the pair of bands which appear at higher frequencies (approximately 2106 and 2047 cm⁻¹) are presumed to be from the same dicarbonyl species observed in Figure 1. Thus, two different dicarbonyl species are observed at the same time.

It is possible, although not certain at this point, that the appearance and growth of the lower frequency dicarbonyl bands (in Figure 2) with exposure to the 3.3% CO/He mixture is a reduction effect accompanied by a breakup of the rhodium ensemble as proposed by Van't Bilk and co-workers.15,16

The possibility of a $Mo(CO)_2$ species leading to the observation of the higher frequency pair of infrared bands was dismissed after examination of the infrared spectra (not shown) of a 4% Mo/SiO₂ catalyst subjected to treatment B. No bands were observed in the infrared region corresponding to CO adsorbates on molybdenum. This is in good agreement with the literature^{17,18} which suggests only very weak adsorption of CO in a linear form on Mo sites.

Miessner et al.¹⁹ have recently observed a rhodium dicarbonyl species appearing at 2118 and 2053 cm⁻¹ in the infrared spectrum of a calcined dealuminated zeolite Y catalyst containing 1% Rh. It is interesting to note that upon reduction with H_2 and treatment with CO the calcined zeolite catalyst exhibits both a high-frequency pair of rhodium dicarbonyl bands (at 2118 and 2053 cm⁻¹) and a lower frequency pair appearing at 2093 and 2036 cm⁻¹. The appearance of the lower frequency bands upon reduction of the zeolite catalyst is not inconsistent with the events occurring in

Figure 2 in which the Rh-Mo/SiO₂ catalyst was exposed to a 3.3% CO/He reducing environment resulting in the simultaneous appearance of both rhodium dicarbonyl species. Miessner et al. have assigned their high-frequency pair of infrared bands to a Rh⁺ dicarbonyl species located inside the zeolite cages while they have assigned the low-frequency pair of bands to a Rh⁺ dicarbonyl species located outside the zeolite cages.

The ease with which the pair of higher frequency dicarbonyl bands disappear in Figure 2d (except for the small peak at 2105 cm^{-1}) upon exposure to H₂ (at 423 K) suggests that the type of rhodium site may differ for the two dicarbonyl species observed. The fact that the bands associated with the new high-frequency species appear at frequencies higher than those usually reported for silica-supported rhodium and the fact that they disappear readily upon exposure to H_2 suggests that the new species is associated with a different, more oxidized rhodium state than the traditional dicarbonyl species which is associated with Rh⁺.⁶ The infrared data also suggest that it is the addition of molybdenum that facilitates the oxidation of rhodium and leads to this new rhodium dicarbonyl species upon treatment with NO-CO mixtures.

Conclusions

The results presented in this paper lead to the following important conclusions:

(1) The addition of molybdenum to silica-supported rhodium catalysts followed by the treatments described previously leads to the formation of a pair of new higher frequency dicarbonyl bands that can be distinguished from the dicarbonyl bands usually seen on Rh/SiO₂ catalysts.

(2) The higher frequency dicarbonyl bands suggest that the addition of molybdenum results in a more oxidized form of rhodium and may lead to a different type of active Rh site.

Registry No. Rh, 7440-16-6; Mo, 7439-98-7; NO, 10102-43-9; CO, 630-08-0.

Interfacial Properties of a Novel Group of Solvatochromic Acid–Base Indicators in Self-Assembled Surfactant Aggregates

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The spectral and acid-base properties of 1-hexadecyl-4-[(oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine (HOED), 1-hexadecyl-5-hydroxyquinoline (H5HQ), and 1-hexadecyl-6-hydroxyquinoline (H6HQ) have been investigated to ascertain their suitability as probes of both the mean interfacial solvent properties and the electrostatic surface potential of self-assembled surfactant aggregates in aqueous solution. The results obtained indicate that the solvatochromic visible absorption band of the conjugate base form of HOED, H5HQ, and H6HQ can be utilized to obtain a reasonable estimate of the mean interfacial solvent properties of self-assembled surfactant aggregates. The factors that are primarily responsible for the apparent pK_a values of HOED, H5HQ, and H6HQ in most types of self-assembled surfactant aggregates have been ascertained. It is concluded that the acid-base properties of HOED, H5HQ, and H6HQ can be utilized to obtain a quantitative measure of the electrostatic surface potential of self-assembled surfactant aggregates in aqueous solution.

Introduction

It has long been recognized¹ that the magnitude of the apparent pK_a , pK_a^{obsd} , of a prototropic moiety residing at or close to a charged interface depends on the electrostatic potential of the charged interface. Indeed²⁻²³

$$pK_{a}^{obsd} = pK_{a}^{0} - \frac{F\Psi}{2.303RT}$$
(1)

where pK_a^{0} is the intrinsic interfacial pK_a of the prototropic moiety, Ψ is the mean field potential at the average site of residence for

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Figure 1. Acid-base equilibria of (a) HOED, (b) H5HQ, and (c) H6HO.

prototropic moiety, F is the Faraday constant, R is the universal gas constant, and T is the absolute temperature. It is clear from eq 1 that acid-base indicators have the capacity to probe the mean electrostatic surface potential, Ψ_0 , at charged interfaces. Before an acid-base indicator can serve as a probe of Ψ_0 , however, (1) its prototropic moiety must reside, on average, in the plane of the interfacial charge, and (2) there must be a way of ascertaining the nonelectrostatic component (i.e., the pK_a^0 contribution) to its pK_a^{obsd} values. The evaluation of the pK_a^{0} component to the pK_a^{obsd} value of an indicator located in an interface with a fixed surface charge density, as is the case for most charged micelles and vesicles, is not a straightforward assignment.^{2,8,18,19,24}

Recently¹⁸ we developed a procedure that utilizes the solvatochromism of the conjugate base form of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide (i.e., $E_T(30)$) to obtain the pK_a^0 component to the pK_a^{obsd} values of interfacially located $E_{\tau}(30)$ molecules. Moreover, we established¹⁸ that (1) the solvatochromic visible absorption band of the conjugate base form of the $E_T(30)$ molecule can be used to provide a good estimate of the mean interfacial solvent properties of cationic micelles, and (2) the apparent acid-base behavior of the $E_T(30)$ molecule can be utilized to obtain a quantitative measure of the electrostatic surface potential of a cationic micelle. We found, that there were problems and uncertainties associated with the use of the $E_T(30)$ molecule in aqueous solutions of other types of charged self-assembled surfactant aggregates. Ideally one would like to have a solvatochromic acid-base indicator that can be used to reliably probe the interfacial properties of all self-assembled surfactant aggregates

In the present paper we report the results of an investigation of the spectral and acid-base properties of 1-hexadecyl-4-[(oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine (HOED), 1-hexadecyl-5-hydroxyquinoline (H5HQ), and 1-hexadecyl-6hydroxyquinoline (H6HQ) in a number of different aqueous self-assembled surfactant solutions. The long hydrocarbon chain substituents of HOED, H5HQ, and H6HQ ensure that they are incorporated in the self-assembled phase. The surface-active nature of each aromatic moiety ensures that the average site of

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residence for the solvatochromic chromophores is the interfacial microenvironment of the self-assembled surfactant aggregates.²⁵ The structures and acid-base equilibria of HOED, H5HQ, and H6HQ are shown in Figure 1.

The primary objective of the present investigation was to ascertain whether or not these three solvatochromic acid-base indicators can be employed as probes of both the mean interfacial solvent properties and the electrostatic surface potential of selfassembled surfactant aggregates.

Several previous studies have utilized the solvatochromic behavior of the conjugate base form of HOED, a homologue of HOED, or a closely related analogue of HOED to probe the solvent properties of the lipid/water interfacial microenvironment of self-assembled surfactant aggregates.²⁶⁻²⁹ The acid-base behavior of this type of solvatochromic indicator in aqueous self-assembled surfactant solution has not hitherto been examined. This is the first report on the spectral and acid-base properties of H5HQ and H6HQ in aqueous self-assembled surfactant solutions.

Interfacial Acid-Base Equilibria

When pH titrations are performed with acid-base indicators that have their prototropic moieties located within the interfacial microenvironment of self-assembled surfactant aggregates, it is the proton activity in the bulk aqueous phase and the concentrations of the conjugate acid and conjugate base forms of the indicators in the self-assembled phase that are monitored. Consequently, there is a distinct difference between the "two-phase" apparent pK_a values determined in these types of experiments and the "single-phase" pK_a values determined in either pure water or organic solvent/water mixtures. Nevertheless, providing the intrinsic interfacial acid-base equilibria are unperturbed by any specific solute-solvent interactions or "salt-effects" and the mean solvent properties of the interfacial microenvironments can be mimicked by organic solvent/water mixtures, there is a connection between the apparent pK_a values of indicators residing in selfassembled surfactant aggregates and the pK_a values of the indicators in organic solvent/water mixtures.8

The apparent "two-phase" acid-base equilibrium of an indicator that has its prototropic moiety located within the interfacial microenvironment of a self-assembled surfactant aggregate can be represented as

$$HIN_{i}^{z} \rightleftharpoons H_{w}^{+} + IN_{i}^{z-1}$$
(2)

where HIN^z is the conjugate acid form of the indicator with a charge of z, H^+ is the proton, and IN^{z-1} is the conjugate base form of the indicator with a charge of z - 1. The subscripts i and w in equilibrium 2 denote the interfacial phase and the bulk aqueous phase, respectively. The "two-phase" thermodynamic acid-base equilibrium constant for equilibrium 2 is defined by

$$pK_{a}^{s} = -\log \frac{a_{IN}}{a_{HIN}} a_{H^{+}}^{w}$$
(3)

where a_{IN}^{i} , a_{HIN}^{i} , and $a_{H^{+}}^{w}$ are the activities of the various species in the phases. pK_a^{s} differs from the experimentally determined apparent pK_a , which has the form

$$pK_{a}^{obsd} = -\log \frac{[IN_{i}]}{[HIN_{i}]}a_{H^{+}}^{w}$$
(4)

where the square brackets denote concentrations. Hence

$$pK_{a}^{obsd} = pK_{a}^{s} + \log \frac{\gamma_{IN}}{\gamma_{HIN}^{i}}$$
(5)

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where γ_{IN}^{i} and γ_{HIN}^{i} are the activity coefficients of the conjugate base and conjugate acid forms of the indicator referred to the interfacial phase at infinite dilution.

The "two-phase" thermodynamic acid-base equilibrium constant, pK_a^s , and the standard Gibb's free energy of the "two-phase" reaction, ΔG° , are related and with ΔG° expressed in terms of the standard chemical potentials for species involved in the equilibrium:⁸

$$pK_{a}^{s} = \frac{1}{2.303RT} (\mu_{H^{+}}^{\circ w} + \mu_{IN}^{\circ i} - \mu_{HIN}^{\circ i}) - \frac{F\Psi}{2.303RT}$$
(6)

where the mean field potential term is set equal to zero when an uncharged interface is considered. In addition, it is convenient to define

$$pK_{a}^{i} = pK_{a}^{s} + \frac{F\Psi}{2.303RT} = \frac{1}{2.303RT}(\mu_{H^{+}}^{\circ w} + \mu_{IN}^{\circ i} - \mu_{HIN}^{\circ i})$$
(7)

Also note that the pK_a^0 component of eq 1 and pK_a^i are related and

$$pK_a^{\ 0} = pK_a^{\ i} + \log \frac{\gamma_{\rm IN}^{\ i}}{\gamma_{\rm HIN}^{\ i}}$$
(8)

The acid-base equilibrium for an indicator in an organic solvent/water mixture (m) can be represented as

$$\operatorname{HIN}_{m}^{z} \rightleftharpoons \operatorname{H}_{m}^{+} + \operatorname{IN}_{m}^{z-1}$$
(9)

The single-phase thermodynamic acid-base equilibrium constant for this reaction is defined by

$$pK_{a}^{m} = -\log \frac{a_{IN}^{m}}{a_{HIN}^{m}} a_{H^{+}}^{m} = \frac{1}{2.303RT} (\mu_{H^{+}} \circ m + \mu_{IN} \circ m - \mu_{HIN} \circ m)$$
(10)

If one assumes that (1) there are no specific solute-solvent interactions that interfere with the interfacial acid-base equilibrium and (2) the solvent properties of an interfacial microenvironment can be approximated by an organic solvent/water mixture with equivalent solvent properties, then for the particular equivalent organic solvent/water mixture

$$\mu_{\rm IN}^{\circ i} - \mu_{\rm HIN}^{\circ i} \equiv \mu_{\rm IN}^{\circ m} - \mu_{\rm HIN}^{\circ m}$$
(11)

and pK_a^{i} and pK_a^{m} differ solely by the work required to transfer the proton from the bulk aqueous phase to the interfacial microenvironment, i.e.

$$pK_{a}^{i} = pK_{a}^{m} - \frac{1}{2.303RT}(\mu_{H^{+}}^{\circ m} - \mu_{H^{+}}^{\circ w})$$
(12)

The change of free energy for the transfer process

$$H^+(std state, w) \rightarrow H^+(std state, m)$$
 (13)

is related to the medium effect on the proton, $_{m}\gamma_{H^{+}}$, where

$${}_{\mathrm{m}}\gamma_{\mathrm{H}^{+}} = \gamma_{\mathrm{H}^{+}}{}^{\mathrm{w}}/\gamma_{\mathrm{H}^{+}}{}^{\mathrm{m}} \tag{14}$$

by the formula³⁰

$$\mu_{\rm H^+}^{\circ m} - \mu_{\rm H^+}^{\circ w} = 2.303 RT \log_{\rm m} \gamma_{\rm H^+}$$
(15)

and as a result

$$pK_{a}^{i} = pK_{a}^{m} - \log_{m}\gamma_{H^{+}}$$
 (16)

Experimental Section

Solvatochromic Indicators. The hexadecyl homologues of the solvatochromic acid-base indicators were synthesized by I.C.I. Australia Operations Pty. Ltd., while the propyl homologues were

synthesized in-house. Analytical grade reagents were used in all the syntheses. The following procedures were employed in the syntheses.

1-Hexadecyl-1-[(oxocyclohexadienylidene)ethylidene]-1,4dihydropyridine (HOED) and 1-Propyl-4-[(oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine (POED).27,31 The appropriate alkyl iodide, either hexadecyl iodide or propyl iodide (20 mmol), and 4-methylpyridine were refluxed in dry toluene (10 mL) for 5 h. The solution was cooled to room temperature, and the white precipitate filtered off, washed with toluene, and dried. The white solid, 1-alkyl-4-methylpyridinium iodide (18 mmol), was dissolved in warm ethanol (20 mL) and piperidine (2.4 mL). A solution of 4-hydroxybenzaldehyde (18 mmol) in ethanol (10 mL) was added, and the mixture refluxed for 3 h. The reaction mixture was cooled, and the orange-red precipitate collected and washed with cold ethanol. This precipitate was suspended in a KOH solution (2 g, in 100 mL of water) and heated at 50-60 °C for 30 min. The red suspension was cooled, and the product filtered off and recrystallized from ethanol to give dark red-purple crystals. Based on 4-methylpyridine, the yield of HOED was 32% and that of POED was 51%. NMR, UV-vis, and IR spectra confirmed that the expected products were obtained.

Anhydro Salts of 1-Hexadecyl-5-hydroxyquinoline (H5HQ), 1-Propyl-5-hydroxyquinoline (P5HQ), 1-Hexadecyl-6-hydroxyquinoline (H6HQ), and 1-Propyl-6-hydroxyquinoline (P6HQ).^{32,33} The 5- (or 6-) hydroxyquinoline (13 mmol) and the appropriate alkyl iodide (28 mmol) were heated in dry toluene (5 mL) at 100-120 °C for 12-15 h with constant stirring. After the heating was stopped, diethyl ether was added very slowly and cautiously to the rapidly stirred viscous reaction mixture. The addition of excess ether caused the precipitation of the colored quinolinium iodide salt (orange for 5-hydroxy, gray for 6-hydroxy). The cooled solution was filtered off, and the crude salt washed with ether and recrystallized twice from ethanol-ether to give the pure quinolinium iodide salt. This salt was placed in an aqueous H_2CO_3 solution (27.6 g in 100 mL of water), and the anhydro salt extracted into dichloromethane. The anhydro salt was isolated from the dichloromethane extracts by precipitation (red for 5-hydroxy, orange for 6-hydroxy). The NMR and UV-vis spectra were consistent with those expected.

Preliminary experiments with the 1-propyl derivatives in 1,4dioxane/water mixtures indicated that there was no difference between the spectral and acid-base properties of a pyridinium/ quinolinium iodide salt and those of the related anhydro salt. The POED, P5HQ, and P6HQ results reported in the present work were obtained with the pyridinium/quinolinium iodide salts.

Surfactants. The nonionic surfactants n-dodecyloctaoxyethylene glycol monoether ($C_{12}E_8$) and *n*-dodecyl β -D-maltoside (DM) were obtained from Nikko Chemical Co. and Calbiochem, respectively. Hexadecyltrimethylammonium chloride (CTAC), hexadecyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium chloride (DTAC), dodecyltrimethylammonium bromide (DTAB), and dodecyl benzenesulfonate (DBS) were purchased from Tokyo Kasei Kogyo Co. Sodium dodecyl sulfate (SDS) and dihexadecyl phosphate (DHP) were supplied by Sigma Chemical Co. Oleic acid was obtained from BDH Chemicals Pty. Ltd. Dr. J. Brady and Professor D. F. Evans of the University of Minnesota kindly donated didodecyldimethylammonium bromide (DDDAB) and dihexadecyldimethylammonium bromide (DHDAB). L- α -Dimyristoylphosphatidylcholine (DMPC) and L- α -dipalmitoylphosphatidylcholine (DPPC) were puriss grade from Fluka AG Buchs. The solid cationic and anionic surfactants were recrystallized prior to use. The rest of the surfactants were used as received.

Solvents and Inorganic Reagents. Millipore filtered water (conductivity $< 1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ and air/water surface tension

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Solvatochromic Indicators in Surfactant Aggregates



Figure 2. UV-vis absorption spectrum of 2.5×10^{-5} mol dm⁻³ HOED in a 10 mmol dm⁻³ $C_{12}E_8$ solution as a function of bulk aqueous pH: (A) 11.98; (B) 10.15; (C) 9.91; (D) 9.71; (E) 9.49; (F) 9.26; (G) 9.02; (H) 8.72; (I) 6.01.



Figure 3. UV-vis absorption spectrum of 5.1×10^{-5} mol dm⁻³ H5HQ in a 10 mmol dm⁻³ C₁₂E₈ solution as a function of bulk aqueous pH: (A) 10.17; (B) 6.70; (C) 6.35; (D) 6.19; (E) 5.87; (F) 5.68; (G) 5.45; (H) 5.05; (I) 2.84.



Figure 4. UV-vis absorption spectrum of 5.2×10^{-5} mol dm⁻³ H6HQ in a 10 mmol dm⁻³ C₁₂E₈ solution as a function of bulk aqueous pH: (A) 10.60; (B) 8.29; (C) 7.97; (D) 7.77; (E) 7.56; (F) 7.43; (G) 7.29; (H) 7.16; (I) 6.88; (J) 2.97.

= 72.0 mN m⁻¹ at 25 °C) was employed to prepare the aqueous solutions. The 1,4-dioxane was UV spectroscopic grade from Fluka and was dried immediately before use by passing it through an aluminum oxide column (active neutral Brockmann grade 1, BDH). The inorganic reagents NaBr and NaCl were purum grade from Fluka and were used as received.

Methods. The experiments were performed at 25 °C. The UV-visible absorption spectra were obtained on a Varian Cary Model 210 spectrophotometer. The reference cell contained a solution, minus the solvatochromic indicator, equivalent to the one in the sample cell.

Unilamellar vesicle dispersions of DHP, DDDAB, DHDAB, DMPC, and DPPC were prepared by following the methods outlined in ref 19.

The acid-base equilibrium of each of the solvatochromic indicators examined in the present investigation is analogous to the acid-base equilibrium of the $E_T(30)$ molecule. Hence the same type of procedure was employed to obtain the pK_a values of the solvatochromic indicators from their spectra as a function of pH.¹⁸ Representative examples of the change in the UV-visible absorption spectrum of HOED, H5HQ, and H6HQ as a function of pH are shown in Figures 2-4.

The experimental setup for the pH titrations was identical with the one described in ref 18. The method of Van Uitert and Haas³⁴



Figure 5. λ_{max} for the solvatochromic absorption band of POED (O), P5HQ (\bullet), and P6HQ (\bullet) as a function of the dielectric constant of 1,4-dioxane/water mixtures.



Figure 6. $\Delta p K_a^m$ (O) and $\Delta p K_a^i$ (\bullet) values for POED as a function of the dielectric constant of 1,4-dioxane/water mixtures ($p K_a^w = 8.50 \pm 0.01$).



Figure 7. $\Delta p K_a^m$ (O) and $\Delta p K_a^i$ (\bullet) values for P5HQ as a function of the dielectric constant of 1,4-dioxane/water mixtures ($p K_a^w = 6.06 \pm 0.05$).

was used to obtain the proton activity from the pH meter reading in 1,4-dioxane/water mixtures. Our use of this method will be described in more detail in a future publication.²⁴

In general, extreme care was taken to ensure that the pK_a values referred to media in which the intrinsic ionic strength had not been significantly altered. The pK_a^{obsd} values of HOED in anionic self-assembled surfactant solutions were an unavoidable exception. The reasons for this are discussed later.

Results

In order to characterize what effect varying the properties of the solvating medium has on the spectral and acid-base properties of HOED, H5HQ, and H6HQ, we ascertained the properties of their water-soluble propyl homologues in 1,4-dioxane/water mixtures. The positions of the solvatochromic long-wavelength absorption band maximum of the conjugate base form of POED, P5HQ, and P6HQ in pure water and in various 1,4-dioxane/water

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Figure 8. $\Delta p K_a^{m}$ (O) and $\Delta p K_a^{i}$ (\bullet) values for P6HQ as a function of the dielectric constant of 1,4-dioxane/water mixtures ($pK_a^w = 7.08 \pm$ 0.08).

TABLE I: Comparison between the λ_{max} and pK_{a} Values Found for POED, P5HQ, and P6HQ in Pure Water and Literature Values for Their Methyl Homologues (Denoted MOED, M5HQ, and M6HQ) in **Pure Water**

indicator	λ _{max} , nm	pK _a ^w	ref
POED	444	8.50 ± 0.01	this work
MOED	442	8.57 ± 0.05	36
MOED	442	8.54	37
MOED	443	8.37	38
P5HQ	460	6.06 ± 0.05	this work
M5HQ	460	6.1-6.2	33
M5HQ	462	6.12 ± 0.04	39, 40
P6HQ	408	7.08 ± 0.08	this work
M6HQ	408	7.1-7.2	33
M6HQ	408	7.15 ± 0.03	39, 40

mixtures are shown in Figure 5. Figures 6-8 display the $\Delta p K_a^m$ (i.e., $pK_a^{m} - pK_a^{w}$) and ΔpK_a^{i} (i.e., $pK_a^{i} - pK_a^{w}$) values of POED, P5HQ, and P6HQ, respectively, in a number of 1,4-dioxane/water mixtures. Data were obtained in 1,4-dioxane/water mixtures with from 0 to 80 wt % 1,4-dioxane. In Figures 5-8 there is an interval of 10 wt % between each data point. The dielectric constants of the 1,4-dioxane/water mixtures were acquired from the work of Critchfield et al.35

Equation 16 was used to obtain the reference pK_a^{i} values from the p K_a^m values. The medium effect on the proton, $_m\gamma_{H^+}$, can only be estimated by making nonthermodynamic assumptions. In the present study the procedure of Fernandez and Fromherz⁸ has been followed, and it has been assumed that for a particular 1,4-dioxane/water mixture the log $_{m}\gamma_{H^{+}}$ values can be approximated by the log $_{m}\gamma_{\pm}$ value for HCl in the same mixture. The method employed to obtain the log $_{m}\gamma_{\pm}$ values for HCl in the 1,4-dioxane/water mixtures has been detailed elsewhere.¹⁸

The λ_{max} and pK_a values found for POED, P5HQ, and P6HQ in pure water can be compared with literature values for their methyl homologues.^{33,36-40} This is done in Table I. It is clear from Table I that the values determined in the present study are in good accord with previously obtained results.

Tables II-IV contain the λ_{max} and pK_a^{obsd} values found for HOED, H5HQ, and H6HQ, respectively, in the self-assembled surfactant solutions investigated. As well, these tables contain $\epsilon_{\rm eff}$ and p K_a^i values. The $\epsilon_{\rm eff}$ values were determined by comparing the λ_{max} values of the solvatochromic indicators in the self-assembled surfactant solutions with the relevant plot in Figure 5. These ϵ_{eff} values were then employed to obtain the p K_a^i values from the appropriate plot of pK_a^{\dagger} as a function of solvent dielectric constant (Figures 6-8).

In some preliminary pH titrations with HOED in aqueous micellar $C_{12}E_8$, CTAB, and SDS solutions and POED in pure

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TABLE II: λ_{max} , ϵ_{eff} , pK_a^i , and pK_a^{obsd} Values Obtained with HOED in the Aqueous Self-Assembled Surfactant Solutions

surfactant	concn, mmol dm ⁻³	λ_{max}, nm	$\epsilon_{\rm eff}$	pKa ⁱ	${ m p}K_{ m a}^{ m obsd}$
C_{1}, E_{8}	10	494	29	9.61	9.13 ± 0.03
DM	10	490	32	9.54	8.68 ± 0.03
CTAC	50	493	29	9.61	7.52 ± 0.04
СТАВ	50	493	29	9.61	7.74 ± 0.04
DTAC	50	485	36	9.44	7.73 ± 0.05
DTAC/4M NaCl	50	486	35	9.46	9.04 ± 0.04
DTAB	50	488	34	9.49	7.86 ± 0.06
DTAB/4M NaBr	50	482	39	9.38	9.40 ± 0.03
SDS ^a	50	476	46	9.22	11.00 ± 0.04
DBS ^a	50	478	44	9.26	10.61 ± 0.03
oleate ^a	50	478	44	9.26	11.35 ± 0.03
DDDAB	2.5	480	41	9.33	6.91 ± 0.04
DHDAB	2.5	480	41	9.33	6.45 ± 0.12
DH₽⁴	2.5	470	51	9.10	11.82 ± 0.20
DMPC	2.5	479	43	9.28	10.68 ± 0.14
DPPC	2.5	478	44	9.26	10.38 ± 0.20

^a Ionic strength of solution high (see text).

TABLE III: λ_{max} , ϵ_{eff} , pK_{a} ,ⁱ and pK_{a}^{obsd} Values Obtained with H5HQ in the Aqueous Self-Assembled Surfactant Solutions

	concn,	\		. TZ İ	te obsid
surfactant	mmol am	λ_{max}, nm	€eff	pK _a	pK _a oosa
C ₁₂ E ₈	10	490	26	6,11	5.90 ± 0.05
DM	10	486	33	6.14	5.56 ± 0.03
CTAC	50	488	30	6.13	4.20 ± 0.03
CTAB	50	486	33	6.14	4.43 ± 0.01
DTAC	50	486	33	6.14	4.67 ± 0.01
DTAC/4M NaCl	50	490	26	6.11	6.04 ± 0.02
DTAB	50	486	33	6.14	4.76 ± 0.03
DTAB/4M NaBr	50	487	31	6.14	6.45 ± 0.04
SDS	50	478	46	6.12	8.62 ± 0.04
DBS	50	476	49	6.11	8.21 ± 0.02
DDDAB	2.5	482	40	6.14	3.41 ± 0.19
DHDAB	2.5	487	31	6.14	3.31 ± 0.17
DHP ^a	2.5	475	51	6.10	10.17 ± 0.22
DMPC ^b	2.5	486	33	6.14	6.8 ± 0.4
DPPC ^b	2.5	482	40	6.14	6.8 ± 0.5

^a Unspecified ionic strength (see text). ^bSee text.

TABLE IV: λ_{max} , ϵ_{eff} , pK_a^{i} , and pK_a^{obsd} Values Obtained with H6HO in the Aqueous Self-Assembled Surfactant Solutions

surfactant	concn, mmol dm ⁻³	λ _{max} , nm	€eff	pK_a^{i}	$\mathrm{p}K_\mathrm{a}^\mathrm{obsd}$
$\overline{C_{12}E_8}$	10	431	29	7.41	7.44 ± 0.11
DM	10	426	40	7.32	7.04 ± 0.06
CTAC	50	435	22	7.47	6.10 ± 0.03
CTAB	50	435	22	7.47	6.32 ± 0.02
DTAC	50	432	27	7.43	6.36 ± 0.01
DTAC/4M NaCl	50	432	27	7.43	7.97 ± 0.04
DTAB	50	430	31	7.40	6.56 ± 0.05
DTAB/4 M NaBr	50	427	38	7.34	8.25 ± 0.05
SDS	50	420	53	7.24	9.84 ± 0.08
DBS	50	419	55	7.21	9.38 ± 0.05
DDDAB	2.5	423	47	7.26	5.45 ± 0.10
DHDAB	2.5	425	43	7.30	4.94 ± 0.09
DHP ^a	2.5	418	58	7.20	10.86 ± 0.16
DMPC ^b	2.5	430	31	7.40	8.6 ± 0.4
DPPC ^b	2.5	426	42	7.30	8.8 ± 0.3

^aUnspecified ionic strength (see text). ^bSee text.

water it was found that the spectra as a function of pH were ill-defined. Moreover the spectra did not exhibit distinct isosbestic points. Similar behavior has been reported for MOED in pure water by Steiner et al.³⁷ These researchers attributed this type of phenomenon to the fact that only the trans isomer of the conjugate base form is photochemically stable, while for the conjugate acid form both the cis and trans isomers, which have different molar extinction coefficients, are photochemically stable and exist in equilibrium. In the present study it was found that the problems associated with the cis/trans isomerization process

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could be avoided if the pH of the solution was initially adjusted so that there was a 100% population of the trans isomer of the conjugate base form, and pH titrations were performed by commencing at this high pH and progressing to lower pH values. The spectra of HOED and POED obtained in this manner as a function of pH were consistently reproducible and possessed sharp isosbestic points. From this finding it can be inferred that the duration of the above pH titration procedure was such that the cis isomer of the conjugate acid form had insufficient time to build up to problem amounts. All the pK_a values for HOED and POED reported in this work were determined from pH titrations performed in the manner just described. A consequence of this procedure, however, was that the anionic self-assembled surfactant solutions had a high intrinsic ionic strength (Table II).

The apparent pK_a of a phosphate head group in a 50% ionized DHP vesicle is ca. 6.⁴¹ Consequently, DHP vesicles act as buffers. In the solutions containing DHP vesicles it was necessary to add the requisite quantity of NaOH to completely ionize all the phosphate head groups before the pH titrations with the solvatochromic indicators could commence. Unfortunately, this resulted in the DHP solutions having an unspecified and not very reproducible ionic strength. This was also the case for the aqueous self-assembled DHP solutions employed in earlier works.^{18,19}

Each addition of a small aliquot of HCl or NaOH to the vesicular DMPC and DPPC solutions caused the background absorbance of the solutions to increase slightly. This may have been due to either surfactant precipitation or alkali/acid-induced growth of the vesicles. Because HOED has a large extinction coefficient, this occurrence had a negligible effect on both the nature and the analysis of the HOED spectra as a function of pH in these solutions. However, the smaller extinction coefficients of H5HQ and H6HQ meant that the spectra of both H5HQ and H6HQ as a function of pH in DMPC and DPPC solutions were devoid of a sharp isosbestic point. Moreover only rough estimates of the pK_a^{obsd} values of these indicators in DMPC and DPPC solutions could be obtained (Tables III and IV).

Characterizing the mean interfacial solvent properties in terms of an effective dielectric constant is not meant to imply that the electronic transition energy, $E_{\rm T}$, of the conjugate base form of a solvatochromic indicator is affected only by the polarity of the solvating media. It is recognized that the E_{T} value will reflect contributions from the polarity, polarizability, and hydrogen-bond donor properties of the interfacial microenvironments. The ϵ_{eff} parameter is utilized because it is expedient to describe the mean interfacial solvent properties in terms of a macroscopic solvent property of a reference solvent series.

Discussion

Solvatochromism. The solvatochromism of the conjugate base form of the methyl homologue of HOED, i.e., MOED, and closely related analogues of MOED has been extensively studied.⁴²⁻⁴⁸ The following is the most widely accepted rationalization of the dramatic solvatochromism of MOED. The electronic transition from the ground to the excited state $(\pi \rightarrow \pi^*)$ involves intramolecular charge transfer, i.e., upon excitation electron density migrates from the negative pole of MOED to the positive pole. As a result of this electron redistribution the excited state is much less dipolar than the ground state. Moreover, there is a solvent-associated variation in the relative contributions of the two extreme resonance forms to the resonance hybrid structure of the electronic ground



Figure 9. Electronic transition energy, E_{T} , of the solvatochromic absorption band of POED (O), P5HQ (O), and P6HQ (O) versus the electronic transition energy of the solvatochromic absorption band of the $E_T(30)$ molecule in 1,4-dioxane/water mixtures.

state of MOED (cf. Figure 1). A decrease in the polarity of the solvating medium therefore shifts the balance of the ground-state resonance hybrid structure in the direction of the nonpolar quinonoid resonance form, and since the structure of the excited state resembles the nonpolar quinonoid resonance form, there is a decrease in the energy difference between the ground and excited states.

To date the solvatochromism of the conjugate base form of the 1-alkylhydroxyquinolines has not been thoroughly examined. Thus, to clearly ascertain the nature of the solvatochromic behavior of the conjugate base form of the 1-alkylhydroxyquinolines, the spectral properties of POED, P5HQ, and P6HQ in 1,4-dioxane/ water mixtures have been compared with those of the $E_T(30)$ molecule. The $E_{T}(30)$ results given in ref 18 have been used for this comparison.

Figure 9 demonstrates that for 1,4-dioxane/water mixtures there is a linear relationship between the electronic transition energy, $E_{\rm T}$, of the solvatochromic absorption band of POED, P5HQ, and P6HQ and the electronic transition energy of the solvatochromic absorption band of the $E_T(30)$ molecule. The relationships are expressed in eq 17–19. The correlation coefficient, r, for each

$E_{\rm T}(\rm POED) = 0.609(E_{\rm T}(30)) + 25.9$ $r = 0.99^{\circ}$	7 (1	7)
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$$E_{\rm T}({\rm P5HQ}) = 0.359(E_{\rm T}(30)) + 39.6$$
 $r = 0.997$ (18)

$$E_{\rm T}({\rm P6HQ}) = 0.396(E_{\rm T}(30)) + 45.2$$
 $r = 0.997$ (19)

relationship is also given. The excellent linear correlations described by eq 17-19 indicate that the solute-solvent interaction for POED, P5HQ, and P6HQ in 1,4-dioxane/water mixtures must be closely related to that for the $E_T(30)$ molecule in 1,4-dioxane/water mixtures.^{45,46,49,50} Furthermore, from the excellent linear correlations and positive gradients of eq 18 and 19 it can be inferred that (1) the conjugate base forms of both P5HQ and P6HQ undergo a decrease in dipole moment upon excitation, (2) in a manner analogous to MOED the balance of the resonance hybrid structure of the ground state of the conjugate base form of P5HQ is shifted toward that of the nonpolar resonance form (see Figure 1) as the polarity of the solvating medium is decreased, and (3) the ground state of the conjugate base form of P6HQ becomes less dipolar, i.e., the charge is delocalized, as the polarity of the solvating medium is decreased.

Figure 10 shows that, in contrast to the findings in 1,4-dioxane/water mixtures, there is a relatively poor correlation between $E_T(30)$ and E_T of HOED, H5HQ, and H6HQ in many of the self-assembled surfactant solutions investigated. Two factors may be responsible for this relatively poor correlation. Within the interfacial microenvironment of the self-assembled aggregates the chromophores of the solvatochromic indicators may either experience unique solute-solvent interactions or have different average sites of residence (cf. ref 18).

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Figure 10. Electronic transition energy, E_T , of the solvatochromic absorption band of HOED (O), H5HQ (\bullet), and H6HQ (\bullet) versus the electronic transition energy of the solvatochromic absorption band of the $E_T(30)$ molecule in the self-assembled surfactant solutions: (A) $C_{12}E_s$; (B) DM; (C) CTAC; (D) CTAB; (E) DTAC; (F) DTAC/4 M NaCl; (G) DTAB; (H) DTAB/4 M NaBr; (I) SDS; (J) DBS; (K) oleate; (L) DHP; (M) DMPC; (N) DPPC. The dashed lines indicate the relationships between the E_T of the *n*-propyl homologues and $E_T(30)$ in 1,4-dioxane/water mixtures.

Davidson and Jencks³⁸ have shown that the conjugate base form of MOED exhibits spectral changes in concentrated aqueous electrolyte solutions that are consistent with the formation of a 1:1 complex between MOED and a component of the electrolyte. With the information at hand, Davidson and Jencks were unable to decide whether the cations complexed with the negative pole or the anions complexed with the positive pole of MOED. It was evident, however, that the complexed form of MOED had spectral properties different from the uncomplexed form. In particular, the electronic transition energies of the two forms were not the same in aqueous solution. Our own evidence (vide infra) suggests that an ion pair is formed between the positive nitrogen moiety of MOED and an anion. The acid-base behavior of HOED, H5HQ, and H6HQ in cationic micelles are consistent with the occurrence of this type of ion pair formation (vide infra). Considering the findings with MOED in concentrated aqueous electrolyte solutions, it is most likely that ion pair formation affects the electronic transition energy of HOED, H5HQ, and H6HQ in some of the self-assembled surfactant aggregates. Thus, the formation of ion pairs between the positive nitrogen moieties of HOED, H5HQ, and H6HQ and anionic species within the interfacial microenvironments is believed to be at least partially responsible for the relatively poor correlation between $E_{T}(30)$ and E_{T} (Figure 10). These anionic species may in principle be either the surfactant head groups or the counterions depending on the kind of self-assembled surfactant. So far, however, there is only evidence for the counterions of aggregates complexing with the positive nitrogen atoms of the solvatochromic indicators (vide infra). It should also be mentioned that the low effective interfacial dielectric constant and high effective concentration of counterions and surfactant head groups within the interfacial microenvironment combine to ensure that ion pair formation is much more energetically favorable within the interfacial phases of the selfassembled aggregates than it is in aqueous solution.

The plots displayed in Figure 10 are somewhat deceptive and may leave one with the impression that solvatochromic indicators cannot be employed to obtain estimates of the mean solvent properties of interfacial microenvironments. In this context, it is enlightening to compare the various $\epsilon_{\rm eff}$ estimates for the interfacial microenvironments of the self-assembled surfactant aggregates. To facilitate the comparison, the $\epsilon_{\rm eff}$ estimates, based on 1,4-dioxane/water mixtures as the reference media, have been collated in Table V. From Table V it is clear that each solvatochromic acid-base indicator "reports" a fairly similar interfacial $\epsilon_{\rm eff}$ for a particular self-assembled surfactant aggregate. Moreover, where comparisons can be made, the $\epsilon_{\rm eff}$ estimates are also in

TABLE V: ϵ_{eff} Estimates Based on 1,4-Dioxane/Water Mixtures as the Reference Solvent Series, for the Interfacial Region of Select Self-Assembled Surfactant Aggregates As Deduced from the Visible Absorption Spectra of the Solvatochromic Acid-Base Indicators

	€eff						
surfactant	E _T (30)	HOED	H5HQ	H6HQ			
C ₁₂ E ₈	29	29	26	29			
DM	41	32	33	40			
CTAC	34	29	30	22			
CTAB	33	29	33	22			
DTAC	39	36	33	27			
DTAC/4M NaCl	31	35	26	27			
DTAB	36	34	33	31			
DTAB/4M NaBr	29	39	31	38			
SDS	56	46	46	53			
DBS	58	44	49	55			
oleate	49	44					
DDDAB		41	40	47			
DHDAB		41	31	43			
DHP	51	51	51	58			
DMPC	27	43	33	31			
DPPC	43	44	40	42			

accord with those deduced from the solvatochromic visible absorption spectra of nitroxides⁵¹ and fluorescence emission spectra of a p-(N,N-dialkylamino)benzylidenemalononitrile.^{52,53} Therefore, it is inferred that any unique solute-solvent interaction, e.g., ion pair formation, experienced by a solvatochromic indicator residing within the interfacial microenvironment of a self-assembled surfactant aggregate does not markedly affect its ability to "report" the mean interfacial solvent properties.

Interestingly, we found the λ_{max} values of the conjugate base forms of POED, P5HQ, and P6HQ in aqueous 4 M NaCl solution to be blue shifted by 6, 3, and 3 nm, respectively, from their λ_{max} values in pure water. Therefore the low interfacial ϵ_{eff} values for the self-assembled surfactant aggregates cannot be ascribed to a "Hasted-type" ion induced dielectric saturation effect.⁵⁴

It should also be pointed out that there are several indications that the $E_T(30)$ molecule provides the most accurate estimate of the interfacial ϵ_{eff} of a particular cationic micelle. For example, the $E_T(30)$ interfacial ϵ_{eff} estimates for a series of DTAB/NaBr and DTAC/NaCl micelles correlate with the surface area per surfactant head group.²¹ As well, there is very good agreement between a cationic micellar Ψ_0 value determined with $E_T(30)$ and that determined with 4-heptadecyl-7-hydroxycoumarin by utilizing the $E_T(30) \epsilon_{eff}$ estimate.¹⁸ The $E_T(30)$ molecule probably provides the best interfacial ϵ_{eff} estimates for cationic micelles because its very large solvatochromic response swamps the effect that ion pair formation, if present (vide infra), has on the electronic transition energy.

Acid-Base Equilibria. Nonionic Micellar Solutions. Table VI shows that the pK_a^0 value of H6HQ in micellar $C_{12}E_8$ solution is in excellent agreement with the pK_a^i value, while the pK_a^0 value of H5HQ in micellar $C_{12}E_8$ solution is in reasonable accord with the pK_a^i value. However, there is a blatant disparity between the pK_a^0 value of HOED in micellar $C_{12}E_8$ and the pK_a^i value. This disparity indicates that HOED must experience some form of specific solute-solvent interaction in the interfacial microenvironment of $C_{12}E_8$ micelles. Why HOED is the only solvatochromic indicator to be markedly affected by this type of interaction is not known. Table VI also indicates that there is a clear disparity between the pK_a^0 and pK_a^i values of HOED, H5HQ, and H6HQ in micellar DM solution.

It is also noteworthy that for the $E_T(30)$ molecule the pK_a^{W} is 8.63 ± 0.03, the pK_a^{obsd} in micellar DM solution is 8.46 ± 0.04, and the pK_a^{obsd} in micellar octyl β -D-glucoside (OG) solution is 8.49 ± 0.06, whereas the pK_a^{i} value determined for the DM and

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TABLE VI: Comparison of pK, and pK, Values for HOED, H5HQ, and H6HQ in the Aqueous Nonionic and Cationic Micellar Solutions

		HOED		H5HQ			H6HQ			
surfactant	Ψ_0 , mV	pK _a ⁱ	p <i>K</i> _a ⁰	$\Delta p K_a^{0i}$	pK _a ⁱ	p <i>K</i> _a ⁰	$\Delta p K_a^{0i}$	pK_a^{i}	p <i>K</i> _a ⁰	$\Delta p K_a^{0i}$
C ₁ ,E ₈	0	9.61	9.13	-0.48	6.11	5.90	-0.21	7.41	7.44	+0.03
DM	0	9.54	8.68	-0.86	6.14	5.56	-0.58	7.32	7.04	-0.28
CTAC	+158	9.61	10.19	+0.58	6.13	6.87	+0.74	7.47	8.77	+1.30
CTAB	+141	9.61	10.12	+0.51	6.14	6.81	+0.67	7.47	8.70	+1.23
DTAC	+129	9.44	9.91	+0.47	6.14	6.85	+0.71	7.43	8.54	+1.11
DTAC/4M NaCl	+47	9.46	9.83	+0.37	6.11	6.83	+0.72	7.43	8.76	+1.33
DTAB	+118	9.49	9.85	+0.36	6.14	6.75	+0.61	7.40	8.55	+1.15
DTAB/4M NaBr	+18	9.38	9.70	+0.32	6.14	6.75	+0.61	7.34	8.55	+1.21

OG solutions is 9.55.55 Furthermore the visible absorption spectrum of the $E_T(30)$ molecule as a function of the bulk aqueous pH in micellar DM and OG solutions is unlike that seen in 1,4dioxane/water mixtures and other types of self-assembled surfactant solutions. To be precise, it possesses an isosbestic point at 400 nm (cf. Figures 1 and 2 in ref 18). Thus "aberrant" acid-base behavior in micellar alkyl saccharide solutions appears to be common to the phenol betaine class of compounds. A number of explanations for the difference between the pK_a^0 and pK_a^{i} values of $E_T(30)$, HOED, H5HQ, and H6HQ in aqueous micellar DM solution can be considered.

Hydrogen bonding between the oxygen atom of the conjugate base form of an indicator and a hydroxyl group of the disaccharide head group would stabilize the conjugate base form and thus could account for the pK_a^0 values. However, it is expected that this type of hydrogen bonding would also stabilize the dipolar nature of the electronic ground state of the conjugate base form of a solvatochromic indicator.^{49,56} On the basis that the electronic excited state of an indicator residing within the interfacial microenvironment of DM micelles remains much less dipolar than the electronic ground state, as is the case in protic homogeneous solvents and organic solvent/water mixtures, the λ_{max} values, (or more precisely the electronic transition energies) for the indicators in the aqueous micellar DM solutions argue against the existence of an extremely dipolar ground state. Hence, although the pK_a^0 values can be rationalized by invoking hydrogen bond formation, the spectral properties of the indicators do not appear to support this hypothesis.

The concordancy of the interfacial ϵ_{eff} estimate deduced from the acid-base behavior of methyl orange, neutral red, bromocresol green, and bromothymol blue in micellar OG solution²⁴ suggests that explanations that invoke either the presence of a positive micellar dipole potential or an anomalous proton activity within the interfacial microenvironment of the alkyl saccharide micelles are inappropriate.

It is known that the acid-base properties of the solvatochromic indicators are influenced by the positive charge on the nitrogen atoms (vide infra). An enhancement of this charge effect as a result of specific solute-solvent interaction within the interfacial microenvironment of the DM micelles can be ruled out however, because it is inconsistent with the spectral properties of the conjugate base forms of the indicators (vide supra).

At this stage, we are unable to rationalize unambiguously the acid-base behavior of $E_T(30)$, HOED, H5HQ, and H6HQ in aqueous micellar alkyl saccharide solutions.

Cationic Self-Assembled Surfactant Solutions. For the $E_T(30)$ molecule in cationic micellar solution it has been demonstrated that the pK_a^{0} value is equivalent to the calculated pK_a^{i} value.¹⁸ However, for HOED, H5HQ, and H6HQ in cationic micellar solution the pK_a^0 value, determined from eq 1 employing the known Ψ_0 values¹⁸ and the pK_a^{obsd} values, and the pK_a^i value are not equivalent. The pK_a^0 and pK_a^i values are compared in Table VI.

The p K_a^0 and p K_a^i values would have been equivalent if all of the following conditions had been met:¹⁸ (1) the prototropic moiety of the solvatochromic indicator resides, on average, in the plane of the charged surfactant head groups of the micelles; (2) the TABLE VII: $\Psi_0(1)$ and $\Psi_0(2)$ Values Determined from the Acid-Base Behavior of H5HQ and H6HQ in Micellar SDS and DBS Solutions^a

	$\Psi_{0}(1)$), mV	$\Psi_0(2), mV$		
surfactant	H5HQ	H6HQ	H5HQ ^b	H6HQ ^c	
SDS DBS	-148 ± 2 -124 ± 1	-154 ± 5 -128 ± 3	-107 ± 2 -83 \pm 1	-70 ± 5 -43 ± 3	

^aSee the text for the definition of $\Psi_0(1)$ and $\Psi_0(2)$. ^b p $K_a^0 = 6.81$. $^{\circ} \mathrm{p}K_{\mathrm{s}}^{0} = 8.65.$

position of the solvatochromic absorption band maximum of the indicator in micellar solution reflects the ϵ_{eff} of the interfacial microenvironment; (3) the effect of the mean interfacial solvent properties on the acid-base equilibrium of an indicator is mimicked by a 1,4-dioxane/water mixture that has a dielectric constant equivalent to the interfacial ϵ_{eff} value; (4) the principal factors responsible for the difference between the pK_a^w and pK_a^{obsd} values of an indicator are the micellar surface potential and the low ϵ_{eff} of the interfacial region, i.e., the intrinsic interfacial acid-base equilibrium is not influenced by either specific solute-solvent interactions or interfacial "salt-effects". It is obvious from the results of Table VI that one or more of these conditions are not met when HOED, H5HQ, and H6HQ are in cationic micellar solution.6

On the basis of the findings of a great deal of other work^{8,18,19,23,24} we considered it highly unlikely that conditions 1-3 were not satisfied. As alluded to earlier, the formation of an ion pair between the positive nitrogen atom of a solvatochromic indicator and a halide ion is believed to be responsible for the disparity between the pK_a^0 and pK_a^i values.

A charged group affects the pK_a of a neighboring acid-base group in the molecule. The magnitude of this effect may be formalized in the equation⁵⁷⁻⁵⁹

$$pK_{a} = pK_{a}^{n} - \frac{Z_{n}e^{2}}{2.303DdkT}$$
(20)

where pK_a^n is the intrinsic pK_a of the acid-base group, Z_n is the charge (partial or otherwise) of the neighboring group, D is the effective dielectric constant separating the charged group and the acid-base group, d is the distance between the two groups, e is the electronic charge, and k is the Boltzmann constant.

The assumption that within the interfacial microenvironment of the cationic micelles HOED, H5HQ, and H6HQ are ion paired with a halide ion that causes the charge on their nitrogen atom to be electrically neutralized leads to

$$pK_{a}^{i} = pK_{a}^{n} - \frac{Z_{n}e^{2}}{2.303DdkT}$$
(21)

$$pK_a^{\ 0} = pK_a^{\ n} \tag{22}$$

$$\Delta p K_a^{0i} = \frac{Z_n e^2}{2.303 D d k T}$$
(23)

Hence the difference in the $\Delta p K_a^{0i}$ value for HOED, H5HQ, and H6HQ in a particular cationic micellar solution (Table VI) can

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TABLE VIII: $\Psi(1)$ and $\Psi(2)$ Values Determined from the Acid-Base Behavior of HOED, H5HQ, and H6HQ in Vesicular DMPC and DPPC Solutions^a

		$\Psi(1), mV$			$\Psi(2), \mathrm{mV}$			
phosphatidylcholine	HOED	H5HQ	H6HQ	HOED ^b	H5HQ ^c	H6HQ ^d		
DMPC	-83 ± 8	-39 ± 24	-71 ± 24	-44 ± 8	$+1 \pm 24$	$+3 \pm 24$		
DPPC	-66 ± 12	-39 ± 30	-89 ± 18	-27 ± 12	$+1 \pm 30$	+9 ± 18		

^a See the text for the definition of $\Psi(1)$ and $\Psi(2)$. ^b $pK_a^{\ 0} = 9.93$. ^c $pK_a^{\ 0} = 6.81$. ^d $pK_a^{\ 0} = 8.65$.

be rationalized in terms of the different distances between the charged nitrogen atom and the prototropic hydroxy group in each indicator and also the magnitude of Z_n , i.e., the partial positive charge on the nitrogen atom in the absence of ion pair formation, for each indicator.

In the $E_T(30)$ molecule the distance between the positive pyridinium nitrogen atom and the prototropic hydroxy group is considerably less than the distance between the same groups in HOED. Why then is the acid-base behavior of an $E_T(30)$ molecule that is located within the interfacial microenvironment of a cationic micelle seemingly unaffected by complexation with a halide ion?¹⁸ There are two possible explanations. Either the $E_{T}(30)$ molecules does not form an ion pair with a halide ion, or in the $E_T(30)$ molecule the positive charge is sufficiently delocalized over the pyridinium ring and screened by the phenyl groups^{49,60} so that complexation of the pyridinium nitrogen with a halide ion has a negligible effect on the acid-base properties of an interfacially located $E_T(30)$ molecule. We consider the latter explanation to be the more reasonable one.

The $E_T(30)$ molecule cannot be used to determine the surface potential of DDDAB and DHDAB vesicles.¹⁸ HOED, H5HQ, and H6HQ can, however, be utilized to obtain a Ψ_0 estimate for these vesicles in aqueous solution. It is reasonable to expect the average pK_a^0 value of the solvatochromic indicator in the alkyltrimethylammonium halide micelles (Table VI) to be a good approximation for the pK_a^0 value in DDDAB and DHDAB vesicles. Substituting this average pK_a^0 value and the pK_a^{obsd} value of the indicator (Tables II-IV) into eq 1 yields Ψ_0 values of 190 \pm 13 and 211 \pm 11 mV for the DDDAB and DHDAB vesicles, respectively, in aqueous solution without added electrolyte. The acid-base behavior of 4-heptadecyl-7-hydroxycoumarin in vesicular DDDAB solution also yields a Ψ_0 value of 190 mV when an interfacial ϵ_{eff} of 41 is taken into account.¹⁹

The DDDAB and DHDAB vesicles are of a size where the planar solution to the Poisson-Boltzmann equation can be employed to approximate the relationship between the surface charge density, σ_0 , and Ψ_0 :

$$\sigma_0 = -(8n_0\epsilon\epsilon_0 kT)^{1/2}\sinh\frac{e\Psi_0}{2kT}$$
(24)

where n_0 is the number density of ions in the bulk solution, ϵ is the dielectric constant of the bulk solution, ϵ_0 is the permittivity of a vacuum, and the other parameters are defined as before. Substituting the average value of Ψ_0 and the CVC^{61,62} into eq 24 gives a σ_0 of 0.030 and 0.012 C m⁻² for DDDAB and DHDAB vesicles, respectively. This σ_0 value of 0.021 ± 0.009 C m⁻² quantitatively agrees with the σ_0 value obtained by fitting the results of direct double-layer force measurements between two DHDAB bilayers to the DLVO theory.⁶³ Hence, our results are an entirely independent confirmation of the results of Pashley et al.63

Anionic Self-Assembled Surfactant Solutions. To ascertain whether or not the pK_a^{0} value is equivalent to the pK_a^{i} value in anionic self-assembled surfactant solutions, we used two methods to obtain a Ψ_0 value for the anionic surfactant aggregates. In the first method $\Psi_0(1)$ values were calculated by assuming that the pK_a^0 value was equal to the pK_a^i value. In the second method $\Psi_0(2)$ values were calculated by assuming that the p K_a^0 value was equal to the average pK_a^0 value found in cationic micellar solution. The $\Psi_0(1)$ and $\Psi_0(2)$ values determined with H5HQ and H6HQ in micellar SDS and DBS solutions are contained in Table VII. The HOED results were not examined in this manner because of the high ionic strength of the anionic self-assembled surfactant solutions (vide supra). As well, the H5HO and H6HO results in DHP solution were not analyzed because of the unspecified ionic strength of the DHP solutions (vide supra).

The concordancy of the H5HQ and H6HQ $\Psi_0(1)$ values for both the SDS and the DBS micelles suggests that the pK_a^0 value is equivalent to the pK_a^{\dagger} value in these systems. Evidently the anionic sulfate and sulfonate head groups do not form intimate ion pairs with the positive nitrogen atoms of these solvatochromic indicators.

Phosphatidylcholine Vesicular Solutions. It has been established elsewhere^{18,19} that the acid-base behavior of an indicator residing within the interfacial microenvironment of a zwitterionic phosphatidylcholine vesicle is not influenced by the net surface charge (i.e., zero). Instead it is influenced by the local electrostatic potential, Ψ , at the average site of residence of the indicator's prototropic group in the interfacial region. As shown in Table V, the $E_T(30)$ molecule, HOED, H5HQ, and H6HQ all report a similar interfacial ϵ_{eff} for the DMPC and DPPC vesicles. This suggests that the different solvatochromic chromophores have a similar average site of residence within the interfacial microenvironment of the DMPC and DPPC vesicles and should therefore "sense" a similar Ψ value. The $E_{\rm T}(30)$ molecule "senses" a Ψ value of -56 mV in both DMPC and DPPC vesicles.¹⁸

The $\Psi(1)$ and $\Psi(2)$ values determined with HOED, H5HQ, and H6HQ in vesicular DMPC and DPPC solutions are given in Table VIII. The $\Psi(1)$ and $\Psi(2)$ values were determined by methods analogous to those employed to gain the $\Psi_0(1)$ and $\Psi_0(2)$ values for the anionic micellar solutions. It is clear from the results in Table VIII that the $\Psi(1)$ values agree best with the Ψ value "sensed" by the $E_T(30)$ molecule. This suggests that the p K_a^{C} values of HOED, H5HQ, and H6HQ in vesicular DMPC and **DPPC** solutions without extraneous electrolyte are equivalent to the pK_a^i values. Furthermore, it indicates that the anionic phosphate moiety of the zwitterionic phosphatidylcholine head group does not form an intimate ion pair with the positive nitrogen atom of HOED, H5HQ, or H6HQ.

Conclusions

In the present investigation it has been established that (1) the solvatochromism of the conjugate base forms of HOED, H5HQ, and H6HQ can be utilized to obtain a reasonable estimate of the mean interfacial solvent properties of self-assembled surfactant aggregates, (2) the acid-base behavior of HOED, H5HQ, and H6HQ in cationic micellar solutions is consistent with the formation of an intimate ion pair between the positive nitrogen atom of the indicator and a halide ion, (3) the intrinsic acid-base behavior of H5HQ and H6HQ in micellar SDS and DBS solutions is not markedly affected by any specific solute-solvent interaction or interfacial "salt effects", and (4) the acid-base behavior of HOED, H5HQ, and H6HQ in vesicular DMPC and DPPC solutions with no extraneous electrolyte is not markedly affected

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by any specific solute-solvent interaction.

It is concluded that HOED, H5HQ, and H6HQ can be employed as probes of the electrostatic surface potential of self-assembled surfactant aggregates. However, for each particular system being investigated it is essential to determine whether or not the indicator is complexed with an anion. This determination is necessary in order to ensure that the correct pK_a^0 value is used.

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Registry No. HOED, 58346-32-0; H5HQ, 113451-64-2; H6HQ, 113451-65-3; POED, 70850-53-2; P5HQ, 113451-66-4; P6HQ, 113451-67-5; $C_{12}E_8$, 3055-98-9; DM, 69227-93-6; CTAC, 112-02-7; CTAB, 57-09-0; DTAC, 112-00-5; DTAB, 1119-94-4; Na DBS, 25155-30-0; SDS, 151-21-3; Na DHP, 60285-46-3; DDDAB, 3282-73-3; DHDAB, 70755-47-4; DMPC, 18194-24-6; DPPC, 63-89-8; oleic acid, 112-80-1.

Photolonization of N, N, N', N'-Tetramethylbenzidine in Anionic–Cationic Mixed Micelles of Sodium Dodecyl Sulfate–Dodecyltrimethylammonium Chioride: Electron Spin Resonance and Electron Spin Echo Modulation Studies

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Electron spin echo modulation (ESEM) and electron spin resonance (ESR) spectra of the photogenerated N,N,N',N' tetramethylbenzidine cation radical (TMB⁺) in frozen mixed micelles of dodecyltrimethylammonium chloride (DTAC) and sodium dodecyl sulfate (SDS) have been studied as a function of the mixed micelle composition. ESEM effects due to TMB⁺ interactions with deuterium in D₂O show a decrease of the TMB⁺-water interaction that depends on the SDS-DTAC mixed micelle composition and reaches a minimum for the equimolar mixed micelle. The efficiency of charge separation upon photoionization of TMB to produce TMB⁺ measured by ESR correlates with the degree of water penetration into the micelle. ESEM effects due to interaction of x-doxylstearic acid nitroxide probes with deuterium in D₂O show that the decrease of water penetration is due to higher surface packing due to electrostatic attraction among the polar headgroups of the two surfactants.

Introduction

The influence of organized media such as micelles and vesicles on photoinduced charge separation is well documented.¹ The photoionization of a solute like N,N,N',N'-tetramethylbenzidine (TMB) in micellar solution can be controlled by changing the chemical properties of the host assembly. It has been demonstrated that the photoionization efficiency is affected by micellar charge, micellar size, counterion variation, and added cosurfactants.²⁻⁶ In frozen solutions the photoionization in positively charged micelles (dodecyltrimethylammonium chloride, DTAC) has been found to be about twice as efficient as in negatively charged micelles (sodium dodecyl sulfate, SDS). Electron spin echo modulation (ESEM) results have also shown that the photoionization yield correlates, in frozen micellar solution, with the degree of water penetration into the micellar surface.^{6,7}

In a recent study Bernas et al.⁸ showed that at room temperature the water-TMB⁺ interaction amplitude, which is an essential factor governing the decay rate, is not an independent parameter but is correlated with the effective micellar charge.

In the present work we study the variation of the photoionization yield of TMB by varying, in a controlled way, the charge density of a mixed micelle that is generated by changing the surfactant mixing ratio of an anionic (SDS) and a cationic (DTAC) surfactant. In this way the net surface charge of the resulting mixed micelle decreases until neutralization for 1:1 mole ratio. The results obtained for frozen micellar solutions show how the degree of water interaction of the photoproduced cation and how the degree of water organization of the micellar interface affect the photoionization yield.

Experimental Section

SDS and DTAC were purchased from Eastman Kodak, TMB was obtained from Aldrich, 1-butanol (HPLC grade) and NaCl

were obtained from Fisher, and x-doxylstearic acid spin probes (x-DSA), were obtained from Molecular Probes, Inc. All these products were used as received.

A stock solution of TMB was prepared in chloroform. Stock solutions of 0.1 M surfactant were prepared in triply distilled and deoxygenated water and in deuteriated water (Aldrich). The surfactant solution was added to a film of TMB generated by evaporating the chloroform. The film was solubilized by sonicating for 30 min and by stirring the solution for 3 h at 50 °C in a nitrogen atmosphere.

The concentrations of the solutions were 0.1 M SDS, 0.1 M DTAC, and 1×10^{-4} M TMB. The samples were prepared by mixing these solutions according to the different mole fractions of surfactant studied.

Stock solutions of x-DSA probes were prepared in chloroform. Films of the spin probes generated by evaporating the chloroform were dissolved in the surfactant solution in a nitrogen atmosphere.

The samples having a mole fraction from 0.3 to 0.6, in which a phase separation occurs at room temperature, were heated for several hours at about 50 °C to obtain a homogeneous micellar solution. The other solutions were mixed for several hours at room temperature. All the samples were sealed in 2-mm i.d. \times 3-mm o.d. Suprasil quartz tubes and frozen rapidly in liquid nitrogen.

Photoirradiation of the TMB was carried out at 77 K for 6 minutes with a 150-W xenon lamp (Cermax) filtered with 10 cm

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