Kinetics of reduction of [Co(NH$_3$)$_5$N$_3$]Cl$_2$ by iron (II) in CTAB/$n$-heptane/butanol/water reverse micelles

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The kinetic study of reduction of pentaammineazidocobalt(III) chloride complex by Mohr’s salt (ammonium ferrous sulphate) has been carried out in the water pools of cationic reverse micelles of cetyltrimethylammonium bromide (CTAB). The reaction is first order each in Co(III) complex and iron(II) in all water-to-surfactant molar ratios, i.e. at all $W$ values. The observed pseudo first order rate constant ($k_{obs}$) versus $W$ plot shows highest rate at $W = 8.33$. The kinetics has been accounted for by a mechanism involving bimolecular azido-bridged inner-sphere intermediate complex formation between Co(III) complex and iron(II). The significant increase of rate in reverse micellar media as compared to that in aqueous medium is due to the lower micropolarity of the water pool and bound state of reactants in this reverse micellar media, both facilitating the intermediate formation. The activation parameters (standard enthalpy of activation, $\Delta^\circ H^\ddagger$ and standard entropy of activation, $\Delta^\circ S^\ddagger$) of the reaction at different $W$ values have been calculated which corroborate the kinetics of the reaction.

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Several surfactants are able to aggregate in non-aqueous solvents to yield reverse micelles$^{12}$, in which the polar head groups of the surfactant monomers cluster to form a micellar core and are directed towards the centre of the assembly, and the hydrophobic tails extend outwards into the bulk organic phase.$^3$ Both experimental$^4$ and theoretical$^5$ approaches show that key structural parameter of reverse micelle is the [water]/[surfactant] molar ratio ($W$) which determines the micellar size as well as the unique physicochemical properties of the entrapped water. Reverse micelles, therefore, represent a typical organized molecular assembly that offers the unique advantage of monitoring dynamics of embedded molecules with graded hydration. A wide range of physicochemical properties of the micellar water such as micro polarity, micro viscosity, dielectric constant, water activity, freezing point, proton transfer efficiency and the hydrogen bonding potential of the water in the reverse micellar core can be experimentally varied with $W$, providing a unique and versatile reaction medium.

One of the several advantages of a reverse CTAB micellar system is that the size of the water pool can be controlled precisely at the nanometer scale through the molar ratio of water to surfactant. Therefore, size effect on chemical and physical properties in nanometer dimension can be studied by the use of CTAB reverse micelles.

Several transition metal complexes have been used for studying electron-transfer reactions.$^6$ Amongst them, octahedral Co(III) complexes, which are substitutionally inert, are ideal for theoretical and experimental studies. The kinetics of reduction of Co(III) complexes is free from complications arising due to reversible electron transfer, aquation, substitution and isomerisation reactions. Diebler and Taube,$^7$ Watts et al.$^8,9$ and other researchers$^{10}$ have studied the kinetics and mechanism of reduction of Co$^{II}$ by Fe$^{II}$ in aqueous and non-aqueous medium. Various effects on this reaction are reported$^{11}$. Besides this, many researchers$^{12-14}$ have been studying the micellar and reverse micellar effect on the rate of different types of reactions. We present here the kinetics and mechanism of the reduction of Co$^{III}$ by the reducing agent, Fe$^{II}$ in micelles and reverse micelles. This reaction has been shown to proceed through an inner-sphere mechanism. The effect of micellar environment on the electron transfer rate has also been examined.

Experimental

Cetyltrimethylammonium bromide (CTAB) of Loba Chemie, India was used. $n$-Heptane of spectroscopic grade, Mohr’s salt and ammonium sulphate of analytical grade, and spectrophotometric quality of sulphuric acid were used, as obtained from Merck, India. Aqueous solutions were prepared in deionised and doubly distilled water. The complex was prepared by a standard procedure. For the kinetic measurements, stock solutions of the complex (ca. $4.0 \times 10^{-2} M$) in water and of Mohr’s salt (ca. $4.0 \times 10^{-1} M$) in 0.4 $M$ sulphuric acid solution were prepared. All kinetic and spectral measurements were recorded on an Agilent 8453E UV-vis spectroscopy system. Quartz cells (1.0 cm path length) from Hellma were used.
To prepare a pseudo-quaternary system of CTAB/water/1-butanol/n-heptane reverse micelles using its phase diagram\textsuperscript{15} (Fig. 1), requisite amounts of the cationic surfactant and CTAB were dissolved in n-heptane-butanol mixture in 20 mL stoppered test tubes. Butanol was used as a co-surfactant. Then, water was added and shaken to form the reverse micelles. Solutions of different concentrations were prepared by varying the amount of CTAB. Mohr’s salt solution (in doubly distilled water) and required amount of complex solution were added to the CTAB solution and shaken to obtain a transparent solution with required concentration of Mohr’s salt and \( W \) value that can be regarded as a reverse micellar system.

Before each kinetic run, all solutions were thermostated to a specific temperature. The required amount of Mohr’s salt solution was added to CTAB solution during preparation of reverse micellar system in a 20 mL stoppered test tube. Finally, required amount of complex solution was added to the mixture and shaken again to obtain a transparent solution and to initiate the reaction. Since all the reactants of the reaction are ionic, they can exist only in the water pool, and not in the organic phase. Due to confinement of the reactants in the small volume of the water pool in bulk organic phase, the effective concentration of Mohr’s salt, \( [\text{Fe}^{\text{II}}]_0 \), is equal to the volume fraction \( f \) of solubilized water \( (f = \text{volume of water/total volume of the system}) \). The rate data was analyzed by taking this effective concentration in the water pool.

The kinetics of the reactions between \([\text{Co(NH}_3\text{)}_5\text{N}_3\text{]Cl}_2\) and Mohr’s salt (ammonium ferrous sulphate) in reverse micellar medium of CTAB were studied spectrophotometrically under pseudo-first-order condition with large excess amount of Mohr’s salt at 298 K. In all experiments, the initial molar concentration of Mohr’s salt, \( [\text{Fe}^{\text{II}}]_0 \), was at least ten times than that of initial molar concentration of cobalt(III) complex, \( [\text{Co}^{\text{III}}]_0 \), to maintain the pseudo-first-order condition. Solutions of different concentrations were prepared by accurate dilution of stock solutions. All experiments were performed at 298 K (otherwise mentioned) by mixing required volumes of the thermostated reactants with proper dilution to the required volume in the quartz cell (1 cm path length). The change of spectra of the reaction mixture proceeds through a decrease in absorbance at \( ca. 516 \text{ nm} \). The decrease in absorbance \( (A_t) \) of the reaction mixture with time was recorded at 520 nm. \( A_\infty \) was measured after completion of reaction (~ after 24 h of mixing) when the absorbance became constant. Observed pseudo first order rate constants \( (k_{obs}) \) and their standard deviations were calculated by linear regression using a computer-based program Microcal-Origin Ver 6.1. The \( k_{obs} \) values were obtained from the plots of \( A_t \) versus Time(s) for the reaction using Microcal-Origin version 6.1. The integrated rate equation used for the plots is:

\[
A_t = A_\infty + a_1 \exp(-k_{obs} \cdot t),
\]

which is first order exponential decay equation. The standard error in determination of \( k_{obs} \) value was within ± 3%.

**Results and discussion**

**Effect of variation of reactant concentration on rate**

This redox reaction between oxidizing agent, Co\textsuperscript{III} complex salt (\([\text{Co(NH}_3\text{)}_5\text{N}_3\text{]Cl}_2\)) and reducing agent, Fe\textsuperscript{II} salt in aqueous medium follows the second order kinetics: first order in each \([\text{Co}^{\text{III}}]\) and \([\text{Fe}^{\text{II}}]\). Its mechanism is well established. This reaction proceeds through a bimolecular azido-bridged inner sphere complex. An electron can be transferred from Fe\textsuperscript{II} to Co\textsuperscript{III} through the azide bridge.

The rate of same reaction was studied in CTAB micellar medium and there is about 3 times acceleration in rate as compared to aqueous medium. CTAB is a cationic surfactant, above its CMC (~ 0.7 mM at 298 K). It forms normal micelles of colloidal size; occupies much space in the reaction volume which ultimately increases the local concentration of reacting species, Co\textsuperscript{III} complex and hydrated Fe\textsuperscript{II} ion. In CTAB micellar medium, the reaction is also first order.
order in Co III complex since the plot of Absorbance versus Time fits well with first order exponential decay curve on Microcal-Origin version 6.1 and $k_{obs}$ values \{(1.30 ± 0.06)×10^{-3} \, \text{s}^{-1}\} of the reaction are almost constant with variation of $[\text{Co}^{\text{III}}]_0$ \{1.07-5.33 × 10^{-3} \, \text{M}\} when all other variables \{[$\text{Fe}^{\text{II}}]_0 = 5.33 \times 10^{-2} \, \text{M}$, temperature = 298 K, $[\text{CTAB}]_0 = 0.1 \, \text{M}$ and ionic strength \(\approx 3.25 \, \text{M}\}\} are constant. The variation of $[\text{Fe}^{\text{II}}]_0$ increases the $k_{obs}$ values (Table 1) and the linear plot of $k_{obs}$ versus $[\text{Fe}^{\text{II}}]_0$ indicates that the reaction is also first order in $\text{Fe}^{\text{II}}$ in CTAB micellar medium. The slope of the plot shows that the rate constant ($k$) corresponds to second order reaction.

This reaction rate has also been studied in CTAB reverse micellar cavity and there is 17.5 times acceleration in rate at $W = 8.33$ as compared to aqueous medium. In presence of reverse micelles of CTAB, the reaction occurs in water present in a reverse micellar cavity, referred to as ‘water pool’, since all the reactants are ionic in nature. In this microenvironment, effective concentration of both cationic reacting species increases. This accelerates the formation of a bimolecular azido-bridged inner sphere complex, which ultimately increases its rate. The $k_{obs}$ values have been measured at different values of $[\text{Fe}^{\text{II}}]_0$ and at different $W$ values.

The plots of $k_{obs}$ versus $[\text{Fe}^{\text{II}}]_0$ at different $W$ values \{5.56-18.06\} are linear passing through origin with positive slope, indicating that the reaction in CTAB reverse micellar cavity at these $W$ values \{5.56-18.06\} is also first order in $[\text{Fe}^{\text{II}}]$ beside its order in $[\text{Co}^{\text{III}}]$ complex is unity. The slope of the plot shows that the rate constant ($k$) corresponds to the second order reaction. The $k$ values are $4.68 \times 10^{-2}$ at $W = 5.56$; $15.40 \times 10^{-2}$ at $W = 8.33$; $8.90 \times 10^{-2}$ at $W + 11.11$; $6.40 \times 10^{-2}$ at $W = 13.90$ and $4.50 \times 10^{-2} \, \text{M}^{-1} \, \text{s}^{-1}$ at $W = 18.06$. The rate increases with $W$, i.e. cavity size up to 8.33. Beyond that, it decreases.

**Effect of variation of ionic strength and temperature on rate**

It is found that the effect of ionic strength on the reaction rate is almost insignificant. In presence of cationic micellar environment, effect of ionic strength may be masked. We could not maintain the constancy of ionic strength of reactions in reverse micellar cavity. The second order rate constants of the reaction in CTAB micellar medium have been determined at different temperatures. The standard enthalpy of activation, $\Delta^\ddagger H^\circ \approx 49.1 \pm 8.5$ and standard entropy of activation, $\Delta^\ddagger S^\circ \approx -111 \pm 18$ have been calculated from Eyring plot. The second order rate constants of the same reaction in the reverse micellar cavity of CTAB have been determined at different temperatures. The activation parameters (standard enthalpy of activation $\Delta^\ddagger H^\circ$ and standard entropy of activation $\Delta^\ddagger S^\circ$) have been calculated at different $W$ values from Eyring plot (Table 2).

<table>
<thead>
<tr>
<th>$W$</th>
<th>Temp. (K)</th>
<th>$10^2 k_{obs}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$10^2 k$ (M$^{-1}$ s$^{-1}$)</th>
<th>$\Delta^\ddagger H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta^\ddagger S^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
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<tr>
<td>5.56</td>
<td>298</td>
<td>0.47</td>
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<td>-132 (± 7)</td>
<td>43.8 (± 6.2)</td>
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<td>0.64</td>
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<td>11.11</td>
<td>303</td>
<td>1.18</td>
<td>313</td>
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<td>1.51</td>
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<td>1.94</td>
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The second order rate constant \((k)\) data and standard enthalpy of activation \((\Delta^2 H)\) data corroborate each other. The decreasing order for rate constant is: \(k\) (in CTAB reverse micellar cavity at \(W = 8.33\)) >> \(k\) (in CTAB micellar medium) >> \(k\) (in aqueous medium) whereas the order for \(\Delta^2 H\) is just reverse of \(k\).

**Effect of variation of micellar, reverse micellar concentration and of \(W\) on rate**

The variation of [CTAB] on reaction rate in the concentration range 0.1-0.5 \(M\) does not have any significant effect on rate though its presence accelerates rate about 3 times. The variation of water pool size on reaction rate in reverse micellar medium has been studied at different values of \(W\) (2.78-20.83) (Table 3) and the variation of CTAB concentration (0.1-0.8 \(M\)) at different values of \(W\) (4.17-15.28) (Table 3) have a significant effect on rate. The rate initially increases with \(W\), reaches a maximum at \(W = 8.33\) and then it decreases. The reactants being ionic cannot exist in bulk oil phase; the reaction only can take place either in the water pool or in the micellar interface or in both. The increase in CTAB concentration at fixed \(W\) increases the micellar concentration and hence the area of the interface, although there is no change in the micellar composition or other properties. The increase in rate with [CTAB] shows that the reaction is taking place on the micellar interface. The reactants are also present in water pool. Thus, reaction takes place partly on the micellar interface and partly in the water pool. The increase in the surfactant concentration at constant different \(W\) values increases, the interfacial area and ionic strength that ultimately increases rate. With increase of [CTAB], two things may happen; firstly the water pool size may be smaller and secondly number of reverse micellar aggregates may increase. In both the cases, the reaction rate would be facilitated (Table 3).

The variation of \(W\) on the rate of concentration and other variables has been studied (Table 3). When \(W\) is very small, almost all the water molecules are used up to hydrate the surfactant head groups. So, the dissolved reactants are in a bound state and have very low mobility. Hence, the reaction rate is small. With graded hydration, the reactants become more mobile. Also, their local concentration is quite high resulting increase in the rate. When the water pool size is very large, i.e. at very high \(W\), the water content at the reverse micellar core is so high that it virtually behaves like the bulk water phase; hence the local concentration of the reactants decreases and rate decreases (Table 3).

The study shows that the redox reaction between oxidizing agent, Co\(^{III}\) complex salt ([Co(NH\(_3\))\(_5\)N\(_3\)]Cl\(_2\)) and reducing agent, Fe\(^{II}\) salt (Mohr’s salt) in aqueous, in CTAB micellar and reverse micellar cavity follows the second order kinetics: first order in each [Co\(^{III}\)] and [Fe\(^{II}\)]. This reaction proceeds through a bimolecular azido-bridged inner sphere complex. An electron is transferred from Fe\(^{II}\) to Co\(^{III}\) through the azide bridge. The rate is influenced significantly in presence of cationic micelle as compared to aqueous medium and also influenced significantly when the same reaction occurs inside the reverse micellar cavity of cationic surfactant, CTAB. With increase in size of water pool, rate initially increases, reaches a maximum and then it decreases.

**Table 3 — Second order rate constants \((k)\) at different [CTAB]\(_0\) and at different water to surfactant ratios \((W)\). [Temp. = 298 K]**

<table>
<thead>
<tr>
<th>[CTAB] ((M))</th>
<th>(W = 4.17)</th>
<th>(W = 5.56)</th>
<th>(W = 6.94)</th>
<th>(W = 8.33)</th>
<th>(W = 9.72)</th>
<th>(W = 11.11)</th>
<th>(W = 12.50)</th>
<th>(W = 13.90)</th>
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<td>0.59</td>
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References