was not determined separately by GLC at low conversion. Calculated and observed quantum yields are reported in Table I. Di-*tert*-butyl(dichloromethoxy)amine (**7**) was not sufficiently stable for isolation. It was characterized from the $^1$H NMR spectrum ($DCCl_3$) which showed singlets at $\delta$ 1.28 (18 H) and 7.80 (1 H).

**Determination of Quantum Yields of Product Formation from Irradiation of DTBN in Methylene Chloride.** The quantum yield of formation of 2-methyl-2-nitrosopropane (**1**) from irradiation of 0.10 M DTBN in methylene chloride at 300 ± 10 nm was determined spectrophotometrically at low conversion (vide supra). The quantum yield of formation of di-*tert*-butyl-*tert*-butoxyamine (**2**) was determined in the same experiment by GLC (vide supra). The ratio of the quantum yields of formation of di-*tert*-butylhydroxylammonium chloride (**3**) and di-*tert*-butyl(chloromethoxy)amine (**8**) was determined as follows. A 2.8-mL sample of 0.10 M DTBN in methylene chloride was irradiated for 3 h at 300 ± 10 nm at which time the solution was a blue green color. Vacuum distillation of all volatile materials was followed by $^1$H NMR analysis. Integration of the NMR spectrum showed the ratio of **3** to **8** to be 0.97. Di-*tert*-butyl(chloromethoxy)amine (**8**) was not sufficiently stable for isolation. It was characterized from the $^1$H NMR spectrum ($CH_2Cl_2$) which showed singlets at $\delta$ 1.41 (18 H) and 5.53 (2 H). Because 2-methyl-2-nitrosopropane is photolabile and absorbs light at wavelengths less than 300 nm, determination of the relative quantum yields of formation of the volatile products by $^1$H NMR spectroscopy after irradiation to completion was impossible. The calculated and observed quantum yields are reported in Table I.

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# Reactivity Control in Micelles and Surfactant Vesicles. Kinetics and Mechanism of Base-Catalyzed Hydrolysis of 5,5′-Dithiobis(2-nitrobenzoic acid) in Water, Hexadecyltrimethylammonium Bromide Micelles, and Dioctadecyldimethylammonium Chloride Surfactant Vesicles

**Janos H. Fendler*[1] and Willie L. Hinze[2]**

*Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843, and Wake Forest University, Winston-Salem, North Carolina 27109.*
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**Abstract:** Rate constants have been determined for the hydrolysis of 5,5′-dithiobis(2-nitrobenzoic acid) (DTNB) as functions of hydroxide ion concentrations in water, micellar hexadecyltrimethylammonium bromide (CTAB), and dioctadecyldimethylammonium chloride (DODAC) surfactant vesicles. The observed second-order rate constants at 26.4 °C in micellar CTAB (8.4 $M^{-1}$ $s^{-1}$) and in DODAC surfactant vesicles (840 $M^{-1}$ $s^{-1}$) are approximately 15- and 1500-fold larger than that in water (0.54 $M^{-1}$ $s^{-1}$). The rate–concentration profiles in both surfactant systems fit the pseudophase-type models of micellar catalysis. The "true" second-order rate constants in the pseudophases of micelles and surfactant vesicles are 0.1–1.1 and 0.75–7.7 $M^{-1}$ $s^{-1}$, respectively. Rate enhancements are the consequences of highly increased DTNB and hydroxide ion concentrations in the micelles and surfactant vesicles. Binding constants for the association of DTNB with micellar CTAB and DODAC vesicles, determined spectrophotometrically as well as derived from the kinetic treatments, are approximately (1–3) × $10^4$ and (1–4) × $10^4$ $M^{-1}$. Binding constants for the hydroxide ion association with CTAB micelles and DODAC vesicles, determined from the kinetic data, are (1–2) × $10^2$ and (3–8) × $10^2$ $M^{-1}$, respectively. Kinetic treatments derived from micellar catalysis are also applicable to surfactant vesicles.

## Introduction

The influence of environmental factors on chemical reactions in various organized systems is of considerable current interest. Incorporation of reactants in micellar aggregates dramatically affects their apparent reactivity compared to that observed in water.[3] Enhanced rate effects have been rationalized in terms of favorable reagent distribution and/or changes in the apparent dissociation constants of ionizable functional groups.[4-6] Several quantitative kinetic treatments have been developed to assess the intrinsic reactivity in micelles.[4-12]

Completely synthetic surfactant vesicles have also been utilized as models for interfacial effects on chemical reactivity and for membrane-mediated processes.[13] Vesicles readily form upon

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sonication of simple anionic or cationic long-chain dialkyl surfactants. Whereas micellar aggregates are in dynamic equilibrium with their monomer units, vesicles are more static entities that can bind a relatively large number of guest molecules per aggregate.[13] A wide variety of reactions have been studied and characterized in synthetic vesicles.[14-24] Very little attention has been given, however, to a comparison of micelles and surfactant vesicles as reaction media.[25] The present study was undertaken to examine the comparative effectiveness of micelles and vesicles as catalytic media. Hence, rate constants for the reaction of hydroxide ion with Ellman's reagent, 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB), in water, in the presence of cationic micelle-forming detergent, hexadecyltrimethylammonium bromide (CTAB), and in vesicle-forming surfactant, dioctadecyldimethylammonium chloride (DODAC), have been determined. The applicability of the kinetic treatments for describing reactivity in surfactant vesicles has been demonstrated.

The alkaline hydrolysis of disulfides (such as DTNB) has been briefly examined by several workers.[26-33] The generally accepted hydrolysis mechanism can be represented by the initial attack of hydroxide ion on sulfur to give a thiol anion and a sulfenic acid (eq 1) which rapidly disproportionates into another thiol anion

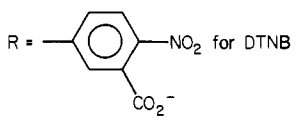
$$RSSR + {}^{-}OH \xrightarrow{slow} RS^{-} + RSOH \qquad (1)$$

and a sulfinate ion (eq 2). The overall reaction stoichiometry

$$RSOH \xrightarrow{rapid} {}^{1}/_{2}RS^{-} + {}^{1}/_{2}RSO_2^{-} + H^{+} \qquad (2)$$

is shown in eq 3.

$$RSSR + 2OH^{-} \rightarrow {}^{3}/_{2}RS^{-} + {}^{1}/_{2}RSO_2^{-} + H_2O \qquad (3)$$




DTNB was chosen since it has been used as a model compound in disulfide cleavage reactions.[26,29,34-36] Sulfur–sulfur bonds play an important role in biological systems because of the frequency with which the disulfide linkage occurs in such relevant substances as enzymes. Consequently, mechanistic studies of reactions involving scission of disulfides should be interesting and valuable in its own right both theoretically and in regard to its dominant role in protein biosynthesis.[37-39] Additionally, DTNB is a reagent commonly used in the spectrophotometric determination of cyanide,[40] sulfide,[41] and thiols.[42] Thus, information concerning its basic hydrolysis should also be useful in these analytical applications.

## Experimental Section

**Materials and Reagents.** Ellman's reagent, 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB) was purchased from Aldrich and purified using an established procedure.[28] Purification of hexadecyltrimethylammonium bromide (CTAB),[3,43] as well as the synthesis, purification, and characterization of dioctadecyldimethylammonium chloride (DODAC),[19,44] has been previously described. The thiol reaction product 2-nitro-5-thiobenzoate anion (TNB) was independently synthesized using a slightly modified procedure of Riddles et al.[28] All other materials used were the best available reagent grade. The water used in the experiments was purified by deionization and subsequent distillation in an all-glass still and then purged with nitorgen.

The typical DODAC vesicle preparation consisted of the sonic dispersion of DODAC (15.0–45.0 mg in 2.0–6.0 mL of distilled water) at 50–68 °C using either the microprobe of a Braunsonic 1510 sonifier set at ca. 70 W[19,44] or a standard 19-mm probe of a Fisher Model 300 sonic dismembrator set at 25–40% power. Using this procedure, optically transparent solutions of the vesicles were obtained within about 20–30 min sonication time. The desired DODAC surfactant concentration could then be achieved by appropriate dilution.

**Methods.** The concentration of CTAB stock solutions was determined by bromide ion titration.[45] DTNB concentrations were determined spectrophotometrically at 324 nm via use of a Beer's law calibration plot. Hydroxide ion concentrations were determined by volumetric and potentiometric titrations using a standardized hydrochloric acid solution (British Drug House). Additionally, the pH of the solutions was measured before and after each kinetic run using a Radiometer Model 28 or Fisher Accumet Model 320 pH meter that had been calibrated with standard buffers to ±0.02 pH unit. Values of the critical micelle concentrations (cmc) of CTAB were obtained using standard techniques.[3] Although it is known to be somewhat unreliable since incorporation of the dye may in itself induce micellization,[46] variations of the dye method were employed[47,48] to ascertain the cmc in the presence of buffer, hydroxide ion, and/or DTNB. Cmc's were determined from breaks in the plots of either the absorbance of bromophenol blue (at 590 or 603 nm) or the fluorescence intensity of eosin or fluoroscein ($5 \times 10^{-6}$ M) vs. the surfactant concentration. Absorption spectra were recorded and absorbance measurements made using either a Cary Model 118C or 219 recording spectrophotometer. An Aminco-Bowman spectrofluorimeter was used in the fluorescence work.

**Kinetics.** Rate constants were determined by adding an appropriate aliquot (20–50 μL) of a concentrated stock DTNB solution (10–15 mM in ethanol) to standardized sodium hydroxide solutions (10.00 mL each, 7–200 mM in [$^{-}$OH]), or to micellar CTAB or DODAC surfactant vesicles containing appropriate base concentrations.[49] Reaction solutions

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Table I. Spectral Data for DTNB and TNB in Different Media at 25.0 °C[a,b]

| medium | DTNB | | TNB[e] | |
|---|---|---|---|---|
| | λ, nm[c] | $10^{-4}\epsilon$, $M^{-1}$ $cm^{-1}$ | λ, nm[d] | $10^{-4}\epsilon$, $M^{-1}$ $cm^{-1}$ |
| $H_2O$, pH 6.8–8.0 | 324<br>(324–5)[28,40] | 1.78 ± 0.08[f]<br>(1.80 ± 0.50)[28,41] | 410[g]<br>(410–12)[28] | 1.42 ± 0.05[h]<br>(1.48 ± 0.07)[28] |
| $H_2O$, 0.01 M HCl | 324 | 1.74 ± 0.06 | 330<br>(329.5)[28] | 0.84 ± 0.04<br>(0.88)[26] |
| CTAB, ≥$4.0 \times 10^{-4}$ M | 312<br>(~310)[29] | 1.11 ± 0.02<br>(~1.2)[29] | 435 | 1.47 ± 0.04 |
| DODAC, ≥$4.0 \times 10^{-4}$ M | 312 | 1.15 ± 0.10 | 445 | 1.44 ± 0.08 |

[a] Literature values, where available, are given in parentheses. [b] Both DTNB and TNB obey Beer's law in the 0.025–2.50 × $10^{-4}$ M concentration range in all of the solvent and surfactant systems studied. [c] The absorption of DTNB is due to a $\pi \rightarrow \pi^*$ transition.[53] [d] The absorption of TNB is assigned to a $\pi \rightarrow \pi^*$ transition that has considerable intramolecular charge-transfer character.[52c,54,55] [e] The spectral properties of in situ generated TNB were virtually the same as those observed for the independently synthesized product. [f] The molar absorptivity, ε, of DTNB exhibits a slight thermochromatic temperature effect.[28] [g] The $\lambda_{max}$ of TNB is solvent sensitive (refer to Figure 1). [h] The molar absorptivity, ε, of TNB has been reported to exhibit a dependence upon the pH of the solution (e.g., at pH 6.9, $10^{-4}\epsilon = 1.29$, while at pH 10.7, $10^{-4}\epsilon = 2.26$).[56]

were quickly transferred to 1.00-cm quartz cells and the reaction progress monitored spectrally (absorbance vs. time) within 10 s of mixing. In some instances (i.e., at relatively high pH and/or increased temperature), the rapidity of the hydrolysis reaction necessitated the use of the stop-flow technique. Typically, 250 mL of a 0.06–0.10 mM DTNB solution was prepared in either water or an aqueous surfactant solution of the appropriate CTAB or DODAC concentration. Next, a series of solutions (usually 25.0 mL of each) containing a constant concentration of hydroxide ion, but of varying surfactant concentration (0–50 mM), were prepared by appropriate dilution of standard hydroxide and surfactant solutions with water. Then the solution of DTNB was mixed 1:1 with the desired hydroxide-surfactant solution in the cuvette (2.0-cm path length) of a Durrum Model D-130 stop-flow spectrophotometric system.[49] The rates were determined from Polaroid photographs taken of the oscilloscope absorbance vs. time curves.

The temperature for all the kinetic runs was maintained to within ±0.1 °C of the desired value by means of circulating water and a Haake thermostated water bath setup. The solutions were always equilibrated at the desired temperature for 15–25 min prior to initiation of the reaction. All solutions were flushed and stored under nitrogen in order to prevent oxidation of the released thiol reaction product (TNB) by air.[51a-c] The Ellman reagent, DTNB ($pK_a$ in $H_2O$ = 4.75),[27a] and its product thiol, TNB ($pK_a$ in $H_2O$ = 4.53),[28] are essentially completely ionized at the hydroxide ion concentrations employed in these studies.[52] In all kinetic runs, the final organic solvent content (ethanol) never exceeded 0.50% (v/v). All kinetic work done using the DODAC surfactant vesicles was carried out on freshly prepared solutions (i.e., ≤6 h old).

The reactions were monitored spectrophotometrically by following either the appearance of the TNB product at 410, 435, and 440–50 nm or the disappearance of the DTNB reactant at 324, 312, and 325 nm, respectively, in water, micellar CTAB, and DODAC vesicles as a function of time (Table I). Under all conditions, the DTNB showed no appreciable absorption at the wavelength maximum for TNB (and vice versa). Except as otherwise mentioned, pseudo-first-order conditions prevailed (i.e., [hydroxide]/[DTNB] ≥ 75) in all of the kinetic runs. The apparent pseudo-first-order rate constants, $k_\psi$, were obtained from linear plots of either ln $[A_\infty - A_t]$ (for product TNB formation) or ln $[A_t - A_\infty]$ (for reactant DTNB decay) vs. time. The activation parameters were determined from the rate dependence on temperature in the 8–40 °C range in the usual manner.

**Determination of Distribution Constants.** The distribution or "binding" constants of DTNB to the cationic surfactant systems were determined spectrophotometrically using modified literature procedures.[43,57,58] A series of solutions (10.0 mL each total volume) were prepared of varying cationic surfactant concentration (0–18 mM) with and without added buffer (pH 7.2 and 10.3). Next, a small amount of a concentrated DTNB stock solution (10–60 μL of 4–15 mM) was successively added to each of the surfactant-containing solutions using a calibrated Hamilton microsyringe. After mixing, an aliquot (2.50 mL) was transferred to a 1-cm quartz cuvette that was thermostated at the desired temperature and the absorbance recorded in the 300–360-nm wavelength region vs. an appropriate reference. Binding constants ($K_{DTNB}$, Table II) were calculated from[57,58]

$$K_{DTNB} = f/[(1-f)([D] - cmc) - f(1-f)[DTNB]] \quad (4)$$

The fraction, $f$, of micellar or vesiclar-bound DTNB at various surfactant (CTAB or DODAC) concentrations, [D], can be estimated from:

$$f = (A - A_{aq})/(A_{mv} - A_{aq}) \quad (5)$$

where $A_{aq}$ is the absorbance of DTNB in pure water, $A$ the absorbance in the presence of added surfactant, and $A_{mv}$ the limiting absorbance resulting from complete incorporation of DTNB into the micellar or vesiclar pseudophase.[57,58] Beer's law was found to be obeyed in all of these systems (see Table I).

Table II. Summary of Critical Micelle Concentrations and Binding Constants for the Incorporation of DTNB in the CTAB Micelle and DODAC Vesicle Pseudophases at 25.0 °C[a]

| supporting medium | CTAB | | DODAC |
|---|---|---|---|
| | $10^4$cmc, M | $10^{-4} \times K_{DTNB}$, $M^{-1}$ | $10^{-4} \times K_{DTNB}$, $M^{-1}$ |
| $H_2O$ | 8.4[b]–9.8[c]<br>(9 ± 1)[3,48] | | |
| $H_2O$ + 0.05 M NaOH (pH 12.7) | 3.4 ± 0.2[b]<br>(3.2)[48] | | |
| $H_2O$ + $5 \times 10^{-5}$ M DTNB at pH 7.2 | 0.6 ± 0.3[b] | 2.0 ± 1.0 | 2.0 ± 0.5 |
| $H_2O$ + $5 \times 10^{-5}$ M DTNB at pH 10.3 | 0.4 ± 0.3[b] | 3.0 ± 1.5 | 4.0 ± 1.5 |

[a] Literature values are given in parentheses for comparison. [b] Determined using dye method (bromophenol blue).[48] [c] Determined from the conductivity method.

## Results and Discussion

**Characterization of the Reaction System.** The cmc's for CTAB micelles in the presence of additives, determined in the usual manner, are summarized in Table II. In the absence of additives the experimentally determined values agree well with that given in the literature. Cmc values of CTAB are seen to be depressed by DTNB, hydroxide ion, and the TNB reaction product. This finding is in accord with the reported lowering of cmc by base[48] and/or aromatic substrates.[59]

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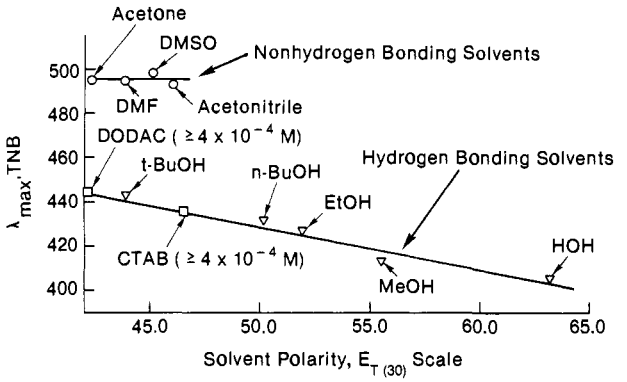


**Figure 1.** Absorption maximum ($\lambda_{max}$, nm) of TNB vs. the solvent polarity parameter ($E_{T(30)}$, kcal/mol) for the $\pi \rightarrow \pi^*$ intramolecular charge-transfer transition.

There is a minimum concentration below which surfactant vesicles cannot form. For DODAC vesicles these concentrations in the absence and in the presence of $5 \times 10^{-5}$ M DTNB were determined to be $(8.0 \pm 4.0)10^{-6}$ and $(9.0 \pm 4.0)10^{-6}$ M, respectively. Similar values [$(3.8 \pm 0.8)10^{-6}$ M] have been reported previously for minimum concentrations of DODAC necessary to form vesicles.[47,60] It should be emphasized that the minimum concentration of surfactant needed to form vesicles is not equivalent to the concept of cmc used for micelles. Once formed, vesicles cannot be destroyed by dilution. Surfactant vesicles have, in fact, been detected at as low a stoichiometric concentration as $10^{-8}$ M.[22]

The absorption spectral parameters ($\lambda_{max}$ and $\epsilon$) of DTNB and TNB in aqueous media (Table I) are in good agreement with published values.[26,40,41,61] In the presence of monomeric CTAB or DODAC surfactants, the spectra are essentially the same as that observed in aqueous media alone. However, in micellar CTAB or in DODAC surfactant vesicles, a surfactant concentration dependent hyposochromic $\lambda$ and hypochromic $\epsilon$ shift was observed for DTNB. Above $3\text{-}4 \times 10^{-4}$ M surfactant concentration, absorption spectra of DTNB remain unaltered as functions of surfactant concentration.[62] These data are interpreted in terms of the partitioning of the dianionic DTNB to the cationic micellar CTAB or DODAC vesicle pseudophase. The spectral parameters of the fully bound DTNB in these systems are summarized in Table I. The product TNB's spectral $\lambda_{max}$ surfactant concentration dependence is similar to that of DTNB except that the TNB experiences a rather large bathochromic $\lambda$ shift (25–40 nm compared to water). Its molar absorptivity, $\epsilon$, however, remains essentially unchanged in micelles or in vesicles. Additionally, it was observed that the $\lambda_{max}$ for this TNB $\pi \rightarrow \pi^*$ charge-transfer band[63] is very solvent sensitive. Figure 1 illustrates the solvent dependency of the TNB absorption maximum in terms of the $E_{T(30)}$ solvent polarity parameter.[64] The transition energies (expressed in $\lambda_{max}$) do not correlate with the $E_{T(30)}$ indexes for solvent polarity; rather, they seem to indicate two lines, one for hydrogen-bonding solvents and another for aprotic solvents. The $\lambda_{max}$ is insensitive to the polarity of the aprotic solvents whereas a fair correlation is observed between $\lambda_{max}$ and the $E_{T(30)}$ values for the hydroxylic solvents (Figure 1).

Using this correlation as a sort of spectroscopic ruler, the effective polarity and degree of hydrogen-bonding ability of the surface of CTAB micelles and DODAC vesicles can be assessed. TNB in CTAB micelles experiences a micropolarity similar to that in *n*-butyl alcohol ($E_{T(30)} = 51$), whereas in the DODAC vesicles it senses a less polar and/or reduced hydrogen bonding surrounding ($E_{T(30)} = 43$, similar to *tert*-butyl alcohol).[65] The loss of hydrogen-bonding ability purportedly plays an essential role in the red shifts observed for other probes.[52c,66] The reduced tendency of intramicellar water to hydrogen bond[67] could account for the rather large bathochromic shifts observed in this study for the TNB in cationic micelles or DODAC vesicles. The environment of TNB in DODAC vesicles appears to be slightly more hydrophobic than that in CTAB micelles. This finding is in good qualitative agreement with other estimates of the surface micropolarity.[23,68]

Absorbance changes of DTNB (at 324 nm) as a function of the added surfactant concentration (in the concentration region from the cmc to approximately $4 \times 10^{-4}$ M) allowed the calculation (via use of eq 4 and 5) of the equilibrium binding constant, ($K_{DTNB}$), for the incorporation of DTNB into the CTAB micelles or DODAC vesicles:[57]

$$DTNB_{aq} + (CTAB)_n \rightleftharpoons^{K_{DTNB}} [DTNB\cdot(CTAB)_n] \quad (6)$$

$$DTNB_{aq} + (DODAC)_n \rightleftharpoons^{K_{DTNB}} [DTNB\cdot(DODAC)_n] \quad (7)$$

where $(CTAB)_n$ or $(DODAC)_n$ represent the portion of the micelle or vesicle consisting of $n$ surfactant molecules that are necessary for the incorporation of one DTNB anion. Binding constants for CTAB and DODAC under the kinetic experimental conditions were found to be quite similar (i.e., $K_{DTNB} \approx (1\text{-}4) \times 10^4$ $M^{-1}$; see Table II). The rather large errors associated with these reported values stem from the uncertainty in the respective surfactant cmc values and from the fact that the DTNB reacts with the hydroxide ion (vide supra, eq 1–3) under the experimental conditions employed.

It is informative to compare these experimentally determined binding constants with those that can be predicted using an approach first described by Berezin.[7,9] Binding constants for incorporation of DTNB into the CTAB micelles (or DODAC vesicles) are defined by:

$$K = (P - 1)\bar{V} \quad (8)$$

where $P$ is the partition coefficient and $\bar{V}$ the partial molar volume of the monomer in the micelle or vesicle. The partition coefficient of an ionic species such as DTNB between an aqueous phase and the micellar or vesicle pseudophase can be estimated from:

$$P = e^{-Z\psi/25.69} \text{ (at 25.0 °C)} \quad (9)$$

where $Z$ is the ionic charge on the substrate (DTNB) and $\psi$ is the surface potential of the micelle or vesicle.[7,9,69] The surface potential for CTAB has been reported to be in the range of 50–175 mV[70,71] with $\bar{V} = 0.32\text{–}0.37$ $M^{-1}$ [43,72] whereas the same values for

(60) Henglein, A.; Proske, T.; Schnecke, W. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 956.
(61) Paul, C.; Kinschner, K. Haenisch, G. *Anal. Biochem.* **1980**, *101*, 445.
(62) The effect of tetramethylammonium bromide (TMAB) and tetrabutylammonium bromide (TBAB) on the absorbance of DTNB was also briefly studied. The addition of either TMAB or TBAB up to 0.01 M did not change the absorbance of $6.7 \times 10^{-5}$ M DTNB. Both TMAB and TBAB have the same ionogenic group as do CTAB and DODAC except that they are incapable of forming micelles or vesicles. This indicates that the presence of micellar CTAB or DODAC vesicles, rather than just formation of hydrophobic ion pairs, is required for the binding of DTNB observed in this study.
(63) (a) It should be noted here that the TNB absorption has been variously misassigned as being due to a $n \rightarrow \pi^*$ or regular $\pi \rightarrow \pi^*$ transition in the literature.[63b,c] However, the magnitude of its $\epsilon(\sim 10^4$ $M^{-1}$ $cm^{-1}$, Table I) and its $\lambda_{max}$–solvent dependence (Figure 1) are inconsistent with both of these assignments. The absorption is most probably attributed to a $\pi \rightarrow \pi^*$ transition that has considerable intramolecular charge-transfer character[54] as has been recently reported by Porter and Minch for similar species.[52c,63d] (b) Parker, A. J. *Acta Chem. Scand.* **1962**, *16*, 855. (c) Gillian, A. E.; Stern E. S. "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry"; Edward Arnold: London, 1971. (d) Kerber, R. C.; Porter, A. *J. Am. Chem. Soc.* **1969**, *91*, 366.
(64) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29.
(65) Although no apparent similar correlation was found for the $\pi \rightarrow \pi^*$ DTNB band, its absorption maximum, when bound to the surfactant systems, was similar to that in ethanol or *n*-butyl alcohol ($E_{T(30)} \simeq 50\text{–}52$).
(66) Minch, M. J.; Shah, S. S. *J. Org. Chem.* **1979**, *44*, 3252.
(67) Figueras, J. *J. Am. Chem. Soc.* **1971**, *93*, 3255.
(68) Okahata, Y.; Ando, R.; Kunitake, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3647.
(69) Davis, J. T. "Surface Phenomena in Chemistry and Biology"; Danieli, J. F.; Pankhurst, K. G. Riddiford, A. C., Eds.; Pergamon Press: New York, **1958**.
(70) Bhalekar, A. A.; Engberts, J.B.F.N. *J. Am. Chem. Soc.* **1978**, *100*, 5914.
(71) Bunton, C. A.; Sepulveda, L. *J. Phys. Chem.* **1979**, *83*, 680.

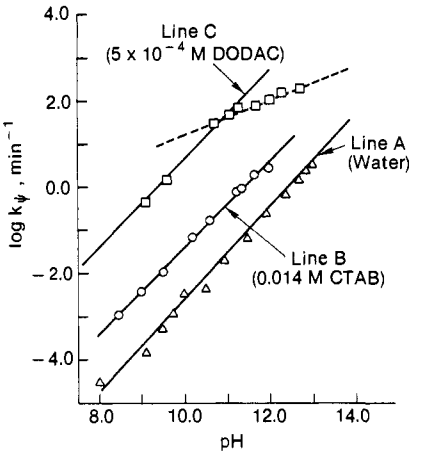


**Figure 2.** Plot of log $k_\psi$ ($min^{-1}$) vs. pH of solution for the hydrolysis of DTNB in water (△), 0.014 M CTAB (○), and $5 \times 10^{-4}$ M DODAC (□).

DODAC are estimated to be 64–100 mV[13] and 0.44[19]–0.54 $M^{-1}$,[73] respectively. Using these values, the predicted binding constant for the interaction of the divalent DTNB anion to CTAB or DODAC would be expected to range from ca. $10^3$ to $5 \times 10^5$ $M^{-1}$. The experimentally determined values $(2–4)10^4$ $M^{-1}$ are well within this predicted range. A similar calculation using this approach predicts a binding constant in the range 7–500 $M^{-1}$ for the binding of the other reactant, hydroxide ion, to the CTAB or DODAC pseudophase. A problem with using this approach stems from the uncertainty in assigning proper values to the surface potential since it is highly sensitive to the experimental conditions (i.e., pH, ionic strength, type of counterions present, etc.).[74] Nevertheless, the binding constants estimated by means of eq 8 and 9 agree with those determined experimentally and obtained from a treatment of the kinetic data (vide infra). Equations developed by Berezin[7,9] for estimation of the degree of binding substrates to micelles appear to be also applicable to surfactant vesicles.

**Alkaline Hydrolysis of DTNB in Water.** Although several articles have briefly described the hydrolysis of DTNB in water,[26–33] there are some discrepancies in the published work[75] and no definitive systematic investigation of this reaction has been conducted.

If the rate-limiting step is as reported (eq 1), then the rate will be given by:

$$\frac{-d[DTNB]}{dt} = \frac{d[TNB]}{dt} = k[DTNB][^-OH] \qquad (10)$$

Pseudo-first-order rate constants, $k_\psi$, have been determined at several base concentrations in the pH 9–13 range (Figure 2). The linear dependence of $k_\psi$ on $[^-OH]$ and the fact that the rates determined from following the decrease of reactant [DTNB] equal to those obtained from following the appearance of the product [TNB] support the indicated mechanism and rate law expression. Additionally, it was noted that the absorbance change observed for TNB (at 412 nm) per mole of DTNB reacted was 0.75 that obtained when 1 mol of DTNB was completely converted to 2 mol of TNB owing to the addition of dithiothretiol. This suggests that for every 2 mol of DTNB consumed in the hydrolysis reaction, 3 (not 4) mol of product TNB forms, which is in agreement with the overall stoichiometry shown in eq 3 based upon earlier literature reports.[26–33] A plot of log $k_\psi$ vs. pH was linear with a slope of 1.06 which clearly indicates that the reaction is first order with respect to hydroxide ion in the pH range studied (refer to line A of Figure 2).[76] Second-order rate constants, determined from $k_\psi = k_2[OH^-]$, were obtained at the indicated temperatures (with literature values in parentheses where available): at 13.5 °C, $k_2 = 0.16$ $M^{-1}$ $s^{-1}$; at 37.0 °C, $k_2 = 1.26$ $M^{-1}$ $s^{-1}$ (1.4 $M^{-1}$ $s^{-1}$ reported at 35 °C[34] and 1.3 $M^{-1}$ $s^{-1}$ reported at 40 °C[26]); and at 25.0 °C, $k_2 = 0.54$ $M^{-1}$ $s^{-1}$ (0.41–0.53 $M^{-1}$ $s^{-1}$ reported[28]). Using our data, the energy of activation, $E_a$, was found to be 15.0 ± 0.3 kcal/mol with the Arrhenius constant (log $A$) equal to 10.7. These values compare favorably with those determined previously at a single hydroxide ion concentration ($E_a$ = 14.9 ± 0.3 kcal/mol, log $A$ = 10.6).[26] Free energy ($\Delta G^*$), enthalpy ($\Delta H^*$), and entropy ($\Delta S^*$) of activation were calculated to be 11.0 kcal/mol, 14.4 kcal/mol, and 11.5 ± 0.3 eu, respectively.

Table III. Observed Pseudo-First-Order Rate Constants for the Reaction of DTNB with Hydroxide Ion in the Presence of CTAB at 26.4 °C[a,b]

| | $10^2k_\psi$, $s^{-1}$ | |
|---|---|---|
| $10^3$[CTAB], M | pH 12.40 | pH 11.70 |
| 0.00 | 1.35 | 0.27 |
| 0.10 | | 0.92 |
| 0.13 | 3.50 | |
| 0.26 | 10.7 | 4.28 |
| 0.51 | | 5.00 |
| 0.64 | 20.0 (24.4) | |
| 0.77 | | 6.15 (9.52) |
| 0.93 | 21.5 (23.2) | |
| 1.03 | 22.9 (23.0) | 8.73 (10.10) |
| 2.06 | 19.6 (19.0) | 7.53 (7.30) |
| 2.58 | 19.8 (17.9) | |
| 3.09 | 16.5 (16.6) | 5.95 (5.92) |
| 4.12 | 14.5 (14.9) | 5.7 (5.00) |
| 5.14 | 13.9 (13.6) | 4.2 (4.35) |
| 10.27 | 10.4 (9.7) | 3.4 (2.70) |
| 20.54 | 6.7 (6.5) | 2.1 (1.60) |
| 30.81 | 5.7 (5.0) | 1.7 (1.11) |
| 41.08 | 4.5 (4.1) | 1.3 (0.90) |
| 51.35 | 3.9 (3.5) | 1.1 (0.70) |

[a] Rates determined from the product TNB buildup monitored at 435 nm. The DTNB concentration was $2.79 \times 10^{-5}$ M. [b] Pseudo-first-order rate constants given in parentheses were calculated from eq 22 using a value of $K_{OH/Br} = 0.08$, $\alpha = 0.20$, $K_{DTNB} = 2 \times 10^4$ $M^{-1}$, and $k_m/V = 0.33$ or 0.42 $s^{-1}$ at pH 11.70 and 12.40, respectively.

In summary, our results indicate that the basic hydrolysis of DTNB in water alone can indeed be adequately described by eq 1–3 in the pH range from about 7.0 to 13.0. Above pH 13.4, the kinetics become more complicated in that there is observed rapid formation of an oxygen-sensitive reddish-brown transient which subsequently decays at a somewhat slower rate. This result can be explained in terms of a recently proposed mechanistic scheme:[77–79]

$$RSSR + {}^-OH \xrightarrow{\text{rapid}} RS^- + RSO^- + H^+ \qquad (11)$$

$$RSO^- \xrightarrow{\text{slow oxidation}} RSO_2^- \text{ or } RO^- + SO_3^{2-} \qquad (12)$$

which involves the relatively rapid formation of the transient sulfenate ion (eq 11). The 3-carboxylato-4-nitrobenzenesulfenate

(72) Yatsimirski, A. K.; Martinek, K.; Berezin, I. V. *Tetrahedron* **1971**, *27*, 2855.
(73) (a) Estimated according to Berezin's procedure (ref 7) using the molecular weight of DODAC as 529.5 g/mol and the density of the "dry surfactant" as ~1.0 g/mL.[73b] (b) Mukerjee, P. *J. Phys. Chem.* **1962**, *66*, 1733.
(74) Pelizzetti, E.; Pramauro, E. *Inorg. Chem.* **1980**, *19*, 1407.
(75) For instance, one study reported that the basic hydrolytic decomposition rate of DTNB at pH 7.0 was 0.10%/h while another reported no apparent hydrolysis.[27a]
(76) Additionally, the reaction was conducted under pseudo-unimolecular conditions with respect to DTNB (i.e., at constant hydroxide ion concentration). Under these conditions, eq 10 reduces to $k_\psi' = k_2'[DTNB]$ and the observed linear dependence of $k_\psi'$ on the DTNB concentration is in accord with the outlined mechanistic scheme.
(77) Davis, F. A.; Friedman, A. J. *J. Org. Chem.* **1976**, *41*, 898.
(78) (a) Hogg, D. R.; Stewart, J. *J. Chem. Soc., Perkin Trans. 2* **1974**, *43*. (b) Blakeley, R. L.; Zerner, B. *J. Am. Chem. Soc.* **1980**, *102*, 6587.
(79) (a) This complication can be circumvented by merely monitoring the rate of DTNB disappearance due to the rapid step in eq 11 using stop-flow techniques and calculating the results via Guggenheim's method.[79b] If this is done, the rates determined agree fairly well with those expected for this reaction (eq 11) that is first order with respect to hydroxide ion. (b) Guggenheim, E. A. *Phil. Mag.* **1926**, *2*, 538.

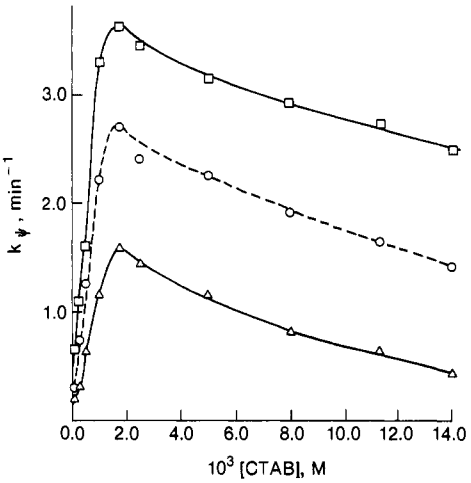


**Figure 3.** Plot of the pseudo-first-order rate constant for the hydrolysis of DTNB ($4.0 \times 10^{-5}$ M), $k_\psi$, vs. CTAB surfactant concentration at pH 11.94 (△), 12.33 (○), and 12.64 (□) at 13.5 °C.

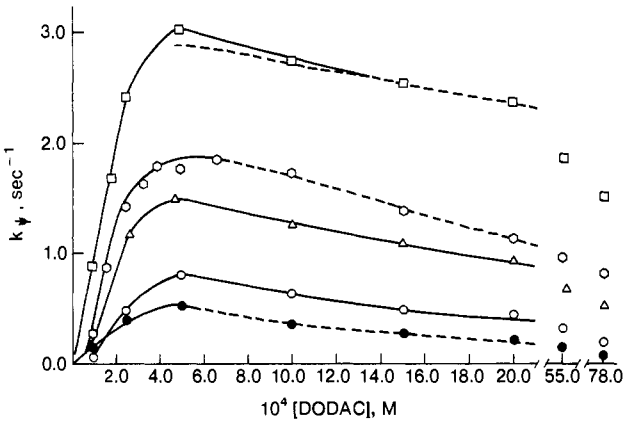


**Figure 4.** Plots of the observed pseudo-first-order rate constants, $k_\psi$, for the hydrolysis of DTNB ($2.67 \times 10^{-5}$ M) vs. the concentration of DODAC surfactant at the following hydroxide ion concentrations: $5 \times 10^{-4}$ M (●), $1.25 \times 10^{-3}$ M (○), $5 \times 10^{-3}$ M (△), $10 \times 10^{-3}$ M (○); and 50 $\times 10^{-3}$ M (□) at 26.3 °C. The broken lines represent the calculated rates from use of eq 22.

ion subsequently undergoes oxidation to form either 3-carboxylato-4-nitrobenzenesulfinate ion (in 3–5 M OH) or 3-carboxylato-4-nitrophenoxide and sulfite ions (in 15–17 M OH) as shown in eq 12. In agreement with this possibility is the observation that the amount of TNB formed per mole of DTNB reacted is one. This is exactly what would be expected if the sulfenic acid decomposition reaction is no longer rapid in comparison to its formation. Similar conclusions were reached in a recent study.[28,78b]

**Kinetics in the Presence of CTAB and DODAC.** Table III and Figure 3 show the pseudo-first-order rate constants obtained for the basic hydrolysis of DTNB as a function of CTAB concentration and of pH, at 26.4 and 13.5 °C, respectively. Figure 4 illustrates the experimental results obtained for the same reaction in the presence of DODAC at 26.3 °C for several pH values. The plots of the pseudo-first-order rate constants for the hydrolysis of DTNB vs. concentration of CTAB (Figure 3) and of DODAC (Figure 4) show the characteristic pattern of a micellar-catalyzed reaction.[3-12] Similar profiles have been observed for numerous other basic hydrolysis reactions.[3-7,80-82] At surfactant concentrations below the cmc, rates are little affected, but close to the cmc, rates start increasing sharply to a maximum value after which they slowly decrease with increasing CTAB or DODAC concentration. For the CTAB micellar system, the maximum rate enhancement occurs at a surfactant concentration of $1.0 \times 10^{-3}$ M at 26.4 °C ($1.75 \times 10^{-3}$ M at 13.5 °C) while in the DODAC vesicle system, it occurs at about $5.0 \times 10^{-4}$ M DODAC at 26.3 °C. The concentrations at which these maxima occur for both surfactant systems appear to be independent of the pH of the solution (Figures 3 and 4).[83]

Figure 2 illustrates the data obtained for this hydrolytic reaction in water alone, and at constant surfactant concentration ([CTAB] = 0.014 M or [DODAC] = $5.0 \times 10^{-4}$ M) as a function of pH. The slopes of the solid lines for DODAC (in the 8.0–11.3 pH range), CTAB, and water are all approximately unity. In water alone, the slope of 1.06 indicates that the reaction is first order in hydoxide ion. Since the pH in the pseudophases of micelles or vesicles cannot be determined, the bulk pH was measured and used in constructing the graphs. Thus, the fact that the lines for the CTAB or DODAC systems are parallel suggests that the concentration of hydroxide ion in the micellar CTAB or DODAC vesicle pseudophase is at least linearly dependent on the hydroxide ion concentration in the bulk aqueous phase over the pH range employed.

It should be noted that for the DODAC system, above pH 11.3, there is a levelling off of the rate (expressed as log $k_\psi$) with increasing pH. This could be due to saturation of the vesicle surface with hydroxide ion, the fact that the amount of hydroxide ion bound to the DODAC phase is no longer a linear function of the total added hydroxide ion,[12a] or charge neutralization induced vesicle–vesicle fusion.[84] Most likely, the latter two factors are operative. Although one might anticipate a linear dependence of log $k_\psi$ on pH at any fixed DODAC vesicle concentration, it has been pointed out by Chaimovich that the amount of bound hydroxide ion is not necessarily at linear function of the total hydroxide concentration.[12a]

Catalytic factors (i.e., the ratios of the maximum rate observed in the presence of the surfactant compared to that in water), determined from the differences between the appropriate sets of parallel lines[82] in Figure 2, are 13 for 0.014 M CTAB, 17–32 for $1.0 \times 10^{-3}$ M CTAB, and 1500 for $5.0 \times 10^{-4}$ M DODAC in the pH range of 8–11.3. Vesicles are apparently 100 times more effective than CTAB micelles in catalyzing the basic hydrolysis of DTNB.

Before continuing with a more quantitative analysis of the data, there are two points that need to be mentioned. First, the rate of the DTNB hydrolysis reaction was found to be dependent upon the age of the DODAC solutions employed. Under given constant conditions, the observed pseudo-first-order rate constants *decreased* as the age of the solutions *increased*. By analyzing the data obtained at pH 12.0 for DODAC solutions that had been prepared 0, 3, 13, and 37 h before the initiation of the reaction, it appears that the observed rates decrease approximately 0.5–1.2%/h. Thus, in order to obtain reproducible and precise results, reactions have been initiated at a constant time after the preparation of the vesicle solutions. The reason for the observed time dependence is most likely due to the changing structures of DODAC vesicles. Vesicles have been reported to undergo fusion with formation of larger and more polydisperse aggregates on prolonged standing.[13,84] As in the case with liposomes,[85a] additives (such as $^-$OH and DTNB) can probably accelerate this fusion process.[84] The size distribution of distearoylphosphatidylcholine vesicles has been found to change as a function of time at all temperatures below the phase-transition temperature, but remained constant at the transition temperature or above.[85b] Significantly, for the DODAC system, it was observed

(80) (a) Quina, F. H.; Politi, M. J.; Cuccovia, I. M.; Baumgarten, E.; Franchetti, S. M.; Chaimovich, H. *J. Phys. Chem.* **1980**, *84*, 361. (b) Bonilha, J. B. S.; Chaimovich, H.; Toscano, V. G.; Quina, F. *Ibid.* **1979**, *83*, 2463.
(81) (a) Politi, M.; Cuccovia, I. M.; Chaimovich, H. *Tetrahedron Lett.* **1978**, *2*, 115. (b) Broxton, T. J.; Duddy, N. W. *Aust. J. Chem.* **1979**, *32*, 1717.
(82) Nome, F.; Schwingel, E. W.; Ionescu, L. G. *J. Org. Chem.* **1980**, *45*, 705.
(83) The surfactant concentration at which the maxima occur in both the DODAC and CTAB systems is dependent upon the ionic strength. Additionally, the observed rate constants decrease as the ionic strength is increased.[26,29]
(84) Tunuli, M. S.; Fendler, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2507.
(85) (a) Sunamoto, J.; Hamada, T.; Muruse, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2773. (b) Larrabee, A. L. *Biochemistry* **1979**, *18*, 3321.

that the rate did not change as a function of time when the hydrolysis reaction was carried out above the phase-transition temperature.

Second, above pH 11.0 in DODAC vesicles and to a lesser extent in the CTAB micellar system at pH >12.0, the reddish-brown transient sulfenate anion formed (eq 11).[77-79] Transient sulfenate formation at lower pH's in the surfactant systems than in water alone is explicable in terms of two possible factors. (1) The micellar or vesicle systems concentrate $^-OH$ ions in the pseudophase where the hydrolysis reaction occurs.[3-13] The "local concentration" of $^-OH$ ion is thus much greater than the calculated stoichiometric hydroxide ion concentration. (2) The stability of sulfenate ion has been reported to increase as the polarity and/or hydrogen-bonding ability of the solvent decreases.[77,78] CTAB and DODAC aggregates provide, of course, less polar and decreased hydrogen-bonding environments than water (Figure 1).

The fact that sulfenic acid anion appears at lower pH's in DODAC vesicles than in CTAB micelles is due to the less polar environment of DODAC and/or to its greater ability to concentrate hydroxide ions. DODAC vesicles are particularly good at concentrating hydroxide ions.[86] For instance, when the bulk aqueous pH is adjusted to 8.75, the apparent pH of the DODAC pseudophase is in excess of 10 as determined by the pH-sensitive probe pyranine.[86] Interestingly, on comparing rate data shown in Figure 2 (line C for DODAC and line A for water) one finds that the rate of reaction in DODAC at pH 8.75 can only be achieved in water alone at a pH around 11.5.

**Quantitative Treatment of the Kinetic Data in the Presence of the CTAB Micelles and DODAC Surfactant Vesicles.** During the past 10 years, several comprehensive kinetic theories have been described by Berezin,[7,9] Romsted-Cordes,[5,8,10] and Chaimovich-Quina[12,18] in order to explain and analyze the catalysis exhibited by micelles on chemical reactions. Our purpose in this section is to show that the general quantitative treatments of the kinetic data provide an adequate description of the alkaline hydrolysis of DTNB in micellar CTAB or in DODAC surfactant vesicles. These treatments allow for calculation of the degree of partitioning or binding of the reagents to the surfactant pseudophase as well as yield a "corrected" rate constant that represents the true rate for the reaction in the micelle or vesicle.

The general form of the Berezin relationship that quantitatively describes the micellar effects on a bimolecular reaction is given by:

$$k = \frac{k_{mv}P_{DTNB}P_{OH}C\bar{V} + k_w(1 - C\bar{V})}{[1 + (P_{DTNB} - 1)C\bar{V}] + [1 + (P_{OH} - 1)C\bar{V}]} \quad (13)$$

where $k_{mv}$ and $k_w$ represent the rate constants in micelles or vesicles and in water, respectively; $P_{DTNB}$ and $P_{OH}$ represent the partition coefficient of the DTNB and hydroxide ion respectively between micelles (or vesicles) and water; $\bar{V}$ is the partial molar volume of the appropriate surfactant molecule in the micelle or vesicle; and $C$ is the stoichiometric surfactant concentration minus its cmc.[7,9] Because both $P_{DTNB}$ and $P_{OH}$ are greater than unity and since, at low surfactant concentrations [where $(C\bar{V} << 1)$], the $(1\text{-}C\bar{V})$ term will approximately equal 1, eq 13 may be simplified by use of eq 8 to:[7,9]

$$k = \frac{(k_{mv}/\bar{V})K_{DTNB}K_{OH}C + k_w}{(1 + K_{DTNB}C)(1 + k_{OH}C)} \quad (14)$$

where $K_{DTNB}$ and $K_{OH}$ represent the binding constants (vide supra).

If $k_w < [k_{mv}K_{DTNB}K_{OH}C/\bar{V}]$, then the rate–surfactant concentration profiles will exhibit a maximum rate enhancement at a particular surfactant concentration, $C_{opt}$, that can be described by:[7]

$$C_{opt} = 1/(K_{DNTB}K_{OH})^{1/2} \quad (15)$$

from which one can easily calculate the product of the reactants' binding to the surfactant systems.

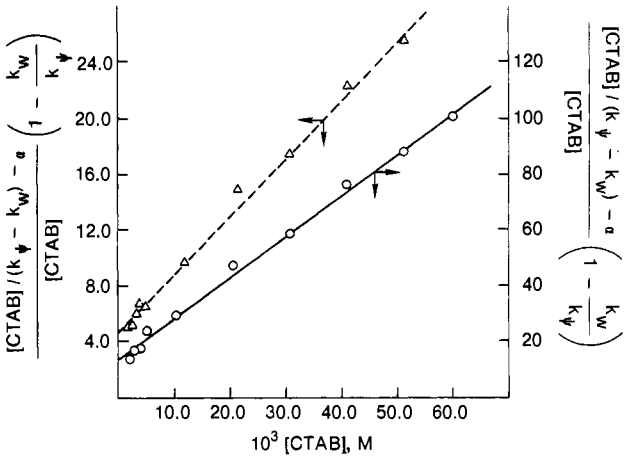


**Figure 5.** Plot of left side of eq 16 vs. [CTAB] for the hydrolysis of DTNB at pH 11.70 (solid line, O) and 12.40 (dashed line, Δ) at 26.4 °C.

For graphical treatment, eq 14 can be transformed into:[7,9,82]

$$\frac{C/(k_\psi - k_w) - \alpha\left(1 - \frac{k_w}{k_\psi}\right)}{C} = \beta + \gamma C \quad (16)$$

where

$$\alpha = \frac{\bar{V}}{k_{mv}K_{DTNB}K_{OH}} \quad (17)$$

$$\beta = \bar{V}(K_{DTNB} + K_{OH})/k_{mv}K_{DTNB}K_{OH} \quad (18)$$

$$\gamma = \bar{V}/k_{mv} \quad (19)$$

Two types of plots can be made which will yield values of either $\alpha$, $\beta$, and/or $\gamma$. Firstly, $\alpha$ can be determined from a plot of eq 16 as $C/(K_\psi - K_w)$ vs. $C$ ($\alpha$ is the intercept or limiting value as $C$ approaches zero). Values of $\alpha$ thus determined are usually not very reliable (±35%) since this analysis requires the use of experimental data points in the region where the surfactant concentrations are lower than $C_{opt}$ but not much greater than the cmc under the kinetic conditions ($C_{opt}$ > [surfactant] > cmc) and show considerable scatter.[82,87] Additionally, uncertainties in the cmc complicate the situation.[87] Alternatively, a plot of the left-hand term of eq 16 vs. $C$ should yield a straight line with slope $\gamma$ and intercept $\beta$.[7,9] The values of $\gamma$ thus obtained are more reliable (typically ±20%) because, at surfactant concentrations greater than $C_{opt}$, the left-hand term of eq 16 becomes insensitive to the errors associated with $\alpha$[82] as well as to the uncertainties in the cmc. Figure 5 shows such a typical plot of the data for the hydrolysis of DTNB at pH 11.70 and 12.40 in CTAB at 26.4 °C.

Since it has been reported that virtually all bivalent substrate ions (such as DTNB) will be bound to the micelle (provided that the ions are of opposite charge),[24,88,89] the rate of reaction in water, $k_w$, will be negligible. If this assumption is operative, Berezin's eq 14 reduces to:

$$k = \frac{(k_{mv}/\bar{V})(K_{DTNB}K_{OH})C}{1 + (K_{DTNB}K_{OH})C + K_{DTNB}K_{OH}C^2} \quad (20)$$

Equation 20 can be rewritten as eq 21,

$$1/k = \bar{V}/k_{mv}(1/K_{OH}) + C\bar{V}/k_{mw} \quad (21)$$

provided $K_{DTNB} >> K_{OH}$ and the surfactant concentration is sufficiently high (i.e., [surfactant] >> $C_{opt}$).[88,89] Typical plots of $1/k$ vs. $C$ should yield straight lines as illustrated in Figure 6 for the indicated CTAB and DODAC surfactant systems. From these plots, values of $k_{mv}$ and $K_{OH}$ were determined.

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Table IV. Summary of the Kinetic Parameters Obtained for the Reaction of DTNB with Hydroxide Ion in the Presence of Micellar CTAB as a Function of pH at 26.4 and 13.5 °C

| parameter determined | pH 11.70[a] | pH 11.94[b] | pH 12.33[b] | pH 12.40[a] | pH 12.64[b] |
|---|---|---|---|---|---|
| $k_m$, $M^{-1}$ $s^{-1}$ [c] | (0.05 ± 0.01)[d]<br>(0.13 ± 0.04)[e] | (0.009 ± 0.003)[d]<br>(0.02 ± 0.005)[e] | (0.009 ± 0.002)[d]<br>(0.03 ± 0.01)[e] | (0.02 ± 0.01)[d]<br>(0.09 ± 0.02)[e] | (0.009 ± 0.002)[d]<br>(0.04 ± 0.01)[e] |
| $K_{OH}$, $M^{-1}$ | (100 ± 10)[d]<br>(150 ± 30)[e] | (300 ± 50)[d,e] | (80 ± 20)[d,e] | (100 ± 15)[d]<br>(150 ± 25)[e] | (50 ± 15)[d]<br>(40 ± 10)[e] |
| $K_{DTNB}$, $M^{-1}$ | (~$10^4$)[d,e] | (~0.1 × $10^4$)[d,e] | (~0.4 × $10^4$)[d,e] | (~0.9 × $10^4$)[d,e] | (~$10^4$)[d,e] |
| $K_{DTNB}K_{OH}$, $M^{-2}$ [f] | $10^6$ | 3.3 × $10^5$ | 3.3 × $10^5$ | $10^6$ | 3.3 × $10^5$ |

[a] Data obtained at 26.4 °C. [b] Data obtained at 13.5 °C. [c] For comparison, the rate in water at 26.4 °C is 0.54 $M^{-1}$ $s^{-1}$ while at 13.5 °C it is 0.16 $M^{-1}$ $s^{-1}$. [d] Determined from plots of the data according to eq 16-19. [e] Determined from plots of the data according to eq 21. [f] Determined from a graph of $k_\psi$ vs. [CTAB] and use of eq 15.

Table V. Summary of the Kinetic Parameters Obtained for the Hydrolysis of DTNB in the Presence of DODAC as a Function of pH at 26.3 °C

| parameter determined | pH 10.70 | pH 11.10 | pH 11.70 | pH 12.00 | pH 12.60 |
|---|---|---|---|---|---|
| $k_v$, $M^{-1}$ $s^{-1}$ | (0.75 ± 0.25)[a,b] | (0.70 ± 0.10)[a,b] | (0.66 ± 0.20)[a,b] | (0.56 ± 0.12)[a,b] | (0.22 ± 0.04)[a,b] |
| $K_{OH}$, $M^{-1}$ | (800 ± 300)[a] | (500 ± 50)[a] | (220 ± 40)[a] | (200 ± 25)[a] | (130 ± 25)[a] |
| $K_{DTNB}$, $M^{-1}$ | (~0.5 × $10^4$)[a] | (~1 × $10^4$)[a] | (~2 × $10^4$)[a] | (~2 × $10^4$)[a] | (~3 × $10^4$)[a] |
| $K_{DTNB}K_{OH}$, $M^{-2}$ [c] | | | (~4.0 × $10^6$)[d] | | |

[a] Determined from plots of the data according to eq 21. [b] Determined from plots of the data according to eq 16-19. [c] Determined from plot of $k_\psi$ vs. [DODAC] and use of 15. [d] The product of the binding constants appear to be independent of the pH.

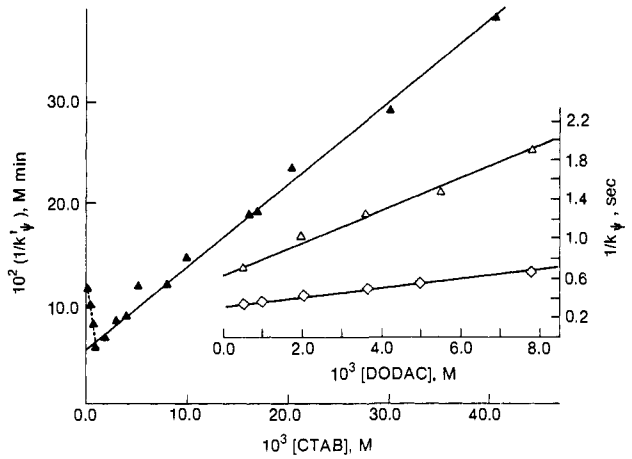


Figure 6. Plot of $1/k_\psi'$ (M min) vs. molar concentration of CTAB for the hydrolysis of DTNB at pH 11.70 (▲) at 26.4 °C. The insert shows a plot of $(1/k_\psi)$ vs. [DODAC] according to eq 21 for the basic hydrolysis of DTNB at pH 11.70 (△) and 12.70 (◇) at 26.4 °C.

By combining the information obtained from the slopes and intercepts of these three types of plots and use of eq 15, 17-19, and 21, estimates of the "true" rate constants, $k_{mv}$, for the hydrolysis reaction in the micellar or vesiclar pseudophase can be made as well as binding constants for the partitioning of DTNB and hydroxide ion to the respective surfactant pseudophase. Experimental results for CTAB micelles and DODAC vesicles determined by this Berezin type of analysis as a function of pH are summarized in Tables IV and V.

As can be seen from Table VI, the "true" second-order rate constants in the CTAB micellar phase (0.03-0.11 $M^{-1}$ $s^{-1}$) and the phase of DODAC vesicles (0.56-0.75 $M^{-1}$ $s^{-1}$) are, within experimental error, the same on average in the DODAC systems and slower by a factor of 5-18 in the CTAB system compared to the value observed in water alone (0.54 $M^{-1}$ $s^{-1}$) when the true concentrations of the reactants in the pseudophase are used. Although it may be fortuitous considering the degree of experimental error involved, it appears that the rate in DODAC vesicles decreases as the pH increases (at pH >11) (refer to Table V).

Alternatively, the "true" rate constants and degree of binding of DTNB can be estimated using the treatment developed by Quina and Chaimovich.[12,80] In this, the binding of hydroxide ion is explained in terms of ion exchange with the micellar counterion

Table VI. Summary of Kinetic Parameters for the Base-Catalyzed Hydrolysis of DTNB in Water, Micellar CTAB, and DODAC Vesicles at 26.4 °C

| | $H_2O$ | CTAB micelles | DODAC vesicles |
|---|---|---|---|
| $k(k_m k_v)$, $M^{-1}$ $s^{-1}$ | 0.56 | 0.10 ± 0.04[a]<br>(1.0 ± 0.1)[c] | 0.65 ± 0.10[b]<br>(6.2 ± 1.4)[d] |
| $K_{DTNB}$, $M^{-1}$ [e] | | ~$10^4$ [f,g]<br>(2.0 × $10^4$)[h] | ~$10^4$ [g]<br>(4.0 × $10^4$)[h] |
| $K_{OH}$, $M^{-1}$ [i] | | (1-2)$10^2$ [g] | (3-8)$10^2$ [g] |

[a] Rate constant in the micellar pseudophase determined by treating the data according to eq 21. [b] Rate constant in the pseudophase of DODAC vesicles determined by treating the data according to eq 21. [c] Rate constant in the micellar pseudophase determined by treating the data according to eq 22-25. [d] Rate constant in the vesicle pseudophase determined by treating the data according to eq 22-25. [e] Substrate micelle (or vesicle) binding constant. [f] Determined from plots of the data according to eq 16-19. [g] Determined from plots of the data according to eq 21. [h] Determined from treatment of data according to eq 22-25. [i] Hydroxide ion micelle (or vesicle) binding constant.

while the binding of the substrate (DTNB) is explained in terms of partitioning. If the reaction proceeds only in the micellar phase (supra vide), then eq 22 can be easily derived;[12]

$$k_\psi = \frac{[OH]_T(k_{mv}/\bar{V})(K_{DTNB}K_{OH/X})([X]_{mv}/[X]_w)}{(1 + K_{DTNB}C)(1 + K_{OH/X}[X]_{mv}/[X]_w)} \quad (22)$$

where $[OH]_T$ represents the total concentration of hydroxide ion, $k_{mv}$ the second-order rate constant in the micellar or vesicle phase, $K_{DTNB}$ the binding constant of DTNB to the CTAB or DODAC, and $K_{OH/X}$ the ion exchange constant for the surfactant counterion-hydroxide ion equilibrium (X = Br for CTAB and Cl for DODAC); the subscripts mv and w are used to indicate the micellar or vesicle and water phases, respectively.

To make use of eq 22, the values for the concentration of hydroxide ion in the micellar or vesicle phase and the ratio of the counterion concentration between the micellar (or vesicle) and aqueous phases are required. The concentration of surfactant bound hydroxide ion can be calculated from:[12,80]

$$[OH]_{mw} = \frac{-A + [A^2 + 4(1 - K_{OH/X})[OH]_T K_{OH/X}(1 - \alpha)C]^{1/2}}{2(1 - K_{OH/X})} \quad (23)$$

where $A$ equals

$$A = \alpha C + \text{cmc} + K_{OH/X}[OH]_T + (1 - \alpha)CK_{OH/X} \quad (24)$$

By use of the $[OH]_{mv}$ as calculated from eq 23, the ratio of the surfactant counterion concentration between the micellar or vesicle and aqueous phases can be calculated from:

$$\frac{[X]_{mv}}{[X]_w} = \frac{(1 - \alpha)C - [OH]_{mv}}{\alpha C + \text{cmc} + [OH]_{mv}} \quad (25)$$

Using eq 22–25, it was possible to satisfactorily explain the experimental data (for surfactant concentrations greater than $C_{opt}$).[90] Indeed, the rate data given in parentheses in Table III for CTAB were calculated from eq 22 using values of 0.08 for $K_{OH/Br}$ and $\alpha = 0.20$.[12,80] Values of $2 \times 10^4$ $M^{-1}$ for $K_{DTNB}$ at all pHs and of 0.33 and 0.42 $s^{-1}$ for $k_m/\bar{V}$ at pH values 11.70 and 12.40 were found to give the best fits with the CTAB data at 26.4 °C (refer to Table III). For the DODAC system, the dashed lines in Figure 4 were calculated from eq 22, using values of 0.14 for $K_{OH/Cl}$ and $\alpha = 0.20$ which were chosen by analogy with the tetradecyltrimethylammonium chloride micellar system.[80b] Values of $4 \times 10^4$ $M^{-1}$ for $K_{DTNB}$ at all pHs and 3.2, 3.2, and 3.8 $s^{-1}$ for $k_v/\bar{V}$ at hydroxide ion concentrations of $5 \times 10^{-4}$, $1 \times 10^{-2}$, and $5 \times 10^{-2}$ M, respectively, were found to give the best fits with the DODAC rate data (Figure 4).

Roughly the same conclusions can be reached from these results as those that were obtained from use of the Berezin approach. Namely, the "true" second-order rate constants are about six- to eight-fold greater in the DODAC vesicle phase compared to that of the CTAB micelle phase. Both kinetic treatments yield binding constants for the incorporation of DTNB into the micellar or vesicle phase that are in good agreement with those determined independently from spectroscopic studies. The main difference in the results as obtained from the two kinetic approaches is that the ion-exchange treatment yields "true" second-order rate constants (0.9–1.2 $M^{-1}$ $s^{-1}$ for CTAB and 4.8–7.6 $M^{-1}$ $s^{-1}$ for DODAC) that are about 10-fold greater than those obtained from Berezin's treatment.

The results from these two treatments of the data indicate that the observed rate enhancements in CTAB and DODAC aggregates (15× and 1500×, respectively) are primarily due to the increased concentration of the reactants in the micelle or vesicle phase. This is a consequence of their efficient binding to the respective pseudophases which effectively reduces their volume element. The higher "catalytic" factor of DODAC as compared to CTAB can be attributed to the increase in the binding constants of the reactants to their respective pseudophase ($\sim 4 \times 10^6$ $M^{-2}$ for DODAC compared to $\sim 10^6$ $M^{-2}$ for CTAB) and/or possibly to a small microscopic polarity effect, since the polarity and hydrogen-bonding ability of the DODAC environment is somewhat diminished compared to that of CTAB (vide supra).

In view of the assumptions and approximations involved, the good agreement between spectroscopically and kinetically determined binding constants for the incorporation of DTNB into the CTAB micelles and DODAC vesicles is remarkable and lends credence to the validity of the treatments employed. The apparent rate enhancements as well as the similar or slightly retarded "true" second-order rate constants observed in many other types of bimolecular reactions[3-12,43,81,82,91] in the presence of micelles (and in one previous instance in vesicles[19]) have been rationalized in an analogous manner and appear to be a general phenomenon in surfactant catalysis.

## Conclusions

Rate enhancements for the basic hydrolysis of DTNB can be explained entirely on the basis of concentration of the reagents in the pseudophases of micelles and vesicles. Intrinsic effects of the pseudophases on reactivity are of little or no importance. The obtained results provide additional much needed information on the analysis of kinetic data in surfactant vesicles and allow for further comparison and assessments of catalysis in vesicles and micelles. Most importantly, the results of this work indicate applicability of kinetic treatments derived for micellar catalysis to surfactant vesicles.

The present work is also significant in the context of analytical applications. It has shown the importance of selecting the correct wavelength for measuring TNB absorptions in the quantitative determinations of cyanide, sulfite ions, and thiols in alcohols, surfactants, and polymers.[29,56,92-95]

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(90) The experimental rate data obtained at surfactant concentrations below $C_{opt}$ (i.e., $< 5 \times 10^{-4}$ M for DODAC and $< 1 \times 10^{-3}$ M CTAB) do not fit the calculated values. This is due to the fact that our simplistic approach neglects incorporation of appropriate ion-exchange constants ($K_{DTNB/X}$, $K_{OH/DTNB}$) that would describe the competitive binding of the ionic DTNB substrate to the cationic surfactant phase. Consequently, the strong binding of the dianionic DTNB will exert a significant influence on the amount of hydroxide ion bound to the CTAB or DODAC pseudophases, especially at the lower surfactant concentrations.[80a] Another problem with this type of calculation at very low surfactant concentrations stems from the assumption that the concentration of monomeric surfactant is constant and equal to the cmc[91] (especially for substances such as DTNB that can induce micellization and markedly perturb the aggregate structure and cmc).

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