Deprotonation of Indole Derivatives in Aqueous Cationic Surfactants

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Deprotonations of 5-nitroindole, **1a**, and its 2-carboxylate ion, **2a**, have been monitored in 0.01, 0.1, and 0.5 M NaOH in micellar solutions of cetyl trialkylammonium bromide, alkyl = Me, Et, *n*Pr, *n*Bu, CTABr, CTEABr, CTPABr, CTBABr. Extents of deprotonation (% *f*) have been fitted using the pseudophase model of micellar effects with interionic competition described by ion exchange or by independent association constants. Both treatments indicate that base dissociation constants in dilute OH^- are lower than in water by factors of ca. 3–11, and decrease with increasing bulk of the head groups, and that these factors increase modestly as the OH^- concentration increases to 0.5 M.

Introduction

Ionic micelles influence indicator equilibria in water; for example cationic micelles increase, and anionic micelles decrease, the extents of deprotonation of weak acids.[1] The relationships between micellar effects and the charge-type of reaction have also been investigated for the rates of bimolecular ionic reactions.[2]

Quantitative treatments of micellar effects upon reaction rates and equilibria generally involve the assumption that micelles, or other association colloids, and water can be treated as distinct reaction regions. Thus, for bimolecular reactions, overall rates depend on local concentrations and rate constants in each region, and this pseudophase formalism can also be applied to equilibria.[2,3,4] However, although a very large range of rate constants can often be covered experimentally, only relatively small variations of indicator ratios (approximately 10−90% deprotonation) can be monitored spectrophotometrically.

A weakness of comparisons of treatments of reactivities in association colloids, relative to those in water, is that the colloids exert a kinetic medium effect depending on the structure of the activated complex, which is uncertain,[2,3] but for equilibria the initial and final structures are defined.

We have examined deprotonations of 5-nitroindole (**1**) and 5-nitroindole-2-carboxylate ion (**2**) at high pH in a variety of surfactant assemblies.

Indoles are very weak acids and are only deprotonated in aqueous alkali more concentrated than that covered by the pH scale. Yagil[5] set up a scale that gave $pK_a = 14.75$ and 14.91 for **1a** and **2a**, respectively, and the equilibria can be monitored at 398−400 and 392−393 nm, respectively. Values of K_b are 5.6 and 8.3 M for **1a** and **2a**, respectively, but because cationic micelles increase the extent of deprotonation[1] we can monitor them even in dilute OH^-.[4,6]

The effects of aqueous cationic micelles on acid−base equilibria have been examined and treated in terms of pseudophase models which treat water and micelles, or other association colloids, as distinct reaction regions.[2−4,6] Variations of overall equilibrium (or rate) constants with concentrations of surfactants or reactants depend on reactant transfer between the aqueous and micellar pseudophases and local equilibrium (or rate) constants in each region.[2−4] For deprotonations of **1a** and **2a** we assume that **1** and **2**, which are charge-dispersed anions, will bind quantitatively to cationic micelles, except in very dilute surfactant, and that **2a** will also be fully micellar-bound (Scheme 1). There is extensive evidence of micellar binding of nonionic compounds[2,7] and that of **1** has been examined physically.[6c]

The transfer of some ions between water and micelles can be monitored electrochemically or by NMR spectroscopy[2,3] and diazo trapping of weakly basic solutes directly determines local concentrations in association colloids.[8] These methods are inapplicable to OH^-, and a variety of treatments have been used to estimate the extents of ionic transfer and interionic competition. These treatments

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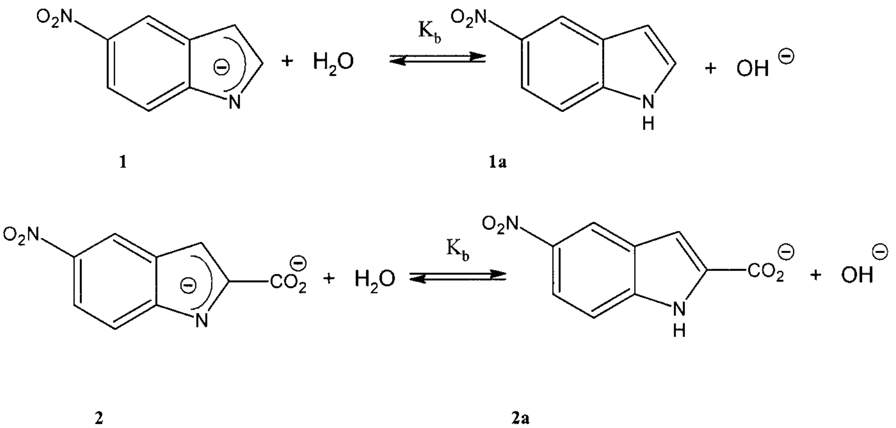

Scheme 1

involve assumptions and approximations that limit their general applicability, although they fit extensive kinetic and equilibrium data, especially for dilute electrolyte.[2,3,9]

The pseudophase, ion-exchange (PIE) model involves the assumptions that the interfacial, surface region is saturated with competing counterions, i.e., that the fractional charge neutralization, β, is constant, and that ions compete specifically, e.g., for OH^- and Br^- (see ref.[3a,4]):

$$K_{Br}^{OH} = \frac{[OH^-]_W[Br^-]_M}{[OH^-]_M[Br^-]_W} \tag{1}$$

Concentrations are written in terms of total solution volumes, not as local concentrations in the aqueous and micellar pseudophases, and subscripts *W* and *M* denote aqueous and micellar pseudophases. This treatment fits extensive data, but reaction rates in moderately concentrated OH^- are typically higher than predicted by the PIE model.[10] These rate increases were first explained on the assumption that OH^- in the aqueous pseudophase could react directly with micellar-bound substrate, i.e., that a new reaction path is introduced at high $[OH^-]$.[10a,10b] Subsequently the kinetic data were fitted in terms of "invasion" of the micellar interfacial region by OH^- and other hydrophilic ions, which means that the postulated constancy of β breaks down at high ionic concentrations.[3a,10c]

The present work had two main aims. The first was to examine deprotonation in moderately concentrated OH^-, i.e., 0.5 M, because the introduction of a new reaction path[10a,10b] could affect reaction rates, but not equilibria. The second was to examine the effects of an increase in the head-group size of cationic, cetyl (hexadecyl) surfactants, viz., $n\text{-}C_{16}H_{33}N^+R_3\ Br^-$; R = Me, Et, *n*Pr, *n*Bu, CTABr, CTEABr, CTPABr, or CTBABr. Effects of changes in head group size on reactivities have been examined, but not their effects on acid−base equilibria.[2]

The earlier analyses of micellar effects on deprotonation of indoles were in terms of the PIE treatment[3a,4,6] and we followed this approach. Other treatments of interionic competition have been developed as alternatives to the PIE model, but some, such as that based on an ionic distribution in terms of the Poisson−Boltzmann equation,[11,12] apply to colloidal particles with a smooth surface, and may not apply to micelles with large cationic head groups. The fitting of ionic distribution in this treatment depends upon the surface charge density of the association colloid and upon its radius and aggregation number.[11,12]

An alternative approach is to describe ionic transfer in terms of mass-action-like equations with the form of a Langmuir isotherm.[13] For a single ionic system, e.g., CTAOH, we write:

$$K'_{OH} = \frac{[OH^-]_M}{[OH^-]_W([CTAOH - cmc - [OH^-]_M)} \tag{2}$$

and for OH^- added to CTABr, for example, we write (see ref.[14]):

$$K'_{OH} = \frac{[OH^-]_M}{[OH^-]_W([CTABr - cmc - [OH^-]_M - [Br^-]_M)} \tag{3}$$

A corresponding equation can be written for the transfer of Br^-, or other inert anion.

These equations retain the concept of interionic competition, but allow neutralization of the fractional head-group charge, β, to increase to the hypothetical limit of 1. With a strongly interacting anion, e.g., Br^-, the value of β is initially high, increases slowly with increasing ionic concentration, and is not very sensitive to small changes in the value of K'_{Br}, but it is initially low and increases sharply for OH^-, where K'_{OH} is small relative to K'_{Br}.

Values of the ionic-binding parameters, e.g., K'_{OH} and K'_{Br}, have been estimated by fitting kinetic data for reactions in reactive counterion micelles,[2] although as noted above kinetic data for reactions of Br^- can often be fitted by a range of values of K'_{Br}.[15]

Results and Discussion

Deprotonation in Cationic Micelles

Extents of deprotonation of **1a** and **2a** over a range of $[OH^-]$ are shown in Figures 1 and 2. The data for depro-

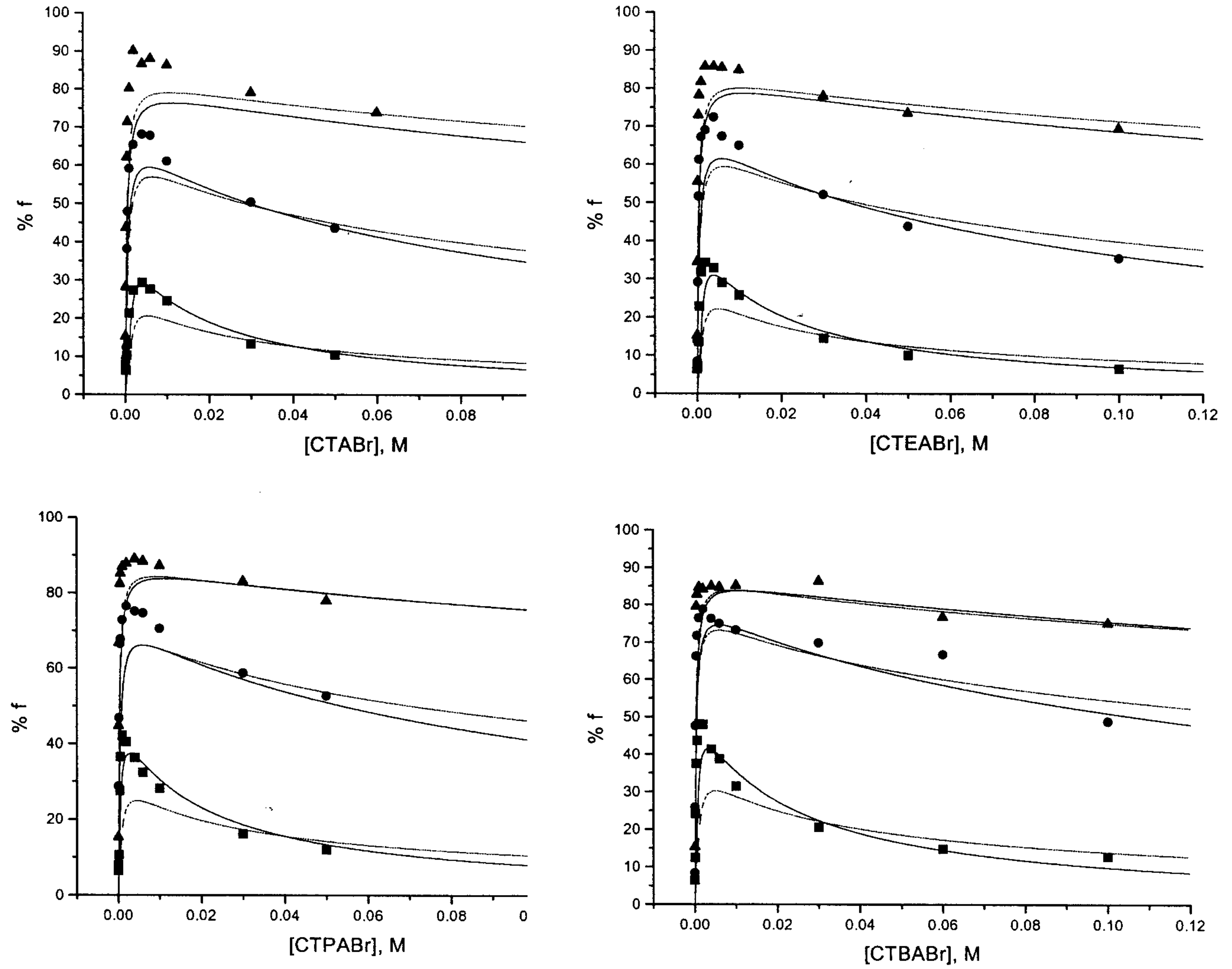

Figure 1. Extents of deprotonation, *f*, of 5-nitroindole in: [CTABr], [CTEABr], [CTPABr], and [CTBABr]; 0.01 M NaOH (black square); 0.1 M NaOH (black circle), 0.5 M NaOH (black triangle); lines are as calculated from Langmuir isotherms: dotted line; PIE, solid line

tonation of **1a** in CTABr and dilute NaOH differ slightly from those given earlier,[6c] but those for **2a** agree with earlier results.[6a,6b]

Concentrations of **1a** and **2a** were $9 \cdot 10^{-5}$ M, in order to obtain reasonable absorbance changes on deprotonation. As a result, fitting of data in dilute surfactants is unreliable because increases in absorbances could be due to interactions between the indicators and free quaternary ammonium ions or premicellar clusters of them.[16] In general observed and predicted values are least satisfactory in these conditions.

The PIE Treatment

In fitting the data we assume that except in very dilute surfactant **1**, **2**, and **2a** are fully micellar-bound and that binding of nonionic indole, BH, fits Equation (4).[2,3,7]

$$\frac{[BH]_M}{[BH]_T} = \frac{K_S[D_n]}{1+K_S[D_n]} \tag{4}$$

In Equation (4) $[BH]_M$ and $[BH]_T$ are concentrations in the micellar pseudophase and total concentration, respectively, in terms of total solution volume and D_n is micellized surfactant (detergent) with the concentration of free surfactant given by the critical micelle concentration, cmc, under the conditions of the experiment.[3a,3b,3c]

Deprotonation in the micellar pseudophase is given by:

$$K_b^M = \frac{[BH]_M m_{OH}^s}{[B^-]_M} \tag{5}$$

where BH and B^- are respectively the protonated and deprotonated forms of the indole indicator and:

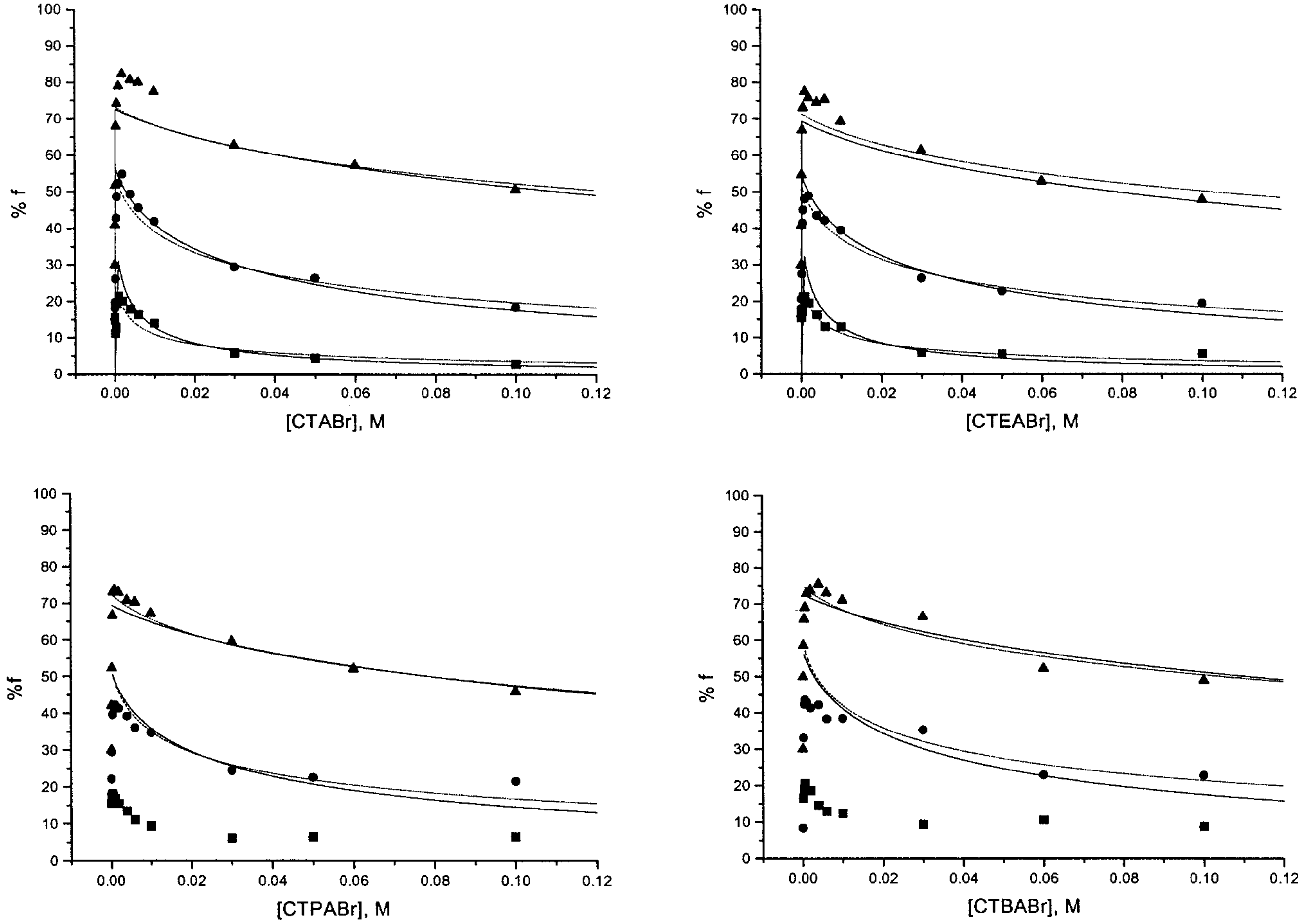

Figure 2. Extent of deprotonation, *f*, of 5-nitroindole-2-carboxylate in: [CTABr], [CTEABr], [CTPABr], and [CTBABr]; 0.01 M NaOH (black square), 0.1 M NaOH (black circle), 0.5 M NaOH (black triangle); lines are as specified in the caption to Figure 1

$$m^s_{OH} = \frac{[OH^-]_M}{[D_n]} \tag{6}$$

The competition between OH^- and Br^- is given by Equation (1), which with constant β and mass balance gives (ref.[4]):

$$(m^s_{OH})^2 + m^s_{OH}\left(\frac{[OH^-]_T + K^{OH}_{Br}[Br^-]_T}{[D_n](K^{OH}_{Br}-1)} - \beta\right) - \frac{[OH^-]_T\beta}{[D_n](K^{OH}_{Br}-1)} = 0 \tag{7}$$

where β, the charge neutralization of the micelle, is:

$$\beta = \frac{[OH^-]_M + [Br^-]_M}{[D_n]} \tag{8}$$

Variations of $m^s{}_{OH}$ with changes in $[D_n]$, and $[Br^-]_T$ can be treated by using Equation (7), because $[OH^-]_T$, the total hydroxide concentration, is constant at 0.01 M, 0.1 M, or 0.5 M in our experiments.

These equations have been used extensively in treating micellar rate and equilibrium data and are combined to predict variations of % *f*, in terms of $K_b{}^M$ and $m^s{}_{OH}$ (see refs.[2,3a,3b,3c,4]):

$$f = \frac{[B^-]_M}{[B^-]_M[BH]_M} = \frac{m^s_{OH}}{m^s_{OH} + K^M_b} \tag{9}$$

In fitting the data we took $K^{OH}{}_{Br} = 14$ and $\beta = 0.8$ because similar values had been used earlier for OH^- and CTABr.[6] However, β decreases with increasing bulk of the head group and we note below the effect of treating the data for CTBABr with $\beta = 0.6$. The value of the cmc is not critical because the necessary relatively high concentration of the indicators, $9 \cdot 10^{-5}$ M, makes fits unreliable in dilute surfactant.

The fits are shown in Figures 1 and 2, and the fitting parameters are in Tables 1 and 2. For both **1a** and **2a** values of $K_b{}^M$ decrease with increasing $[OH^-]$. A decrease in β for CTBABr to 0.6 allows reasonable fits to the data, but with $K_b{}^M = 0.07$ for **1a** in 0.1 and 0.5 M NaOH and 0.38 and 0.22 for **2a** in 0.1 and 0.5 M NaOH, respectively. This de-

Table 1. Deprotonation of 5-nitroindole

Surfactant[a]	[NaOH], *M*[b]	K_b^M		K_b^V, *M*		K_b/K_b^V	
		Langmuir form	PIE	Langmuir form	PIE	Langmuir form	PIE
CTABr	0.01	0.33	0.28	2.4	2.0	2.3	2.8
	0.1	0.26	0.24	1.9	1.7	3.0	3.3
	0.5	0.16	0.16	1.1	1.2	5.1	4.7
CTEABr	0.01	0.30	0.26	2.1	1.9	2.7	2.9
	0.1	0.25	0.22	1.8	1.5	3.1	3.7
	0.5	0.16	0.14	1.1	1.0	5.1	5.6
CTPABr	0.01	0.18	0.23	1.3	1.6	4.3	3.5
	0.1	0.16	0.18	1.1	1.3	5.1	4.3
	0.5	0.10	0.10	0.7	0.7	8	8
CTBABr	0.01	0.12	0.18	0.9	1.3	6.5	4.3
	0.1[c]	0.10	0.07	0.7	0.5	8	11.2
	0.5[c]	0.10	0.07	0.7	0.5	8	11.2

[a] Values of 10^4 cmc, M, in 0.01, 0.1, and 0.5 M NaOH, are, respectively: CTABr, 7, 0.1, 0; CTEABr, 6, 0.1, 0; CTPABr, 1, 0.1, 0; CTBABr, 1, 0.1, 0. [b] With $\beta = 0.8$, $K_{Br}^{OH} = 14$, $K_S = 400$ M^{-1}. [c] $\beta = 0.6$.

Table 2. Deprotonation of 5-nitroindole-2-carboxylate

Surfactant	[NaOH], *M*[a]	K_b^M		K_b^V, *M*		K_b/K_b^V	
		Langmuir form	PIE	Langmuir form	PIE	Langmuir form	PIE
CTABr	0.01	0.80	0.80	5.7	5.7	1.5	1.5
	0.1	0.70	0.60	5.0	4.3	1.7	2.0
	0.5	0.36	0.30	2.6	2.1	3.2	3.9
CTEABr	0.01	0.70	0.80	5.0	5.7	1.7	1.5
	0.1	0.70	0.65	5.0	4.5	1.7	1.8
	0.5	0.38	0.35	2.7	2.4	3.1	3.5
CTPABr	0.1	0.65	0.75	4.6	5.2	1.8	1.6
	0.5	0.33	0.35	2.4	2.4	3.5	3.5
CTBABr	0.1[b]	0.45	0.38	3.2	2.7	2.6	3.1
	0.5[b]	0.30	0.22	2.1	1.6	3.9	5.2

[a] Values of β, K_{Br}^{OH} and the cmc are as in Table 1. [b] $\beta = 0.6$.

crease in β does not affect our qualitative conclusions regarding the effects of [OH$^-$] on values of K_b^M, and is consistent with other evidence that increasing the bulk of a cationic head group decreases binding of anions.[2,17]

Fitting with Langmuir Isotherms

The fitting follows the general approach described earlier with use of the PIE [Equations (7) and (8)] except that transfer of OH$^-$ from the aqueous to the micellar pseudophase is given by Equations (2) and (3),[13,14] with kinetically derived values of K'_{OH} and K'_{Br} (Tables 1 and 2). Reaction rates had not been examined in CTBAOH but the value of K'_{OH} was expected to be lower than that for CTPAOH. Values of K'_{OH}, M^{-1} are: 55, 45, 25 and 20 for CTAOH, CTEAOH, CTPAOH, and CTBAOH, respectively. Values of K'_{Br}, M^{-1} are: 1000, 800, 700, and 600 for CTABr, CTEABr, CTPABr, and CTBABr, respectively. The significant difference in counterion binding for such diverse anions as Br$^-$ and OH$^-$ is well documented in the literature.[2,18] These values are lower than those used in fitting kinetic data for nucleophilic reactions of Br$^-$,[17] but those fits were not very sensitive to values of K'_{Br} which could be varied significantly without impairing the fits. We note that fits fail for CTPABr and CTBABr in dilute (0.01 M) NaOH, in part due to a modest change in the extent of deprotonation.

Fitted plots are in Figures 1 and 2, and the derived parameters are in Tables 1 and 2. As for the PIE treatment, values of K_b^M decrease with increasing [OH$^-$].

Comparisons of Base Dissociation Constants

The base dissociation constant, K_b^M, is written with concentration as a mole ratio of bound ion to micellar head groups, and second-order rate constants in the micellar pseudophase can be written on the same basis. Classical equilibrium constants and second-order rate constants in solution are generally written with concentrations as molarities, and comparison of data in micelles and water requires estimation of local molarities in the micellar pseudophase.[2,3a,3b,3c]

Provided that we treat the micellar interfacial reaction region as of uniform composition with molar volume, V_M, we can relate concentrations by using Equation (10).

$$[OH^-_M] = \frac{m^s_{OH}}{V_M} = \frac{[OH^-]_M}{[D_n]V_M} \tag{10}$$

where subscript M inside the square brackets denotes local molarity, and outside the brackets it indicates molarity in terms of total solution volume.

Base dissociation constants, $K_b{}^V$, in terms of local molarity of OH^- are given by:

$$K_b{}^V = K_b{}^M / V_M \tag{11}$$

Values of $K_b{}^V$ and K_b in water have the same dimensions and are comparable, but comparison involves the value of V_M, which is uncertain. In examining dissociations for **1a** and **2a** in micelles of trimethylammonium-ion surfactants we took V_M = 0.14 M^{-1} on the assumption that it would be less than half the molar volume of the micelle whose apolar interior should exclude ions,[6,9] and then $K_b/K_b{}^V$ was ca. 3 for **1a** and ca. 2 for **2a**. However, the values of K_b of 5.6 and 8.3 M for **1a** and **2a** in water are calculated thermodynamically and referred, by extrapolation, to the pH scale,[5] whereas those in micelles are calculated by using estimated molarities. The values of $K_b/K_b{}^V$ in Tables 1 and 2 are similar to those estimated earlier for reaction in micelles of N^+Me_3 surfactants in dilute OH^-.[6a,6b] We note that in ref.[6b] Figures 5 and 6 were mislabeled; the former pertains to deprotonation of **2a** and the latter of **1a**. The data in Tables 1 and 2 of that reference are correct.

Comparisons of rate or equilibrium constants in the aqueous and micellar pseudophases in terms of these simple models imply that the interfacial region is uniform in composition and that ionic distribution between it and water follows a step function. These approximations become more unsatisfactory as the ionic concentration and the head group bulk are increased.

An increase in ionic concentration in the interfacial region changes its properties in several respects, even when ions are regarded as point-charges, e.g., screening of electrostatic repulsions of the head groups reduces their separation, and sequestrating water molecules changes polarity in the region. A change from NMe_3 to NBu_3 head groups reduces the volume of the interfacial region accessible to solutes, although it may increase the apparent volume of the region.

The implicit assumption of the pseudophase models that ionic distribution follows a step function becomes less reliable with increasing ionic concentration, because in the limit of very high electrolyte concentration the distinction between the interfacial region and bulk solvent should disappear.[11,12] This condition may not be reached experimentally because of phase separation, but the trend towards it is evident both in models which explicitly include electrostatic ion−micelle interactions[11,12] and in the "invasion" concept applied to micellar effects on reaction rates for relatively concentrated ions.[10c] However, it is always possible that 0.5 M OH^- changes the micellar interfacial properties so as to stabilize a charge-delocalized indolate anion relative to its parent acid. In these conditions the relatively small decreases in $K_b{}^M$ (or $K_b{}^V$) may be due to a change in micellar properties rather than to an increase in $[OH^-{}_M]$. These considerations also apply to reactions which involve charge-dispersed transition states, e.g., bimolecular eliminations.[19]

The concept of a molar volume of the interfacial region is complicated in going from N^+Me_3 to N^+Bu_3 head groups. For a hypothetical cationic micelle of aggregation number = 100, radius 30 Å and a 3-Å thick interfacial region its overall volume is approximately 10,000π Å^3. The approximate volumes of the 300 CH_3 groups is 3180π Å^3 and of the C_4H_9 groups is 6300π Å^3, which means that the free volume in the interfacial region is reduced by a factor of approximately 2. This comparison is artificial, because interfacial interactions and those with counterions will change the micellar structure, but it indicates a problem in estimating quantitatively reliable values of V_M on any rational basis. At the same time introduction of bulky alkyl groups changes the polarity of the interfacial region.

Despite the qualitative nature of the pseudophase model of reactivity and equilibria in association colloids, extensive data can be analyzed in terms similar to those applied to solvent effects on reactivity and equilibria. Some of the uncertainties are similar to those involved in discussions of reactions in mixtures of water and organic solvents, where the significance of "reactant concentration" in terms of total solution volume is also not obvious.

Conclusions

The observed classical base dissociation constants of the anions of 5-nitroindole and its 2-carboxylate ion decrease with increasing $[OH^-]$ and increasing bulk of head groups of micellized cationic surfactants. The trends are interpreted qualitatively in terms of pseudophase treatments of micellar effects on reaction rates and equilibria.

Experimental Section

Preparation and purifications of **1a** and **2a**[5,6] and of the surfactants[20] have been described. Solutions were made up in redistilled, CO_2-free water.

Deprotonation: The fraction, *f*, of deprotonated indicator was monitored spectrophotometrically at 398 and 393 nm for **1a** and **2a** respectively. Values are least reliable when extents of deprotonation are low or high because they depend on small differences between large numbers. Absorbances were measured under conditions giving complete deprotonation, i.e., 0.36 M surfactant with OH^- as counterion and 1 M NaOH, and Beer's Law was obeyed showing that deprotonation was complete. Spectra were monitored on a Hewlett−Packard diode-array spectrophotometer at 25.0 °C.

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