Effect of Sodium Dodecyl Sulfate Micelles on Complex Formation of -2Nitroso-1-Naphthol with Iron (II) Ion in Aqueous Urea Solutions

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Abstract:

The effect of sodium dodecyl sulfate (SDS) micelles on the observed rate constant \(k_{\text{obs}}\) for complex formation of 2-nitroso-1-naphthol (NAPH) with iron (II) ion (Fe\(^{2+}\)) in the presence of 0.02 M NaOH at 25°C was studied at different urea concentrations. Typical saturation behavior was observed at \([\text{NAPH}] \geq 0.001\) M and \([\text{Fe}^{2+}] \geq 0.015\) M, which allows the electron transfer rate constant \(k_{\text{et}}\) between NAPH and Fe\(^{2+}\) in the micellar pseudophase to be evaluated. The increase in urea concentration from 0.0 to 4.0 M has three effects. It increases \(k_{\text{et}}\) from 0.072 to 0.239 s\(^{-1}\), decreases the critical micelle concentration (cmc) from 6.5 to 3.5 mM and increases the NAPH binding constant to SDS micelles (K) from 20 to 170 M\(^{-1}\). At constant SDS concentration, the complex formation constant (KIP) increases with increasing urea concentration.

Key words: Sodium dodecyl sulfate, Complex, 2-Nitroso-1-naphthol, Iron (II) ion, Urea

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2-Nitroso-1-naphthol is currently used as a complexing agent in the analysis of cobalt and iron (Foretic and Burger, 2002; Foretic and Burger, 2000; Sugawara et al., 1982). It is also a sensitive and specific histochemical reagent for fluorimetric determinations of tyrosine residues in proteins and peptides (Foretic and Burger, 2002; Sundler et al., 1976). Along with other phenols and naphthols, it belongs to biologically important compounds, especially, because of its cytotoxic action (Portela et al., 1996). It makes part of noxious substances in the industry of polymers, cosmetic and pharmaceutical preparations, dyes and pesticides (Korenman et al., 1994); hence, the methods of determining 2 nitroso-1-naphthol may be of practical importance.

One of the most effective means for modulating the reactivity of species in solution is altering the nature of the solute-solvent interactions (Frenandez et al., 1995; Salem et al., 2002). Non electrolytes such as urea have been found to be efficient modifiers of the properties of aqueous micellar solution (El–Aila, 2005; Baraka et al., 2002; Enea and Jolicoeur, 1982).

The examination of the equilibrium and kinetics of metal complex formation reactions in relevance to solvent extraction processes is an active area of research in the laboratory (Cai et al., 1995). Electron transfer at interfaces is of fundamental importance in understanding charge transfer occurring in biological systems (Tanford, 1973). To acquire better insight in the factors that control this phenomenon, micelles are often chosen as systems, which mimic the reaction environment of biological interfaces (Bunton, et al., 1978). Reaction trends in aqueous and micellar aqueous solutions can be altered by varying the reaction temperature or modifying the properties of the aqueous solvent (Sanchez et al., 1997).

In this work, we carried out a systematic kinetic study of complex formation between iron(II) ion (Fe²⁺) and 2-nitroso-1-naphthol (NAPH) in basic medium in the presence of anionic surfactant (SDS) at different concentrations of urea.

**Experimental Materials**

Sodium dodecyl sulfate (SDS) purchased from Across Organics (Fairlawn, NJ, USA), 2-nitroso-1-naphthol obtained from Riedel-de-Haen (Seelze,
Germany), and FeSO4.6H2O purchased from Fluka Chemical Co. (Buchs, Switzerland) were used as received. The other materials used were also reagent grade products. All solutions were prepared using deionized water.

To prepare sample solution (El–Aila, 2005), a proper volume of FeSO4.6H2O (from stock solution) was prepared in one glass tube (tube A). A reagent mixture of suitable volume of NAPH + urea + NaOH in a second tube (tube B) was prepared. The same process was carried out in micellar solutions, except that tube B contained the proper concentration of SDS + NAPH + urea + NaOH. A suitable volume of deionized distilled water was added to tube B in either case to keep the total volume of reaction mixture in all experiments fixed (10 mL). Before mixing, the contents of both tubes A and B were thermostated separately for at least 20 min at 25°C. The contents of tube B was added to the contents of tube A. Immediately the time of reaction was recorded by using stop watch (within accuracy of 1 / 100 s).

All runs employed a large excess of Fe2+ (0.015 M) over NAPH (0.001 M) concentration to obtain pseudo first-order rate conditions. The same procedure was employed to study the effects of Fe2+, NAPH, NaOH, SDS, and urea.

**Kinetics**

The rate of formation of complex of Fe2+ with NAPH in basic aqueous or micellar solutions in the presence of different urea concentrations was studied spectrophotometrically by monitoring the decrease in the absorbance of NAPH as a function of time at 430 nm (Foretic and Burger, 2002, Foretic and Burger, 2000) and 25.0 ± 0.1°C using CECILL 1020 UV–VIS spectrophotometer. All measurements were carried out in the presence of 0.02 M NaOH (pH ~12). The ionic strength was kept constant by adding the required amount of NaNO3 salt. The uncertainty in the observed rate constant (kobs, s⁻¹) was estimated to be less than 4%.

The critical micellar concentration (cmc) of SDS in the presence of the reactants was estimated by surface tension method by carrying out series of measurements at increasing SDS concentration at 25°C with drop method. The instrument employed is called a stalagomete (Mee and Speakman 1968) with relative accuracy of about 3%. The cmc value was obtained from the point showing discontinuity in the plots of the measured surface tension versus surfactant concentration profile. (El–Aila, 2005; Salem, 2002; Frenandez et al., 1995; Korenman et al., 1994).

**Results and Discussion**

The rate of complex formation of Fe2+ by NAPH was studied in the absence and the presence of 0.15 M SDS in different concentrations of urea at 25°C and at different concentrations of NaOH. The observed rate constant values (kobs) were found to be independent on [NaOH] within the range 0.015 to 0.05 M in the presence and absence of 0.15 M SDS. Therefore, the reaction of NAPH with Fe2+ to form the
complex, Tris(2-nitroso-1-naphtholate) ferrate(II) (Proskurnin et al., 2003) can be written as follow:

\[
K_{IP} \quad \text{NAPH} + \text{Fe}^{2+} \leftrightarrow (\text{NAPH})_3/\text{Fe}^{2+} \\
(\text{NAPH})_3/\text{Fe}^{2+} \rightarrow \text{complex}
\]

The observed rate constant \(k_{obs} \) is a composite parameter. It contains contributions from the equilibrium complex formation step and the electron transfer step (Salem et al. 2002; Baraka et al., 2002, (a) Rodriguez, et al., 1996) Under these condition \([\text{Fe}^{2+}] \gg [\text{NAPH}]\) the observed data were found to fit equation (1)

\[
k_{et} K_{IP} [\text{Fe}^{2+}] \quad k_{obs} = \frac{k_{et} K_{IP} [\text{Fe}^{2+}]}{1 + K_{IP}[\text{Fe}^{2+}]} (1)
\]

where \(K_{IP}\) is the complex formation constant and \(k_{et}\) is the electron transfer rate constants. The observed rate constants at different \(\text{Fe}^{2+}\) concentrations in the presence of 0.15 M SDS at different concentrations of urea are shown graphically in Figure 1 and Table 1. The \(K_{IP}\) and \(k_{et}\) values can be obtained from linear plots of 1/ \(k_{obs}\) against 1/ \([\text{Fe}^{2+}]\) as expected from equation (1), results were shown in Figure 2. The values obtained for \(K_{IP}\) are summarized in Table 1. A large \(K_{IP}\) value of is consistent with greater destabilization of the initial state of the reactants than of ion / ligand complex \((\text{NAPH})_3/\text{Fe}^{2+}\) in SDS micelle as increasing of urea concentration(Cai et al., 1995 ; (b)Rodrigues et al., 1996). The increase in solvated urea molecules in the micellar surface, which may in
turn create regions within the micellar interfacial region capable of formation of complex, indicates that the transition state is more solvated in the urea solution of anionic micelles.

On the basis of equation (1) and in the presence of high \(\text{Fe}^{2+}\) concentration, kinetic saturation behavior might be expected, i.e. where the observed rate constant is independent on the complex formation constant \(K_{IP}\) with \(K_{IP}[\text{Fe}^{2+}] \gg 1\). Hence equation (1) reduces to \(k_{obs} \approx k_{et}\). Saturation was shown in different concentrations of urea in the presence of 0.15 M SDS. In all cases, kinetic saturation was reached at \([\text{Fe}^{2+}] \geq 0.01\) M (Figure 1).

The complex formation of \(\text{Fe}^{2+}\) with NAPH in the presence of SDS micelles was increased by increasing the concentration of surfactant. Data were depicted in Table 2 and Figure 3. This increment in \(k_{obs}\) mainly attributed to the attraction between negative charge of SDS micelle and positive charge of \(\text{Fe}^{2+}\). This behavior allows \(\text{Fe}^{2+}\) ion coming near little bite from NAPH which adsorbed at the surface of surfactant through a physical bonds. This process shows that surfactant forms a bridge to maximize interaction between NAPH and \(\text{Fe}^{2+}\). A constant value for \(k_{obs}\) would be expected according to pseudophase model

\[
k_{obs} = \frac{k_{et}^w + k_{et}^m K_{[SDS]}}{1 + K_{[SDS]}} (2)
\]

Where \(k_{et}^w\) and \(k_{et}^m\) are the electron transfer rate constants between NAPH and \(\text{Fe}^{2+}\) in the bulk water phase and micellar pseudophase, respectively, K
is an equilibrium constant for binding NAPH to the surfactant micelles and [SDS] is the micellized surfactant concentration \([\text{[SDS]}] - \text{cmc}\). To evaluate \(k^m_{et}\) and \(K\) from equation (2), the exact value of the cmc under kinetic conditions is needed. Critical micelle concentrations in the absence and presence of reactants at 25°C in SDS systems were determined from intersection points of their surface tension vs. surfactant concentration profiles (Proskurnin et al., 2003; Rodrigues et al., 1996) and typical plots are shown in Figure 4. The cmc values were obtained under different conditions, i.e. in water as solvent, water + Fe\(^{2+}\) and water + NAPH. The respective cmc values are 7, 6.5, 4.5 mM. These results reveal that cmc of SDS is quite sensitive to the nature of reactants and reaction conditions, which could not be detected by surface tension measurements owing the variation to the concentration of reaction species during the course of reaction. An alternative graphical kinetic method (Baraka et al., 2002; Sanchez et al., 1997) for determining the cmc at different urea concentrations was employed. In this method, the cmc value was obtained from the point of intersection of two linear plots of \(k_{\text{obs}}\) vs. [SDS] drawn through the observed points below the cmc and just above cmc as shown in Figure 5. These cmc values, as well as the calculated values for \(k^m_{et}\) and \(K\) at different urea concentrations, are summarized in Table 1. Before analyzing the effect of urea addition on \(k^m_{et}\) and \(K\), it is interesting to note that penetration of the benzene moiety of NAPH into micellar palisade layer takes place with the hydrophilic groups [-OH, -NO] remaining in the outer region of the micelle. (Baraka et al., 2002; Sanchez et al., 1997; Rodrigues et al 1998). Urea also penetrates near the head groups by replacing some water molecules which may behave as a medium for Fe\(^{2+}\) and NAPH to form complex (Baraka et al., 2002; Zourab et al 2003).

Increasing the urea concentration from 0.0 to 4.0 M increased \(k^m_{et}\) from 0.072 to 0.239 s\(^{-1}\) and \(K\) from 20 to 170 M\(^{-1}\) (Table 1). The most plausible explanation for these observations may be given as follows: The increase in \(k^m_{et}\) values can be interpreted as consequence of adsorption of Fe\(^{2+}\) at micellar interfacial region. In addition, the changes in \(k^m_{et}\) values are the consequences of changes in the characteristics of the reaction media, the micellar and the aqueous regions, when urea is added. These changes will affect the reorganization energy and reaction free energy of the electron transfer (Kresheck, 1975). The addition of urea creates regions and facilitates interaction of Fe\(^{2+}\) with NAPH at the palisade part of surfactant, which results in an increase in \(k^m_{et}\) with slight increase in NAPH binding constant, \(K\), values. Another factor is the change in the microenvironment properties; in fact, an increase in [urea] from 0.0 to 4.0 M decreases cmc value from 6.5 to 3.5 mM. This means that the micellar concentration increases with increasing [urea]; this would lead to an increase in the effective charge of head groups and the electrical potential at the SDS, micelle surface would become more negative (Bunton, et al 1999).
The presence of Fe$^{2+}$ did not modify the cmc value obtained in any reactant. In the presence of NAPH, it seems that hydrophobic bonding with the exposed hydrocarbon on the micellar surface overcomes the electrostatic contribution of the ion head group interaction, because NAPH will be solubilized in the micellar palisade layer with the hydrophilic part of NAPH exposed close to the head group region. This is responsible for the decrease in the cmc of SDS. Addition of urea clearly increases the hydrophobic interaction by decreasing the solubility of the surfactant monomers and therefore, increases the micelles formation and then the cmc should decrease, as was indeed observed, with increasing urea concentration; this is shown in Figure 6.

In conclusion, complex formation between Fe$^{2+}$ ion and NAPH legends is strongly increased by the negatively charged micelles. The rate of activation was mainly due to a concentration effect in the vicinity of the micellar surface. Urea served to promote complex formation at the palisade region of surfactant.

References


Table 1
KIP values and kinetic parameters of Eq.(2) to simulate kobs – [SDS] Profiles at different urea concentration

<table>
<thead>
<tr>
<th>[Urea] (M)</th>
<th>KIP (M⁻¹)</th>
<th>103ketw (s⁻¹)a</th>
<th>ketm (s⁻¹)</th>
<th>K (M⁻¹)</th>
<th>103cmc (M)</th>
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<tr>
<td>0.0</td>
<td>430</td>
<td>7.17</td>
<td>0.072</td>
<td>20</td>
<td>6.5</td>
</tr>
<tr>
<td>0.5</td>
<td>446</td>
<td>9.60</td>
<td>0.082</td>
<td>40</td>
<td>6.0</td>
</tr>
<tr>
<td>1.0</td>
<td>526</td>
<td>13.0</td>
<td>0.103</td>
<td>65</td>
<td>5.5</td>
</tr>
<tr>
<td>2.0</td>
<td>606</td>
<td>16.0</td>
<td>0.141</td>
<td>90</td>
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</tr>
<tr>
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<td>26.0</td>
<td>0.191</td>
<td>120</td>
<td>4.5</td>
</tr>
<tr>
<td>4.0</td>
<td>952</td>
<td>33.0</td>
<td>0.239</td>
<td>170</td>
<td>3.5</td>
</tr>
</tbody>
</table>

a Electron transfer constant, K_{etw}, obtained in the absence of SDS micelles.

Table 2
Effect of [SDS] on kobs for NAPH / Fe²⁺ complex formation at different concentration of urea and 25°C. [NAPH] = 0.001 M, [Fe²⁺] = 0.015 M and [NaOH] = 0.02 M

<table>
<thead>
<tr>
<th>[SDS]B (M)</th>
<th>Urea = 0.0 M</th>
<th>0.5 M</th>
<th>1.0 M</th>
<th>2.0 M</th>
<th>3.0 M</th>
<th>4.0 M</th>
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<td>0.01</td>
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<td>0.0150</td>
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</tr>
<tr>
<td>0.02</td>
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<td>0.0090</td>
<td>0.0120</td>
<td>0.0150</td>
<td>0.0170</td>
<td>0.0200</td>
</tr>
<tr>
<td>0.03</td>
<td>0.0015</td>
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<td>0.0140</td>
<td>0.0160</td>
<td>0.0190</td>
<td>0.0220</td>
</tr>
<tr>
<td>0.04</td>
<td>0.0020</td>
<td>0.0120</td>
<td>0.0160</td>
<td>0.0170</td>
<td>0.0220</td>
<td>0.0240</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0025</td>
<td>0.0140</td>
<td>0.0180</td>
<td>0.0190</td>
<td>0.0240</td>
<td>0.0260</td>
</tr>
<tr>
<td>0.06</td>
<td>0.0030</td>
<td>0.0150</td>
<td>0.0200</td>
<td>0.0210</td>
<td>0.0260</td>
<td>0.0280</td>
</tr>
<tr>
<td>0.08</td>
<td>0.0035</td>
<td>0.0160</td>
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<td>0.0220</td>
<td>0.0280</td>
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</tr>
<tr>
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</tr>
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<tr>
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<td>0.0270</td>
<td>0.0330</td>
<td>0.0370</td>
</tr>
<tr>
<td>0.20</td>
<td>0.0070</td>
<td>0.0190</td>
<td>0.0240</td>
<td>0.0280</td>
<td>0.0340</td>
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<tr>
<td>0.30</td>
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<td>0.0200</td>
<td>0.0260</td>
<td>0.0300</td>
<td>0.0360</td>
<td>0.0400</td>
</tr>
<tr>
<td>0.40</td>
<td>0.0080</td>
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<td>0.0310</td>
<td>0.0370</td>
<td>0.0410</td>
</tr>
</tbody>
</table>
Figure 1. Effect of [Fe²⁺] on $k_{obs}$ for NAPH/Fe²⁺ complex formation in 0.15 M SDS aqueous solutions at different concentration of urea and 25°C. [NAPH] = 0.001 M, [NaOH] = 0.02 M.

Figure 2. Plot of $1/k_{obs}$ vs. $1/[\text{Fe}^{2+}]$ at different concentrations of urea and 25°C, [NAPH] = 0.001 M and [NaOH] = 0.02 M.
Figure 3. Effect of [SDS] on $k_{obs}$ for NAPH / Fe$^{2+}$ complex formation at different concentration of urea and 25°C. [NAPH] = 0.001 M, [Fe$^{2+}$] = 0.015 M and [NaOH] = 0.02 M.

Figure 4. Surface tension measured in water in the absence of the reactants versus [SDS] at 25°C.
Figure 5. Plots of $k_{obs}$ versus [SDS]_T for the Fe^{2+}/NAPH complex formation at different urea concentration and 25°C. [Fe^{2+}] = 0.015 M, [NAPH] = 0.001 M, [NaOH] = 0.02 M.

Figure 6. Effect of [Urea] on the cmc of SDS micellar solutions under kinetic conditions at 25°C.