2b)$$

$$\Delta G_{transfer}^{\circ} = \Delta G_{HA(m)\rightarrow A^-(m)+H^+}^{\circ} - \Delta G_{HA\rightarrow A^-+H^+}^{\circ} = \Delta G_{A^-\rightarrow A^-(m)}^{\circ} - \Delta G_{HA\rightarrow HA(m)}^{\circ} \quad (2c)$$

In addition to the calorimetric measurements, we present a thermodynamic analysis of the difference in the electrostatic Gibbs energy for the transfer of a dodecanoate ion and a dodecanoic acid molecule from a bulk solution into a micelle. In the developed model, the general Poisson−Boltzmann

equation[7-9] is used to calculate the thermodynamic transfer properties of the charged and uncharged species. In the model, we focus on the electrostatic contributions, but the presence of other contributions is also touched upon.

It deserves to be mentioned that the problem treated here has some biological implications, namely, in the context of molecular association in fat digestion. This was realized at an early stage by Hofmann, who performed experiments related to ours in dispersions of bile salts and oleic acid−sodium oleate.[10] Other related work has been carried out and is described in refs 11 and 12. A common result of these studies, as well as of the studies of pH indicators referred to above,[5,6] and of NMR-based investigations of the same phenomena,[13] is that the pK_a value of an acid probe inserted in anionic, zwitterionic, or nonionic colloidal aggregates is shifted to higher values as compared with the values in water.

Experimental Section

Materials. The anionic surfactant sodium dodecyl sulfate (SDS) was supplied by Sigma, St. Louis, MO. The cationic surfactants dodecyltrimethylammonium chloride (DTAC) and dodecyltrimethylammonium bromide (DTAB) were purchased from Kasei, Tokyo, Japan. They were used as received. The prototropic probe molecule dodecanoic acid ($C_{12}H_{24}O_2$) was from Acros Organics, New Jersey, and a GC reference product. Sodium hydroxide (NaOH), analytical grade, was obtained from MERCK, Germany.

Sample Preparation. The aqueous solutions were prepared using Millipore filtered water (conductivity $<10^{-6}$ Ω^{-1} cm^{-1}). The samples were prepared by weighing appropriate amounts of surfactant, dodecanoic acid, and boiled water into glass tubes, which were immediately sealed off. They were stirred vigorously and heated in a water bath until a clear solution was obtained. The concentration of the surfactants used was 5 wt %, and the ratio of the number of surfactant molecules to the number of solubilized dodecanoic acid molecules was chosen to be about 60:1. Therefore, there should be on average one dodecanoic acid molecule in each micelle, considering the aggregation number of these micelles. The concentrations used are between 165 and 190 mM for the surfactants. In all cases, this is more than 10 times the critical micelle concentration (cmc) of the surfactants used.

Calorimetric Measurements. The titration calorimetric measurements were performed at 25.0 °C by using a twin heat-conduction microcalorimeter with a 20 mL vessel (Thermometic AB, Järfälla, Sweden). Weighed amounts of sample solution were titrated with 0.2 M NaOH that was injected stepwise from a gastight Hamilton syringe through a thin stainless steel capillary. The amount of sample was 16.9 g and the injection volume 29.7 μL, corresponding to 5.94 μmol of NaOH. A microprocessor-controlled motor-driven syringe drive was used to monitor the 10 consecutive additions. The fast titration procedure was used with 15 min between each injection.[14] All experiments were repeated twice, and the reproducibility was good. Although ΔH is measured, we will take this as $\Delta H°$ in the calculations. This approximation amounts to neglecting any dependence in the measured ΔH values on the fatty acid concentration.
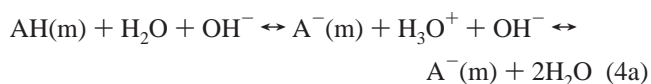
pH Titrations. The pH values were determined on identical samples to the ones investigated by calorimetry in separate experiments by using a Radiometer Copenhagen PHM 210 pH meter, which was calibrated before and after the experiments with pH 4 and pH 10 buffer solutions from Radiometer. No deviation in the calibration was detected, when comparing the results before and after the experiments. The titrations were carried out in a dynamic mode with increments of added NaOH varied according to the rate of the pH change and were stopped when the pH reached 10. The temperature was not regulated in the experiments, but it was measured each time and was typically about 25 °C. Titrations of acetic acid under a number of different conditions were used as control experiments in order to ascertain the validity of the pH measurements. Thus, the presence of both cationic and anionic surfactants below the cmc values had no influence on the obtained pK_a value for acetic acid. The same was true for the presence of SDS above its cmc.

Data Treatment. The heat evolved when NaOH is added to the reaction vessel originates from the following two reactions: (1) the dissociation of the dodecanoic acid and (2) the production of water from the reaction between H$^+$ and OH$^-$.

$$q_{\text{evolved}} = \Delta n_{\text{A}^-}(-\Delta H°_{\text{HA(m)}\rightarrow\text{A}^-\text{(m)+H}^+}) + \\ \Delta n_{\text{H}_2\text{O}}(-\Delta H°_{\text{H}^++\text{OH}^-\rightarrow\text{H}_2\text{O}}) \quad (3)$$

The Δn_{A^-} and $\Delta n_{\text{H}_2\text{O}}$ values can be obtained from the stoichiometric relations. We thus neglect any effects due to the difference in the degree of solubilization between the dodecanoic acid and dodecanoate ion. The studied reaction can be written as

$$\text{AH(m)} + \text{H}_2\text{O} + \text{OH}^- \leftrightarrow \text{A}^-\text{(m)} + \text{H}_3\text{O}^+ + \text{OH}^- \leftrightarrow \\ \text{A}^-\text{(m)} + 2\text{H}_2\text{O} \quad (4a)$$

and the equilibrium equation for the reaction is

$$\frac{[\text{A}^-\text{(m)}]}{[\text{AH(m)}]a_{\text{OH}^-}} = \frac{[\text{A}^-\text{(m)}]a_{\text{H}_3\text{O}^+}}{[\text{AH(m)}]K_\text{w}} = \frac{K_\text{a}^{\text{obsd}}}{K_\text{w}} = 10^{pK_\text{w}-pK_\text{a}^{\text{obsd}}} \quad (4b)$$

Please note that we write the observed dissociation constant as a mixed equilibrium constant, containing both activities and concentrations. As a consequence, any change in K_a^{obsd} reflects changes in the activity coefficients of A$^-$ and HA (see discussion in ref 1).

The amount of acid that is titrated and the amount of water formed in the reaction vessel can be written as

$$\Delta n_{\text{A}^-} = C_{\text{AH(m)+A}^-\text{(m)}}V\left(\frac{1}{1+10^{pK_\text{a}^{\text{obsd}}-\text{pH}}} - \\ \frac{1}{1+10^{pK_\text{a}^{\text{obsd}}-\text{pH}_{\text{start}}}}\right) \quad (5a)$$

$$\Delta n_{\text{H}_2\text{O}} = \Delta n_{\text{A}^-} + V(10^{-\text{pH}_{\text{start}}} - 10^{-\text{pH}}) \quad (5b)$$

where $C_{\text{AH(m)+A}^-\text{(m)}}$ is the total concentration of dodecanoic acid/dodecanoate and V is the volume of the sample (we neglect any dilution; note that the total added volume of sodium hydroxide is approximately 60 μL into a total volume of around 17×10^3 μL). If eqs 5a and b are used in eq 3, the equation for the heat evolved in the experiment becomes

$$q_{\text{evolved}} = -V(10^{-\text{pH}_{\text{start}}} - 10^{-\text{pH}}) \\ \left(\frac{C_{\text{AH(m)+A}^-\text{(m)}}(\Delta H°_{\text{HA(m)}\rightarrow\text{A}^-\text{(m)+H}^+} + \Delta H°_{\text{H}^++\text{OH}^-\rightarrow\text{H}_2\text{O}})}{(1+10^{pK_\text{a}^{\text{obsd}}-\text{pH}})(10^{-pK_\text{a}^{\text{obsd}}} + 10^{-\text{pH}_{\text{start}}})} + \\ \Delta H°_{\text{H}^++\text{OH}^-\rightarrow\text{H}_2\text{O}}\right) \quad (6)$$
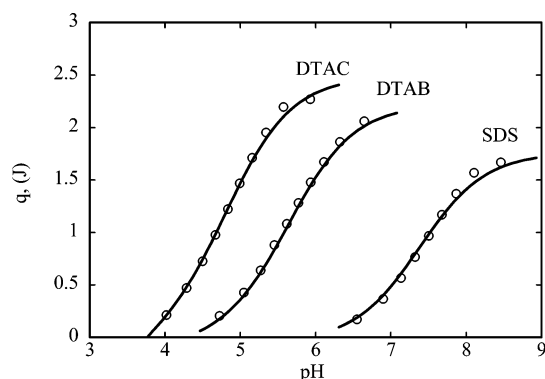
Figure 1. Cumulative heat evolved after the addition of OH⁻ plotted vs the pH. The surfactants in the micelles are from left to right DTAC, DTAB, and SDS, as indicated in the figure. The solid lines are the results of fitting eq 6 to the data. The results of the fits are summarized in Table 1.

TABLE 1: Results of Regressing the Data in Figure 1 onto eq 6 (Also Given Are Data for Acetic Acid in Water)

system	pK_a^{obsd}	$\Delta H^\circ_{HA(m)\rightarrow A'(m)+H^+}$/kJ mol⁻¹
DTAB	5.64 ± 0.04^a	10.0 ± 0.4
DTAC	4.82 ± 0.05	4.7 ± 0.6
SDS	7.45 ± 0.12	18.5 ± 0.7
acetic acid in water	4.8	-0.4 ± 0.1^{23}

a The errors are computed using the Monte Carlo technique described by Alper and Gelb.[24]

TABLE 2: Difference in the Transfer Energies of Charged and Uncharged Dodecanoate/Dodecanoic Acid Species from a Bulk Water Solution to Different Ionic Micelles (See eqs 2a−c)

surfactant	$\Delta H^\circ_{transfer}$/kJ mol⁻¹	$\Delta G^\circ_{transfer}$/kJ mol⁻¹	$\Delta S^\circ_{transfer}$/J(mol K)⁻¹
DTAB	10.0 ± 0.4	4.8 ± 0.2	17.4 ± 1.3
DTAC	4.7 ± 0.6	0.1 ± 0.3	15.4 ± 2.2
SDS	18.5 ± 0.7	15.1 ± 0.4	11.4 ± 2.7

Equation 6 has been used to determine $\Delta H^\circ_{HA(m)\rightarrow A^-(m)+H^+}$ and pK_a^{obsd} from the calorimetric measurements through a nonlinear least-squares procedure. The value used for $\Delta H^\circ_{H^++OH^-\rightarrow H_2O}$ at 25 °C is -55.85 kJ mol⁻¹.[15]

Results and Discussion

Experimental Results. The results of the calorimetric measurements are presented in Figure 1 where we give the cumulative heat evolved as a function of pH for the three ionic surfactants investigated. By fitting the parameters in eq 6 to the data in Figure 1, the pK_a and $\Delta H^\circ_{HA(m)\rightarrow A'(m)+H^+}$ values for the dissociation of dodecanoic acid at the surface of the studied micelles are obtained. The results of the fitting procedure are summarized in Table 1.

Since the thermodynamic properties of the carboxylic group in acetic acid, propionic acid, and butanoic acid change very little when the carbon chain length is increased, it is reasonable to assume that the values for acetic acid in Table 1 can also be used for dodecanoic acid in water.[16] The thermodynamics for the transfer of a charged and an uncharged fatty acid from a bulk solution into an ionic micelle (see eqs 2a−c) can now be determined from the values in Table 1. The obtained values are summarized in Table 2.

Table 1 shows that the titration reaction becomes endothermic when the fatty acid is solubilized in a micelle, while ΔH is approximately zero when the same process occurs in water. We feel that this is the main result of this study, and it reflects the presence of a dielectric discontinuity between the water environment and the interior of the micelle.

Thermodynamic Model for the Titration of a Fatty Acid at the Surface of an Ionic Micelle. As stated above, the dissociation reaction of a fatty acid becomes endothermic when the acid is solubilized in a micelle, and this fact reflects the environment in which the charged species is created.[7]

Since the transition region from the micellar interior to the water is complex, involving mobile charged surfactant headgroups, counterions, and a "rough" micellar surface, it is clear that a detailed modeling of this region is a very difficult task. Our aim in the theoretical interpretation of the experimental data is therefore to seek to identify the major contribution to the observed effect. As a consequence, we do not expect our model to yield quantitative agreement with the experimental data, but we demand of it to give data that are qualitatively correct. Our point of departure is that the main reason for the difference between titration of the acid in water and in a micelle is the fact that the dielectric properties change over a rather narrow transition region at the micellar/water interface.

The model is based on the thermodynamics of four well-defined states, which are (1) dodecanoic acid in a micelle, HA(m); (2) dodecanoic acid in the bulk solution, HA; (3) dodecanoate ion in the bulk solution together with a proton, $A^- + H^+$; and (4) dodecanoate ion in a micelle together with a proton, $A^-(m) + H^+$.

States 4 and 1 are compared when the titration of an acid group at the surface of a micelle is considered, and states 3 and 2 are compared when the titration of a fatty acid in a bulk solution is considered. The difference in Gibbs energy (or enthalpy/entropy) between states 1 and 2 is called the Gibbs transfer energy in the model, $\Delta G^\circ_{AH,transfer}$ (or transfer enthalpy/entropy, $\Delta H^\circ_{AH,transfer}/\Delta S^\circ_{AH,transfer}$), of the fatty acid. The transfer property of a dodecanoate ion depends on states 4 and 3, and we denote it $\Delta G^\circ_{A^-,transfer}$ (or for the transfer enthalpy/entropy, $\Delta H^\circ_{A^-,transfer}/\Delta S^\circ_{A^-,transfer}$).

By comparing states 1−4, it is clear that the difference in the change of the standard thermodynamic properties, when a fatty acid is solubilized in a micelle and in a bulk solution, can be written as (for Gibbs energy, corresponding relations for the enthalpy and entropy are easily obtained):

$$\Delta G^\circ_{AH(m)\rightarrow A^-(m)+H^+} = G^\circ_4 - G^\circ_1 = \Delta G^\circ_{1\rightarrow 2} + \Delta G^\circ_{2\rightarrow 3} +$$
$$\Delta G^\circ_{3\rightarrow 4} = \Delta G^\circ_{2\rightarrow 3} + (\Delta G^\circ_{3\rightarrow 4} - \Delta G^\circ_{2\rightarrow 1}) = \Delta G^\circ_{AH\rightarrow A^-+H^+} + \Delta G^\circ_{transfer} \quad (7)$$

where, according to eqs 2a−c, $\Delta G^\circ_{transfer}$ is given by

$$\Delta G^\circ_{transfer} = \Delta G^\circ_{A^-,transfer} - \Delta G^\circ_{AH,transfer} \quad (8)$$

The corresponding relations for $\Delta H^\circ_{transfer}$ ($\Delta S^\circ_{transfer}$ is obtained by replacing H with S below) are

$$\Delta H^\circ_{AH(m)\rightarrow A^-(m)+H^+} = \Delta H^\circ_{AH\rightarrow A^-+H^+} + \Delta H^\circ_{transfer} \quad (9)$$

with

$$\Delta H^\circ_{transfer} = \Delta H^\circ_{A^-,transfer} - \Delta H^\circ_{AH,transfer} \quad (10)$$

From eqs 7 and 9, it is clear that the thermodynamics involved in the titration of a fatty acid at the surface of a micelle can be calculated from the thermodynamics of the same reaction in a bulk solution if the quantities $\Delta G^\circ_{transfer}$ and $\Delta H^\circ_{transfer}$ are known. Since these quantities are obtained from the experimental

Titration of Fatty Acids Solubilized in Micelles
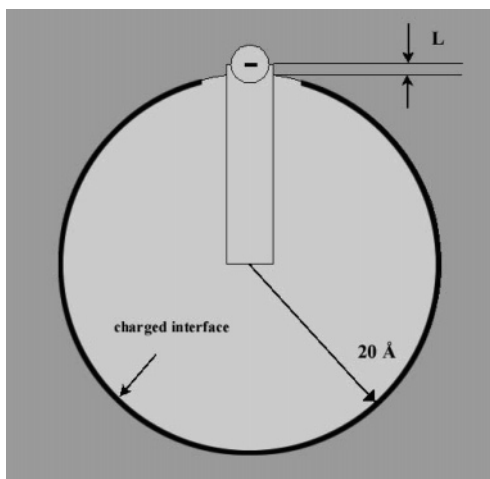
J. Phys. Chem. B, Vol. 110, No. 7, 2006 **3291**

Figure 2. Cross section through the center of a micelle with one solubilized dodecanoate ion. The solubilized dodecanoate ion is assigned an area at the micellar interface of 75 Å^2, and its charge sits in the center of a spherical headgroup with a radius of 2 Å (see text for more details).

data (see Table 2), we will use the outlined model to predict them so that the model can be compared with the experimental data.

The main contribution according to our model to $\Delta G^\circ_{transfer}$ and $\Delta H^\circ_{transfer}$ is the electrostatic interaction between the charged dodecanoate ion and the charges and ions at or near the surface of the micelle. Another contribution is the hydrophobic effect, which of course is the effect responsible for the formation of the micelle in the first place. If there is a difference in the total water−hydrocarbon contact when a charged dodecanoate or uncharged fatty acid species is solubilized in a micelle, there will be a contribution to $\Delta G^\circ_{transfer}$ and $\Delta H^\circ_{transfer}$. However, we will neglect this effect in the model developed here and assume that $\Delta G^\circ_{transfer}$ and $\Delta H^\circ_{transfer}$ can be calculated from the electrostatic interactions, which we shall describe by means of the Poisson−Boltzmann equation.[7,8]

The fatty acid is approximated as a cylindrical hydrocarbon region with a 2.5 Å radius and a spherical headgroup with a 2 Å radius; see Figure 2. The charge of the fatty acid/dodecanoate ion is in the calculation zero/−1 unit charge, and the charge is placed in the center of the spherical headgroup; see Figure 2. Please note that $\Delta G^\circ_{AH,transfer}$ and $\Delta H^\circ_{AH,transfer}$ are not zero, since the properties of the micelle are changed when the (noncharged) fatty acid is introduced in the micelle.

The micelle is approximated as a spherical aggregate with a 20 Å radius. The charged headgroups of the surfactants building the micelle are modeled by a charge density on the surface of the micelle. This surface charge density is assumed to be constant on the micelle except in a 75 Å^2 circular region around the fatty acid/dodecanoate ion where the surface charge density is assumed to be zero. In the case of the dodecanoate ion, one unit charge is placed in the center of a spherical headgroup with a radius of 2 Å (see Figure 2). In the calculations, the surface charge density is assumed to be +0.2 C m^{-2} for the DTAC and DTAB micelles and −0.2 C m^{-2} for the SDS micelle (corresponding to one unit charge per 75 Å^2). Different distances between the center of the spherical headgroup and the surface of the micelle, L in Figure 2, have been used in the calculations.

The dielectric constant in the micelle and in the fatty acid/dodecanoate ion is assumed to be 2 at all temperatures, and the dielectric constant in the water solution outside the micelle is
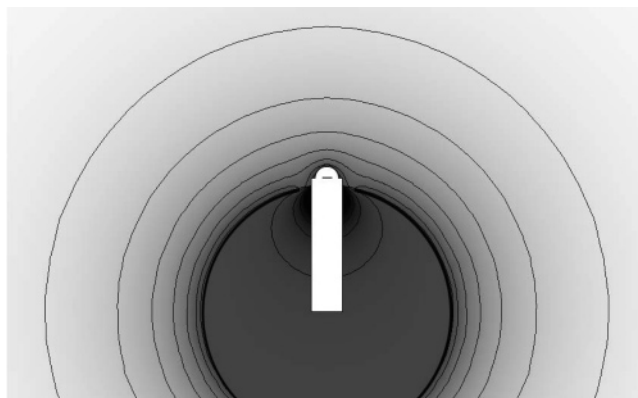

Figure 3. Potential profile around a charged dodecanoate ion solubilized in an anionic micelle. The contour line represents the (reduced) potentials $e\phi/k_BT = -1.0, -2.0$, and so on beginning at the largest radius.

assumed to follow the temperature dependence given in eq 11 (with T in K).[17]

$$\epsilon_r = 307.1 \exp\left(-\frac{T}{218.3}\right) \qquad (11)$$

In all calculations, the salt concentration is assumed to be 0.01 M in the solution surrounding the micelles, which is close to the cmc values for the surfactant used here. To solve the Poisson−Boltzmann differential equation for the system specified in Figure 2, a finite element method was used. Thus, the FEMLAB program[18] was used to numerically solve the general form of the Poisson−Boltzmann equation.

The electrostatic Gibbs energy of the system is calculated as a function of the distance, L (cf. Figure 2), for a charged dodecanoate and an uncharged fatty acid at three different temperatures, 296.15, 298.15, and 300.15 K. From these values, both the electrostatic Gibbs energy and the electrostatic enthalpy of the system are calculated by using the Gibbs−Helmholtz equation. A typical potential profile around a dodecanoate ion solubilized in a SDS micelle is given in Figure 3, while the results for $\Delta G^\circ_{transfer}$ and $\Delta H^\circ_{transfer}$ are presented in Figures 4 and 5, where also the experimental values from Table 2 are included. Please note that there are no adjustable parameters in the calculations.

Discussion. The effect of the electrostatic interaction between the charged dodecanoate species and the charges on the micellar surface depends on the sign of the charge of the micelle. For the case of an anionic micelle, the base form of the fatty acid is destabilized (disregarding all other effects than electrostatic interactions between the surfactants and the carboxylate probe) which would make the acid *weaker* than in water, and this is observed. However, for the case of a cationic micelle, the base form is stabilized which would make the acid *stronger* than in water, and this is not observed (cf. Table 1). This observation indicates that the dielectric discontinuity at the micellar interface does indeed play a role in determining the acid/base properties of the solubilized probe. We note that a fatty acid becomes a weaker acid when solubilized in phospholipid vesicles[12] and in nonionic micelles.[1,13] Thus, it seems clear that effects other than the interaction of the carboxylate group with the charges at the micellar interface must play a role. One such effect is provided by the presence of the low dielectric medium of the micellar interior, giving rise to the image charge effect discussed in the Introduction.

On the level of description as given by the model outlined above in Figure 2 and described in the text above, it is clear
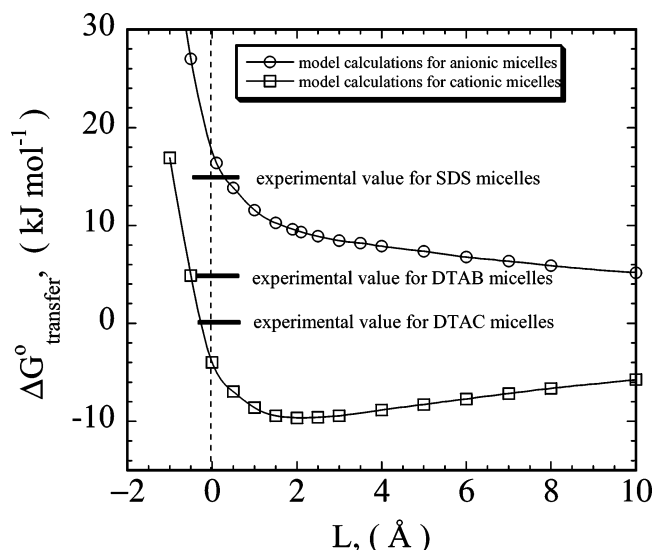
Figure 4. $\Delta G^{\circ}_{\text{transfer}}$ for anionic and cationic micelles as a function of the distance, L (see Figure 2). Experimental values from Table 2 together with corresponding values from the model calculations are given. The calculations have been performed at discrete values of L, as indicated by the symbols. The solid lines through the calculated points are merely guides to the eye.

Figure 5. $\Delta H^{\circ}_{\text{transfer}}$ for anionic and cationic micelles as a function of the distance, L (see Figure 2). Experimental values from Table 2 together with corresponding values from the model calculations are given. The calculations have been performed at discrete values of L, as indicated by the symbols. The solid lines through the calculated points are merely guides to the eye.
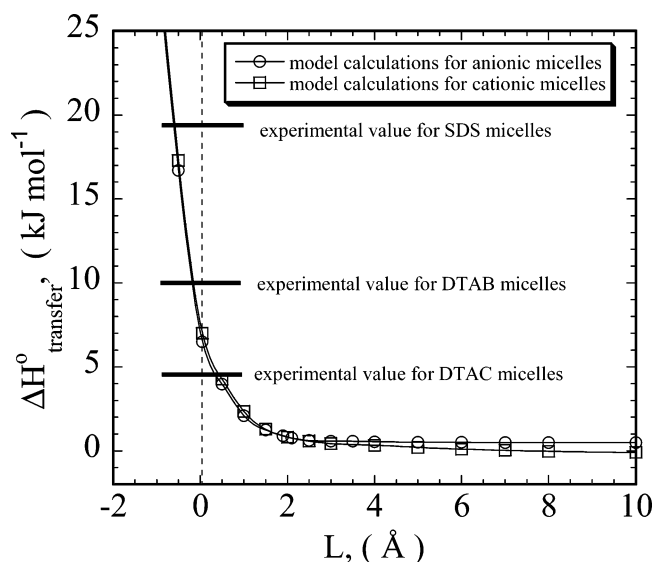
that image charge effects destabilize the base form of the fatty acid in both cationic and anionic micelles as long as the headgroup of the fatty acid is close to the surface of the micelle. This is evident from Figure 4, where the steep increase in $\Delta G^{\circ}_{\text{transfer}}$ at small positive and negative L values is, in the model, a result of the low dielectric constant in the interior of the micelles. Model calculations show that the steep increase disappears if the dielectric constant of the interior of the micelle is set equal to the dielectric constant of the surrounding solution (data not shown). This means that the closest agreement between the results obtained in the experiments and the model calculations is obtained if the interior of the micelle is assumed to have a much lower dielectric constant than the surrounding solution. It is also clear that $\Delta G^{\circ}_{\text{transfer}}$ depends critically on the

value of L. This makes a comparison of the model and the experimentally obtained $\Delta G^{\circ}_{\text{transfer}}$ values difficult, since the calculated values of $\Delta G^{\circ}_{\text{transfer}}$ vary steeply with L around $L = 0$ and since the value of L for a probe in a micelle is not exactly known. We note that, for $L = 0$, we predict the value of $\Delta G^{\circ}_{\text{transfer}}$ reasonably well for SDS, whereas the values for DTAC and DTAB depart more from the experimental values, more so for DTAB. We will return to this specific ion effect below.

The same behavior observed for the $\Delta G^{\circ}_{\text{transfer}}$ values is also seen for the $\Delta H^{\circ}_{\text{transfer}}$ values. As seen in Figure 5, the best agreement between the results from the experiments and the model calculations is obtained if the interior of the micelle is assumed to have a much lower dielectric constant than the surrounding solution. If the dielectric properties of the interior of the micelles in the model calculations are assumed to be the same as those in the surrounding aqueous solution, the $\Delta H^{\circ}_{\text{transfer}}$ values will be very small at all L values (data not shown). As for $\Delta G^{\circ}_{\text{transfer}}$, there is a sharp change in $\Delta H^{\circ}_{\text{transfer}}$ around $L = 0$, which again makes the comparison between the experimental and calculated values difficult. We note that the increase in $\Delta H^{\circ}_{\text{transfer}}$ as L becomes negative reflects the fact that the free energy of a charge in a nonpolar solvent is dominated by enthalpy.[7]

Thus, our calculations do indeed reproduce the observed trends reported in Figures 4 and 5. In particular, we reproduce the observation that the dissociation reaction becomes endothermic when it occurs in the micelle. However, on account of the simplifications made in the descriptions of the micellar interface, the model is not capable of quantitatively reproducing the experimental values.

In conclusion, it is clear that the presence of the dielectric discontinuity is necessary when modeling the change in pK_a when a fatty acid probe is transferred to a micelle from water. It is also clear that the simplified model of a discontinuity of the dielectric constant at the surface of a micelle, as is assumed in the model used here, is probably too simplistic of a model. To obtain a better fit, a more detailed description of the dielectric behavior of the surface region is necessary. One improvement would be to include a region over which the dielectric properties vary continuously from the hydrocarbon value to that of water. It also appears that a detailed description of the dielectric behavior of the surface region is probably more important for the modeling of the $\Delta H^{\circ}_{\text{transfer}}$ values compared with the $\Delta G^{\circ}_{\text{transfer}}$ values, as can be seen from Figures 4 and 5.

Of course, our electrostatic calculations cannot predict the specific ion effects observed for DTAC/DTAB. Such effects are ubiquitous,[19] and their origins are intensely debated.[20,21] In our experiments, the specific ion effect makes the acid probe weaker in the micelles formed from surfactants with bromide counterions as compared to those with chloride counterions, with everything else being equal. This effect can be rationalized in terms of a stronger headgroup screening in the case of Br^- as counterion, caused by a larger degree of counterion binding for Br^- to the micellar surface compared to Cl^-. Ninham and co-workers argue that this specific ion effect is caused by dispersion interactions.[22] Thus, the effect can be attributed to the effect of the larger polarizability of the Br^- ion, compared to the Cl^- ion.

Summarizing Remarks

The main results of this work can be summarized as follows:
(1) We present a combination of calorimetric and potentiometric measurements of the titration behavior of a fatty acid

Titration of Fatty Acids Solubilized in Micelles

J. Phys. Chem. B, Vol. 110, No. 7, 2006 **3293**

probe solubilized in a micelle. The experiments yield a full thermodynamic characterization of the process.

(2) The dissociation reaction of a fatty acid becomes endothermic when it occurs in a micelle.

(3) A thermodynamic model has been devised which yields results that are directly comparable with the experimental data.

(4) The model is solved on the general Poisson–Boltzmann level, in which the fatty acid probe is described with molecular detail.

(5) Experiments and model calculations show that effects of the dielectric discontinuity are important and must be included in the analysis of the titration behavior of acid functionalities close to a dielectric discontinuity.

(6) The model does not provide quantitative agreement with the experimental data. This is due to the lack of detail in the description of the micellar surface region and the omission of specific, nonelectrostatic effects.

(7) Specific ion effects are observed for Br^- and Cl^- counterions.

References and Notes

(1) da Silva, F.; Bogren, D.; Söderman, O.; Åkesson, T.; Jönsson, B. *J. Phys. Chem. B* **2002**, *106*, 3515.

(2) Kesavatera, T.; Jönsson, B.; Thulin, E.; Linse, S. *J. Mol. Biol.* **1996**, *259*, 828.

(3) da Silva, F.; Jönsson, B.; Penfold, R. *Protein Sci.* **2001**, *10*, 1415.

(4) Mukerjee, P.; Bannerjee, K. *J. Phys. Chem.* **1964**, *68*, 3657.

(5) Fernández, M. S.; Fromherz, P. *J. Phys. Chem.* **1977**, *81*, 1755.

(6) Drummond, C. J.; Warr, G. G.; Grieser, F.; Ninham, B. W.; Evans, D. F. *J. Phys. Chem.* **1985**, *89*, 2103.

(7) Evans, D. F.; Wennerström, H. *The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet*, 2nd ed.; VCH Publishers: New York, 1999.

(8) Israelachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1992.

(9) Jönsson, B. The Thermodynamics of Ionic Amphiphile-Water Systems–A Theoretical Analysis. Thesis, Lund University, 1981.

(10) Hofmann, A. *Adv. Chem. Ser.* **1968**, *84*, 53.

(11) Parks, J.; Cistola, D.; Small, D. M.; Hamilton, J. A. *J. Biol. Chem.* **1983**, *258*, 9262.

(12) Cistola, D. P.; Small, D. M. *J. Clin. Invest.* **1991**, *87*, 1431.

(13) Whiddon, C. R.; Bunton, C. A.; Söderman, O. *J. Phys. Chem. B* **2003**, *107*, 1001.

(14) Bäckman, P.; Bastos, M.; Hallén, D.; Lönnbro, P.; Wadsö, I. *J. Biochem. Biophys. Methods* **1994**, *28*, 85.

(15) Hepler, L. G.; Wooley, E. M. *Water: A comprehensive Treatise*; Plenum Press: New York, 1973; Vol. 3.

(16) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1977; Vol. 3.

(17) *Handbook of chemistry and physics*, 52nd ed.; Weast, R., Ed.; The Chemical Rubber Co.: Cleveland, OH, 1971.

(18) See: http://www.comsol.com.

(19) Kunz, W.; Nostro, P. L.; Ninham, B. W. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 1.

(20) Kunz, W.; Belloni, L.; Bernard, O.; Ninham, B. W. *J. Phys. Chem. B* **2004**, *108*, 2398.

(21) Manciu, M.; Ruckenstein, E. *J. Phys. Chem. B* **2004**, *108*, 20479.

(22) Ninham, B.; Yaminski, V. *Langmuir* **1997**, *13*, 2097.

(23) Olofsson, G. *J. Chem. Thermodyn.* **1984**, *16*, 39.

(24) Alper, J. S.; Gelb, R. I. *J. Phys. Chem.* **1990**, *94*, 4747.