Micellar Effects upon the Deprotonation of the 5-Nitroindole-2-carboxylate Ion

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Deprotonation of the 5-nitroindole-2-carboxylate ion (**1**) at high pH is markedly increased by micelles of cetyltrimethyl ammonium bromide and hydroxide (CTABr and CTAOH). On the assumption that (**1**) and its dianion are fully micellar-bound the fraction, *f*, of deprotonated (**1**) can be related directly to the amount of micellar-bound OH^- and the basicity constant in the micelle is slightly smaller than in water.

Micellar effects upon indicator equilibria are well known and cationic micelles increase deprotonation of weak acids at high pH.[1] They also speed attack of OH^- and other nucleophilic or basic anions upon substrates which bind to the micelles.[2]

These effects upon bimolecular reaction rates and equilibria can be treated quantitatively by assuming that micelles act as a pseudophase and bring reactants together, or keep them apart. The problem then is to estimate the concentrations of both reactants in the micellar pseudophase, but there is a problem when inert and reactive counterions compete for the micelle. The general approach is to assume that the ions compete, as shown in equation (1) for OH^- and Br^-.[3]

$$K_{Br}^{OH} = [OH_W^-][Br_M^-]/[OH_M^-][Br_W^-] \qquad (1)$$

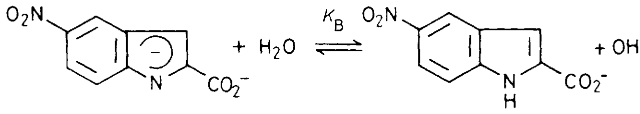
Provided that the fractional ionization of a micelle, α, is constant, the amounts of the ions in water and in the micelles, designated by the subscripts W and M, respectively, can be calculated in terms of the exchange constant, K_{Br}^{OH}.[3-6]

An alternative approach is to make the micellar counterion the reactive ion, so that if α is constant the micellar surface, the so-called Stern layer, should be saturated with reactive ions.[7] The variation of the rate constant for such a reaction should then follow the distribution of the substrate between water and micelles. This simple model fits data for reactions of such ions as H_3O^+, CN^-, N_3^-, and Br^-,[7,8] but for hydrophilic ions, *e.g.*, OH^- or F^-, reaction rates do not become constant, even with fully micellar-bound substrate, but increase on addition of the anion.[9] Thus the Stern layer is apparently not saturated with counterions under all conditions, and micellar rates and equilibria in cetyltrimethylammonium hydroxide (CTAOH) have been described quantitatively in terms of a distribution which follows a mass action equation.[9] However, one might also assume that OH^- in the aqueous pseudophase might react with micellar-bound substrate, *i.e.*, that reaction can occur across the micelle–water interface.[7,10]

To date, the mass action model has been tested for a variety of reactions in CTAOH and similar surfactants.[9,11-14] Most of the tests have been on reaction rates, but the model has also been applied successfully to equilibrium deprotonation of 5-nitroindole at high pH,[13] and to the formation of a Meisenheimer complex.[14]

A problem in interpreting deprotonation data on 5-nitroindole is that the extent of micellar binding of the neutral indicator is an adjustable parameter, because it cannot be measured directly at high pH.[9,13] We have therefore examined deprotonation of 5-nitroindole-2-carboxylate ion (**1**) because this relatively hydrophobic anion should bind very strongly to cationic micelles of CTAOH and the corresponding bromide, CTABr.

In water the dianion (**2**) is a slightly stronger base than the anion of 5-nitroindole, and K_B = 5.6 and 8.3M for 5-nitroindole anion and (**2**), respectively.[15]



(**2**) (**1**)

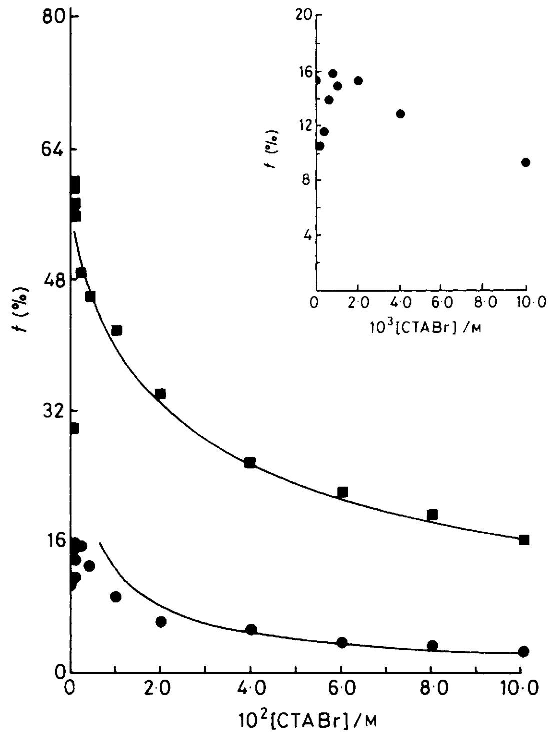


Figure 1. Extent of deprotonation of 5-nitroindole-2-carboxylate ion in CTABr + NaOH: ●, 0.01 and ■, 0.1M NaOH. The lines are calculated

Results and Discussion

Deprotonation in CTABr.—The extents of deprotonation, *f*, go through maxima with increasing [CTABr] in 0.01 and 0.1M NaOH (Figure 1). The maxima are in very dilute CTABr, below the critical micelle concentration, cmc, which is *ca.* 8 × 10^{-4}M in water.[16] In these dilute surfactant solutions the anionic

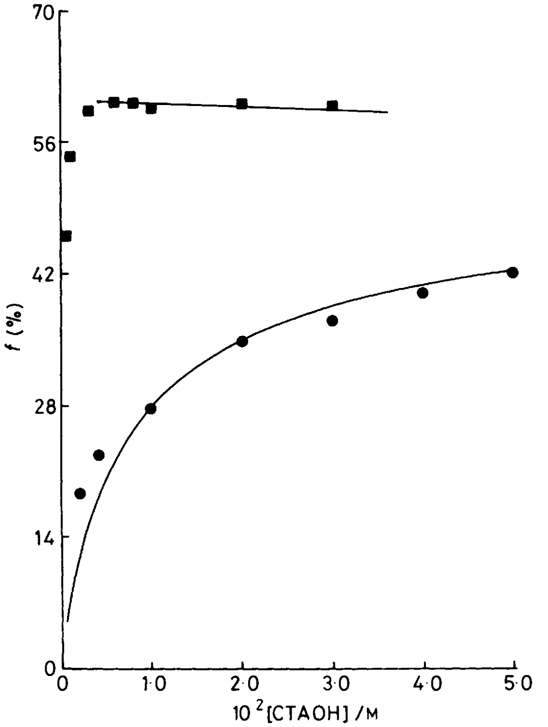


Figure 2. Extent of deprotonation of 5-nitroindole-2-carboxylate ion in CTAOH: ●, with no added NaOH and ■, 0.1M NaOH. The lines are calculated

indicator is probably binding to monomeric surfactant cation, or to small submicellar aggregates of it.

Deprotonation in CTAOH.—The extent of deprotonation, *f*, increases very sharply with increasing [CTAOH], especially in solutions containing 0.1M NaOH (Figure 2). As in CTABr, *f* increases at [CTAOH] below the cmc.

The cmc of CTAOH is higher than that of CTABr,[9,17] because of the hydrophilicity of OH^-, and, because it seems to depend upon the method of measurement; we question whether CTAOH has a sharp, well defined, cmc.

Quantitative Treatment of Deprotonation.—We assume that 5-nitroindole-2-carboxylate ion is fully micellar-bound under all conditions, so that its deprotonation depends only upon the amount of OH^- in the micellar pseudophase. [We assume also that the dianion (**2**) is fully micellar-bound.]

We define deprotonation in terms of equation (2), where BH denotes monoanionic (**1**), B^- dianionic (**2**), and X = Br or OH.

The concentration of OH^- in the micellar pseudophase is defined in terms of the mole ratio, $m_{OH}{}^s$, which in CTABr can be estimated from the mass balance equation (3),[13] where β is the degree of counterion binding, and ion-exchange, equation (1).

$$K_B{}^M = \frac{[BH]m_{OH}{}^s}{[B^-]} = \frac{[BH][OH_M{}^-]}{[B^-]([CTAX] - cmc)} \qquad (2)$$

$$m_{OH}{}^s + m_{Br}{}^s = \beta \qquad (3)$$

Provided that β and $K_{Br}{}^{OH}$ are constant under the experimental conditions we estimate $m_{OH}{}^s$ from the quadratic equation (4), where subscript *T* denotes total concentration.*

Equation (2) gives equation (5), provided that the indicator is fully micellar-bound. The fraction, *f*, of deprotonated 5-nitroindole can be written in terms of equation (6).

$$(m_{OH}{}^s)^2 + m_{OH}{}^s\left(\frac{[OH_T{}^-] + K_{Br}{}^{OH}[Br_T{}^-]}{([CTABr] - cmc)(K_{Br}{}^{OH} - 1)} - \beta\right) - \frac{[OH_T{}^-]\beta}{([CTABr] - cmc)(K_{Br}{}^{OH} - 1)} = 0 \qquad (4)$$

$$K_B(app.) = K_B{}^M[OH_T{}^-]/m_{OH}{}^s \qquad (5)$$

$$f = [OH_T{}^-]/\{[OH_T{}^-] + K_B(app.)\} \qquad (6)$$

The various equations are combined and the data are treated by computer simulation.[6,13]

For deprotonation in CTAOH we assume that the distribution of OH^- is given by the mass action equation,[9] equation (7).

$$K_{OH}' = [OH_M{}^-]/[OH_W{}^-]([CTAOH] - cmc - [OH_M{}^-]) \qquad (7)$$

This equation is combined with equations (2), (5), and (6) to allow computer simulation of the data. We did not attempt to fit the data for 0.01M NaOH and [CTABr] < 10^{-2}M.

Estimation of $K_B{}^M$.—We estimate $K_B{}^M$ by comparing experimental and calculated values of *f* (Figures 1 and 2). For CTABr we used the values of $K_{Br}{}^{OH}$ = 15 and β = 0.78, which were used in treating the deprotonation of 5-nitroindole.[13] These values are in the ranges estimated independently,[4,6,18,19] although we recognize that reasonable fits can often be obtained by taking other values for these parameters.[6]

For CTAOH we took K_{OH}' = 55M^{-1} because this value fits a variety of rate and equilibrium data.[9,12–14] For both CTAOH and CTABr the fits are worst in dilute surfactant because of uncertainties in the appropriate value of the cmc and the possible formation of submicellar aggregates.

The parameters used in fitting the data are in the Table.

Basicity Constants in Water and Micelles.—The values of $K_B{}^M$ are approximately 0.7 (Table), but they cannot be compared directly with those of K_B in water because of the difference in dimensions. We estimate the (classical) value of the basicity constant, K_B, in the micellar pseudophase, written in terms of molarity of OH^-, by converting $m_{OH}{}^s$ into a molarity in the Stern layer. If we take the molar volume of the Stern layer to be 0.14 l we obtain equation (8)†, so that $K_B{}^V \approx$ 5M. This value is

$$K_B{}^V = K_B{}^M/0.14 \qquad (8)$$

slightly smaller than that of K_B = 8.3M in water.[15] Similar, but larger, differences were obtained for deprotonation of 5-nitroindole, for which $K_B/K_B{}^V \approx 5.6$[13] and of arylimidazoles for which $K_B/K_B{}^V \approx 2$.[6b] Favourable interactions between the cationic micellar head groups should stabilize the indicator base relative to its conjugate acid.

The stabilization is greater when the conjugate base is monoanionic rather than dianionic, but, as in micellar rate enhancements, concentration of OH^-, for example, in the small bulk of the micelles is of key importance.

Our treatment depends on the assumption that equilibria and kinetics in micelles and similar aggregates can be treated as if micelles and water are distinct reaction media.[2,7,10] Despite the success of the model we recognize that it is no more than a crude description of the situation. In addition, we assume the

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* There was a typographical error in the sign in the corresponding equation (5) in reference 13.

† The small differences in basicity constants (Table) may be related to a shrinkage of the volume element of reaction, which is assumed to be the Stern layer, with increasing [OH^-].

Table. Micellar effects upon deprotonation

Medium	10^4 cmc (M)	K_B^M
CTABr + 0.01M NaOH	6	0.75[a]
CTABr + 0.1M NaOH	4	0.60[a]
CTAOH	8	0.75[b]
CTAOH + 0.1M NaOH	4	0.60[b]

[a] Calculated by taking $\beta = 0.78$ and $K_{Br}^{OH} = 15$. [b] Calculated by taking $K_{OH}' = 55\text{M}^{-1}$.

volume element of reaction to be that of the Stern layer. The existence of a Stern layer seems to be warranted when the counterions are not very hydrophilic and interact strongly and specifically with micellar head groups.[20] The situation is less simple with strongly hydrated anions such as OH^- and F^-, which have less tendency to bind tightly in the intermediate environs of the head groups, and away from hydrophobic substrates which bind strongly to micelles. Thus our binding parameter, K_{OH}', equation (7),[9] may reflect a gradual distribution of OH^- away from the micellar surface, rather than specific binding, especially in the presence of large amounts of added OH^-, and Evans and Ninham have recently considered various ways of describing the binding of counterions to micelles.[21] However, the treatment is self-consistent and allows discussion of data from a variety of apparently unrelated systems,[20d] despite the artificiality of the boundary between the micellar Stern layer and bulk solvent.

There is, however, the paradox that micelles of CTAOH or CTAF differ from those with less hydrophilic counterions, *e.g.*, CTACl or CTABr, in several respects. The cmc is large,[9,17] and not well defined, the aggregation numbers appear to be low,[17] and micellar charge, as estimated by dynamic light scattering, is high, so that micelles of CTAOH show little growth even in high NaOH.[22] All these features suggest that the micellar surfaces of CTAOH should be different from those of CTABr or CTACl, because of the balance of forces in micellization, and geometrical requirements for formation of various aggregates.[23] But rate and equilibrium constants for reactions of OH^- are similar for the various micelles, as are binding constants of hydrophobic solutes.[7,9,11-14] Therefore rate and equilibrium constants of bimolecular reactions at micellar surfaces are not good indicators of the detailed structure of the micellar surface, although rates of spontaneous unimolecular reactions seem to be sensitive to the nature of the surface.[24]

Experimental

Materials.—5-Nitroindole-2-carboxylic acid was prepared by cyclization of the 4-nitrophenyl hydrazone of ethyl pyruvate in polyphosphoric acid, and its ester was saponified.[25] The acid was recrystallized (EtOH) and had m.p. 325—326 °C (lit.,[25] 326—328 °C). Preparation and purification of the surfactants has been described.[13]

Solutions of CTAOH were prepared from $(CTA)_2SO_4$ under an atmosphere of N_2 and were tested for contamination by CO_3^{2-} or SO_4^{2-} by the addition of $BaCl_2$, and for Ba^{2+} by addition of Na_2SO_4.

Deprotonation.—The fraction, *f*, of deprotonated (**1**) was measured spectrophotometrically at 25 °C. The indicator concentration was 9×10^{-5}M, and $f = [2]/([1] + [2])$. Solutions were made up in redistilled, deionized water under N_2 to exclude CO_2. The molar absorptivities of the dianion (**2**) are 6 900 and 6 680 at 387 and 393 nm, respectively, and measurements were made at these wavelengths.

Acknowledgements

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