ISSN 1061-933X, Colloid Journal, 2014, Vol. 76, No. 6, pp. 765–773. © Pleiades Publishing, Ltd., 2014.

Micellar Effect on Hydrolysis of 4-Methyl-2-Nitroaniline Phosphate[1]

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Received February 28, 2013

Abstract—The effect of anionic surfactant sodium dodecyl sulfate (SDS) on the hydrolysis of a substrate (mono-4-methyl-2-nitroaniline phosphate) by HCl was studied at 303 K. The reaction followed the first-order kinetics with respect to both HCl and the substrate. SDS effectively catalyzes this reaction, which rate increases with the concentration of SDS due to an increase of dielectric constant of the medium. The kinetic data were fitted to Menger–Portnoy, Piszkiewicz and Berezin kinetic models to explain the observed micellar effects. The various activation parameters both in the presence and absence of SDS were evaluated; a reasonable mechanism was proposed. The rate constant in micellar phase, binding constant and index of cooperativity were calculated accordingly.

DOI: 10.1134/S1061933X14060027

INTRODUCTION

Organic phosphates are very important substances utilized in various branches of chemistry. Phosphate esters exhibit interesting biological and pharmacological properties that make them useful as pesticides and drugs. Phosphate mono- and diesters are the key components of many biochemical reactions [1], first of all, of phosphate ester hydrolysis, which underlies energy metabolism and various cellular transduction pathways in biological system. In living organisms, there is a wide variety of monophosphate, diphosphate and triphosphate compounds (essential esters). Some of them, such as adenosine diphosphate and adenosine triphosphate, plays especially important role in metabolism [2, 3]. These esters are widely used as solvents and as fuel additives for explosion control. The widespread use of toxic phosphates and phosphonates as insecticides, and their use as chemical weapons, has led to investigation of the fast detoxification and decontamination method [4]. Organophosphorous compounds are widely used as pesticides, insecticides, and chemical warfare agents [5]. The field of organophosphate chemistry is one of the most rapidly growing in the chemical industry [6].

Surfactant molecules when dissolved in water in concentration above certain critical value (critical micellar concentration, CMC) form aggregates which are called micelles. Micellar effect represents the most extensively studied example of surfactant influence on the kinetics of organic reactions in water and aqueous-organic mixtures [7–12]. Micellar systems allow for controlling the rate of chemical transformations proceeding within the colloidal phase. Acceleration of organic reactions in micellar solution is determined mainly by the concentration of the reactants in the micellar pseudophase [13–15]. The micelle forms specific microenvironments for different fragments of the reactant molecules; that is, a non-polar hydrophobic core binds similar hydrophobic species, whereas the outer, charged polar shell can interact with the hydrophilic groups. This micro-heterogeneity of the micellar environment underlies a catalytic action of micellar solutions. The ionic micelles enhance the rate of bimolecular reactions by increasing the concentration of the reactants within the small volume of Stern layer of the micelle. Duynstee and Grunwald were first [16], who found that anionic surfactants inhibited the rate of alkaline fading of several dyes, whereas the cationic surfactants exhibited an opposite tendency. The consideration of electrostatic and hydrophobic interactions between the reactants and micelles can account qualitatively for the kinetic effect on the reactions in micellar solutions. Surfactants and polymers are widely used as micellar matrices for medicine and industrial applications such as production of cosmetics, food, detergents, textiles and paints. A significant amount of systematic kinetic results have been reported in the literature on the effects of micelles on various organic reactions [17, 18].

Recently, a number of theoretical and experimental approaches have been used to address the problem of hydrolysis of anthropogenic organophosphorus ester, paraoxon [19]. The catalytic systems so far developed for cleavage of paraoxon include metal ion catalysis

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[20, 21], hydrolysis using nucleophiles [22], enzymatic degradation [23] and reactions in colloidal aggregates [24]. Although several studies on the catalytic degradation of phosphate esters have been recently published [25], the hydrolysis of phosphate esters in the presence of surfactants remains poorly explored. Ghosh et al. [26] studied the kinetic of hydrolytic decompositions of organophosphate and triphosphate by N-hydroxyamide in cationic micellar solution. The rate enhancement has been observed upon the nucleophilic attack of cationic micelles at phosphorus center. The interfacial ion exchange, which controls of the interfacial nucleophile concentration, and the reactivity at the micellar interface have been explained.

Hydrolysis is a chemical process, in which a certain molecule splits in two parts by the addition of a molecule of water. One fragment of the parent molecule binds a hydrogen ion (H^+) from water molecule, whereas the other group attaches the remaining hydroxyl group (OH^-). Hydrolysis is an important process in energy metabolism and storage in plants and animal. All living cells require a continuous energy supply for the biosynthesis and also for the active transport of ions and molecules across cell membranes. The study of hydrolysis of a variety of organic phosphates has become the subject of intense biochemical research. Metal ions can catalyze the enzymatic and non-enzymatic hydrolysis of a large number of phosphate esters [27]. Metals ions enhance the rate of hydrolysis through a formation of complex that results in neutralization of charge, enhancement of nucleophilicity, polarization of P–O bonds and appropriate alignment of reactants and, thereby, facilitates the reaction.

Herein, we report the micellar effect on the kinetics of hydrolysis of organophosphate and the effect of surfactant, sodium dodecyl sulfate (SDS), on the rate of various reactions under different experimental conditions such as chemistry of solvent and temperature.

EXPERIMENTAL

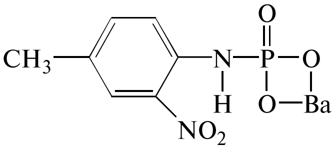
Materials

Ammonium molybdate: 8.3 g of ammonium molybdate was dissolved in 100 mL of distilled water under continuous shaking.

Hydrochloric acid: Hydrochloric acid of A.R. quality was used. It was standardized by 0.1 N sodium tetraborate (Borax) solution.

Amidol reagent: 1.4 g of amidol (impure, brownish black in color) was taken in a conical flask covered with a carbon paper; 2.0 g of activated charcoal and 10.0 mL of distilled water were added into the flask and then were shaken for 20 min. The colorless amidol solution was filtered into the flask containing 100 mL of 20% sodium metabisulphite. The as-prepared reagent was kept in a dark and cool place.

Synthesis of Mono-4-methyl-2-nitroaniline Phosphate



Mono-4-methyl-2-nitroaniline phosphate (MNP) has been synthesized by Cavalier method [28]. The method involves the reaction of 4-methyl-2-nitroaniline with phosphorylating agent phosphorous pentaoxide (P_2O_5) in 1 : 1 molar ratio. Saturated solution of barium hydroxide was added drop by drop to aqueous solution of mono-4-methyl-2-nitroaniline phosphate until the solution becomes pink-colored. A white precipitate was obtained which was filtered and washed several times with distilled water having few drops of acetic acid to remove inorganic phosphate. It was then dried to obtain barium salt of mono-4-methyl-2-nitroaniline phosphate. All the chemicals used were of A.R. grade.

The confirmation of the compound was done by comparing the theoretical and observed percentage of elements and also with the recorded IR spectrum as shown below.

a—Elemental analysis—theoretical (observed): C, 22.1 (23.65); H, 2.67 (2.19); N, 5.33 (4.45).

b—IR absorption spectra: The IR spectrum of mono-4-methyl-2-nitroaniline phosphate was recorded on Shimadzu FTIR Model-136 using KBr pallets.

(ν, cm^{-1})—Theoretical (observed): N–H, 3330–3050 (3065); O–H stretching, 3570–3200 (3350); C–H stretching, 2960–2835 (2944); C=C aromatic stretching, 1600–1450 (1557); P=O stretching, 1299–1250 (1257); P–N stretching, 850–650 (834); C–N stretching, 1065–953 (1023).

Kinetic Measurements

Allen's modified spectrophotometric method was used for the kinetic study of the hydrolysis of all esters. This procedure involves the measurement of inorganic phosphate formed from the ester during hydrolysis. Phosphomolybdate complex $[NH_4)_3PO_4 \cdot 12MoO_3]$ is formed by the reaction of inorganic phosphate with ammonium moybdate. This complex is reduced to molybdenum blue, a soluble complex, by the addition of 2,4-diaminophenol dihydrochoride (amidol) solution. The reaction-produced blue color is fully developed within ten minutes and remains stable for thirty minutes at room temperature. The intensity of the blue color is directly proportional to the amount of the free phosphoric acid. The optical density of the blue color followed Beer's law and was measured by Systronic 105 spectrophotometer at a wavelength (λ_{max}) of 735 nm.

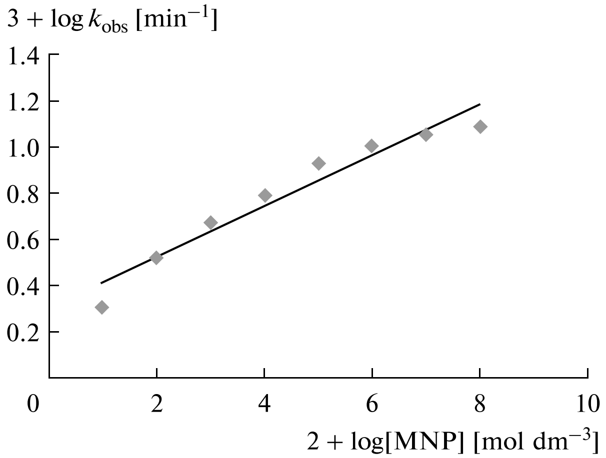


Fig. 1. Plot of logk_{obs} versus [MNP] obtained under experimental conditions (see Experimental section).

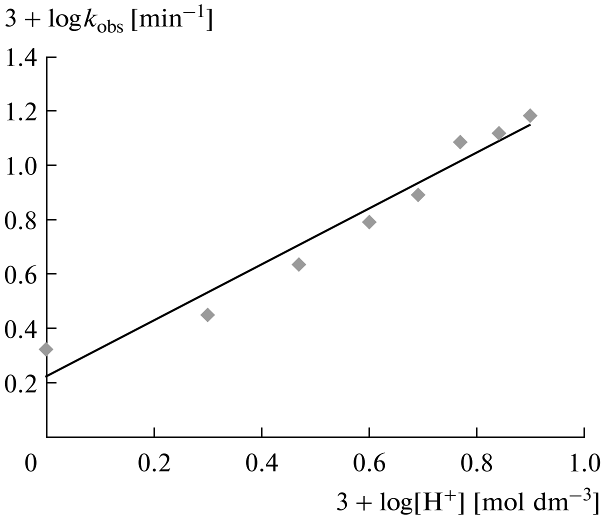


Fig. 2. Plot of logk_{obs} versus [H$^+$] for the SDS-catalyzed hydrolysis of MNP.

RESULTS AND DISCUSSION

The detailed kinetic investigations were performed under pseudo-first order conditions, when [MNP] $\gg$ [HCl]. The kinetics of hydrolysis of the phosphate was investigated at 303 K. 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. 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.

Effect of Variation of [MNP]

Hydrolysis was carried out in solutions with MNP concentration varied from 1.0×10^{-2} to 8.0×10^{-2} mol dm^{-3}. The results show that the rate of hydrolysis increases with concentration of substrate (S). The plot of logk_{obs} versus log[MNP] yields a straight line with a positive slope indicating that the order with respect to MNP concentration is a positive fractional value (Fig. 1).

Effect of Variation of [HCl]

Hydrolysis was studied for the systems with HCl concentration varied from 1.0×10^{-3} to 10.0×10^{-3} mol dm^{-3}. The data suggest that the rate of hydrolysis increases with HCl concentration. The plot of logk_{obs} versus log [HCl] also yields a straight line with a positive slope (Fig. 2).

Effect of Temperature

The reaction was studied at five different temperatures with 5°C interval in the range from 25 to 40°C. The rate of the reaction increased with temperature both in absence and presence of SDS. Thermodynamic activation parameters such as the enthalpy of activation ($\Delta H^{\neq}$), the entropy of activation ($\Delta S^{\neq}$) and Gibb's free energy of activation ($\Delta G^{\neq}$) were obtained from the Arrhenius equation (Table 1).

Activation parameters provide useful information about the environment in which chemical reactions take place. In order to obtain more information regarding the microenvironment of submicroscopic aqueous micelles, a series of kinetic runs were carried out at different temperatures with constant reactants concentration both in the absence and presence of SDS micelles. Gibb's free energy, enthalpy, entropy and heat capacity of activation are widely used to evaluate experimental reaction rates, especially for organic reactions in solution. In the absence as well as in the presence of surfactant, the plots of logk_{obs}, versus $1/T$ were linear with a negative slope (Fig. 3) which confirms the applicability of Arrhenius equation. The large negative value of entropy of activation ($\Delta S^{\neq}$) indicates that more ordered activated complex is formed in the presence of SDS with respect to the assemble in the SDS-free solution. The high values of free energy of activation ($\Delta G^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) suggests that the transition state is highly solvated.

Table 1. Thermodynamic parameters for the hydrolysis of MNP in presence and absence of SDS

System	E_a, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$-\Delta S^{\neq}$, J K^{-1} mol^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}
With SDS	46.08	47.83	58.51	65.55
Without SDS	34.47	34.20	120.9	70.80

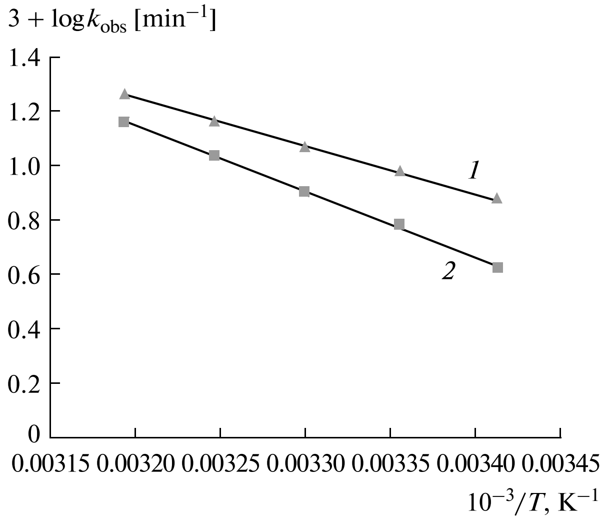


Fig. 3. Plots between logk_{obs} and $1/T$ in the presence of SDS (*1*) and in the SDS-free system (*2*).

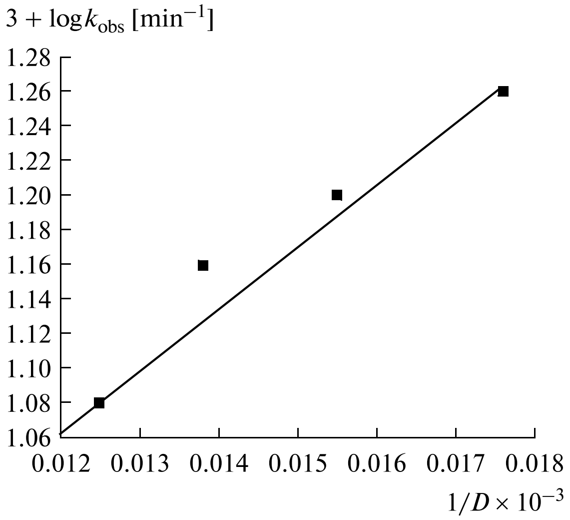


Fig. 4. Plot of logk_{obs} versus $1/D$ for the hydrolysis reaction catalyzed with SDS.

Effect of Polarity

In order to determine the effect of polarity of the medium on the rate of the reaction, the micellar-catalyzed acidic hydrolysis of MNP was studied in the systems with varied concentration of 1,4-dioxane (Table 2). The obtained data suggested that the reaction rate increased with the concentration of 1,4-dioxane, that is, the reaction proceeded faster upon an increase of the polarity of the medium. The influence of polarity on the rate of a reaction between two ions has been described by the well-known equation [29] given below

$$\log k_{obs} = \log k'_0 - (Z_A Z_B e^2 N/2.303(4\pi\varepsilon_0)d_{AB}RT) \times 1/D, \quad (1)$$

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 an absolute temperature and D is the dielectric constant of the medium. Equation (1) predicts a linear relationship between logk_{obs} versus $1/D$. In our system, a plot of logk_{obs} versus $1/D$ gave a straight line with a negative slope (Figs. 4, 5) corroborating the involvement of two dipoles into the process.

Table 2. Effect of change in percentage of 1,4-dioxane content on the rate of MNP hydrolysis in presence and absence of SDS

Percentage of dioxane, v/v	$1/D \times 10^3$	$k_{obs} \times 10^3$ (min^{-1}) in presence of SDS	$k_{obs} \times 10^3$ (min^{-1}) in absence of SDS
0.00	0.0125	12.13	3.11
10%	0.0138	14.33	4.15
20%	0.0155	16.14	5.17
30%	0.0176	18.20	6.55

The results suggest that the rate constant gradually increased upon the addition of solvent. The observed solvent-induced effect is in a good agreement with Chanley's observation [30].

On the basis of experimental findings, the following reaction scheme was proposed for the micellar effect on the hydrolysis of the phosphate (MNP):

$$S + H^+ \overset{K}{\rightleftharpoons} SH^+, \quad (2)$$

$$SH^+ \xrightarrow[\text{slow}]{k} \text{Product}. \quad (3)$$

Scheme 1.

Considering Eqs. (2), (3) of Scheme 1, we construct the following rate equations:

$$\text{rate} = k[SH^+], \quad (A)$$

$$\text{rate} = kK[S][H^+]. \quad (B)$$

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

Measurements of Critical Micellar Concentration

Surfactants undergo spontaneous aggregation above CMC, which value and dependence on experimental parameters is important for understanding the self-assembly of surfactant molecules. Micelles act as microreactors which can either accelerate or inhibit some reactions [31]. Micelles influence chemical reactivity by binding or excluding reactants from the reaction space as well as by changing the free energy of activation. The CMC values of the SDS were determined from specific conductivity versus surfactant concentration graphs obtained in the presence and in the absence of reactants (Fig. 6). The difference between the CMC values results from the well-known

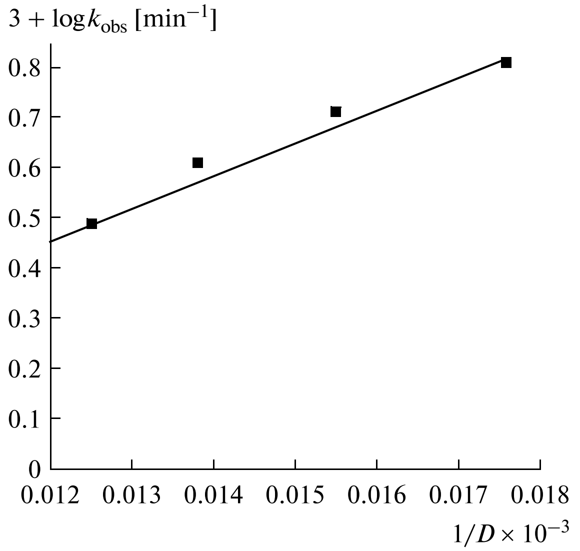


Fig. 5. Plot of $\log k_{obs}$ versus $1/D$ for the hydrolysis of MNP in the absence of SDS.

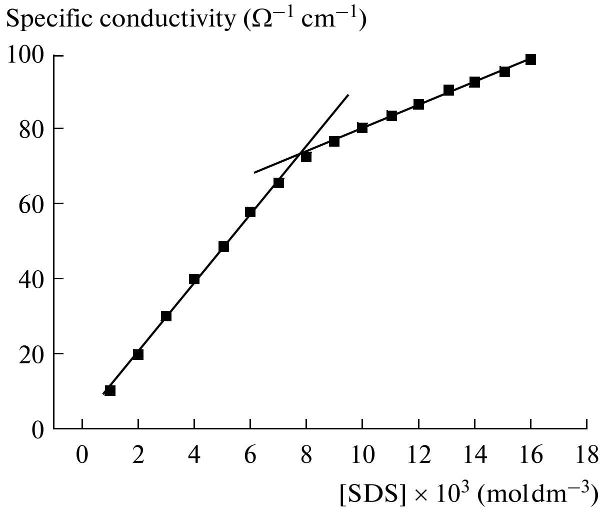


Fig. 6. Dependence of specific conductance of the reaction system on the concentration of SDS.

effect of added electrolyte which decreases the CMC due to the decrease of repulsion between the polar head groups on the micellar surface. Our results are in agreement with our earlier observations of micelle formation at relatively low surfactant concentrations.

Influence of SDS on Rate Constant

Micelles constitute an unusual medium, which may affect the rate of reactions. Catalysis by micelles involves at least three main steps: (i) binding of the substrate to the micelle; (ii) the actual chemical transformation within the micelle (most often on the micellar surface), and (iii) the release of product(s). The process, which underlies micellar catalysis or inhibition, is the binding of the counter ion to the micelle. Micelle can either attract the reactive ions or repel them depending on the electrical charge of the head groups of surfactant molecules. Micelle can either harbor the solubilized substrate and reactive ions together or separate them, and, thereby can cause either catalytic or inhibition effect. The effect of SDS micelles on the reaction rate was investigated by performing the experiment in the presence of varied amounts of SDS. On increasing SDS concentration up from 0 to 8.0×10^{-3} mol dm^{-3} at constant concentrations of the substrate and HCl at 30°C, the pseudo-first order rate constant (k_{obs}) increased from 2.10×10^{-3} to 12×10^{-3}. At higher concentrations of the surfactant, a decrease of rate constant was, however, observed (Fig. 7).

Most of the micellar-mediated organic reactions are believed to occur either inside the Stern layer or at the junction region of Stern and Gouy–Chapman layers. The main factor involved in the kinetic micellar effects is therefore the electrostatic repulsion between the substrate and surfactant. In our case, negatively charged micellar surface repels the ionized substrate bearing negative charge in the Stern layer. Upon an increase of the concentration of SDS, the local molarity of reactants in the Stern layer increased, leading to the increase of k_{obs}.

Kinetic Models of Micellar Effect

One of the most important properties of micellar system is its ability to influence the rate of chemical reaction. Micellar catalysis of reactions in aqueous solutions is usually explained on the basis of a distribu-

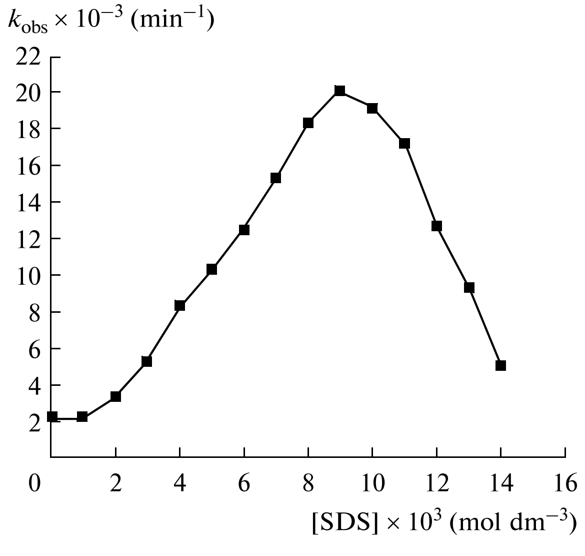


Fig. 7. Plot of k_{obs} versus [surfactant] for the SDS-catalyzed hydrolysis of MNP.

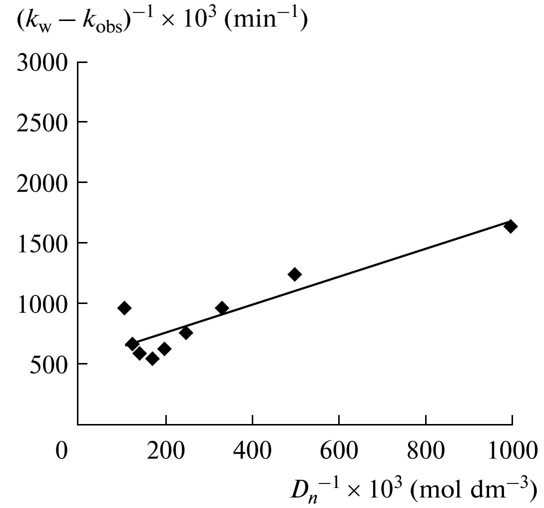
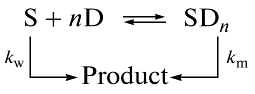


Fig. 8. Fitting of the experimental kinetic data to Menger–Portnoy's model.

tion of reactants between water and the micellar "pseudo-phase." The reaction occurs at different rates in the two media. If the solubility of the reactants is greater in the micelles than in water, then the local concentration is increased in the micelle, often with suitable orientation of the reactants bound in the micelle. Surfactant catalysis can be ascertained by plotting a graph between k_{obs} versus [SDS] by the model proposed by Menger and Portnoy for bimolecular reactions.

Menger and Portnoy's model. Catalysis by micelle involves at least three main steps: (a) binding of the substrate to the micelle, (b) its chemical transformation in the micelle, most often, on the micelle surface, and (c) release of product(s). Menger and Portnoy [14] developed a pseudo-phase model which has been fitted to various micelle-catalyzed reactions. According to this model, rate constant is generally treated on the assumption that a substrate "S" is distributed between the aqueous and micellar phases as shown in Scheme 2



Scheme 2.

where D$_n$ is the micellized surfactant. This model leads to the following relationship for micellar catalysis

$$\frac{1}{k_{obs} - k_w} = \frac{1}{k_m - k_w} + \frac{1}{(k_m - k_w)K_s[D_n]}. \tag{4}$$

According to Eq. (4), the plot of $(k_{obs} - k_w)^{-1}$ versus $[D_n]^{-1}$ (D_n = [D] – CMC) should give a straight line exhibiting a positive intercept with the $(k_{obs} - k_w)^{-1}$ axis as it is shown in Fig. 8. The Menger and Portnoy model allows determination of the binding constant k_s and the rate constant k_m in the micellar phase. The values of k_s and k_m were calculated from the slope and the intercept of the plot of $(k_{obs} - k_w)^{-1}$ versus $[D_n]^{-1}$ and were found to be 5.0×10^{-3} mol^{-1} dm^{-3} and 6.5×10^{-3} mol^{-1} dm^{-3}, respectively.

Piszkiewic's model. The micellar catalysis or inhibition can be modeled theoretically by simplifying the mechanism and assuming that only one substrate is incorporated into the micelle and that the aggregation number of the micelle is independent of the presence of substrate. Piszkiewicz [32] 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) undergoes aggregation with n number of surfactant molecules (D) forming a catalytic associate (D$_n$S). This aggregate then reacts to yield a product as described in Scheme 3.

$$nD + S \underset{K_D}{\rightleftharpoons} D_nS,$$
$$D_nS \xrightarrow{k_m} \text{Product},$$
$$S \xrightarrow{k_w} \text{Product}.$$

Scheme 3.

For the micelle-catalyzed reactions, the rate constant, as a function of the surfactant concentration, is given by

$$k_{obs} = \frac{k_m[D]^n + k_w K_D}{K_D - [D]^n}, \tag{5}$$

where k_{obs} is the rate constant in the presence of surfactant. On rearrangement and taking a logarithm, the above equation gives

$$\log[(k_{obs} - k_w)/(k_m - k_{obs})] = n\log[D] - \log K_D, \tag{6}$$

where K_D is the dissociation constant of micelle into its components. Here, n is an index of cooperativity, [D] is the total concentration of surfactant within the system, and k_m and k_w are the rate constants in micellar and aqueous pseudo-phases, respectively. To determine the values of k_w and k_{obs} for the acidic hydrolysis, the reaction was studied in absence of SDS to obtain k_w and in the presence of SDS to calculate k_{obs}. The correct value of k_m can not be determined experimentally; therefore its value was calculated using Menger–Portnoy approach. Figure 9 shows a straight line for the plot of $\log[(k_{obs} - k_w)/(k_m - k_{obs})]$ versus log[D]. The slope of this line gives the value of n (4.273×10^{-3}).

Berezin's model. Berezin and coworkers developed the first general pseudo-phase model and successfully simulated bimolecular reactions between neutral and organic reactants. The inhibition of the hydrolysis at high concentration of SDS can be explained using Berezin's model [33], which involves solubilization of both reactants in the micellar phase. According to this

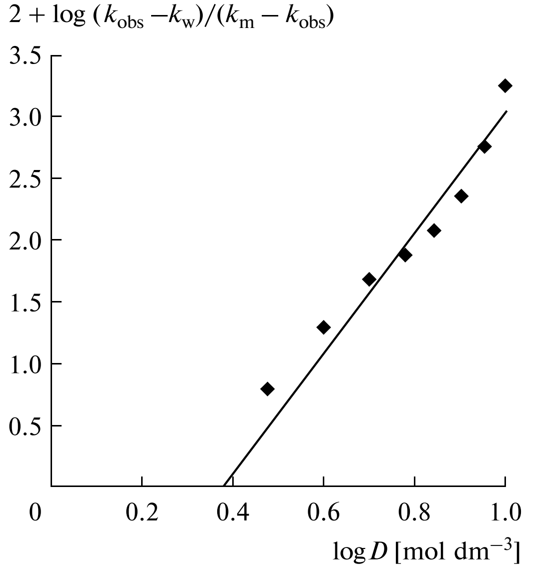


Fig. 9. Fitting of the experimental kinetic data to Piszkiewicz's model.

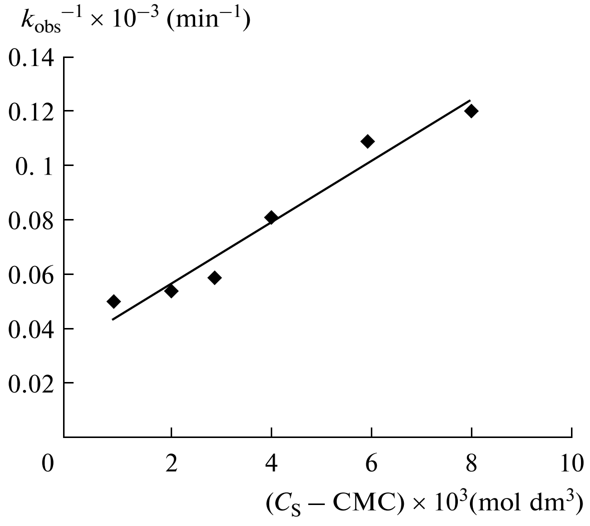
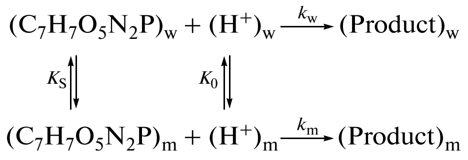


Fig. 10. Fitting of the experimental kinetic data to Berezin's model.

approach, a solution existing above the CMC may be considered as a two-phase system, consisting of an aqueous phase and a micellar pseudo-phase.



$$\begin{tikzcd}(C_7H_7O_5N_2P)_w + (H^+)_w \arrow[r, "k_w"] \arrow[d, shift left, "K_S"'] & (\mathrm{Product})_w \\ (C_7H_7O_5N_2P)_m + (H^+)_m \arrow[r, "k_m"] \arrow[u, shift left, "K_0"'] & (\mathrm{Product})_m\end{tikzcd}$$

Scheme 4.

A quantitative expression for the rate of bimolecular reaction (Scheme 4) occurring only in aqueous (k_w path) and micellar (k_m path) phase for the pseudo-first order rate constant is drawn as follows:

$$k_{obs} = \frac{k_w + k'_m K_S K_0 (C_{surf} - \mathrm{CMC})}{[1 + K_S(C_{surf} - \mathrm{CMC})][1 + K_0(C_{surf} - \mathrm{CMC})]}, \qquad (7)$$

where K_S and K_0 are the association constants of MNP and HCl respectively, C_{surf} is the analytical concentration of SDS ($k'_m = k_m/V$), V is a molar volume of the micelle and k_w and k_m are the pseudo-first order rate constants in absence and presence of micelles, respectively. The charged species involved into the hydrolysis of MNP are small molecules; the hydrophobic and electrostatic interactions between them can be considered as minor ones. When C_{surf} is small, $k_w \gg k_m^1 K_S K_0 (C_{surf} - \mathrm{CMC})$. Based on this assumption, Eq. (7) gives the following relation

$$k_{obs} = \frac{k_w}{[1 + (K_S + K_0)(C_{surf} - \mathrm{CMC}) + K_S K_0 (C_{surf} - \mathrm{CMC})^2]}. \qquad (8)$$

Since (C_{surf} − CMC) is very small, the terms containing (C_{surf} − CMC) may be neglected, and the Eq. (8) may be rearranged as

$$\frac{1}{k_{obs}} = \frac{1}{k_w} + \frac{K_S K_0}{k_w}(C_{surf} - \mathrm{CMC}). \qquad (9)$$

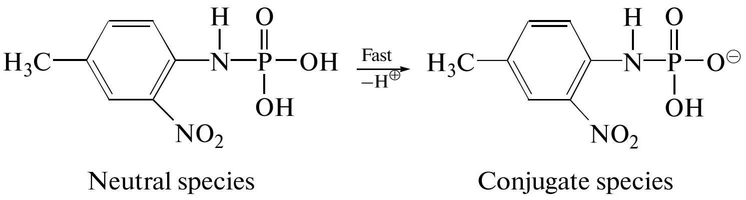
According to Eq. (9), a plot of k_{obs}^{-1} versus (C_{surf} − CMC) should give a straight line with a positive slope (Fig. 10).

In bimolecular micelle-catalyzed reactions, the reaction rate increases due to the changes in the environment of reactants which reduce the difference in free energy between the initial and transition states. This effect can be attributed to an increase in the frequency of molecular collisions as a result of the close association of the two reacting species at the micellar interface.

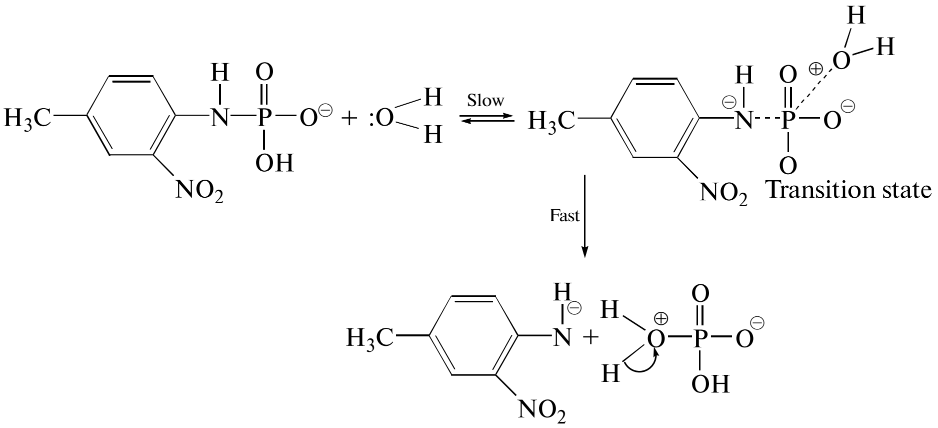
Mechanism of Micellar Catalysis

Based on the above modelling of the experimental observations, we suggested the possible mechanism of micellar catalysis of the hydrolysis of MNP in the SDS micellar solution.

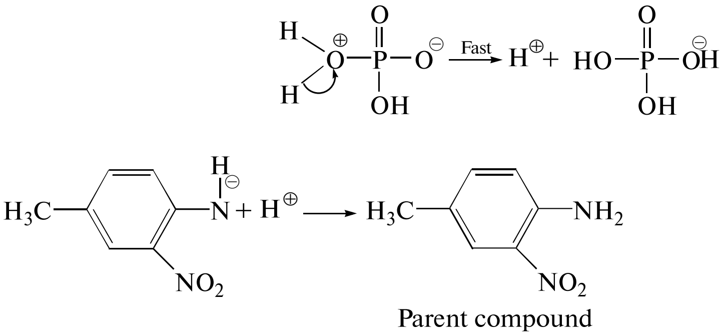
A. Formation of mononegative acid species



B. Bimolecular nucleophilic attack of water on phosphorous via mononegative species



C.



CONCLUSION

Herein, we reported the study of the micellar-catalyzed hydrolysis of 4-methyl-2-nitroaniline phosphate in the aqueous acidic solution of SDS at 303 K. The results suggest that the rate of the reaction is accelerated by the presence of anionic surfactant. According to the calculation of thermodynamic activation parameters, the value of activation energy in presence of SDS is lower that in the SDS-free system, that explains observed enhancement of the rate of hydrolysis in the micellar solution.

ACKNOWLEDGMENT

We thank reviewers for the critical and useful comments.

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