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PHYSICAL CHEMICAL STUDIES OF THE AGGREGATION AND CATALYTIC PROPERTIES OF THE SURFACTANT CETYLDIMETHYLETHYLAMMONIUM BROMIDE (CDEAB)

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ABSTRACT

The micellization of cetyldimethylethylammonium bromide (CDEAB) in water was studied by means of surface tensiometry. The critical micellar concentration (CMC) was determined at 25°, 32° and 40 °C and thermodynamic properties such as the free energy of micellization (ΔG^o_{mic}), enthalpy (ΔH^o_{mic}) and entropy (ΔS^o_{mic}) of micellization were measured. The CMC at 25 °C was 9.05×10^{-4} M and the corresponding values of the thermodynamic parameters were: $\Delta G^o_{mic} = -4.15$ kcal/mol; $\Delta H^o_{mic} = -1.37$ kcal/mol and $\Delta S^o_{mic} = +9.33$ e.u. Micelles of the surfactant CDEAB were good catalysts for the alkaline hydrolysis of p-nitrophenyl diphenyl phosphate (NPDPP) with a maximum catalytic factor of approximately 80, comparable to that of CTAB. Typical activation parameters measured for 0.005 M NaOH were: $E_a = 9.0$ kcal/mol; $\Delta H^{o\neq} = 8.4$ kcal/mol; $\Delta G^{o\neq} = 19.2$ kcal/mol and $\Delta S^{o\neq} = -36.3$ e.u. The kinetic results were also analyzed in terms of the pseudo-phase ion exchange models (PPIE) and showed that the model is applicable and gave reasonable fits.

KEYWORDS: cetydimethylethylammonium bromide; micellization; micellar catalysis; phosphate esters

RESUMO:

A micelização do brometo de cetildimetiletilamônio (CDEAB) em água foi estudada por métodos de tensiometria superficial. A concentração micelar crítica (CMC) foi determinada a 25°, 32° e 40 °C e propriedades termodinâmicas tais como a energia livre (ΔG^o_{mic}) de micelização, entalpia (ΔH^o_{mic}) e entropia (ΔS^o_{mic}) de micelização foram medidas. A CMC a 25 °C foi $9,05 \times 10^{-4}$ M e os valores correspondentes para os parâmetros termodinâmicos foram os seguintes: $\Delta G^o_{mic} = -4,15$ kcal/mol; $\Delta H^o_{mic} = -1,37$ kcal/mol e $\Delta S^o_{mic} = +9,33$ e.u. Micelas do surfactante CDEAB foram bons catalisadores para a hidrólise alcalina do p-nitrofenil difenil fosfato, com um fator catalítico máximo de aproximadamente 80, comparável ao do CTAB. Parâmetros de ativação representativos medidos experimentalmente para 0,005 M NaOH foram: $E_a = 9,0$ kcal/mol; $\Delta H^{o\neq} = 8,4$ kcal/mol; $\Delta G^{o\neq} = 19,2$ kcal/mol and $\Delta S^{o\neq} = -36,3$ e.u. Os resultados cinéticos também foram analisados em termos do modelo de pseudo-fase de troca iônica (PPIE) e mostraram que o modelo é aplicável e satisfatório.

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INTRODUCTION

The present paper deals with the study of the micellization process of surfactant cetyldimethylethylammonium bromide or hexadecyldimethylethylammonium bromide [CDEAB, $CH_3CH_2N^+(CH_3)_2CH_2(CH_2)_{14}CH_3\ Br^-$] and its use as a catalyst for the alkaline hydrolysis of p-nitrophenyl diphenyl phosphate.

In the past, as a part of our systematic investigation of the process of micellization we have studied many surfactants in water, non-aqueous solvents and water solutions containing various co-solvents or additives by means of a variety of experimental techniques including surface tensiometry, nuclear magnetic resonance (NMR) and quasi-elastic light scattering (QELS)[1-14]. The surfactant CDEAB was chosen because of its similarity to cetyltrimethylammonium bromide (CTAB).

Phosphate esters are compounds with interesting biological and physiological properties and are widely used as pesticides, drugs and nerve gases. Their accumulation and their effect in the environment are of paramount importance[15,16].

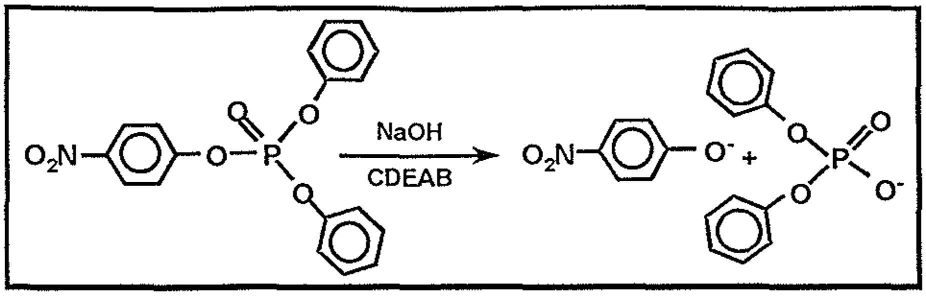
In studies reported in the literature we have shown that the hydrolysis of di- and tri-substituted phosphate esters is catalyzed by micelles of cetyltrimethylammonium bromide [$C_{16}H_{33}N^+(CH_3)_3\ Br^-$], N,N-dimethyl-N-hydroxyethyldodecylammonium bromide [DHEDAB, n-$C_{12}H_{25}N^+(CH_3)_2CH_2CH_2OH\ Br^-$] and N,N-dimethyl-N-hydroxyethylcetylammonium bromide [CHEDAB, n-$C_{16}H_{33}N^+(CH_3)_2CH_2CH_2OH\ Br^-$][17]. The last two, CHEDAB and DHEAB are among the first examples of surfactants that form functional micelles.

Micellar aggregates of DHEDAB and CHEDAB are excellent catalysts for the hydrolysis of both lithium p-nitrophenyl ethyl phosphate (LiPNEP) and p-nitrophenyl diphenyl phosphate (NPDPP) in the presence of hydroxide ions, with over a 300-fold rate enhancement for the hydrolysis of the triaryl phosphate in the presence of CHEDAB. The dependence of the reaction rate on hydroxide ion concentration and the catalytic effect have been explained in terms of nucleophilic participation of the alkoxide ion of DHEDAB and CHEDAB, with pK_a of 12.4 and 12.9, respectively for the ionization of the hydroxyl groups[17]. For reactions with fluoride ion, the hydroxy-substituted surfactants are no better catalysts than the corresponding alkyltrimethylammonium bromides, suggesting that electrophilic catalysis is relatively unimportant. Cetylpyridinium bromide [CPBr, $C_5H_5N^+C_{16}H_{33}\ Br^-$] is similar to CTAB at low hydroxide concentration and has a slightly more pronounced effect with fluoride ion. Zwitterionic surfactants such as lauryl carnitine chloride (LCCl) and palmityl carnitine chloride (PCCl) have little effect on the rate of hydrolysis of LiPNEP[18,19].

The addition of primary amines enhanced the rate of reaction in the presence of CTAB and CHEDAB for the triaryl phosphate, but much of the increase was due to attack by amine on the aryl group. In the absence of micelles, amines increased the overall rate of the reaction by attacking the aryl group without markedly catalyzing hydrolysis[20].

The micellar catalyzed oxidative cleavage of a carbon-carbon bond in Dicofol$^{(TM)}$[21] and the micellar catalyzed dehydrochlorination of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) and some of its derivatives have also been subject of our investigations[22,23]. In recent studies we have reported results obtained for the hydrolysis of p-nitrophenyl diphenyl phosphate in aqueous solutions in the presence of micelles of diethyl heptadecyl imidazolinium ethyl sulfate (DEHIES) and CTAB, sodium hydroxide and dimethylsulfoxide (DMSO) and analyzed the effect of internal pressure of the medium, dielectric constant, donor number and polarity of the solvent and the effect of DMSO on micellization[24-28].

The present paper deals with the study of the hydrolysis of p-nitrophenyl diphenyl phosphate (NPDPP) in the presence of micelles of cetyldimethylethylammonium bromide (CDEAB) in aqueous solutions containing NaOH, as illustrated by the following scheme:



EXPERIMENTAL PROCEDURE

Materials. The p-nitrophenyl diphenyl phosphate (NPDPP) was prepared using standard methods[29,30]. A sample was also obtained from Prof. Fred Menger, Emory University, Atlanta, Georgia, USA. The surfactant cetyldimethylethylammonium bromide (CDEAB) was purchased from Chem. Service, West Chester, Pa., USA. The sodium hydroxide was analytical reagent grade and was purchased from Merck Co.

Surface Tension Measurements. All solutions were prepared volumetrically with deionized double distilled water and contained a series of at least fifteen different concentrations of CDEAB. The surface tension of the CDEAB-H_2O solutions was measured at 25°, 32° and 40 °C by means of a Fisher Model 21, Semi-Automatic Tensiometer. Ten milliliters aliquots of the solutions were placed in a Petri dish with a diameter of 6 cm. The temperature of the solutions was brought to the chosen temperature using a water bath and the Petri dish was kept at the desired temperature by placing it in a container through which water was circulated from the constant temperature bath. The tensiometer was set a constant height. The final surface tension of any solution was the average of at least three independent measurements.

The critical micellar concentrations (CMC's) were determined from plots of the surface tension of the solutions versus the concentration or log concentration of CDEAB. The marked change in the plots was taken as an indication of micelle formation and the inflection point was considered to correspond to the CMC.

The thermodynamic parameters ΔG^{o}_{mic}, ΔH^{o}_{mic} and ΔS^{o}_{mic} were determined using standard equations[31,32] derived on the basis of the assumption that the process of micellization involves the formation of a distinct micellar phase at the CMC and that the concentration of monomers in solution is constant, once micelles are formed. The experimental accuracy in the values determined for ΔG^{o}_{mic} is about ± 100 cal/mole. On the other hand, ΔH^{o}_{mic} and ΔS^{o}_{mic} are more approximate since they were calculated on the basis of measurements at three temperatures only.

Kinetic Measurements. The hydrolysis of p-nitrophenyl diphenyl phosphate was studied spectrophotometrically by measuring the rate of appearance of the p-nitrophenoxide anion at 4030 Å with a Varian DMS-80 spectrophotometer equipped with a temperature controlled cell compartment. The reaction was studied at 15°, 25° and 35°C at various concentrations of NaOH and CDEAB. The pseudo-first order rate constant (k_ψ), in s^{-1}, was determined from linear plots of logarithm of absorbance versus time and the second order rate constants (k_{2m}) in the micellar phase and (k_2^0) in the aqueous phase, in $s^{-1}M^{-1}$, were calculated from k_ψ and the hydroxide ion concentration. Activation parameters such as the activation energy (E_a), the activation entalphy ($\Delta H^{o\neq}$) and the activation entropy ($\Delta S^{o\neq}$) were determined from experimental k_ψ values measured at three different temperatures using the following equations.

$$\ln k_\psi = \ln A - (E_a/R)(1/T) \quad (1)$$

$$\Delta H^{o\neq} = E_a - RT \quad (2)$$

$$\Delta S^{o\neq} = 4.576\,(\log k_\psi - 10.753 - \log T + E_a/4.576T) \quad (3)$$

$$\Delta G^{o\neq} = \Delta H^{o\neq} + \Delta S^{o\neq} \quad (4)$$

where, R corresponds to the gas constant and T to the absolute temperature.

RESULTS AND DISCUSSION

Some typical experimental results obtained for the surface tension of CDEAB in water solutions at 25° and 32°C are illustrated in Figure 1.

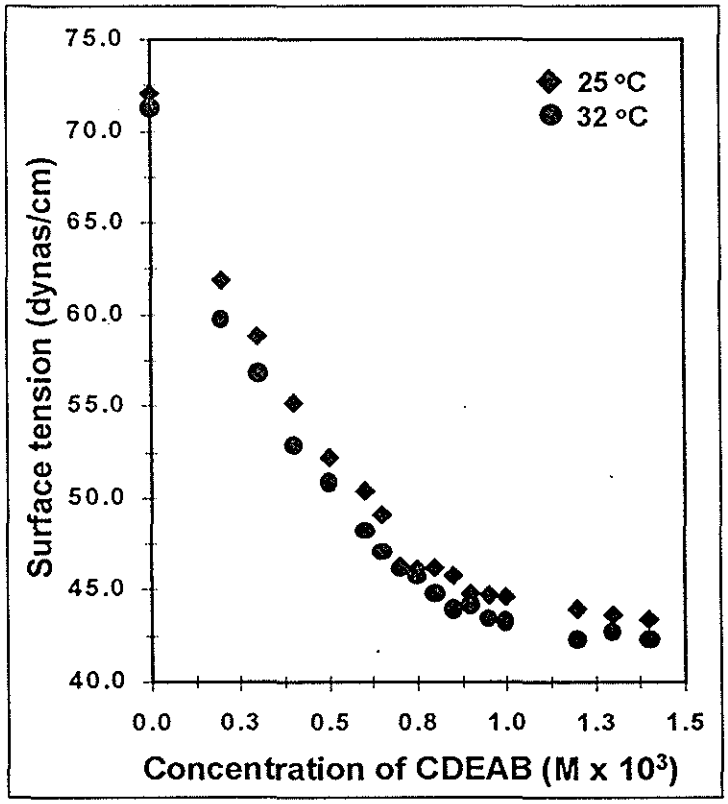


Figure 1. Plot of Surface Tension versus Concentration of Cetyldimethylethylammonium Bromide (CDEAB) in water at 25° and 32°C.

All plots of surface tension versus the concentration of CDEAB exhibited initial marked drops and subsequent leveled off. The inflection point in the given curve was taken as the CMC. At times, plots of surface tension versus the logarithm of the concentration of surfactant gave a better determination for the CMC. Such results are shown in Figure 2 for the same temperatures.

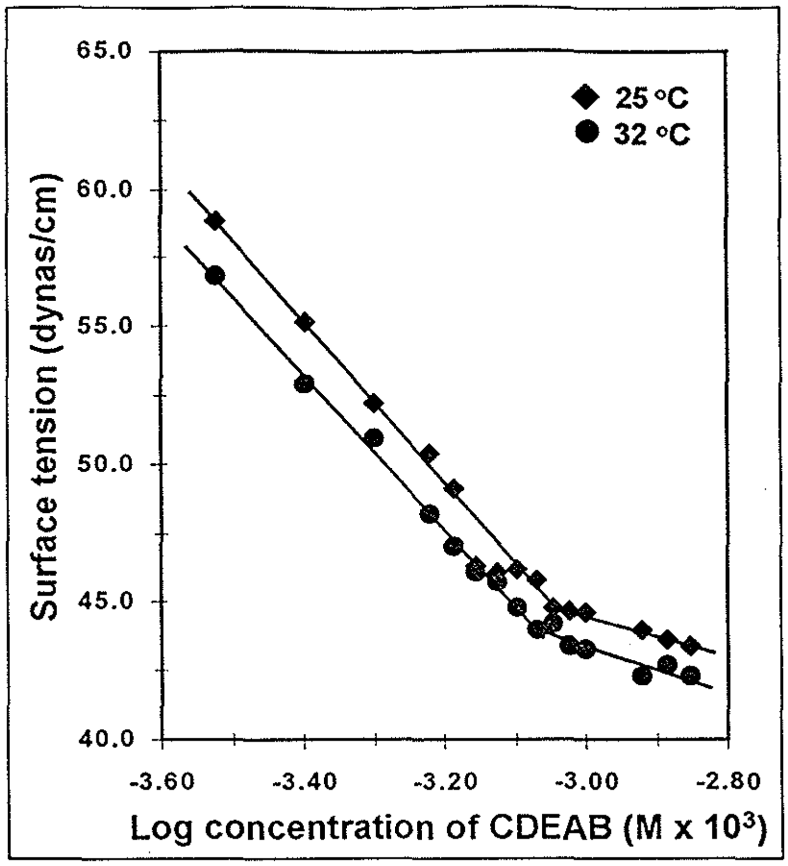


Figure 2. Plot of Surface Tension versus Logarithm of the Concentration (M x 10^{-3}) of Cetyldimethylethylammonium Bromide (CDEAB) in water at 25° and 32°C.

The experimental values determined for the critical micellar concentration (CMC) are summarized in Table I and compared to cetyltrimethylammonium bromide (CTAB). Table II illustrates the experimental values obtained for the thermodynamic functions, i.e., the standard free energy of micellization, ΔG^{o}_{mic}, the enthalpy, ΔH^{o}_{mic}, and the standard entropy of micellization ΔS^{o}_{mic} at 25°C, again compared to CTAB[7,11,14]. As expected, the difference between the experimental values obtained for the CMC and the thermodynamic properties is very small; the difference in the structure of the two surfactants being only the substitution of one of the head CH_3- groups by an ethyl group.

Table I. Critical Micellar Concentration (CMC) of Cetyldimethyethyllammonium Bromide (CDEAB) in Aqueous Solutions Compared to CTAB[14]

Surfactant	Temperature (°C)		
	25	32	40
CDEAB	9.05 x 10^{-4} M	9.30 x 10^{-4} M	10.0 x 10^{-4} M
CTAB	9.20 x 10^{-4} M	---	10.0 x 10^{-4} M

Table II. Some Thermodynamic Properties for the Formation of Micelles of Cetyldimethylethylammonium Bromide (CDEAB) in Water at 25 °C Compared to CTAB[14]

Surfactant	Free Energy of Micellization at 25 °C ΔG^o_{mic} (kcal/mole)	Enthalpy of Micellization ΔH^o_{mic} (kcal/mole)	Entropy of Micellization at 25 °C ΔS^o_{mic} (e.u.)
CDEAB	-4.15	-1.37	+9,33
CTAB	-4.14	-1.03	+10.43

Typical profiles for the pseudo-first order rate constant, k_ψ, as a function of the concentration of CDEAB for the hydrolysis of p-nitrophenyl diphenyl phosphate (NPDPP) at 25°C in aqueous solutions containing various concentrations of NaOH, ranging from 0.001 M to 0.010M are shown in Figure 3.

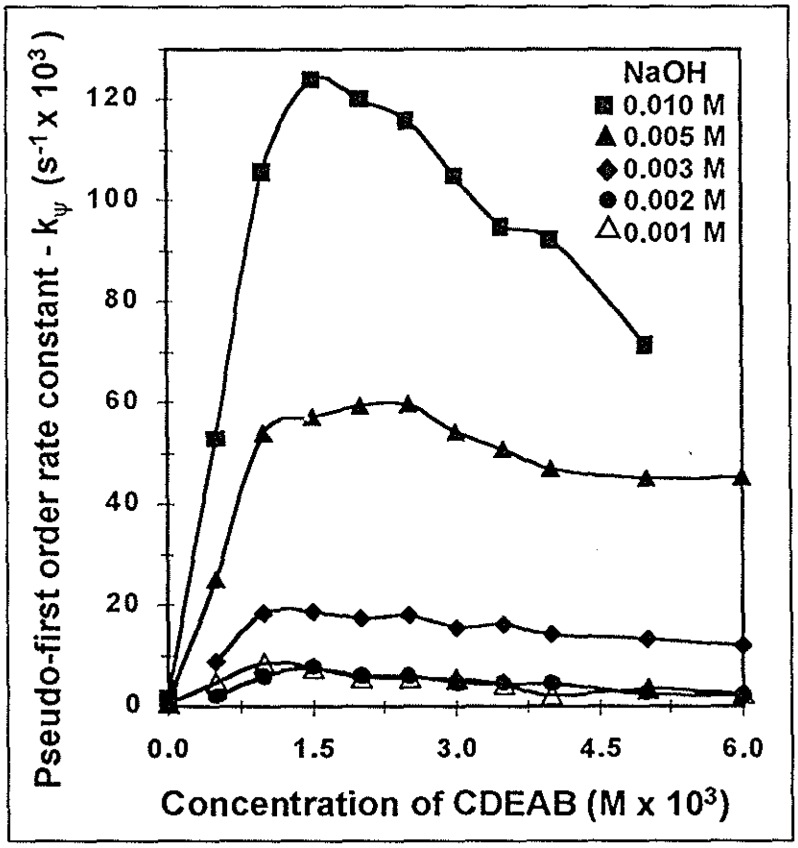


Figure 3. Rate Profiles for the Hydrolysis of p-Nitrophenyl Diphenyl Phosphate in Aqueous Solutions of NaOH and Various Concentrations of CDEAB at 25°C.

The experimental rate profiles obtained are characteristic of micellar catalyzed reaction in aqueous solutions with a maximum at 2.0 x 10^{-4} M CDEAB, similar to that measured for CTAB. The addition of CDEAB to the reaction medium causes an increase in the rate of hydrolysis up to a point (the maximum in rate) where there is total incorporation of the substrate in the micellar phase. Subsequent addition of the surfactant causes a decrease in the reaction rate, probably due to the dilution of the reactive counter-ions in the Stern layer of a higher number of micelles.

Typical activation parameters measured for the reaction with CDEAB are shown in Table III. As can be seen from the analysis of the results the activation parameters for the two surfactants are very similar and comparable to others measured for micellar catalyzed reactions. The addition of the surfactant in the form of micelles causes a decrease of approximately 5 kcal/mol in the activation energy.

Table III. Activation Parameters for the Hydrolysis of p-Nitrophenyl Diphenyl Phosphate in Aqueous Solutions of 0.005 M NaOH in the Presence of CDEAB and CTAB[28] at 25 °C.

Surfactant	Concentration ($M \times 10^4$)	E_a (kcal/mole)	$\Delta H^{0\neq}$ (kcal/mole)	$\Delta G^{0\neq}$ (kcal/mole)	$\Delta S^{0\neq}$ (e.u.)
--	--	+ 15.2	+14.6	+21.3	-22.2
CDEAB	18	+ 9.0	+ 8.4	+19.2	-36.3
CTAB	15	+11.4	+10.8	+18.7	-26.6
CTAB	20	+10.5	+ 9.9	+18.8	-29.9

Most of the models proposed for micellar catalysis[31-38] consider the partition coefficient for the substrate between the micellar and aqueous phase and the distribution of the reagents between the two phases. The hydrolysis of NPDPP with hydroxide ion in the presence of CDEAB may be considered a bimolecular reaction of OH^- ion and the substrate. Since the concentration of OH^- in the micellar phase is dependent on the concentration of both bromide ions and surfactant, a quantitative treatment of the reaction rate must consider ion exchange on or near the micellar surface. For the reaction under consideration, the model proposed by Quina and Chaimovich[38] reduces to Equation 5, that gives the theoretical dependence of the pseudo-first order constant, k_ψ, as a function of the total hydroxide ion concentration

$$k_\psi = \frac{\{(k_{2m}/V)\, K_S K_{OH/Br}\, [(Br)_m/(Br)_w] + k_2{}^0\}(OH)_T}{(1+K_S C_D)\,[1+K_{OH/Br}\,(Br)_m\,(Br)_w]} \qquad (5)$$

where, C_D is the concentration of micellized surfactant, V is the molar volume of the reactive region at the micelar surface, k_ψ is the pseudo-first order rate constant, k_{2m} is the second order rate constant in the micellar phase, $k_2{}^0$ is the second order constant in the aqueous phase, $K_{OH/Br}$ is the ion exchange constant, K_s is the binding constant for the substrate, $(Br)_m$ is the concentration of Br^- in micellar phase, $(Br)_w$ is the concentration of Br^- in aqueous phase, $(OH)_T$ is the total concentration of hydroxide ions and V is the molar volume of surfactant.

With substrates such as p-nitrophenyl diphenyl phosphate that are very insoluble in water and are solubilized by CDEAB the expression for $k_\psi$can be reduced to a simpler form given by Equation (6):

$$k_\psi = \frac{k_{2m}}{C_D V}\,(OH)_T\,\frac{K_{OH/Br}[(Br)_m/(Br)_w]}{[1+K_{OH/Br}\,(Br)_m\,(Br)_w]} \qquad (6)$$

The concentration of Br^- in the micellar and aqueous phases can be obtained using the following equations[39,40]:

$$A_1 = C_D + CMC + K_{OH/Br}\,(OH)_T + (1 - \alpha)\,C_D\,K_{OH/Br} \qquad (7)$$

$$(OH)_m = \frac{(-A_1) + [(A_1)^2 + 4\,(1 - K_{OH/Br})\,(OH)_T\,K_{OH/Br}\,(1 - \alpha)\,C\,]^{0.5}}{2\,(1 - K_{OH/Br})} \qquad (8)$$

$$(B_r)_m = (1 - \alpha)\,C_D - (OH)_m \qquad (9)$$

$$(Br)_w = \alpha\,C_D + CMC + (OH)_m \qquad (10)$$

where CMC is the critical micellar concentration, α is the degree of ionization of the micelle and $(OH)_m$ is the concentration of OH^- in the micellar phase.

We have calculated the theoretical values of k_ψ for the reaction discussed above using $\overline{V}$ = 0.37 l/mol; $K_{OH/Br}$ = 0.08; α = 0.20 and various concentrations of CDEAB and NaOH. The results obtained for the calculated values of k_ψ using different values for k_{2m} compared to the experimental data are illustrated in Figure 4.

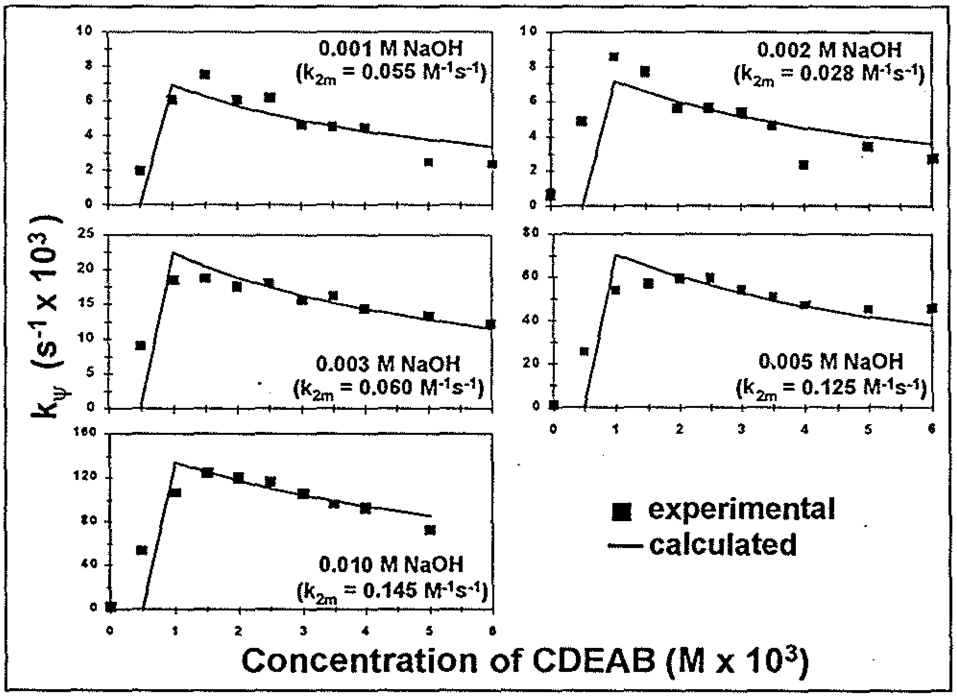


Figure 4. Experimental and Theoretical k_ψ Values for the Hydrolysis of p-Nitrophenyl Diphenyl Phosphate in Aqueous Solutions of NaOH and Various Concentrations of CDEAB at 25°C.

The best fits between the experimental and theoretical k_ψ values are obtained using a variable k_{2m}, between 0.028 $M^{-1}s^{-1}$ and 0.145 $M^{-1}s^{-1}$ indicating that the pseudo-phase ion exchange model (PPIEM) gives a reasonable agreement for this micellar catalyzed reaction.

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