Using the Optical Probe Methyl Orange To Determine the Role of Surfactant and Alcohol Chain Length in the Association of 1-Alkanols with Alkyltrimethylammonium Bromide Micelles

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We have used the optical probe methyl orange to characterize the interaction of primary alcohol additives with micelles assembled from a series of alkyltrimethylammonium bromide (C_nTAB) surfactants in aqueous solution. The anionic methyl orange (MO) interacts electrostatically with the cationic C_nTAB headgroups to reveal micellar properties through variations in the probe's absorption wavelength maximum. The sensitivity of the absorbance of methyl orange to its microenvironment is interpreted to reflect the nature of the association of 1-alkanols with C_nTAB micelles, an association dependent on both the surfactant and alcohol chain lengths. From the observed effect of alcohol addition on the methyl orange absorption λ_{max}, we propose three distinct roles for 1-alkanols: cosolvent at the micellar surface, coaggregate within the micellar palisade layer, and cosurfactant via extension of the alcohol into the micellar core. Our suggestions for the surfactant and 1-alkanol chain length criteria that determine the role of alcohol additives within C_nTAB micelles are presented.

Introduction

Micelles formed by ionic amphiphilic molecules in aqueous solution are dynamic associations of surfactant molecules that achieve segregation of their hydrophobic portions from the solvent via self-assembly. Both attractive (e.g., hydrophobic associations) and repulsive (e.g., electrostatic interactions) forces govern the micellization of ionic amphiphiles. Numerous techniques have been employed in the investigation of the effect of additives on the micellization process and on the structure of the resulting micelles.[1] Studies of alcohol−surfactant−water ternary systems have been of particular interest for a variety of scientific and technological applications, including drug delivery, micellar catalysis, and tertiary oil recovery.[2,3] For cationic alkyltrimethylammonium bromide micelles (C_nTAB, $n = 12-16$), both the incorporation of water-soluble short-chain 1-alkanols and the solubilization of amphiphilic higher-chain primary alcohols have been characterized.[2−12]

One observation of these investigations has been the dependence of the site of incorporation or solubilization of 1-alkanols on alcohol chain length. Discrepancies exist among data obtained using different experimental techniques and different ranges of alcohol chain lengths, [3,9,10,12] but results have been generally interpreted in terms of effects on two distinct regions of the micelle. The main localization sites are (1) the palisade layer, an outer micellar region in contact with water and consisting of the ionic surfactant headgroups and the initial segment of the hydrophobic surfactant tail, and (2) the inner micellar core not in contact with water and containing the remaining portions of the surfactant tails interacting via hydrophobic forces.[1,6] For cationic alkyltrimethylammonium bromide micelles (C_nTAB, $n = 12-16$), investigations suggest that the solubilization of 1-alkanols of two to seven carbons occurs mainly at the palisade layer near the micelle/water interface.[1,3] For higher alcohols (specifically, 1-octanol and 1-decanol), a deeper location of the alcohol within the C_nTAB micellar core is proposed, consistent with cosurfactant behavior.[6] These positionings optimize the interaction between the -OH group of the alcohol and the headgroup of the ionic surfactant and maximize the hydrophobic associations between surfactant and alcohol nonpolar tails.[10] Thus, the polar hydroxyl group is anchored at the micellar surface, and the differing locus of solubilization of the aliphatic alcohols reflects the extension of those hydrocarbon chains of sufficient length into the micellar core.

In general, these investigations have neglected the role of the surfactant alkyl chain length in dictating the nature of the association of an added alcohol with a micelle structure. A call for a comparative study of solubilization of amphiphilic additives of different chain lengths as a function of surfactant chain length has been made.[6] The need for such a study is further substantiated by the results of an earlier investigation[13] that suggest a change in the mechanism of solubilization for 1-octanol and especially for 1-decanol as surfactant chain length increases. Thus, we present here the results of a comprehensive comparative study of the addition of a series of homologous 1-alkanols ($C_nH_{2n+1}OH$, $n = 1-10$) to a series of alkyltrimethylammonium bromide (C_nTAB, $n = 12$, 14, 16, 18) micelles. We use one of three standard procedures to monitor the effect of added alcohols on micelles in which surfactant concentration is kept constant and the volume percentage of alcohol is progressively increased.[4] While this approach is often avoided because of the differential effects that can be induced by disparate additives, it is precisely this information that we seek to obtain.

We have monitored the absorbance properties of the optical probe methyl orange to determine the locus of solubilization of the 1-alkanols. MO exhibits an extreme sensitivity of absorption wavelength to the polarity of the probe's environment, for example, ranging from $\lambda_{max} = 396 \pm 1$ nm in heptane to 462 $\pm$ 1 nm in neutral aqueous solutions.[14] As an anionic azo dye, methyl orange (MO) interacts electrostatically with the cationic alkyltrimethylammonium headgroups of C_nTAB micelles to reveal the properties of the micellar surface.[14−24] The observed MO absorption wavelength in the 425−430 nm region (λ_{max} dependent on surfactant) arises from the combined effects of the solvation of MO by highly polar water molecules and the

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electrostatic interaction with the C_nTAB micelles that reduces electron density in the MO chromophore. We propose that variations in the MO λ_{max} upon the incorporation of alcohol additive within the micelle structure will reflect changes in the MO microenvironment at the micellar surface. In particular, alcohol-induced structural changes in the micelle will likely alter such properties as the degree and nature of solvation of the surfactant headgroups. From the observed MO absorption λ_{max} values in C_nTAB micelles with alcohol additives, the influence of both alcohol and surfactant chain length on the site of alcohol solubilization can be ascertained. In this study the sensitive and reproducible response of MO absorption to its immediate surroundings provides a more detailed and complete picture of alcohol partitioning within C_nTAB micelles that reveals the influence of both 1-alkanol and surfactant chain length on alcohol−micelle associations.

Experimental Section

Reagents Used. Methyl orange (Allied Chemical and Dye Corp.) was recrystallized four times from deionized water. Four alkyltrimethylammonium bromide (C_nTAB) cationic surfactants were used without further purification: dodecyltrimethylammonium bromide (DTAB, $n = 12$, Aldrich, 99%), myristyltrimethylammonium bromide (MTAB, $n = 14$, Aldrich, 99%), cetyltrimethylammonium bromide (CTAB, $n = 16$, Calbiochem, >99.9%), and octadecyltrimethylammonium bromide (OTAB, $n = 18$, Aldrich, 99%). The following alcohols were used without further purification (supplier was Aldrich, unless otherwise noted): methanol (99.9+%), ethanol (Quantum, 200 proof, dehydrated), 1-propanol (99.5+%), 1-butanol (99.4+%), 1-pentanol (99%), 1-hexanol (98%), 1-heptanol (98%), 1-octanol (99%), 1-nonanol (98%), 1-decanol (99%), 1,5-pentanediol (Eastman), and 1,7-heptanediol (95%). Surfactant solutions were prepared using 18.2 MΩ ultrapure water obtained from a Milli-Q Millipore water filtration system. Additional solvent studies were performed using *p*-dioxane (Aldrich, reagent), acetic acid (E. M. Science, reagent), D_2O (Norrell), ethylene glycol (Aldrich, spectrophotometric), dimethyl sulfoxide (Spectrum, reagent), dimethylformamide (Eastman, spectrophotometric), heptane (Aldrich, spectrophotometric), cyclohexane (Aldrich, HPLC), benzene (Aldrich, HPLC), chlorobenzene (Matheson, reagent), acetone (Aldrich, reagent), and acetonitrile (Aldrich, reagent). For studies with added counterion, potassium bromide (Spectrum, IR grade) was employed.

Absorbance Measurements. Absorption spectra over the range 350−500 nm were recorded at 25 °C on a Beckman DU-650 UV/vis spectrophotometer at a scan rate of 1200 nm/min. In addition to investigations with C_nTAB micelles, methyl orange absorption spectra were recorded in each alcohol studied and in additional selected solvents. A nonlinear least-squares fitting routine (PeakFit, Jandel Scientific) was used to deconvolute individual absorption spectra into a sum of overlapping Gaussian functions with frequency as the independent variable. All spectra were fit using an iterative Marquardt−Levenberg fitting algorithm to obtain the minimum number of absorbing components that yielded an r^2 of at least 0.999 with a random scattering of residuals. The center, amplitude, width, and area of each Gaussian function were characterized.

Addition of Alcohols to C_nTAB Micelles. Surfactant concentrations were chosen above the critical micelle concentration (cmc) in water and maintained micellar aggregation in the presence of the added alcohols, as added alcohol depresses the cmc.[3,4,6] Cmc values were spectroscopically determined[14] by the appearance of an absorption band at 425−428 nm,[14−24] reflecting the interaction of MO with the micellar surface. (A concurrent disappearance of an absorption band at 376−377 nm is also observed, indicating the absence of 1:1 probe−surfactant ion pairs that form at surfactant concentrations below the cmc.[14,22]) For DTAB, a cmc of 15 mM was determined; for MTAB, 3.0 mM; for CTAB, 0.8 mM; and for OTAB, 0.15 mM. Cmc values were found to be independent of MO concentration in the range of 30−70 μM. For investigations with alcohol additives, surfactant concentrations were fixed at the following values: 100 mM DTAB, 15 mM MTAB, 15 mM CTAB, and 8 mM OTAB. A MO concentration of 50 μM was selected to ensure that essentially all added MO was located at the micellar surface, with little free in aqueous solution (as revealed by λ_{max}[14]). The low [MO] also reduces the probability of multiple probe molecules per micelle. Probe:micelle ratios ranged from ∼0.03:1 for DTAB micelles (using a micellar aggregation number of 55[25]) to ∼0.7:1 for OTAB micelles (using an estimated[25] micellar aggregation number of 105) in the absence of added alcohol. Absorption spectra were recorded for varying volume percentages of alcohol until a constant λ_{max} value was observed (interpreted as no further change in alcohol location and/or amount within the micelle) or immiscibility occurred (i.e., maximum amount of alcohol incorporated within the micelle). With this approach only total alcohol volume percentages are known; free and incorporated alcohol volumes are not directly measured. At least two separate investigations of each combination of surfactant and alcohol were conducted (three series of investigations were routinely conducted for studies involving the first surfactant DTAB), and the absorption results reported reflect averages of measured values.

Addition of Bromide Ion to Surfactant Micelles. To interpret the results of alcohol additives, the effect on the MO absorption λ_{max} of low concentrations of added bromide counterion was investigated. Added KBr concentrations were chosen to achieve a reduction in headgroup spacing without substantial micellar growth (i.e., without increased aggregation number).[26] Absorption spectra were recorded for C_nTAB micelles in the absence and presence of 0.005−0.100 M KBr. To effect the micellar structural change, bromide ions were added before the addition of methyl orange. As the reduction in electrostatic repulsion between headgroups may alter the extent of interaction of MO with the micellar surface (i.e., increasing the amount of free MO), PeakFit analyses of the MO absorption spectra were conducted to differentiate the absorption bands of free and bound MO in order to monitor solely the variation in λ_{max} of bound MO.

Results

Spectral Characterization of Methyl Orange in 1-Alkanols and Varying Solvents. We monitored the dependence of methyl orange absorption on solvent medium and observed a wide variation in absorption λ_{max} from 462 ± 1 nm in water to 394 ± 1 and 396 ± 1 nm in cyclohexane and heptane, respectively. We found the λ_{max} value of 50 μM MO solutions to be rather invariant in 1-alkanols, occurring at 420 ± 1 nm in methanol, at 417 ± 1 nm in 1-alkanols $C_nH_{2n+1}OH$ with $n =$ 2−7, 9 and at 416 ± 1 nm for 1-octanol and 1-decanol. Methyl orange exhibited limited solubility in 1-nonanol and 1-decanol. Table 1 summarizes the observed MO absorption wavelength maxima.

Effect of Added 1-Alkanol on Absorption λ_{max} of Methyl Orange in C_nTAB Micelles. For all alcohols, the absorption λ_{max} of MO decreased upon the initial addition of alcohol. For 1-alkanols with $n \geq 3$, λ_{max} achieved a minimum value at a particular alcohol volume percentage with no further changes in λ_{max} with higher alcohol volume percentages. For the shorter-

TABLE 1: Dependence of λ_{max} of Absorption of Methyl Orange on Solvent

solvent	λ_{max}/nm[a]	solvent	λ_{max}/nm[a]
cyclohexane	394	1-$C_nH_{2n+1}OH$, $n = 2-7, 9$	417
heptane	396	methanol	420
benzene	406	dimethylformamide	421
chlorobenzene	411	1,7-heptanediol	422
p-dioxane	412	1,5-pentanediol	426
acetone	412	dimethyl sulfoxide	429
acetonitrile	416	ethylene glycol	442
decanol	416	deuterium oxide	462
octanol	416	water	462

[a] λ_{max} values expressed with an uncertainty of ± 1 nm.

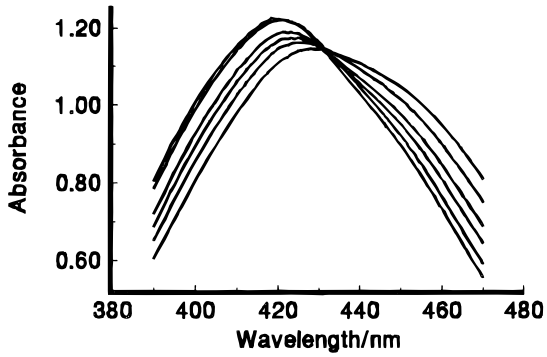

Figure 1. A portion of the full absorption spectrum of methyl orange in CTAB ($n = 16$) micelles treated with increasing amounts of 1-hexanol. The spectrum in the absence of added alcohol exhibits the longest λ_{max}; the spectrum shifts to shorter wavelength as additional alcohol is incorporated within the micelles. The corresponding volume percentages of hexanol added as spectra shift to shorter wavelength are 0.0, 0.3, 0.6, 0.9, 1.1, and 1.4%, respectively.

chain alcohols ($n = 1$ and 2), λ_{max} typically reached a minimum value at a certain alcohol volume percentage and then increased with larger alcohol volume percentages. Figure 1 illustrates the shift in λ_{max} as increasing amounts of 1-hexanol are added to CTAB ($n = 16$) micelles, with a minimum λ_{max} of 421.0 ± 0.5 nm observed at 1.1% 1-hexanol by volume. Table 2 summarizes the observed minimum MO absorption λ_{max} values for addition of 1-alkanols to C_nTAB surfactant micelles and the volume percentages required to achieve the minimum λ_{max}. As the alcohol chain length increased, the alcohol volume needed to achieve a constant (and minimum) absorption λ_{max} value decreased significantly. For each surfactant, Figure 2 presents the λ_{max} results as a function of alcohol chain length. Several generalizations can be stated: (1) Overall, for a given surfactant, as alcohol chain length increases, λ_{max} decreases. (2) For DTAB ($n = 12$), two plateaus in the dependence of λ_{max} on alcohol chain length are observed: at C_5-C_7 (average $\lambda_{max} \approx 423.5$ nm) and at C_8-C_{10} ($\lambda_{max} = 417$ nm). (3) For MTAB ($n = 14$), a single plateau is observed for C_5-C_8 (average $\lambda_{max} \approx 421.5$ nm) and a decrease in λ_{max} for higher-chain alcohols. (4) For the longer surfactants, CTAB ($n = 16$) and OTAB ($n = 18$), a single plateau is observed for C_5-C_{10} ($\lambda_{max} = 421$ nm for CTAB and average $\lambda_{max} \approx 419.5$ nm for OTAB). (5) The λ_{max} observed at the first (or only) plateau decreases slightly with increasing surfactant alkyl chain length: from 423.5 nm for DTAB to 419.5 nm for OTAB.

PeakFit analyses of the absorption spectra yielded a two-component fit, with the minor Gaussian peak (i.e., contributing generally $\leq 6 \pm 2\%$ of the total area of the spectrum) reflecting free MO absorbing at 455−465 nm. Since the majority of added methyl orange was associated with the micelle, variations in the observed λ_{max} noted in Figure 2 and in Table 2 exactly parallel the variations noted in the major Gaussian peak in the deconvoluted spectra. To confirm this point, Table 3 summarizes the center of the principal Gaussian MO absorption band resolved by PeakFit analysis of the absorption spectra of C_n-TAB micelles with alcohol additives. Thus, as previously noted, the selected MO concentration of 50 μM ensures that essentially all added MO is located at the micellar surface, and the observed absorption λ_{max} is an accurate and convenient means of monitoring the association of 1-alkanols with C_nTAB micelles.

Effect of Added 1,5-Pentanediol and 1,7-Heptanediol on Absorption λ_{max} of Methyl Orange in C_nTAB Micelles. A blue shift in λ_{max} occurred only at small volume percentages of these diols, with increasing diol volume percentages either not changing the absorption maximum further or red-shifting the spectrum. Table 2 presents the observed minimum absorption λ_{max} values for addition of these diols to C_nTAB surfactant micelles and the diol volume percentage at which these minimum λ_{max} values were recorded.

Effect of Added Bromide Counterion on Absorption λ_{max} of Methyl Orange. Table 3 also presents the effect of low concentrations of added bromide on the methyl orange absorption spectrum of micelles with no alcohol additives. The Gaussian absorption band attributed to MO at the micellar surface shifts to shorter wavelength upon the addition of bromide ion. For DTAB micelles the λ_{max} value did not shift any further

TABLE 2: Variation of λ_{max} of Absorption of Methyl Orange in C_nTAB Micelles with Alcohol Additives at Given Volume Percentages

	CTAB surfactant							
alcohol additive	DTAB (n=12)		MTAB (n=14)		CTAB (n=16)		OTAB (n=18)	
	λ_{max}[a]	% V[b]	λ_{max}[a]	% V[b]	λ_{max}[a]	% V[b]	λ_{max}[a]	%V[b]
none	433.0		432.5		428.5		428.5	
methanol	431.0	8 ± 2[c]	431.0	20 ± 5[c]	427.0	34 ± 10[c]	425.0	26 ± 5[c]
ethanol	431.0	6.4 ± 0.4[c]	430.0	7.1 ± 0.7[c]	427.0	6 ± 1	424.0	13 ± 2[c]
1-propanol	430.0	11 ± 2[c]	428.0	9 ± 2	425.0	9 ± 2	423.0	10 ± 2
1-butanol	426.5	5.7 ± 0.7	425.0	4.3 ± 0.7	422.0	5.7 ± 0.7	421.0	7 ± 1
1-pentanol	423.0	3.3 ± 0.2	422.0	2.9 ± 0.4	421.0	2.1 ± 0.3	420.0	2.3 ± 0.3
1-hexanol	424.0	0.6 ± 0.1	422.0	1.1 ± 0.2	421.0	1.1 ± 0.2	420.0	1.1 ± 0.2
1-heptanol	423.0	0.3 ± 0.1	421.0	0.9 ± 0.1	421.0	0.6 ± 0.1	419.0	0.6 ± 0.1
1-octanol	417.0	0.6 ± 0.1	421.0	0.6 ± 0.1	421.0	0.6 ± 0.1	420.0	0.9 ± 0.1
1-nonanol	417.0	0.23 ± 0.03	419.0	0.23 ± 0.03	421.0	0.24 ± 0.01	419.0	0.40 ± 0.03
1-decanol	417.0	0.06 ± 0.03	415.0	0.23 ± 0.03	421.0	0.17 ± 0.01	419.0	0.34 ± 0.03
1,5-pentanediol	432.0	8 ± 3	430.0	13 ± 3	426.0	11 ± 2	426.0	6 ± 1
1,7-heptanediol	431.0	6 ± 1	429.0	4 ± 1	427.0	6 ± 1	425.0	6 ± 1

[a] λ_{max} values expressed with an uncertainty of ± 0.5 nm. [b] Unless otherwise noted, volume percentages refer to the volume needed to achieve a minimum MO absorption λ_{max} value with no change in λ_{max} with higher alcohol volume percentages. [c] Volume percentages expressed as a range of values giving rise to the stated minimum absorption λ_{max}. Alcohol volume percentages outside of the stated range led to larger λ_{max} values.

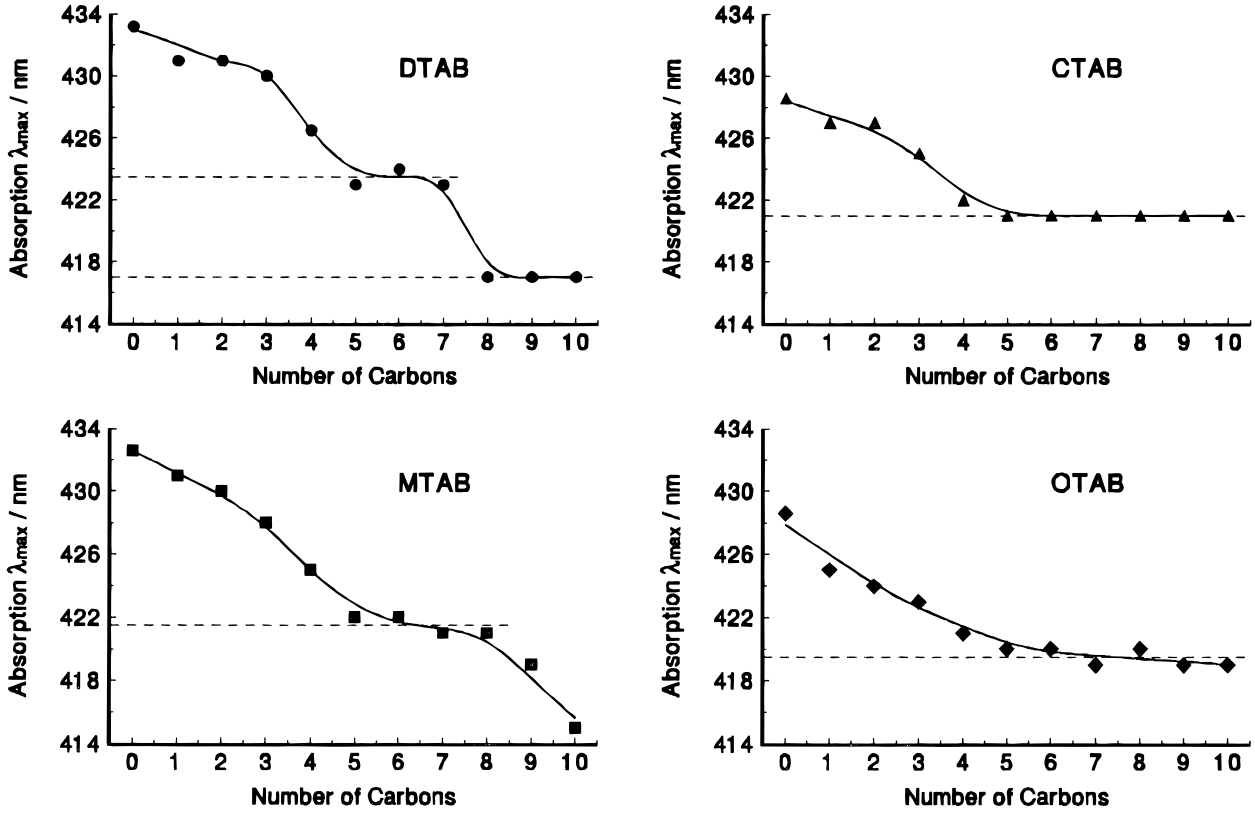

Figure 2. Dependence of experimental absorption λ_{max} of methyl orange in 1-alkanol-treated C_nTAB micelles as a function of alcohol chain length. (a) DTAB ($n = 12$) micelles; (b) MTAB ($n = 14$) micelles; (c) CTAB ($n = 16$) micelles; (d) OTAB ($n = 18$) micelles. The fitted curves are locally weighted regression plots using a piecewise linear least-squares fit at each data point (i.e., a *lowess* plot using Axum graphical software).

TABLE 3: Variation of λ_{max} of Absorption of Methyl Orange in C_nTAB Micelles with Alcohol Additives Using PeakFit Analysis

	C_nTAB surfactant			
alcohol additive	DTAB (n=12) λ_{max}[a]	MTAB (n = 14) λ_{max}[a]	CTAB (n=16) λ_{max}[a]	OTAB (n=18) λ_{max}[a]
none	432.1	431.6	432.4	431.8
methanol	430.0	430.8	431.1	429.1
ethanol	429.0	432.1	430.8	426.9
1-propanol	429.0	431.0	428.4	425.2
1-butanol	425.7	425.9	423.8	422.7
1-pentanol	426.1	422.3	423.6	422.5
1-hexanol	424.8	422.1	422.6	421.2
1-heptanol	418.3	421.3	423.3	421.3
1-octanol	416.3	422.2	423.1	422.2
1-nonanol	416.7	418.7	421.7	420.3
1-decanol	415.2	415.4	422.0	421.1
1,5-pentadiol	433.7	432.0	427.8	427.9
1,7-heptadiol	433.0	429.4	425.5	427.8
KBr[b]	427.3	425.9	425.0	424.6

[a] λ_{max} values expressed with an uncertainty of ±0.5 nm. [b] Added KBr in the absence of any alcohol additive. The λ_{max} value reported is the shortest value observed over the [KBr] range from 0.005 to 0.100 M, occurring at [KBr] ≥ 0.050 M for DTAB micelles and at 0.100 M for MTAB, CTAB, and OTAB micelles.

above 0.050 M KBr. The lowest λ_{max} value observed upon bromide addition is summarized in Table 3.

Discussion

Absorption and emission studies have previously presented[14−24] evidence for the electrostatic interaction of methyl orange with the cationic headgroups on the surface of C_nTAB micelles. With the ionic nature of methyl orange anchoring the chromophore at the micellar surface, the absorption signature of MO can serve as a sensitive indicator of variations in the environment of the surfactant headgroups. In particular, decreases in the degree of solvation of the C_nTAB headgroups by water would be reflected by a concomitant decrease in the MO absorption λ_{max}, as supported by both our solvent studies and bromide counterion studies. Factors that reduce the electrostatic repulsion between C_nTAB headgroups, yielding a tighter packing of surfactant molecules, would effect such an enhanced exclusion of water solvent molecules from the palisade layer. Alternatively, a displacement of MO from the micellar surface to the bulk aqueous region would be indicated by an increase in λ_{max} toward the value observed in aqueous solution.

In the present study, the effect of the added alcohol on the MO absorption λ_{max} (and hence on micellar structure) depends on *both* the chain length of the added alcohol and the length of

the hydrophobic tail of the surfactant. To interpret these observations, the hydroxyl group of the alcohol is presumed to be fixed in the vicinity of the C_nTAB headgroups. This assumption is justified by the results of other investigations[10] of the solubilization of neutral polar organic solutes within ionic micelles which support a strong interaction between the polar moiety of the additive and the ionic headgroup of the surfactant. Depending on the relative lengths of the hydrophobic chains of both surfactant and 1-alkanol, we suggest that this tethering of the hydrophilic moiety of the additive creates *three* distinct roles for the alcohol: *cosolvent*, *coaggregate*, and *cosurfactant*. For cosolvent behavior, the alcohol alkyl chain remains at the micellar surface, a thermodynamically favorable situation for short-chain alcohols. As a coaggregate, the alcohol is solubilized within the palisade layer, while an alcohol serving as cosurfactant extends appreciably into the micellar core. We present a brief analysis of our results to support this proposed model.

***n*-Alkanols as Cosolvents.** For short-chain alcohols, the absorption λ_{max} of methyl orange reflects a microenvironment that is similar to that in untreated micelles in terms of the polarity and/or the degree of water accessibility of the microregion. The high water solubility of these alcohols and their relatively short alkyl chains dictate their role as cosolvents, slightly modifying the characteristics of the water solvent medium but not penetrating the micellar palisade layer. As a consequence of similarities in the value of MO λ_{max} in alcohol-treated micelles to that in untreated micelles, we assign C_1-C_3 alcohols as cosolvents in DTAB micelles and C_1 and C_2 alcohols as cosolvents in both MTAB and CTAB micelles. The investigations with 1,5-pentanediol and 1,7-heptanediol can be used to confirm these assignments as well as to suggest which alcohols might serve a cosolvents in OTAB micelles. These diols most likely behave as bolaamphiphiles or bolaphiles, with two hydrophilic headgroups at either end of a single hydrophobic hydrocarbon chain. The polar hydroxyl groups would presumably anchor the diols on the micellar surface, thermodynamically limiting a sterically strained insertion of the short five- and seven-carbon chains into the micelle interface. The water-soluble diols would thus act as cosolvents of the C_nTAB headgroups. On the basis of MO absorption λ_{max} values in 1-alkanol-treated micelles that are comparable to the λ_{max} values observed in diol-treated micelles, we can support the assignments of cosolvent alcohols for DTAB, MTAB, and CTAB micelles and further suggest the role of at least methanol as a cosolvent for OTAB micelles.

***n*-Alkanols as Coaggregates.** Moderate-chain 1-alkanols likely act as coaggregates with the C_nTAB surfactants by anchoring the polar hydroxyl group of the alcohol on the micellar surface and aligning the alkyl chain of the alcohol within the micellar palisade layer. This thermodynamically preferred arrangement would induce a reduction in surface charge that would effect a closer packing of surfactant molecules. The absorption λ_{max} of MO should reflect a slight reduction in the polarity and/or water accessibility of this interfacial region (i.e., a shift to lower wavelength), consistent with an increased exclusion of water as alcohols align and as surfactant headgroups increase in proximity. On the basis of the observed absorption parameters, coaggregation presumably occurs with alcohols of chain length C_4-C_7 for DTAB; C_3-C_9 for MTAB; $\geq C_3$ for CTAB; and $\geq C_2$ for OTAB. Optimal coaggregation of a 1-alkanol with the C_nTAB surfactants (as measured by achieving the MO absorption λ_{max} value of the first plateau in each panel of Figure 2) appears to require an alcohol chain length of at least five.

***n*-Alkanols as Cosurfactants.** For long-chain alcohols, behavior of the alcohol as a cosurfactant would lead to the closest packing of surfactant molecules and the most limited degree of water penetration into the surfactant aggregations. With a greater similarity in alkyl chain length to the C_nTAB surfactant, these alcohols can act as cosurfactants by inserting between or even replacing surfactant monomers within the micelle. Such an incorporation would be expected to decrease intramicellar Coulombic repulsive forces and increase hydrophobic forces among the monomers. This additional hydrophobic effect present in cosurfactant behavior could be the origin of the observed MO λ_{max} values (e.g., 415−419 nm) that are shorter than those observed for C_nTAB micelles with added bromide counterion (e.g., 425−427 nm). These favorable cosurfactant conditions would further reduce headgroup repulsion and decrease the surface area occupied per headgroup.[27] Thus, on the basis of the further blue-shift of the MO λ_{max}, alcohols of length C_8-C_{10} appear to function as cosurfactants for DTAB ($n = 12$) micelles; for MTAB ($n = 14$), only C_{10} is a possible cosurfactant. Even 1-decanol does not sufficiently extend into the micellar core of CTAB and OTAB micelles to act as a cosurfactant. Hence, for a given C_nTAB surfactant, the ability of a given alcohol to act as a cosurfactant decreases with increasing surfactant chain length. As a consequence, as the difference in alcohol and surfactant chain lengths increases, the stability of their association as cosurfactants is reduced. DTAB and MTAB results suggest that the most effective cosurfactant behavior is achieved when the chain length of a 1-alkanol is no fewer than four carbons shorter than the given surfactant.

Conclusions

We have used the absorption properties of the anionic molecular probe methyl orange to reveal the incorporation of alcohol additives within the various regions of alkyltrimethylammonium bromide micelles. Our results are consistent with the anchoring of the polar hydroxyl group of the alcohol at the micellar surface. We further suggest that the alkyl chain length of the alcohol and the dimensions of the micellar palisade layer as dictated by the length of the surfactant hydrocarbon tail determine the extent of incorporation of the aliphatic chain of the alcohol into the palisade layer and the micellar core. The positioning of the alcohol within the micelle can influence the spacing between cationic surfactant headgroups by enhancing the micellar packing and reducing the water accessibility of the palisade layer. Variations in the absorption λ_{max} of MO are consistent with these alcohol-induced changes in interfacial properties. Our results suggest that 1-alkanols (represented by $C_mH_{2m+1}OH$) of short chain length do not appreciably penetrate the micelle structure, acting as cosolvents on the C_nTAB micellar surface and modifying the solvent properties of water. As the alkyl chain length of the surfactant increases, the length of the alcohol carbon chain leading to cosolvent behavior decreases (e.g., at $n = 12$, $m = 1-3$ for cosolvency; at $n = 18$, $m = 1$ for cosolvency). Alcohols with moderate chain lengths (i.e., $5 \leq m \leq n - 4$) presumably most optimally coaggregate with the surfactant, with the alkyl chain of the alcohol primarily residing within the palisade layer of the micelle. In this configuration, interactions between the OH group and the headgroup of the ionic surfactant would reduce the electrostatic repulsion between neighboring headgroups and lead to a greater exclusion of water from this interfacial region. We attribute the observed reduction in MO absorption λ_{max} to the decrease in polarity of the MO microenvironment. Alcohols of longer chain length (and therefore with a greater similarity in length to the surfactant

tail group, i.e., $n - m \leq 4$) have a greater probability to act as a cosurfactant with the C_nTAB monomers comprising the micelle. Such an incorporation is expected to enhance the micellar packing through both increased hydrophobic interactions within the micellar core and reductions in headgroup repulsion at the micellar surface. The concomitant decrease in the surface area occupied per headgroup[27] and the further expulsion of solvating water molecules are proposed to account for the most extensive alcohol-induced shift in MO absorption λ_{max} to shorter wavelength. While this model is based on the use of a single spectroscopic technique and on the spectral properties of only a single probe, it offers both a reasonable and an insightful new physical picture of the association of surfactant molecules with neutral organic solutes that may be investigated in other micellar systems.

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