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NUCLEOPHILIC AROMATIC SUBSTITUTION IN TWIN - TAILED HYDROXIDE ION SURFACTANTS

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Summary: The effects of didodecyldimethylammonium hydroxide and chloride upon reactions of OH^- with 2,4-dinitrochloro-benzene and naphthalene are treated quantitatively in terms of the pseudophase model of micellar kinetics.

The pseudophase, ion exchange, model with assumed constancy of fractional micellar charge,α, has been applied extensively to the treatment of reactions of hydrophilic ions in aqueous micelles.[1-4] It is assumed that the micellar reaction occurs in the Stern layer, and the assumption of constant α appears to be satisfactory for reactions in solutions containing both reactive and inert counterions, and in several reactive-ion micelles.[5] The treatment fails with reactive-ion micelles which have very hydrophilic counteranions[5a], e.g., OH^- and F^-, but here kinetics can be treated on the assuption that α is large and decreases on addition of the reactive ion.[6]

Didodecyldimethylammonium hydroxide (DDDAOH) is reported to form vesicles spontaneously,[7] and we examined reactions of 2,4-dinitrochlorobenzene and 2,4-dinitrochloronaphthalene (DNCB and DNCN) in its solutions, where there is no competition between reactive and inert counteranions, and in DDDACl + NaOH (Fig. 1).

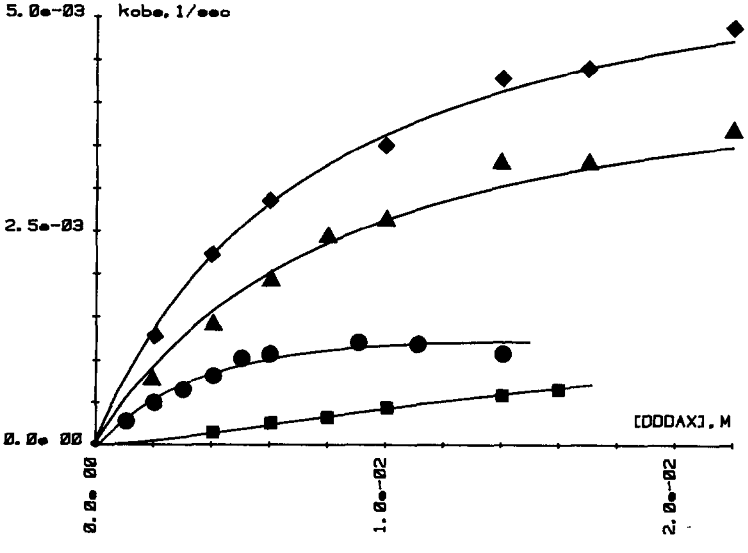

Fig. 1. Reaction of DNCB in DDDAOH and DDDACl at 25.0°C.
In DDDAOH,
■ no added OH^-;
▲ 0.1 M $[OH_T^-]$;
◆ 0.2 M $[OH_T^-]$.
In DDDACl,
● 0.05 M NaOH.

The hydroxide (DDDAOH) was made from the bromide via the sulfate by methods described for single chain surfactants.[6] The substrates are chemically similar but have different reactivities and hydrophobicities.[6a]

The rates enhancements in DDDAOH and DDDACl are similar to those in micellar solutions of single-tailed surfactants, but occur at somewhat lower [surfactant].[6a] Understanding of these rate enhancements requires isolation of the factors responsible for the rate enhancement and calculation of the second order rate constants at the vesicular surface.

The curves shown in Fig.1 for reaction of DNCB at 25.0°C are theoretical and are derived using equations applied earlier to reactions in cetyltrimethylammonium hydroxide (CTAOH) and in CTACl + NaOH.[3,6]

The first order rate constant with respect to substrate, S, is given by eq. 1:

$$k_{obs} = \frac{k_W[OH^-_W] + k_M K_s m^s_{OH}([D]-cmc)}{1 + K_s([D]-cmc)} \qquad (1)$$

where K_s is the substrate binding constant and [D]-cmc is the concentration of aggregated surfactant. (Subcripts W and M denote aqueous and micellar pseudophases respectively). The second order rate constant in the micellar or vesicular pseudophase, k_M, is written in terms of the mole ratio of bound OH^-, and $m^s_{OH} = [OH^-_M]/([D]-cmc)$.[3,5,6]

For mixtures of DDDACl and NaOH m^s_{OH} (or $[OH^-_M]$) is calculated from the ion-exchange equation (2)[1-4]

$$K^{OH}_{Cl} = [OH^-_W][Cl^-_M] \;/\; [OH^-_M][Cl^-_W]) \qquad (2)$$

For DDDAOH we apply the mass action equation which has been applied to the binding of OH^- and F^- to reactive-ion micelles:[6a]

$$K'_{OH} = [OH^-_M]/[OH^-_W]\,([D]-cmc-[OH^-_M]) \qquad (3)$$

These treatment have been described[3,6], and the parameters used in Fig. 1 are in Table I, which also contains parameters for DNCN. The cmc of DDDACl is $1.8\text{x}10^{-4}$ M by conductivity, c.f. ref. 8,9, but surfactant concentrations are sufficiently high that the fitting is insensitive to the cmc. In fitting the rate data we chose values of K'_{OH}, K^{OH}_{Cl}, k_M and K_s similar to those used for micelles.[3,6] For DNCB in CTAOH $K_s = 10^2\ M^{-1}$ and $k_M \approx 5\text{x}10^{-3}\ s^{-1}$, and in CTABr the corresponding values are 70 M^{-1} and $3.5\text{x}10^{-3}\ s^{-1}$. For DNCN in CTAOH $K_s = 1.6\text{x}10^3\ M^{-1}$ and $k_M \approx 0.1\ s^{-1}$ and from data for several reactions $K'_{OH} = 55\ M^{-1}$ and $K^{OH}_{Cl} = 4$.[3a,6a] The fit between theory and experiment is satisfactory (Fig. 1) except at DDDACl > 10^{-2}M where solutions in NaOH become viscous, c.f. ref.7.

Table I

Reactions of DNCB and DNCN[a]

substrate	medium	$[OH_T^-]$, M	k_M, s^{-1}	K_s, M^{-1}
DNCB	DDDAOH	0-0.016	0.003	100
DNCB	DDDAOH	0.1	0.006	110
DNCB	DDDAOH	0.2	0.007	130
DNCB	DDDACl[b]	0.05	0.0055	100
DNCN	DDDAOH	0-0.016	0.065	$1.6x10^3$
DNCN	DDDAOH	0.1	0.08	$1.6x10^3$
DNCN	DDDAOH	0.2	0.08	$1.6x10^3$
DNCN	DDDACl[b]	0.05	0.085	$1.6x10^3$

[a] At 25.0°C with $K'_{OH} = 55\ M^{-1}$, $K_{Cl}^{OH} = 4$ and cmc = $1.5x10^{-4}$ M, and zero for $[OH^-] > 0.1M$

[b] $\alpha = 0.3$.

The values of k_M are very similar for reactions in DDDAOH, DDDACl and in normal micelles, despite differences in the nature of the aggregates and the counterions. We note that reaction of OH^- with 5,5'-dithiobis (2-nitrobenzoic acid) has a similar form in cationic micelles and sonicated vesicles but second order rate constants are different in the micelles and vesicles, and depend to some extent on [surfactant] and pH, and the method of treatment of the data. To some extent this may be because the reaction rates depended upon the extent of sonication which apparently affected the vesicle size and shape. Because DDDAOH (and probably DDDACl) spontaneously assemble[7] they should provide vesicles uniformly.

Overall rate enhancements are often larger in vesicles than in micelles,[10-12] and a striking example of this effect is ester thiolysis in cationic vesicles.[12] However, in these systems, as in the present work, the major source of the rate enhancement is the high concentration of both reactants in the small volume of the vesicles. Overall rate enhancements can be very large in sonicated vesicles[10-12] simply because reactants are fully bound at very low concentrations of surfactant.

In treating our vesicular data we do not differentiate between reactions on the interior and exterior surfaces[13] because the nonionic substrate should move rapidly between these surfaces, although OH^- may not,[7] but see ref. 10. Our evidence suggests that the pseudophase model of micellar kinetics is applicable to reactions of hydrophilic ions in reactive-ion vesicles as well as to systems containing both inert and reactive counterions. Comparison of second order rate constants in water and in micelles or vesicles requires estimation of the volume element of reaction in the aggregates,[1-3] and in micelles this element can be regarded as that of the micelles or of their Stern layers. These molar volumes are assumed to be in the range 0.14 - 0.3L.[1-4] If the lower estimate[3] is taken for DDDAOH and DDDACl the second order rate constants for DNCB are ca. 10^{-3} $M^{-1}s^{-1}$, and for DNCN ca. 10^{-2} $M^{-1}s^{-1}$, whereas the corresponding values in water are 1.4×10^{-4} and 6.4×10^{-3} $M^{-1}s^{-1}$.[6a] (The second order rate constants will be correspondingly larger if a volume element of 0.3L is used). Nucleophilic aromatic substitution by hydrophilic anions appears to be somewhat faster in micellar and vesicular pseudophases than in water, but this effect is much less important than that of increased reactant concentration. These didodecyl vesicles and micelles have very similar kinetic parameters for reactions of OH^- suggesting that the surfaces are not very different.

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