Kinetic and thermodynamic characteristics of the hexacyanoferrate II/III redox system in t-butanol/water mixed solvent

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The kinetic and thermodynamic parameters controlling the hexacyanoferrate II/III redox reaction in t-butanol/water mixtures have been derived using a gold rotating disc electrode with a standard potentiostatic technique. The effect of temperature on the current-voltage characteristics of the gold rotating disc electrode in the hexacyanoferrate redox system at different compositions of the solvent mixture has been studied and thermodynamic parameters have been evaluated. The presence of t-butanol in the solvent mixture enhances the rate of charge transfer reactions with respect to the diffusion controlled reactions. From the thermodynamic point of view, the rate of the cathodic process is independent of both the enthalpy or the entropy of the process and compensation effect is present. The anodic process obeys an entropy-controlled mechanism. Chemical potential calculations show that the concentration of the activated complex in the case of the anodic process is lower than that corresponding to the cathodic process.

The importance of the hexacyanoferrate II/III redox reaction for applications in electrochromic devices and catalysis of electron transfer reactions^1,2 makes the electrochemical and spectroscopic investigations^3,4 worthy of further studies. Kinetic studies in some buffer solutions have shown that the increasing exchange current density is due to electrode surface changes^5. The kinetic parameters controlling the anodic and cathodic processes in the hexacyanoferrate systems were best studied by cyclic voltammetry^6,7. Organic hydroxy compounds were found to influence the kinetic and thermodynamic parameters of the redox reaction^6,8,9 and change the membrane permeability by increasing the pore size of the film formed on the electrode surface. Potentiostatic measurements at high scan rates have shown that the redox reaction in such systems is slow^11. The presence of ethanol in the solvent mixture was found to enhance the diffusion controlled processes and to retard the charge transfer kinetics^8 and this was attributed to changes in the structural properties of the solvent or solvent mixture^12.

The activation free energy, \( \Delta G^* \), activation enthalpy change, \( \Delta H^* \), and the activation entropy change, \( \Delta S^* \), were found to play an important role in the mechanism of the processes taking place at the electrode/electrolyte interface^8,10,12,13. Chemical potential and constants of equilibria of any process lead to valuable information concerning the concentration and stability of the activated complex accompanying each step^14,15.

In the present investigation the kinetic and thermodynamic parameters controlling anodic and cathodic processes occurring at the gold rotating disc electrode (Au-rde) in the hexacyanoferrate II/III redox system dissolved in t-butanol/water mixed solvent were evaluated. The change in the chemical potential of the anodic and cathodic process was also calculated. The effect of t-butanol on the mechanism of the electrode processes is discussed.

Materials and Methods

A standard potentiostatic technique was used to carry out the current density-potential curves. The circuit consisted of a multifunction potentiostat (FHI GO50-17) with an interruption unit to compensate and to measure the ohmic overpotential accompanying the electrode processes. The interruption of the current was controlled by an oscilloscope. The current density-potential behaviour was traced using X-Y recorder (JJ-PL-50). The electrochemical cell was a double-walled all glass cell provided with a Teflon stopper with suitable opening for the three electrode system (working, counter and reference electrodes) as well as for the gas inlet and outlet. The working electrode.
was a gold disc of diameter 3 mm attached to the rotating disc system (Metrohm 628-10). The counter electrode was a large area Pt-spiral and the reference electrode was a saturated calomel electrode (sce), which is attached to the cell through a salt bridge ending with a lugulli capillary placed adjacent to the working electrode. Details of the experimental procedure were described elsewhere.\textsuperscript{8-10} Electrolytic solutions were prepared using analytical grade reagents and triply distilled water. All measurements were carried out at $25 \pm 0.1^\circ C$ except those related to the effect of temperature. In most cases, test solutions were deaerated by bubbling with pure $N_2$ for at least 20 min before the measurement. Measured potentials were referred to the normal hydrogen electrode (nhe). Before each experiment the rde was mechanically polished with diamond spray down to 0.25 $\mu m$, washed first in ethanol, then in triply distilled water in an ultrasonic bath.

**Results and Discussion**

**Effect of temperature on the current-voltage behaviour of the Au-rde in the Fe(CN)$_6^{3-/4-}$-t-butanol/water solution**

To study the general electrochemical behaviour of the Au-rde in the hexacyanoferrate redox system and the effect of both the temperature and the composition of the mixed solvent on such behaviour, experiments were carried out at constant electrolyte concentration-0.01 mol dm$^{-3}$ K$_2$Fe(CN)$_6$-0.01 mol dm$^{-3}$ K$_2$Fe(CN)$_4$-0.5 mol dm$^{-3}$ KNO$_3$. The composition of the solvent mixture was varied between 0 and 30 wt % of t-butanol and the remaining part was also triply distilled water. The measurements were carried out repeatedly in the temperature range 283-323 K at a scan rate of 50 mV s$^{-1}$ and a rotation speed of the Au-rde of 2000 rpm (revolution per min.).

Typical current density-potential curves showing the general electrochemical behaviour and the effect of temperature on that behaviour for the Au-rde in the redox system dissolved in 30% t-butanol are presented in Fig. 1. The figure shows that both the anodic and cathodic processes obey a diffusion controlled mechanism, as can be seen from the limiting currents recorded at each temperature. This behaviour is quite similar to the behaviour of hexacyanoferrate in pure water, ethanol-water, glycerol-water, and ethylene glycol-water mixed solvents.\textsuperscript{7-10}

At the same temperature the diffusion current decreases as the ratio of t-butanol in the solvent mixture increases. It means that the increase in the concentration of t-butanol lowers the diffusion processes, a behaviour similar to that observed with ethylene glycol containing solvents. This behaviour can be attributed to the increased kinematic viscosity of the mixed solvent due to the increasing concentration of t-butanol.\textsuperscript{10}

For the same solvent composition (e.g. 30 wt % t-butanol as in Fig. 1), the diffusion current increases as the temperature increases. It means that the rate of the electrode reaction increases as the temperature increases as it would be expected for kinetic processes controlled either by diffusion of charge transfer.

Near the equilibrium potential (where $\eta$, the polarization, $\eta \leq 20$ mV), the system was found to obey the linear approximation of the Butler-Volmer equation.\textsuperscript{16} The current density-potential behaviour of the Au-rde in the same electrolyte of Fig. 1 and near the equilibrium potential ($|\eta| \leq 20$ mV) for both the anodic and cathodic processes is presented in Fig. 2. From the linear relations of Fig. 2 the exchange current density $i_0$ for both processes can be obtained using Eq. (1):

$$i = i_0 \frac{zF}{R} |\eta|$$

where $|i|$ is the anodic or cathodic current density, $|\eta|$ the corresponding polarization, and $z$, $F$, $R$, and $T$ have their usual meaning. At any polarization interval the ratio between $i$ and $|\eta|$ gives the value of the charge transfer resistance ($R_{ct}$), which is a measure of the kinetic facility of the electrochemical process.\textsuperscript{16}

$$R_{ct} = \frac{|\eta|}{|i|} = \frac{RT}{Fz} \times \frac{1}{i_0}$$

![Fig. 1—Current density-potential behaviour of the Au-rde during anodic and cathodic polarization in the Fe(CN)$_6^{3-/4-}$/t-butanol-water redox system at different temperatures. Speed of rotation is 2000 rpm. Scan rate is 50 mV s$^{-1}$. (1) 283, (2) 293, (3) 298, (4) 303, (5) 313 and (6) 323 K.](image-url)
The exchange current density, charge transfer resistance and limiting currents for the anodic and cathodic processes taking place at the Au-rde in the hexacyanoferrate redox system dissolved in t-butanol/water mixed solvent at different temperatures were calculated and are summarized in Table 1. It can be seen from Table 1 and also from the results presented in Figs 1 and 2, that the increase in temperature is followed by an increase in the exchange current density and a decrease in the charge transfer resistance. The decrease in the charge transfer resistance with increase in temperature for both the anodic and cathodic processes is an indication for an increasing tendency towards charge transfer kinetics. The activation energies of the anodic and cathodic processes at different compositions of the mixed solvent were calculated from the log $|i_0|$ versus $1/T$ plots. Values of the activation energy and limiting current density showing the effect of the composition of the mixed solvent are summarized in Table 2.

![Table 1](image)

The activation energy values presented in Table 2 show that unlike ethanol or glycerol and like ethylene glycol the increase in concentration of t-butanol in the solvent decreases the activation energy of the electrode process. Since the calculated activation energy corresponds to the charge transfer reaction, the increase in concentration of t-butanol enhances the charge transfer kinetics. This is in good agreement with the fact that the limiting current density of the electrode process decreases as the concentration of t-butanol increases which means that the diffusion controlled processes are retarded (cf. Table 2).

**Solvation effect and activation parameters**

The isocomposition activation energy, $E_a^*$, i.e., the energy of activation of a certain process at a given solvent composition, presented in Table 2 for both the anodic and cathodic processes were used to calculate the thermodynamic parameters, i.e., the activation free energy, $\Delta G^*$, the activation enthalpy, $\Delta H^*$, and the activation entropy, $\Delta S^*$. Compound thermodynamic parameters are summarized in Table 3.

The linearity of the best fitting Arrhenius plots show that the enthalpy of activation $\Delta H^*$ is constant over the investigated temperature range. Variations of the activation parameters $\Delta S^*$ and $\Delta H^*$ and $\Delta G^*$ with a mole fraction of the t-butanol in the solvent mixture at 298 K are presented in Fig. 3 (A, B and C respectively). The linear increase in free energy of activation, $\Delta G^*$ with the increased ratio of t-butanol gives an indication of the preferential solvation of the electrode surface in presence of the organic solvent. Preferential solvation of the electrode surface is a characteristic property of organic hydroxy compounds. As a consequence of such solvation the transition of ionic species through the double layer at the electrode/electrolyte interface requires more energy to overcome the energy barrier, and

![Table 2](image)
Table 3—The thermodynamic parameters of the anodic and cathodic processes taking place at the Au-rde/electrolyte interface in the hexacyanoferrate II/III solution in the t-butanol/water mixed solvent

<table>
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<th>Cathodic Process</th>
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<td>24.0</td>
</tr>
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</table>

ΔH* and ΔG* in kJ mol⁻¹ whereas ΔS* in J mol⁻¹ K⁻¹.

Fig. 3—Variation of the activation parameters ΔS* (A), ΔH* (B) and ΔG* (C) with the mole fraction of t-butanol in the mixed solvent at 298 K.

Since the anodic and cathodic processes have two different isokinetic temperature, they should have different reaction mechanisms based on the mechanism of the electrode/solvent interaction.

The interaction mechanism affects the activation of both the enthalpy and entropy of each process however, in different ways. In some cases, the entropy of activation is more effective than the enthalpy of activation and hence the process obeys an entropy-controlled mechanism. In such cases lower isokinetic temperatures compared to experimental temperature should be obtained, as well as in the case of the anodic process of the reaction under investigation. In some other cases, where the enthalpy of activation is more effective than the entropy of activation, the reaction will be enthalpy controlled. The isokinetic temperatures of such systems should be relatively higher than...
According to Atkins\textsuperscript{15}, the molar Gibb's function is given by the chemical potential, i.e.,
\[ G_m = \mu \]  
and hence,
\[ \Delta G_m = \Delta \mu^* = -RT \ln K \]  
where \( K \) is the equilibrium constant of the reactant/activated complex equilibrium. Using the estimated values of \( \Delta \mu^* \) equilibrium constants of the anodic and cathodic reactant/activated complex equilibria could be calculated. For the anodic process a value of \( K_{an} = 2.1 \) and for the cathodic process a value of \( K_{cat} = 2.8 \) were obtained.

These values show that the concentration of the activated complex produced in the cathodic process is higher than that of the anodic and since such complex is relatively stable with respect to the reacting species, the rate of the anodic process, especially near the equilibrium potential will be relatively higher than the rate of the cathodic one. This can be seen clearly in the results presented in Fig. 1 and also reflected on the values of the exchange current density of the anodic and cathodic processes (cf. Table 1). Such a difference indicates that anodic and cathodic processes of the same system obey two different mechanisms which are an entropy-controlled and a linear compensation mechanism.

References