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MICELLAR CATALYZED HYDROLYSIS OF LITHIUM *p*-NITROPHENYL ETHYL PHOSPHATE (LiPNEF) AND THE PSEUDO PHASE ION EXCHANGE MODEL

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ABSTRACT

The hydrolysis of lithium p-nitrophenyl ethyl phosphate (LiPNEF) was studied at 25º, 35º and 45ºC by spectrophotometric techniques in the presence of micelles of cetyltrimethylammonium bromide (CTAB), sodium hydroxide and salt. The concentraion of NaOH used varied from 0,050 to 5,00M and the NaCl ranged from 0,0050 to 0,030 M. Pseudo-first order rate constants (k_ψ) and second order rate constants (k_2) and activation parameters such as E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ were measured. The system was also studied by tensiometric, viscosity and quasi-elastic light scattering methods. At low concentrations of NaOH (below 0,55 M), the reaction can be explained in terms of conventional models of micellar catalysis, including the pseudo-phase ion exchange model. For higher concentration of NaOH, conventional models of micellar catalysis are not applicable. In fact, at high hydroxide concentration, the system no longer contains micelles but liquid crystalline mesophases and a model analogous to phase transfer catalysis appears to be more appropriate.

RESUMO

A hidrólise do lítio p-nitrofenil etil fosfato (LiPNEF) foi estudada a 25º, 35º e 45ºC por métodos espectroscópicos na presença de micelas de brometo de cetiltrimetilamônio (CTAB), hidróxido de sódio e sal. A concentração de NaOH variou entre 0,050 e 5,00 M e de NaCl entre 0,0050 e 0,030 M. Foram medidas constantes de velocidade de pseudo-primeira ordem (k_ψ) e segunda ordem (k_2) e parâmetros de ativação tais como E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$ e $\Delta S^{\neq}$. O sistema também foi estudado por métodos de tensiometria, viscosidade e espalhamento quase-elástico de luz. À concentrações baixas de NaOH (menos de 0,55M) a reação pode ser explicada em termos termos de modelos convencionais de catálise micelar, inclusive o modelo de troca iônica. Para concentrações mais elevadas de NaOH, os modelos convencionais não são aplicáveis. De fato, a concentrações elevadas de NaOH, o sistema não contém mais micelas, mas mesofases líquido-cristalinas e um modelo análogo à catálise por transferência de fase parece mais adequado.

KEYWORDS: Micellar Catalysis, Phosphate Esters, Pseudo Phase Ion Exchange Model, Cetyltrimethylammonium Bromide-CTAB.

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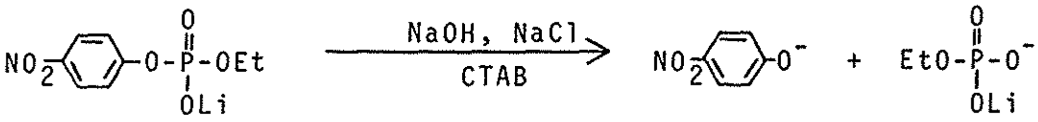
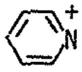
INTRODUCTION

The present paper deals with the hydrolysis of lithium p-nitrophenyl ethyl phosphate (LiPNEF) in aqueous solutions in the presence of micelles or other aggregates of cetyltrimethylammonium bromide (CTAB) and varying concentraions of NaOH and NaCl. The reaction under consideration is illustrated below.



The organophosphorus compound under consideration (LiPNEF) is a common pesticide related to Paroxon and Parathion that have a wide use in agriculture.[1,2]

In previous studies we have shown that the hydrolysis of di- and tri-substituted phosphate esters is catalyzed by micelles of cetyltrimethylammonium bromide $\left[C_{16}H_{33}\overset{+}{N}(CH_3)_3\ Br^-\right.$, $\left.\text{CTAB}\right]$ and also by micelles of N,N-dimethyl-N-hydroxyethyl-dodecylammonium bromide, $\left[\text{DHEDAB},\ n\text{-}C_{12}H_{25}\overset{+}{N}(CH_3)_2CH_2CH_2OH\ Br^-\right]$ and N,N-dimethyl-N-hydroxyethylcetylammonium bromide, $\left[\text{CHEDAB},\ n\text{-}C_{16}H_{33}\overset{+}{N}(CH_3)_2CH_2CH_2OH\ Br^-\right]$.[3] Micelles of DHEDAB and CHEDAB are excellent catalysts for the hydrolysis of both LiPNEF and p-nitrophenyl diphenyl phosphate in the presence of OH^-, with over 300-fold rate enhancement for the hydrolysis of the triaryl phosphate in the presence of CHEDAB. The catalytic effect and the dependence of the reaction rate on hydroxide ion concentration has been explained in terms of nucelophilic 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 group. 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,  $\overset{+}{N}C_{16}H_{33}\ Br^-$] has approximately the same effect as CTAB at low hydroxide concentration and 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 LiPNEF.[4,5]

The addition of primary amines increased the rate of reaction in the presence of CTAB and CHEDAB for the triarylphosphate, 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.[6]

The micellar catalyzed oxidative cleavage of a carbon-carbon bond in Dicofol[7] 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 the subject of our investigations.[8,9]

In more recent studies we have reported results obtained for the hydrolysis of *p*-nitrophenyl diphenyl phosphate in aqueous solutions in the presence of micelles of diethylheptadecylimidazolinium ethyl sulfate (DEHIES) and CTAB, sodium hydroxide and dimethyl sulfoxide (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.[10-12]

EXPERIMENTAL PROCEDURE

Materials. Lithium p-nitrophenyl ethyl phosphate (LiPNEF) was prepared from diethyl phosphate and sodium p-nitrophenoxide using LiCl in dry acetone, followed by precipitation with diethyl ether.[13,14]

The surfactant cetyltrimethylammonium bromide (CTAB) was purchased from Aldrich Chemical Company, Milwaukee, Wisconsin, USA. It was recrystallized from ethanol three times and dried under vacuum. NaOH and NaCl were supplied by Merck do Brasil, S.A., Rio de Janeiro and were of analytical reagent grade. The water was deionized and distilled.

Kinetics. The hydrolysis of LiPNEF was studied spectrophotometrically measuring the rate of appearance of the p-nitrophenoxide ion at 4030 Å. A Varian 634 spectrophotometer, equipped with a water-jacketted cell compartment was used. The pseudo-first order rate constant (k_ψ) was determined at 25^o, 35^o and 45^o C by graphical methods using the integrated form of the rate equation. The second order rate constant (k_2) was calculated from k_ψ and the hydroxide ion concentration. The activation parameters were determined from measurements of the reaction rate at three different temperatures using appropriate equations.[10]

The experimental procedures for quasi-elastic light scattering and viscosity measurements have been described elsewhere in the literature.[15,16]

RESULTS AND DISCUSSION

Some typical experimental results obtained for the pseudo first order rate constant (k_ψ) for the hydrolysis of LiPNEF at 25ºC are illustrated in Figure 1. The values of k_ψ for low concentrations of NaOH (less then 0,55 M) decrease as a function of concentration of NaCl, an observation typical of micellar catalyzed reactions.[3] At higher concentrations of NaOH (more than 1,00 M), however, the experimental values of k_ψ are essentially constant and are not affected by the addition of salt, illustrating the more pronounced electrolyte effect of the hydroxide ion.

Figure 2 shows some typical results obtained for the second order rate constant k_2 $\left[k_2=k_\psi/(OH^-)\right]$ as a function of NaCl concentration for fixed low concentrations of sodium hydroxide. It can be seen that the second order rate constant is highly dependent and decreases in the presence of salt.

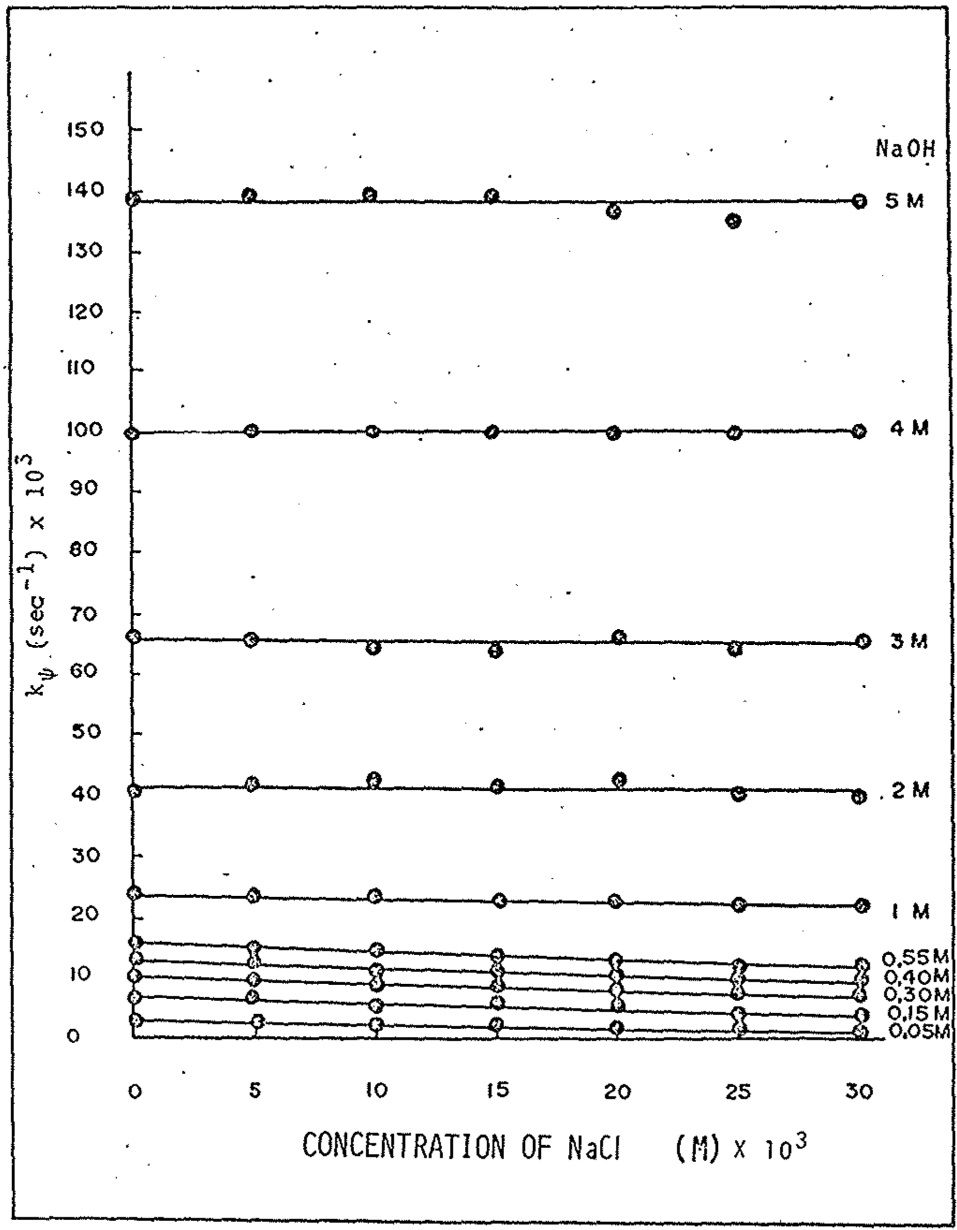


FIG. 1. PLOT OF THE PSEUDO-FIRST ORDER RATE CONSTANT (k_ψ) VERSUS THE CONCENTRATION OF SALT FOR THE HYDROLYSIS OF LiPNEF AT 25°C IN THE PRESENCE OF 0.0088 M CTAB AND DIFFERENT CONCENTRATIONS OF SODIUM HYDROXIDE.

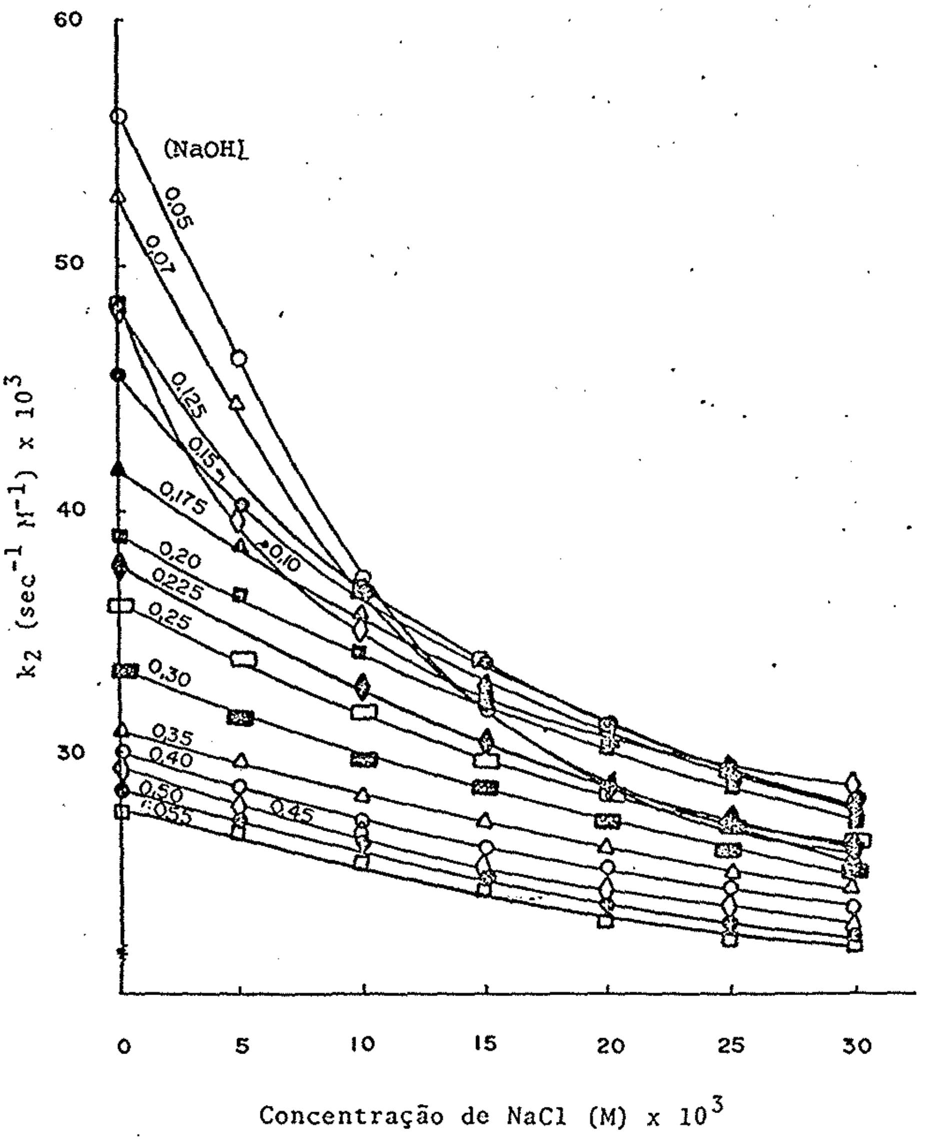


FIG. 2. VARIATION OF THE SECOND ORDER RATE CONSTANT (k_2) VERSUS THE CONCENTRATION OF SALT FOR THE HYDROLYSIS OF LiPNEF AT 25ºC IN THE PRESENCE OF 0,0088 M CTAB AND LOW CONCENTRATIONS OF SODIUM HYDROXIDE.

Figure 3 illustrates the variation of the second order rate constant k_2 as a function of NaCl concentration for fixed high and low concentrations of NaOH. It can be clearly noted that for high concentrations of NaOH (above 1,00 M) the values of k_2 are practically constant and do not depend on the presence of salt.

Figure 4 shows the dependence of the second order rate constant k_2 on the hydroxide ion concentration in the absence of salt and the presence 0,0088 M CTAB. The experimental values of k_2 decrease exponentially at low concentrations of NaOH (0,010 to 2,00 M), reach a minimum at 2,00 M and increase at higher concentrations of NaOH (2,00 to 5,00 M).

Figure 5 illustrates some typical results obtained for the diffusion coefficient (D) of the CTAB-H_2O-NaOH ternary system at 25ºC by means of quasi-elastic light scattering. It is interesting to note the presence of three different types of behavior of the diffusion coefficient D , indicating the presence of spherical micelles (positive slope part), elliptical micelles (zero slope) and stepladder growth with gelatinous and liquid crystalline mesophases (negative slope part). This observation is consistent with viscosity and surface tension measurements for the same system.

The activation parameters were determined from experimental values of k_ψ at 25º, 35º and 45ºC in the presence and absence of salt at different concentrations of NaOH. Some representative are summarized in Tables I and II.

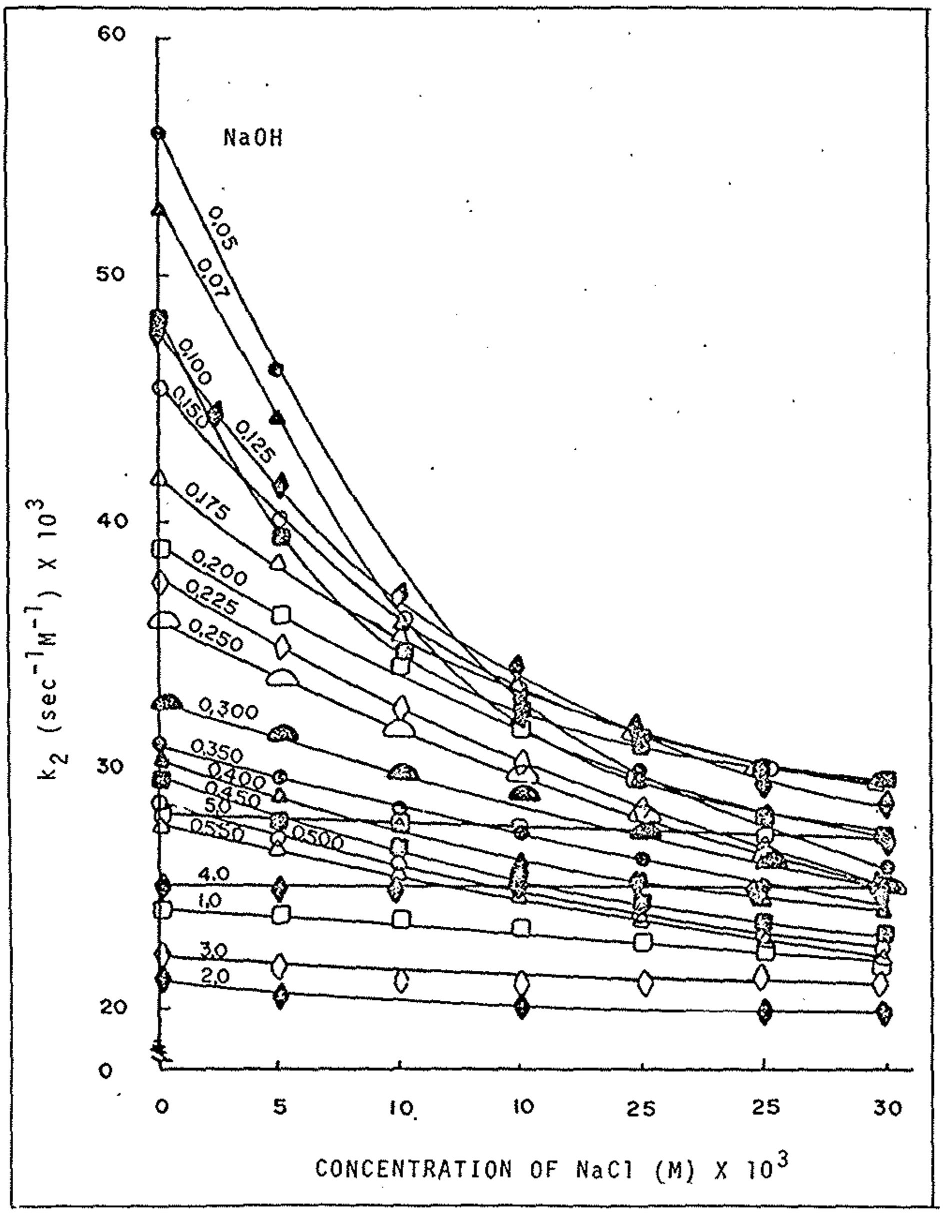


FIG. 3. VARIATION OF THE SECOND ORDER RATE CONSTANT (k_2) VERSUS THE CONCENTRATION OF SALT FOR THE HYDROLYSIS OF LiPNEF AT 25ºC IN THE PRESENCE OF 0,0088 M CTAB AND DIFFERENT FIXED CONCENTRATIONS OF SODIUM HYDROXIDE.

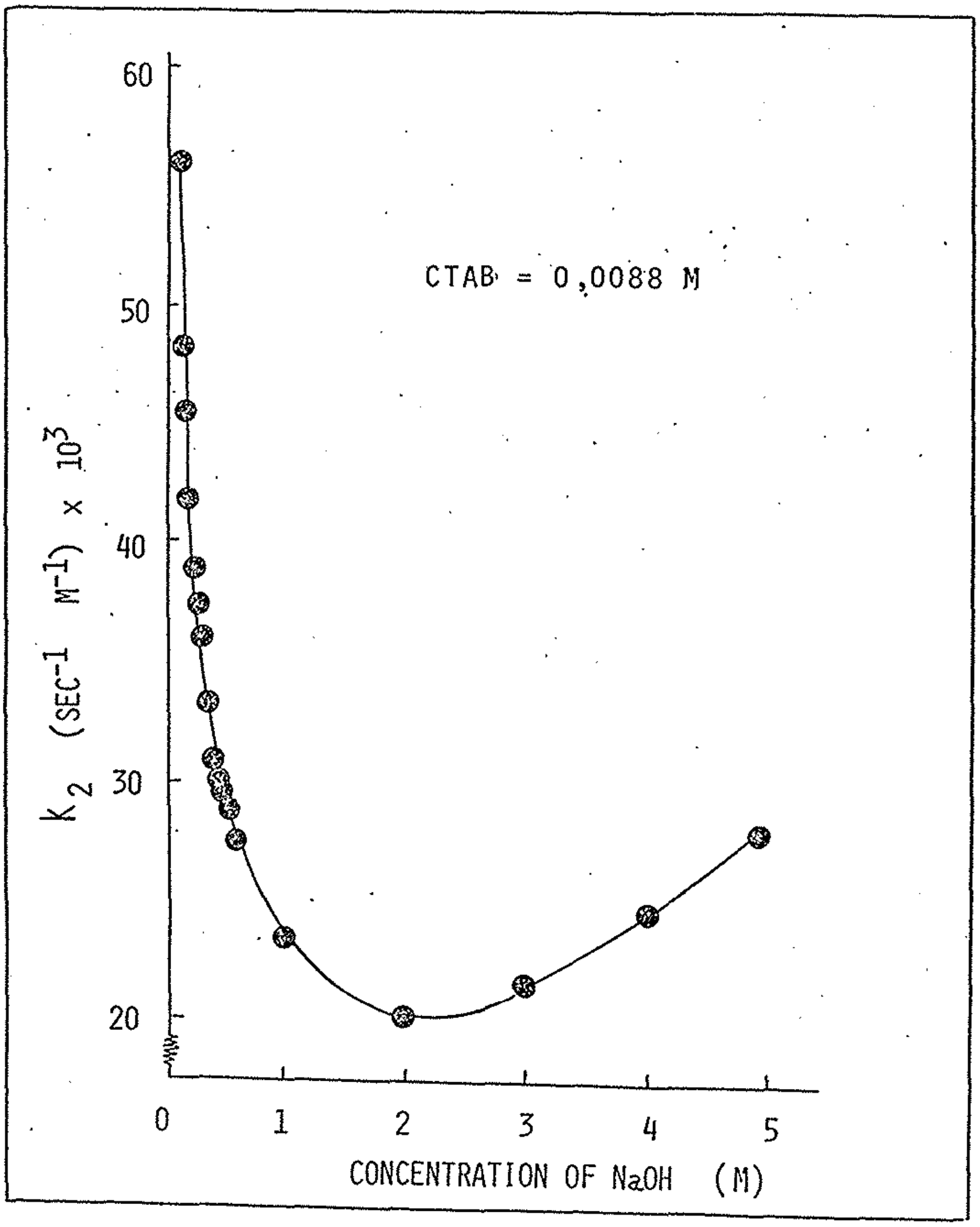


FIG. 4. VARIATION OF THE SECOND ORDER RATE CONSTANT (k_2) AS A FUNCTION OF SODIUM HYDROXIDE CONCENTRATION FOR THE HYDROLYSIS OF LiPNEF AT 25°C IN THE ABSENCE OF SALT.

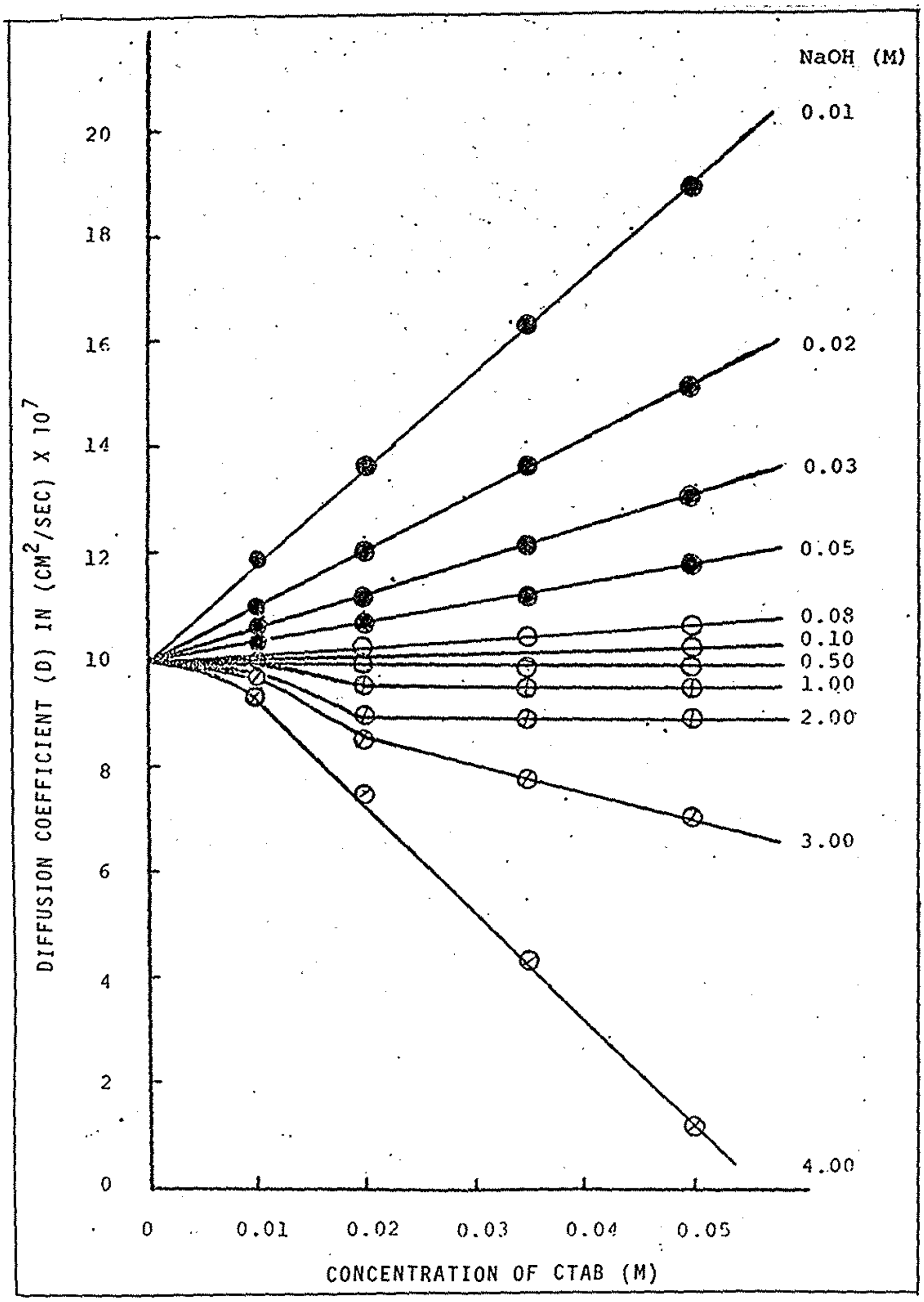


FIGURE 5. DIFFUSION COEFFICIENT (D) FOR THE CETYLTRIMETHYLAMMONIUM BROMIDE-WATER-SODIUM HYDROXIDE TERNARY SYSTEM AT 25°C.

TABLE I. ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF LiPNEF IN THE PRESENCE OF 0,0088 M CTAB, 0,030M NaCl AND DIFFERENT CONCENTRATIONS OF NaOH.

NaOH (M)	E_a (kcal/mole)	$\Delta H^{\neq}$ (kcal/mole)	$\Delta G^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
0,05	14,7	14,1	21,4	- 24,4
0,10	13,4	12,8	20,9	- 27,2
0,50	10,2	9,58	20,1	- 35,3
1,00	9,32	8,73	19,7	- 36,7

TABLE II. ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF LiPNEF IN THE PRESENCE OF 0,0088 M CTAB, THE ABSENCE OF SALT AND DIFFERENT CONCENTRATIONS OF NaOH.

NaOH (M)	E_a (kcal/mole)	$\Delta H^{\neq}$ (kcal/mole)	$\Delta G^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (e.u.)
0,05	14,2	13,6	21,5	-26,4
0,10	13,6	13,0	20,6	-25,6
0,50	11,8	11,2	19,9	-29,4
1,00	11,2	10,6	19,6	-30,4

In general, for low concentrations of sodium hydroxide, the activation parameters are comparable to others obtained for similar reactions catalyzed by micelles[11] and they decrease as a function of NaOH. The addition of NaCl also causes a decrease. It thus appears that the presence of NaOH and NaCl lead to a more structured or ordered transition state.

Most of the models proposed for micellar catalysis[17-22] 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 LiPNEF with hydroxide ion in the presence of CTAB may be considered a bimolecular reaction between OH^- and the substrate. Since the concentration of OH^- in the micellar phase is dependent on the concentration of bromide ion 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[21] reduces to Equation (I) that gives the theoretical dependence of the pseudo first order rate constant, k_ψ , as a function of the total hydroxide ion concentration, $(OH)_T$.

$$k_\psi = \frac{\left[k_{2m/\bar{V}}\ K_s K_{OH/Br}\ (Br)_m/(Br)_w + k_2^o\right](OH)_T}{(1 + K_s C_D)\left[1 + K_{OH/Br}(Br)_m(Br)_w\right]} \qquad (I)$$

where

C_D = concentration of micellized detergent

k_ψ = pseudo first order rate constant

k_{2m} = second order rate constant in the micellar phase

k_2^o = second order rate constant in the aqueous phase

$K_{OH/Br}$ = ion exchange constant

K_s = binding constant for the substrate

$(Br)_m$ = concentration of Br^- in micellar phase
$(Br)_w$ = concentration of Br^- in aqueous phase
$(OH)_T$ = total OH^- concentration
$\bar{V}$ = molar volume of the surfactant

With substrates such as lithium *p*-nitrophenyl ethyl phosphate that are very insoluble in water and are solubilized by CTAB the expression for k_ψ can be reduced to a simpler form given by Equation (II).

$$k_\psi = \frac{k_{2m}}{C_D\bar{V}} (OH)_T \frac{K_{OH/Br}(Br)_m/(Br)_w}{1 + K_{OH/Br}(Br)_m/(Br)_w} \qquad \text{(II)}$$

The concentration of Br^- in the micellar phase can be obtained using the following equations.(Eq. III-VII).[23]

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

where

CMC = critical micellar concentration of CTAB
α = degree of ionization of the micelle

$$(OH)_m = \frac{(-A_1) + \left[(A_1)^2 + 4(1-K_{OH/Br})OH_T K_{OH/Br}(1-\alpha)C\right]^{1/2}}{2(1-K_{OH/Br})} \qquad \text{(IV)}$$

where $(OH)_m$ = concentration of OH^- in micellar phase

$$(Br)_m = (1-\alpha)C_D - (OH)_m \qquad \text{(VI)}$$

$$(Br)_w = \alpha C_D + CMC + (OH)_m \qquad \text{(VII)}$$

We have calculated the theoretical values of k_ψ for the reaction discussed above using various concentrations of OH^-, $\overline{V}$ = 0,37 l/mole; $K_{OH/Br}$ = 0,08; α = 0,20 and CTAB = 0,0088 M.

Table III summarizes some parameters used for the calculation of the pseudo first order rate constant (k_ψ) and Table IV presents the experimental values of k_ψ and values calculated for k_ψ using the ion exchange model and different fixed concentrations of k_{2m}.

Figure 6 illustrates plots of the experimental pseudo first order rate constant k_ψ for the hydrolysis of LiPNEF at 25ºC versus the hydroxide ion concentration and calculated k_ψ values using the ion exchange model and different values of k_{2m}. As can be seen, there is some agreement between the experimental data and the theoretically calculated results only at lower concentrations of hydroxide ion.

Figure 7 illustrates the same results using an expanded scale for the hydroxide ion concentration in the range of 0,00 to 0,55 M , where there is good agreement between the experimental and calculated values of k_ψ.

Figure 8 shows a plot of the experimental pseudo first order rate constant k_ψ for the hydrolysis of LiPNEF at 25ºC versus hydroxide ion concentration giving the best fit of the experimental data with the pseudo phase ion exchange model and using a value of 0,0035 s^{-1} M^{-1} for k_{2m}.

TABLE III.SOME PARAMETERS USED FOR THE CALCULATION OF THE PSEUDO FIRST ORDER RATE CONSTANT (k_ψ) USING THE ION EXCHANGE MODEL.

$(OH)_T$	Exp. k_ψ	A_1	$(OH)_m$	$(Br)_m$	$(Br)_w$	$(Br)_m/(Br)_w$
0,05	0,00280	0,01428	0,001770	0,005630	0,004450	1,264939
0,08	0,00370	0,01628	0,002297	0,005103	0,004977	1,025329
0,10	0,00482	0,01828	0,002712	0,004688	0,005392	0,869591
0,13	0,00600	0,02028	0,003050	0,004350	0,005730	0,759137
0,15	0,00683	0,02228	0,003334	0,004066	0,006014	0,676193
0,18	0,00730	0,02428	0,003576	0,003824	0,006256	0,611336
0,20	0,00845	0,02628	0,003785	0,003615	0,006465	0,559070
0,25	0,00900	0,03028	0,004132	0,003268	0,006812	0,479717
0,30	0,01000	0,03428	0,004408	0,002992	0,007088	0,422064
0,35	0,01080	0,03828	0,004634	0,002766	0,007314	0,378119
0,40	0,01200	0,04228	0,004823	0,002577	0,007503	0,343430
0,45	0,01330	0,04628	0,004984	0,002416	0,007664	0,315304
0,50	0,01420	0,05028	0,005122	0,002278	0,007802	0,292011
0,55	0,01520	0,05428	0,005242	0,002158	0,007922	0,272388
1,00	0,02350	0,09028	0,005887	0,001513	0,008567	0,176672
2,00	0,04020	0,17028	0,006395	0,001005	0,009075	0,110700
3,00	0,06530	0,25028	0,006592	0,000808	0,009272	0,087090
4,00	0,09940	0,33028	0,006697	0,000703	0,009377	0,074933
5,00	0,13800	0,41028	0,006762	0,000638	0,009442	0,067518

* All parameters are defined within the text.

TABLE IV. CALCULATED PSEUDO FIRST ORDER RATE CONSTANTS ($k\psi$) FOR DIFFERENT FIXED VALUES OF k_{2m} USING THE ION EXCHANGE MODEL.

		Calculated k_ψ for different fixed values of k_{2m}			
$(OH)_T$	Exp. k_ψ	0,0025	0,0030	0,0035	0,0040
0,05	0,00280	0,003528	0,004234	0,004939	0,005645
0,08	0,00370	0,004365	0,005239	0,006112	0,006985
0,10	0,00482	0,004994	0,005993	0,006992	0,007990
0,13	0,00600	0,005495	0,006594	0,007693	0,008792
0,15	0,00683	0,005911	0,007093	0,008275	0,009457
0,18	0,00730	0,006265	0,007518	0,008771	0,010024
0,20	0,00845	0,006574	0,007889	0,009204	0,010519
0,25	0,00900	0,007094	0,008513	0,009932	0,011351
0,30	0,01000	0,007524	0,009028	0,010533	0,012038
0,35	0,01080	0,007890	0,009468	0,011047	0,012625
0,40	0,01200	0,008212	0,009855	0,011497	0,013140
0,45	0,01330	0,008501	0,010201	0,011901	0,013602
0,50	0,01420	0,008764	0,010516	0,012269	0,014022
0,55	0,01520	0,009006	0,010807	0,012608	0,014410
1,00	0,02350	0,010701	0,012841	0,014981	0,017121
2,00	0,04020	0,013480	0,016176	0,018872	0,021568
3,00	0,06530	0,015937	0,019125	0,022312	0,025500
4,00	0,09940	0,018301	0,021961	0,025622	0,029282
5,00	0,13800	0,020625	0,024750	0,028875	0,033000

* All parameters are defined within the text.

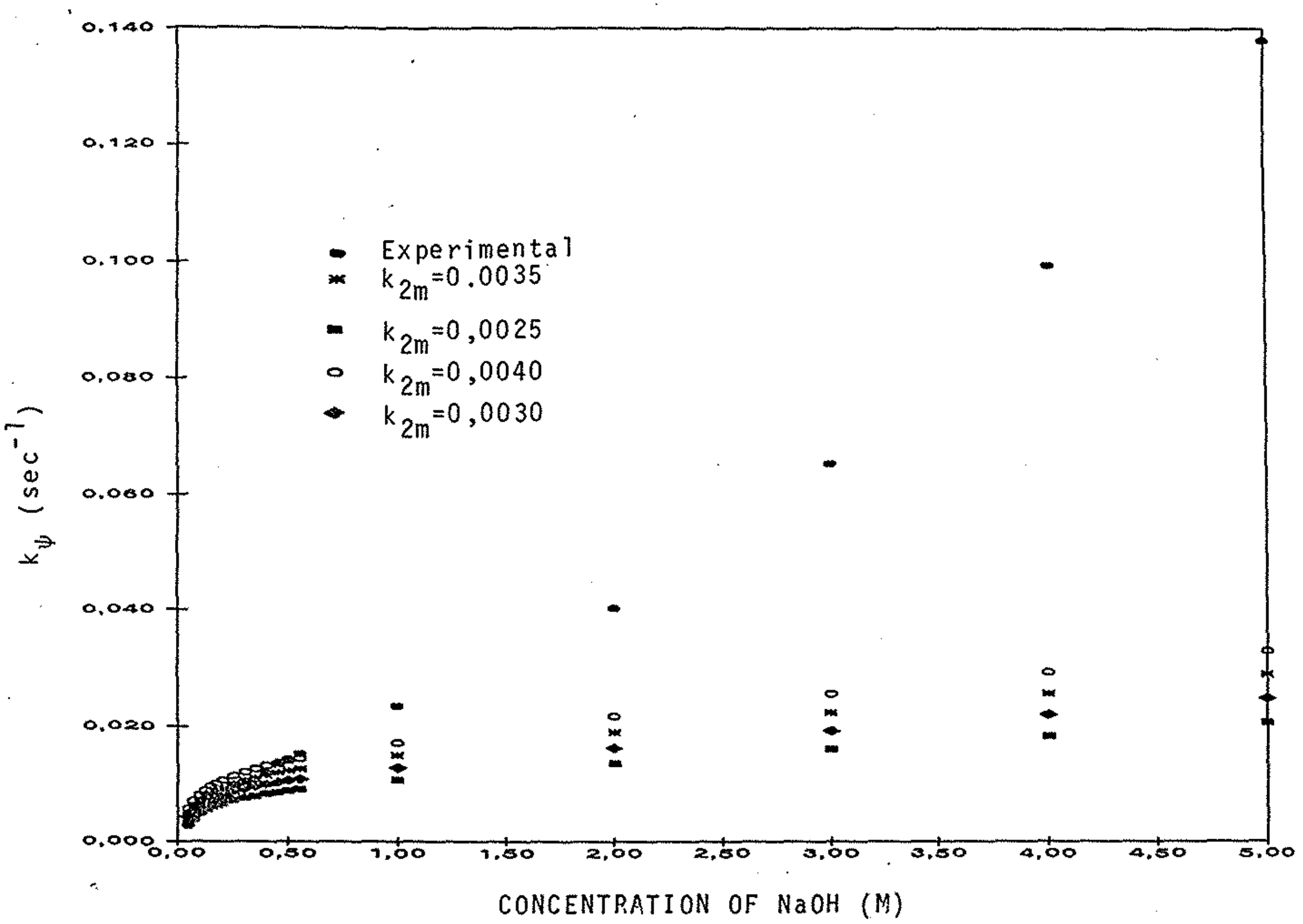


FIGURE 6. PLOTS OF THE EXPERIMENTAL PSEUDO FIRST ORDER RATE CONSTANT k_ψ FOR THE HYDROLYSIS OF LiPNEF AT 25ºC VERSUS HYDROXIDE ION CONCENTRATION AND FITS OF THE EXPERIMENTAL DATA WITH THE ION EXCHANGE MODEL USING DIFFERENT VALUES OF k_{2m}.

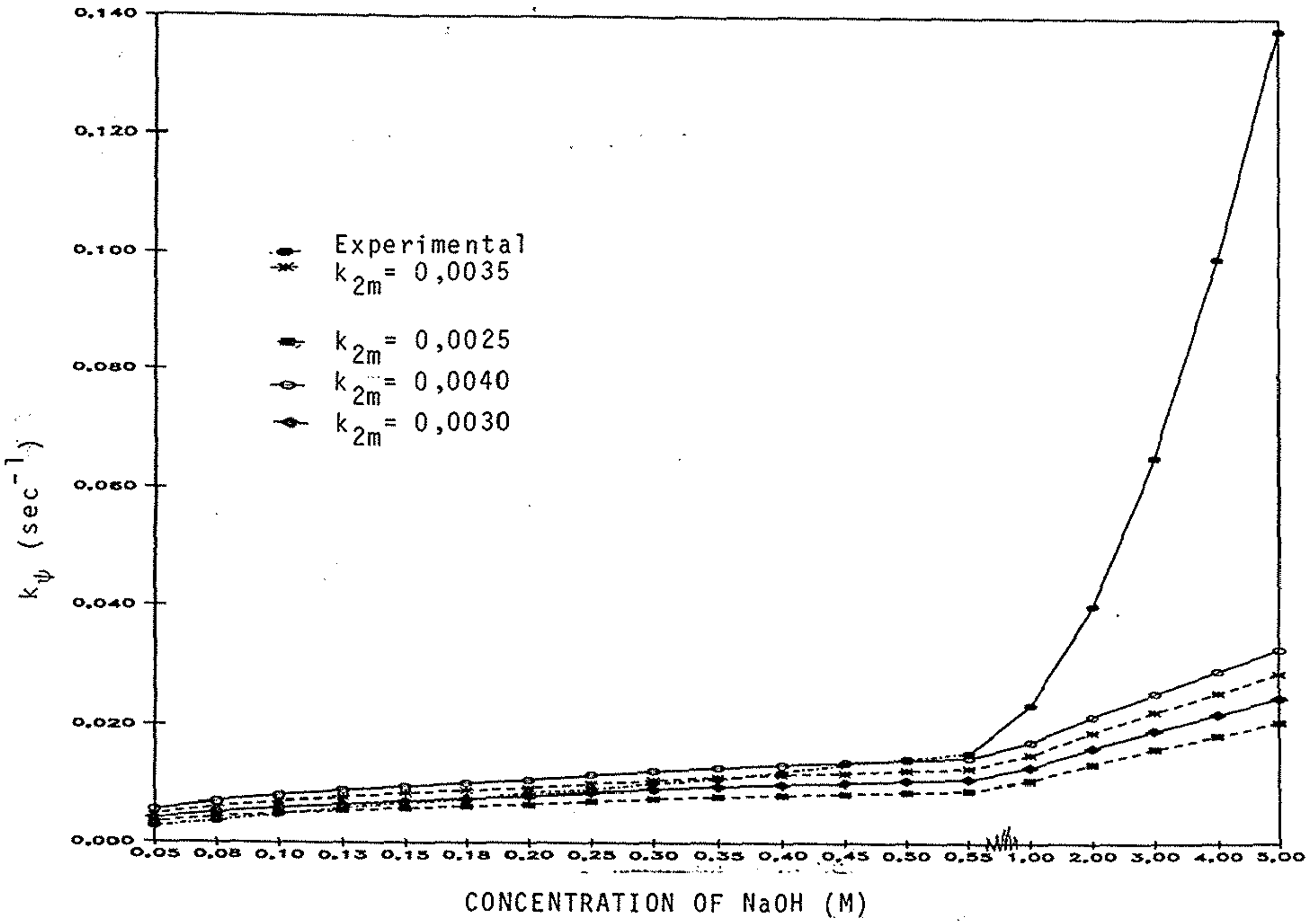


FIGURE 7. PLOTS OF THE EXPERIMENTAL PSEUDO FIRST ORDER RATE CONSTANT k_ψ FOR THE HYDROLYSIS OF LiPNEF AT 25ºC VERSUS HYDROXIDE ION CONCENTRATION AND FITS OF THE EXPERIMENTAL DATA WITH THE ION EXCHANGE MODEL USING DIFFERENT VALUES OF k_{2m} WITH AN EXPANDED SCALE AT LOW HYDROXIDE CONCENTRATION.

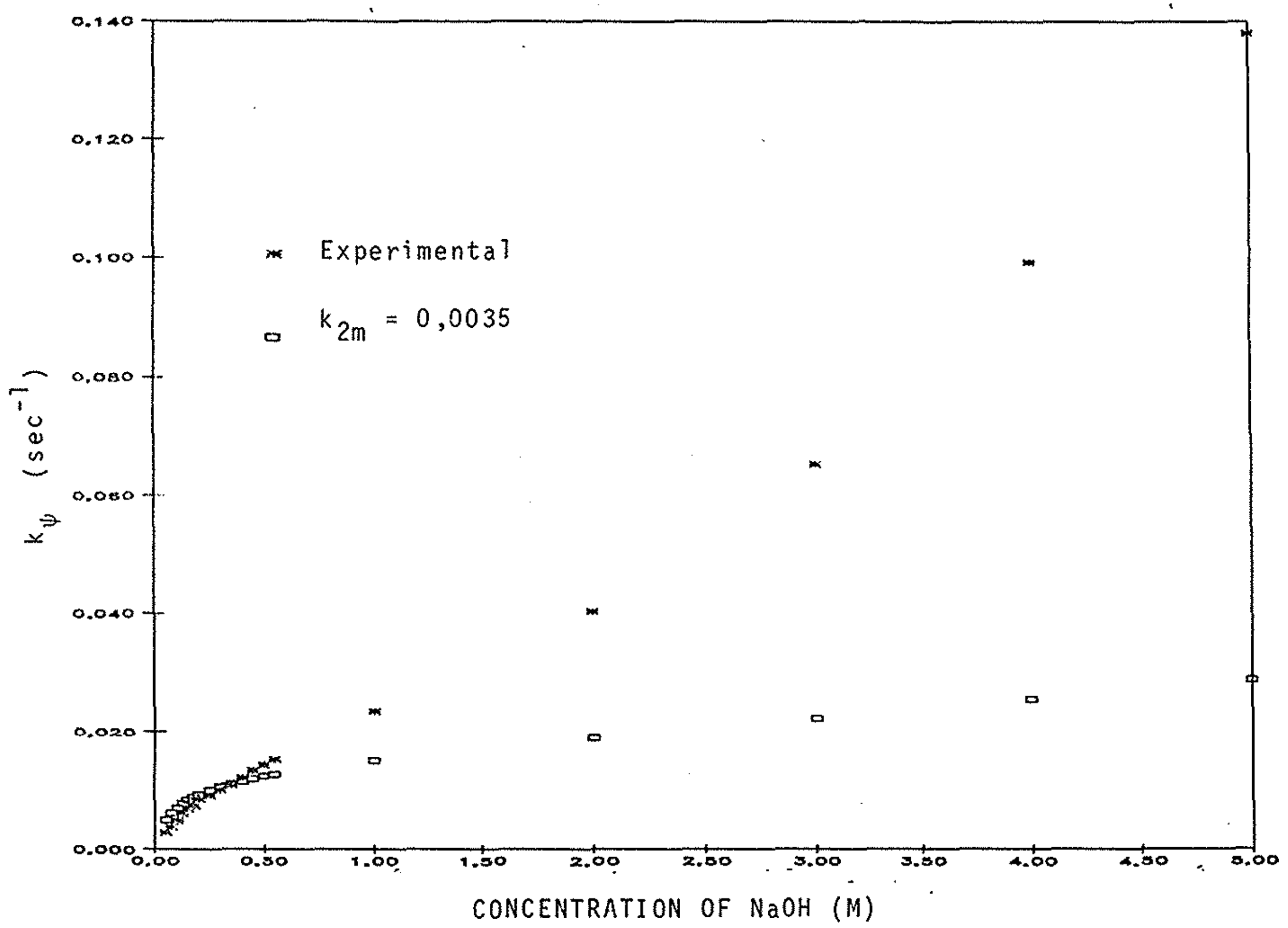


FIGURE 8. PLOT OF THE EXPERIMENTAL PSEUDO FIRST ORDER RATE CONSTANT k_ψ FOR THE HYDROLYSIS OF LiPNEF AT 25ºC VERSUS HYDROXIDE ION CONCENTRATION AND BEST FIT OF THE EXPERIMENTAL DATA WITH THE ION EXCHANGE MODEL USIG A VALUE OF k_{2m} OF 0,0035 s^{-1} M^{-1} .

Attempts to explain the experimental results obtained for the hydrolysis of LiPNEF using the pseudo phase ion exchange models presented in the literature[18-23] lead to failure of the models at higher hydroxide concentrations. Such failure at high hydroxide ion concentration has first been observed by Bunton, Romsted and Savelli[24] and by Lapinte and Viout[25]. The limitation of these models is not surprising, since they assume a constant micellar structure and involve partitioning of the substrate and the reactant between the aqueous and micellar phases and a fixed number of sites. All of them assume a closed thermodynamic system for a case when the kinetics under consideration may be more similar to flow kinetics, particularly when the micelles change in form, size and shape or undergo transitions to liquid crystalline mesophases.

More recent models, such as those proposed by D.G. Hall[26] that considers the transition state and by Bunton and Moffatt[27,28] that suggest a Coulombic Model and use the Poisson-Boltzmann Equation take into considerations some of shortcomings mentioned above.

Bunton, Romsted and Savelli[24] in their paper that may be considered a major breakthrough im micellar catalysis, explained the discrepancy between the theoretical models and the experimental results by considering an additional reaction pathway across the micellar boundary at the shear surface between the Stern and the Gouy-Chapmnan layers of the micelle. We have suggested that conceptually this interfacial boundary or micelle-water interface, as it has been called, should not be very different from the interface present in systems where phase transfer catalysis is taking place.[8,9,29,30]

Quasi elastic light scattering, viscosity and surface tension studies of the CTAB-H_2O-NaOH (See Figure 5) and CTAB-H_2O-NaCl [15,16] systems clearly indicate changes in size and shape of the CTAB micelles and formation of liquid crystalline mesophases as a function of electrolyte concentration.

Consideration of the kinetic results presented above in light of the structural changes occuring in the system excludes the theoretical pseudo phase ion exchange models presented in the literature[18-23] for concentration of OH^- above 0,55 M. Changes in size, form, shape of the CTAB micelle and formation of lamellar and liquid crystalline mesophases are not taken into account in any of these models.[18-23]

For solutions of surfactants containing higher concentrations of electrolyte, serious consideration should be given to models more akin to phase transfer catalysis or liquid crystalline catalysis. Samori and his collaborators have described liquid crystalline catalysis by smectic B solvents [31,32] and Ramesh and Labes have investigated the control of reaction kinetics by manipulation of micellar size and shape [33,34] and the influence of disc-rod-sphere transitions in nematic lyotropics on a unimolecular isomerization reaction.

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