SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol 16., N° 16, 2008

MICELLAR CATALYZED REACTION IN AQUEOUS GLYCEROL SOLUTIONS AND THE INTERNAL PRESSURE OF THE MEDIUM

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ABSTRACT

The experimental results obtained for the hydrolysis of p-nitrophenyl diphenyl phosphate (NPDPP) in the presence of sodium hydroxide (NaOH), micelles of cetyltrimethylammonium bromide (CTAB) and aqueous solution of glycerol were analyzed taking into consideration the internal pressure and the cohesive forces of the reaction medium. The effect of glycerol on micelle formation and also its influence on the internal pressure of the reaction medium are large enough to affect the micellar catalyzed alkaline hydrolysis of the phosphate ester.

KEY WORDS: Micellar Catalysis, Cetyltrimethylammonium Bromide (CTAB), Phosphate Esters, Solvent Effects, Internal Pressure of Liquids, Cohesive Forces, Glycerol

RESUMO

Os resultados experimentais obtidos para a hidrólise do p-nitrofenil difenil fosfato (NP DPP) na presença de hidróxido de sódio (NaOH), micelas de brometo de cetiltimetilamônio (CTAB) e soluções aquosas de glicerol foram analisados considerando a pressão interna e as forças de coesão do meio reacional. O efeito do glicerol sobre a formação de micelas e a sua influência sobre o meio da reação são suficientemente grandes para ter um efeito sobre a hidrólise alcalina do éster de fosfato na presença de micelas.

PALAVRAS CHAVE : **Catálise Micelar, Brometo de Cetiltrimetilamônio (CTAB), Éster de fosfato, Presssão Interna de Líquidos, Forças de Coesão**

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DOI: 10.48141/SBJCHEM.v17.n17.2008.43_2008.pdf

INTRODUCTION

Phosphate esters are compounds with interesting biological and pharmacological properties and are widely used as pesticides, drugs and nerve gases. Their accumulation and their effect in the environment are of paramount importance [1,9].

In previous studies, described in the literature [3,9], we have shown that the alkaline hydrolysis of di- and tri-substituted phosphate esters is catalyzed by micelles of various surfactants, have analyzed the effect of different additive on the reaction medium and have proposed mechanisms for the reaction.

Regardless of the models chosen for the liquid state, the consideration of cohesive forces or internal pressure is of primary importance. Starting with one of the basic thermodynamic relations that includes the first and the second laws of thermodynamics ($dE = TdS - PdV$) it can be shown, by standard methods that

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P \qquad (1)$$

where the term $(\partial E/\partial V)_T$ is called the internal pressure, P_i, and is related to cohesive or attractive forces in the system [10-15].

For real gases, this term is equal to the attraction term in the Van der Waals equation $[(\partial E/\partial V)_T = (an^2/V)]$. The "cohesive pressure" or internal pressure resulting from attraction forces is responsible for the negative deviation of real gases from ideal behavior and the larger the Van der Waals constant a, the larger the cohesive or internal pressure [10-15]. In general, the internal pressure of gases, P_i, is small compared to the real pressure.

In the case of liquids and solids, the internal pressure, P_i, is usually much greater than the real or external pressure, P. For example, for glycerol the internal pressure is 10,324 atm while for water $P_i = 22{,}355$ atm [14,15].

The analysis of the effect of solvents on the rate of chemical reactions is generally approached in two different ways. The first approach uses transition state theory and analyses the relative solvation between the initial state and the transition state. The solvation of either state reduces the free energy associated with it and increases its stability [14,16]. The change in the reaction medium leads to the reduction of the free energy of activation and to an increase in the rate of the reaction [16].

The second approach takes into consideration the structure of the solvent or the reaction medium, its cohesive or internal pressure and how the solvent-solvent interactions affect the reacting species. Clearly, both solvation and cohesion affects are manifestations of electrostatic interactions in the liquid medium and it is very difficult to separate the two.

For a reaction to take place in solution it is necessary to form cavities in the solvent in order to accommodate the reagents, activated complex and products. The facility with which solvent molecules can be separated from each other to form these cavities is a critical factor and determines the solubility of the solute. The use of internal pressure or "density of energy cohesion", as it has also been called, has been introduced originally by Hildebrand [10] to estimate solubility, and the square root of its value has been called the solubility parameter (δ).

Solvent molecules exhibit attractive and repulsion forces among themselves. In order to create a cavity in a liquid it is necessary to overcome the attractive forces that are responsible for the cohesion of the medium. For reactions where the products exhibit more cohesion than the reagents, the rate of the reaction is increased by solvents with higher internal pressure [17]. The activated complex of a reaction whose rate increases with the internal pressure of the medium occupies less volume than the reagents. In the present case, the reaction medium consists of water, glycerol, micelles and monomers of CTAB, and the nature of the micelle is affected by the amount of glycerol present.

EXPERIMENTAL

The p-nitrophenyl diphenyl phosphate (NPDPP) was prepared using standard methods [18-20]. A sample was also obtained from Prof. Fred Menger, Emory University, Atlanta, Georgia, USA. The surfactant cetyltrimethylammonium bromide (CTAB) was purchased from Aldrich Chemical Co. and recrystallized three times from absolute ethanol before use. Glycerol and sodium hydroxide were analytical reagent grade and were purchased from Merck Co.

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, CTAB and glycerol. The pseudo-first order rate constant (k_ψ), in sec^{-1}, was determined from linear plots of logarithm of absorbance versus time and the second order rate constants (k_2), in $sec^{-1}.mol^{-1}$, were calculated from k_ψ and the hydroxide ion concentration. Activation parameters such as the activation energy (E_a), the activation Gibbs free energy ($\Delta G^{\neq}$), the activation entalphy ($\Delta H^{\neq}$) and the activation entropy ($\Delta S^{\neq}$) were determined from experimental k_ψ values measured at three different temperatures using the following equations.

$$\ln k_\psi = \ln A - (E_a/R)(1/T) \qquad (2)$$

$$\Delta H^{\neq} = E_a - RT \qquad (3)$$

$$\Delta S^{\neq} = 4.576 (\log k_\psi - 10.753 - \log T + E_a/4.576T) \qquad (4)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\,\Delta S^{\neq} \qquad (5)$$

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

RESULTS AND DISCUSSION

The reaction under consideration is the hydrolysis of p-nitrophenyl diphenyl phosphate in aqueous solutions containing 0.010M NaOH, various concentrations of CTAB and glycerol ranging from 0 to 90% by volume and is illustrated in Figure 1.

Some typical profiles of the pseudo-first order rate constants, k_ψ, as a function of the concentration of CTAB for the hydrolysis of NPDPP at 25°C in aqueous solutions containing 0.010 M NaOH and concentrations of glycerol varying from 10 to 90% by volume are presented in Figure 2. The rate profiles obtained are characteristic of micellar catalyzed reactions in aqueous solutions. The addition of CTAB to the reaction medium causes an increase in the rate of hydrolysis up to a point where there is total incorporation of the substrate in the micellar phase. More 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. There is a maximum in all the rate profiles at 20×10^{-4}M CTAB. This maximum has the same value as that observed for CTAB-H_2O-NaOH. This behavior is totally different from that observed for solutions containing CTAB-H_2O-NaOH-DMSO (dimethylsulfoxide) and H_2O-NaOH-DMSO-DEHIES (diethyl heptadecyl imidazolinium ethylsulfate) where the maximum shifts for higher concentration of DMSO and the profiles exhibit three different types of behavior, indicating changes in the mechanism of the reaction [7,8,14,15].

For the case of CTAB-H_2O-NaOH-G (glycerol), the mechanism of the micellar catalyzed reaction apparently does not change, but the catalytic effect of CTAB (ratio of the reaction rate in the presence and absence of surfactant under the same experimental conditions) is reduced by the addition of glycerol.

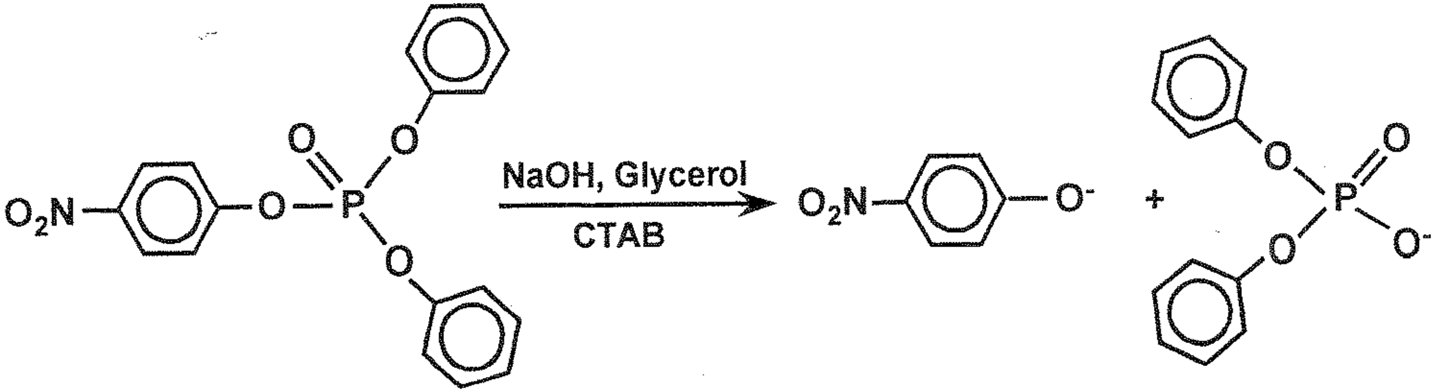

Figure 1 - Hydrolysis of p-nitrophenyl diphenyl phosphate (NPDPP) in aqueous solutions containing sodium hydroxide, glycerol and micelles of CTAB.

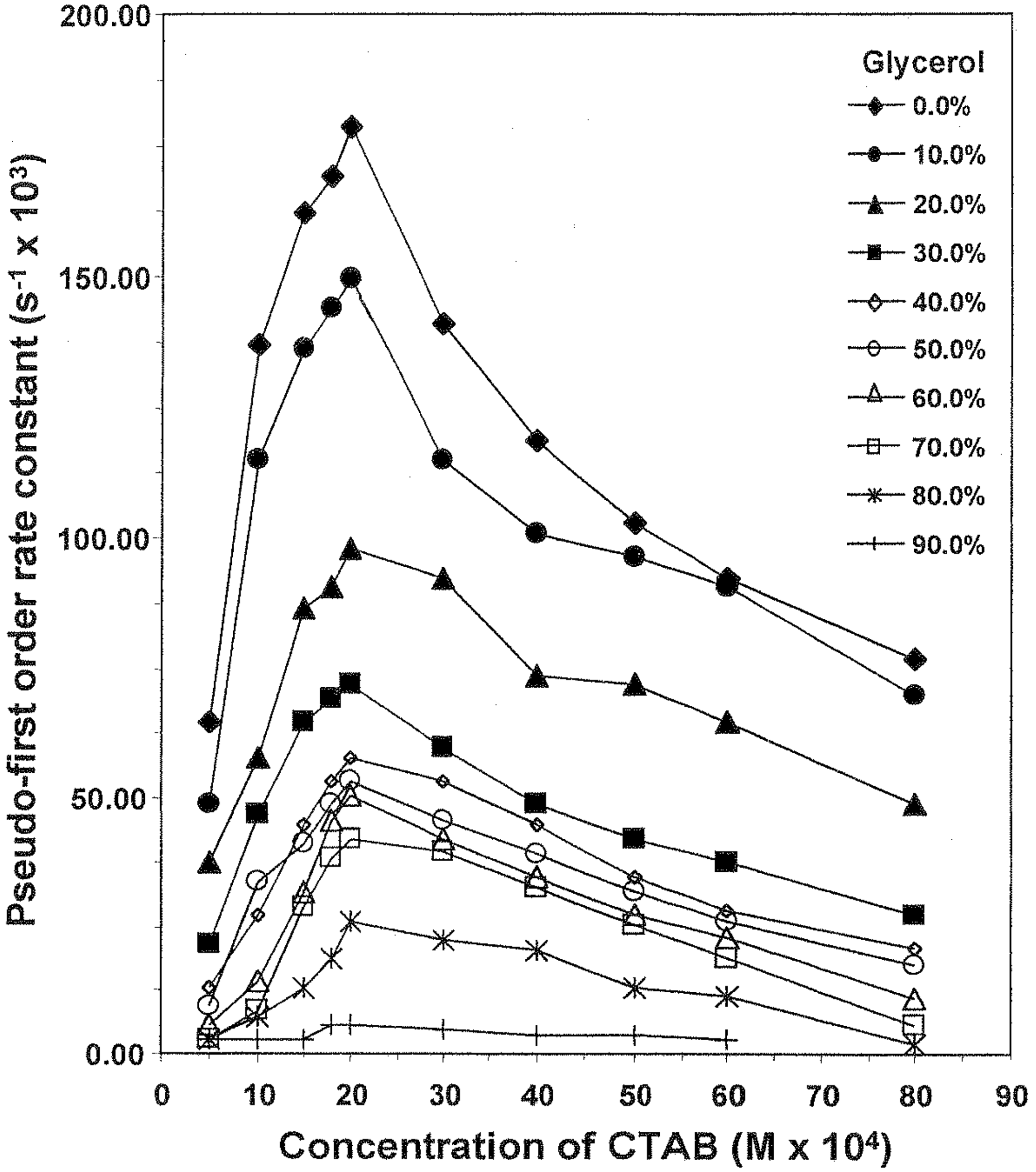

Figure 2 - Rate profiles for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C in aqueous solutions containing 0.010 M NaOH in presence of CTAB and concentrations of glycerol varying from 0 to 90% by volume.

Figure 3 illustrates a plot of the pseudo-first order rate constant for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C as a function of the mole fraction of glycerol for solutions containing 0.010M NaOH and 20 x 10^{-4} M CTAB. As can be seen, the pseudo-first order rate constant decreases exponentially as a function of the mole fraction of glycerol.

It is well known that glycerol decreases the spontaneity of the micellization process in water and that the critical micellar concentration (CMC) of the surfactant in aqueous solutions increases as a function of glycerol [21-25]. Figure 4 illustrates a plot of the dependence of the critical micellar concentration of CTAB at 25°C and 40°C ~~from~~ CTAB-H_2O-G solutions and clearly shows that the CMC increases exponentially as a function of the mole fraction of glycerol [23,24]. Formamide (F), ethylene glycol (EG) and glycerol (G) are solvents similar to water and micelle formation is common in these solvents, although it is less spontaneous than in water. The solvophobic effect per methylene group (-CH_2-) measured for acylcarnitines was -2.89 $kJ.mol^{-1}$ for water, -0.75 $kJ.mol^{-1}$ for glycerol, -0.71 $kJ.mol^{-1}$ for ethylene glycol and -0.70 $kJ.mol^{-1}$ for formamide [21,22].

The effect of these three cosolvents on the micellization process in water can be explained in terms of their breaking up the structure of water and diminishing the hydrophobic effect in the ternary systems (surfactant-water-cosolvent). The breaking up of the water structure results from the formation of complexes of the type EG.$2H_2O$, F.H_2O and G-$2H_2O$ through hydrogen bonding. Experimental studies involving various techniques, including NMR, for aqueous solutions of ethylene glycol and glycerol, have shown the existence of inter and intramolecular hydrogen bonding and have indicated

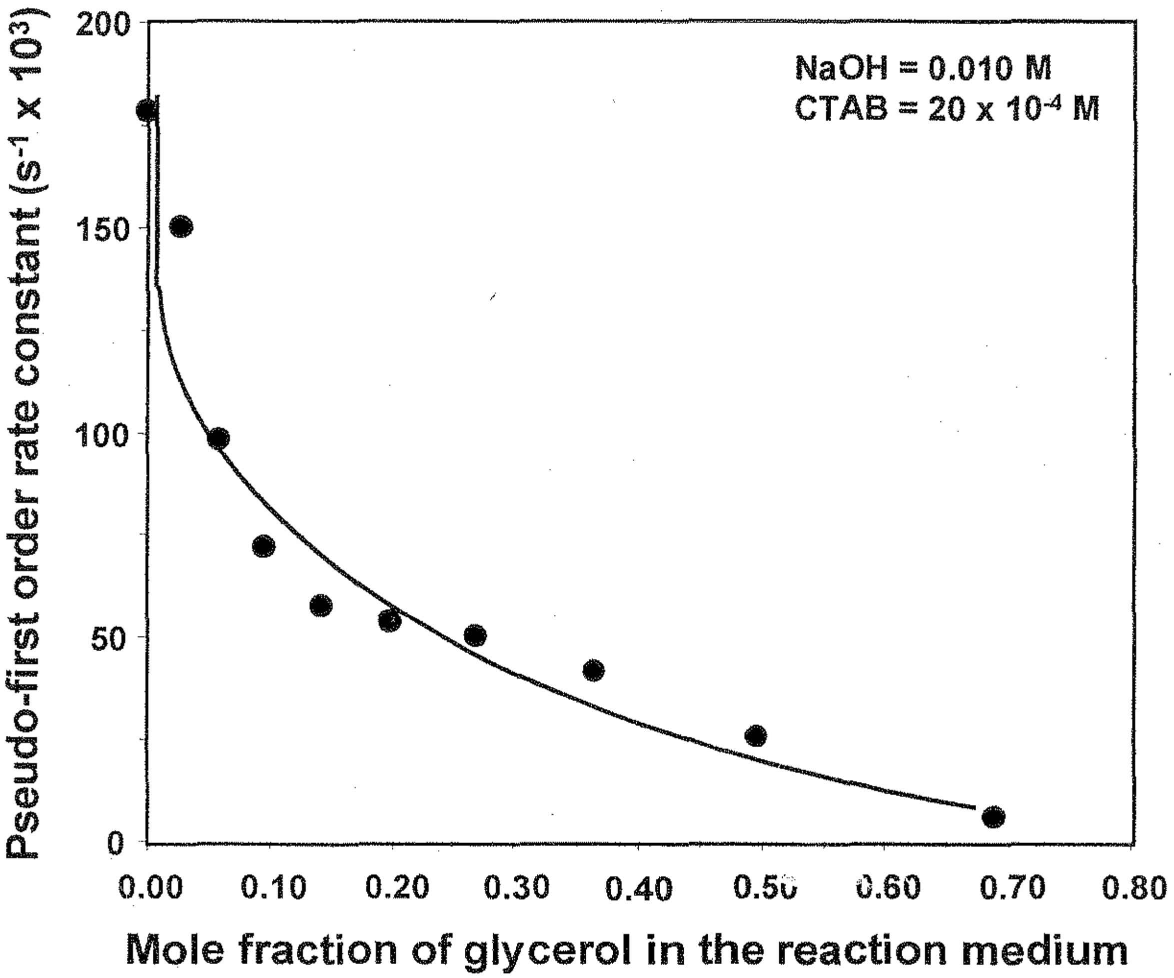

Figure 3- Plot of the pseudo-first order rate constant for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C as a function of the mole fraction of glycerol.

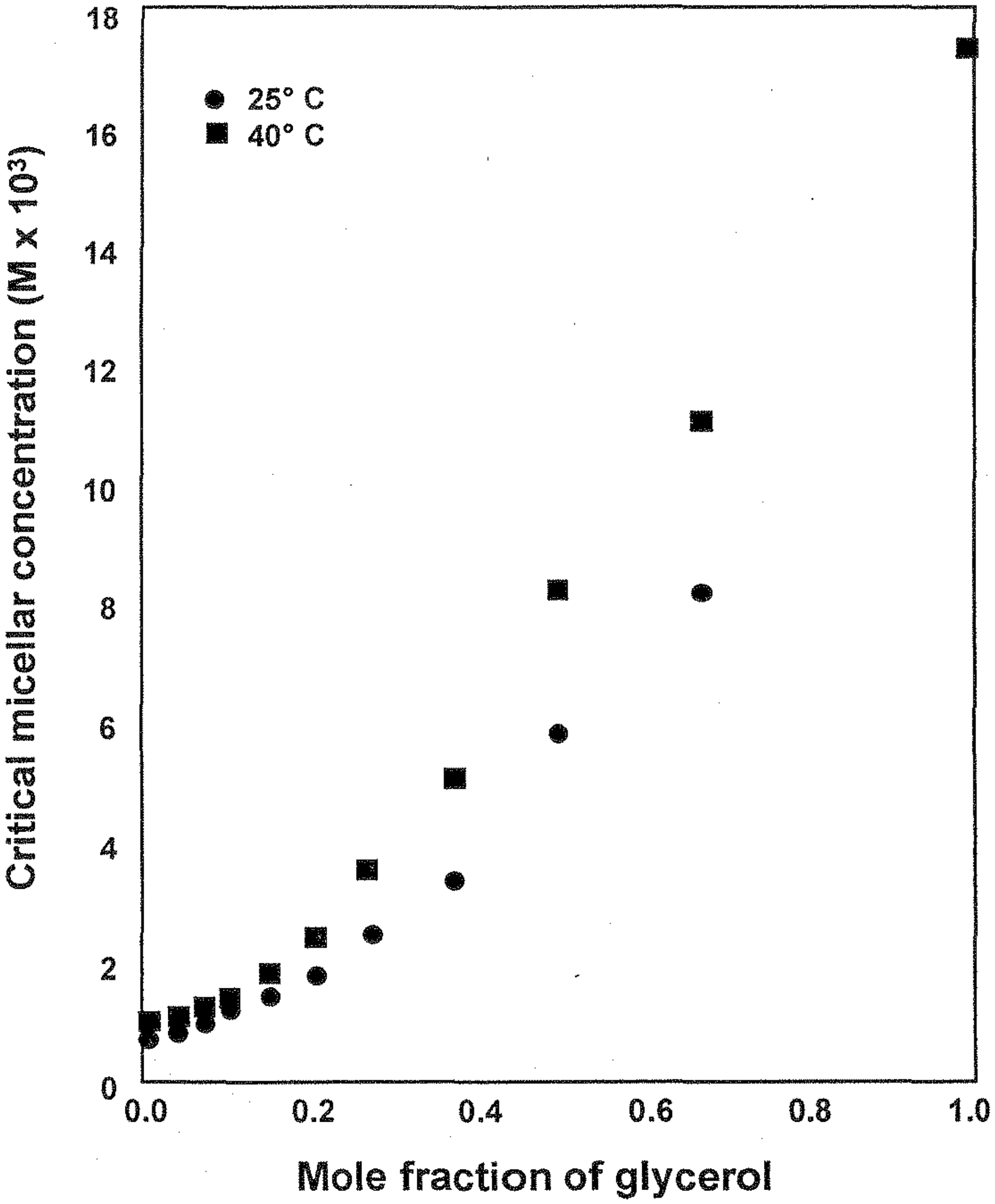

Figure 4 - Dependence of the critical micellar concentration (CMC) of CTAB in aqueous solutions as a function of the mole fraction of glycerol.

that the hydrogen bonds between either one of the two and water are stronger than those among themselves [26-28].

Table I shows some typical activation parameters for the reaction at 25°C in the presence and absence of CTAB and cosolvents such as glycerol and dimethylsulfoxide. As can be seen, addition of CTAB in the form of micelles in the reaction medium reduces the activation energy, E_a, of about 5 kcal/mole as compared to aqueous solutions containing only NaOH. The entropy of activation under the same conditions varies from -22.2 to -29.9 e.u., indicating that the presence of micelles leads to a more structured transition state. The addition of glycerol and dimethylsulfoxide (10% by volume) decreases slightly more the activation energy. When the reaction is carried out in the presence of 10% cosolvent by volume, the entropy of activation is reduced even more (-31.6 e.u. for glycerol and -33.5 e.u. for dimethylsulfoxide).

The internal pressure, Pi, of the reaction medium was calculated according to Equation (6) using the appropriate mole fraction of water and glycerol [15].

$$P_i\,(\text{medium}) = X_{\text{water}}\, P_{i\ \text{water}} + X_{\text{glycerol}}\, P_{i\ \text{glycerol}} \qquad (6)$$

The internal pressure used for water was 22,355.0 atm and for glycerol was 10,324.2 atm. Figure 5 illustrates a plot of the logarithm of the pseudo-first order rate constant versus the internal pressure of the medium for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C in the presence of 0.010 M NaOH and 20 x 10^{-4} M CTAB. As can be seen, the plot of log k_ψ versus internal pressure gives essentially a straight line and the rate of the reaction increases with the internal pressure. This indicates that the products

Table 1 - Activation parameters for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C in aqueous solutions of 0.010 M NaOH in the presence and in the absence of CTAB and of glycerol or DMSO .

Concentrations		**E_a**	**$\Delta H^{o\neq}$**	**$\Delta S^{o\neq}$**
Cosolvent (% by volume)	**CTAB ($M \times 10^4$)**	**($kcal.mole^{-1}$)**	**($kcal.mole^{-1}$)**	**(e.u.)**
-	-	+15.2	+14.6	-22,2
-	15	+11.4	+10.8	-26.6
-	20	+10.5	+ 9.9	-29.9
Glycerol (10%)	18	+10.3	+9.7	-30.1
Glycerol (10%)	20	+10.0	+9.4	-31.6
Glycerol (10%)	30	+9.4	+8.8	-34.2
DMSO (10%)	-	+18.7	+18.2	- 9.4
DMSO (10%)	20	+ 9.3	+ 8.7	-33.5

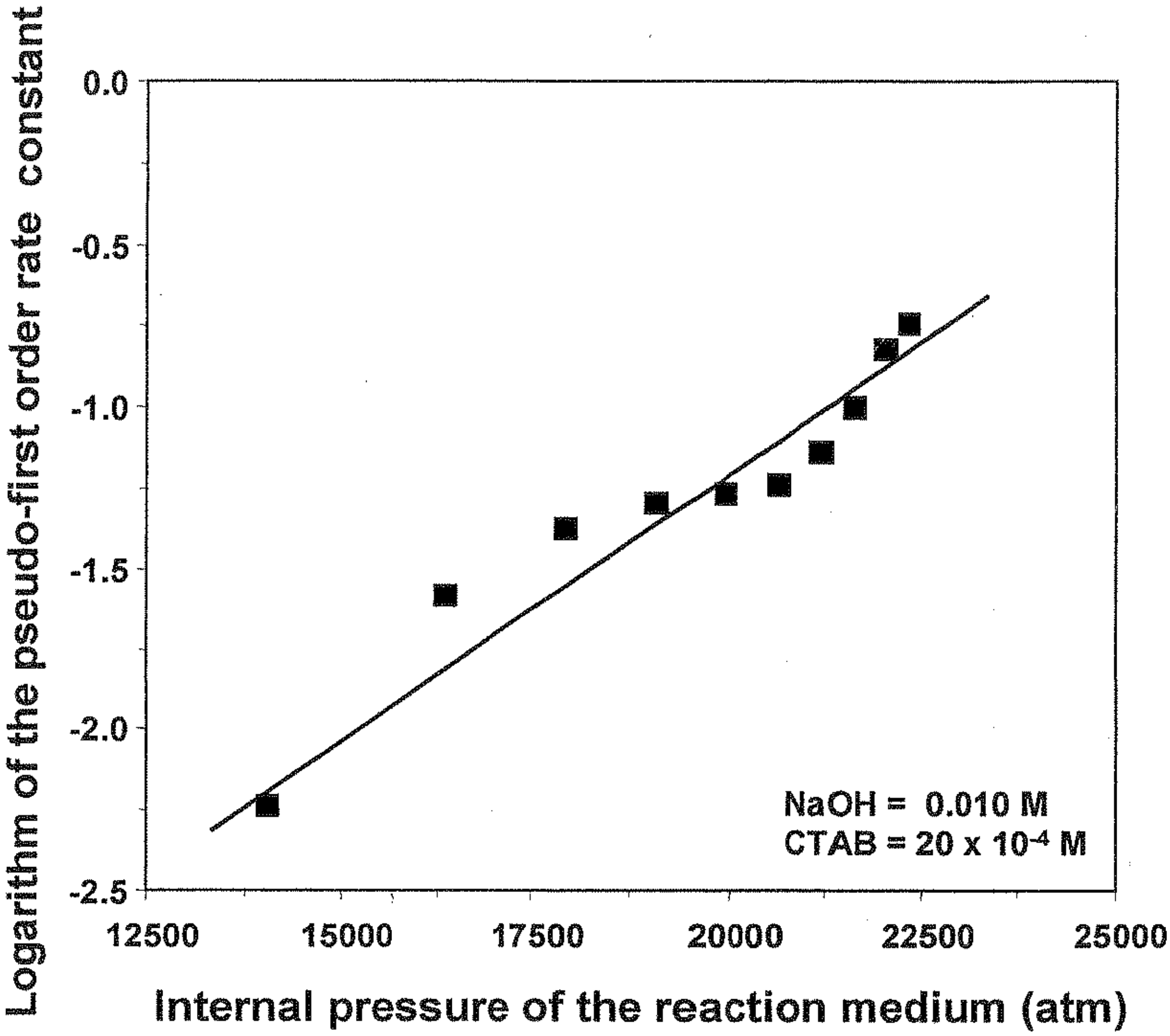

Figure 5 - Plot of the logarithm of the pseudo-first order rate constant for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C in 0.010 M NaOH and 20 x 10^{-4} M CTAB as a function of the internal pressure of the reaction medium.

exhibit more cohesion than the reagents and that the activated complex occupies less volume than the reagents. In the presence of micelles (as is the case in consideration) the activated complex is in the interior or near the surface of the micelle. The addition of glycerol to the H_2O-CTAB medium that contains the micelles leads to the diminution of the internal pressure and the aggregates. The activated complex now formed occupies a smaller volume than the reagents and the rate of the reaction continues to decrease as long as micelles are still present in the liquid medium. This is in fact what is being observed for the case of micellar catalysis in aqueous solutions containing glycerol.

CONCLUSIONS

The addition of glycerol to the reaction medium has a effect on micellar catalyzed alkaline hydrolysis of p-nitrophenyl diphenyl phosphate which is caused not only by the formation of the complex $G.2H_2O$ and reduction of CTAB micellization but also by the changes in the internal pressure of the medium.

ACKNOWLEDGEMENTS

The authors acknowledge the sample of p-nitrophenyl diphenyl phosphate obtained from Prof. Fred M. Menger, Emory University, Atlanta, Georgia, USA. LGI acknowledges the financial support from CNPq and Sarmisegetusa Research Group. EFS acknowledges the financial support from FAPESP.

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