

Kinetic investigation of the oxidation of N-alkyl anilines by peroxomonophosphoric acid in anionic surfactant sodium lauryl sulphate

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Abstract. Kinetics of oxidation of N-methyl and N-ethyl aniline by peroxomonophosphoric acid (PMPA) in aqueous and 5% (v/v) acetonitrile medium respectively have been studied in presence of anionic micelles of sodium lauryl sulphate (SLS) at different *pH*. Oxidation rate of both the substrates increases up to a certain [SLS] much below the critical micellar concentration (cmc) after which the rate is retarded. Kinetic data have been used to compute the binding constants of both substrate and oxidant with the micelle. A scheme explaining the kinetic data has been proposed.

Keywords. Anionic surfactants; peroxomonophosphoric acid; oxidation of N-alkyl anilines.

1. Introduction

The effect of organised assemblies on the equilibrium and rate of reactions has attracted attention in recent years¹. This is primarily due to the realisation that many biochemical processes proceed in a microheterogeneous system containing an aqueous and liophilic moiety². Redox processes represent reactions of primary importance in biological systems³. In order to understand the mechanism of these biochemical processes several attempts have been made to study redox processes arising out of electron transfer from substrates to metal ions in surfactant molecules^{4,5}. However, redox processes involving atom transfer do not appear to have been undertaken in surfactant media. Oxidations by per acids and their derivatives mainly proceed through oxygen atom transfer⁶. Oxidation of amines⁷ using peroxomonophosphoric acid which proceeds by oxygen atom transfer provides an interesting system. As there is no report of these reactions having been investigated in surfactant medium, it was considered worthwhile to undertake the kinetic study of oxidation of N-methyl and N-ethyl aniline by peroxomonophosphoric acid (PMPA) in the presence of micelles. This communication therefore incorporates the result of kinetic study of the aforesaid reaction in presence of sodium lauryl sulphate (SLS).

2. Experimental – Materials and methods

Analar grade reagents were used. N-alkyl anilines were distilled before use. Solutions of N-methyl aniline were prepared in aqueous medium, whereas N-ethyl aniline solutions

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were prepared in 5% (v/v) acetonitrile medium. Peroxomonophosphoric acid (PMPA) was obtained by hydrolysis of potassium peroxodiphosphate (FMC) in 1 N H₂SO₄ at 40°C for one and a half hours. The strength of PMPA was fixed by iodometry in presence of 2 ml of conc. HCl and 2 drops of ammonium molybdate to avoid diffused end-point due to presence of H₂O₂ obtained as a hydrolytic product. Before making up PMPA solutions, appropriate amounts of buffers were used to bring pH of the PMPA solution to the desired value which was checked with the help of a systronics digital pH-meter (model 335). Progress of the reaction was followed by measuring the residual amount of PMPA at different time intervals in 5 ml aliquots of the reaction mixture. Surfactants were always added to the oxidant flask before making up and the reactants were stable under the experimental conditions. Rate constants were reproducible within 5%.

Table 1. Pseudo first-order rate constants for the oxidation of N-methyl aniline by PMPA in presence of SLS, at temperature 40°C.

pH	10 ⁴ [PMPA] (mol dm ⁻³)	10 ³ [substrate] (mol dm ⁻³)	10 ³ [SLS] (mol dm ⁻³)	10 ³ k _p (min ⁻¹)
1.2	5.0	5.0	0.0	3.97
			1.0	8.25
			2.0	8.37
			3.0	9.19
			4.0	8.58
			6.0	6.47
			8.0	6.48
			10.0	6.28
			12.0	5.74
			14.0	6.40
			16.0	5.97
2.0	5.0	5.0	0.0	4.55
			2.0	8.14
			4.0	12.50
			6.0	11.69
			8.0	9.01
			10.0	8.39
			12.0	7.91
2.5	5.0	5.0	0.0	7.77
			1.0	11.70
			2.0	18.93
			2.0	17.81 ^a
			2.0	18.47 ^b
			4.0	14.79
			6.0	12.77
			8.0	11.44
			10.0	10.03
			14.0	10.45
			16.0	8.17
20.0	8.76			

^aIn presence of 0.01 M K₂SO₄; ^b0.02 M K₂SO₄

Table 2. Pseudo first-order rate constants for the oxidation of *N*-ethyl aniline by PMPA in presence of SLS in 5% acetonitrile medium, at temperature 40°C.

<i>pH</i>	10^4 [PMPA] (mol dm ⁻³)	10^3 [substrate] (mol dm ⁻³)	10^3 [SLS] (mol dm ⁻³)	$10^3 k_p$ (min ⁻¹)
1.2	5.0	5.0	0.0	1.03
			2.0	4.17
			4.0	5.78
			6.0	3.31
			8.0	3.39
			14.0	2.29
			16.0	1.63
			18.0	2.52
			20.0	1.20
			2.1	5.0
2.0	4.77			
4.0	6.57			
6.0	5.05			
8.0	4.52			
14.0	4.81			
16.0	4.55			
18.0	4.97			
20.0	5.05			
2.7	5.0	5.0		
			2.0	5.79
			4.0	8.93
			6.0	7.35
			8.0	7.10
			10.0	8.22
			12.0	5.37
			14.0	4.85
			16.0	5.55
			18.0	6.06
			20.0	6.63
			22.0	3.78

3. Results and discussion

It has been already reported that the oxidation rate of *N*-methyl aniline in aqueous medium and *N*-ethyl aniline in acetonitrile–water by peroxomonophosphoric acid⁸ (PMPA) exhibits first-order dependence in both substrate and oxidant whereas dependence in [H⁺] is fractional. These observations have been rationalised. The present work includes oxidations by PMPA at three different *pH* values, over varying sodium lauryl sulphate concentrations. The pseudo first-order rate constants in the presence of added SLS have been tabulated in tables 1 and 2. The plots are given in figures 1 and 2. Rates measured in the presence of varying [K₂SO₄] (table 1) shows constancy of k_p values. As there was no effect on oxidation rate in presence of added salts, constant ionic strength was not maintained. Examination of the data in tables 1 and 2 and figures 1 and 2 suggest that the oxidation rate increases as SLS concentration increases, reaches a maximum at around 0.002–0.005 M (SLS) and then decreases asymptotically. The

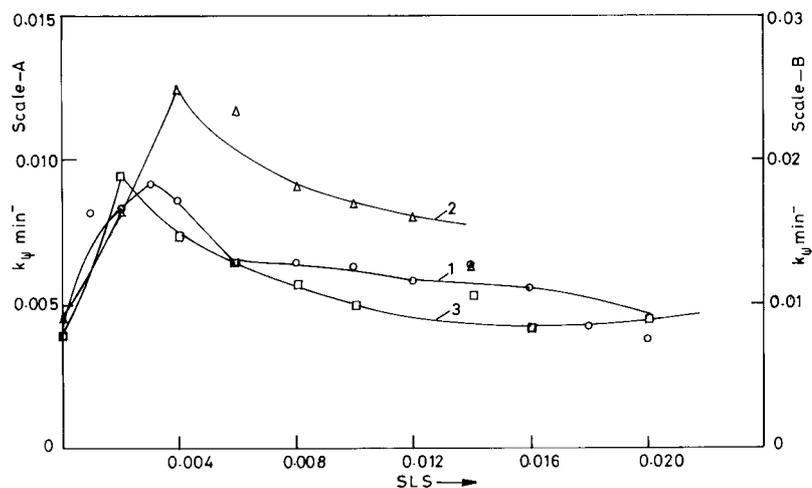


Figure 1. Plot of pseudo first-order rate constants ($k_p \text{ min}^{-1}$) at 40°C for the oxidation of N-methyl aniline by PMPA vs [SLS] at different values of pH. Plot 1, pH = 1.2 (scale A), plot 2, pH = 2.0 (scale A), plot 3, pH = 2.5 (scale B).

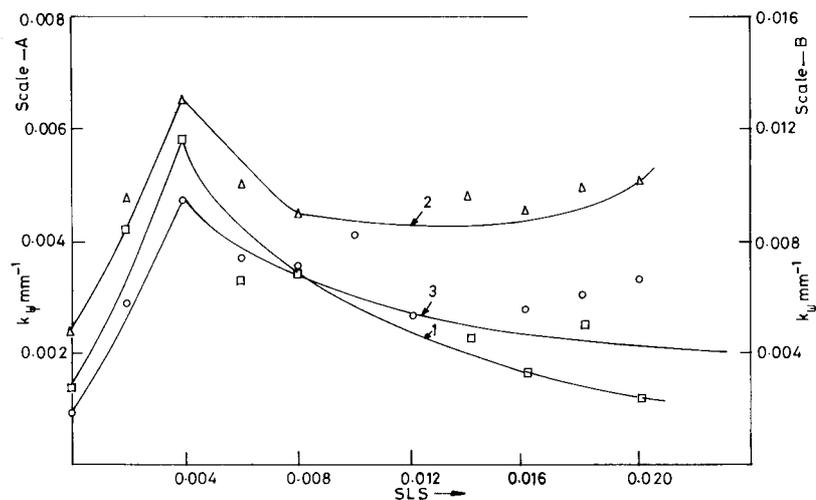
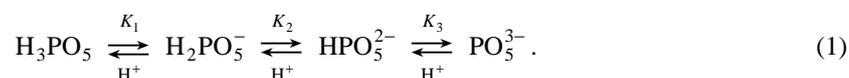


Figure 2. Plot of pseudo first-order rate constants ($k_p \text{ min}^{-1}$) for the oxidation of N-ethyl aniline by PMPA vs [SLS] at different values of pH. Plot 1, pH = 1.2 (scale A), plot 2, pH = 2.1 (scale A), plot 3, pH = 2.7 (scale B).

maximum occurs much below the reported critical micellar concentration (cmc) value of SLS, i.e. 0.008M. The maximum rates observed in the pre-micellar region might be due to concentration of the reactants in submicellar aggregates⁹ or the substantial decrease in cmc for a micelle in presence of added molecules¹⁰⁻¹² or H^+ ions.

Before attempting an explanation of the effect observed due to presence of the anionic surfactant, i.e. SLS, it is necessary to consider the identity of the active species of the

oxidant, namely PMPA. Peroxomonophosphoric acid (H_3PO_5) exists in equilibrium with various dissociated species as below.



pK_1 , pK_2 and pK_3 values are respectively 1.10, 5.38 and 12.8 at 25°C ¹³. Oxidation studies of N-methyl and N-ethyl aniline in aqueous medium by PMPA have suggested that in the pH range 0–4, though H_3PO_5 and H_2PO_5^- are present, the oxidation rate due to H_3PO_5 species is about two orders of magnitude higher than that due to H_2PO_5^- ¹⁴. Therefore, in the present study, in the presence of added SLS, the effective oxidant species was taken to be H_3PO_5 .

Plot of k_ψ against (SLS) (figures) shows a maximum as already stated. In the presence of negatively charged aggregates, partitioning between the bulk aqueous phase and the micellar pseudo phase has to be considered for all the species involved in the reaction of N-alkyl anilines with PMPA since both electrostatic and hydrophobic interactions are operative. Therefore in the present case the reaction shown in scheme 1 applies. Such a scheme has been proposed by Carbone *et al* to explain the complex formation¹⁴ between Ni(II) and pyridine-2-azo *p*-dimethyl aniline. The apparent rate constant is \bar{k}_m given by (2) where $k_m = k_m/v$ (where v is a quantity related to the volume element for the reaction) and K_s and K_o are the binding constants of the substrate and oxidant in the micelle respectively.

$$k_\psi = \frac{k_w + \bar{k}_m K_s K_o C}{(1 + K_s C)(1 + K_o C)}. \quad (2)$$

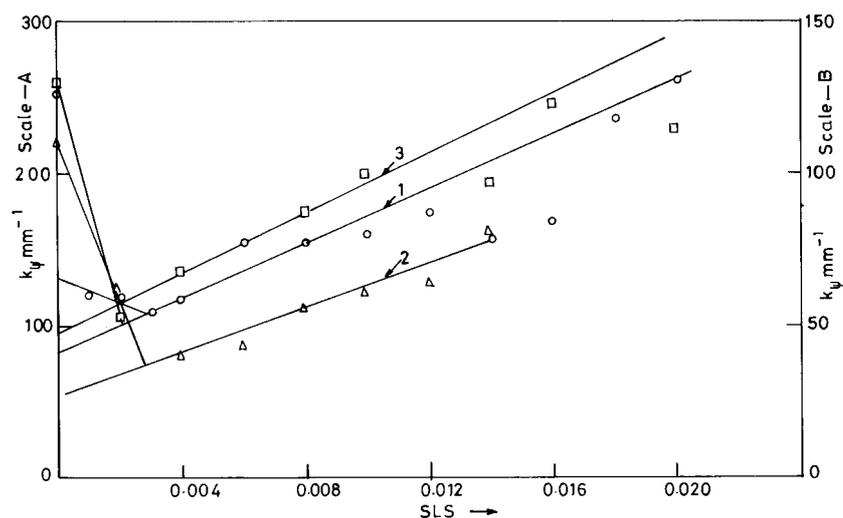
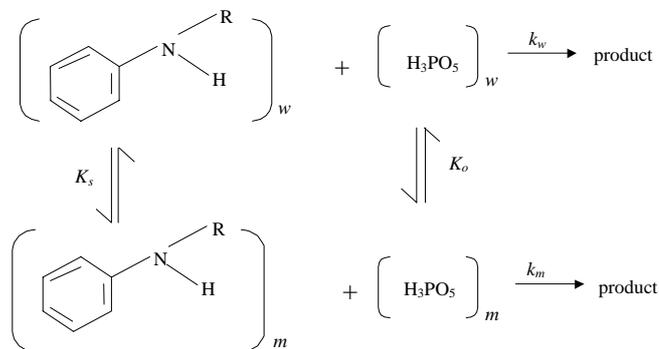


Figure 3. Plot of k_ψ^{-1} vs [SLS] (N-methyl aniline–PMPA reaction). Plot 1, pH = 1.2 (scale A), plot 2, pH = 2.0 (scale A), plot 3, pH = 2.5 (scale B).



Scheme 1.

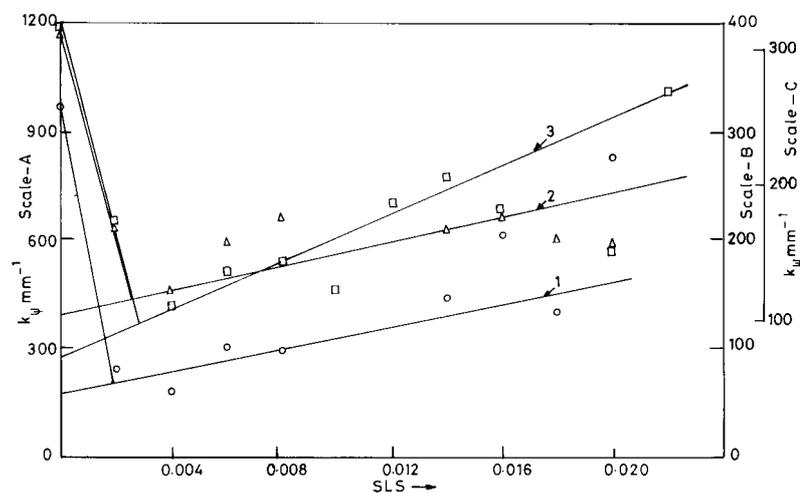


Figure 4. Plot of k_p^{-1} vs [SLS] (N-ethyl aniline-PMPA reaction). Plot 1, $\text{pH} = 1.2$ (scale A), plot 2, $\text{pH} = 2.1$ (scale B), plot 3, $\text{pH} = 2.7$ (scale C).

Since the rate decreases from a maximum as the anionic surfactant concentration increases, k_w can be neglected with respect to the other term in the numerator of (2) and the rearrangement of this expression yields

$$\frac{1}{k_p} = \frac{1}{\bar{k}_m K_s K_o C} + \frac{K_s + K_o}{\bar{k}_m K_s K_o} + \frac{C}{\bar{k}_m} \quad (3)$$

According to (3) the plot of $1/k_p$ against C i.e. (SLS) would show a minimum¹⁵ at the value $C_{\min} = 1/(K_s K_o)^{1/2}$ and $1/k_p$ would be linearly dependent on C , for values of C greater than C_{\min} . In fact, the plot of $1/k_p$ against $C > C_{\min}$ shows that a linear dependence exists between $1/k_p$ and C (figures 3 and 4). The slope of the plot yields \bar{k}_m and the intercept is equal to $(K_s + K_o)/K_s K_o$. Using the slope and intercept values and the relationship $C_{\min} = 1/(K_s K_o)^{1/2}$, K_s and K_o have been computed. These values at different pH levels are collected in tables 3 and 4.

Table 3. Binding constants, transfer free energies of oxidant (PMPA) and substrate (N-methyl aniline) and \bar{k}_m at different values of pH.

pH	$10^4 \bar{k}_m$	$10^{-2} K_s$	$10^{-2} K_o$	$-\Delta\mu_s^0$ (kJ mol ⁻¹)	$-\Delta\mu_{ox}^0$ (kJ mol ⁻¹)
1.2	1.45	9.23	1.20	118.53	96.25
2.0	1.4	7.61	1.67	116.42	99.88
2.5	2.05	24.98	1.11	129.41	95.36

Table 4. Binding constants, transfer free energies of oxidant (PMPA) and substrate (N-ethyl aniline) and \bar{k}_m at different values of pH.

pH	$10^4 \bar{k}_m$	$10^{-2} K_s$	$10^{-2} K_o$	$-\Delta\mu_s^0$ (kJ mol ⁻¹)	$-\Delta\mu_{ox}^0$ (kJ mol ⁻¹)
1.2	0.69	32.05	0.86	132.13	92.64
2.1	1.73	32.88	0.45	132.41	85.50
2.7	1.14	9.43	1.35	118.77	97.53

Examination of the binding constants reveals that K_s values are much larger than K_o values. Larger values of binding constants for the substrate, i.e. *N*-alkyl aniline, can be attributed to both hydrophobic and hydrophilic binding with the micellar phase compared to location of H_3PO_5 in the Stern layer bound only hydrophilically. This is evident from the transfer free energy¹⁶ values which are calculated from the relationship,

$$(\mu_m^o - \mu_w^o) = \Delta\mu^o = -RT \ln(55 \cdot 5 K),$$

where K is the relevant binding constant. $\Delta\mu^o$ values for both substrate and oxidant are collected in tables 3 and 4. Magnitude of $\Delta\mu^o$ for one of the reactants, i.e. the substrate is decisively larger than that for the other, clearly suggesting that one reactant is more inside the core of the micelle as compared to the other. It is however reasonable to suggest that the reaction occurs in the palizade layer that is an intermediate region between the hydrophilic micellar surface and the hydrophobic core.

A look at the \bar{k}_m values of *N*-methyl aniline and *N*-ethyl aniline makes it clear that the reaction rate in the micellar phase is not significantly affected in spite of an additional $-CH_2$ group present in the latter. This is at variance with the finding that every methylene group makes a definite contribution to the transfer free energy of the molecule, from water to the micellar phase.

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