

RESEARCH ARTICLE



**EFFECT OF SODIUM DODECYL SULPHATE ON THE KINETICS OF REACTION BETWEEN
PERSULPHATE AND IODIDE IONS**

AVIJIT SAHA

Department of Chemistry, Jogesh Chandra Chaudhuri College, 30 Prince Anwar Shah Road,
Kolkata – 700 033, India

Corresponding Author: asaha22@rediffmail.com

Abstract

The kinetics of the reaction between potassium persulphate and potassium iodide has been studied iodometrically in aqueous solutions of sodium dodecyl sulphate (SDS) at various surfactant concentrations. It is observed that from low concentrations up to the c.m.c, the surfactant behaves like a normal electrolyte exhibiting primary kinetic salt effect. In presence of micelles it is observed that rate constant decreases with increase of ionic strength between cmc and 32 m mol dm^{-3} of SDS and at very high concentrations of SDS the reaction rate increases slowly in keeping with the fact that owing to micellisation the concentration of monomeric SDS increases slowly with increase in the total concentration of SDS.

Keywords: Sodium dodecyl sulphate, Ionic strength, Micelle, Primary kinetic salt effect

Introduction

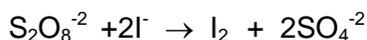
Study of the normal and reverse micelles (Hinze, 1979) on various types of physicochemical phenomena is a subject of current interest. For example, reaction rates are greatly influenced by micellar media (Sahu and Panigrahi, 1996; Hodges and De Aruzo 1982; Menero et al., 1983; Dash et al, 1990), absorption and emission properties (Kalyanasundaram, and Thomas, 1977; Turley, and Often, 1986; Saroja, and Samanta, 1996) and chemiluminescence (McCapra, 1976) of many dyes. These phenomena are utilized for the determination of critical micelle concentrations (c.m.c) and micellar aggregation number of surfactants (Stam et al., 1998). For reactions where one of the reactants is partitioned between the inner and outer regions of the micelle there is the well established Menger-Portnoy model (Menger and Portnoy, 1967) for studying the kinetics. Kinetic model based on chemical affinity describes the kinetics of crystal growth process for CHClF_2 hydrate formation in presence of surfactant (Karamoddin, et al., 2014).

A number of reactions of this type have been studied fairly recently (Sahu and Panigrahi, 1996; Pradhan, et al., 1996; Vasi, et al., 2003.). However, although the effect of ionic strength on reactions between ions is a well known phenomenon, the effect of increasing concentration of the anionic surfactant, sodium dodecyl sulphate (SDS), on the rate of the reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- ions has not yet been studied. The object of the present work is to make an investigation along this line.

Materials and method

Commercial G.R. grade potassium persulphate and potassium iodide (E.Merck) and extra pure quality sodium dodecyl sulphate (SDS) from Sisco Research Laboratories, Bombay, were used without further purification.

The kinetics of the reaction



was followed by iodometric titration with standardized sodium thiosulphate solution.

Even below c.m.c, aqueous solution of SDS shows turbidity when an electrolyte solution is added at temperatures within 309K. This was tested with the electrolytes KCl, NaCl, BaCl₂, Na₂S₂O₃, K₄[Fe(CN)₆] and K₂Cr₂O₇. From and above 313K the added electrolytes do not cause flocculation irrespective of whether the SDS concentration is below or above c.m.c. So the experiment was carried out at 313K. With normal concentrations of I⁻ and S₂O₈⁻ ions, the working formula for the second order reaction (first order with respect to each of I⁻ and S₂O₈⁻ ions) can be shown to be,

$$V_t/(V_\infty - V_t) = 2akt \quad \dots\dots(1)$$

where, V_t = the volume of a standard thiosulphate solution required for titration of a definite volume of reaction mixture (aliquot) at time t and V_∞ is that

required on completion of the reaction. In equation (1) a is the initial concentration of I⁻ ion

Results and discussion

Rate constants were determined titrimetrically using equation (1). One typical plot according to equation (1) is shown in Fig. 1. The correlation coefficients of such plots at various concentration of SDS are above 0.98. Since it is known that the reaction path may change if long time is allowed, only the data up to ~30mins. were taken and rate constants were calculated by least square fitting.

Variation of rate constant with concentration of SDS at 313K is shown in Fig. 2 where it is observed that log k increases linearly with [SDS] up to 6 m.mol.dm⁻³, showing primary kinetic salt effect. This linear portion is shown in Fig. 3 with an expanded scale for clarity. Least square fitting gives a slope of 2.13 for the line in Fig. 3, which is close to the value expected from the equation,

$$\log k = \log k_0 + 2AZZ'/\sqrt{\mu} \quad \dots\dots(2)$$

Table: 1 Rate constants at different concentrations of SDS at 313 K

Concentration of SDS (m.mol dm ⁻³)	Rate constant(k) (dm ³ .mol ⁻¹ min ⁻¹)
0	0.18 ± 0.004
0.1	0.17 ± 0.005
0.3	0.17 ± 0.005
0.5	0.17 ± 0.008
0.8	0.18 ± 0.004
2	0.19 ± 0.004
4	0.22 ± 0.008
6	0.23 ± 0.006
7	0.21 ± 0.007
8	0.20 ± 0.003
9	0.19 ± 0.006
10	0.19 ± 0.004
12	0.19 ± 0.002
16	0.18 ± 0.008
24	0.18 ± 0.003
32	0.17 ± 0.005
55	0.22 ± 0.012
80	0.25 ± 0.009

Fig.1. Plot for determination of rate constant of the reaction at $[SDS]= 0.8 \text{ m.mol.dm}^{-3}$ according to equation 1.

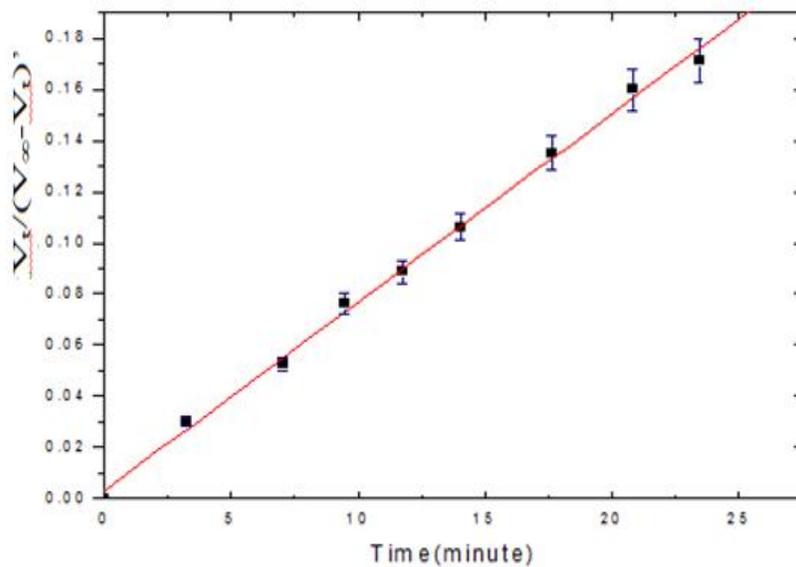


Fig.2. Plot of $\log k$ against ionic strength ($=\sqrt{[SDS]}$), in the entire range of surfactant concentrations.

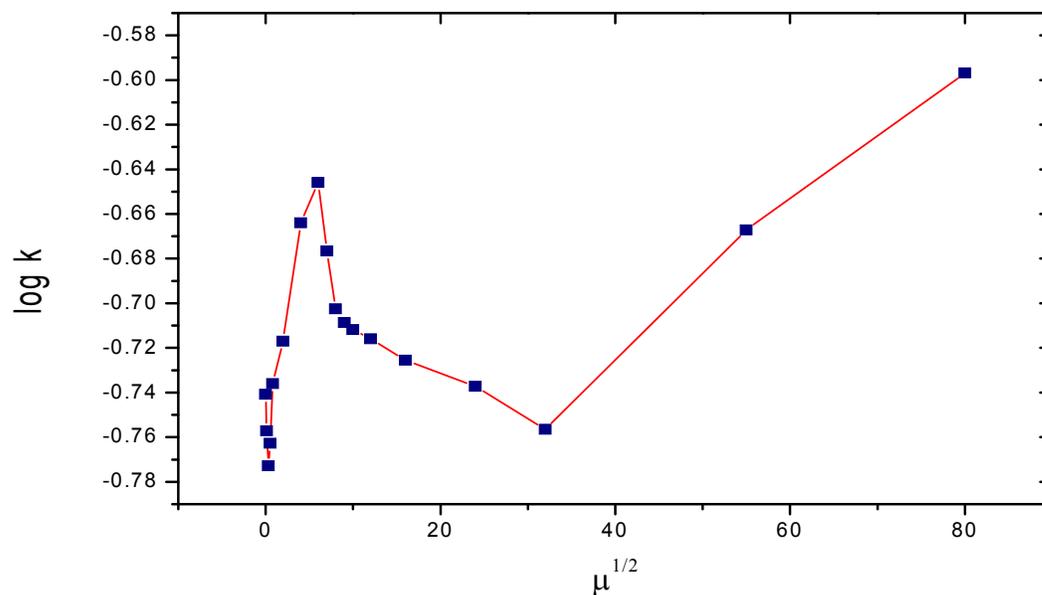
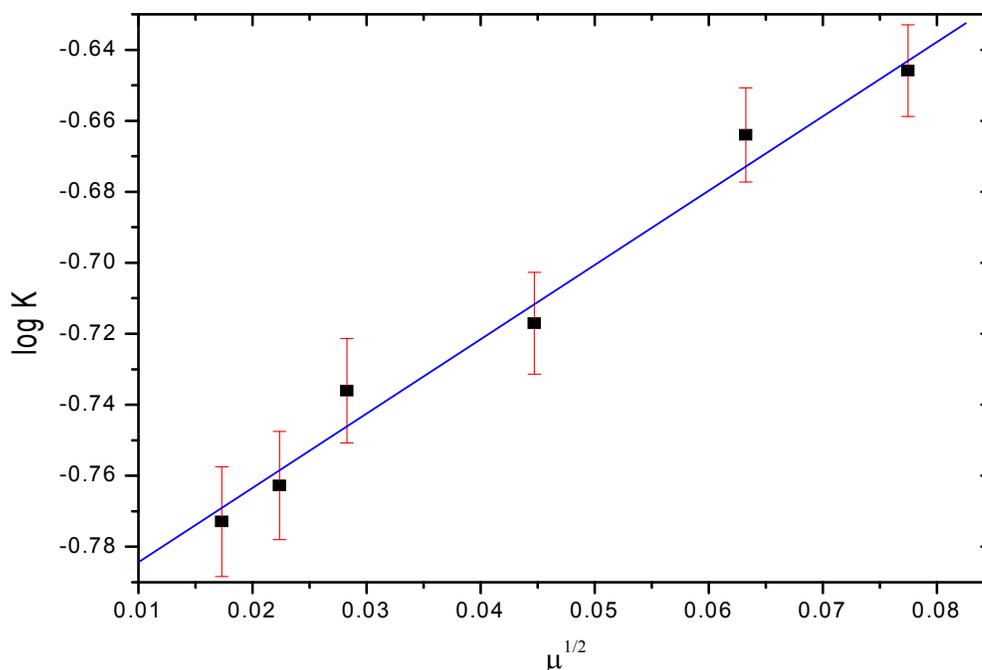


Fig. 3. Primary kinetic salt effect exhibited by SDS below c.m.c.



where A is the Debye-Huckel constant (about 0.51 in water at 298K to 313K), Z and Z' are the valences of the reactant ions and μ is the ionic strength of the medium (in this case $\mu \approx [\text{SDS}]$). At $[\text{SDS}] = 6 \text{ m.mol.dm}^{-3}$, there is a break, $\log k$ decreases non-linearly upto 32 m.mol.dm^{-3} , and then again increases slowly. Thus c.m.c is obtained as 6 m.mol.dm^{-3} , a value slightly less than that reported (8 m.mol.dm^{-3}) in literature (Hinze, 1991). The lower c.m.c value even above room temperature may be due to the presence of electrolytes. The non-linear increase of $\log k$ with $[\text{SDS}]$ at high concentrations above c.m.c is not easy to explain quantitatively. At lower concentration region above cmc, concentration of micelle increases more than the concentration of monomeric $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-$ ions with increase in total concentration of SDS.

The ionic reactants $\text{S}_2\text{O}_8^{2-}$ and I^- are repelled by the negatively charged micelles, the reactant anions reside well within the bulk away from the micellar surface. In presence of micelles it is observed that rate constant decreases with increase of ionic strength between cmc and 32 m.mol dm^{-3} of SDS. This effect can be explained by the competition

between reactant anions for berth into the core position of the micelle. Between these two, reactant anions which have higher mobility are trapped first in the micelles. So concentration of free reactants decreases with increase of conc of SDS and a consequent decrease of the rate constant. At higher concentration of SDS, concentration of monomeric $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-$ ions increases slowly with increase in total concentration of SDS resulting in slow increase of rate constant in the high concentration region of SDS.

Acknowledgement

The Author would like to thank Dr. Asok K. Mukherjee, former Professor, Department of Chemistry, The University of Burdwan for affectionate guidance and valuable advice for research. Sincere thanks are also extended to the University Grants Commission, India for financial assistance in the minor research project.

References

Dash, A. C., Prusti, J., Pradhan, J., and Das, P. K., 1990. Micellar Effects upon the Reactions of

- Complex Ions in Solution J. Chem. Soc. Faraday Trans., 86(3), 507-510
- Hinze, W. L. 1979. Solution chemistry of surfactant edited by Mittal, K. L., (Plenum Press, New York),1, 79-128.
- Hinze, W.L., Srinivasan, N., Smith, T. K., Igarashi, S., and Hishino, H., 1991. Advances in *Multi dimensional Luminescence*, vol 1, (JAI Press Inc.) 149-206.
- Hodges H. L., and De Aruzo, M. A., 1982. Kinetic investigation of the equilibrium between mono- and bis(1,10-phenanthroline)copper(I) in aqueous and sodium dodecyl sulfate solution. *Inorg Chemistry*,21, 3236-3239.
- Kalyanasundaram, K., and Thomas, J. K., 1977. Environmental effects on vibronic band intensities in pyrene monomer fluorescence and their application in studies of micellar systems. *J Amer Chem.Soc*, 99, 2039.
- Karamoddin, M., Varaminian, F., and Daraee, M., 2014. Kinetic study on the process of CHCl₃ (R22) hydrate formation in the presence of SDS surfactant based on chemical affinity Journal of Natural Gas Science and Engineering 19, 46–51
- McCapra, F., 1976. Chemical mechanisms in bioluminescence. *Acc. Chem Res.* 9, 201-208.
- Menero, C., Pramauro, E., Pelizzetti, E. and Miesel, D., 1983. One-electron transfer equilibriums and kinetics of N-methylphenothiazine in micellar systems. *J Phys Chem.*,87, 399-407.
- Menger, F. M., and Portnoy, C. E., 1967. Chemistry of reactions proceeding inside molecular aggregates. *J.Amer.Chem. Soc.* 89, 4698-4703.
- Pradhan, D. K., Panigrahi, A. K., and Sinha, B. K., 1996. Effect of Organised Surfactant System on the Kinetics of Acid-catalysed Hydrolysis of Ethyl Acetate. *J Indian Chem.Soc.* 73, 203
- Sahu, S. K. and Panigrahi, G. P., 1996. Micellar Catalysis- Effect of Sodium Lauryl Sulphate in the Oxidation of Cyclopentanol by Chromic-acid', *J Indian Chem Soc*,73, 576.
- Saroja, G., and Samanta, A., 1996. Photophysical studies on a fluorescence probe labelled fatty acid: chain folding in a micellar environment. *J Chem Soc. Faraday Trans.* 92. 2697-2701.
- Stam. J.v.,Depaemelaere, S., De Schryver, F. C., 1998. Micellar Aggregation Numbers - A Fluorescence Study. *J Chem Education*, 75, 93 and referceces cited Therein.
- Turley, W. D., and Often, H. W., 1986. Lipid microviscosity of DMPC vesicles at high pressures. Dipyrenylpropane excimer fluorescence. *J Phys Chem.*90, 1967.
- Vasi , V., akar, M., Savi , J., Petrovi , B., Nedeljkovi , J., Bugar i , Z., 2003. Influence of sodium dodecyl sulfate on the kinetics of complex formation between [PdCl(dien)]⁺ and sulfur containing ligands L-cysteine and glutathione. *Polyhedron* 22, 279–285