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Effect of micelles on hydrolysis of di-2,3-dichloroaniline phosphate

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The effect of anionic surfactant, di-octylsodium sulphosuccinate (AOT) and nonionic surfactant, polyoxyethylene sorbitanmonooleate (Tween-80) on the hydrolysis of di-2,3-dichloroaniline phosphate was studied spectrophotometrically at 303 K. The influence of inorganic salts on the reaction rate was studied. The added salts viz. KCl, KNO₃, and K₂SO₄ accelerated the rate of the reaction in the presence of anionic and nonionic micelles. The role of anionic and non-ionic micelle has been explained by the Menger-Portnoy, and Piszkiwicz models. The binding constant (K_s), rate constant (k_{ψ}) in the micellar phase, co-operativity index (n) and various thermodynamic activation parameters viz. ΔE_a , ΔS^\ddagger , ΔH^\ddagger , ΔG^\ddagger etc. have been evaluated. Possible reaction mechanism has been proposed on the basis of the observed kinetic data.

Keywords: Hydrolysis, Di-2,3-dichloroanilinephosphate, Menger-Portnoy's, Piszkiwicz's, Berezin models

Phosphate esters are key ingredients in biological systems. These esters are involved in countless biological processes, most prominently the storage and transmission of genetic information involving DNA and RNA. Phosphate esters are widely used as surfactants in many fields, such as textile, leather, household and personal care products, paint, extractants for metal ions, and so on, due to their outstanding emulsibility, antistatic property, biodegradability, low cutaneous irritation, and dispersity^{1,2}. Phosphate esters are used as pesticides for protection against agricultural and household pests^{3,4}. The hydrolysis of phosphate esters has been the subject of numerous experimental and theoretical studies over many years⁵. Phosphate ester hydrolysis is a crucially important reaction in biological systems, being involved in, among other things, signal and energy transduction, biosynthesis, protein synthesis, and replication of the genetic material⁶⁻⁸.

Surfactants are surface active substances which reduce the liquid surface tension when dissolved in aqueous solution⁹. Surfactants have a wide range of applications in agriculture, industries, detergent, textile, food, cosmetics and the drug or pharmaceutical¹⁰⁻¹². Due to their immense application potential, surfactant-based systems are a topic of major research interest for both academician and industrialist¹³. Surface-active molecules self-assemble in aqueous media to form nano-sized aggregates

called micelles. Micelle formations are important in clinical or pharmaceutical applications specifically in physiological conditions; since they directly affect DNA/cationic surfactant interaction driven by both electrostatic attraction and hydrophobic effect¹⁴⁻¹⁸. The micelles have a tendency to influence the reaction rates by enhancing it or by retarding the rates of reaction¹⁹. The effects of surfactant and its micelle on chemical reactions are always an interesting field of research for chemists and biologists²⁰.

Micelles have been the subject of intense investigation for a number of years. Formation of micelles and their dependence on environmental factors, temperature, additives and catalyzing functions, etc. are important physicochemical aspects, which are used for both fundamental understanding and application prospects. Due to analogy between enzyme catalyzed and micellar catalyzed reactions, the micellar catalysis has received a considerable attention of investigators²¹. Micelles and similar colloids assemblies generally increase the nucleophilic reactivity and their hydrolytic reactions with different surfactants. The use of novel surfactants in assisting a variety of organic reactions is highly promising for basic and applied research. Therefore the effect of surfactant on chemical reactions is an interesting field of research for chemists and biologists. Hydrolytic studies of phosphate esters have been done mostly in the

presence of metal ions or other catalysts and very limited literature is available for studies of phosphate ester hydrolysis in presence of micellar aggregates. The micellar catalyzed hydrolysis of phosphate diester in acidic medium is not very much explored. This prompted us to probe the catalytic activity of anionic and nonionic micelles in the hydrolysis of phosphate-diester. In kinetic study of micellar catalyzed hydrolytic reactions, the substrate form micelles by electrostatic force in micellar medium or it gets chemically bonded in it, resulting its interaction with diester for finding the conditions in which micelles would hydrolyse phosphate ester. In present investigation, we report the influence of anionic di-octyl sodium sulphosuccinate (AOT), and non ionic polyoxyethylene sorbitanmonooleate (Tween-80) on the rate of acidic hydrolysis of di-2,3-dichloroaniline phosphate.

Materials and Methods

Ammonium molybdate (98%, Sigma Aldrich), amidol (98% Sigma Aldrich), di-octyl sodium sulphosuccinate (99%, Merck) and polyoxyethylene sorbitanmonooleate (99%, Merck) were used to prepare stock solutions. 2,3-dichloroaniline was purchased from Sigma Aldrich and it was used to synthesize di-phosphate. Other reagents like HCl, KCl, K_2SO_4 and KNO_3 were of analytical grade. All the solutions were prepared in triply distilled water and were used throughout the kinetic experiments.

Di-2,3-dichloroaniline phosphate was synthesized by the literature method²² in the laboratory. This method involves the reaction of 2,3-dichloroaniline (parent compound) and phosphorylating agent phosphorus oxychloride ($POCl_3$) in 2:1 mole ratio. 2,3-dichloroaniline was dissolved in benzene and kept in a water bath. Then phosphorus 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 dissolved 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 recrystallized by dissolving in ammonia and reprecipitating by HCl

to get pure sample. It was then dried to obtain di-2,3-dichloroaniline phosphate.

Elemental and IR spectrum analysis data were used to confirm the compound as shown below:

- Elemental analysis (%); calculated (observed): C, 37.50 (37.46); H, 2.34 (2.30); N, 7.29 (7.24).
- IR spectrum analysis: The IR spectrum of di-2,3-dichloroaniline phosphate was recorded by ATR-FTIR (model: Nicolet iS10). ν (zinc selenite crystals) (cm^{-1}): 3150.00 (N-H); 3369.22 (O-H); 1540.93 (C=C); 1261.54 (P=O); 778.55 (P-N); 2851.74 (C-H); 967.27 (C-N).

The kinetic study of di-2,3-dichloroaniline phosphate was carried out at 303 K in 30% dioxane-water mixture in presence and absence of surfactants. The progress of hydrolytic study was measured by Allen's modified method²³. This method involves the estimation of inorganic phosphate produced during ester hydrolysis. The inorganic phosphate reacts with ammonium molybdate and forms phosphomolybdate complex $[(NH_4)_3PO_4.12MoO_3]$. 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 color is directly proportional to the amount of the free phosphoric acid. The optical density of the blue color was measured by Systronic spectrophotometer (model: 105) at wavelength of 735 nm.

Results and Discussion

The kinetic investigations were carried out in aqueous medium at different concentration of HCl under pseudo-first-order conditions. The concentration of HCl was taken in the range from $3.5 \times 10^{-3} \text{ mol dm}^{-3}$ to $21.0 \times 10^{-3} \text{ mol dm}^{-3}$. The concentration of diphosphate was kept constant at $5 \times 10^{-4} \text{ mol dm}^{-3}$. The observed values of rate constant (k_w) increased linearly with the increase in [HCl]. The slope of the plot of $3 + \log k_w$ versus $\log [H^+]$ was found to be 0.63 (with $r^2 > 0.99$), indicating that the order of the reaction is close to unity.

The kinetics of hydrolysis of the di-2,3-dichloroanilinephosphate in micellar medium 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 AOT influenced the rate of hydrolysis of the ester. The observed values of rate constants were increased with the increase in [AOT]. The values of rate constant attained maximum values and then started to decrease on further increasing the anionic [surfactant]. The observed higher rate in AOT 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 non ionic micelles of Tween-80 enhanced the rate of hydrolysis of the ester. The observed values of rate constants were increased with the increase in [Tween-80]. The values of rate constant attained maximum values and then started to decrease on further increasing the concentration of non ionic surfactant.

Effect of substrate

Hydrolysis was carried out in solution with di-2,3-dichloroaniline phosphate concentration varied from 1.0×10^{-4} to 5.5×10^{-4} mol dm⁻³. 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 (Fig. 1).

Effect of [HCl]

To determine the effect of [H⁺], acid concentration was varied in the range of 3.5×10^{-3} mol dm⁻³ to 21.0×10^{-3} mol dm⁻³ at constant concentration of other reactants. Pseudo-first order rate coefficients are presented in Table 2. With increasing [H⁺] the rate

constant values increased and the order with respect to H⁺ was found to be positive fractional (Fig. 2). The acceleration by [H⁺] may be mainly attributed to the conversion of the less reactive neutral species of di-2,3-dichloroaniline to the more reactive protonated species.

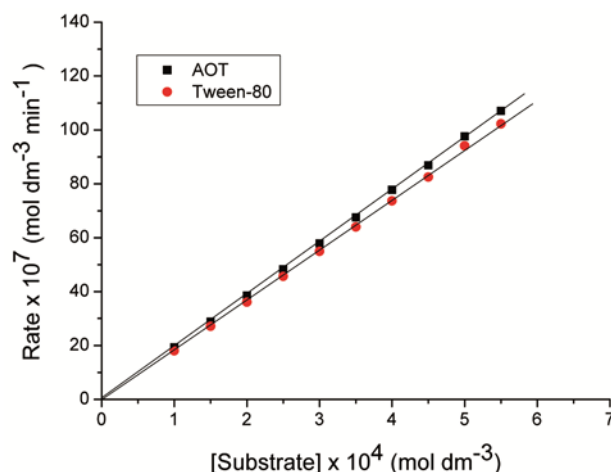


Fig. 1 — Plot of rate of reaction vs. [Substrate] for the hydrolysis of di-2,3-dichloroaniline phosphate.

Table 2 — Effect of [H⁺] on the reaction rate of hydrolysis of di-2,3-dichloroaniline phosphate in micellar media

HCl x 10 ³ (mol dm ⁻³)	k _w x 10 ³ (min ⁻¹)	
	AOT	Tween-80
3.5	16.81	15.23
7.0	25.42	23.12
10.5	32.01	28.20
14.0	36.65	31.62
17.5	42.50	36.18
21.0	46.15	40.53

Reaction conditions: T = 303 K, [Substrate] = 5.0×10^{-4} mol dm⁻³, [AOT] = 6.0×10^{-3} mol dm⁻³, [Tween-80] = 18.0×10^{-6} mol dm⁻³

Table 1 — Effect of substrate on the reaction rate of hydrolysis of di-2,3-dichloroaniline phosphate in micellar media

[Substrate] x 10 ⁴ (mol dm ⁻³)	AOT		Tween-80	
	k _w x 10 ³ (min ⁻¹)	Rate x 10 ⁷ (mol dm ⁻³ min ⁻¹)	k _w x 10 ³ (min ⁻¹)	Rate x 10 ⁷ (mol dm ⁻³ min ⁻¹)
1.0	19.22	19.22	18.03	18.03
1.5	19.18	28.77	18.10	27.15
2.0	19.26	38.52	18.06	36.12
2.5	19.32	48.30	18.26	45.65
3.0	19.28	57.84	18.32	54.96
3.5	19.30	67.55	18.28	63.98
4.0	19.43	77.72	18.41	73.64
4.5	19.31	86.89	18.34	82.53
5.0	19.53	97.65	18.82	94.10
5.5	19.48	107.1	18.61	102.3

Reaction conditions: T = 303 K, [H⁺] = 5.0×10^{-3} mol dm⁻³, [AOT] = 6.0×10^{-3} mol dm⁻³, [Tween-80] = 18.0×10^{-6} mol dm⁻³

Effect of temperature

The thermodynamic activation parameters provide useful information regarding the environment in which chemical reactions take place. The effect of temperature on the micellar-catalyzed reaction of di-2,3-dichloroaniline phosphate were studied at the temperature range 298–318 K in presence and absence of surfactant. The results are shown in Table 3. From the Arrhenius plot (Fig. 3), the value of energy of activation (ΔE_a), enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and Gibb's free energy of activation (ΔG^\ddagger) were calculated. These values are summarized in Table 4. A lower value of ΔE_a in presence of surfactant shows the catalytic effect on the rate of reaction. Observed negative entropy of activation in the hydrolysis of di-2,3-dichloroaniline phosphate in the presence of surfactant supports the rate determining step of the

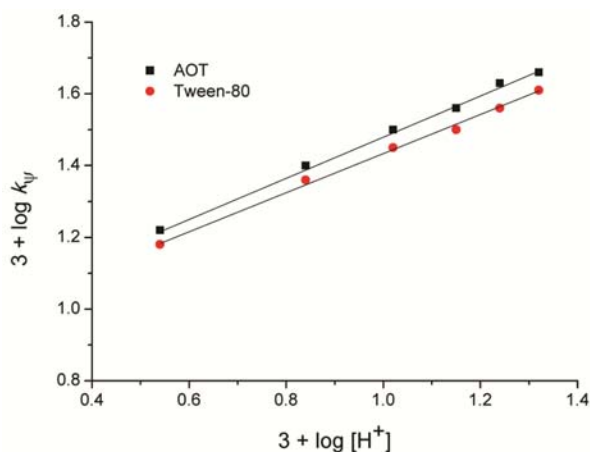


Fig. 2 — Plot of $(3 + \log k_\psi)$ vs. $(3 + \log [H^+])$ for the hydrolysis of di-2,3-dichloroaniline phosphate.

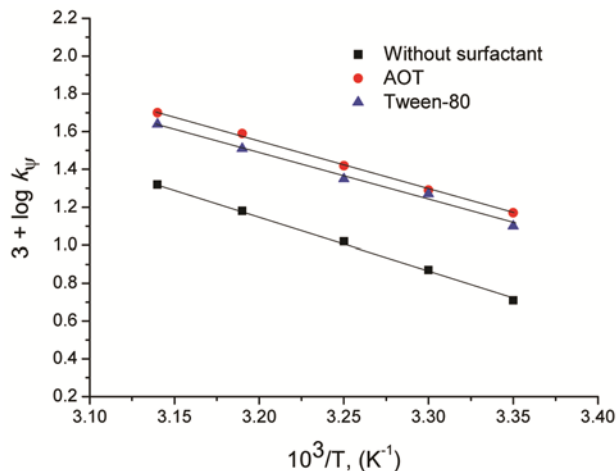


Fig. 3 — Plot between $(3 + \log k_\psi)$ and $(1/T \times 10^3)$ in the presence and absence of surfactants.

proposed mechanism. The proposed mechanism is also supported by the moderate values of energy of activation and other activation parameters. The larger negative value of ΔS^\ddagger in the presence of surfactant indicates that more ordered activated complex is formed in the presence of surfactant²⁴. The fairly positive values of ΔH^\ddagger and ΔG^\ddagger indicate that the transition state is highly solvated. Nearly same value of ΔG^\ddagger in absence as well as in presence of the surfactant has been observed which indicates the same reaction mechanism in aqueous and micellar medium (Table 5 & 6).

Effect of dielectric constant

To study the effect of dielectric constant (polarity) of the medium on the rate of reaction, the micellar catalyzed hydrolysis of di-2,3-dichloroaniline

Table 3 — Rate constant values obtained from Arrhenius plot data for di-2,3-dichloroaniline phosphate with and without surfactants

T (K)	$k_w \times 10^3$ (min ⁻¹) Without Surfactant	$k_\psi \times 10^3$ (min ⁻¹) With surfactant	
		AOT	Tween-80
298	5.12	15.06	12.71
303	7.47	19.53	18.82
308	10.5	26.31	22.54
313	15.3	39.51	32.56
318	20.1	50.38	43.51

Reaction conditions: $[H^+] = 5.0 \times 10^{-3}$ mol dm⁻³, [Substrate] = 5.0×10^{-4} mol dm⁻³, [AOT] = 6.0×10^{-3} mol dm⁻³, [Tween-80] = 18.0×10^{-6} mol dm⁻³

Table 4 — Arrhenius parameters for the di-2,3-dichloroaniline phosphate with and without surfactant

Parameters	Without surfactant	With surfactant	
		AOT	Tween-80
ΔE_a (kJ mol ⁻¹)	55.22	49.17	47.67
ΔH^\ddagger (kJ mol ⁻¹)	52.70	46.65	45.15
$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	111.9	123.9	129.2
ΔG^\ddagger (kJ mol ⁻¹)	86.62	84.20	84.29

Table 5 — Effect of change in percentage of 1,4-dioxane content on the rate of diphosphate hydrolysis in the presence and absence of surfactant

Percentage of 1,4-Dioxane (v/v)	$1/D_c \times 10^3$	$k_w \times 10^3$ (min ⁻¹) Without surfactant	$k_\psi \times 10^3$ (min ⁻¹) With surfactant	
			AOT	Tween-80
0.00	0.0128	8.320	19.53	18.82
10.0	0.0142	9.110	21.81	19.56
20.0	0.0159	10.06	23.23	21.41
30.0	0.0181	11.28	25.46	22.21
40.0	0.0209	12.53	27.63	25.28

Table 6 — Effect of change in percentage of DMSO content on the rate of diphosphate hydrolysis in the presence and absence of surfactant

Percentage of DMSO (v/v)	$1/D_c \times 10^3$	$k_w \times 10^3$ (min ⁻¹)	$k_\psi \times 10^3$ (min ⁻¹) With surfactant	
			Without surfactant	AOT Tween-80
0.00	0.0128	8.320	19.53	18.82
10.0	0.0134	9.110	22.45	20.20
20.0	0.0139	10.06	25.18	22.16
30.0	0.0146	11.28	29.05	25.08
40.0	0.0153	12.53	33.27	28.74

phosphate was studied in various composition of 1,4-dioxane and Di-methyl sulfoxide (DMSO). The results clearly reveal that the rate increases with increase in the percentage of

1,4-dioxane and DMSO, i.e. with increasing dielectric constant of the medium (Tables 5 and 6). 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^{25,26}. The modifications in the reaction medium, that is, by adding organic solvents or by adding surfactant molecules also affect the solvating power and thus alter the hydrolytic rate.^{27,28} 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 state²⁹. 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.

$$\log k_\psi = \log k'_0 - \frac{Z_A Z_B e^2 N}{2.303 (4\pi\epsilon_0) d_{AB} RT} \frac{1}{D_c} \quad \dots (1)$$

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 the absolute temperature and D_c is the dielectric constant of the medium. Eqn (1) predicts a linear relationship between $\log k_\psi$ versus $(1/D_c)$. In the present investigations a plot of $(3 + \log k_\psi)$ versus $(1/D_c)$ gave a straight line with a positive slope which clearly supports the involvement of two dipoles (Figs 4 and 5). The result shows that the rate constant values gradually increased with the addition of

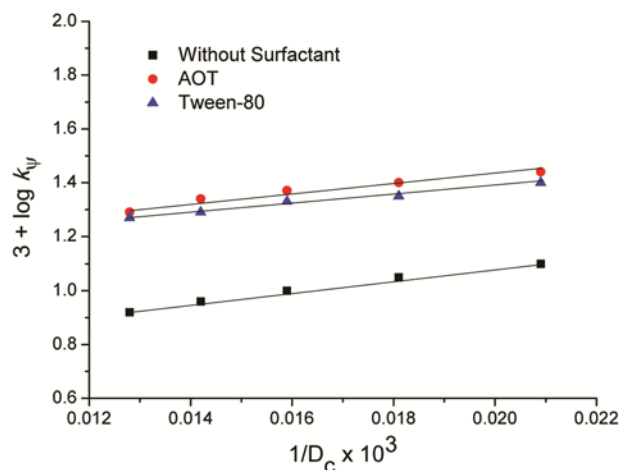


Fig. 4 — Plot of $(3 + \log k_\psi)$ vs. $1/D_c$ with and without surfactant (1,4-Dioxane).

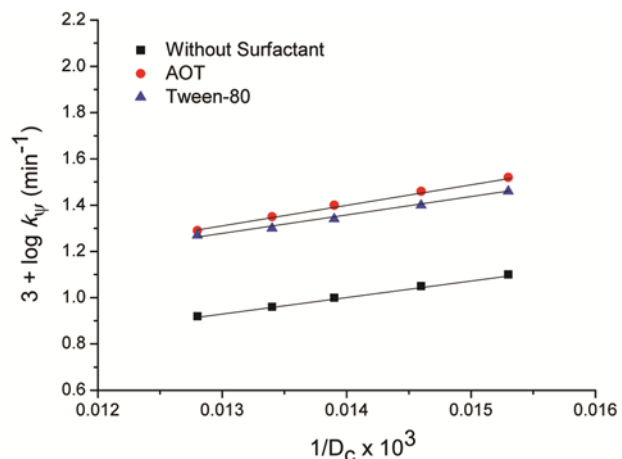
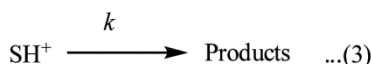
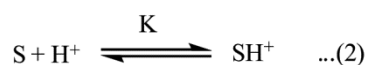


Fig. 5 — Plot of $(3 + \log k_\psi)$ vs. $1/D_c$ with and without surfactant (DMSO).



Scheme 1

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 observation³⁰. On the basis of experimental finding, the reaction Scheme 1 may be proposed for the effect of micelle for the hydrolysis of phosphate ester.

Considering Eqn (2) and (3) of Scheme 1 and also applying steady-state approximation, we construct the following rate equation:

$$\text{rate} = \frac{kK[S]_T [H^+]}{1+K [H^+]} \quad \dots (4)$$

The rate relation is in a good agreement with the experimental results.

Effect of electrolytes

The effect of added salts on the rate of reaction was also explored because salts as additives, in micellar systems, acquire a special ability to induce structural changes which may, in turn, modify the substrate-surfactant interaction leading to acceleration of reaction rate³¹. 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 and Fig. 6 a–c). The rate enhancing affects largely depends upon the nature of counter ions and the hydrophilic character. The counter ions from the added electrolyte compete with the reactive counter ions 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.

Critical micelle concentration (CMC) determinations

Micelles are observed only above a certain concentration, called the critical micelle concentration (CMC) in micellar solution. The CMC can most conveniently be defined as the concentration below which only single chains are present but above which both single chains and micellar aggregates can be found³². CMC is a measure of the ability of a surfactant to form micelles. Lower the CMC, the greater the ability and vice-versa. CMC can be obtained by measuring any surfactant solution property (e.g., surface tension, density, speed of sound, light scattering intensity, light absorption, molar conductivity, etc.) as a function of surfactant

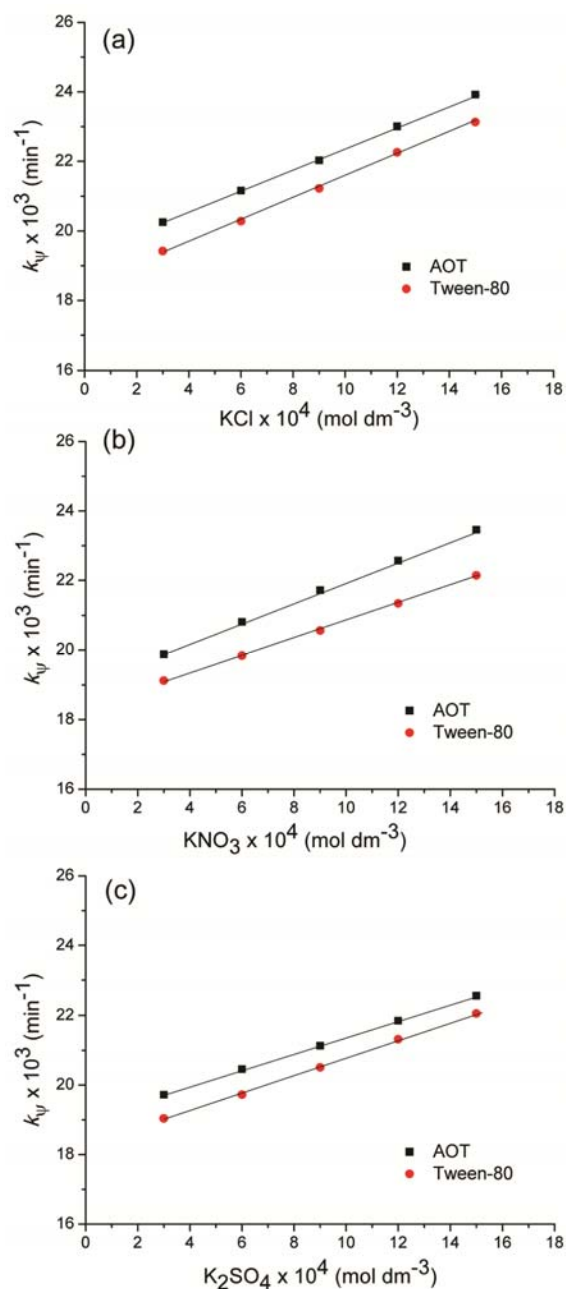


Fig. 6 — Effect of variation of inorganic salt: (a) KCl, (b) KNO₃ and (c) K₂SO₄.

Table 7 — Salt effect on the rate of hydrolysis of di-2,3-dichloroaniline phosphate in the presence of surfactant

[Salt] × 10 ⁴ (mol dm ⁻³)	KCl		KNO ₃		K ₂ SO ₄	
	AOT	Tween-80	AOT	Tween-80	AOT	Tween-80
	$k_p \times 10^3$ (min ⁻¹)					
3	20.25	19.42	19.88	19.12	19.72	19.04
6	21.16	20.28	20.81	19.84	20.46	19.72
9	22.03	21.22	21.72	20.56	21.13	20.51
12	23.01	22.26	22.57	21.34	21.85	21.32
15	23.92	23.13	23.46	22.15	22.57	22.06

concentration. An abrupt change of slope on the plot of the physical property versus surfactant concentration marks the CMC³³. Surface tension illustrates the hydrophobic and hydrophilic sections of micelle. The surface activity of a particular surfactant depends on the balance between its hydrophilic and hydrophobic properties. For a homologous series of surfactants, an increase in the length of the hydrocarbon chain (hydrophobic) increases the surface activity. An increase in surface activity means a decrease in surface tension. An increase of the length of the ethylene oxide chain (hydrophilic) of a polyoxyethylated non-ionic surfactant results in a decrease of surface activity. Non-ionic surfactants generally have very much lower CMC values and higher aggregation numbers than their ionic counterparts with similar hydrocarbon chains. An increase in the ethylene oxide chain length of a non-ionic surfactant makes the molecule more hydrophilic and the CMC increased.

A digital conductivity meter (model: 304, Systronics) was used to determine CMC values of ionic surfactant (AOT) and surface Tensiometer (model: 253, Jencon) was used to determine CMC values of non-ionic surfactant (Tween-80) at a constant temperature. The point of intersection of two linear portions from the plots of specific conductance vs. [surfactant] and surface tension vs. log [surfactant] for studied systems corresponds to CMC for the aqueous surfactant solution. The CMC values of surfactant measured under different experimental conditions are summarized in Table 8.

Effect of surfactants

The effect of AOT micelles on the reaction of di-2,3-dichloroaniline phosphate was studied by performing the reaction in presence of varying amounts of AOT. On increasing AOT from nil $\times 10^{-3}$ to 6.0×10^{-3} mol dm⁻³ at fixed [Substrate] and [HCl] at 303 K the pseudo-first-order rate constants (k_{ψ}) increase from 7.47×10^{-3} to 19.53×10^{-3} min⁻¹ (Table 9). The value of binding constant was also calculated. However at higher concentrations of surfactant (from 7.0×10^{-3} to 12.0×10^{-3} mol dm⁻³), 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

Table 8 — CMC values of surfactants in different experimental conditions

Solution	CMC (mol dm ⁻³)
Water + AOT	6.0×10^{-3}
Water + Tween-80	18.0×10^{-6}
Water + AOT + Substrate + HCl	3.0×10^{-3}
Water + Tween-80 + Substrate + HCl	4.0×10^{-6}

Reaction conditions: [Substrate] = 5.0×10^{-4} mol dm⁻³, [HCl] = 5.0×10^{-3} mol dm⁻³, T = 303 K

Table 9 — Effect of AOT concentration on the rate of hydrolysis of di-2,3-dichloroaniline phosphate

AOT $\times 10^3$ (mol dm ⁻³)	$k_{\psi} \times 10^3$ (min ⁻¹)
0	7.47
1	10.42
2	12.01
3	14.36
4	16.16
5	18.21
6	19.53
7	19.42
8	17.58
9	15.21
10	13.04
11	10.56
12	9.05

hydrophobic interaction between substrate and surfactant increases the concentration of reactants into a small volume. In present case, negatively charged micellar surface attracts the ionized substrate bearing the positive charge in the Stern layer. With increase in concentration of AOT, the local molarity of reactants increases in the Stern layer resulting in the enhancement of rate constant k_{ψ} for the hydrolysis of substrate (Fig. 7). The Tween-80 concentration was varied in the range of 0.0 to 24.0×10^{-6} mol dm⁻³ and the rate constant values first increased from 7.47×10^{-6} min⁻¹ to 18.82×10^{-6} min⁻¹ and after that it decreased on further increasing the concentration of surfactant (Fig. 8). The results are shown in Table 10. The increase in rate constant was observed at [Tween-80] < 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 (dimers, trimers, tetramers, etc.) exist below CMC; these small submicellar aggregates can interact physically with the reactants forming catalytically active entities. The maxima in the rate surfactant profile are produced by

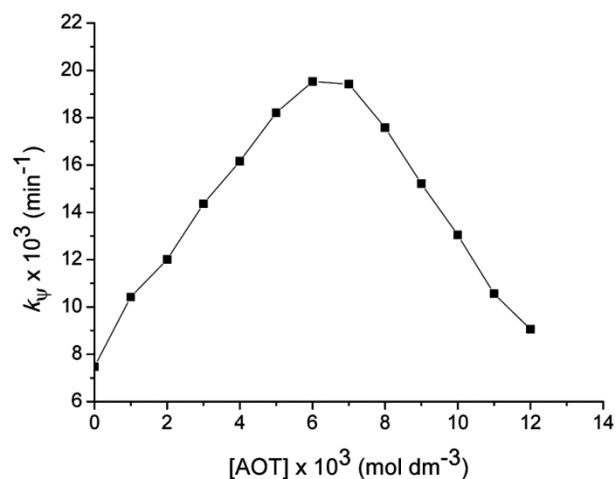


Fig. 7 — A plot of k_{ψ} vs. $[AOT]$ for the hydrolysis of di-2,3-dichloroaniline phosphate.

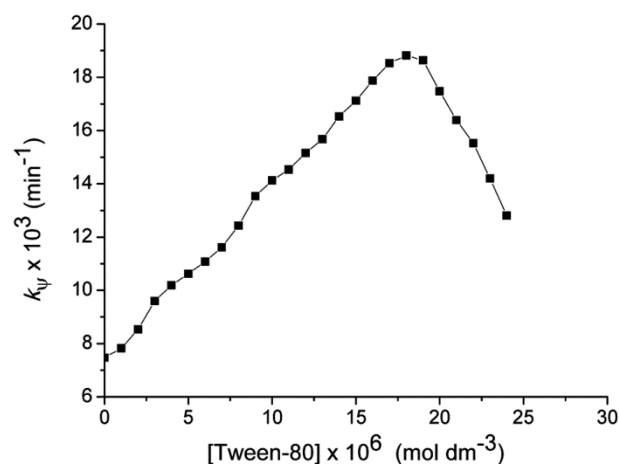


Fig. 8 — A plot of k_{ψ} vs. $[Tween-80]$ for the hydrolysis of di-2,3-dichloroaniline phosphate.

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 counter ions dilution of the reactants within the micellar pseudophase with increasing surfactant concentration.

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. The kinetic data were fitted to

Table 10 — Effect of Tween-80 concentration on the rate of hydrolysis of di-2,3-dichloroaniline phosphate

Tween-80 x 10 ⁶ (mol dm ⁻³)	k _ψ x 10 ³ (min ⁻¹)
0	7.47
1	7.82
2	8.53
3	9.60
4	10.19
5	10.62
6	11.08
7	11.61
8	12.43
9	13.54
10	14.13
11	14.54
12	15.16
13	15.68
14	16.53
15	17.12
16	17.88
17	18.53
18	18.82
19	18.64
20	17.48
21	16.39
22	15.53
23	14.20
24	12.81

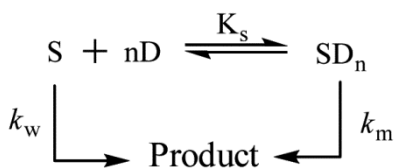
Menger-Portnoy, Piszkiwicz and Berezin models to explain the observed micellar effects.

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 “pseudophase”, 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.

Menger and Portnoy's model

The catalysis of the reaction in the presence of aqueous micellar solution of AOT and Tween-80 may also be explained by the micellar kinetic pseudo phase model proposed by Menger and Portnoy³⁴ and modified by Bunton *et al.*³⁵⁻³⁷. According to this model, the substrate “S” is distributed between the aqueous and micellar phases as given in Scheme 2.

In Scheme 4, K_s is the association constant with micellized surfactant, nD_n whose concentration is that



Scheme 2

of the total surfactant, less that of monomer, which is taken to be the CMC. This model leads to the following relationship for micellar catalysis:

$$\frac{1}{k_w - k_\psi} = \frac{1}{k_w - k_m} + \frac{1}{(k_w - k_m)K_s[D_n]} \quad \dots (5)$$

Where Eqn (5) predicts that the plot of $(k_w - k_\psi)^{-1}$ versus $[D_n]^{-1}$, ($D_n = [D] - \text{CMC}$) is linear (Figs 9a & b). The Menger and Portnoy 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.

Piszkievic’s model or co-operative model

At lower concentrations of a surfactant, the micellar catalysis has been explained by the kinetic model developed by Piszkievicz³⁸ which is analogous to Hill model³⁹. According to this model a substrate (S) aggregates with n number of detergent molecules (D) to form critical micelle (D_nS) 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:

$$k_\psi = \frac{k_m[D]^n + k_wK_D}{K_D + [D]^n} \quad \dots (6)$$

$$\log \left(\frac{k_\psi - k_w}{k_m - k_\psi} \right) = n \log[D] - \log K_D \quad \dots (7)$$

Here k_ψ represents the rate constant in the presence of surfactant. K_D is dissociation constant of micellized detergent back to its free components, n is index of cooperativity, D is the total [surfactant], k_m and k_w are rate constants in micellar and aqueous pseudophases, respectively. To determine the k_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_m cannot be determined experimentally; therefore its value is computed using Menger-Portnoy’s approach. Fig. 10(a & b) gives a straight line for the plot of $\log [(k_\psi - k_w)/(k_m - k_\psi)]$ vs. log

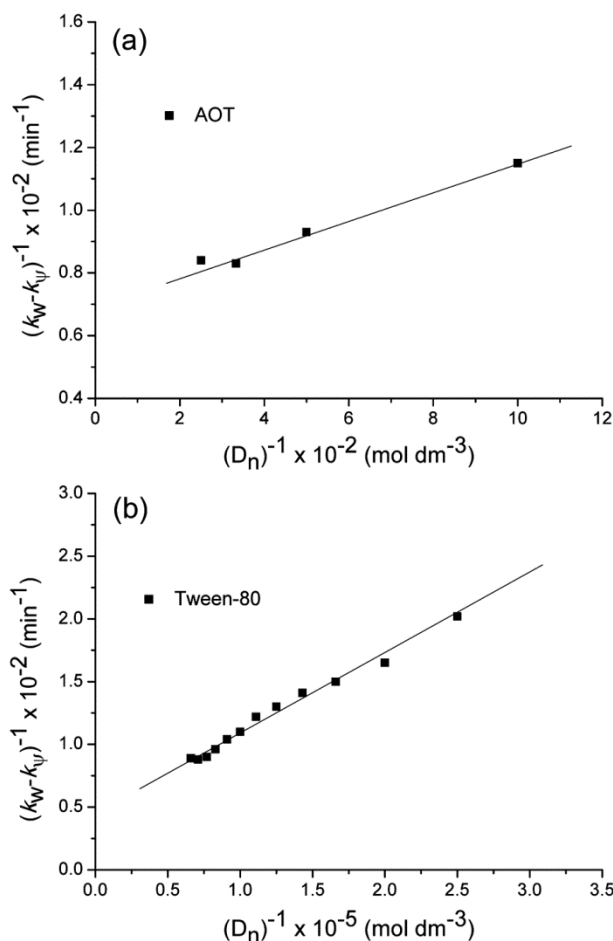


Fig. 9 — Fitting of the experimental kinetic data to Menger-Portnoy’s model: (a) AOT and (b) Tween-80.

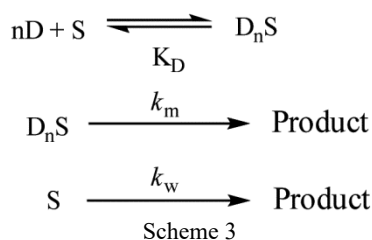


Table 11 — Some parameters of surfactant and different constant calculated from various models

Parameters	Values of parameters	
	AOT	Tween-80
K_s ($\text{mol}^{-1} \text{dm}^{-3}$)	1.59×10^3	7.95×10^4
k_m (m^{-1})	1.17×10^{-3}	1.35×10^{-2}
K_D	70.07	5.94
N	0.11	1.89

D. The values of n and K_D were determined from the gradient and intercept (Table 10). Some thermodynamic parameters are given in Table 11.

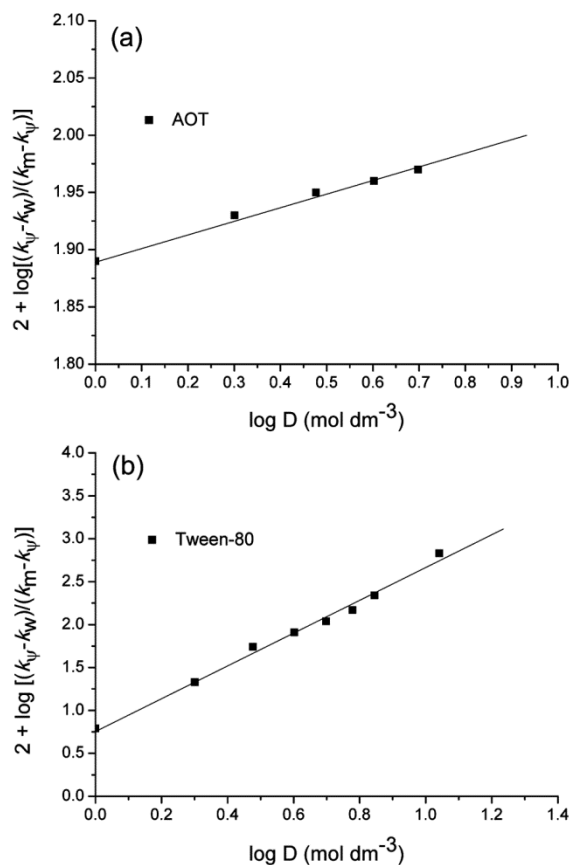


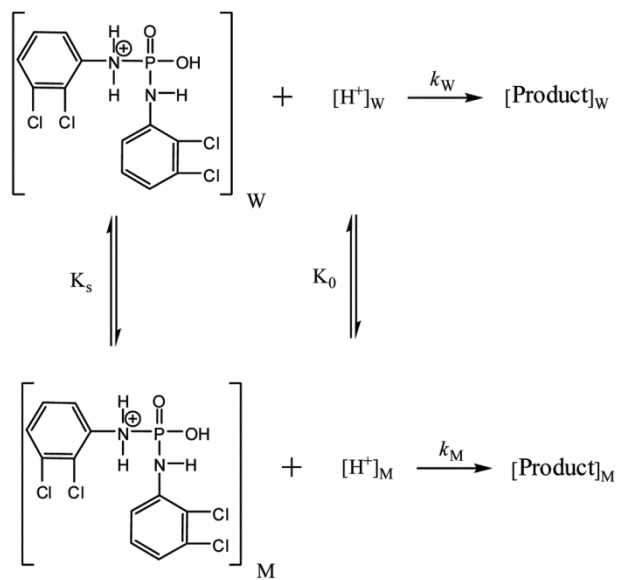
Fig. 10 — Fitting of the experimental kinetic data to Piszkiwicz's model: (a) AOT and (b) Tween-80.

Berezin's model

The kinetic results of the effect of varying [surfactant] on the rate of reaction (Table 9 & 10) and the inhibition of rates at higher concentration of surfactant may be explained by means of the pseudophase model proposed by Berezin's *et al.*,⁴⁰ which takes into consideration solubilization of both reactant into the micellar phase. According to this approach, a solution above the CMC may be considered as a two-phase system, consisting of an aqueous phase and a micellar pseudophase. 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 in Scheme 4.

$$k_{\psi} = \frac{k_w + [k'_m K_S K_0 (C_{\text{surf}} - \text{CMC})]}{[1 + K_S (C_{\text{surf}} - \text{CMC})][1 + K_0 (C_{\text{surf}} - \text{CMC})]} \quad \dots (8)$$

Where, K_S and K_0 are the association constants of substrate and HCl, respectively, with AOT and Tween-80. C_{surf} is the analytical concentration of AOT



Scheme 4

and Tween-80, ($k'_m = k_m/V$), V being molar volume of the micelle and k_w and k_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_S and K_0 will be low. Since C_{surf} is small, it may be possible that $k_w \gg [k'_m K_S K_0 (C_{\text{surf}} - \text{CMC})]$ so that the above equation takes the form as follows:

$$k_{\psi} = \frac{k_w}{[1 + (K_S + K_0)(C_{\text{surf}} - \text{CMC}) + K_S K_0 (C_{\text{surf}} - \text{CMC})^2]} \quad \dots (9)$$

Since $(C_{\text{surf}} - \text{CMC})$ is negligible so Eqn (9) may be rearranged to:

$$\frac{1}{k_{\psi}} = \frac{1}{k_w} + \frac{(K_S + K_0)}{k_w} (C_{\text{surf}} - \text{CMC}) \quad \dots (10)$$

Plot k_{ψ}^{-1} vs. $(C_{\text{surf}} - \text{CMC})$, is linear (Figs 11a & 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, that is, $(K_S + K_0)$. 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

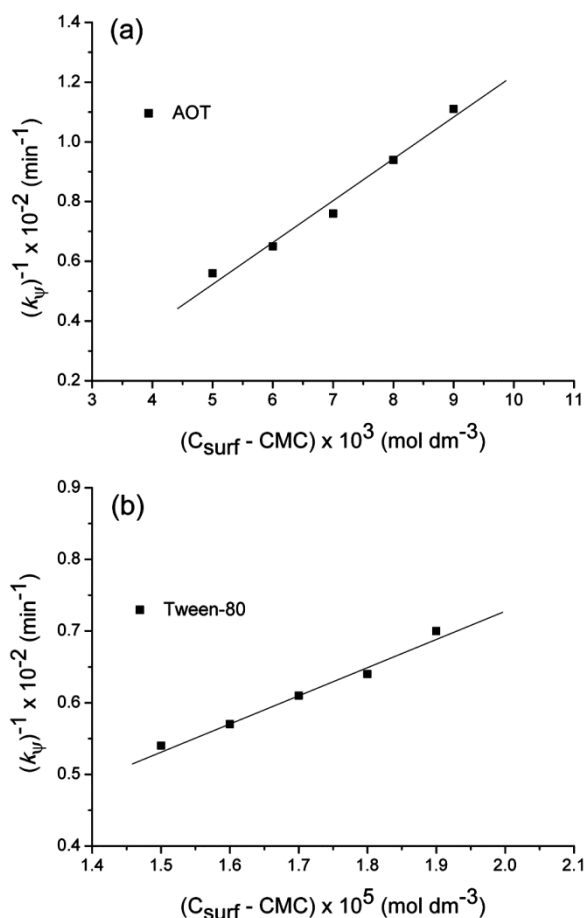
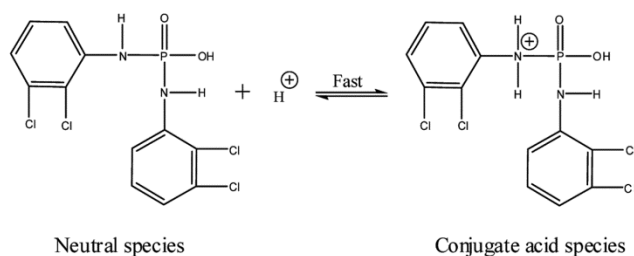


Fig. 11 — Fitting of the experimental kinetic data with surfactants to Berezin model: (a) AOT and (b) Tween-80.



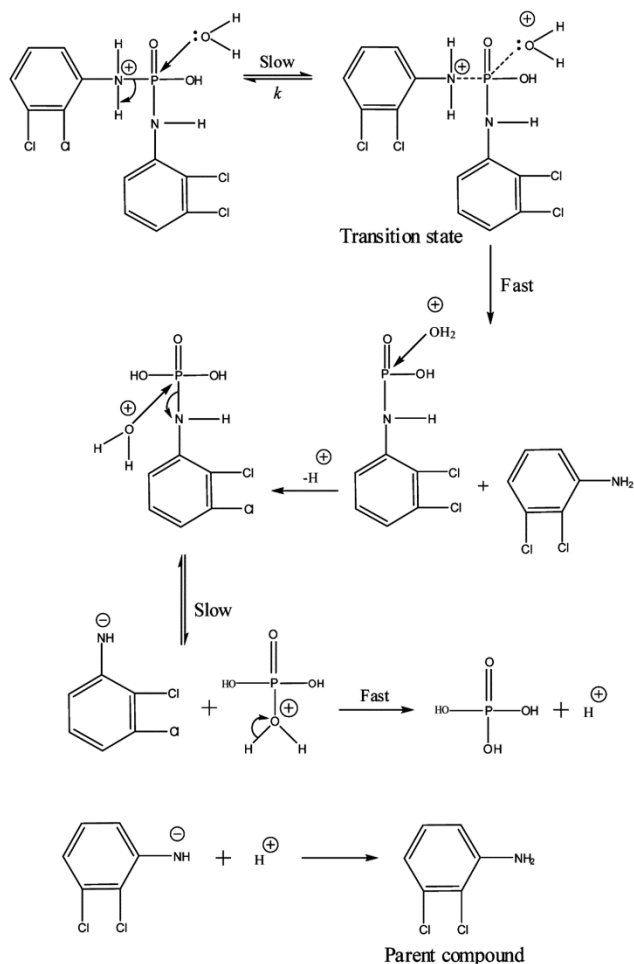
Formation of conjugate acid species

Scheme 5

the ionization of HCl by micelles indicates that the transition state is stabilized more than the ground state.

Mechanism of micellar catalysis

On the basis of experimental observations⁴¹, we suggested the possible mechanism of micellar catalysis of the hydrolysis of di-2,3-dichloroaniline phosphate in the different micellar solution (Scheme 5 & 6).



Scheme 6

Conclusions

The kinetics of the hydrolysis of di-2,3-dichloroaniline phosphate was investigated in presence and absence of anionic (AOT) and non-ionic (Tween-80) surfactants. The CMC values lower than those given in the literature for aqueous solutions of surfactants indicates that acid decreases the CMC values. In both uncatalyzed and micellar catalyzed reactions, the reactions follow the first-order kinetics with respect to di-2,3-dichloroaniline phosphate and HCl under pseudo-first-order reaction conditions. 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 AOT and Tween-80, the rate of hydrolysis first increased and after attaining maxima (peak), it decreased with increasing concentration of surfactant. Hydrolysis products were identified and thermodynamic activation parameters were evaluated. The added salts viz. KCl, KNO₃, and K₂SO₄ enhanced

the rate of reaction in the presence of micelles. Positive effects of $[Cl^-]$, $[NO_3^-]$ and $[SO_4^{2-}]$ was found on the rate of reaction. Increasing the $[Cl^-]$, $[NO_3^-]$ and $[SO_4^{2-}]$ the rate constant is increased because $[Cl^-]$, $[NO_3^-]$ and $[SO_4^{2-}]$ will be solubilized in the micelle palisade layer close to the head group region. Therefore, in addition to neutralization of micellar positive charge, they will restrict solubilization sites to hydrophobic substrates. Thus, they catalyze the reaction by virtue of increased concentration of di-2,3-dichloroaniline phosphate, in the Stern layer. The behaviour of micellar catalyzed reaction could be explained by theoretical models: Menger-Portnoy, Piszkiwicz and Berezin models. The kinetic parameters like k_m , K_s , etc., were determined using rate-[surfactant] profile.

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