MICELLAR CATALYZED HYDROLYSIS OF A PHOSPHATE ESTER IN AQUEOUS SOLUTIONS CONTAINING DIMETHYL SULFOXIDE

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ABSTRACT

The hydrolysis of p-nitrophenyldiphenyl phosphate was studied in aqueous solutions containing micelles of diethylheptadecylimidazolinium ethyl sulfate (DEHIES), sodium hydroxide and various concentrations of dimethyl sulfoxide (DMSO). Pseudo-first order (k_ψ) and second order rate constants (k_2) were determined at 15º, 25º and 35 ºC and activation parameters such as E_a, $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were also measured. The rate profiles obtained for solutions containing 10-50% DMSO by volume exhibited clear maxima that shifted to higher concentrations of DEHIES as a function of DMSO added. For solutions containing 60-80% DMSO there was no maximum in the rate profile and inhibition of the reaction took place. Solutions containing 90% by volume of DMSO exhibited much higher reaction rates and considerably more catalysis. The experimental results are explained in terms of the Hughes-Ingold Theory, specific solvent effects, polarity and internal pressure of the reaction medium. The interpretation and discussion of the results takes into consideration the formation of the stoichiometric hydrate DMSO·2H₂O and the inhibitory effect of dimethyl sulfoxide on the formation of micelles of DEHIES.

RESUMO

A hidrólise do p-nitrofenildifenilfosfato foi estudada em soluções contendo micelas de dietilheptadecil-etilsulfato-imidazolínio (DEHIES), hidróxido de sódio e várias concentrações de dimetilsulfóxido (DMSO). Foram determinadas constantes de velocidade de pseudo-primeira ordem (k_ψ), segunda ordem (k_2) e parâmetros de ativação tais como E_a, $\Delta G^{\neq}$, $\Delta H^{\neq}$ e $\Delta S^{\neq}$. Para soluções contendo 10-50% de DMSO por volume os perfis de velocidade apresentam um máximo bem definido, deslocado para concentrações mais elevadas de DEHIES em função de DMSO adicionado. Para soluções com 60-80% DMSO não há um máximo no perfil de velocidades e ocorre uma inibição da reação. Para soluções contendo 90% por volume de DMSO, as velocidades de reação são consideravelmente mais elevadas com catálise muito pronunciada. Os resultados experimentais são explicados em termos da Teoria Hughes-Ingold, dos efeitos específicos do solvente, da polaridade e da pressão interna do meio de reação. A discussão e interpretação dos resultados leva em consideração a formação do hidrato estequiométrico DMSO·2H₂O e o efeito inibitório do DMSO sobre a formação de micelas de DEHIES.

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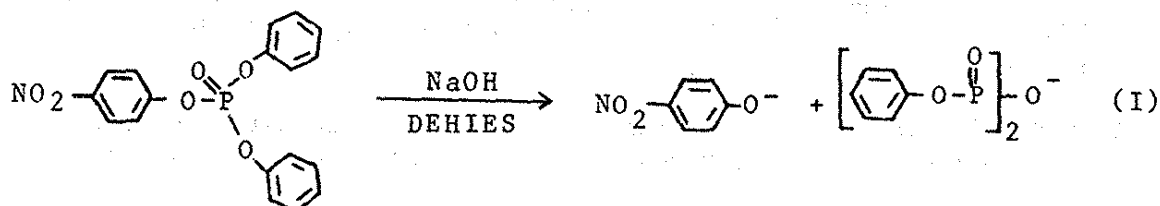§ *PPGEMM-UFRGS*

INTRODUCTION

Phosphate esters represent a group of compounds with interesting biochemical and pharmacological properties and have a wide use as pesticides, drugs and nerve gases.[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 (CTAB) and also by micelles of N,N-dimethyl-N-hydroxyethyldodecylammonium bromide (DHEDAB) and N,N-dimethyl-N-hydroxyethylcetylammonium bromide (CHEDAB).[3] Micelles of DHEDAB and CHEDAB are excellent catalysts for the hydrolysis of both lithium *p*-nitrophenyl ethyl phosphate (LiPNEF) and *p*-nitrophenyldipnehyl phosphate (PNFDF) in the presence of OH⁻, with over a 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 nucleophilic participation of the alkoxide ions of DHEDAB and CHEDAB, with values of 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 (functional micelles) are no better catalysts than the corresponding alkyltrimethyl ammonium bromides, suggesting that electrophilic catalysis is relatively unimportant. Cetylpyridinium bromide (CPBr) 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)[4,5] have little effect on the rate of hydrolysis of LiPNEF.

The addition of primary amines increased 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 micells, amines increased the overall rate of the reaction by attacking the aryl group without markedly catalyzing hydrolysis.[6]

The study of the micellar catalyzed dehydrochlorination of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) and some of its derivatives, as well as the hydrolysis of lithium *p*-nitrophenyl ethyl phosphate (LiPNEF) in the presence of higher concentrations of hydroxide ion (0,10 to 5,0 M) in the presence and absence of salts, showed that the pseudo-phase ion exchange model fails and does not explain experimental results. In fact, some systems contain liquid crystalline mesophases and a model analogous to phase transfer catalysis seems more appropriate.[7-15]

The present paper deals with the study of the hydrolysis of *p*-nitrophenyl diphenyl phosphate in aqueous solutions containing sodium hydroxide, micelles of diethylheptadecylimidazolinium ethyl sulfate (DEHIES) and dimethyl sulfoxide (DMSO). The reaction under consideration is illustrated below.

$$NO_2 - \langle \rangle - O - P \overset{O}{\underset{}{}} (O-\langle \rangle)_2 \quad \xrightarrow[\text{DEHIES}]{\text{NaOH}} \quad NO_2 - \langle \rangle - O^- + \left[\langle \rangle - O - \overset{O}{\underset{}{P}} \right]_2 O^- \quad (I)$$

EXPERIMENTAL PROCEDURE

MATERIALS. The phosphate ester, *p*-nitrophenyl diphenyl phosphate (PNFDF) was prepared by standard methods[16-19]. A sample was also obtained from Prof. Fred M. Menger, Emory University, Atlanta, Georgia, USA. The surfactant, diethylheptadecylimidazolinium ethyl sulfate (DEHIES) was obtained from Chem Service Inc., West Chester, Pennsylvania, USA. Dimethyl sulfoxide (DMSO) and sodium hydroxide were analytical reagent grade and were purchased from Merck do Brasil, Rio de Janeiro. They were used without further purification.

MICELLE FORMATION. The critical micellar concentration (CMC) of the surfactant DEHIES was determined at 25°, 32° and 40°C by measurement of the surface tension of DEHIES-H_2O-DMSO solutions using a Fisher Model 21 Semi-Automatic Tensiometer. The thermodynamic parameters for micellization including the free energy, ΔG_m^o, enthalpy, ΔH_m^o and the entropy of micellization, ΔS_m^o, were calculated from CMC data using standard equations.[20-22]

KINETICS. The hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNFDF) was studied spectrophotometrically measuring the rate of appearance of the *p*-nitrophenoxide ion at 4030 Å. A Varian DMS-80 spectrophotometer equipped with a water-jacketted cell compartment was used. The reaction was studied at 15°, 25° and 35° C at various concentrations of NaOH, DMSO and DEHIES. The pseudo-first order rate constant ,k_ψ , in sec^{-1} was determined from linear plots of $\ln(A_\infty - A_t)$ versus time. The second order rate constants (k_2) were calculated from k_ψ and the hydroxide ion concentration. Activation parameters such as E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ were also determined using the following equations.

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

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

$$\Delta S^{\neq} = 4,576(\log k_\psi - 10,753 - \log T + E_a/4,576T) \qquad (IV)$$

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

RESULTS AND DISCUSSION

Some representative results obtained for the critical micellar concentration (CMC) of DEHIES at 25° and 40°C are illustrated in Table I. The CMC values were obtained from the inflection point of plots of surface tension versus concentration or logarithm ($\log_{10}$) of the concentration for fixed amounts of DMSO. As can be seen, the critical micellar concentration of the surfactant increases both as a function of temperature and DMSO added. The addition of DMSO

hinders the formation of micelles in the DEHIES-H_2O-DMSO ternary system.

TABLE I. CRITICAL MICELLAR CONCENTRATION OF DIETHYLHEPTADECYL-
IMIDAZOLINIUM ETHYL SULFATE IN AQUEOUS SOLUTIONS
CONTAINING DIMETYL SULFOXIDE AT 25º AND 40º C.

Percent DMSO (by volume)	Mole Fraction (X_{DMSO})	CMC at 25ºC ($M \times 10^3$)	CMC at 40ºC ($M \times 10^3$)
0	0.000	0,25	0,28
10	0,028	0,40	0,45
20	0,060	0,44	0,50
30	0,099	0,55	0,66
40	0,145	1,10	1,32
50	0,203	2,75	3,47
60	0,277	5,13	6,61

TABLE II. THERMODYNAMIC PARAMETERS FOR THE FORMATION OF MICELLES
OF DIETHYLHEPTADECYLIMIDAZOLINIUM ETHYL SULFATE IN
AQUEOUS SOLUTIONS OF DIMETHYL SULFOXIDE AT 25ºC.

Percent DMSO (by volume)	Mole Fraction (X_{DMSO})	ΔG°_m (kcal/mol)	ΔH°_m (kcal/mol)	ΔS°_m (eu)
0	0,000	-4,91	-1,41	+11,8
10	0,028	-4,64	-1,47	+10,6
20	0,060	-4,58	-1,59	+10,0
30	0,099	-4,45	-2,27	+ 7,3
40	0,145	-4,04	-2,26	+ 6,0
50	0,203	-3,49	-2,28	+ 2,1
60	0,277	-3,12	-3,15	+ 0,1

Table II summarizes the thermodynamic parameters obtained for the micellization of DEHIES in aqueous solutions of DMSO at 25ºC. The standard free energy of micellization, ΔG^o_m , varies almost linearly from -4,64 kcal/mole to -3,12 kcal/mole with increasing concentration of DMSO. The value of ΔG^o_m determined for DEHIES alone in pure water was -4,91 kcal/mole, indicating that the micellization process is more spontaneous in pure water. The enthalpy of micellization, ΔH^o_m , calculated experimentally is exothermic and similar to water for low concentrations of DMSO (-1,41 to -1,59 kcal/mole). For higher concentrations it becomes more pronounced (more exothermic), indicating stronger inter- actions between H_2O and DMSO. ΔS^o_m decreases gradually from +11,8 to +0,1 eu.

Similar results have been reported for the cetyltrimethyl- ammonium - water-dimethyl sulfoxide system (CTAB-H_2O-DMSO) and have been explained in terms of the formation of the DMSO·$2H_2O$ stoichiometric hydrate.[24-26] As can be seen in Table II from the ΔS^o_m values, an increase in orderliness of the DEHIES-H_2O-DMSO system takes place as the mole fraction of DMSO is increased. In fact, results of proton spin-lattice relaxation studies have shown that the increased structuring of the DMSO-H_2O liquid system resulting in the formation of the stoichiometric hydrate DMSO·$2H_2O$ overcomes the hydrophobic effect of the alkyl chain of CTAB and inhibits totally the formation of micelles at a mole fraction of DMSO (X_{DMSO}) of about 0,33 in accordance with results obtained by surface tensiometry. Under these conditions plots of surface tension for CTAB-H_2O-DMSO versus concentration of CTAB are linear.

Proton spin-lattice relaxation times ($1/T_1$) and average rotational correlation times, $\tau_s(R)$, for the terminal methyl, N-methyl and methylene groups of CTAB as well as effective activation energies obtained for the various relaxation processes in water-dimethyl sulfoxide solutions showed that the surfactant molecules become trapped in the crystalline lattice of the DMSO·$2H_2O$ hydrate.[25-27]

Some typical experimental results obtained for the pseudo- first order rate constant k_ψ for the hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNFDF) at 25ºC as a function of DEHIES and various fixed amounts of NaOH are shown in Figure 1. The rate profiles are representative of micellar catalyzed reactions.The addition of surfactant to the reaction medium causes an increase in the rate of hydrolysis up to a point where there is complete incorporation of the substrate in the micellar phase. Further increase in the concentration of surfactant causes a decrease in the rate of reaction, probably due to dilution of the reactive counterions in the Stern layer. There is a maximum in all rate profiles at about 15 x 10^{-4} M DEHIES as compared to 20 x 10^{-4} M for CTAB. All curves also show a secondary maximum at about 8 x 10^{-4} M DEHIES that is probaly due to the formation of pre- micellar aggregates. For aqueous solutions containing 0,020 M NaOH the catalytic effect (ratio of the rate in the presence and absence of surfactant under the same conditions) is about 40-fold for DEHIES as compared to 80-fold for CTAB.The difference is
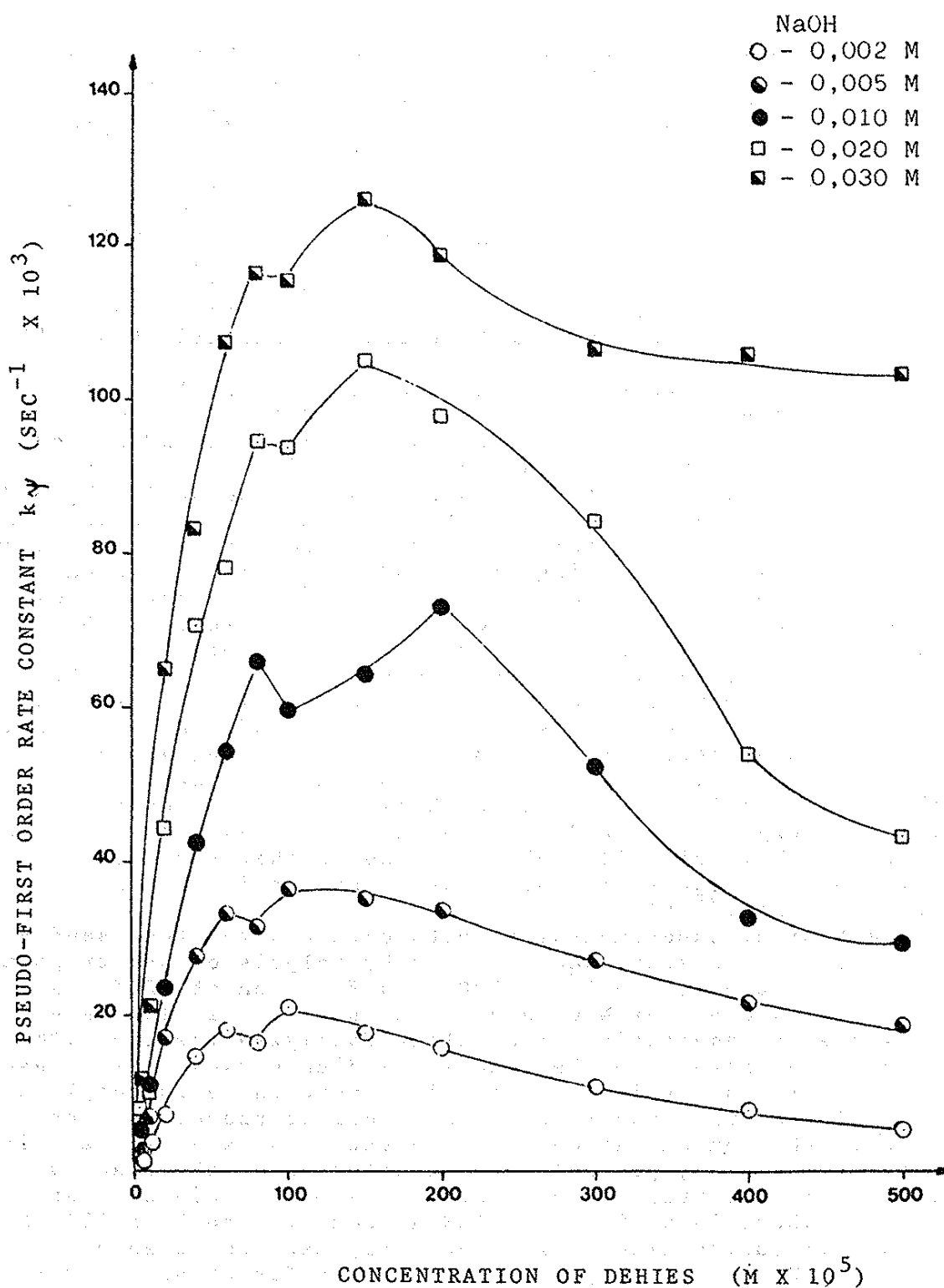
FIGURE 1. RATE PROFILES FOR THE HYDROLYSIS OF *p*-NITROPHENYL
DIPHENYL PHOSPHATE AT 25ºC IN AQUEOUS SOLUTIONS
CONTAINING SODIUM HYDROXIDE AND MICELLES OF DIETHYL-
HEPTADECYLIMIDAZOLINIUM ETHYL SULFATE (DEHIES).

attributed to the large difference in the head group of the two surfactants. Second order rate constants for the reaction (k_2) have an average value of 6,0 sec^{-1} mole^{-1} and the reaction can be essentially considered as second order in hydroxide ion.

Figure 2 illustrates typical rate profiles obtained for the hydrolysis of PNFDF in aqueous solutions containing 0,010 M NaOH and different concentrations of surfactant and dimethyl sulfoxide at 25ºC. For a fixed concentration of 30% DMSO by volume there is a similar behavior to that observed for the aqueous solutions without DMSO, with a maximum in the rate profile shifted to higher concentrations of surfactant. For solutions with 60% DMSO by volume there is a relative inhibition of the reaction, but the reaction rates are slightly higher than for the corresponding DMSO-H$_2$O solutions without surfactant. There is no clear maximum in the rate profile. For solutions containing 90% DMSO by volume the reaction rates measured are considerably higher than under other conditions studied. An inhibition of the reaction takes place at concentrations above 20 x 10^{-4} M DEHIES.

Figure 3 shows the variation of the pseudo-first order rate constant at 25ºC for the reaction under consideration in the absence of surfactant at a fixed concentration of NaOH (0,010M) and varying mole fraction of DMSO.

Figure 4 illustrates the dependence of the pseudo-first order rate constant (k_ψ) on the mole fraction of DMSO for fixed concentrations of NaOH (0,010 M) and surfactant (15 x 10^{-4} M DEHIES).

Figure 5 shows on the same scale the results mentioned above and compares them to those obtained for aqueous solutions containing a fixed concentration of cetyltrimethyl ammonium bromide (CTAB = 20 x 10^{-4} M), at the maxima in the rate profiles.

It can be clearly noted that low concentrations of DMSO have a pronounced effect on the reaction rates in the presence of the two surfactants. At mole fractions of DMSO above 0,2 the rate constants for the three systems H$_2$O-DMSO, H$_2$O-DMSO-CTAB and H$_2$O-DMSO-DEHIES become much less sensitive to the addition of the cosolvent.

A more detailed analysis of Figure 5 shows three different types of behavior of the rate constant as a function of the mole fraction of the cosolvent. In the DMSO mole fraction range where micelle formation takes place (10-60% by volume), an increase in the amount of cosolvent decreases the rate of the reaction. At about 70% by volume of DMSO the rate constant attains minimum values and at concentrations of DMSO above 80% by volume the reaction rates increase considerably.

The three different behaviors of the rate constants (that are essentially similar for CTAB and DEHIES) are explained in terms of the effect of DMSO on micelle formation. At low concentrations of DMSO where micelles exist, but the micellization process is inhibited by DMSO, the addition of the cosolvent decreases the rate constant of the reaction. At higher concentrations of DMSO, where there are no micelles, the system is essentially controlled by the influence of the dipolar aprotic solvent that also acts as a catalyst for the reaction. In the intermediate region (60-70% by volume of cosolvent), where the stoichiometric hydrate DMSO·2H$_2$O forms, the behavior is similar to the solution without
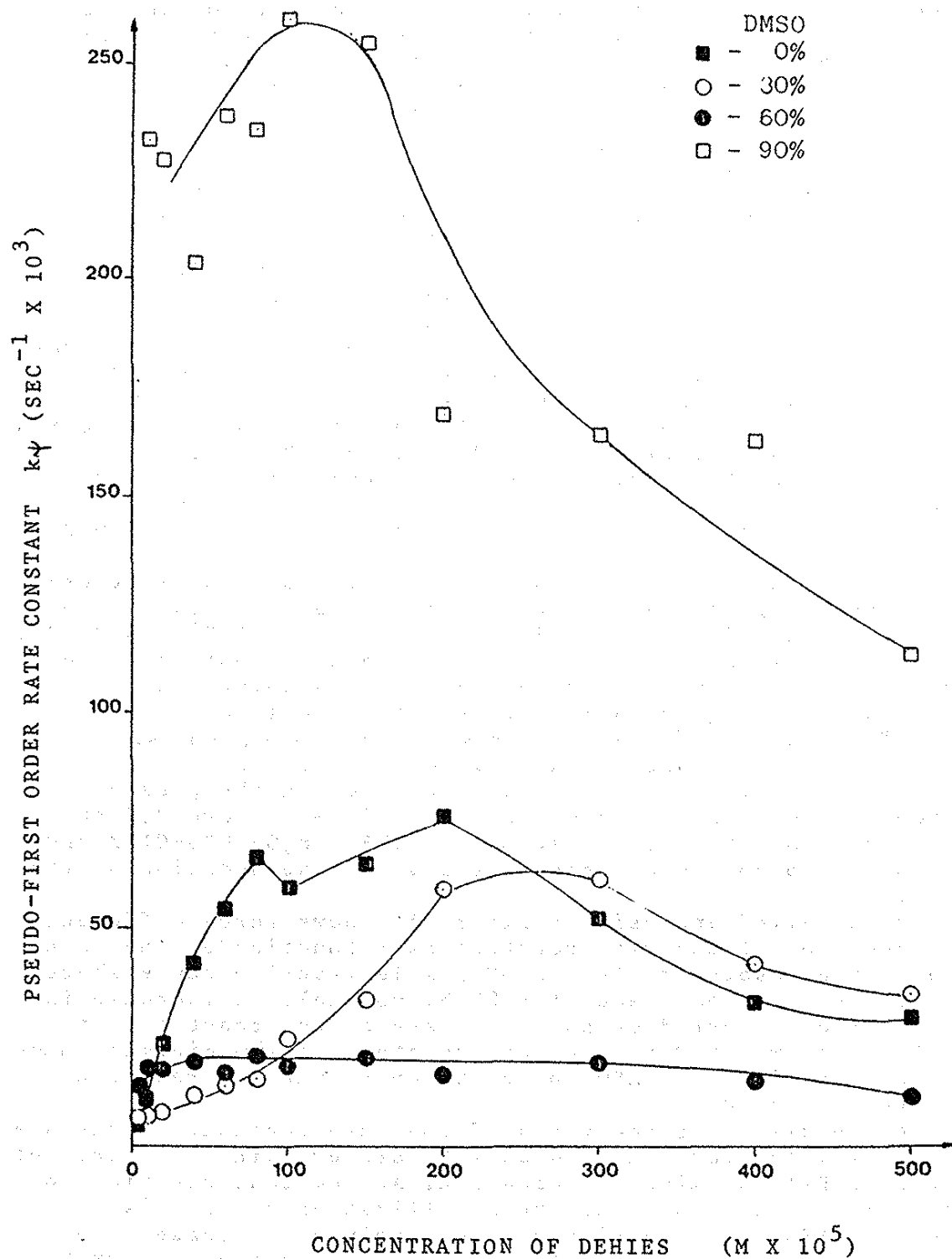
FIGURE 2. RATE PROFILES FOR THE HYDROLYSIS OF p-NITROPHENYL DIPHENYL PHOSPHATE AT 25°C IN AQUEOUS SOLUTIONS CONTAINING 0,010 M SODIUM HYDROXIDE IN THE PRESENCE OF DEHIES AND VARIOUS CONCENTRATIONS OF DMSO.
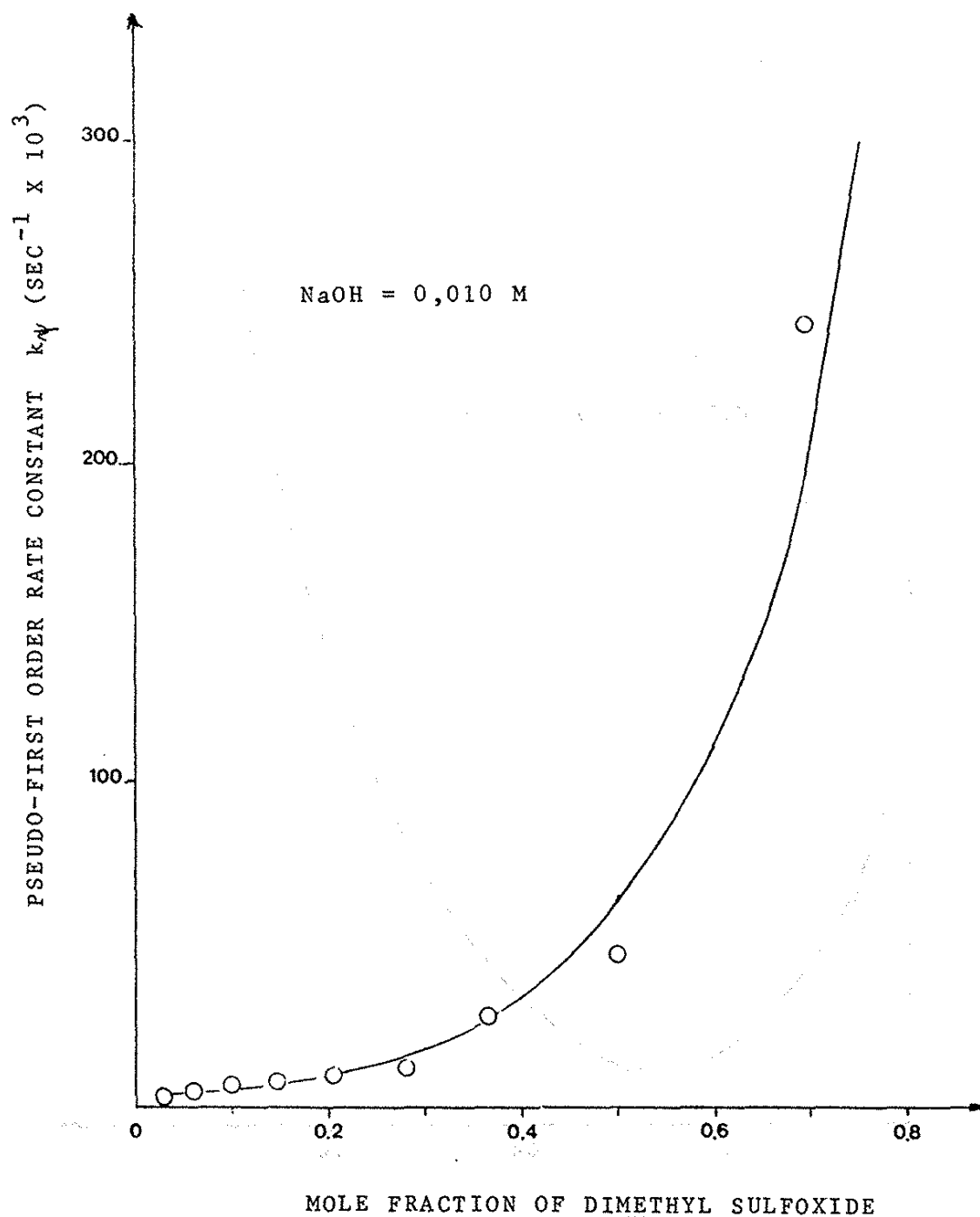
NaOH = 0,010 M

MOLE FRACTION OF DIMETHYL SULFOXIDE

FIGURE 3. PLOT OF THE PSEUDO-FIRST ORDER RATE CONSTANT FOR
THE HYDROLYSIS OF p-NITROPHENYL DIPHENYL PHOSPHATE
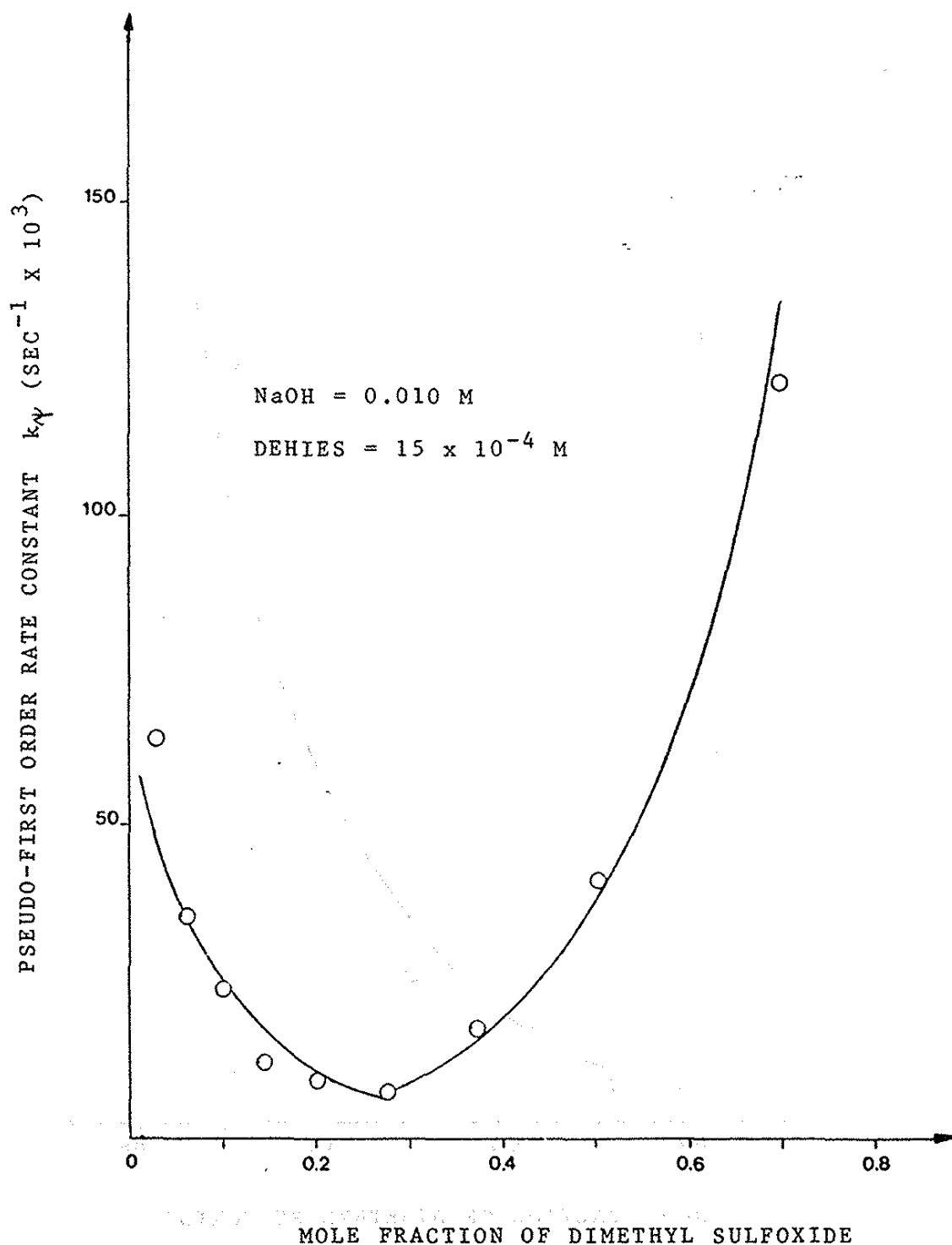AT 25°C AS A FUNCTION OF THE MOLE FRACTION OF DMSO.

FIGURE 4. PLOT OF THE PSEUDO-FIRST ORDER RATE CONSTANT FOR
THE HYDROLYSIS OF p-NITROPHENYL DIPHENYL PHOSPHATE
AS A FUNCTION OF THE MOLE FRACTION OF DMSO FOR
AQUEOUS SOLUTIONS CONTAINING 0,010 M SODIUM HYDROXIDE
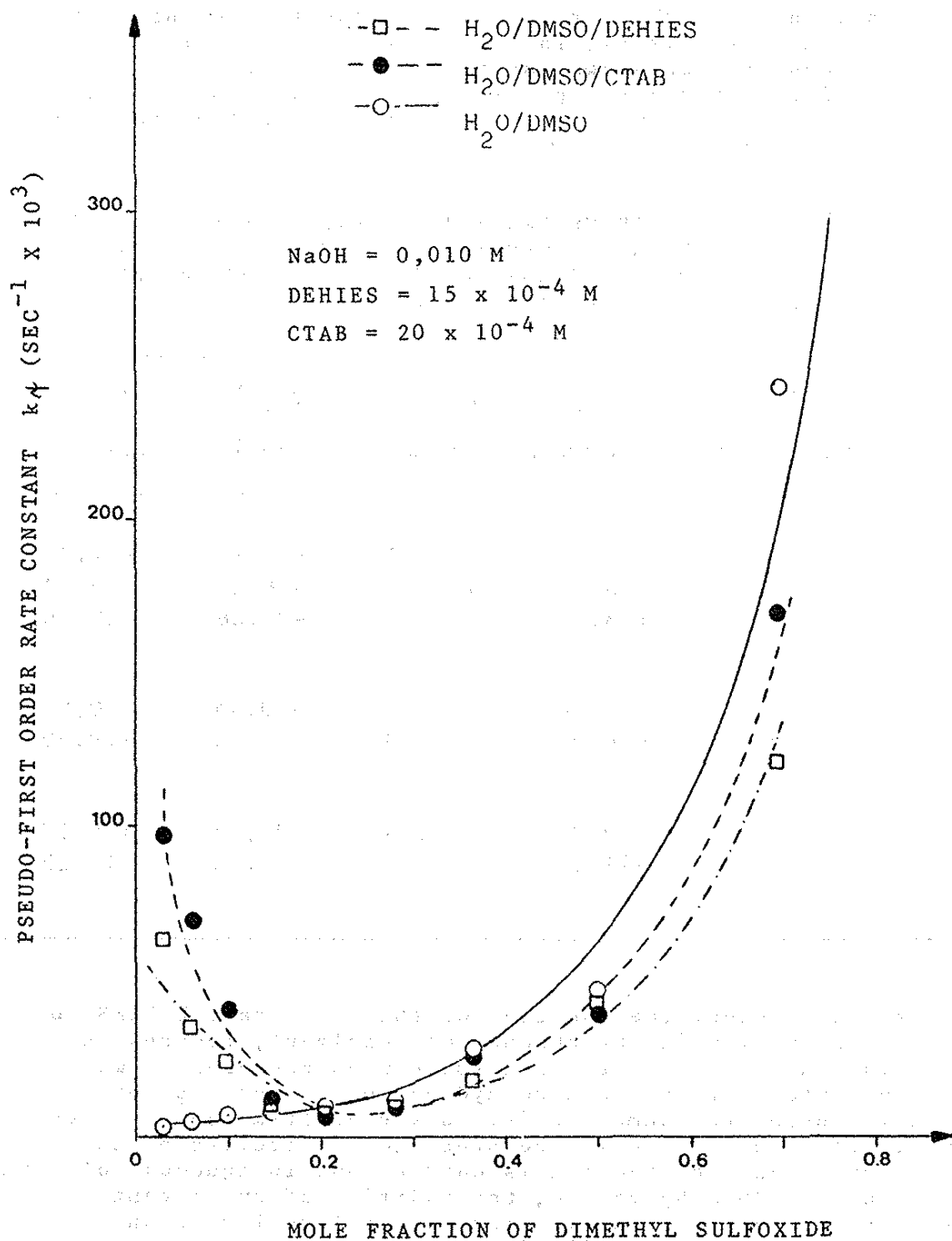AND 15 x 10^{-4} M DEHIES AT 25ºC.

FIGURE 5. PLOT OF THE PSEUDO-FIRST ORDER RATE FOR THE HYDROLYSIS OF p-NITROPHENYL DIPHENYL PHOSPHATE AT 25°C AS A FUNCTION OF THE MOLE FRACTION OF DMSO FOR FIXED CONCENTRATIONS OF NaOH, CTAB AND DEHIES.

surfactant. In fact, the surfactant is present in solution as dispersed monomers, trapped in the crystal lattice of the $DMSO \cdot 2H_2O$ hydrate, as shown for the case of CTAB. [25-27]

Table III summarizes typical experimental results obtained for the activation parameters of the reaction in the presence and absence of DEHIES at 25ºC.

TABLE III. ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF p-NITRO-
PHENYL DIPHENYL PHOSPHATE IN AQUEOUS SOLUTIONS OF
0,010 M SODIUM HYDROXIDE AT 25ºC IN THE PRESENCE
AND ABSENCE OF DEHIES AND DMSO.

Concentration		Ea	$\Delta H^{o \neq}$	$\Delta S^{o \neq}$	$\Delta G^{o \neq}$
DMSO (% vol.)	DEHIES $(M \times 10^3)$	(kcal/mol)	(kcal/mol)	(eu)	(kcal/mol)
–	–	+15,23	+14,64	-22,24	+21,27
–	100	+ 8,82	+ 8,22	-36,60	+19,14
–	150	+ 8,61	+ 8,02	-37,08	+19,08
10	–	+18,74	+18,15	- 9,44	+20,96
10	100	+14,68	+14,08	-17,46	+19,29
90	–	+ 9,03	+ 8,44	-32,64	+18,17
90	100	+11,29	+10,70	-25,26	+18,23

As can be seen, the addition of the surfactant DEHIES to the reaction medium in the absence of cosolvent, reduces the activation energy, E_a, about 7 kcal/mole when compared to water solution containing only sodium hydroxide. The entropy of activation under the same conditions varies from about -22 eu in water to about -37 eu in the presence of micelles of the surfactant. When the reaction is carried out in aqueous solutions containing 10% DMSO by volume, the addition of surfactant decreases the energy of activation about 4 kcal/mole and reduces the entropy of activation from -9 eu to -17 eu. For the case of solutions containing 90% DMSO by volume, the addition of surfactant increases the activation energy about 2 kcal/mole and increases the entropy of activation from about -32 eu to - 25 eu. In summary, the addition of surfactant to pure water solutions

or to water solutions containing 10% DMSO by volume leads to a
more structured transition state (due to the presence of micelles)
and facilitates the occurrence of the reaction.

For solutions containing 90% by volume DMSO, that already
represents a highly structured medium, the addition
of the surfactant, that is now present as dispersed non-aggregated
monomers, causes a destructuring of the transition state and an
inhibition of the reaction. Analysis of the variation of $\Delta G^{\neq}$,
$\Delta H^{\neq}$ and $\Delta S^{\neq}$ as a function of solvent shows that this reaction
follows the isokinetic or compensation law and permits us to
suggest that the presence of micelles in the reaction medium does
not alter the mechanism of the reaction.[28]

Interactions in liquid solutions and the effect of solvents
on the rate of bimolecular reactions are rather complex subjects
and have been treated extensively in the literature.[29-38]

One approach uses the transition state theory and considers
the relative solvation between the initial and transition state.
The solvation of any of these states reduces the free energy and
increases the stability. For a solvent to increase the rate of
reaction it is necessary to reduce the activation free energy
($\Delta G^{\neq}$). This reduction in $\Delta G^{\neq}$ may come about either by the sta-
bilization of the transition state with respect to the initial
state or by destabilization of the initial state with respect to
the transition state.[30]

Another approach considers the structure or cohesion of the
solvent and how solvent-solvent interactions affect the reacting
species.Obviously, the over-all effect of a solvent includes both
solvation and cohesion, but to date it is extremely difficult to
integrate the two points of view. The cohesive forces of a liquid
are electrostatic in nature. At the same time, electrostatic
interactions are responsible for non-specific solvation. It is
thus very diffcult to consider the two effects separately.[32]

There are many theories that can give good predictions about
the solvent effect on reaction rates.

The Hughes-Ingold Theory is based on the fact that reacting
species normally alter their charge distribution during the
passage through the transition state of the reaction.Ionic reagents
form activated complexes that contain less charge, while neutral
molecules form transition states containing some degree of
separation of charge.The Hughes-Ingold Theory analyzes the type of
charge of a given reaction pathway and the effect of polarity on
the charge distribution during the reaction (from initial to
transition state).

The alkaline hydrolysis of *p*-nitrophenyl diphenyl phosphate
is a bimolecular reaction between the hydroxide anion and a neutral
substrate. According to the Hughes-Ingold Theory,this reaction
should be faster when carried out in a polar solvent. In fact,
this theory can be used to explain the experimental results
observed for solutions containing only water and DMSO in the
absence of surfactant. This theory really considers the solvent
as a continuous medium and does not take into account specific
effects.

Common equations proposed show a linear relationship in terms of functions of the dielectric constant ε, such as $(1/\varepsilon)$, $(\log \varepsilon)$ or $(\varepsilon - 1)/(2\varepsilon + 1)$. Such linearity has been observed for reactions in binary solvent systems where the dielectric constant varies with the composition.[37-40]

The dielectric constant of the medium was calculated according to Equation VI.

$$\varepsilon_{medium} = X_{H_2O} \cdot \varepsilon_{H_2O} + X_{DMSO} \cdot \varepsilon_{DMSO} \qquad (VI)$$

where $\varepsilon_{H_2O} = 70,5$ and $\varepsilon_{DMSO} = 48,9$ and X_{H_2O} and X_{DMSO} represent the respective mole fractions of water and dimethyl sulfoxide.[29]

Figure 6 illustrates a plot of the log $k\psi$ for the reaction versus the function $(\varepsilon - 1)/(2\varepsilon + 1)$ of the dielectric constant ε and represents a quantitative correlation of the reaction rate with the dielectric constant. It is really a linear free energy relationship.

An analysis of Figure 6 shows that in the absence of surfactant the plot of log k ψ versus $f(\varepsilon)$ is essentially a straight line (line 1). In the presence of surfactant, however, the plot of log k ψ versus $f(\varepsilon)$ gives two straight lines. One of them (line 2) describes the behavior for solutions containing 10-50% DMSO by volume and line 3 for solutions with 50 to 90% by volume DMSO. One may conclude that the dielectric constant may be used to describe the polarity of the reaction medium. The effect of DMSO on the reaction rate can be described quantitatively in the absence of surfactant (H_2O-DMSO system) or when the surfactant is present in the form of dispersed monomers (60-90 % DMSO by volume for the H_2O-DMSO-DEHIES system). In the presence of micelles, the reaction rate is essentially determined by the micelles themselves and the addition of DMSO to the reaction medium is practically masked.

The internal pressure of liquids is given by Equation VII.[41-44]

$$I\,P = \Delta H_{vap}/M\rho \qquad (VII)$$

where   I P = internal pressure
ΔH_{vap} = latent heat of vaporization
M   = molecular weight
ρ = density of the liquid

The calculated values for the internal pressure of water and dimethyl sulfoxide were 22355,0 atm and 5991,5 atm, respectively.

The internal pressure of the reaction medium was calculated using Equation VIII and the appropriate mole fractions of H_2O and DMSO.

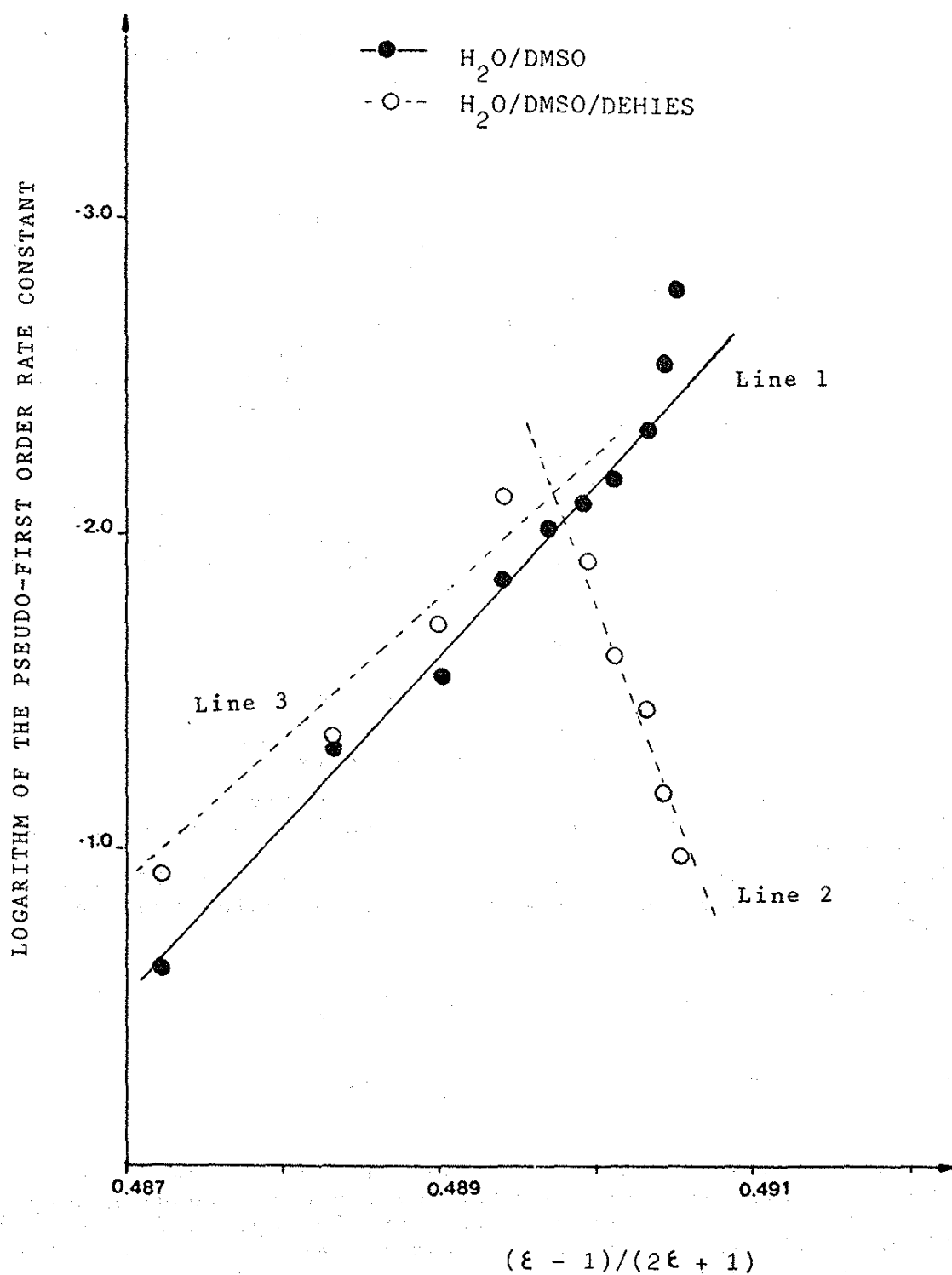$$I\,P_{medium} = X_{H_2O} \cdot I\,P_{H_2O} + X_{DMSO} \cdot I\,P_{DMSO} \qquad (VIII)$$

FIGURE 6. PLOT OF THE LOGARITHM OF THE RATE CONSTANT FOR
THE HYDROLYSIS OF PNFDF AT 25ºC   IN THE PRESENCE
OF 0,010 M NaOH, DMSO AND DEHIES VERSUS A FUNCTION
OF THE DIELECTRIC CONSTANT OF THE MEDIUM.

Figure 7 shows a plot of lóg k_ψ versus the internal pressure of the medium for H_2O-DMSO and H_2O-DMSO-DEHIES solutions at 25°C. For the case of water-dimethyl sulfoxide solutions without surfactants the plot is essentially a straight line (line 1). For the H_2O-DMSO-DEHIES system containing 15×10^{-4} M surfactant, there are two straight lines, one describing the behavior in the reaction medium containing 10 to 60% by volume DMSO (line 2) and the other (line 3) for solutions containing 60 to 90% DMSO. The influence of the internal pressure of the reaction medium on the reaction rate in the absence of surfactant or when it is present in dispersed form (60 to 90% DMSO) indicates that the activated complex formed during hydrolysis of PNFDF in alkaline medium occupies a larger volume than that of the reagents involved in the reaction. In the presence of micelles, the activated complex is in the interior of the micelles and the reaction rate is determined by the micellar medium. The cohesive effect of the solvent medium (H_2O-DMSO) is essentially masked.

A multi-parameter correlation was also done in order to consider specific solute-solvent interactions. The parameters used were polarity (E_T) and donor number (DN), one representing acidity, the other basicity of the solvent.[36] The realation used is given by Equation IX.

$$\log k_\psi = \log k_{\psi 0} + a E_T + b DN \qquad (IX)$$

where E_T = polarity of the solvent

DN = donor number of the solvent

a,b = regression coefficients

The regression coefficients describe the sensitivity of the reaction rate on electrophilic and nucleophilic characteristics of the solvent.

The polarity and donor number of the medium for different concentrations of DMSO present were calculated using Equations X and XI.

$$E_T \text{ medium} = X_{H_2O} \cdot E_{T\ H_2O} + X_{DMSO} \cdot E_{T\ DMSO} \qquad (X)$$

$$DN \text{ medium} = X_{H_2O} \cdot DN_{H_2O} + X_{DMSO} \cdot DN_{DMSO} \qquad (XI)$$

The polarity values used for water and dimetyl sulfoxide were 63,1 and 45,0 cal/mole, respectively and the corresponding donor numbers were 18,0 for water and 29,8 for dimethyl sulfoxide.[29,45]

Figure 8 illustrates a plot of log k_ψ as a function of the mole fraction of DMSO for solutions containing H_2O-DMSO and H_2O-DMSO-DEHIES at 25°C for the multi-parameter correlation function given by Equation IX.
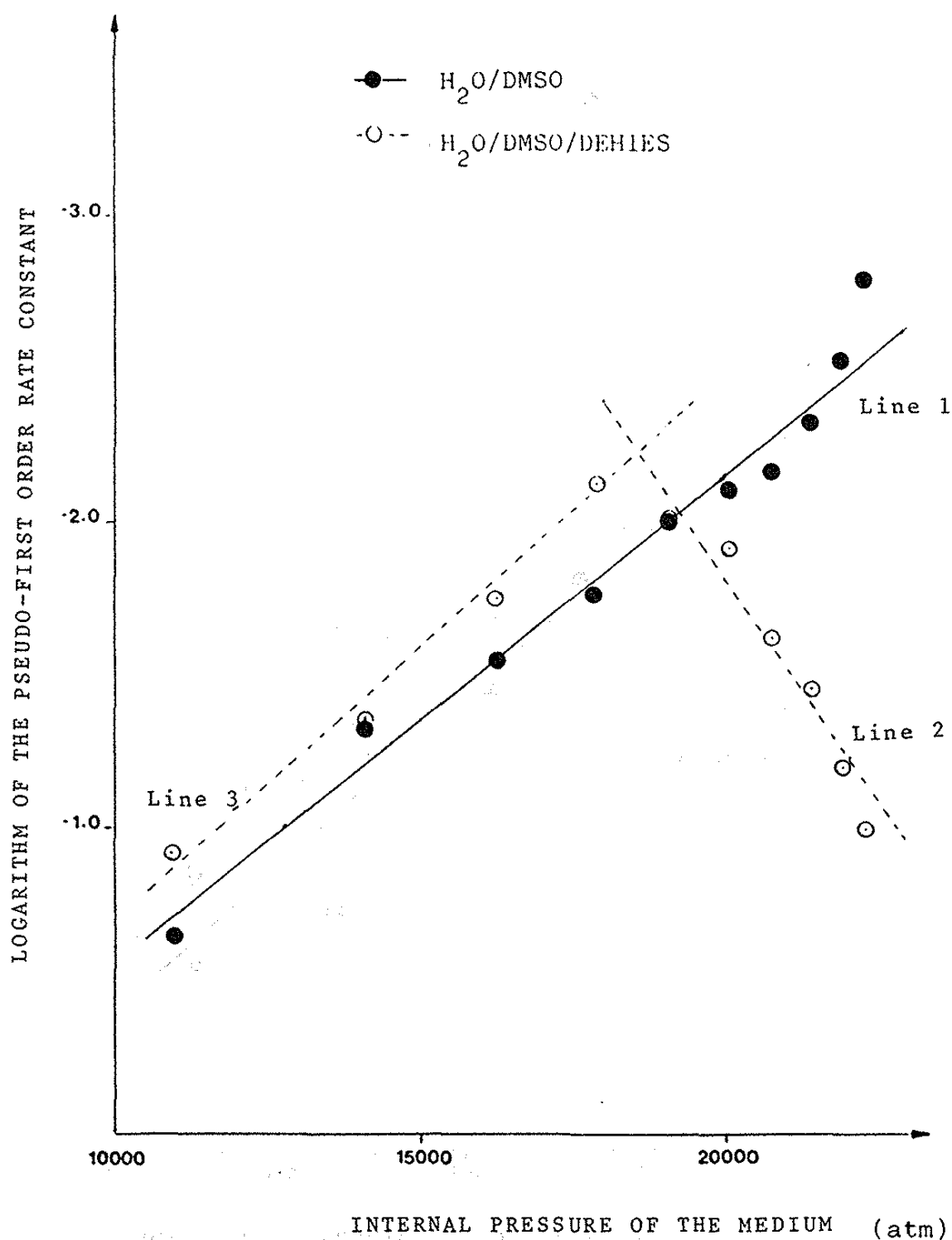
FIGURE 7. PLOT OF THE LOGARITHM OF THE PSEUDO-FIRST ORDER RATE
CONSTANT FOR THE HYDROLYSIS OF PNFDF AT 25ºC IN THE
PRESENCE OF 0,010 M NaOH, DEHIES AND DMSO VERSUS THE
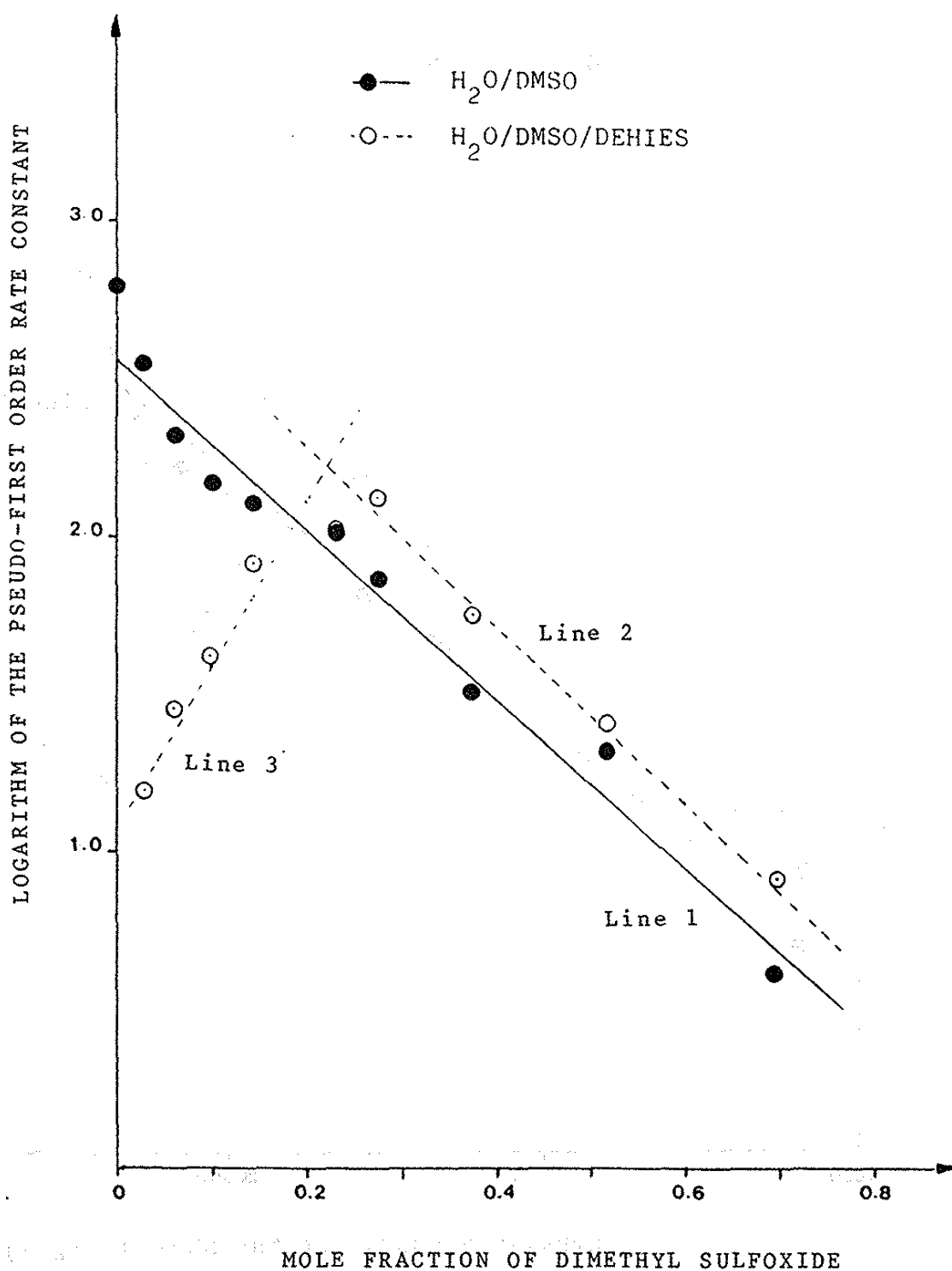INTERNAL PRESSURE OF THE MEDIUM.

FIGURE 8. PLOT OF THE LOGARITHM OF THE PSEUDO-FIRST ORDER
RATE CONSTANT FOR THE HYDROLYSIS OF PNFDF AT 25⁰C
IN THE PRESENCE OF 0,010 M NaOH, DEHIES AND DMSO
VERSUS THE MOLE FRACTION OF DMSO FOR A MULTI-
PARAMETER CORRELATION .

Again, in the absence of surfactant, the result is a straight line (line 1) with a=-0,0423 and b=0,1647. In the presence of 15×10^{-4} M DEHIES the behavior of log k ψ is described by two two straight lines. One of them (line 2) describes the behavior of solutions containing 10-50 % by volume DMSO (a=0,0783 and b=-0,2785) and the other one (line 3) describes the behavior for solutions containing 60-90 % DMSO (a=-0,0593 and b=0,1172). These results indicate that in the absence of surfactant (a=-0,0423 and b=0,1647) or when the surfactant is present in dispersed form (a=-0,593 and b=0,1172) the reaction medium shows a negative influence of the electrophilic character and a positive influence of the nucelophilic character. In the presence of micelles (a=0,0783 and b=-0,2785) the electrophilic contribution becomes positive and the nucleophilic contribution becomes negative.

In summary, we may conclude that all three linear correlation relationships in terms of polarity, internal pressure and multi-parameters give similar results and that the formation of the $DMSO \cdot 2H_2O$ stoichiometric hydrate has a pronounced effect on the formation of micelles and the rate of the micellar catalyzed hydrolysis.

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