Micellar Catalytic Effect of Triton –X-100 on the Oxidation of N, N-Dimethylaniline by Hexacyanoferrate (III)

Dr. Hisham Juma'a El- Aila[*] and Dr. Jamil Kamal Salem[**]

الملخص

تم فى هذا البحث دراسة حركية ثنائى أكسدة ميثل الأنيلين بواسطة حديدى سيانيد البوتاسيوم فى وجود 0.03 مولر من محلول هيدروكسد الصوديوم عند 25 درجة مئوية فى وسط مائي أو فى وجود ميسيلات Triton – X- 100 الفعّالة سطوحياً وكذلك فى وجود الكتروليتات مختلفة و ذلك باستخدام جهاز المطياف الضوئى عند طول موجى 420 نانو متر. ووجد من النتائج أن التفاعل من الرتبة الأولى لكلٍ من ثنائى ميثل الأنيلين وحديدى سيانيد البوتاسيوم. وتبين أن ثابت معدل التفاعل (k_{obs}) ثابت عند تركيز محلول الصودا كاويه مـن 0.03 – 0.1 مولر . إن زيادة معدل التفاعل في وجود الميسيلات تم دراسته من خلال نمـوذج الطـور الكاذب لحركية التفاعل. لقد تم مناقشة اعتماد معدل التفاعل علي نوعية الكاتيون المستخدم.

Abstract

The kinetic oxidation of N,N- dimethylaniline (DMA) by hexacyano-ferrate (III) ($Fe(CN)_6^{3-}$) has been studied in aqueous and micellar solutions of Triton-X-100 (TX-100) in the presence of various electrolytes, using spectrophotometer at 420 nm. The present data showed that the reaction is first – order with respect to $[DMA]_T$ and $Fe(CN)_6^{3}$. Also k_{obs} have constant values within concentration 0.03 - 0.10 M of NaOH. The rate enhancement of the reaction in the presence of micelles has been discussed in term of pseudo-phase model of the kinetics . The dependence of the reaction rate on the nature of the salt cation has also been discussed .

Keywords : N,N- Dimethylaniline, Hexacyanoferrate (III), Triton-X-100, Oxidation .

[*] Assist. Professor of Physical Chemistry, Department of Chemistry,
Al- Aqsa University, Gaza, Palestine, E-mail :ailahesham@hotmail

[**] Assist. Prof. of Physical Chemistry, Department of Chemistry, Al –
Azhar University, Gaza, Palestine.

INTRODUCTION

The rate of bimolecular reaction between organic substrates and inorganic ions are affected by the medium properties of the micellar surface, but they also depend upon how strongly organic substrates and reactive ions bind to micellar surfaces[1]. Aqueous micelles can accelerate, or inhibit, bimolecular reaction by concentrating, or keeping apart, the two reactants at the colloid surfaces [2]. Micelles induced changes in observed rate of chemical reaction are usually attributed to lower polarity of micellar surface compared to water, and depending upon reaction studied, micellar rate constants for completely bound substrates can be greater or less than the rate constants in water [3].

Hexacyanoferrate (III) usually reacts with organic substrates by one – electron abstraction [4]. Dimethylaniline was chosen as the organic substrate since it is known to have a strong tendency to be located near the micelle surface [5].

Triton-X-100 is nonionic surfactant, in which polyoxyethylene chains stay outside the core and move relatively freely in the solvent keeping the micelles stable in solution, regarding the hydrocarbon part of the micelle as a liquid hydrocarbon [6,7].With Triton-X-100 as the bulk solvent, addition of small amount of water creates water pockets with a chemical environment which may be similar to that in reverse micellar systems [7-10]. In the present study, the kinetics of reaction has been studied in aqueous TX100 micellar solution as well as in presence of electrolytes .

EXPERIMENTAL
Materials

Triton-X-100 (TX100) was obtained from BDH Chemical Ltd. Pool England . N,N-Dimethylaniline (DMA) was purchased from Riedel– de-Haen and potassium hexacyanoferrate (III) was obtained from Fluka and were used as received. The other materials used were also reagent grade products . Deionized, distilled water was used. All DMA solutions were prepared in 40 % ethanol - water mixture.

Kinetics

Rates of oxidation of DMA by $Fe(CN)_6^{3-}$ in the presence of hydroxide ions were determined by using the same method described previously [11]. All kinetic runs were carried out in CECILL 1020 UV-VIS spectrophoto – meter. The reactions were initiated with addition of required volume of thermally equilibrated 40 % ethanol – water mixture of DMA to the reaction mixtures in temperature equilibrated cells. The cell compartments was thermostated by circulating water from constant – temperature bath through thermostated cell holder. The reaction was monitored by following changes in the absorbance of the $Fe(CN)_6^{3-}$ at 420 nm over time. The reaction was made pseudo-first-order with respect to $Fe(CN)_6^{3-}$ by the presence of excess DMA. The observed rate constants (k_{obs}, s^{-1}) are calculated from the slopes of the straight lines of $\ln A_o / A_t$ vs. time (t) according to the following equation.

$$\ln A_o / A_t = k_{obs}\ t$$

Where A_o and A_t refer to the $Fe(CN)_6^{3-}$ absorbances at time = 0 and any subsequent time, t, respectively. The uncertainty in the observed rate constant (k_{obs}, s^{-1}) was estimated to be less than 4 % .

The critical micelle concentration (cmc) of TX 100 was estimated by viscosity method . The viscosity of surfactant solutions were measured by using Abbelohde viscometer. The cmc value was obtained from the point showing discontinuity of plots of measured viscosity vs. surfactant concentration profile [12]. The obtained value is in the vicinity of 0.27 mM in agreement with the literature value of 0.26 mM in water at 25 °C [13].

RESULTS AND DISCUSSION

The kinetic rate of oxidation of DMA by $Fe(CN)_6^{3-}$ was studied in the absence and presence of 0.003 M TX 100 in mixed aqueous ethanol solvent containing 40 % (v/v) ethanol at 2 5 °C . The observed rate constants were found to be independent of [OH⁻] with range (0.03- 0.1 M) in presence and absence of 0.003 M TX 100. The observed results are summarized in Table.1 .Therefore, working with [OH⁻] ≥ 0.06 M, we have all the analytical DMA concentration in it's neutral form and avoided the use of buffers by following all the kinetic runs in solutions containing 0.06 M NaOH . Similar observations were also obtained for the reactions of several secondary amines with alkyl nitrites in aqueous basic solution in the presence of micelles [2].

The kinetic of oxidation reaction of DMA by $Fe(CN)_6^{3-}$ in basic media proceeds through a subsequent electron transfer reactions in which $Fe(CN)_6^{3-}$ ion is reduced to $Fe(CN)_6^{4-}$ and DMA is oxidize to formaldehyde and methylphenylamine [14] . The mechanism summarized as

Table 1

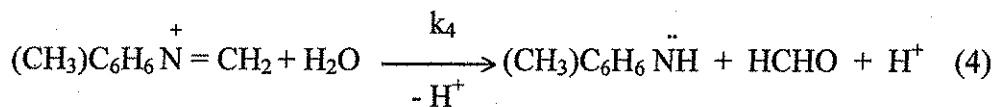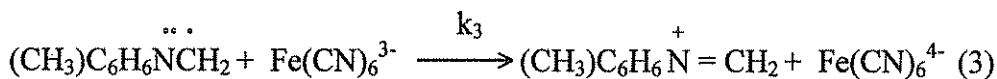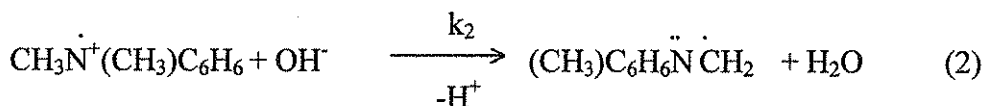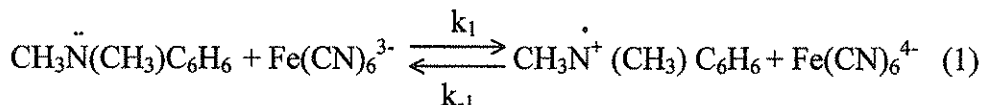Effect of [NaOH] on observed rate constants (k_{obs}) for DMA / $Fe(CN)_6^{3-}$ reaction in the presence of 0.003 M TX 100 in 40 % ethanol - water mixture at 25 ^oC .

[NaOH] (M)	k_{obs} x 10^4(s^{-1})
0.01	24.5 (15.4)
0.02	25.2 (16.0)
0.03	26.2 (16.2)
0.05	26.5 (16.3)
0.06	26.6 (16.6)
0.08	26.7 (16.6)
0.10	27.0 (16.7)

Values in parentheses pertain to absence of TX 100 micelles .
[DMA] = 0.03 M, [$Fe(CN)_6^{3-}$] = 0.001 M

$$CH_3\overset{..}{N}(CH_3)C_6H_6 + Fe(CN)_6^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3\overset{.}{N}{}^+ (CH_3) \, C_6H_6 + Fe(CN)_6^{4-} \quad (1)$$

$$CH_3\overset{.}{N}{}^+(CH_3)C_6H_6 + OH^- \xrightarrow[-H^+]{k_2} (CH_3)C_6H_6\overset{..}{N}\overset{.}{C}H_2 + H_2O \quad (2)$$

$$(CH_3)C_6H_6\overset{..}{N}\overset{.}{C}H_2 + Fe(CN)_6^{3-} \xrightarrow{k_3} (CH_3)C_6H_6\overset{+}{N} = CH_2 + Fe(CN)_6^{4-} \quad (3)$$

$$(CH_3)C_6H_6\overset{+}{N} = CH_2 + H_2O \xrightarrow[-H^+]{k_4} (CH_3)C_6H_6\overset{..}{N}H + HCHO + H^+ \quad (4)$$

The second step is the slow step, so the formation of $(CH_3)C_6H_6N\,CH_2$ is the rate determining step. The following rate equation was established for the oxidation of DMA by $Fe(CN)_6^{3-}$ in basic medium[14].

$$-d\ [Fe(CN)_6^{3-}]\ /\ dt\ =\ k_{obs}\ [Fe(CN)_6^{3-}] \tag{5}$$

with

$$k_{obs} = k_1[DMA]$$

The reaction was carried out with large excess of DMA over the $Fe(CN)_6^{3-}$. In all cases good pseudo-first-order plots were obtained .Table 2 shows the dependence of k_{obs} on DMA and $Fe(CN)_6^{3-}$ concentration. The approximate similarity of k_{obs} values at different $Fe(CN)_6^{3-}$ concentrations from 0.50 to 1.5 Mm, indicating that the reaction is first order with respect to $Fe(CN)_6^{3-}$. The dependence of the observed rate constant on DMA concentration is also shown graphically in figure1. In all cases the observed data shows a linear dependency with DMA concentration in aqueous and in presence of 0.003 M TX 100, indicating a first order behavior in relation to DMA in aqueous and micellar media .This suggests that the oxidation of DMA by $Fe(CN)_6^{3-}$ takes place through the same mechanism in the absence and presence of micelles. Also, it can be observed from Table 2 that the ratios, R [R = k_{obs}(in TX 100) / k_{obs} (in H_2O)] are increased with increasing

Table 2

Effects of $[Fe(CN)_6^{3-}]$ and $[DMA]$ on k_{obs} for DMA / $Fe(CN)_6^{3-}$ reaction in the presence of 0.003 M TX 100 in 40 % ethanol - water mixture at 25 °C.

$[Fe(CN)_6^{3-}]$ x 10^3 (M)	[DMA] (M)	k_{obs} x 10^4 (s^{-1})	R
0.5	0.03	26.6(16.6)	
0.7		26.3(16.3)	
0.9		26.7(16.4)	
1.0		26.6(16.6)	
1.2		27.3(16.7)	
1.5		27.5(16.9)	
1.0	0.01	11.0(7.27)	1.51
	0.02	19.6(12.3)	1.59
	0.03	26.6(16.6)	1.63
	0.04	37.8(23.0)	1.64
	0.05	45.5(27.4)	1.66
	0.06	54.4(31.6)	1.72

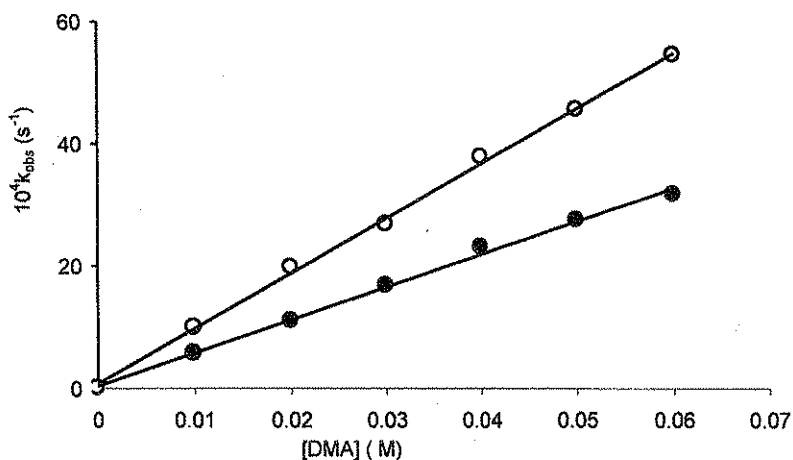Values in parentheses pertain to absence of TX 100 micelles

Fig .1. Effect of [DMA] on k_{obs} for DMA / Fe(CN)$_6^{3-}$ reaction in water (●) and in the presence of 003 M TX 100in 40 % ethanol - water mixture (o) at 25 °C. [Fe(CN)$_6^{3-}$] = 0.001 M .

the [DMA]$_T$ at a fixed [TX 100] . It seems that in the concentration range from 0.01 to 0.06 M of DMA, the micellar surface is still unsaturated with DMA molecules and hence as the [DMA]$_T$ is increased, the DMA concentration becomes more significant in the micellar region (increasing [DMA]$_m$) where micellized Fe(CN)$_6^{3-}$ ions existed.

Figure 2 shows the dependence of the observed rate constant (k_{obs}, s^{-1}) for the oxidation of DMA by Fe(CN)$_6^{3-}$ on surfactant concentration. It is seen from figure 2 that k_{obs} increases with increasing surfactant concentration up to 0.003 M and a plateau is reached at 0.003 M. To rationalize the kinetic data, the following equation based on the pseudo-phase model is considered :

$$k_{obs} = \frac{K'_w + k'_m K_s K_A [D_n][DMA]_T}{(1 + K_s [D_n]) ((1 + K_A [D_n])} \tag{6}$$

Here, subscript w and m denote the aqueous and micellar pseudophases , respectively, quantities in square brackets are concentrations in term of total solution volume , K_s is the equilibrium association constant of Fe(CN)$_6^{3-}$ molecules to the DDAO micelles, K_A is the equilibrium association constant

of DMA molecules to the DDAO micelles, $[D_n]$ is the micellized surfactant whose concentration is given by $[D_n] = [$ surfactant$]_T -$ cmc, k'_w and k'_m are the second order rate constants in the aqueous and micellar pseudo-phase, respectively. k'_w ($M^{-1}s^{-1}$) is written with concentration as molarity and k'_m (s^{-1}) is written with concentration as a mole ratio ($[DMA]_m /\ [D_n]$) . To
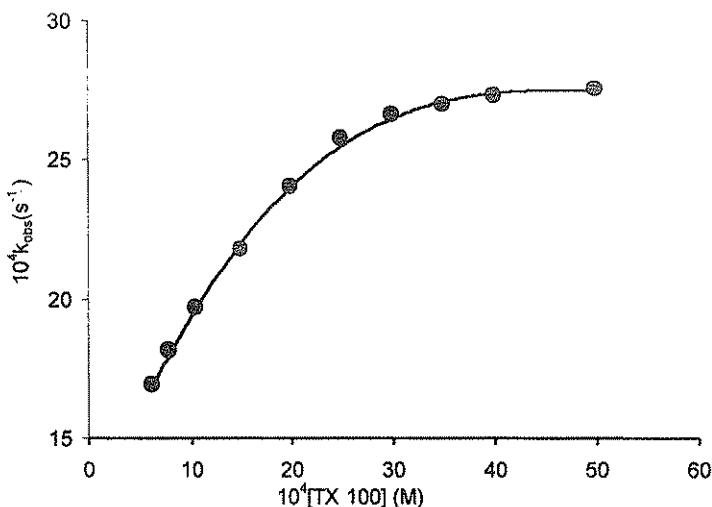

Fig .2. Effect of [TX 100] on k_{obs} for DMA / Fe(CN)$_6^{3-}$ reaction at 25 °C. [DMA] = 0.03 M and [Fe(CN)$_6^{3-}$] = 0.001 M

estimate values of k'_m and K_s by fitting eq.6 to experimental values of k'_w, K_A, D_n, cmc, k_{obs} and $[DMA]_T$ .The equilibrium association constant, K_A was determined independently by following the spectrophotometric method [15]. The value of K_A was found to be 630 M^{-1}, using experimental k'_w equal 55.3 x $10^{-3}\ M^{-1}s^{-1}$ and critical micelle concentration (cmc) = 0.27 mM, the kinetic data were fitted by using eq 6. The obtained values by this fitting k'_m = 0.009 s^{-1} and K_s = 11 M^{-1}. The value of k'_m which has the unit of s^{-1} cannot be utilized for comparison purposes. However , the comparison can be made by considering the volume element of reaction in the micellar pseudo-phase ; that is volume of the reaction region . Thus, the second order in the micellar pseudo-phase can be written with concentration as local molarity, k_m ($M^{-1}s^{-1}$), as

$$k_m = k'_m V_m \qquad (7)$$

Where, V_m is the molar volume of the reaction region at the micellar surface. It's value is uncertain and estimates range from 0.14 to 0.37 M^{-1} for aqueous ionic micelle [16] .

The obtained value of k_m is in the range $1.3 \times 10^{-3} – 3.3 \times 10^{-3}$ $M^{-1}s^{-1}$. This result supports that the bimolecular reaction takes place predominantly nearly at the interface region of the micelles. But the rate enhancement could be explained by considering that the increased concentration of reactants at the micellar surface leads to an increase in the observed rate, where the presence of water which attached to hydroxyl group of surfactant make shielding and minimizing the possibility of repulsion between negatively charged $Fe(CN)_6^{3-}$ ion and pair of electron which freely on hydroxyl group of TX 100 [17]. Incorporation of the reactants into a limited volume decreases the energy of activation and the entropy loss that is associated with bringing both reactants together in the transition state, leading to an increase in the observed rate constant in the presence of micelles.

Activation parameters are believed to provide useful information regarding the environment in which chemical reaction take place. In order to learn more about the micro– environments of submicroscopic assemblies such as aqueous micelles, the temperature effect upon the observed rate constants in water and in the presence of 0.003 M TX 100 were also studied within temperature range 20 - 40 °C. Activation parameters such as ΔH^* and
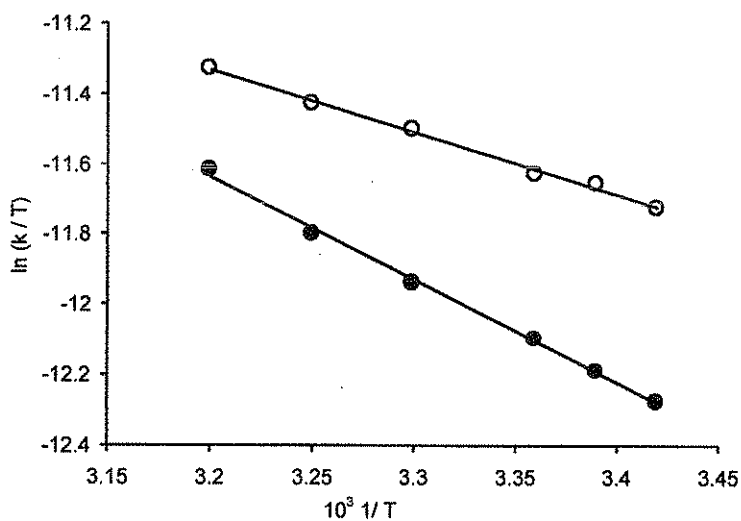

Fig .3. ln (k_{obs} / T) vs. 1/ T of Eyring equation for DMA / Fe(CN)$_6^{3-}$ reaction in water (●) and in0.003 M TX 100 in 40 % ethanol - water mixture (o).

ΔS^* were obtained from Eyring equation [11]. Plots of ln (k_{obs} / T) vs. 1 / T of Eyring equation are shown in figure 3. The obtained values of ΔH^* (kJ mol^{-1}) and ΔS^* (J.K^{-1}.mol^{-1}) were found respectively, to be14, - 197 (water) and 14.8, -243 (TX100). These results indicated that the presence of TX 100 micelles lowers the ΔH^* with a substantial negative ΔS^*. This lowering can not be attributed to dramatic change in reaction pathway . The marked drop in activation parameters that occurs on the addition of surfactant signify that the micelles change the behavior of the system and to be more friendly environments for the reactants . Thus, it will be lead to the adsorption of both the reactants on the micellar surface and stabilize the transition state .

Kinetic salts results show that the observed rate constants generally increase in the presence of added salts (figure 4). The effect depends on the nature of salt cation, and its concentration. For a given salt concentration it
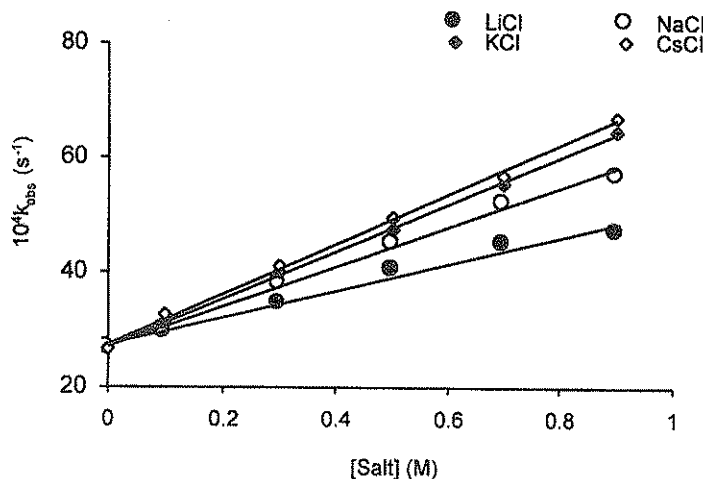

Fig. 4. Effect of [salt] on k_{obs} for DMA / Fe(CN)$_6^{3-}$ reaction in the presence of 0.003 M TX100 in 40 % ethanol - water mixture at 25 °C . [DMA] =0.03 M and [Fe(CN)$_6^{3-}$] = 0.001 M .

was found that k_{obs} (CsCl) > k_{obs} (KCl) > k_{obs} (NaCl) > k_{obs} (LiCl).This indicates that k_{obs} depends on the nature of the cation which comes from the salt and agrees with the same order of increasing cation size. This cation effect can enhance movement of electron from DMA to Fe(CN)$_6^{3-}$ and behave as a bridge for electron transfer [18]. Same observations have been

obtained for oxidation of tertiary amines and amino acids by $Fe(CN)_6^{3-}$ [19 – 21].

So, an increase in k_{obs} is expected to occur through the hydrophilic (charge – dipole) interaction between the dipole group ($O \rightarrow H$) in TX 100 and $Fe(CN)_6^{3-}$ ion. With increasing the polarization power of the salt cation following the trend $Li^+ < Na^+ < K^+ < Cs^+$, the electronneutrality of OH group is decreased which can enhance the dipole moment of the ($O \rightarrow H$) group on the micellar surface. This increase in the dipole ($O \rightarrow H$) will favor the approach of $Fe(CN)_6^{3-}$ to the DMA residing in the micelle surface. Therefore, k_{obs} should be increased in the same order. On this basis, the expected trend would be k_{obs} (LiCl) < k_{obs} (NaCl) < k_{obs} (KCl) < k_{obs} (CsCl), as was found .

Also, in order to explain kinetic salts effects corresponding to different types of salts, formulations of Deby – Huckel equation have been used [22] . As, that in eq. 8 .

$$\log \ k_{obs} = \log k_o - \ A^\backslash I^{1/2} \quad 1 + BI^{1/2} \quad + C\,I \qquad (8)$$

Where, I is the ionic strength of medium, $\log k_o$, $A^\backslash$, B and C are adjustable parameters. In case of electrolytes, a value of unity is taken for B parameter which corresponding to an average distance of closer approach of $4A^o$ [23]. In respect to increase of k_{obs} with increasing concentration of different types of electrolytes, this correspondence to the constancy of coulombic term in eq. 8 . These data can be fitted to eq. 9

$$\log \ k_{obs} = \ \log k_o^\backslash + C\,I \qquad (9)$$

Where, $\log k_o^\backslash = \log k_o - \ A^\backslash I^{1/2} \ / \ 1 + BI^{1/2}$, values of $\log k_o^\backslash$ and C can be obtained from the logarithm of rate constants (k_{obs}) against I . So the value of C is proportional to hydration free energy of electrolytes and their interaction with reactants [22]. Values of $\log k_o^\backslash$ and C are given in Table 3. The high value of C obtained in micelle could be due to the hydrophobic interaction between $Fe(CN)_6^{3-}$ and monomer of surfactant [22], which increases in presence of electrolytes in order CsCl > KCl > NaCl> LiCl.

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Also, in order to explain kinetic salts effects corresponding to different types of salts, formulations of Deby – Huckel equation have been used [22] . As, that in eq. 8 .

$$\log k_{obs} = \log k_o - \quad A^\backprime I^{1/2} \quad 1 + BI^{1/2} \quad + C I \qquad (8)$$

Where, I is the ionic strength of medium, $\log k_o$, $A^\backprime$, B and C are adjustable parameters. In case of electrolytes, a value of unity is taken for B parameter which corresponding to an average distance of closer approach of $4A^°$ [23]. In respect to increase of k_{obs} with increasing concentration of different types of electrolytes, this correspondence to the constancy of coulombic term in eq. 8 . These data can be fitted to eq. 9

$$\log k_{obs} = \log k_o^\backprime + C I \qquad (9)$$

Where, $\log k_o^\backprime = \log k_o - A^\backprime I^{1/2} / 1 + BI^{1/2}$, values of $\log k_o^\backprime$ and C can be obtained from the logarithm of rate constants (k_{obs}) against I . So the value of C is proportional to hydration free energy of electrolytes and their interaction with reactants [22]. Values of $\log k_o^\backprime$ and C are given in Table 3. The high value of C obtained in micelle could be due to the hydrophobic interaction between $Fe(CN)_6^{3-}$ and monomer of surfactant [22], which increases in presence of electrolytes in order CsCl > KCl > NaCl> LiCl.

Table 3
Adjustable parameters values obtained from the fit of experimental data using eq. 9 for different types of salts.

Salt	$\log k_0$	C
LiCl	-2.56	0.28
NaCl	-2.56	0.37
KCl	-2.55	0.41
CsCl	-2.56	0.53

ACKNOWLEDGMENT

REFERENCES

1) Bonadiman Marin, M. A. ; Nome, F. ; Zanette, D. and Zucco, C. : J. Phys. Chem , 99, 10879 – 10885, (1995).

2) Fernandez, A. ; Iglesias, E. ; Luis, G. R. and Leis, J. R. : Langmuir, 11, 1917 - 1922 (1995)300.

3) Bunton, C. A. : "In Kinetic and Catalysis in Microheterogeneous Systems" vol.38 p.13, M. Gratzel , K. Kalyanasudaram Ed ; Marcel Dekker, Inc. NewYork (1991).

4) Stewart, R. : " Oxidation Mechanism " W. A. Benjamin, Inc., New York, (1964).

5) Hlrose, C. and Sepulveda, L. :.J. Phys. Chem., 85, 3689 -3695 (1981).

6) Stainby, G.and Alexander, A. : Trans Faraday Soc., 46,587- 594 (1950).

7) Yuan, H. Z. ; Cheng , G. Z. ; Zhao, S. ; Miao, X. J. ; Yu, J.Y. ; Shen, L. F and Du, Y. R. : Langmuir, 16, 3030- 3035 (2000).

8) Fendler, J. H. and Liu, L.J. : J. Am. Chem.Soc., 97 , 999 – 1004(1975).

9) Fendler, J. H. ; Nome, F. and Van Woert, H.C. : J. Am. Chem.Soc., 96 , 6745 - 6750(1974).

10) Fendler, J. H. : Acc. Chem. Res., 9 , 153- 159 (1976).

11) Salem, J.K.J. ;. Baraka, R. M ; Haboush, T. M. and. EL khaldy, A. A : Tenside Surf. Det., 2, 23 – 28 (2002).

12) Rodrigues, M. P. ; Prieto, G. ; Rega, C. ; Verla, L. M. ; Sarmiento, F. Mosquera, V, Langmuir 14, 4422- 4456 (1998)

13) Andersson, B. and Olofsson, G. J : J. Chem. Soc., Faraday Trans, 184 , 4087 - 4091(1988).

14) Audeh, C. A. and Lindsay Smith, J. R. : J. Chem. Soc.B , 1280-1285 (1970).

15) Bunton, C.A. ; Rivera, F. and Sepulveda, L. : J. Org. Chem., 43, 1166 – 1170 (1978)

16) Bunton, C. A. : J. Mol. Liq., 72, 231- 236 (1997)

17)-Ige, J. ; Lambi, J. N. and Soriyan, O.O. : J. Chem. Soc., Faraday trans,1, 84(1),1(1988).

18) Swinehart, J. H. : J. Inorg. Nuclear Chem., 29 (1967).

19) Lambert, D. G. and Jones, M.M. : J. Am. Chem. Soc., 88, 4615 – 4619 (1966).

20) Rosenblatt, D. H. ; Hull, L. A. ; Deluca, D. C. ; David, G. T. ; Weglein, R. C. and Williams, H. K. R: J. Am. Chem. Soc., 89, 1158 - 1163 (1967).

21) Hull. L. A. ; Davis, G. T. and Rosenblatt, D. H. : J. Am. Chem. Soc., 91, 6247 - 6251(1969).

22) Sanchez, F. ; Moya, M. L. ; Rogriguez, A. ; Jimenez. R. ; Gomez-Herrera, C. ; Yanes, C. ; Lopez – Corrj, P: Langmuir 13, 3084-3089 (1997).

23) Fernandez, B. E. ; Bejarano, M. ; Craciani, M. M. ;