Sodium Dodecylsulfate and Sodium Sulfate Effects on the Oxidation of N, N-dimethylaniline by Hexacyanoferrate(III)

Jamil K .J Salem

Department of Chemistry, Faculty of Science,
Al-Azhar University-Gaza, Gaza-Palestine.
Email: jamils22@yahoo.com

Abstract: *The reaction of oxidation of N,N-dimethylaniline (DMA) by hexacyanoferrate has been studied in micellar solution of sodium dodecyl sulfate(SDS). It is shown that micellization results in an increase of the rate of reaction and the effect is reversed at surfactant concentration below CMC. The effects of* Na_2SO_4 *addition on the rate of reaction in pure water and in SDS solutions have been investigated. These results are rationalized in terms of the extended Debye–Hückel equation and the ion–pairing between reactants and counterions.*

INTRODUCTION

Micelles are believed to affect reactions in several ways. The outer-core region of the micelle, commonly referred to as the palisade layer, may provide a medium of intermediate polarity that affects the energetics of transition-state formation [1]. In many systems, the primary influence of micelles is to concentrate all reactants in or near the micelles. Micellar catalysis exploits the ability of surfactant aggregates to solubilize significant amounts of reactants that are virtually water-insoluble [2,3]. When ionic surfactants are employed, polar or ionic reactants that are freely soluble in water may also be concentrated near the micelles by electrostatic or dipole interactions. The degree to which reaction rates are enhanced depends on a number of factors, including the location of the solubilized reactant in the micelle where nonpolar compounds are found closer to the micelle-water interface. The extent of solubilization, ionic charge of the micelle and the size and shape of the micelle are also important factors.

Recently, the oxidation of amines by hexacyanoferrate has been extensively studied in anionic micellar media and a catalytic effect upon the rate of the reaction was found [4,5]. But an inhibitory effect was observed upon the rate of the oxidation of phenylhydrazinium chloride by hexacyanoferrate in anionic micellar solutions [6,7].

In this work, the effects of sodium dodecyl sulfate micelles and salt addition on the oxidation of N,N-dimethylaniline by hexacyanoferrate are reported.

EXPERIMENTAL

Materials:

Potassium hexacyanoferrate was purchased from Fluka and N,N-dimethylaniline was obtained from Riedel–de–Haen and were used as received. Sodium dodecyl sulfate was obtained from Merck, purity > 99%. All other chemicals used were also reagent-grade products. Double-distilled water was used in all experiments.

Kinetic Measurments:

All the kinetic runs were carried out in a Shimadzu- 1601 UV- visible spectrophotometer. The studied reaction was monitored by following the changes in absorbance of the$[\mathrm{Fe(CN)_6}]^{3-}$ at 420 nm in all solutions. In all the experiments , temperature was maintained constant at 25±0.1 ^{O}C .The kinetics was studied under pseudo-first order conditions by using excess DMA .The observed rate constants (k_{obs} / s^{-1}) were obtained from the slopes of the ln A_0/A_t against time plots , where A_0 and A_t are the absorbances at time =0 and time ,t , respectively .

Conductivity Measurements:

Conductivities in the presence of reactants were measured on an AC-13 conductivity meter with a cell constant of 1.03 cm^{-1} .Solutions in the conductivity cell were thermostated at 25±0.1 ^{O}C.

RESULTS AND DISCUSSION

The oxidation of DMA by $[\mathrm{Fe(CN)_6}]^{3-}$ in basic media takes place through an electron transfer reaction in which Fe(III) is reduced to Fe(II), $[\mathrm{Fe(CN)_6}]^{3-} + e^- \rightarrow [\mathrm{Fe(CN)_6}]^{4-}$. The dependence of the observed reaction rate constant, k_{obs}, on [DMA] was investigated in aqueous and in micellar solutions. The experimental data as shown in Figure1, log k_{obs}, indicate nearly first order behavior with respect to DMA as evidenced from the slopes of the plot which are near unity.

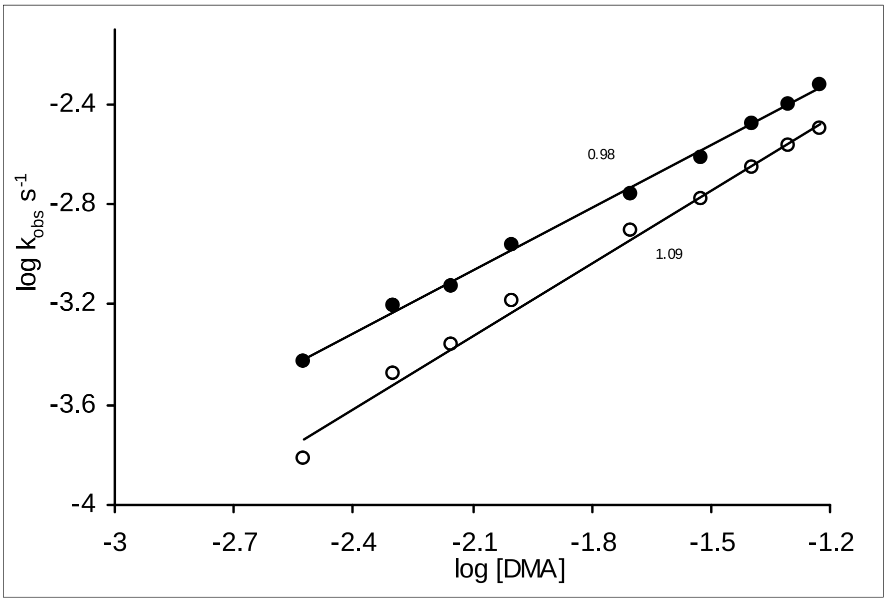
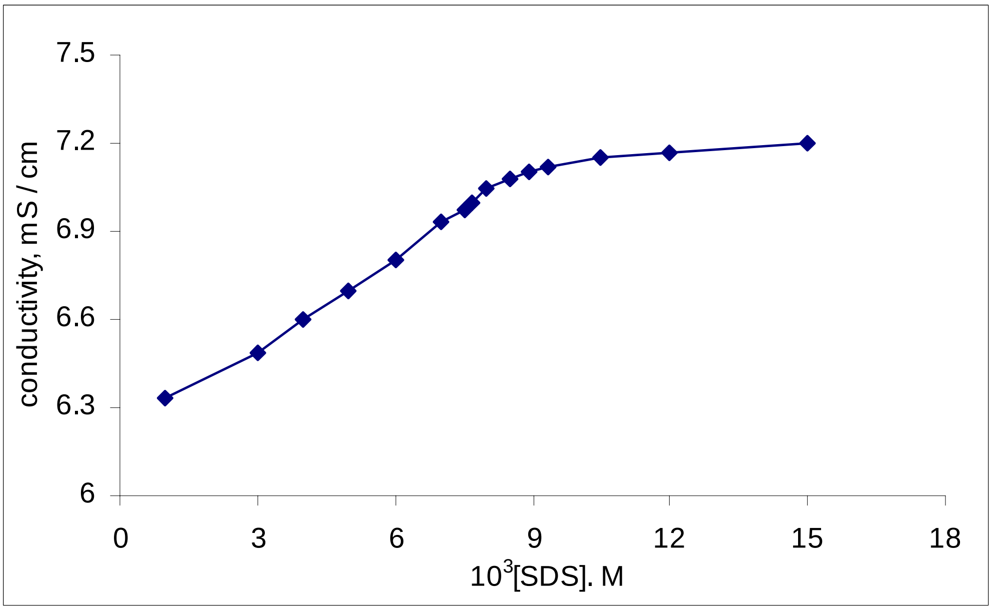


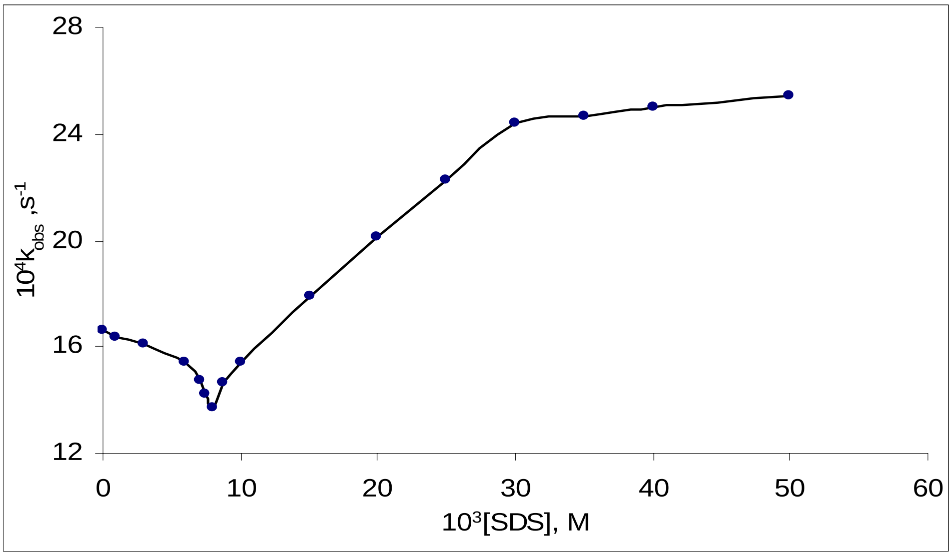
Fig.(1): A Plot of log k_{obs} vs. log [DMA] for the DMA oxidation by 0.001M $Fe(CN)_6^{3-}$ in aqueous solution (o) and in the presence of 0.03 M SDS (•) at 25 ^oC

The CMC of SDS was confirmed to be $8.5x10^{-3}$ M by conductivity measurements (Figure.2). This was in perfect agreement with the literature data [8].



Fig(2): Critical micelle concentration of SDS in presence of 0.001 M $Fe(CN)_6^{3-}$ at 25 ^oC

Figure 3 shows that micellization results in an increase in the observed rate constant above the CMC .An inhibitory effect was observed below the CMC and the rate passes through a minimum as the surfactant concentration approaches the CMC .This inhibition occurs in a region where the surfactant is apparently not micellized and where its concentration is lower than that of the substrate (DMA). This can be due to a formation of submicellar complexes by DMA molecules whereas $[Fe\ (CN)_6]^{3-}$ ions are expected to be mainly in the bulk aqueous phase. The negatively charged $[Fe\ (CN)_6]^{3-}$ ion is highly hydrophilic and it is repelled towards the aqueous phase by the negatively charged micelles. From purely hydrophobic considerations, the DMA molecules can be assumed to reside predominantly in the micelle palisade layer with the dimethylamine group exposed close to the Stern layer [9].



Fig(3): Effect of [SDS] on k_{obs} for the DMA oxidation by 0.001M $Fe(CN)_6^{3-}$ at 25 °C

The oxidation of a set of m- and p- substituted anilines in water provides evidence for a specific catalytic effect, by binding of alkali-metal ions to $[Fe(CN)_6]^{3-}$ through ion-pair formation [10]. Therefore ion pair formation between$[\ Fe\ (CN)_6]^{3-}$ and Na^+ counterions in the Stern layer of micelles appears to be a critical factor in determining the rate . The enhancement of rate about CMC could then be attributed to catalysis by ion-pairing which is a general feature often found in many chemical reactions between charged or an uncharged and a charge species [11-13]. When the SDS concentration increases, the free Na^+ counterion concentration will increase which can attract $[Fe(CN)_6]^{3-}$ ions towards the Stern layer and, thus, increasing the effective concentration of $[Fe(CN)_6]^{3-}$ reactant. So counterions, Na^+, play an important role in assisting $[Fe(CN)_6]^{3-}$ ions to get into the micelles to a significant extent which should depend on the SDS concentration. Hence reaction between $[Fe(CN)_6]^{3-}$and DMA takes place almost exclusively in the interface region of the SDS micelles (i.e. the counterion diffuse layer surrounding the micelles), where the reactants are brought together. To shed more light on the influence of ion-pair formation on the reaction rate, the effect of added $[Na_2SO_4]$ on the reaction rate constant in pure water and in SDS Micellar solution was investigated. Table 1 shows the effect of $[Na_2SO_4]$ on k_{obs} in pure water and in the presence of 0.03M SDS. The results show that the k_{obs} increased linearly in Na_2SO_4 solutions in the absence of SDS micelles. However, in the presence of SDS micelles, an initial decrease was observed in the concentration range from 0.00 - 0.02 M Na_2SO_4.

Table.(1): Effect of $[Na_2SO_4]$ on k_{obs} for the DMA oxidation by $Fe(CN)_6^{3-}$ at 25 °C. [DMA]=0.030M, $[Fe(CN)_6^{3-}]$ =0.0010M.

$[Na_2SO_4]$, M	$10^4\ k_{obs}\ s^{-1}$	
	Aqueous	SDS
0.000	16.60	24.30
0.003	16.78	22.00
0.005	17.00	20.00
0.007	17.40	18.00
0.010	18.30	16.30
0.020	19.00	13.00
0.030	19.70	17.60
0.040	20.40	23.30
0.050	21.00	29.00
0.060	21.50	34.30

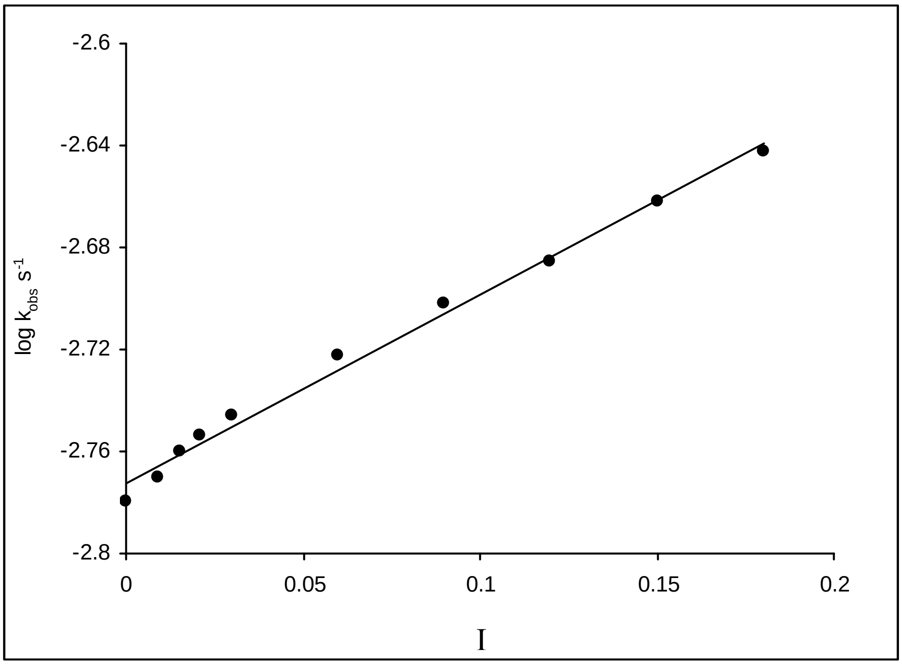
In order to explain the kinetic effect of $[Na_2SO_4]$ addition, the extended Debye - Hückel type of formulation,eq.(1)is considered

$$\log k_{obs} = \log k_o - A I^{1/2} / 1 + B I^{1/2} + C I \qquad (1)$$

Where I is the ionic strength of the solution and log k_o, A, B and C are adjustable parameters. The results corresponding to the absence of SDS micelles show a linear dependence of log k_{obs} on I . the best fit is shown in Figure4. This means that the second term on the right-hand side of eq. (1) is negligible as compared with the third term suggesting that the variations due to the electrostatic interaction are small, in agreement with previous studies [12-15]. So eq. (1) becomes in this case

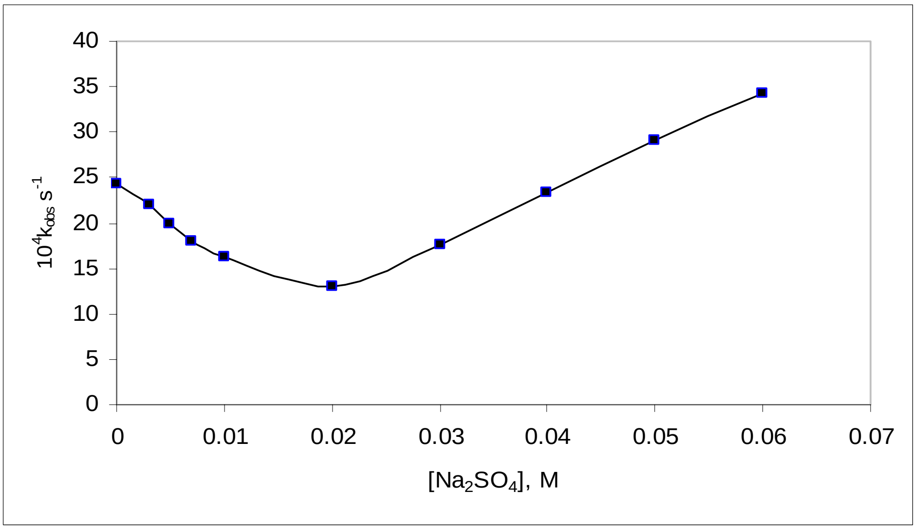
$$\log k_{obs} = \log k_o + CI \qquad (2)$$

Where the parameter C, represents a measure of the ion-pairing between the reactants and added electrolyte [13]. Therefore, association between one (or both) of the reactants and ions which come from the background electrolytes produces ion pairs which react at a different rate from the unassociated reactants.



Fig(4): A plot of log k_{obs} vs. I for oxidation of DMA by 0.001M $Fe(CN)_6^{3-}$ in absence of SDS at 25 °C.

Figure 5 shows the effect of $[Na_2SO_4]$ on k_{obs} in the presence of 0.03M SDS. The addition of electrolytes such as Na_2SO_4 to the surrounding solution at first acts primarily to modify interactions between micelles. As $[Fe(CN)_6]^{3-}$ contains a negative charge, its exclusion from micellar surface is responsible for a rate decrease at low salt concentration. However, at highly Na_2SO_4 concentrations micelles grow above their size in pure water. The progressive addition of Na^+ ions would neutralize the micellar negative charge in addition to its contribution for ion-pair formation. These effects can assist in catalyzing the reaction.



Fig(5): Effect of $[Na_2SO_4]$ on k_{obs} for oxidation of DMA by 0.001M $Fe(CN)_6^{3-}$ in presence of 0.03 M SDS at 25 °C

CONCLUSION

The effect of varying concentrations of added Na_2SO_4 reveals the existence of a specific catalytic effect by binding of Na^+ ions to$[Fe(CN)_6]^{3-}$, so that the formed $Na[Fe(CN)_6]^{2-}$ complex play an important oxidizing role. The origin of the catalytic effect of added SDS above CMC could be also attributed to the formation of $Na[Fe(CN)_6]^{2-}$ complex in the interface region of the SDS micelles. However, at low SDS concentrations below CMC , the interface region of micelles is not formed and the formation of submicellar complexes by DMA molecules is responsible for the inhibition of reaction observed at SDS concentrations below CMC.

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REFERENCES

1. D. Myers, Surfactant Science and Technology, 2nd Ed.; VCH: New York, 1992.
2. M. J. Rosen, Surfactant and Interfacial Phenomena, 2nd Ed. John Wiley and SNS : New York, 1989.

3. Sh. M. Zourab, E. M. Ezzo, H. J. Aila, J. K. Salem, *Dispersion Sci. Technol.,* **2002**, 24, 132.
4. J. K. Salem, H. J. Aila, J. React. *Kinet.Catal. Lett.,* **2003**, 80, 105.
5. J. K. Salem, R. M. Baraka, T. M. Haboush, A. El Khalady, *Tendide Surf. Det.,* **2002**, 2, 23.
6. R. M. Baraka, T. M. Haboush, J. K. Salem, *Colloid Surf.,* **2002**, 202, 181.
7. P. Cornejo, R. Jimeneze, M. Moya, F. Sanchez, *Langmuir*, **1996**, 12, 4981.
8. H. Rehage, H. Hoffmann, *J. Phys.Chem.*,**1988**, 92, 4217.
9. S. J. Bachofer, U. Simonis, *Langmuir*, **1996**, 12, 1744.
10. . J. Leal, P. Domingo, B. Garcia, S. Ibeas, *New J. Chem.*, **1994,** 18, 1233.
11. J. Alexander, H. Gray, *J. Am. Chem. Soc.* **1986**, 90, 4260.
12. D. Jain, F. Nandel**,** *J. Chem. Soc., Dalton Trans.,* **1977**, 949.
13. T. Bockmann, K. Kochi, *J. Am. Chem. Soc., III*, **1989**, 4669.
14. A. Loupy, B. Tchoubar and D. Astruc, *Chem. Rev,* **1992**, 92, 1141
15. M. Dunn, T. Kozak, *J. Chem. Phys.,* **1982**, 76, 984.