Medium effects on the electron transfer processes: Reduction of aquapentaamminecobalt(III) by hexacyanoferrate(II) in glucose-water medium

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The electron-transfer between \(\text{(NH}_3\text{)}_5\text{Co}^{3+}\) and \(\text{Fe(CN)}_6^{3-}\) in glucose-water medium \((0 \leq \text{vol} \% \text{G} \leq 40)\) proceeds via the reactive ion-pair \([\text{(NH}_3\text{)}_5\text{Co}-\text{CoOH}^+ \ldots \text{Fe(CN)}_6^{3-}\]. The first order rate constant \(k\) at 40°C for the ion-pair shows a small decreasing trend with increase in \([\text{glucose}]\) despite the fact that the viscosity \(\eta\) of the medium increases sharply. This is in contrast to the increase in \(k\) with \(\eta\) for ethylene glycol-water and glycerol-water media reported earlier. The activation parameters \(\Delta H^*\) and \(\Delta S^*\) are also insensitive to the composition of glucose-water medium. The results highlight the virtually noninterfering nature of glucose-water medium on the kinetics and energetics of the intramolecular electron transfer process.

It was shown earlier that the electron transfer between \(\text{Co(III)}\) and \(\text{Fe(II)}\) centres in the ion-pair, \([\text{(NH}_3\text{)}_5\text{CoOH}^+ \text{Fe(CN)}_6^{3-}\], is moderately sensitive to the nature of the solvent\(^1,2\). The viscosity of glycerol (G)-water mixture was believed by van Eldik et al.\(^2\) to be a major parameter to control the dynamics and energetics of the process. However, this does not appear to be of a general validity for ethylene carbonate (EC)-water, urea (U)-water and presumably for ethylene glycol (EG) -water media\(^1\). The observed rate sequence \(\text{EC + water} > \text{EG + water} > \text{G + water} > \text{U + water}\) and the dependence of the activation parameters \(\Delta H^*\) and \(\Delta S^*\) on the solvent composition presumably delineate the importance of both electrostatic and non-electrostatic effects on solute-solvent interactions which are the guiding factors for the net electron-transfer process. The molecules of the cosolvents stated above (except \(U\)) are are endowed with hydrophobic property (due to their hydrocarbon skeleton) to different degrees, while the reactive ion-pair is essentially hydrophilic in nature.

The glucose-water is a useful solvent system as: (i) glucose molecule is strongly hydrophilic, (ii) the medium is highly polar (dielectric constant \(= 78-62\) at wt \% \(G = 0-42, 25^\circ\text{C}\))\(^3\), (iii) the six membered ring and glycolic unit in the molecule simulate EC-water and EG-water system (see Fig. 1) and (iv) the viscosity of the medium increases sharply with increasing glucose as it is true for glycerol-water medium\(^4\). Furthermore, glucose-water is a biologically important medium for electron transfer reaction. Based on these considerations, we planned to investigate the outer-sphere electron transfer reaction (OSET) between aquapentaamminecobalt(III) and hexacyanoferate(II) in the glucose water medium. The purpose was to examine how such a solvent system would mediate the kinetics and energetics of this model electron transfer reaction.

**Experimental**

Aquapentaamminecobalt(III) perchlorate was recrystallised before use. Sodium hexacyanoferate(II), glucose and all other reagents used for kinetic study were of AR grade. All solutions were prepared in molar scale using freshly distilled conductivity water. The ionic strength of the reaction mixture was adjusted with \(\text{NaClO}_4\). The electron transfer between \(\text{(NH}_3\text{)}_5\text{CoOH}^+\) and \(\text{Fe(CN)}_6^{3-}\) was studied at \(I = 0.10 \text{ mol dm}^{-3}\) by a fully automated HI-TECH SF 51 stopped flow spectrophotometer; acetate buffer and \(\text{Na}_2\text{EDTA}\) were used to maintain \(\text{pH} \approx 4.7\) and avoid precipitation of \(\text{Co(II)}\). The reaction was monitored at 420 nm at which the \(\text{Fe(CN)}_6^{3-}\) was the only absorbing species under the experimental condition. The details of the procedure adopted were the same as described in our earlier work\(^1\). Minimum of seven
replicate measurements were made to get the pseudo-first order rate constant and its standard deviation. All calculations were made on an Apple II GS PC using least squares programme.

Results and discussion

Under the experimental conditions clean pseudo-first order kinetics was observed in the time scale of measurements. The pseudo-first order rate constant \( k_{\text{obs}} \) versus \([\text{Fe(CN)}_{6}^{3-}]_{T} \) plots at any temperature and solvent composition were nonlinear tending to attain the asymptotic limits at high concentration of the reductant. Typical plots shown in Fig. 2 conform to the reaction shown in Scheme 1.

\[
\begin{align*}
\text{(NH}_3)_5\text{CoOH}_2^{\downarrow} + \text{Fe(CN)}_{6}^{3-} & \rightarrow [\text{(NH}_3)_5\text{CoOH}_2]^{\downarrow} + \text{Fe(CN)}_{6}^{3-} \\
\text{Co(II)} + 5\text{NH}_3 + \text{Fe(CN)}_{6}^{3-} & \end{align*}
\]

Scheme 1

for which the \( k_{\text{obs}} \) is given by

\[
k_{\text{obs}} = \frac{kK[\text{Fe(CN)}_{6}^{3-}]}{1 + K[\text{Fe(CN)}_{6}^{3-}]} \quad \ldots (1)
\]

where \( K \) and \( k \) denote the equilibrium constant for the complex formation and the rate constant of the ion-pair respectively. Values of \( k \) and \( K \) calculated from the intercepts and gradients of the weighted least squares best line plots of \( k_{\text{obs}} \) versus \([\text{Fe(CN)}_{6}^{3-}]_{T} \) are collected in Table 1. The values of activation parameters \( \Delta H^* \) and \( \Delta S^* \) (see Table 1) were calculated using the Eyring equation.

The values of \( K \) are quite expected for \((3+, 4-) \) type of association at low ionic strength\(^{1,2,5}\). It appears that the thermodynamic stability of the ion-pair is little influenced by the net solvent cosphere effects for \((\text{NH}_3)_5\text{CoOH}_2^{\downarrow}, \text{Fe(CN)}_{6}^{3-} \) and the ion-pair as well as the changes in the bulk property of the solvent induced by glucose. It may be noted that the bulk dielectric constant of \( G + H_2O \) system in the range of solvent composition studied decreases only marginally \( 78.6 \leq \varepsilon \leq 62 \) at \( 0 \leq \% \text{ wt } G \leq 42.4 \) at \( 25^\circ \text{C} \)\(^{3,6}\). Interestingly enough, appreciable variations of \( k \) with \% \( G \) is not observed. However, a small but definite decreasing trend of \( k \) with increasing \( [G] \) (= 0-2.22 mol dm\(^{-3}\)) at \( 40^\circ \text{C} \) is evident (see Eq. 2).

\[
k(40^\circ \text{C}) = k(40^\circ \text{C}) - (0.0665 \pm 0.00088)[G] \quad \ldots (2)
\]
Table I—Values of rate constant (k), equilibrium constant (K) and activation parameters (ΔH*, ΔS*) at various temperatures and solvent compositions for glucose water media

<table>
<thead>
<tr>
<th>Temp. °C (±0.1°C)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40% glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.61 ±0.10</td>
<td>6.46 ±0.06</td>
<td>6.34 ±0.14</td>
<td>6.70 ±0.05</td>
<td>5.99 ±0.09</td>
<td>6.25 ±0.09</td>
</tr>
<tr>
<td>(1.47 ±0.06)</td>
<td>(1.48 ±0.06)</td>
<td>(1.56 ±0.11)</td>
<td>(1.19 ±0.02)</td>
<td>(1.65 ±0.06)</td>
<td>(1.81 ±0.08)</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>15.9 ±0.1</td>
<td>14.0 ±0.2</td>
<td>14.5 ±0.3</td>
<td>13.7 ±0.3</td>
<td>13.4 ±0.3</td>
<td>13.6 ±0.1</td>
</tr>
<tr>
<td>(1.00 ±0.02)</td>
<td>(1.46 ±0.03)</td>
<td>(1.36 ±0.07)</td>
<td>(1.53 ±0.08)</td>
<td>(1.70 ±0.12)</td>
<td>(2.34 ±1.16)</td>
<td></td>
</tr>
<tr>
<td>35.0</td>
<td>66.8 ±0.8</td>
<td>65.1 ±0.6</td>
<td>62.1 ±0.4</td>
<td>59.9 ±1.7</td>
<td>62.0 ±1.4</td>
<td>63.9 ±0.7</td>
</tr>
<tr>
<td>(1.05 ±0.03)</td>
<td>(1.33 ±0.04)</td>
<td>(1.26 ±0.04)</td>
<td>(1.58 ±0.09)</td>
<td>(1.62 ±0.10)</td>
<td>(1.53 ±0.04)</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>136.4 ±1.3</td>
<td>134.9 ±2.3</td>
<td>132.8 ±1.1</td>
<td>130.3 ±2.7</td>
<td>128.6 ±2.6</td>
<td>119.7 ±2.3</td>
</tr>
<tr>
<td>(1.25 ±0.03)</td>
<td>(1.28 ±0.05)</td>
<td>(1.41 ±0.02)</td>
<td>(1.57 ±0.10)</td>
<td>(1.65 ±0.08)</td>
<td>(1.87 ±0.12)</td>
<td></td>
</tr>
<tr>
<td>ΔH* /kJ mol⁻¹</td>
<td>110</td>
<td>113</td>
<td>113</td>
<td>110</td>
<td>114</td>
<td>113</td>
</tr>
<tr>
<td>ΔS* /JK mol⁻¹</td>
<td>108</td>
<td>119</td>
<td>118</td>
<td>107</td>
<td>122</td>
<td>117</td>
</tr>
</tbody>
</table>

a) Values in parenthesis are for 10⁻³ K
b) g glucose/100 cm³
c) σ(ΔH*) = ± 2 kJ mol⁻¹, σ(ΔS*) = ± 6 JK⁻¹ mol⁻¹

This is in contrast to the observed increasing trend of k with increase in [ethylene glycol], [ethylene carbonate] and [glycerol] in these aquo + organic solvent systems. It is worth noting that the viscosity (η) of glucose + water system increases steeply at 25°C with increasing proportion of glucose and the relative viscosity (η/ηᵡ) for glucose + water system is significantly greater than that of ethylene glycol + water system under comparable molefractions of the cosolvents (see Fig. 6 or ref. 6). The activation enthalpy and entropy data average to 112 ± 1.7 kJ mol⁻¹ and 115 ± 6 JK⁻¹ mol⁻¹ (0 ≤ % of glucose ≤ 40) with little variation in solvent composition (see Table 1) unlike for ethylene glycol + water, ethylene carbonate + water and glycerol + water systems. The viscosity of the bulk solvent phase has little effect on this intramolecular electron transfer reaction unlike for glycerol + water system as reported by van Eldik et al.².

The observed effect of glucose + water medium on dynamics and energetics of the electron transfer reaction under consideration may be contrasted with the same for the solvolytic reaction of (NH₃)₅CoCl₂⁺ in the same medium reported by Wells et al.⁶. A substantial medium effect, presumably relating to solvent structural effect on the rate and activation parameters of the dissociative activation process was observed. In the present context it is worth mentioning that lack of substantial medium effect may be an advantage for studying electron transfer reaction in glucose + water, a medium of biochemical importance.

Acknowledgement
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References
6 Bush D A & Wells C F, J chem Soc Faradays Trans, 86 (1990) 941 (see Table 1 and Fig. 1 of this reference).