Study of the Polarity and Hydrogen-Bond Ability of Dodecyltrimethylammonium Bromide Micelles by the Kamlet−Taft Solvatochromic Comparison Method

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We have studied the dipolarity/polarizability (π^*), hydrogen-bond donor acidity (α), and hydrogen-bond acceptor basicity (β) of dodecyltrimethylammonium bromide (DTAB) micelles using the Kamlet−Taft solvatochromic comparison method. DTAB micelles were found to be quite polar ($\pi^* = 1.02$), to have relatively strong hydrogen-bond donating ability ($\alpha = 0.700$), and to have moderate hydrogen bond accepting ability ($\beta = 0.486$). These values are compared to the π^*-, α-, and β-values of sodium dodecyl sulfate (SDS) micelles obtained in a previous solvatochromic study and are found to be qualitatively consistent with linear solvation energy relationship studies of both SDS and DTAB micellar systems. The chemical interpretation of these parameters and the nature of DTAB micelles which they reflect are discussed. By comparison to the solvatochromic parameters of representative pure solvents such as DMSO ($\pi = 1.00$), 2-propanol ($\alpha = 0.69$), and ethylbenzoate ($\beta = 0.43$), it is evident that the micellar environments observed by the various indicators are quite dipolar, very strong hydrogen bond donors, and moderately strong hydrogen bond acceptors.

Introduction

Owing to their unique chemical nature, micelles (self-assembled aggregates of surfactant monomers) have been used in a wide variety of applications in many different areas of chemistry. For example, they are used to catalyze organic reactions in aqueous solutions,[1,2] to alter the selectivity of chromatographic[3,4] and electrophoretic separations,[4,5] and to remediate contaminated soil.[6,7] The utility of micelles in these and other applications relies, at least in part, on the interactions between micelles and the organic solutes of interest. These interactions, in turn, are related to the chemical nature of the micelles themselves.

In this study we used the Kamlet−Taft solvatochromic comparison method to characterize the chemical nature of dodecyltrimethylammonium bromide (DTAB) micelles by quantifying their dipolarity/polarizability (π^*), hydrogen-bond acidity (α), and hydrogen-bond basicity (β). The Kamlet−Taft method[8−10,11] has been used extensively to characterize pure fluids, mixed solvent systems, and even supercritical fluids. Its application to the study of sodium dodecyl sulfate (SDS) micelles has been discussed in detail elsewhere.[12,13] Briefly, the method relies on solvent-induced shifts in the wavelength of maximum absorbance (λ_{max}) of indicator molecules to quantify solvents' dipolarities/polarizabilities, hydrogen-bond acidities, and hydrogen-bond basicities relative to reference solvents.

The goal of this study is to characterize DTAB micelles acting as if they were a bulk phase distinct from the aqueous phase in which they are dissolved. Because the indicators used in these studies will be distributed between the bulk aqueous phase and the micellar pseudophase, the spectrum of the indicator in the aqueous phase must be subtracted from the spectrum recorded in the micellar solution in order to characterize only the micelles. The result is the spectrum of the indicator in the micelles, free from contributions of the indicator in the bulk aqueous phase. This spectrum is then used to characterize the micelles as if they were a separate, distinct phase.

The subtraction of the indicator's spectrum in water could be done algebraically if the indicator's distribution coefficient between the bulk aqueous phase and the micellar phase were known. For the indicators used in these studies, however, this is generally not known. Therefore, a different method of spectral curve resolution must be used. For this purpose, we have adapted the curve resolution algorithm of Kubista et al.[14] to make it directly applicable to micellar systems.[13] Briefly, the curve-resolution technique is based on singular value decomposition (SVD) of a matrix of spectra recorded at several different micellar concentrations. Abstract spectra and concentrations obtained from the decomposition are then transformed into real spectra and concentrations by introducing a transformation matrix whose elements are determined using known system parameters coupled with linear regression analysis. The method and its validation have been described in detail elsewhere[13] and applied to the characterization of SDS micelles.[12]

Ultimately, from the λ_{max}-values obtained after curve resolution, we calculate π^*-, α-, and β-values of the micelles, completely independent of spectral contributions of the indicator in the aqueous phase, and thereby quantify the dipolarity/

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polarizability, hydrogen-bond acidity, and hydrogen-bond basicity of the micellar environment.

The π^*-, α-, and β-values obtained for DTAB micelles in this study are compared to the same values obtained in a similar study of SDS micelles. Since both surfactants have the same alkyl chain length, the present work allows us to examine the influence of the headgroup on the chemical nature of the micelles formed by these two surfactants. Additionally, the results are compared to studies based on linear solvation energy relationships (LSERs),[12,15−17] which represent an independent extra-thermodynamic method for characterizing the chemical nature of micelles.

Overall, we find that the solvatochromic and extra-thermodynamic studies are in good qualitative agreement, revealing significant differences between SDS and DTAB micelles, especially regarding their abilities to participate in hydrogen-bond interactions and thereby selectively interact with solutes differing in their hydrogen-bond acidities and basicities.

Experimental Section

Chemicals. The following chemicals were from Aldrich and used without further purification: *p*-ethylnitrobenzene (99+%), *p*-nitroaniline (99+%), *p*-nitrophenol (99+%), and DTAB (99%). The *p*-nitroanisole (97%) used in these experiments was also from Aldrich and was purified using chromatography on silica gel with methylene chloride as the solvent, followed by recrystallization from 2-propanol. *N*,*N*-diethyl-*p*-nitroaniline was from Frinton Laboratories and used as received. The two α-indicators, 2,6-dichloro-*p*-(2,4,6,-triphenyl-*N*-pyridino)phenolate (ET(33)) and bis[α-(2-pyridyl)benzylidine-3,4-dimethylaniline]bis(cyano)iron(II) ($Fe(LL)_2(CN)_2$), were prepared and purified using procedures given in the literature.[18,19] ET(33), which has a pK_a of 4.38,[18] was used instead of the structurally related ET(30), which has a pK_a of 8.65,[18] to avoid Bronsted acid−base complications arising from the protonation of the indicator and subsequent alteration in its solvatochromic behavior. All water was deionized and passed through Barnstead ion exchange and Organic Free cartridges followed by a 0.45-μm filter.

Spectroscopy. A stock solution of each indicator in water was prepared such that the maximum absorbance of the peak of interest was approximately 0.5 (unless solubility-limited in which case an excess of the indicator was stirred in water for approximately 2 days followed by gravity filtration to remove the undissolved material). Indicator solutions of varying DTAB concentrations between 0 and 100 mM were made by preparing a 100 mM DTAB solution using the stock indicator solution as the diluent, followed by serial dilution using the stock aqueous indicator solution. Corresponding aqueous DTAB solutions were prepared using pure water and used as reference solutions.

UV−visible absorbance spectra of *p*-nitroanisole, *N*,*N*-diethyl-*p*-nitroaniline, ET(33), $Fe(LL)_2(CN)_2$, and *p*-nitroaniline were collected using a Varian DMS 200 scanning spectrophotometer, 1-cm quartz cells (Starna Cells, Inc.), a scan rate of 20 nm/min, and a slit width of 0.2 nm. A Cary-17 scanning spectrophotometer controlled with software written in-house was used to collect the spectra of *p*-ethylnitrobenzene and *p*-nitrophenol. A holmium oxide filter was used to calibrate both spectrophotometers. Solutions were allowed to remain in the thermostated sample compartment of the Varian DMS 200 for a minimum of 10 min before the spectra were collected. The temperature was maintained at 25.0 ± 0.2 °C using a Fisher Scientific Isotemp Constant Temperature Circulator (model 800) and a Utile Products Neslab Instruments Inc. (model U-Cool) cooling unit. No temperature control was used with the Cary-17.

Data Analysis. Digitized spectra were collected using DMSSCAN software from Varian (Palo Alto, CA) and software written in-house for the Cary-17 UV−visible spectrophotometer. The data were analyzed using a program based on the curve-resolution algorithm previously described.[12,13] The resolution algorithm yields both the spectra of the indicators in the micellar phase free from contributions of the spectra in the aqueous phase as well as the indicators' molar-based partition coefficients, K_{wm}. This program was written in Matlab for Windows (The Mathworks Inc., Natick, MA). We have assumed that the volume of the micelle is 14.7 L/mol, obtained by multiplying the molar volume of micellized DTAB monomers (0.294 L/mol)[20,21] by the average aggregation number (50).[22,23]

In performing the curve resolution, we vary the range of DTAB concentrations in which data are taken. This reduces the possibility that the results are skewed by any one spectra. In all cases a minimum of four spectra (the indicator in water and the indicator in three different DTAB solutions above the critical micelle concentration) are required by the algorithm. For most indicators, however, we found it necessary to include as many as six spectra taken at different DTAB concentrations above the critical micelle concentration (cmc) before consistent results are achieved. The variations of the results obtained as a function of the DTAB concentration range included in the curve resolution will be discussed below.

Following curve resolution, the spectra of the indicators in DTAB generated by the algorithm are imported into TableCurve (Jandel Scientific, San Rafael, CA) and gently smoothed with its 10% fast Fourier transform (FFT) method, and the "9/10" method of Kamlet, Taft, and Abboud is applied to find λ_{max}.[8] In the 9/10 method, the λ_{max} of a solvatochromic band is taken as the midpoint between the two wavelengths in the peak for which the absorbance is nine-tenths the maximum absorbance.[8] This method was used by Kamlet, Taft, and Abboud to reduce the effects of band overlap, hidden underlying lower intensity bands, and solvent-dependent changes in band shape.[8] The FFT smoothing algorithm transforms the data into the frequency domain via the fast Fourier transform and eliminates high-frequency signals to reduce the noise in the signal. An inverse transformation is then applied to convert the smoothed data back into the standard absorbance spectrum. The "10%" specifies the percent of frequency components that are eliminated in the filtering process. We found that this algorithm causes very little perturbation in the overall peak shape but eliminates enough noise to provide a smooth continuous curve near the peak maxima. This greatly aids in using the "9/10" method since it relies on finding the maximum absorbance value.

Results and Discussion

Partition Coefficients. As mentioned above, in addition to providing the spectra of the indicators in the micellar phase, the curve-resolution technique also yields the indicators' molar-based partition coefficients, K_{wm},[12,13] defined as the ratio of the concentration of the indicator in the micellar phase to that in the aqueous phase. The partition coefficients we obtained after applying curve resolution to the spectral data are shown in Table 1 as a function of the DTAB concentration range included in the curve resolution. As was the case in applying the curve-resolution method to SDS spectra,[12] the partition coefficients determined using only four spectra recorded at the lowest surfactant concentrations are significantly different than those when data recorded at higher concentrations are included. This likely results from a combination of two effects. First, the spectra recorded at the lowest surfactant concentrations exhibit

TABLE 1: Molar-Based Partition Coefficients Obtained for Each Indicator as a Function of the DTAB Concentration Range Analyzed in the Curve Resolution

[DTAB] range (mM)	NNDEA[a]	PENB[b]	PNA[c]	ET(33)[d]	$Fe(LL)_2(CN)_2$[e]	PNP[f]	4NA[g]
0−40	1720	800	260	7090	16 800	1070	170
0−45	1660	790	255	6040	16 300	1200	230
0−50	1550	740	255	5520	15 500	320	270
0−55	1580	680	260	5780	12 100	160	290
0−60	1540	660	260	5560	14 000	170	290
0−65	1520	640	260	5720	19 200	130	270
0−70	1500	620	250	5530	16 000	100	270
0−80	1470	600	240	5060	14 400	100	270
0−90	1440	580	230	4970	12 400	100	270
0−100	1430	570	220	5180	11 000	110	260
average[h]	1500	640	250	5420	14 300	140	270

[a] *N*,*N*-Diethyl-*p*-nitroaniline (NNDEA). [b] *p*-Ethylnitrobenzene (PENB). [c] *p*-Nitroanisole (PNA). [d] 2,6-Dichloro-*p*-(2,4,6,-triphenyl-*N*-pyridino)phenolate (ET(33)). [e] Bis[α-(2-pyridyl)benzylidine-3,4-dimethylaniline]bis(cyano)iron(II) ($Fe(LL)_2(CN)_2$). [f] *p*-Nitrophenol (PNP). [g] *p*-Nitroaniline (4NA). [h] The average value shown for each indicator does not include in the first two partition coefficients obtained at the lowest DTAB concentrations. Spectra recorded in water, 30 mM DTAB, and 35 mM DTAB were included in all of the above analyses.

TABLE 2: Solvatochromic Parameters Obtained with Each Indicator[a] as a Function of the DTAB Concentration Range Analyzed in the Curve Resolution

[DTAB] range (mM)	π^* NNDEA	π^* PENB	π^* PNA	α ET(33)	α $Fe(LL)_2(CN)_2$	β PNP	β 4NA
0−40	1.044	0.995	1.022	0.608	0.798	0.558	0.411
0−45	1.042	0.994	1.024	0.603	0.801	0.557	0.414
0−50	1.042	0.991	1.027	0.602	0.802	0.564	0.414
0−55	1.041	0.987	1.022	0.602	0.800	0.560	0.414
0−60	1.040	0.986	1.021	0.602	0.802	0.561	0.411
0−65	1.040	0.984	1.021	0.605	0.804	0.555	0.408
0−70	1.040	0.983	1.020	0.600	0.791	0.552	0.408
0−80	1.040	0.981	1.020	0.600	0.796	0.561	0.407
0−90	1.039	0.980	1.020	0.599	0.795	0.578	0.406
0−100	1.039	0.978	1.011	0.601	0.798	0.564	0.404
average[b]	1.041	0.986	1.021	0.602	0.798	0.561	0.410

[a] Indicator abbreviations are the same as in Table 1. [b] The average value shown for each indicator includes all of the values shown. Spectra recorded in water, 30 mM DTAB, and 35 mM DTAB were included in all of the above analyses.

the smallest shifts and are therefore more difficult to resolve. Additionally, a minimum of four spectra are required by the curve-resolution algorithm. Thus, the inclusion of more than four spectra represents an overdetermination of the system, which improves the reliability of the method. We note that the spectra obtained for all of the indicators lead to very consistent solvatochromic parameters as a function of DTAB concentration and therefore are not affected by apparent changes in the partition coefficients. The solvatochromic parameters so obtained are discussed below.

Evaluation of the Partition Coefficients. The order of the indicators' partition coefficients is $Fe(LL)_2(CN)_2$ > ET(33) > *N*,*N*-diethyl-*p*-nitroaniline > *p*-ethylnitrobenzene > *p*-nitroaniline ≈ *p*-nitroanisole > *p*-nitrophenol. This order is consistent with the partitioning behavior of other solutes in DTAB micellar systems in that they follow the general observation that large organic molecules tend to partition out of the aqueous phase and into the micellar pseudophase to a greater extent than do smaller, more polar, molecules.[15,24] For example, $Fe(LL)_2(CN)_2$ and ET(33) are the largest indicators and therefore partition to the greatest extent. Additionally, *N*,*N*-diethyl-*p*-nitroaniline partitions to a greater extent than does the related *p*-nitroaniline because of the diethyl derivitization. Furthermore, the methoxy moiety of *p*-nitroanisole is less polar than the hydroxyl moiety of *p*-nitrophenol, increasing the partition coefficient of *p*-nitroanisole relative to that of *p*-nitrophenol. Finally, *p*-ethylnitrobenzene will partition into the micellar phase more than either *p*-nitroanisole or *p*-nitrophenol owing to the presence of the ethyl group relative to the methoxy and hydroxyl groups, which interact more favorably with the aqueous phase than does the ethyl group of *p*-ethylnitrobenzene. Thus, the relative order of the partition coefficients of these three compounds is in agreement with predictions based upon the sizes, polarities, and hydrogen-bonding capabilities of these indicators. This agreement lends qualitative support to the reliability of the curve-resolution technique.

Solvatochromic Parameters. While an examination of the partition coefficients is a necessary part of evaluating the reliability of the curve-resolution method, our true interest lies in the determination of the solvatochromic parameters π^*, α, and β for DTAB micelles. In the following section we present the results of our solvatochromic studies. We note here that the λ_{max}-values for each indicator, and therefore the solvatochromic parameters calculated from them, are quite insensitive to the DTAB concentration range included in the curve resolution. If this were not the case, it would be difficult, if not impossible, to assert anything about the chemical properties of DTAB micelles.

Dipolarity/Polarizability of DTAB. The π^*-values of DTAB micelles obtained with each indicator are shown in Tables 2 and 3 along with the π^*-values for pure water. We used the equations of Kamlet, Taft, and Abboud to calculate π^*-values from the λ_{max}-values obtained after curve resolution was applied to the micellar spectra.[8] An average π^*-value (shown in Table 3) was determined with each indicator by averaging the values obtained at each concentration range we analyzed. An overall π^*_{DTAB}-value of 1.02 was determined by averaging the average π^*-values obtained with each indicator.

Averaging over several indicators in this manner was recommended by Kamlet and Taft to reduce the contributions arising from solvent effects or spectral anomalies specific to any one indicator.[8] This approach, however, has been criticized recently for masking physically meaningful differences in the chemistry of the indicators.[25,26] Therefore, we report the solvatochromic

TABLE 3: Average Solvatochromic Parameters for DTAB, SDS, and Water[a]

indicator[b]	π^*_{DTAB}	π^*_{SDS}	π^*_{water}(DTAB)	π^*_{water}(SDS)
NNDEA	1.04	1.15	1.34	1.34
PENB	0.99	1.00	1.21	1.18
PNA	1.02	1.04	1.08	1.08
average	1.02	1.06	1.21	1.20
indicator[b]	α_{DTAB}	α_{SDS}	α_{water}(DTAB)	α_{water}(SDS)
ET(33)	0.602	0.736	0.938	0.956
$Fe(LL)_2(CN)_2$	0.798	1.010	1.075	1.122
average	0.700	0.873	1.007	1.039
indicator[b]	β_{DTAB}	β_{SDS}	β_{water}(DTAB)	β_{water}(SDS)
PNP	0.561	*c*	0.467	0.459
4NA	0.410	0.401	0.113	0.112
average	0.486	0.401	0.290	0.286

[a] The parameters for water were determined twice—once in conjunction with the SDS data collection and once in conjunction with the DTAB data collection as labeled in parentheses. [b] The indicator abbreviations are the same as in Table 1. [c] The β-value for SDS could not be determined with PNP as discussed in a previous paper.[12]

parameters obtained with each indicator in addition to the average values. We note that in all cases, the conclusions regarding the chemical nature of DTAB micelles based on the analysis of the averaged solvatochromic parameters are the same as those based on an analysis of the individual indicators. Therefore, although effects specific to a particular indicator may be present, they are not large enough to seriously alter the chemical interpretation of the solvatochromic parameters.

The average π^*_{DTAB} value of 1.02 reveals that the indicators are solubilized in the micelle in a region of high dipolarity/polarizability, especially when one compares this π^*-value to the π^*-values of other dipolar solvents such as dimethyl sulfoxide ($\pi^* = 1.00$),[8] formamide ($\pi^* = 1.12$),[8] and water ($\pi^* = 1.21$). This high dipolarity/polarizability most likely arises from a combination of contributions from the charged headgroups, the bound counterions, and the water associated with the headgroup region. Furthermore, the high dipolarity sensed by the indicators suggests that they are localized in the hydrated, polar headgroup region of the micelle and not in the nonpolar core.

One of our purposes in determining the solvatochromic parameters of the micelles is to compare them to predictions made based on a linear solvation energy relationship (LSER) describing solute partitioning between the aqueous and DTAB micellar phases that we obtained in this laboratory (eq 1).[24]

$$\log K_{w/DTAB} = -0.13 + 3.12V_x - 0.14\pi_2^H + 0.42\Sigma\alpha_2^H - 2.71\Sigma\beta_2^H + 0.31R_2 \quad (1)$$

$$n = 28 \qquad \rho = 0.984 \qquad \text{s.d.} = 0.15$$

The partition coefficients used to generate this LSER were measured using headspace gas chromatography.[24] The subscript 2 in the LSER indicates a *solute* parameter in contrast to the bulk liquid properties being determined in this section. The negative coefficient of π_2^H (solute dipolarity/polarizability) means that all else being equal, polar molecules favor being in the aqueous phase rather than in the micellar phase. This implies that water is better able to interact through dipole−dipole and dipole−induced dipole interactions than are DTAB micelles. In other words, the environment experienced by a solute in water is more dipolar than in DTAB micelles. The extent to which this is true is reflected in the magnitude of the coefficient. If the magnitude is large (>∼0.5), then one expects a large difference between the dipolarity of the two solvents. This is exemplified in the LSER describing solute transfer from water to hexadecane shown below in eq 2.[27]

$$\log K_{C16} = 0.09 + 4.43V_x - 1.62\pi_2^H - 3.59\Sigma\alpha_2^H - 4.87\Sigma\beta_2^H + 0.67R_2 \quad (2)$$

$$n = 370 \qquad \rho = 0.998 \qquad \text{s.d.} = 0.12$$

Here, the coefficient of π_2^H is large because of the tremendous difference in the dipolarity of water compared to hexadecane. Thus, the small negative coefficient of π_2^H in the DTAB LSER above (eq 1) suggests that the dipolarity/polarizability of DTAB should be less than that of water, but only slightly so.

This is indeed what we find with the solvatochromic π^*-values of DTAB ($\pi^* = 1.02$) and water ($\pi^* = 1.21$). Thus, the solvatochromic parameters and the LSER are in qualitative agreement, supplying evidence that both methods are reflecting the chemical interactions governing the partition process and the chemical nature of DTAB micelles.

Hydrogen-Bond Donor Strength (α) of DTAB. The α-values of DTAB micelles obtained using ET(33) and $Fe(LL)_2(CN)_2$ are given in Tables 2 and 3 along with the values obtained for pure water using the same indicators. The following equations were used to calculate α from λ_{max}-values.[28]

$$ET(33) = 28\,590/\lambda_{max} = 39.09 + 14.47(\pi^*) + 14.41(\alpha) \quad (3)$$

$$ET(Fe) = 28\,590/\lambda_{max} = 39.71 + 3.31(\pi^*) + 4.50(\alpha) \quad (4)$$

Values of 1.21 and 1.02 were used for the π^* of water and DTAB, respectively. It is important to note here that the use of ET(33), $Fe(LL)_2(CN)_2$, and their corresponding equations for the determination of the micellar hydrogen-bond acidities relies heavily on the assumption that the α-indicators reside in the same micellar environment as do the π^*-indicators. Only in this way can the solvatochromic effects of dipolarity/polarizability on the α-indicators be correctly subtracted from the overall solvatochromic shift to yield information related solely to the hydrogen-bond donating ability of their environment.

On the basis of literature reports,[29−32] it is reasonable to assume that the polar indicators used in this study will reside in approximately the same environment within the DTAB micelles. Specifically, numerous UV−visible and nuclear magnetic resonance studies of polar probes such as acetophenone,[29] benzophenone,[29] *N*,*N*-dimethylaniline,[30] and nitrobenzene[30] in cetyltrimethylammonium bromide (CTAB) micellar systems (note that CTAB and DTAB are structurally closely related) show that polar solutes reside in a polar region of the micelle that includes the headgroup, the bound counterions, and the hydrated methylene units adjacent to the headgroup. These results may also apply to nonpolar, aromatic solutes,[31] although there is some evidence to the contrary.[32]

Thus, although subtle differences in the location of the polar indicators used in this study may exist, there is strong evidence that they will all reside in the polar, hydrated headgroup region of the micelles. Therefore, the use of the π^*-indicators to correct for dipolarity/polarizability effects on the overall solvatochromic behavior of the α-indicators is reasonable.

The α-values determined with ET(33) and $Fe(LL)_2(CN)_2$ are shown in Table 3. They reveal that water (average $\alpha = 1.01$) is a better hydrogen-bond donor than are DTAB micelles (average $\alpha = 0.700$). Other hydrogen bond donating solvents with α-values near that of DTAB are 2-propanol ($\alpha = 0.687$)[9]

and *n*-butanol ($\alpha = 0.710$),[9] indicating that while DTAB micelles are weaker hydrogen-bond donors than is water, they still have rather significant donating ability.

This relatively high α-value of DTAB micelles demands some explanation since DTAB monomers per se have no inherent hydrogen-bond donating ability. A likely explanation is that the hydrogen-bond donating ability arises from water that is associated with the headgroups and the counterions. A number of studies have shown that the headgroups, as well as at least the first two carbons of the alkyl chains attached to the headgroups, have significant amounts of water associated with them.[29,33,34] Thus, the hydrogen-bond acidity of the micelles likely results from this associated water. Given the above explanation of the origin of the hydrogen-bond donating ability of DTAB micelles, we conclude that the indicators must be located in or near the headgroup region of the micelles in order to participate in and sense the hydrogen bonding. This is consistent with the conclusions regarding the localization of indicators that were drawn from the π^*-values discussed above.

The fact that DTAB micelles must have some hydrogen-bond donating ability is predicted by a comparison of the LSERs describing the transfer of solutes from water to DTAB and water to hexadecane (eqs 1 and 2, respectively). It is clear from the large negative coefficient of $\Sigma\beta_2^H$ in the water-to-hexadecane LSER that hexadecane is a significantly weaker hydrogen-bond donor than is bulk water. Chemical intuition dictates that this be true since hexadecane has no inherent hydrogen-bond donating ability.

In contrast, the coefficient of the $\Sigma\beta_2^H$ term in the DTAB LSER (eq 1) is considerably smaller in magnitude than the same coefficient in the hexadecane LSER (eq 2). This means that with regards to hydrogen-bond donating ability, the difference between DTAB and water is smaller than the difference between hexadecane and water. From this we predict that the α-value of DTAB must fall between the α-values of hexadecane ($\alpha = 0.00$) and water ($\alpha = 1.01$), which it does ($\alpha_{DTAB} = 0.700$). Thus, as was the case with the π^*-values, the α-values are in qualitative agreement with the predictions made by comparing LSERs. Again, this lends support that both the LSERs and the solvatochromic parameters are reflecting the chemistry of the system.

Hydrogen-Bond Accepting Ability (β) of DTAB. The β-values determined for DTAB micelles and bulk water using *p*-nitrophenol and *p*-nitroaniline are shown in Table 2 as a function of the DTAB concentration included in the curve-resolution analysis. The average β-values are shown in Table 3. The β-values were determined using the equations of Kamlet and Taft.[10]

We note that in using these equations we are making the assumption that the β-indicators reside in the same micellar environment as do the π^*-indicators. Given the polarity and structural similarity of these indicators, this is a reasonable assumption (see the discussion above concerning the α-indicators).

We point out that prior to resolving the *p*-nitrophenol spectra, small contributions to the spectra from the *p*-nitrophenolate ion were subtracted. The presence of the *p*-nitrophenolate ion results from a combination of the pK_a of *p*-nitrophenol (7.15 at 25 °C)[35] and the pH ($\sim$5.3) of the unbuffered micellar solutions. To determine the absorbance values to be subtracted at each wavelength in each micellar spectrum, the spectrum of *p*-nitrophenolate was recorded in an aqueous solution made basic (pH = 12) with sodium hydroxide. The absorbance values at four different wavelengths at which *p*-nitrophenol does not absorb (450, 440, 430, and 420) were found for this basic spectrum. The absorbance values at these same wavelengths were found in the DTAB micellar spectra and ratioed to the values found in the aqueous basic solution. The average of these four ratios were then determined for each micellar spectrum. For each micellar spectrum, the entire aqueous basic spectrum was multiplied by the average ratio and subtracted from the micellar spectrum to eliminate the contribution for the *p*-nitrophenolate ion, even in regions where the spectra of *p*-nitrophenol and *p*-nitrophenolate overlap. Finally, the resulting *p*-nitrophenol spectra were normalized to their individual maximum absorbance values so that all spectra had an apparent maximum absorbance of 1.0. This was done to satisfy the assumption of the curve-resolution algorithm that all micellar spectra have the same indicator concentration.[12,13] Since the magnitudes of these corrections were generally quite small we believe little perturbation, if any, occurred in the *p*-nitrophenol spectra. The fact that the β-values determined with *p*-nitrophenol show very little fluctuation as a function of DTAB concentration supports this assertion.

The β-values in Table 3 for both *p*-nitrophenol and *p*-nitroaniline reveal that DTAB micelles are stronger hydrogen-bond acceptors than is bulk water, with DTAB micelles having an average β-value of 0.486 and water having an average β-value of 0.290. This result is again in agreement with that predicted by the DTAB LSER shown in eq 1. The positive coefficient of solute hydrogen-bond acidity ($\Sigma\alpha_2^H$) in the DTAB LSER means that hydrogen-bond donating solutes prefer to interact with DTAB micelles rather than remaining in the bulk aqueous phase, all else being equal. This implies that DTAB micelles are stronger hydrogen-bond acceptors than is bulk water, which is borne out by the β-values determined for DTAB ($\beta = 0.486$) and water ($\beta = 0.290$).

Possible explanations for the origin of this basicity have been discussed extensively elsewhere[15,24] as it is somewhat puzzling given that the dodecyltrimethylammonium ion monomers which form the micelles have no inherent hydrogen-bond accepting ability. The basicity probably arises either directly or indirectly from the well-documented hydrogen-bond basicity of bromide counterions[36] associated with the micelles and possibly from the water that hydrates the counterions and the headgroups (provided that these waters of hydration have an increased basicity relative to bulk water owing to interactions with the headgroups and the counterions).

The hydrogen-bond basicity of bromide ions was clearly demonstrated in a study by Marcus, Kamlet, and Taft in which they examined the chemical interactions controlling partitioning of ions between water and organic solvents.[36] Using linear solvation energy relationships (LSERs) they were able to elucidate the distinct roles played by the dipolarity/polarizability, hydrogen-bond acidity, and hydrogen-bond basicity of the solvents in determining the extent of ion partitioning. They found that the partitioning of bromide ions decreases with increasing hydrogen-bond acidity of the organic solvents.[36] This implies that a bromide ion must be a hydrogen-bond base, otherwise the hydrogen-bond acidity of the solvents would not influence the partitioning of the ions. Furthermore, their results show that the hydrogen-bond basicities of the halide ions decrease in the order $F^- > Cl^- > Br^- > I^-$.[36] This is the order of charge density on the ions and is therefore consistent with chemical intuition regarding the expected order of hydrogen-bond basicity. This lends confidence to the reliability of the LSER analysis and its implications as to the hydrogen-bond basicity of bromide ions.

General Conclusions from the Solvatochromic Parameters. Overall, the π^*-, α-, and β-values determined with all of the indicators are in qualitative agreement with and further support the DTAB LSER shown in eq 1. This lends confidence to the assertion that both the LSER and the solvatochromic comparison methodologies are reflecting the chemical nature of DTAB micelles.

Additionally, the fact that the partition coefficients are in agreement with the order predicted on the basis of their size, polarity, and hydrogen-bond ability, as well as the fact that the solvatochromic parameters are generally insensitive to the surfactant concentration range used in the determinations, provides further confidence that the curve-resolution technique is reliable and applicable to all micellar systems that satisfy the criteria detailed in an earlier paper.[13]

Finally, we note that the solvatochromic parameters of water determined when the data for SDS were collected are in good agreement with the same parameters determined when the data for DTAB were collected (see Table 3). Thus, the reproducibility of the method is quite good, implying that the performance of the spectrophotometer and the quality of the indicators have not degraded during the time in which these data were taken.

Comparison of SDS and DTAB Solvatochromic Parameters and LSERs. We can use the LSERs describing solute transfer in SDS[37] and DTAB[24] (shown below) to make predictions about the nature of these two types of micelles relative to one another. These predictions can then be checked by comparing the solvatochromic parameters for the two systems.

water-to-SDS LSER[37]

$$\log K_{w/SDS} = 0.31 + 3.02V_x - 0.58\pi_2^* - 0.37\Sigma\alpha_2^H - 1.65\Sigma\beta_2^H \quad (5)$$

$$n = 22 \qquad \rho = 0.998 \qquad \text{s.d.} = 0.07$$

water-to-DTAB LSER[24]

$$\log K_{w/DTAB} = -0.13 + 3.12V_x - 0.14\pi_2^H + 0.42\Sigma\alpha_2^H - 2.71\Sigma\beta_2^H + 0.31R_2 \quad (6)$$

$$n = 28 \qquad \rho = 0.984 \qquad \text{s.d.} = 0.15$$

First, the small coefficients of π_2^H indicate that both SDS and DTAB micelles should have π^*-values close to, but less than, that of water. Additionally, from the coefficients shown above we predict that SDS micelles should have a slightly lower π^*-value than DTAB micelles. It must be pointed out, however, that in LSERs obtained in this laboratory using micellar electrokinetic capillary chromatography (MEKC) data,[24] the coefficients of π_2^H of SDS and DTAB were both found to be -0.36.[24] These values lead to the prediction that SDS and DTAB micelles should have equivalent π^*-values.

The solvatochromic parameters for SDS and DTAB micelles are shown in Table 3. It is seen that the π^*-values for SDS and DTAB micelles are indeed nearly equivalent and are both less than the π^* of water and therefore are in good agreement with the MEKC-based LSERs. These π^*-values are such that they disagree with the prediction made from eqs 1 and 2 that SDS should have a slightly smaller π^*-value than DTAB. The disagreement is small, however, and does not therefore seriously alter our conclusions as to the characteristics of the chemical nature of the micelles.

The coefficients of $\Sigma\beta_2^H$ in eqs 5 and 6 lead to the prediction that the hydrogen-bond acidity (α-value) of SDS micelles should be greater than that of DTAB micelles, and water should be a stronger hydrogen-bond donor than either SDS or DTAB micelles. This same prediction is made on the basis of our MEKC LSERs.[24] The α-values shown in Table 3 are in agreement with these predictions. For both indicators the order of decreasing α-values is $\alpha_{water} > \alpha_{SDS} > \alpha_{DTAB}$. Thus, the LSERs and the solvatochromic parameters lead to the same conclusions regarding the relative hydrogen-bond donating abilities of water, SDS micelles, and DTAB micelles. This aids greatly in our understanding of the differences in the chemical nature of these systems and can also lead to predictions regarding the ability of these systems to interact with solute molecules. For example, these α-values suggest that hydrogen-bond accepting solutes will interact more with SDS micelles than with DTAB micelles, all else being equal. This can be a valuable piece of information in designing a chromatographic separation of hydrogen-bond donating solutes or in planning the removal of contaminants from environmental samples.

We note here that conclusions based on the average α-values are the same as would be drawn by examining the α-values obtained with the individual indicators. We note also that there are significant differences in the α-values obtained with different indicators, which lead to the large apparent variances in the average α-values. We stress, however, that these are *not* random experimental uncertainties. Rather, they are determinate in nature and are related to the specific solvatochromic behavior of each indicator, a topic that has been discussed in detail elsewhere.[28,37] This assertion is supported by the reproducibility of the solvatochromic parameters for water (Table 3), which show that the long-term precision of solvatochromic measurements is generally better than 0.02. Thus, while the variance in an *average* solvatochromic parameter is large and therefore greatly limits the utility of *average* values in quantitative comparisons, comparisons based on *single* solvatochromic parameters obtained with specific indicators are useful and instructive.

The coefficients of solute hydrogen acidity ($\Sigma\alpha_2^H$) in eqs 5 and 6 are dramatically different in that they have opposite signs. This same result is found in our MEKC-based LSERs, with the exception that the magnitude of the coefficient in the MEKC DTAB LSER (0.99) is larger than that shown in eq 6.[24] From these coefficients we predict that the β-values of water, SDS micelles, and DTAB micelles should follow the order $\beta_{DTAB} > \beta_{water} > \beta_{SDS}$.

We do, in fact, find that DTAB micelles have a higher β-value than water. However, when 4-nitroaniline is used as the indicator, the β-value of SDS micelles is equal to that of DTAB micelles (given the 0.02 reproducibility discussed above) and is higher than that of water. This disagrees with the prediction one makes from the LSER in eq 5. The β-value of SDS micelles could not be determined using *p*-nitrophenol owing to a lack of a discernible shift in its spectra in the presence of SDS micelles. This could be taken to indicate that the hydrogen-bond donating ability of SDS micelles that is sensed by *p*-nitrophenol is nearly equivalent to that of water. Even so, this result does not agree with the prediction that the β-value of SDS micelles should be lower than that of water. Possible sources for these discrepancies between SDS and water were discussed in detail elsewhere[12] and are therefore not repeated here.

Overall, the solvatochromic parameters of water, SDS micelles, and DTAB micelles are in good agreement with

predictions made on the basis of the LSERs describing solute transfer from water to micelles. Thus, the LSERs and the solvatochromic studies generally lead to the same conclusions regarding the chemical nature of SDS and DTAB micelles and their relative abilities to interact with solutes via specific chemical forces.

Comparison of Literature LSER Equations. We note that the DTAB LSER we obtained using partition coefficients measured by HSGC[24] is in relatively poor agreement with one reported in the literature,[15] especially with regards to their coefficients of solute hydrogen-bond basicity. The two LSERs are shown below.

HSGC DTAB LSER[24]

$$\log K_{w/DTAB} = -0.13 + 3.12V_x - 0.14\pi_2^H + 0.42\Sigma\alpha_2^H - 2.71\Sigma\beta_2^H + 0.31R_2 \quad (7)$$

$$n = 28 \qquad \rho = 0.984 \qquad \text{s.d.} = 0.15$$

literature DTAB LSER[15]

$$\log K_{s(w/DTAB)} = -0.87 + 2.98V_x - 0.40\pi_2^H + 0.28\Sigma\alpha_2^H - 1.82\Sigma\beta_2^H + 0.57R_2 \quad (8)$$

$$n = 39 \qquad \rho = 0.975 \qquad \text{s.d.} = 0.16$$

We can compare the solvatochromic parameters determined for SDS and DTAB to test which LSER is in better agreement with the solvatochromic parameters and which, therefore, is supported by an independent method of characterizing the chemical nature of micelles. To make this comparison we must also discuss the SDS LSER generated using HSGC measurements[38] and the one reported in the same literature study mentioned above.[15] These LSERs are shown below.

HSGC SDS LSER[37]

$$\log K_{w/SDS} = 0.31 + 3.02V_x - 0.58\pi_2^* - 0.37\Sigma\alpha_2^H - 1.65\Sigma\beta_2^H \quad (9)$$

$$n = 22 \qquad \rho = 0.998 \qquad \text{s.d.} = 0.07$$

literature SDS LSER[15]

$$\log K_{s(w/SDS)} = -0.62 + 3.25V_x - 0.57\pi_2^H - 0.08\Sigma\alpha_2^H - 1.84\Sigma\beta_2^H + 0.32R_2 \quad (10)$$

$$n = 66 \qquad \rho = 0.990 \qquad \text{s.d.} = 0.13$$

We must also reiterate that although the large spread in solvatochromic values produces large variances in the average values, which makes quantitative comparisons difficult, examining individual indicators so as to eliminate specific chemical differences in the behavior of the indicators allows for these comparisons to be made.

It is seen in the literature LSERs that the coefficient of solute hydrogen-bond basicity ($\Sigma\beta_2^H$) is approximately -1.8 in both SDS and DTAB.[15] This implies that SDS and DTAB micelles should have nearly equivalent hydrogen-bond donating abilities.

Contrary to this result, our LSERs obtained with HSGC[24] (and in fact those also obtained using MEKC)[24] indicate that the hydrogen-bond donating ability of SDS micelles should be much greater than that of DTAB micelles.

The average α-values shown in Table 3 do in fact show a significant difference in the hydrogen-bond donating abilities of SDS micelles ($\alpha = 0.873$) and DTAB micelles ($\alpha = 0.700$), as do the α-values obtained with each individual indicator. Thus, the HSGC and MEKC-based LSERs are in considerably better agreement with the solvatochromic parameters, at least with regards to the relative hydrogen-bond donating abilities of SDS and DTAB micelles.

It must also be noted that although the difference in the coefficients of solute hydrogen-bond acidity ($\Sigma\alpha_2^H$) in eqs 7 and 8 do not seem that large, our MEKC-based DTAB LSER has a coefficient of $\Sigma\alpha_2^H$ of 0.99,[24] making the difference considerably larger. A large difference in the coefficients of $\Sigma\alpha_2^H$ suggests that there should be a large difference in the hydrogen-bond basicity of SDS and DTAB micelles. The β-values that we determined, however, do not reveal a large difference. In fact, the β-values determined with 4-nitroaniline suggest that SDS and DTAB micelles are similar in their hydrogen-bond accepting abilities. Furthermore, we were unable to measure a β-value of SDS using *p*-nitrophenol as the indicator. We must note here that the β-values determined with 4-nitroaniline are highly questionable owing to possible influences from electrostatic effects that may contribute to the apparent basicity measured with this indicator.[39] This concern is discussed in detail elsewhere.[11] Thus, the β-values are not firmly established and therefore are not highly reliable measurements of the hydrogen-bond basicity of the micellar systems being compared. Therefore, we suggest that these values be used with great caution when making assertions about the relative hydrogen-bond donating abilities of SDS and DTAB micelles and about the reliability of LSERs with regard to the relative magnitudes of the coefficients of solute hydrogen-bond acidity.

Conclusions

We have determined the π^*-, α-, and β-values of DTAB micelles. They are 1.02, 0.70, and 0.49, respectively. These values indicate that DTAB micelles are quite dipolar/polarizable and have considerable hydrogen-bond donating and accepting abilities. Additionally, they were shown to be in good qualitative agreement with LSERs describing the transfer of solutes from water to DTAB micelles. Comparing these values to those for SDS micelles, we found that the two systems are quite similar in their dipolarity/polarizability. Additionally, the DTAB micelles are weaker hydrogen-bond donors and stronger hydrogen-bond acceptors than are SDS micelles. These results are in good agreement with predictions made using our HSGC-based LSERs for SDS and DTAB systems. Furthermore, they indicate that there are considerable differences in the chemical environments in SDS and DTAB. This will undoubtedly influence the ability of these two types of micelles to solubilize compounds that differ in their hydrogen-bond accepting and donating strengths. These differences will affect the performance of micelles in their roles as catalysts, emulsifiers, separation enhancers, and models of biological systems.

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References and Notes

(1) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975.

(2) Cordes, E. H. *Pure Appl. Chem.* **1978**, *50*, 617−625.
(3) Dorsey, J. G. In *Ordered Media in Chemical Separations*; Hinze, W. L., Armstrong, D. W., Eds.; ACS Symposium Series 342; American Chemical Society: Washington, DC, 1987.
(4) Pramauro, E.; Pelizetti, E. *Surfactants in Analytical Chemistry: Applications of Organized Amphiphilic Media*; Elsevier: Amsterdam, 1996.
(5) Terabe, S.; Otsuka, K.; Ando, T. *Anal. Chem.* **1985**, *57*, 834−841.
(6) Abdul, A. S.; Ang, C. C. *Groundwater* **1994**, *32*, 727−734.
(7) Pennell, K. D.; Jin, M.; Abriola, L. M.; Pope, G. A. J. *Contam. Hydrol.* **1994**, *16*, 35−53.
(8) Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027−6038.
(9) Taft, R. W.; Kamlet, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 2886−2894.
(10) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377−383.
(11) Carr, P. W. *Microchem. J.* **1993**, *48*, 4−28.
(12) Vitha, M. F.; Weckwerth, J. D.; Odland, K.; Dema, V.; Carr, P. W. *J. Phys. Chem.* **1996**, *100*, 0, 18823−18828.
(13) Vitha, M. F.; Weckwerth, J. D.; Odland, K.; Dema, V.; Carr, P. W. *Anal. Chem.* **1997**, *69*, 9, 2268−2274.
(14) Kubista, K.; Sjoback, R.; Albinsson, B. *Anal. Chem.* **1993**, *65*, 994−998.
(15) Quina, F. H.; Alonso, E. O. Farah, J. P. S. *J. Phys. Chem.* **1995**, *99*, 11708−11714.
(16) Yang, S.; Khaledi, M. G. *Anal. Chem.* **1995**, *67*, 499−510.
(17) Carr, P. W. *Microchem J.* **1993**, *48*, 4−28.
(18) Kessler, M. A.; Wolfbeis, O. S. *Chem. Phys. Lipids* **1989**, *50*, 51−56.
(19) Burgess, J. *Spectrochim. Acta*, **1970**, *26A*, 1957−1962.
(20) Bahri, H.; Bouguerra, S.; Letellier, P. In *Surfactants in Solution*; Mittal, K. L., Bothorel, P., Eds.; Plenum Press: New York, 1986; Vol. 4.
(21) Musbally, G. M.; Perron, G.; Desnoyers, J. E. *J. Colloid Interface Sci.* **1974**, *48*, 494−501.
(22) Moulik, S. P.; Haque, M. E.; Jana, P. K.; Das, A. R. *J. Phys. Chem.* **1996**, *100*, 701−708.
(23) Bach, J. B.; Blandamer, M. J.; Bijma, K.; Engberts, J. B. F. N.; Kooreman, P. A.; Kacperska, A.; Rao, K. C.; Subha, M. C. S. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1229−1235.
(24) Vitha, M. F. Thermodynamic and Solvatochromic Studies of the Fundamental Chemical Forces Governing Solute Interactions with Surfactant Micelles. Ph.D. Thesis, University of Minnesota, 1997.
(25) Laurence, C.; Nicolet, P.; Dalati, M. T.; Abboud, J. L. M.; Notario, R. *J. Phys. Chem.* **1994**, *98*, 5807−5816.
(26) Laurence, C.; Nicolet, P.; Helbert, M.; *J. Chem. Soc., Perkin Trans. 2* **1986**, 1081−1090.
(27) Abraham, M. H.; Chadha, H. S.; Whiting, G. S.; Mitchell, R. C. *J. Pharm. Sci.* **1994**, *83*, 1085- 1100.
(28) Park, J. H.; Dallas, A. J., Chau, P.; Carr, P. W. *J. Phys. Org. Chem.* **1994**, *7*, 757−769.
(29) Fendler, J. H.; Fendler, E. J.; Infante, G. A.; Shih, P. S.; Patterson, K. L. *J. Am. Chem. Soc.* **1975**, *97*, 89−95.
(30) Eriksson, J. C.; Gillberg, G. *Acta Chem. Scand.* **1966**, 20, 2019−2027.
(31) Wasylishen, R. E.; Kwak, J. C. T.; Gao, Z.; Verpoorte, E.; MacDonald, J. B.; Dickson, R. M. *Can. J. Chem.* **1991**, *69*, 822−833.
(32) Grätzel, M.; Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 7869−7874.
(33) Abu-Hamdiyyah, M.; Rahman, I. A. *J. Phys. Chem.* **1985**, *89*, 2377−2384.
(34) Sepulveda, L.; Lissi, E.; Quina, F. *Adv. Colloid Interface Sci.* **1986**, *25*, 1−57.
(35) *CRC Handbook of Chemistry and Physics*, 71st ed., *1990−1991*; Lide, D. R., Ed.; CRC Press: Ann Arbor, MI 1990.
(36) Marcus, Y.; Kamlet, M. J.; Taft, R. W. *J. Phys. Chem.* **1988**, *92*, 3613−3622.
(37) Park, J. H.; Dallas, A. J.; Chau, P.; Carr, P. W. *J. Chromatogr. A* **1994**, 677, 1−9.
(38) Vitha, M. F.; Dallas, A. J.; Carr, P. W. *J. Colloid Interface Sci.* **1997**, *187*, 179−183.
(39) Maria, P. C.; Gal, J. F.; de Franceschi, J.; Fargin, E. *J. Am. Chem. Soc.* **1987**, *109*, 483−492.