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Kinetic and mechanistic study of micellar effect of hydrolytic reaction of di-2methoxy-4-nitroaniline phosphate

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Abstract

The effect of anionic surfactant (sodium dodecyl sulphate) and non-ionic surfactant (Brij-35) on the hydrolysis of di-2-methoxy-4-nitroaniline phosphate was studied spectrophotometrically at 303 K. The influence of salts on the reaction rate was studied. The presence of inorganic salts (KCl, KNO₃, and K₂SO₄) exhibited positive effect on the reaction rate. The thermodynamic activation parameters were calculated from Arrhenius equation. On the basis of the experimental findings a suitable mechanism has been proposed. The binding constants between the reactants and the surfactants evaluated from the kinetic models proposed by Menger-Portnoy, Piszkiewicz and Berezin have been found in good agreement.

Graphical Abtract:



KEYWORDS: Hydrolysis, Di-2-methoxy-4-nitroaniline phosphate, Menger-Portnoy's, Piszkiewicz's and Berezin models.

1. INTRODUCTION

Phosphate ester hydrolysis is an important process in biology as it is being used in protein synthesis, signal, and energy transduction, as well as the replication of the genetic material [1-3]. Phosphate esters have been the subject of extensive experimental [3-10]and theoretical studies [11–16]. Phosphate mono- and diesters are the key components of many biochemical reactions. Compared with phospho-triesters and monoesters, the recognition, binding and cleavage of phosphodiesters, especially of nucleic acids, are currently of utmost importance in biological systems. Many hydrolytic processes in enzymes involve metal cations that are assumed to activate a water molecule or other nucleophilic groups as well as the electrophilic center of the substrate [17]. Extensive investigations were carried out by many researchers on micelles [18, 19] and vesicles [20] due to effective catalytic media, as they can provide a hydrophobic environment, which may affect the catalytic process [21]. Micellar catalysis of a large number of reactions is an area of current research because of the parallel behavior of macromolecules and enzymes [22-24]. In the micellar pseudo phase, micelles can affect the rates of chemical reactions that involve the incorporation of reactants. Kinetic study of some reactions provides information about the reaction mechanism in these media, and about the solubilization of reagents [25].

Surfactants generally form spherical micelles in aqueous solutions above the critical micelle concentration [CMC]. The micelles can affect the rate of reaction by concentrating the reactants and providing a reaction environment that is different from that of the aqueous solution [26]. Thus, rate acceleration or inhibition of organic reactions in micellar solutions will result from two factors: (a) different rates of reaction in the micellar phase and in bulk solution and (b) the altered distribution of the substrate between these two phases (i.e., a concentration effect) [27]. Surfactants are widely used and found a large number of applications because of their remarkable ability to influence the property of surface and interfaces. In the years that have passed, micellar solutions have proven to be an extremely versatile topic of research. The catalytic potential of micellar aggregates has received special attention and kinetic study of esters are the most challenging and interesting areas of research worldwide [28, 29]. Surfactants are widely involved in various strategies such as nanotechnology, gene delivery, drug solubilization, micellar catalysts, emulsifiers, inhibitors of corrosion, enhancing the solubility of sparingly soluble substrates and so forth [30–33]. During past few decades, systematic kinetic results have been reported on the effect of micelle on various organic reactions [34, 35]. However; such studies with phosphate hydrolysis appeared to be scare in literature. So, the kinetic and mechanistic aspects of micellar catalysis have been undertaken in detail.

2. EXPERIMENTAL

2.1 Materials & Methods

The solution of amidol was prepared in triply distilled water and was stored in dark and cool place. Freshly prepared solutions of ammonium molybdate, HCl (A. R. Grade), in triply distilled water were used throughtout the experiments. The surfactants, Sodium dodecyl sulfate (SDS, 99%, Merck), polyoxyethylene (23) lauryl ether (Brij-35, 99%, Merck) were used during the experiment. The solutions of surfactants were prepared in triply distilled water. Other reagents KCl, K₂SO₄, KNO₃ etc. used were of A. R. grade and their solutions were also prepared in triply distilled water.

2.2 Synthesis Of Di-2-Methoxyl-4-Nitroaniline Phosphate

Di-2-methoxy-4-nitroaniline phosphate was synthesized in the laboratory by Rudert [36] method. The method involves the reaction of 2-methoxy-4-nitroaniline phosphate (parent compound) with phosphorylating agent phosphorous oxychloride (POCl₃) in 2:1 mole ratio. 2-methoxy-4-nitroaniline was dissolved in benzene and kept in a water bath. Then phosphorous oxychloride with benzene was added drop wise with heating of reaction mixture on the water bath. After complete addition, the temperature was raised to 120°C using oil bath for half an hour. The whole reaction mixture in the heated condition was poured in a beaker containing 100 ml of distilled water. Two layers were separated; the aqueous layer was rejected as it contained monoester, while the benzene layer was then digested by dilute alkali (5% NaOH), the chloridate dissolve in alkali by forming a soluble sodium salt. The solution was filtered and obtained crude diester as a solid. The crude product so obtained was recrystalized by dissolving in ammonia and reprecipitating by HCl to get pure sample. It was then dried to obtain di-2methoxy-4-nitroaniline phosphate. Elemental and IR spectrum analysis data were used to confirm the compound as shown below:

(a) Elemental analysis (%); calculated (observed): C, 42.22 (42.19); H, 3.77 (3.78); N, 14.07 (14.02).

(b) IR absorption spectra: The spectrum of di-2-methoxy-4-nitroaniline phosphate was recorded by FTIR Model 136 Shimadzu. υ (KBr) (cm⁻¹) : 3326.21 (N-H); 3407.43 (O-H); 1513.62 (C=C); 1215.35 (P=O); 758.88 (P-N); 2918.51 (C-H); 1730.78 (NO₂); 1024.84 (C-N).

2.3 Kinetic Measurements

The required volume of substrate, HCl, surfactants were mixed in the reaction vessel; which was kept at 303 K. The progress of hydrolytic study was measured by Allen's modified method [37]. This procedure involves the measurement of inorganic phosphate formed from the ester during hydrolysis, Phosphomolybdate complex [(NH₄)₃PO₄.12MoO₃] is formed by the reaction of inorganic phosphate with ammonium molybdate. This complex is reduced to molybdenum blue, a soluble complex by addition of 2, 4-diaminophenol dihydrochloride (i.e. Amidol) solution. The intensity of the blue colour is directly proportional to the amount of the free phosphoric acid. The optical density of the blue color was measured by Systronic spectrophotometer at wavelength of 735 nm.

3. RESULTS AND DISCUSSION

3.1 Hydrolysis In Aqueous Medium

The kinetic investigations were carried out at different concentration of HCl under pseudo-first order conditions. The concentration of HCl was taken in the range from 2.5 × 10^{-3} mol dm⁻³ to 15.0×10^{-3} mol dm⁻³ for di-2-methoxy-4-nitroaniline phosphate. The concentration of di phosphate was kept constant at 5 x 10^{-4} mol dm⁻³. The observed values of rate constant (k_w) increase linearly with the increase in [HCl]. The slope of the plot of log (k_w) versus log [H⁺] was found to be 0.30 (with r² > 0.93), indicating that the order of the reaction is close to unity.

3.2 Hydrolysis In Micellar Medium

The kinetics of hydrolysis of the di-2-methoxy-4-nitroaniline phosphate was investigated at 303 K. Pseudo-first order rate constant was determined in each experimental set to establish the dependence of reaction rate on concentration of each reactant as well as on the order of the reaction. To study the effects of the concentration of different reactants on the kinetics of the hydrolysis reaction and to propose a suitable reaction mechanism, concentration of each reactant was varied keeping concentration of other reactants constant. The anionic micelles of SDS influenced the rate of hydrolysis of the ester. The observed values of rate constants were increased with the increase in [SDS]. The values of rate constant attained maximum values and then started to decrease on further increasing the anionic [surfactant]. The observed higher rate in SDS could be attributed to the adsorption of substrate on the micellar surface, thereby, increasing the local molarities of the complex in the Stern layer.. The nonionic micelles of Brij-35 enhanced the rate of hydrolysis of the ester. The observed values of rate constants were increased with the increase in [Brij-35]. The values of rate constant attained maximum values and then started to decrease on further increasing the nonionic [surfactant].

3.2.1 Effect Of Substrate

Hydrolysis was carried out in solution with di-2-methoxy-4-nitroaniline phosphate concentration varied from 1.0×10^{-4} to 8.0×10^{-4} . Pseudo first order rate constants are summarized in Table 1. The results show that the rate of hydrolysis increases with concentration of substrate (S). The plot of rate of reaction versus [Substrate] produces a straight line passing through the origin, indicating the order of reaction with respect to substrate is one [Figure 1].

3.2.2 Effect Of [Hcl]

Hydrolysis was studied for the system with HCl concentration varied from 2.5×10^{-3} to 15.0×10^{-3} mol dm⁻³. Pseudo first order rate coefficients are presented in Table 2. The data suggest that the rate of hydrolysis increases with increasing HCl concentration. A plot of log k_{ψ} versus log [HCl] gave a straight line with positive slope having positive intercept, indicating that order with respect to HCl concentration is positive fractional [Figure -2].

3.2.3 Effect Of Temperature

Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place. The effects of temperature on the micellar-catalyzed reaction of di-2-methoxy-4-nitroaniline phosphate were studied within the temperature range 298 to 318 K in presence and absence of surfactant. The results are shown in Table 3. From the Arrhenius plot (Figure -3), the value of energy of activation (E_a) , enthalpy of activation (ΔH^{\neq}) , entropy of activation (ΔS^{\neq}) and Gibb's free energy of activation (ΔG^{\neq}) were calculated for catalyzed and uncatalyzed reaction. These values are summarized in Table 4. Observed negative entropy of activation in the hydrolysis of di-2methoxy-4-nitroaniline phosphate in the presence of surfactant supports the rate determining step of the proposed scheme 2. The proposed mechanism is also supported by the moderate values of energy of activation and other activation parameters. The large negative value of ΔS^{\neq} in the presence of surfactant again indicates a more ordered, rigid transition state in surfactant media [38]. The nearly identical value of ΔG^{\neq} in the absence and in the presence of surfactants indicates the operation of a similar reaction mechanism in aqueous or surfactant media.

3.2.5 Effect Of Solvent

To study the solvent effect, several experiments were carried out in various percentage of 1,4-Dioxane and DMSO; the data are summarized in Table 5 & 6. These results indicate that the rate of reaction increases with increase in the percentage of solvent (Dioxane and DMSO). The presence of water as solvent changes the rate and mechanism of hydrolysis reactions in many ways such as nucleophilic reagent, as a high dielectric-constant; and as a specific solvating agent for organic reactants and products [39, 40]. The modifications in the reaction medium i.e. by adding organic solvents or by adding surfactant molecules also affect the solvating power and thus alter the hydrolytic rate [41, 42]. The variation in

the values of rate constant with the alteration in the medium may involve the interaction of the solvent medium with the reactants, transition states and/or products. The rate of hydrolysis of ester increases when the transition state is better solvated or stabilized by the H-bonding than the initial state [43]. The effect of dielectric constant of the medium on the rate constant of a reaction between two ions has been described by the well known equation.

$$\log k_{\psi} = \log k'_{0} - \frac{Z_{A} Z_{B} e^{2} N}{2.303 (4\pi\epsilon_{0}) d_{AB} RT} \frac{1}{D_{c}}$$

Where k'_0 is the rate constant in a medium of infinite dielectric constant, Z_A and Z_B are the charges of reacting ions, d_{AB} refers to the size of activated complex, T is the absolute temperature and D_c is the dielectric constant of the medium. Equation (i) predicts a linear relationship between log k_{ψ} versus $1/D_c$. In the present investigations a plot of log k_{ψ} versus $1/D_c$ gave a straight line with a positive slope which clearly supports the involvement of two dipoles (Figure 4 & Figure 5). The result shows that the rate constant values gradually increased with the addition of solvent. The effect of solvents on rate of hydrolysis indicates the transition state in which charge is dispersed and this is accordance with Chanley's observation [44]. On the basis of experimental finding the following reaction scheme may be proposed for the effect of micelle for the hydrolysis of phosphate ester

Considering equation (ii), (iii) of Scheme 1 and also applying steady state approximation, we construct the following rate equations:

$$rate = \frac{kK[S]_{T}[H^{+}]}{1+K[H^{+}]}$$

These rate relations are in a good agreement with the experimental results.

3.2.6 Effect Of Electrolytes

The effects of added salts on the rate were explored because salts, as additives, in micellar system acquire a special place due to their ability to induce structural changes [45]. The effects of salt on the catalytic reactions were studied in the presence of different surfactants at 303 K, keeping other variables constant. The addition of KCl, KNO₃ and K₂SO₄ to the different surfactants increased the rate of reaction {Table 7 & Figure 6 (a, b, c)}. The rate enhancing effect largely depends upon the nature of counterions and the hydrophilic character. The counterions from the added electrolyte compete with the reactive counterions for micellar binding. The enhancing of micellar catalysis by the added electrolytes may also be interpreted by considering the change of size of the micelles in the presence of salts. The presence of salts decreases the aggregation number (and consequently the shape and size) of the micelles. A decrease in aggregation number will increase the number of micelles and as a result the catalytic efficiency of the micelle increases.

3.2.7 Critical Micelle Concentration (CMC) Determinations

The process of micelle formation in aqueous solution occurs when the concentration of free amphiphiles reaches the critical micelle concentration (CMC) [46]. The biological important micelles are capable of forming a new reaction medium, concentrating the reagents at the lipid/water interface, the stern layer micelle-forming surfactants self-aggregate in a cooperative manner, forming stable but highly dynamic clusters above the

critical micelle concentration [47]. Such surfactants as SDS & Brij-35 exhibit a tendency to change their activity through self-assembly that, in turn, may influence the kinetics of hydrolysis or oxidation processes. Determination of critical micelle concentration (CMC) is an important step in studying oxidation process, which is catalyzed by surfactants in a micellar form. A digital conductivity meter was used to measure CMC values at a constant temperature. The CMC values were determined graphically, using a plot of specific conductivity versus surfactant concentration. The intercept point of nearly two straight-line portions in the plot was indicative for micelle formation and corresponded to the CMC of surfactant. The CMC values of surfactant measured under different experimental conditions are summarized in Table 8.

3.2.8 Effect Of Surfactants

The effects of SDS micelles on the reaction of di-2-methoxy-4-nitroaniline phosphate were studied in the presence of varying amounts of SDS. On increasing SDS from nil x 10^{-3} to 7.0×10^{-3} mol dm⁻³ at fixed [Substrate] and [HCI] at 303 K the pseudo-first order rate constants (k_{ψ}) increase from 6.28×10^{-3} to 14.63×10^{-3} (min⁻¹) (Table 9). The value of binding constant was also calculated. However at higher concentrations of surfactant, a decrease in rate constant was observed, this is in confirmation with bimolecular reaction catalyzed by micelles. Most of the micellar mediated organic reactions are believed to occur either inside the Stern layer or at the junction region of Stern or Gouy–Chapman layer. The main factor involved in the kinetic micellar effect is the electrostatic and hydrophobic interaction between substrate and surfactant increases the concentration of reactants in to a small volume. In present case, negatively charged micellar surface Downloaded by [Orta Dogu Teknik Universitesi] at 11:09 23 April 2016

attracts the ionized substrate bearing the positive charge in the Stern layer. With increase in concentration of SDS, the local molarity of reactants increases in the Stern layer resulting the enhancement of rate constant k_{ψ} for the hydrolysis of substrate (Figure - 7).

The Brij-35 concentration was varied in the range of nil x 10^{-3} to 7.0×10^{-3} mol dm⁻³ and the rate constant values first increased from $6.28 \times 10^{-3} \text{ min}^{-1}$ to $13.96 \times 10^{-3} \text{ min}^{-1}$ and after that it decreased on further increasing the concentration of surfactant (Figure 8). The results are shown in Table 8. The increase in rate constant was observed at [Brij-35] < CMC. This fact is usually interpreted as reactants inducing micelle formation. This type of catalysis is also known as submicellar catalysis or pre-micellar catalysis. The feasibility can be sought in the fact that small aggregates of the surfactants (dimmers, trimers, tetramers etc.) exit below CMC; these small submicellar aggregates can interact physically with the reactants forming catalytically active entities. The maxima in the ratesurfactant profile are produced by two opposite effects. Binding of reactants in the stern layer begins as soon as the micelle formation starts and these reactants are transferred into a small volume of the micellar pseudophase. There is thus a concentration effect which is responsible for acceleration. This concentration effect is opposed by the counterions dilution of the reactants within the micellar pseudophase with increasing surfactant concentration.

3.3 Qualitative Treatment Of Micellar Catalysis

The experimental data obtained by variation of surfactant may be applied to some models developed for micellar catalysis reactions. These models explain the catalysis and inhibition of reaction by surfactant and give some qualitative characteristics of surfactant for the reaction.

3.3.1. Kinetic Model To Explain The Micellar Effects

The effect of surfactants on reaction kinetics is known as micellar catalysis which involves several contributing factors. On the basis of a distribution of reactants between water and the micellar "pseudo-phase", in aqueous solution micellar catalysis of reaction is explained. Catalytic effect increases with increasing hydrophobicity of the micelles and reactants. Surfactant catalysis can be ascertained by plotting a graph between k_{ψ} versus [Surfactants], for the verification of bimolecular reactions.

3.3.2. Menger And Portnoy's Model

The observed effect of micelles on the kinetics hydrolysis can be explained in terms of Menger and Portnoy model [48].

Where K_s is the association constant with micellised surfactant, nD_n whose concentration is that of the total surfactant, less that of monomer, which is taken to be the critical micelle concentration. This model leads to the following relationship for micellar catalysis:

$$\frac{1}{k_w - k_{\psi}} = \frac{1}{k_w - k_m} + \frac{1}{(k_w - k_m)K_s[D_c]}$$
(iv)

Where equation (iv) predicts, the plot of $(k_w - k_{\psi})^{-1}$ versus $[D_n]^{-1}$, $(D_n = [D]$ -CMC) is linear {Figure – 9 (a, b)}. The Menger and Portony model allows us to determine kinetically the binding constant K_s and the rate constant k_m in the micellar phase. From the plot of $(k_w - k_{\psi})^{-1}$ versus $[D_n]^{-1}$, K_s and k_m values were calculated. The K_s and k_m values of the micelle, under the present conditions of kinetics were found are shown in Table 11.

3.3.3 Piszkiewic's Model Or Co-Operative Model

Piszkiewicz [49] suggested a kinetic model analogous to well-known Hill model to explain the catalysis of molecular reactions by surfactants. According to this model a substrate (S) aggregates with n number of detergent molecules (D) to form critical micelle (D_n S) which may react to yield product as given in Scheme 3.

For the micelle catalyzed reactions which show positive cooperativity, the rate constant, as a function of the detergent concentration, is given by

$$k_{\psi} = \frac{k_m [D]^n + k_w K_D}{K_D + [D]^n}$$
(v)
$$\log\left(\frac{k_{\psi} - k_w}{k_w - k_w}\right) = n \log[D] - \log K_D$$
(vi)

Here k_{ψ} represents the rate constant in the presence of surfactant. $K_{\rm D}$ is dissociation constant of micellized detergent back to its free components, *n* is index of cooperativity, D is the total [surfactant], $k_{\rm m}$ and $k_{\rm w}$ are rate constants in micellar and aqueous pseudo-phases respectively. To determine the $k_{\rm w}$ and k_{ψ} for the hydrolysis reaction of substrate, in acidic medium, the reaction was studied in both absence and presence of surfactant. The correct value of $k_{\rm m}$ cannot be determined experimentally; therefore its value is computed using Menger–Portnoy's approach. Figure 10 (a, b) gives a straight line for the plot of log [$(k_{\psi} - k_{\rm w}) / (k_{\rm m} - k_{\psi})$] vs. log D. The values of *n* and $K_{\rm D}$ were determined from the gradient and intercept (Table 10).Some thermodynamic parameters are given in Table 11. Regression coefficient of Fig.1-6 and 9-11 are given in Table 12 for the linearity of the graphs.

3.3.4 Berezin's Model

Berezin and coworkers developed the first general treatment based on the pseudo-phase model and successfully simulated for bimolecular reactions. The inhibition of rates at higher concentration of surfactant may be explained with the help of Berezin model [50], which involves solubilization of both the reactants in the micellar phase. According to this approach, a solution above the critical micelle concentration may be considered as a two-phase system, consisting of an aqueous phase and a micellar pseudo-phase. The distribution of reactants may be as shown in Scheme 4.

A quantitative rate expression for a bimolecular reaction (Scheme 3) occurring only in aqueous and micellar phase for the pseudo-first order rate constant is given below:

$$k_{\psi} = \frac{k_{\psi} + k'_{m} K_{S} K_{0} (C_{\text{Surf}} - \text{CMC})}{\left[1 + K_{S} (C_{\text{Surf}} - \text{CMC})\right] \left[1 + K_{0} (C_{\text{Surf}} - \text{CMC})\right]}$$
(vii)

Where, $K_{\rm S}$ and K_0 are the association constants of substrate and HCl, respectively with SDS and Brij-35. $C_{\rm surf}$ is the analytical concentration of SDS and Brij-35, ($k'_{\rm m} = k_{\rm m}/V$), V being molar volume of the micelle and $k_{\rm w}$ and $k_{\rm m}$ are the pseudo-first order rate constant in absence and presence of micelle, respectively. Since the intermediate product (SH⁺) is charged species and the substrate is large molecules, the hydrophobic and electrostatic interactions will be large and hence it may be expected that $K_{\rm S}$ and K_0 will be low. Since C_{surf} is small it may be possible that $k_W \gg k'_m K_S K_0 (C_{surf} - CMC)$ so that the above equation takes the form as below

(ix)

$$k_{\psi} = \frac{k_{\psi}}{1 + (K_{S} + K_{0})(C_{\text{Surf}} - CMC) + K_{S}K_{0} (C_{\text{Surf}} - CMC)^{2}}$$
(viii)

Since (C_{Surf}- CMC) is negligible so, the equation (viii) may be rearranged to:

$$\frac{1}{k_{\psi}} = \frac{1}{k_{w}} + \frac{(K_{s} + K_{0})}{k_{w}} (C_{\text{surf}} - CMC)$$

Plot k_{ψ}^{-1} versus (C_{surf} - CMC), is linear {Figure 11(a, b)}, slope is $(K_s+K_0)/k_w$ and intercept is $1/k_w$. From slope and intercept we calculated the binding constant between HCl and substrate in the micelle, i. e. (K_s+K_0) . The binding constant of the micelle-HCl complex cannot be directly correlated with the catalytic effect without considering the relative binding of the transition state with the micelle. If the binding of the transition state with the micelle is greater than that of the ground state of the HCl with the micelle, rate enhancement would be there. The very high catalytic efficiency observed for the ionization of HCl by micelles indicates that the transition state is stabilized more than the ground state.

3.4 Mechanism Of Micellar Catalysis

On the basis of experimental observations [51], we suggested the possible mechanism of micellar catalysis of the hydrolysis of di-2-methoxy-4-nitroaniline phosphate in the different micellar solution.

(A) Formation of conjugate acid species:



(B) Bimolecular nucleophilic attack of water on phosphorous via conjugate acid species $S_N^2(P)$:



4. CONCLUSIONS

The kinetics of the hydrolysis of di-2-methoxy-4-nitroaniline phosphate studied in aqueous and micellar media. The CMC values lower than those given in the literature for aqueous solutions of surfactants indicates that acid decreases the CMC values. Hydrolysis products were identified and thermodynamic activation parameters were evaluated for the catalyzed as well as unanalyzed reactions. The added salts *viz*. KCl, KNO₃, K₂SO₄ enhanced the rate of reaction in the presence of micelles. Micelles affect rates of reactions by increasing local concentration in the micellar reaction region and changing rate constants in that region. In the presence of SDS and Brij-35, the rate of hydrolysis first increased and after attaining maxima (peak), it decreased with increasing concentration of surfactant. Application of different kinetic models confirms the behavior of micellar catalyzed reactions. The rate–[surfactant] profile was used to determine kinetic parameters like k_{m} , k_s etc.

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[Substrate]	SDS		Brij-35		
$\times 10^4$	$k_{\psi} \times 10^3$	Rate $\times 10^7$	$k_{\psi} \times 10^3$	Rate $\times 10^7$	
(mol dm^{-3})	(min ⁻¹)	mol dm ⁻³	(min ⁻¹)	mol dm ⁻³	
		min ⁻¹		min ⁻¹	X
1.0	14.52	14.52	13.82	13.82	N
2.0	14.57	29.04	13.89	27.78	
3.0	14.53	43.59	13.87	41.61	
4.0	14.61	58.44	13.93	55.72	
5.0	14.63	73.15	13.96	69.80	
6.0	14.68	88.08	13.98	83.88	
7.0	14.72	103.04	13.99	97.93	
8.0	14.67	117.36	13.95	111.60	

Table 1. Effect of substrate on the reaction rate in micellar media

Experimental Conditions: T = 303 K, $[H^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[SDS] = 7.0 \times 10^{-3} \text{ mol}$

dm⁻³, [Brij-35] = 9×10^{-5} mol dm⁻³

$[\text{HCl}] \times 10^3$	$k_{\Psi} \times 10^3 (\mathrm{min}^{-1})$		
$(\text{mol } \text{dm}^{-3})$	SDS	Brij-35	
2.5	12.52	12.21	
5.0	14.63	13.96	
7.5	16.24	14.78	(
10.0	17.85	16.11	
12.5	18.93	17.89	
15.0	20.47	18.96	

Table 2. Effect of $[H^+]$ on the reaction rate in micellar media

Experimental Conditions: T= 303 K, [Substrate] = $5.0 \times 10^{-4} \text{ mol dm}^{-3}$, [SDS] = 7.0×10^{-5}

 3 mol dm⁻³, [Brij-35] = 9 × 10⁻⁵ mol dm⁻³

Temperature	$k_{\rm w} \times 10^3 ({\rm min}^{-1})$	$k_{\psi} \times 10^3 (\text{min}^{-1})$	
T(K)	without Surfactant	SDS	Brij-35
298	4.41	9.93	9.88
303	6.28	14.63	13.96
308	7.84	18.34	19.57
313	10.39	25.77	27.16
318	14.08	35.13	38.69

Table 3. Arrhenius plot data for Di-2-methoxy-4-nitroaniline phosphate with and without surfactants

Experimental Conditions: $[H^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[SDS] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$, [Brij-

 $35] = 9 \times 10^{-5} \text{ mol dm}^{-3}$

Table 4. Arrhenius parameters for the Di-2-methoxy-4-nitroaniline phosphate with and without surfactant

Without surfactant	$\Delta E_a (kJ mol^{-1})$	$\Delta H^{\neq}(kJ mol^{-1})$	$-\Delta S^{\neq} (Jk^{-1} mol^{-1})$	$\Delta G^{\neq} kJ mol^{-1}$)
	10.52	8.03	35.92	18.91
SDS	11.44	8.96	31.21	18.42
Brij-35	12.81	10.32	26.76	18.42

Table 5. Effect of change in percentage of 1,4-dioxane content on the rate of phosphate ester hydrolysis in the with and without of surfactant

Percentage of 1, 4-	$1/D_c \times 10^3$	$k_{\rm w} \times 10^3 ({\rm min}^{-1})$	$k_{\psi} \times 10^3 (\text{min}^{-1})$	
dioxane (v/v)		without surfactant	SDS	Brij-35
0.00	0.0127	6.28	14.63	13.96
5.00	0.0134	7.03	15.40	14.89
10.00	0.0141	7.89	16.21	15.78
15.00	0.0149	8.76	17.24	16.55
20.00	0.0158	9.75	18.19	17.61

Table 6. Effect of change in percentage of DMSO content on the rate of phosphate ester

Percentage of	$1/D_c \times 10^3$	$k_{\rm w} \times 10^3 ({\rm min}^{-1})$	$k_{\psi} imes 10^3 (\mathrm{min}^{-1})$	
DMSO (v/v)		without surfactant	SDS	Brij-35
0.00	0.0127	6.28	14.63	13.96
5.00	0.0130	7.15	15.61	14.91
10.00	0.0133	8.07	16.58	16.06
15.00	0.0136	8.98	17.66	17.15
20.00	0.0139	9.91	18.76	18.29

hydrolysis in the with and without of surfactant

Table 7. Salt Effect

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$[Salt] \times 10^4$	$k_{\psi} \times 10^{-1}$	$^{3}(\min^{-1})$					
(mol dm^{-3})	KC1		KNO ₃		K ₂ SO ₄		
	SDS	Brij-35	SDS	Brij-35	SDS	Brij-35	
2	14.82	14.22	14.76	14.16	14.71	14.10	
4	15.07	14.49	14.98	14.37	14.87	14.25	R
6	15.32	14.73	15.11	14.65	14.98	14.37	
8	15.52	14.98	15.39	14.82	15.09) 14.52	
10	15.78	15.24	15.55	15.03	15.29	14.68	

Table 8. Critical micelle concentration (CMC) values of surfactants in different

experimental conditions

Solution	CMC (mol dm ⁻³)
Water + SDS	8×10^{-3}
Water + SDS + Substrate + HCl	2×10^{-3}
Water + Brij-35	9×10^{-5}
Water + Brij-35 + Substrate + HCl	3×10^{-5}

[Substrate] = 5×10^{-4} mol dm⁻³, [HCl] = 5×10^{-3} , T = 303 K.

Table 9. Effect of SDS

$SDS \times 10^3 \text{ (mol dm}^{-3}\text{)}$	$k_{\psi} \times 10^3 (\mathrm{min}^{-1})$
0	6.28
1	6.72
2	7.08
3	7.65
4	8.26
5	9.90
6	12.06
7	14.63
8	13.49
9	12.51
10	11.74
11	10.45
12	9.70
<u> </u>	

Table 10. Effect of Brij-35

	Brij-35 $\times 10^5$ (mol dm ⁻³)	$k_{\psi} imes 10^3 (ext{min}^{-1})$	
	0	6.28	
	1	6.47	
	2	6.94	X
	3	7.45	
	4	7.83	
	5	8.65	
	6	9.55	
	7	10.12	
	8	11.70	
	9	13.96	
	10	12.44	
	11	11.98	
	12	11.36	
			I
C	Ņ		
5			

Table 11. Some thermodynamic parameters and different constants calculated from various models

Parameters	Value		
	In the presence of SDS	In the presence of Brij-35	
$K_{\rm s}$ (mol ⁻¹	2.10×10^2	1.73×10^{4}	\sim
dm ³)			\mathbf{Q}^{\dagger}
$k_{\rm m} ({\rm m}^{-1})$	6.03 × 10 ⁻²	1.40×10^{-4}	
K _D	4.03	1.84	
n	0.562	0.949	
		0	

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SI. 1NO.	Figure No.	Regression Coefficients			
		Without	SDS	Brij-35	
		Surfactant			
1.	2	-	0.27	0.24	
2.	3	-2.35	-2.52	-2.82	
3.	4	63.51	32.31	32.17	
4.	5	166.6	93.33	99.00	
5.	6 (a)	-	0.118	0.126	
6.	6 (b)	-	0.099	0.109	
7.	6 (c)	-	0.069	0.071	
8.	9	-	0.755	0.058	
9.	10		0.56	0.95	
10.	11		0.70	0.005	
6	20				

Table 12. Regression Coefficients Values



Figure 1. Plot of Rate of reaction versus [Substrate] for the hydrolysis of Di-2-methoxy-



Figure 2. Plot of log k_{ψ} verses [H⁺] for the hydrolysis of Di-2-methoxy-4-nitroaniline phosphate



Figure 3. Plot between log k_{ψ} and 1/T with and without surfactants



Figure 4. Plot of log k_{ψ} versus 1/D_c with and without Surfactants (1, 4-Dioxane)



Figure 5. Plot of log k_{ψ} versus 1/D_c with and without Surfactants (DMSO)

Figure 6.



(c) Effect of variation of Inorganic Salt (K₂SO₄)

Figure 7. A plot of k_{ψ} verses SDS concentration for the hydrolysis of Di-2-methoxy-4nitroaniline phosphate



Figure 8. A plot of k_{ψ} verses Brij-35 concentration for the hydrolysis of Di-2-methoxy-4nitroaniline phosphate



Figure 9.

(b) Fitting of the experimental kinetic data to Menger-Portnoy's model (Brij-35)

Figure 10.

(b) Fitting of the experimental kinetic data to Piszkiewicz's model (Brij-35)

Figure 11

(b) Fitting of the experimental kinetic data to Berezin model (Brij-35)

Scheme 1

Scheme 2

Scheme 3

Scheme 4

