

Micellar and Substituent Effects on the Redox Reaction of Phenylsulfinylacetic Acid and Cr(VI) in SDS Medium.

P. Subramaniam^{1*} & N. Thamilselvi²

¹Research Department of Chemistry, Aditanar College of Arts and Science,
Tiruchendur-628 216, Tamil Nadu.

²Govindammal Aditanar College for Women, Tiruchendur-628 215, Tamil Nadu,

ABSTRACT

The oxidative decarboxylation of phenylsulfinylacetic acid by Cr(VI) was investigated in SDS micellar medium under pseudo-first-order-conditions. The reaction kinetics show unit-order dependence each with respect to PSAA, Cr(VI) and H⁺. SDS produces a catalytic effect in the reaction rate in a continuous fashion without maximum. The study of substituent effect indicates a rate accelerating effect by electron-releasing groups and an opposite effect by electron-withdrawing groups. The Hammett correlation gives a straight line with a negative ρ value which supports the formation of sulfonium cation intermediate as a result of an S_N2 type attack of sulfur atom of PSAA on the Cr atom of the oxidizing species, HCrO₃⁺ in a slow step. The observed micellar and kinetic effects are explained by applying Menger-Portnoy model and Piskiewicz cooperative model.

Keywords: Phenylsulfinylacetic acid, micellar effect, sodium dodecyl sulfate, S_N2 type mechanism, pseudo-phase kinetic model.

Corresponding Author: Subramaniam. P

INTRODUCTION

Catalytic reactions within micelles have been studied extensively [1-5] since the micelle catalyzed reactions are similar to those of many regulatory enzymes that show positive homotropic interaction. Micelles act as pseudo-phase reaction regions which are distinct from the bulk solvent and can accelerate the reaction rate by incorporating more reactant molecules inside the micellar phase. Theoretical treatments and the kinetic evidence of reactants partitioning between water and micelles allow the determination of rate constants in the micellar pseudo-phase for bimolecular reactions. Several pseudo-phase models [6-10] have been developed to explain the kinetic effects and the mechanism by different researchers. The catalytic effect in micellar media may be due to the solubilization of the reactants in micellar surfactant solutions which often leads to drastic changes in their chemical and physical properties [11]. Phenylsulfinylacetic acid (PSAA) is an excellent synthetic agent and precursor for many pharmaceutical preparations [12-16]. In continuation with our recent reports on the oxidative decarboxylation of PSAA by Cr(VI) [17], Cr(VI) in presence of oxalic acid [18] and by oxo(salen)chromium(V) complexes [19], we herewith report the results of the kinetic study between PSAA and Cr(VI) in anionic micellar medium.

MATERIALS AND METHODS

Preparation of phenylsulfinylacetic acids

PSAA and several meta- and para-substituted phenylsulfinylacetic acids were prepared from the corresponding phenylmercaptoacetic acids by controlled oxidation using H_2O_2 [20]. The PSAAs were recrystallized from suitable solvents [21] and their purity was checked by LCMS and m.pt. techniques. They were stored in vacuum desiccator and used for the kinetic study.

Kinetic measurements

The redox reaction between PSAA and Cr(VI) was performed in anionic surfactant, sodium dodecyl sulfate (SDS) medium under pseudo-first-order conditions by maintaining a large excess of [PSAA] over the concentration of Cr(VI). The progress of the reaction was monitored by following the decrease in [Cr(VI)] spectrophotometrically in 95% water-5% CH_3CN medium and the overlay spectrum of the reaction is given in Figure 1.

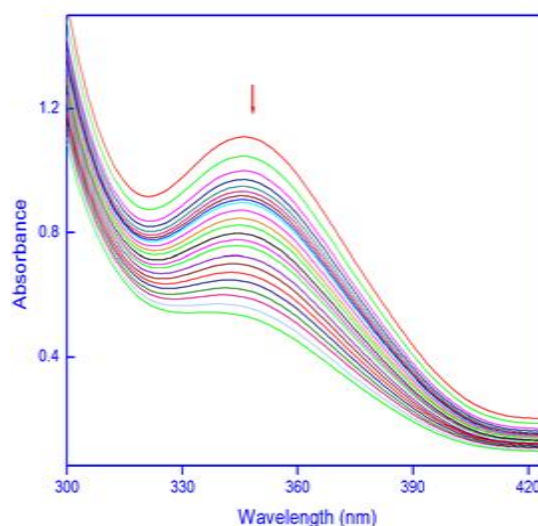


Fig 1: Overlay spectrum of the reaction mixture in the presence of SDS

Product analysis

Methyl phenyl sulfone is identified as the oxidation product of the reaction using FT-IR and LC-MS spectral studies. The ultimate product of Cr(VI) is identified as Cr(III) in the free state from the absorption spectrum of the reaction mixture after completion of the reaction which displays two absorption peaks at 410 nm and 580 nm corresponding to the d-d transitions of Cr(III). This observation is in contradiction with the result observed in the reaction without micelles [18] where a blue shift has been observed in the absorption peaks of Cr(III) at 410 nm and 580 nm and it is proposed that Cr(III) forms complex with the organic product methyl phenyl sulfone. In SDS micellar medium the product, methyl phenyl sulfone may solubilize deeply into the micelle by hydrophobic interaction and becomes inaccessible for complexation with Cr(III) which exists in the aqueous phase.

RESULTS

Effect of [Cr(VI)] and [PSAA] on reaction rate

The kinetics of the reaction was carried out at different initial concentrations of reactants, Cr(VI) and PSAA at fixed concentrations of other reaction ingredients and the rate data are given in Table 1. Linear pseudo-first-order plots at different concentrations of Cr(VI), constant second-order rate constants at different [PSAA] and excellent linear log-log plots of

the pseudo-first-order rate constants and [PSAA] yielding unit slope clearly show the first-order dependence of the reaction each on Cr(VI) and PSAA in the presence of SDS.

Table 1. Effect of [Cr(VI)] and [PSAA] on the rate of SDS mediated reaction

10^2 [PSAA] (mol dm ⁻³)	10^4 [Cr(VI)] (mol dm ⁻³)	$10^4 k_1$ (s ⁻¹)	$10^3 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
1.0	5.0	0.558±0.01	5.58 ± 0.10
3.0	5.0	1.69 ± 0.03	5.63 ± 0.10
5.0	5.0	2.94 ± 0.07	5.88 ± 0.14
7.0	5.0	3.63 ± 0.08	5.18 ± 0.11
10	5.0	5.77 ± 0.10	5.77 ± 0.10
5.0	3.0	3.03 ± 0.15	6.06 ± 0.30
5.0	7.0	2.89 ± 0.09	5.78 ± 0.18

[H⁺] = 5.0 x 10⁻¹ mol dm⁻³; [SDS] = 5.0 x 10⁻² mol dm⁻³; solvent = 95% H₂O-5% CH₃CN (v/v);
I = 6.5 x 10⁻¹ mol dm⁻³.

Effect of H⁺ and SDS on reaction rate

Perchloric acid is used to maintain [H⁺] and the order with respect to H⁺ is unity in the presence of SDS as assessed from the unit slope of the log-log plots of k_1 vs. [H⁺] and from the constant value of $k_1 / [H^+]$. The pseudo-first-order rate constants presented in Table 2 and Figure 2 show that SDS produces a positive catalytic effect in a continuous fashion in the entire range of concentration studied which is typical for reactions catalyzed by micelles.

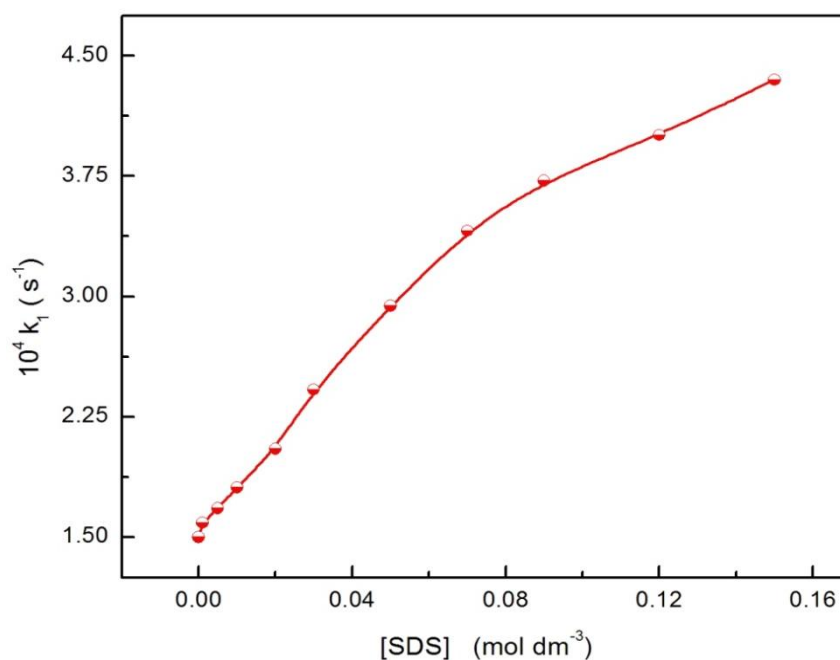


Fig 2: Effect of [SDS] on pseudo-first order rate constant

Table 2. Effect of SDS on the rate of reaction

$10^2[\text{SDS}]$ (mol dm ⁻³)	$10^4 k_1$ (s ⁻¹)
0	1.50 ± 0.05
0.1	1.59 ± 0.02
0.5	1.68 ± 0.04
1.0	1.81 ± 0.06
2.0	2.05 ± 0.03
3.0	2.42 ± 0.08
5.0	2.94 ± 0.07
7.0	3.41 ± 0.06
9.0	3.72 ± 0.02
12	4.01 ± 0.04
15	4.35 ± 0.02

[Cr(VI)] = 5.0×10^{-4} mol dm⁻³; [PSAA] = 5.0×10^{-2} mol dm⁻³; [H⁺] = 5.0×10^{-1} mol dm⁻³;
I = 6.5×10^{-1} mol dm⁻³; solvent = 95% H₂O-5% CH₃CN (v/v).

Effect of temperature and activation parameters

The influence of temperature on the rate of the reaction in presence of SDS was studied by following the reaction at different temperatures in the range 20°C to 35°C keeping all other parameters constant. The thermodynamic parameters evaluated from the intercept and slope of the Eyring's plot are $\Delta^\ddagger S = -44.9 \pm 11.1 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\Delta^\ddagger H = 73.8 \pm 3.18 \text{ kJ mol}^{-1}$.

Substituent effect

The study of substituent effect with several *meta*- and *para*-substituted PSAAs at 30°C in the presence of SDS shows that the rate of the reaction is accelerated by electron-donating groups and retarded by the electron-withdrawing groups present in the phenyl ring of PSAAs (Table 3).

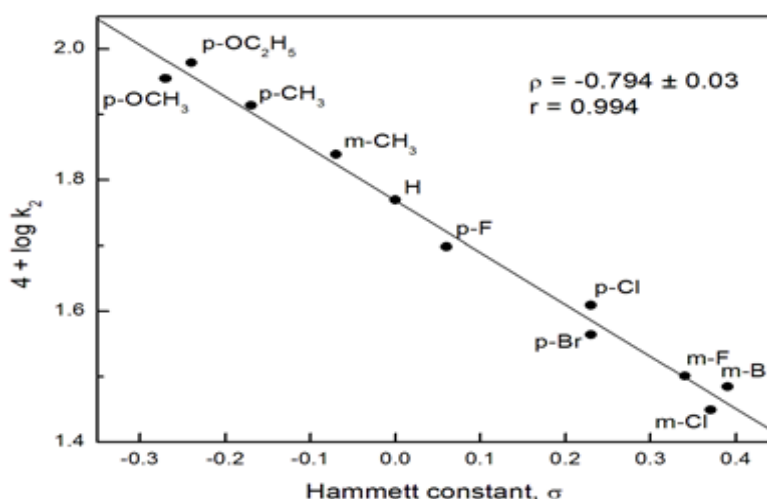


Fig 3: Hammett plot at 30°C for the SDS mediated reaction.

The Hammett correlation (Figure 3; $r = 0.994$) affords a negative slope value ($\rho = -0.794 \pm 0.03$) which indicates the formation of a positively charged intermediate in the slow step.

Table 3. Second-order rate constants for the reaction of PSAAs with Cr(VI) in SDS medium

X	$10^3 k_2$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
<i>m</i> -Br	3.05 ± 0.12
<i>m</i> -Cl	2.81 ± 0.10
<i>m</i> -F	3.17 ± 0.15
<i>p</i> -Cl	4.06 ± 0.12
<i>p</i> -Br	3.66 ± 0.10
<i>p</i> -F	4.99 ± 0.11
H	5.88 ± 0.14
<i>m</i> -CH ₃	6.90 ± 0.12
<i>p</i> -CH ₃	8.20 ± 0.10
<i>p</i> -OC ₂ H ₅	9.53 ± 0.12
<i>p</i> -OCH ₃	9.02 ± 0.10
ρ	-0.794 ± 0.03
r	0.994

$[\text{X-C}_6\text{H}_4\text{SOCH}_2\text{COOH}] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Cr(VI)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$; $\text{I} = 6.5 \times 10^{-1} \text{ mol dm}^{-3}$; solvent = 95% H₂O- 5% CH₃CN (v/v).

Mechanism in micellar media and interpretation of micellar effect

The SDS mediated reaction follows unit order dependence on each reactant as observed in the absence of micelles [17]. The observed UV-vis absorption spectra (Figure 4) of the reaction mixture in both aqueous and SDS media which display similar pattern of absorption peaks may be taken as the positive evidence for the existence of same type of intermediate in both aqueous and SDS mediated reactions.

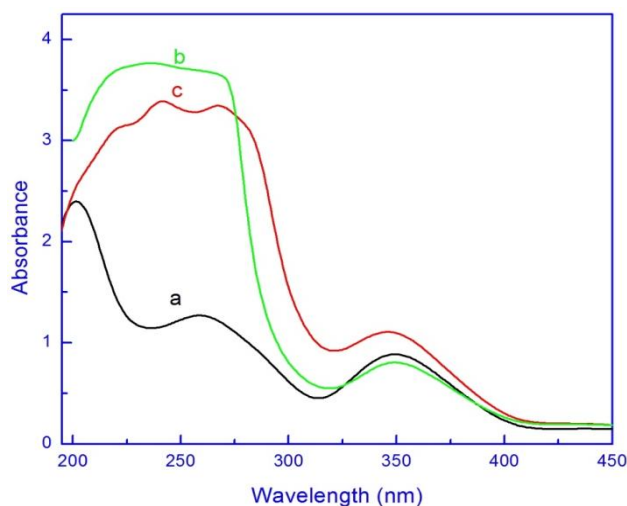
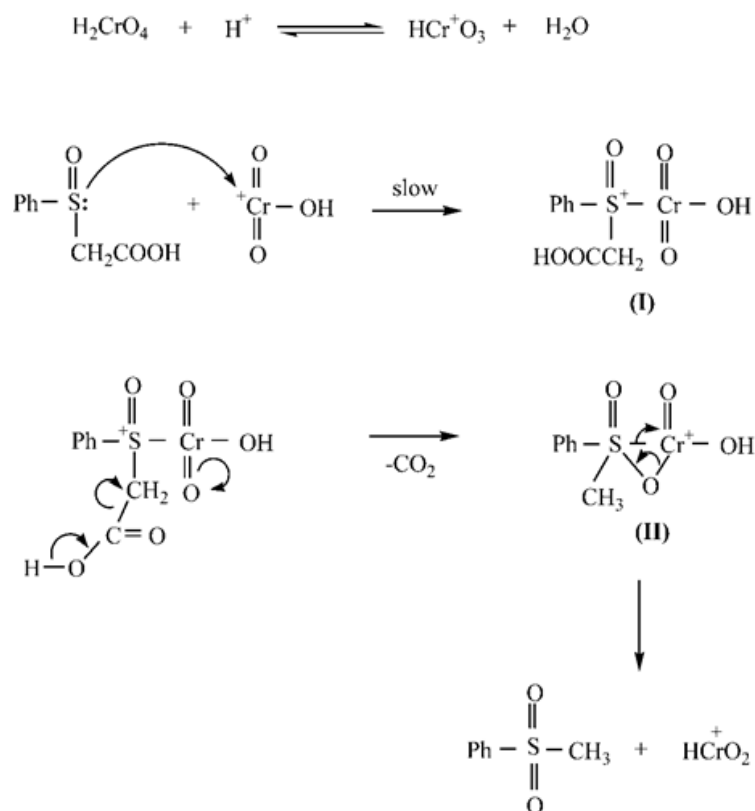


Fig 4. UV-vis spectra of (a) Cr(VI); (b) reaction mixture in aq. Medium;
(c) reaction mixture in SDS medium

$[\text{PSAA}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Cr(VI)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$;
solvent = 95% H_2O -5% CH_3CN (v/v); $[\text{SDS}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$.

The observed kinetic and spectral data along with substituent effect and product formation support the operation of same mechanism with identical active oxidizing species in SDS medium as in the absence of micelle (Scheme 1). The reaction follows an $\text{S}_{\text{N}}2$ type of mechanism involving nucleophilic attack of S of PSAA on Cr of HCrO_3^+ species resulting in the formation of sulfonium ion intermediate in the rate-determining step.



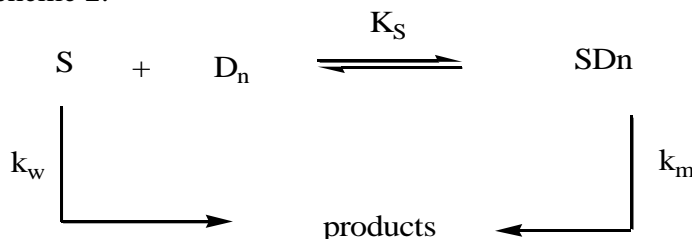
Scheme 1

It is well established that most of the micellar reactions involving ionic and neutral reactants are believed to take place either inside the Stern layer or at the interface between the micellar surface and bulk solvent, water [22]. The active oxidizing species, HCrO_3^+ obviously interact with the anionic micelle, SDS through electrostatic interactions. The observed rate acceleration in anionic surfactant, SDS may be due to the preferential partitioning of positively charged active oxidizing species HCrO_3^+ by electrostatic attraction and the neutral reactant PSAA by hydrophobic interaction into the micellar phase. Thus, SDS allows both the reactants to enter into the micellar pseudo-phase, enhances their stoichiometric concentration in the micellar phase and permit the reaction to proceed much faster which results in the overall rate benefit. With the increase in $[\text{SDS}]$, the extent of partitioning of the reactants in the micellar phase increases followed by increase in rate constant continuously at all the concentrations of SDS studied. Further, the development of positive charge on the sulfur due to the electron transfer from PSAA to HCrO_3^+ in the rate-determining step is also favoured in the anionic micellar medium.

RATE LAW AND MATHEMATICAL TREATMENT

Menger-Portnoy model

To interpret the catalytic activity of SDS and to evaluate the binding constant between the substrate and surfactant the kinetic data were analyzed in terms of the pseudo-phase kinetic model proposed by Menger and Portnoy [6] and its modified forms [23-25]. This model considers the partitioning of the substrate PSAA between the aqueous and micellar pseudo-phases as given in Scheme 2.



Scheme 2

where D_n , S and SD_n represent micellar surfactant, free substrate and associated substrate respectively. According to Scheme 2 the observed rate constant, k_ψ may be derived as,

$$k_\psi = (k_w + k_m K_s [\text{D}_n]) / (1 + K_s [\text{D}_n]) \quad (1)$$

where k_w and k_m are the pseudo-first-order rate constants in aqueous and micellar phases respectively, K_s is the binding constant of the substrate with the surfactant and $[\text{D}_n]$ is the concentration of the micellar surfactant which is related to stoichiometric concentration of the surfactant ($[\text{D}]_T$) and critical micelle concentration (cmc) as $[\text{D}_n] = ([\text{D}]_T - \text{cmc})$. The cmc value of the SDS micelle required for the calculation is taken from the literature as $8 \times 10^{-3} \text{ mol dm}^{-3}$ [6,26].

For micellar catalysis the equation 1 can be rearranged to the form,

$$1 / (k_\psi - k_w) = 1 / (k_m - k_w) + 1 / (k_m - k_w) K_s [\text{D}_n] \quad (2)$$

The eq. 2 has been verified in many cases of continuous micellar catalysis. In the present reaction, the plot of $1 / (k_\psi - k_w)$ versus $1/[\text{D}_n]$ is linear (Figure 5) with positive slope of $1 / (k_m - k_w) K_s$ and intercept of $1 / (k_m - k_w)$ showing the validity of Menger-Portnoy's model to the SDS catalyzed reaction of PSAA.

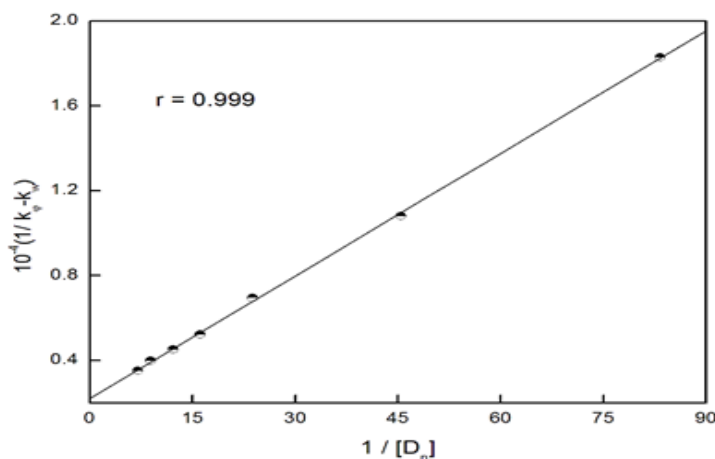
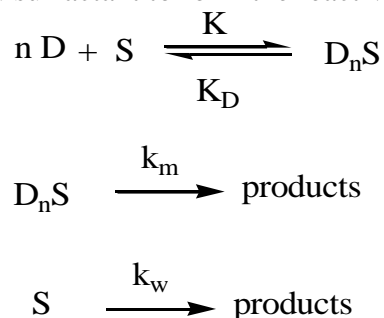


Fig 5. Validity of Menger-Portnoy's model.

The binding constant, K_s and the rate constant for the reaction in the micellar phase, k_m determined from the slope and intercept of the linear plot utilizing Menger-Portnoy's model are $11.37 \text{ mol dm}^{-3}$ and $6.06 \times 10^{-4} \text{ s}^{-1}$ respectively. The observed low binding constant value compared with other reported systems account for the marginal rate accelerating effect. Thus it is assumed that the substrate PSAA is partitioning in both aqueous and micellar pseudo-phases and the reaction between PSAA and Cr(VI) species is also assumed to take place in both the media.

Piskiewicz cooperative model

Many micellar reactions have been explained by the cooperative model developed by Piskiewicz [7] which is analogous to the Hill model applied to enzyme catalyzed reactions. The Piskiewicz model relates the cooperativity between the neutral species of the reaction, in this case PSAA and surfactant to form the reactive micelles as in Scheme 3.



Scheme 3

From the Scheme 3 the observed rate constant, k_ψ can be expressed as a function of the concentration of surfactant as,

$$k_\psi = k_m [D]^n + K_D k_w / K_D + [D]^n \quad (3)$$

The eq. 3 can be rearranged to

$$\log [(k_\psi - k_w)/(k_m - k_\psi)] = n \log [D] - \log K_D \quad (4)$$

where, k_ψ is the observed rate constant at a given surfactant concentration $[D]$, k_m is the rate constant at the micellar phase under the conditions of complete binding of the substrate to the micelles, k_w is the rate constant of the reaction in the absence of micelle, n is the index of cooperativity and K_D is the dissociation constant of micellized substrate back to its free components and its inverse is K which is the association constant of the micelle-substrate complex.

The observed rate constant for the SDS catalyzed reaction continued to increase with increase in the $[SDS]$ without any maxima or saturation. In order to analyze the data according to eq. 4, the rate constant k_m obtained from Menger-Portnoy's model is utilized as done by several other researchers for the systems involving continuous rate enhancement without maxima [27,28]. The plot of $\log [(k_\psi - k_w)/(k_m - k_\psi)]$ vs. $\log [D]$ show linear

behaviour for this reaction (Figure 6) and the parameters, n and K_D determined respectively from the slope and intercept of the linear plot are 1.11 and 7.79×10^{-2} .

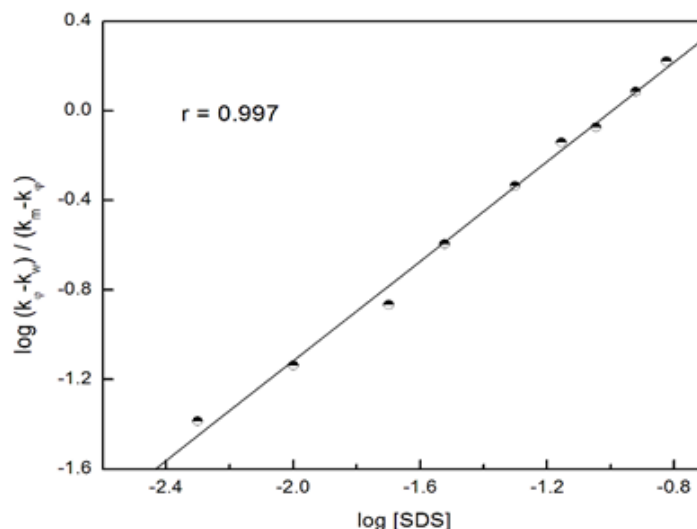


Fig 6. Validity of Menger-Portnoy's model.

The value of n obtained in the present case indicates the formation of catalytically active sub-micellar aggregates. The value of n is far less than the aggregation number (20-100) of the surfactants which indicate the formation of catalytically productive sub-micellar aggregates [7]. The linear plot supports the positive cooperativity between PSAA and micelle to form reactive micelles which indicate that the substrate, PSAA molecules are included into the micellar phase.

CONCLUSION

The micellar and substituent effects on the redox reaction of PSAA and Cr(VI) have been investigated in SDS medium. The reaction is catalyzed by SDS and the observed kinetic data have been subjected to mathematical treatments and explained on the basis of pseudo-phase models, Menger-Portnoy model and Piszkiwicz cooperativity model.

REFERENCE

- [1] Islam, M.; Saha, B.; Das, A. K. *Int. J. Chem. Kinet.* **2006**, 38, 531.
- [2] Ghosh, S. K.; Saha, R.; Ghosh, A.; Basu, A.; Mukherjee, K.; Saha, I.; Saha, B. *J. Korean Chem. Soc.* **2012**, 56, 720.
- [3] Mandal, J.; Chowdhury, K. M.; Paul, K. K.; Saha, B. *The Open Catalysis Journal* **2008**, 1, 1.
- [4] Saha, B.; Das, M.; Mohanty, R. K.; Das, A. K. *J. Chin. Chem. Soc.* **2004**, 51, 399.
- [5] Bayen, R.; Islam, M.; Das, A.K. *Indian J. Chem.* **2009**, 48A, 1055.
- [6] Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, 89, 4698.
- [7] Piszkiwicz, D. *J. Am. Chem. Soc.* **1977**, 99, 1550.
- [8] Das, A. K. *Coord. Chem. Rev.* **2004**, 248, 81.
- [9] Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. *Acc. Chem. Res.* **1991**, 24, 57.
- [10] Berezin, I. V.; Martinek, K.; Yatsmirskii, A. K. *Russ. Chem. Rev.* **1973**, 42, 787.
- [11] Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley, New York, **1982**.
- [12] Jaxa-Chamiec, A. A.; Sammes, P. G.; Kennewell, P. D. *J. Chem. Soc. Perkin Trans. I* **1980**, 170.

-
- [13] Cass, Q. B.; Jaxa-Chamiec, A. A.; Sammes, P. G. *J. Chem. Soc. Chem. Commun.* **1981**, 248.
- [14] Zhang, Z.; Bao, M.; Liu, B. *Hecheng Huaxue* **2002**, 10, 241.
- [15] Allmendinger, T. *Tetrahedron* **1991**, 47, 4905.
- [16] Lee, K. *Bull. Korean Chem. Soc.* **2011**, 32, 3477.
- [17] Subramaniam, P.; Thamil Selvi, N. *Am. J. Anal. Chem.* **2013**, 4, 20.
- [18] Subramaniam, P.; Thamil Selvi, N.; Sugirtha Devi, S. *J. Korean Chem. Soc.* **2014**, 58, 17.
- [19] Subramaniam, P.; Sugirtha Devi, S.; Anbarasan, S. *J. Mol. Catal. A: Chem.* **2014**, 390, 159.
- [20] Walker, D.; Leib, J. *Can. J. Chem.* **1962**, 40, 1242.
- [21] Kenney, W. J.; Walsh, J. A.; Davenport, D. A. *J. Am. Chem. Soc.* **1961**, 83, 4019.
- [22] Cordes, E. H. *Pure Appl. Chem.* **1978**, 50, 617.
- [23] Bunton, C. A. *Catal. Rev. Sci. Eng.* **1979**, 20, 1.
- [24] Bunton, C. A. *J. Mol. Liq.* **1997**, 72, 231.
- [25] Vera, S.; Rodenas, E. *Tetrahedron* **1986**, 42, 143.
- [26] Balakumar, P.; Balakumar, S.; Subramaniam, P. *Der Chemica Sinica* **2012**, 3, 959.
- [27] Sarada, N. C.; Ajit Kumar Reddy, I. *Asian J. Chem.* **1993**, 5, 19.
- [28] Katre, Y.; Goyal, N.; Sharma, R.; Singh, A. K. *Indian J. Chem.* **2013**, 52A, 732.