Ionic Interactions of Fatty Acid Monolayers Studied by Ellipsometry

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Monolayers of fatty acids with chain lengths of 15, 16, 18, and 22 carbons at the air/water interface were studied on aqueous substrates containing hydrochloric acid, cadmium chloride, and lead chloride by using phase-modulated ellipsometry. The change in ellipsometric phase angle $\delta\Delta$, which is the phase difference between the orthogonal s and p waves, was found to be linearly dependent on chain length with the same coefficient for all three cations whereas the magnitude of $\delta\Delta$ was shown to be different. The proportionality constant with respect to chain length was modeled in terms of the refractive index contributions of the hydrocarbon tails, giving thicknesses in agreement with those obtained by other techniques. The magnitudes of $\delta\Delta$ were analyzed in terms of film refractive index anisotropy, whereby our results were shown to be consistent with anisotropic refractive indices obtained by other methods. They were also examined relative to pH values and cation concentration, and the results are discussed in terms of a refractive index increase due to the interaction of carboxylates with divalent cations.

Introduction

The structure of surfactant monolayers at liquid interfaces has implications for a wide range of surface phenomena such as on membranes, emulsions, and transferred Langmuir-Blodgett (L-B) films. Techniques used in the study of fatty acid monolayers on liquid interfaces include X-ray scattering,[1-5] neutron scattering,[4,6] ellipsometry,[7,8] and nonlinear optical techniques.[9,10] The application of techniques to structural studies of transferred L-B multilayers includes X-ray scattering,[3,6,11-13] neutron scattering,[4,6] spectroscopy,[14-17] and ellipsometry.[18]

The majority of the above studies concerns fatty acids in the presence of divalent cations because of their use in L-B films. Therefore, an important variable for ionized fatty acids in these systems is the nature of their interactions with multivalent cations. This has been pursued for monolayers and L-B films as a function of chain length, cation concentration, and pH.[1,16,19-23]

The sensitivity of ellipsometry at the air/liquid interface at low degrees of surface coverage, where surface density is readily manipulated, is illustrated by several recent reports.[7,8,24-27] Due to the occurrence of multiphasic surface regions at the air/water interface,[11,28] we have restricted our investigation to the homogeneous regions where $\delta\Delta$ is relatively independent of small changes in density. This has allowed us to concentrate on the effects of chain length and interactions of multivalent cations on a single phase. Despite evidence for various phenomena ascribed to the two-dimensional phase behavior of fatty acids obtained by ellipsometry,[8] it is generally difficult to interpret the results in terms of macroscopic properties, such as thickness or refractive index. In this paper, we present results on several fatty acids in the condensed state. We show that the increase in the ellipsometric phase angle $\delta\Delta$ with chain length is due to an increase in monolayer thickness and the magnitude of

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$\delta\Delta$ for a given chain length is attributed to an association of cations (Cd^{2+} and Pb^{2+}), resulting in increases of the head group refractive index of the fatty acid. The pH and cation concentration have been shown to control the degree of interaction of these cations.

Experimental Section

Materials. Pentadecanoic acid, designated here as C_{15}, was purified as described elsewhere[28] and was kindly supplied by Dr. Brian Pethica. Stearic acid, C_{18} (99+% purity, Applied Science Labs), was recrystallized 3 times from *n*-hexane (99.9%, spectrophotometric grade, Aldrich). Palmitic acid, C_{16} (99%, Fluka), and behenic acid, C_{22} (97%, Aldrich), were used as received.

HPLC grade hexane (American Brudick and Jackson, supplied by American Scientific Products) was used as the spreading solvent for C_{15}, C_{16}, and C_{18}, and chloroform (Fisher Scientific, ACS grade) was used for C_{22}. The concentrations of the spreading solutions were 1.5–2.5 mg/mL.

The subphase water was in-house deionized water with a Millipore Milli-Q filtering system with one carbon and two ion-exchange stages. The pH of the subphase solutions was adjusted with solutions of HCl (Baker Chemical Co., 37%, ACS grade) and of NaOH (Baker Chemical Co., 98%). The two metal chlorides, CdCl$_2$ (99.999%, Gold label, Aldrich) and PbCl$_2$ (99.999%, Gold label, Aldrich), were used as received.

Methods. All experiments were performed at room temperature (23.0 ± 0.2 °C) on a Teflon-coated Lauda trough (area of 700 cm^2). The surface pressure was measured by using the Langmuir film balance technique by monitoring the horizontal force of the monolayer against a Teflon barrier. The surface concentration of fatty acid monolayers was adjusted with a sliding Teflon barrier or by continuous addition of fatty acid using a microsyringe. The surface was cleaned by aspiration and checked before each run by a 30-fold compression. In all cases, the surface pressure changed by less than 0.1 dyn/cm.

Our instrument is based on modulation ellipsometry principles which have been reviewed previously.[29] The experiments were performed at a fixed incident angle in air (ϕ_0 = 64.1° ± 0.1° measured relative to the outward normal to the surface) by using a 5-mW He–Ne laser beam with λ = 6328 Å (1-mm beam diameter).

An expression for films with dimensions small compared to the wavelength of light has been formulated by Drude[30] and extended by den Engelsen and co-workers[7,35] for birefringent thin films:

$$[\tan\Psi' \exp(i\Delta')]/[\tan\Psi \exp(i\Delta)] = [1 + i4\pi d_1 \cos\phi_0 \times$$
$$\sin^2\phi_0 n_2{}^2 M]/[\lambda(n_2{}^2 - n_0{}^2)(n_0{}^2\sin^2\phi_0 - n_2{}^2\cos^2\phi_0)] \quad (1)$$

where Ψ is the amplitude attenuation, Δ the phase difference, d_1 the film thickness, n_0 = 1.0 the refractive index of air, and n_2 = 1.332 the refractive index of water. ϕ_0 and λ are as defined above. The monolayer-covered surface and the clean water surface are represented by Ψ', Δ' and Ψ, Δ, respectively. The parameter M is defined as

$$M = n_0{}^2 + n_2{}^2 - (n_x{}^2 + n_0{}^2 n_2{}^2/n_z{}^2) \quad (2)$$

where the anisotropy in the film refractive index is defined by two indices: n_z, which is in the direction normal to the surface, and $n_x = n_y$, which are in the plane parallel to the surface.

In our phase-modulated experiment, absolute values of Δ' or Δ were not determined. Only the change in the ellipsometric

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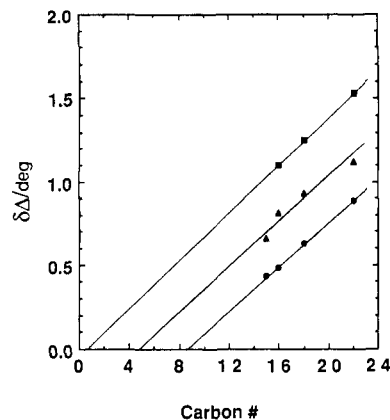

Figure 1. Change in ellipsometric phase angle $\delta\Delta$ vs carbon number for fatty acid monolayers on 1 mM PbCl$_2$ (squares), 1 mM CdCl$_2$ (triangles), and 10 mM HCl (circles). The lines are drawn through the data to illustrate the trend. See text for other details.

Table I. Chain Length Dependence of $\delta\Delta$ (in Degrees)

| | $\delta\Delta$ | | |
carbon	HCl[a]	CdCl$_2$[b]	PbCl$_2$[b]
15	0.43 ± 0.03	0.66 ± 0.04	
16	0.48 ± 0.02	0.81 ± 0.04	1.10 ± 0.03
18	0.63 ± 0.02	0.93 ± 0.04	1.25 ± 0.02
22	0.89 ± 0.04	1.12 ± 0.04	1.53 ± 0.02

[a] pH = 2. [b] pH = 5.5 ± 0.2. Errors are estimated from one standard deviation of replicative determinations of phase angles.

phase angle $\delta\Delta$ was measured:

$$\delta\Delta = \Delta' - \Delta \quad (3)$$

The Drude equations show directly[7,35] that the difference in amplitude attenuation

$$\delta\Psi = \Psi' - \Psi \quad (4)$$

is approximately zero for nonadsorbing substrates so all monolayer information must be determined from $\delta\Delta$. Thus, $\delta\Psi$ was not measured in this study. The thickness d_1 and $\delta\Delta$ are related by

$$\delta\Delta = \alpha d_1 \quad (5)$$

where the proportionality constant α can be calculated by using eq 1. Since the only quantity determined is $\delta\Delta$, either the refractive index or film thickness must be known or assumed. Measurements of n_1 for transferred L–B films of fatty acids[18,33–35] indicate that they are birefringent. Thus one can in principle determine the birefringence of the monolayer at A/W; however, that is yet to be accomplished experimentally. Under such a circumstance, one could attempt to estimate n_z and n_x, which should substantially complicate the analysis because many combinations of n_z and n_x give the same apparent result in terms of α.

Results

Fatty Acids in the Presence of 10 mM HCl, 1 mM CdCl$_2$, and 1 mM PbCl$_2$. Values of $\delta\Delta$ vs carbon number are plotted in Figure 1, and listed in Table I, for various saturated fatty acids spread on 10 mM HCl, pH 2.0, and solutions containing different cations at pH 5.5. The precision of $\delta\Delta$ was 0.02°, and the reproducibility, as determined by one standard deviation of replicate runs, was 0.04° or less. The $\delta\Delta$ values for C_{16}, C_{18}, and C_{22} on HCl were found to be constant within experimental error between surface pressures of 1–30 dyn/cm. Because of the presence of a LE/LC phase transition at 7–8 dyn/cm for C_{15} on HCl, $\delta\Delta$ values were measured between 10 and 20 dyn/cm and found to be constant. A surface pres-
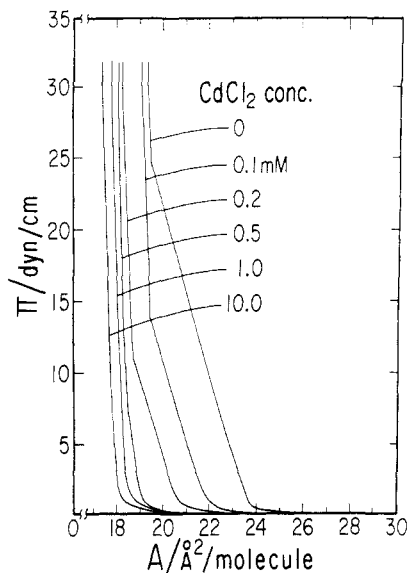
Figure 2. Surface pressure (Π) vs surface area for C_{18} monolayers on aqueous substrates with the $CdCl_2$ concentrations in units of mM indicated in the figure. The isotherms are obtained by averaging over several compression–expansion cycles at a rate of 8 cm^2/min of surface area change, which amounts to about 0.6 $\mathring{A}^2/molecule$ per min.

Table II. Subphase Cadmium Concentration Dependence of Stearic Acid at pH 5.5

$CdCl_2$ concn, mM	$\delta\Delta$, deg	kink pressure,[a] dyn/cm
0.0	0.63 ± 0.04	25 ± 0.2
0.1	0.78 ± 0.04	14 ± 0.5
0.2	0.89 ± 0.04	11 ± 0.5
0.5	0.85 ± 0.03	7 ± 0.5
1.0	0.93 ± 0.02	no kink
10.0	0.95 ± 0.03	no kink

[a] This is the inflection of the Π–A isotherms at the liquid-condensed/solid transition.

sure range of 1–30 dyn/cm amounts to a monolayer density change of about 15%. The observed constancy of $\delta\Delta$ over this range of the density variation is difficult to explain, although we speculate that once the hydrocarbon tails are lifted off the A/W interface the refractive index of monolayer depends insensitively on the mass density of the monolayer. In the absence of divalent cations, the results for C_{22} were independent of pH from 2 to 7. The intercept at about 8 carbons for pH 2 in Figure 1 is consistent with the results of den Engelsen and de Koning[7] under similar conditions of negligible amounts of divalent cations.

In the presence of 1 mM $CdCl_2$ or 1 mM $PbCl_2$ at pH 5.5 ± 0.2, the isotherms for all chain lengths were indistinguishable within experimental error (see Figure 2 for 1 mM $CdCl_2$). As expected, $\delta\Delta$ was independent of surface pressure for Π = 1–30 dyn/cm within experimental error; it is ascribed to an insignificant change in the monolayer refractive index over the surface pressure range of 1–30 dyn/cm due to a monolayer density change of less than 5%.

All values of $\delta\Delta$ were confirmed to be reversible, by performing two or three full compression–expansion cycles. For C_{16}, C_{18}, and C_{22}, it was found that the $\delta\Delta$ values were independent of the number of compression cycles and of surface pressure in the range 1–30 dyn/cm, consistent with X-ray reflection experiments on PbC_{18} (designating stearic acid in the presence of $PbCl_2$), which showed almost no change in X-ray intensity, peak position, or peak width over the same range.[2] The only exception was C_{22} at 1 mM $PbCl_2$. Upon compressing for the first time, this sample gave a more "expanded" isotherm and a lower value of $\delta\Delta$ than the one in Table I. Expanded isotherms for higher chain length fatty acids where Π begins to increase in the range 25–30 $\mathring{A}^2/molecule$ have been reported previously in the presence of lead.[23] We found that upon compressing and expanding for a second and third time, the isotherm was condensed with a limiting area at zero surface pressure of ~18.5 $\mathring{A}^2/$ molecule and the $\delta\Delta$ values had reached the constant value given in Figure 1 and Table I. We speculate that the enhanced rigidity of the monolayer of C_{22}, due to the

longer chain length, somehow decreases the initial interaction of Pb^{2+} with the fatty acid. The enhanced rigidity could decrease the mobility of the fatty acid head groups or alternatively alter the water structure in the vicinity of the head groups. As a consequence, compressing the monolayer to ~5 dyn/cm leads to complete association with Pb^{2+} as the negatively charged carboxylate groups are neutralized as they are forced together during compression. No further changes are seen in $\delta\Delta$ for the second and third compression cycles. Thus, this process is termed a "compression-initiated" formation of lead dibehenate (PbC_{22}).

One crucial aspect of the interaction of divalent cations is the effect of pH. It is known that the degree of association of a divalent cation is partially regulated by an effective pK_a of the fatty acid in a monolayer. For example, at higher pHs the carboxylic group is dissociated leading to enhanced association with divalent cations. The extent of association also depends on the strength of the binding of the divalent cations to the carboxylic group. A large difference has been reported for Pb^{2+} and Cd^{2+}, where at pH 5.5 the fatty acid monolayers are ~100% in the form of lead distearate[20] while due to the decreased strength of binding of Cd^{2+} only 40–50% association is found at the same pH;[1,16,22] it is not known whether stearic acid is in the form of cadmium distearate or monostearate. At pH 6.8 and greater, 100% cadmium distearate formation[1,16,22] results. Preliminary experiments with CdC_{18} at pH 9 gave $\delta\Delta = 1.12°$ as compared to $\delta\Delta = 0.93°$ at pH 5.5. These experiments at pH 9, however, are subject to error because the monolayers were found to dissolve, as judged by poor reproducibility upon performing more than one compression–expansion cycle. They are consistent with the fact that more cadmium stearate is formed at high pH values due to the increased degree of ionization of the acid groups.[1,16,22]

Cadmium Concentration Dependence. The effect of different concentrations of $CdCl_2$ from 0 to 10 mM on C_{18} is summarized in Table II. For each of the experiments, a surface pressure–surface area (Π–A) isotherm was obtained. These isotherms, shown in Figure 2, exhibit a marked dependence on the substrate $CdCl_2$ concentration, shifting toward smaller areas as the concentrations increase. We emphasize here that these isotherms are found to be completely reversible as we compress or expand the area at a rate of 8 cm^2/min, or equivalently 0.5–0.6 $\mathring{A}^2/molecule$ per min. To relate $\delta\Delta$ for different concentrations of Cd^{2+} more quantitatively, we report in Table II the corresponding effects of Cd^{2+} on the kink point in the isotherm, which occurs in the surface pressure isotherm as the monolayer goes from the "liquid-condensed" phase to a more "solid-like" phase.[11] As the Cd^{2+} concentration is increased, this kink moves to lower pressures, and the solid phase covers a wider surface pressure range. In fact, at 1 mM $CdCl_2$ and above, there is

no liquid-condensed phase as the kink disappears. Consistent with the trend in the degree of monolayer condensation with Cd^{2+} concentration, the values of $\delta\Delta$ increased substantially from the pure water value of 0.63° ± 0.02° to 0.78° ± 0.04° at 0.1 mM $CdCl_2$. From 0.2 to 10 mM $CdCl_2$, the values of $\delta\Delta$ increase only slightly (Table II). An earlier report[22] gives results which agree qualitatively in terms of Cd^{2+} concentration dependence. The Cd^{2+} binding tends to be stronger at lower concentrations in the study of ref 22 because of higher pH. Our data were collected after waiting 20–30 min for equilibration upon spreading the monolayer. Immediately after the monolayer was spread on the $CdCl_2$ substrates, the values of $\delta\Delta$ could be seen to increase with respect to time. The values of $\delta\Delta$ reached asymptotic values in a few minutes. Once the initial steady-state values of $\delta\Delta$ were reached, two or three full compression–expansion cycles were performed to ascertain that the state of compression or expansion did not change the results. The $\delta\Delta$ values were independent of the number of compression–expansion cycles and were constant for $\Pi = 1$–30 dyn/cm.

Discussion

The plot of $\delta\Delta$ vs carbon number (Figure 1) gives slopes which are identical within experimental error for fatty acid monolayers on 10 mM HCl, 1 mM $CdCl_2$, and 1 mM $PbCl_2$ solutions. The intercept of about eight carbons for HCl is consistent with previous results.[7] A number of factors could contribute to this unexpectedly low intercept including water structure in the head-group region, water penetration into the monolayer, or refractive index anisotropy. Negative values of $\delta\Delta$ for chain lengths less than eight are not physically reasonable, and due to fatty acid stability problems with the smaller chain lengths, it is not known whether the linear extrapolation to $\delta\Delta = 0$ is valid.

Comparing the intercepts of these plots, one finds the magnitude of $\delta\Delta$ decreases in the order $PbCl_2$, $CdCl_2$, and HCl. Since the fatty acid monolayers with and without Cd^{2+} have the same thickness,[4] the magnitude of $\delta\Delta$ is attributed to an increase in refractive index due to carboxylate of the fatty acids binding to Pb^{2+} or Cd^{2+}. Consistent with earlier discussion, the values of $\delta\Delta$ in the presence of Pb^{2+} are greater than Cd^{2+} since the fatty acid is nearly 100% associated with Pb^{2+} while only partially associated with Cd^{2+} at pH 5.5.[1,16,22]

Regardless of the intercepts, the values of $\delta\Delta$ in Figure 1 increase because of a change in hydrocarbon chain thickness for a given ionic environment. This is consistent with a two-layer model, where the bottom layer consists of the head groups and the top one of the hydrocarbon tails. Ellipsometrically, the head-group layer would contribute to a constant background independent of chain length and would not affect the results in Figure 1, which give a slope of 0.070 ± 0.002 deg/carbon. For the sake of comparison, multiplying this slope for the zero intercept case times 18 gives $\delta\Delta = 1.26$ for C_{18}, similar to what is seen for PbC_{18} experimentally. This value is divided by the thickness of a C_{18} monolayer $d_1 = 24.4$ Å for BaC_{18} L–B multilayers[33] and $d_1 = 24.6$ Å for MnC_{18} L–B multilayers,[12] giving $\alpha = 0.051 ± 0.001$ deg/Å, which can be readily compared to values calculated with the Drude equations as a function of refractive index. The same value ($\alpha = 0.051 ± 0.001$ deg/Å) is obtained by using the slope and dividing by thicknesses for other chain lengths, including $d_1 \sim 27$ Å for CdC_{20} L–B multilayers,[35] $d_1 = 27.1$ Å for CdC_{20} monolayer on water,[3] and $d_1 \sim 30$ Å for CdC_{22} on water.[4]

Table III. Anisotropic Refractive Indices and Estimates of Phase Angle Coefficient α

system	n_x	n_z	α, deg/Å	ref
experimental α			0.051[a]	
amorphous PE	c	c	0.0480[b]	36
crystalline PE	1.52	1.582	0.0480[b]	36
BaC_{18}	1.491	1.551	0.0359[b]	33
CdC_{20}	1.522	1.59	0.0478[b]	38
CdC_{20}	1.518	1.549	0.0530[b]	35
BaC_{16}	1.43	1.59	−0.0054[b]	37

[a] The slopes in Figure 1 were used assuming the intercept to be at the origin. These values of $\delta\Delta$ were then divided by the literature thicknesses to calculate an "experimental" α. [b] These values of α were calculated by using eq 1. [c] $n_{isotropic} = 1.49$.

One could use the reverse of this logic and calculate α using estimated values of the refractive index and then use 0.070 ± 0.002 deg/carbon to calculate the thickness, using eq 5 for a specified chain length. Unfortunately, refractive index anisotropy causes this approach to be ambiguous, as is illustrated in Table III, where isotropic and anisotropic refractive indices[36] for polyethylene (PE) give the same result. It is also found that many different combinations of the anisotropic refractive index give the same value of α for PE, and those for CdC_{20} agree qualitatively with that obtained from the experimental data. Two other cases are included in Table III to indicate the sensitivity of the calculated values of α to the anisotropy. The refractive indices of Blodgett and Langmuir[33] for BaC_{18} give values of α which deviate slightly, while the huge anisotropy reported by Tomar and Srivastava[37] for BaC_{16} and BaC_{17} even indicates a sign reversal in the calculated α which is equivalent to a sign change in $\delta\Delta$. The latter values are not consistent with those of Honig et al.[31] and illustrate the effect that different film-transfer techniques may have on the anisotropy.[34] The refractive indices determined for transferred L–B films applied to the analysis of films at the air/water interface are only qualitative because L–B films give rise to a combination of the head group and hydrocarbon tail contributions. The literature values for anisotropic refractive indices for L–B films, collected in Table III, impart an idea of how the anisotropy, if present, would affect the experimental results. We must also note here that our implicit assumption of identical chain conformation of fatty acids on L–B films and monolayers has been supported by several recent studies.[3,4,6]

Summary

The ellipsometric phase angle $\delta\Delta$ was measured for the monolayers of fatty acids at the air/water interface with chain lengths of 15, 16, 18, and 22. The magnitude of $\delta\Delta$ relative to aqueous substrate was found to increase in the order HCl, $CdCl_2$, and $PbCl_2$ for a given fatty acid monolayer. For a given substrate, $\delta\Delta$ increased monotonically with fatty acid chain length. The observed dependence on the chain length can be regarded as a simple manifestation of monolayer thickness variation with respect to the chain length. By use of literature values of thicknesses, the refractive index of the hydrocarbon chains is directly calculated assuming an isotropic refractive index. The chain length dependence of $\delta\Delta$ is seen to be consistent with some anisotropic refractive indices reported in the literature for L–B multilayers. In this case, however, there are too many experimental variables to determine unique values of the anisotropic refractive index.

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The increase in the refractive index of the fatty acid monolayer in the presence of divalents such as Cd^{2+} and Pb^{2+} was attributed to an increase in the refractive index of fatty acid head groups caused by association with multivalent cations. Preliminary experiments were performed as a function of Cd^{2+} concentration and pH to support this claim.

Transfer Free Energies of p-Alkylphenols and p-Alkylphenoxides from Water to Mixed Micelles Formed by a Cationic and a Nonionic Surfactant

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Association constants (K_a) of p-alkylphenols and p-alkylphenoxides to mixed micelles formed by a cationic surfactant, cetyltrimethylammonium bromide (CTAB), and nonionic surfactant, poly(oxyethylene) 23-lauryl ether (Brij 35), were determined and expressed as the transfer free energies ($\Delta\mu^\circ_{Ar}$) of the substrates from water to the mixed micelles. The hydrophobic contribution due to the CH_2 groups of the alkyl residue ($\Delta\mu^\circ_c$), the contribution of the aryl moiety ($\Delta\mu^\circ_{Ar}$), and the electrostatic contribution ($\Delta\mu^\circ_e$) to $\Delta\mu^\circ_t$ were calculated. $\Delta\mu^\circ_c$ has a value of about –0.3 kcal/mol independent on the composition of the mixed micelles. A high value of –5.0 kcal/mol was calculated for $\Delta\mu^\circ_{Ar}$ at all compositions of the mixed micelles. As expected, the $\Delta\mu^\circ_e$ contribution decreases as the mixed micelle composition approaches that of pure Brij 35, indicating a gradual decrease in the surface micellar potential. No association of phenoxide ions to pure Brij 35 or to mixed micelles containing less than 20% of CTAB was detected.

Introduction

In previous works,[1-3] transfer free energies ($\Delta\mu^\circ_t$) of p-alkylphenols and p-alkylphenoxides from water to cationic micelles were reported. The contributions due to the p-alkyl and aromatic residues of the substrates as well as the electrostatic contribution to the total μ°_t were estimated. This kind of study shows that important information can be inferred about the factors that determine the nature and magnitude of the association of solutes in micelles.

One relevant parameter that is always present in the association of solutes to ionic micelles is the micellar surface potential Ψ_0, which, in turn, is also a function of the electrical charge density of micelles. In this context, our interest is to know how Ψ_0 or the micellar charge density affects the capability of micelles to associate ionic and nonionic solute molecules containing hydrophobic and hydrophilic moieties. It is then of interest to know to what extent any molecular residue is affected by the micellar surface potential in the association process.

A systematic and gradual change in surface micellar potential can be easily obtained by mixing ionic with nonionic surfactants at convenient molar fractions. On the other hand, the family of p-alkylphenols and phenoxides provides the solutes necessary to complete the study.

In this work, we have determined the association constants K_a of p-alkylphenols and their corresponding phenoxide species to mixed micelles composed of the cationic surfactant cetyltrimethylammonium bromide (CTAB) and the nonionic surfactant polyoxyethylene 23-lauryl ether (Brij 35). The K_a values were finally analyzed in terms of the different free energy contributions to the solutes–mixed micelle association.

Experimental Section

Reagents. Phenol, cresol, p-ethylphenol, p-propylphenol, and p-tert-butylphenol from Matheson were purified by distillation under vacuum. Brij 35, Atlas Co., was used as received, but its average molecular weight was determined by an NMR method recently described,[4] giving a value of 1111. CTAB from Matheson was recrystallized twice from ethanol–ether mixtures.

Association Constants (K_a). Mixtures of CTAB and Brij 35 containing a molar fraction X_{CTAB} (X_{CTAB} = [CTAB]/([CTAB] + [Brij 35])) of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 were pre-

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* Published posthumously with the assistance of H. Rios.
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