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Determination of the Heterogeneous Rate Constant of $Fe(CN)_6^{3-/4-}$ in Aqueous Solutions with Different Supporting Electrolyte and Viscosity at Glassy Carbon Electrode

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The apparent standard rate constant, k^0, for a $Fe(CN)_6^{3-/4-}$ electrode process, known to be strongly dependent on the nature of supporting electrolyte, display a lateral dependence on the solution viscosity (water/glucose mixture, 1 M in KCl, NaCl and CsCl). k^0, is inversely proportional to the solution viscosity. The viscosity performance is complementary to the catalytic effect of cations and seems to operate independently. The catalytic role of cations is discussed in term of the pre-equilibrium concept, considering the influence of a double-layer potential on the effective concentration of reactant ions at the active site near the electrode.

Key Words: Supporting electrolyte, Catalytic effect, Glassy carbon.

INTRODUCTION

A number of research papers have been published on the heterogeneous outer-sphere electron exchange at bare metal (Au, Pt, Hg) electrodes, in which the medium viscosity was varied either by adding of inert viscous substances, by solvent variation or through the variation of applied pressure, the following dependence of the heterogeneous rate constant on the solution viscosity, η, has been observed[1-8]:

$$k \alpha \eta^{-\delta} \tag{1}$$

where δ is an empirical parameter with the typical value within the range of $0 < \delta < 1$.

In the present work, the dependence of the heterogeneous rate constant of the $Fe(CN)_6^{3-/4-}$ electrode process on the solution viscosity (varied by the addition of glucose) was rigorously investigated using of three representative electrolytes *i.e.*, KCl, NaCl and CsCl (exhibiting different catalytic effects) and the same experimental technique. The obtained results together with the data on the catalytic effect of cation are discussed in terms of the pre-equilibrium concept, considering the influence of a double-layer potential on the effective concentration of reactant ions at the electrode and involving the solvent friction mechanism of the elementary electron-transfer step, within the framework of charge transfer theory.

EXPERIMENTAL

Cyclic voltammetry: A three-electrode configuration cell with the platinum plate as an auxiliary electrode and the Ag/AgCl reference electrode, the surface area of the glassy carbon working electrodes of 0.135 cm^2, was determined electrochemically.

In order to reduce the uncompensated resistance in the cell, the reference electrode was positioned near the working electrode by Luggin capillary. Working electrodes were polished with 0.3 and 0.05 alumina powder (Buehler) on a Buehler polishing cloth, washed with ultra-pure water.

The implemented solutions contained 1 M KCl, NaCl or CsCl as supporting electrolytes and 1 mM $K_3Fe(CN)_6$ and 1 mM $K_4Fe(CN)_6$.

The viscosity of solutions was varied by addition of anhydrous (+)-glucose. Glucose concentration of 0, 200, 402 and 602 g L^{-1} were used providing the relative viscosity values of 1.06, 1.78, 3.75 and 9.92 (25 ºC).

Rotating disk electrode (RDE): The diffusion coefficients, D_o, of the reactant oxidized from $Fe(CN)_6^{3-/4-}$ are determined in 1 M NaCl, KCl and CsCl solutions at different concentrations of glucose (0, 200, 402, 602 g/L) from the slope of the $I_L/\omega^{1/2}$ characteristic (I_L = limiting current/A, ω = angular velocity = 2πf/s^{-1}, f = rotating frequency/s^{-1}).

$$(I_L = 0.62nFC^oD^{2/3}\omega^{1/2}\nu^{-1/6}) \quad (2)$$

RESULTS AND DISCUSSION

According to the Stokes-Einstein theory the diffusion coefficient of a diffusing particle is related to the solution viscosity by the following expression:

$$D = k_BT/\theta\pi r\eta \quad (3)$$

where k_B is Boltzman constant, η is the plot of D (present experimental data) *vs.* 1/η.

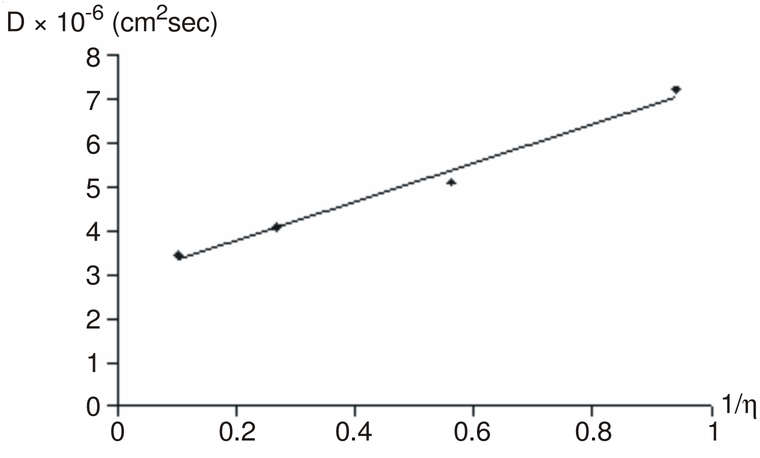

Fig. 1. Typical Stokes-Einstein relationship for $Fe(CN)_6^{3-/4-}$ ion in 1M KCl supporting electrolyte

The rate constants of heterogeneous electron exchange were determined from the cyclic voltammetry peak-to-peak separation, ΔE_p, according to the method of Nicholson[9,10] by using the numerically evaluated relationship between ΔE_p and the Ψ function:

$$\Psi = \frac{(D_o / D_R)^{\alpha 1/2} (RT)^{1/2} k_o}{(\pi n F D_o \nu')^{1/2}} \tag{4}$$

where α is the transfer coefficient, for the present case known to be 0.5, D_o and D_R are the diffusion coefficient of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, respectively, ν is the scan rate and n is the number of transferred electrons (here n = 1). At lower scan rates, the cyclic voltammetry peak-to peak separation was 58 ± 2 mV, corresponding to the electrochemi cally reversible process. The observed ΔE_p can be corrected by applying the following equation[11]:

$$\Delta E_{p,corr} = \Delta E_{p,obs} - 2 \mid i \mid R_u \tag{5}$$

where $\Delta E_{p,corr}$ is the corrected ΔE_p (in V), i is the voltammetric peak current (in A), and R_u is the uncompensated cell resistance (in Ω) . R_u can be determined from the slope of a plot of $\Delta E_{p,obs}$ *versus* i from voltammograms at a common scan rate for solutions of varying concentrations.

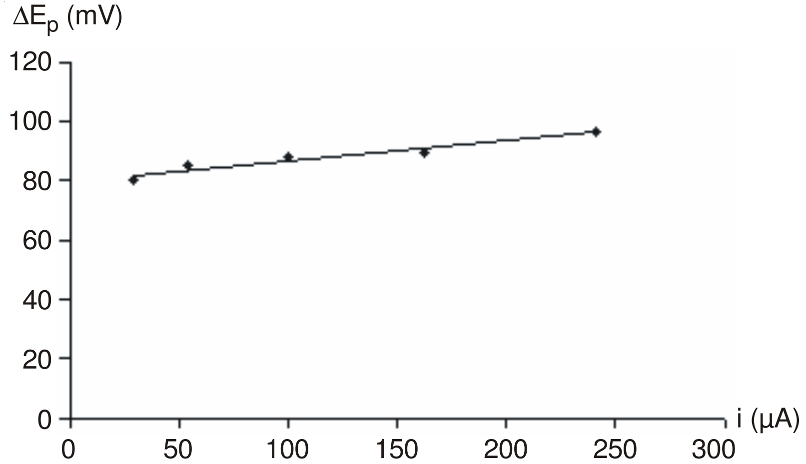

Fig. 2. Plote of ΔE_p *versus* peak current from cyclic voltammetry (ν = 100 mv/s) of $Fe(CN)_6^{3-}$ (1 M KCl) .The concentration of $Fe(CN)_6^{3-}$ was varied from 1 to 10 mM to affect the different peak current .The slope of each least-squares, linear fit yields $2R_u$

Tables 2 to 4 illustrate the procedure of the k^0 determination through the values of ΔE_p and Ψ for the given η. Several scans at different ν were performed and the average values at each η were determined in order to improve the statistics. The diffusion coefficients of reactant's oxidized the reduced forms, D_o and D_R, to be used in eqn. 4, independently determined in RDE experiments.

TABLE-1

DETAILED DATA FROM CYCLIC VOLTAMMETRY OF $Fe(CN)_6^{3-/4-}$ in 0.05 M KCl

Glucose (g/L)	R_u (Ω)	$\Delta E_{p,obs}$ (mv)	$\Delta E_{p,corr}$ (mv)
0	67.28	80.01	76.17
200	83.29	86.00	80.63
402	110.29	90.03	86.71
602	164.80	94.00	90.20

TABLE-2

DIFFUSION COEFFICIENT OF THE $Fe(CN)_6^{3-}$ AND $Fe(CN)_6^{4-}$ IONS, D_o AND D_R IN 0.05M CsCl AND HETEROGENEOUS ELECTRON EXCHANGE RATE CONSTANTS, k^0, Ψ AND ΔE AT DIFFERENT CONCENTRATIONS OF ADDED GLUCOSE AND RELATIVE VISCOSITY

Glucose (g/L)	D_o (cm^2/s)	D_R (cm^2/s)	ΔE_{obs}	ΔE_{corr}	Ψ	k^0 (cm/s)
0	7.62×10^{-6}	6.95×10^{-6}	78.95	75.13	1.60	0.0143
200	5.43×10^{-6}	4.11×10^{-6}	84.21	79.36	1.40	0.0092
402	4.18×10^{-6}	2.53×10^{-6}	89.04	85.01	0.98	0.0047
602	3.50×10^{-6}	1.97×10^{-6}	92.32	88.73	0.70	0.0030

TABLE-3

DIFFUSION COEFFICIENT OF THE $Fe(CN)_6^{3-}$ AND $Fe(CN)_6^{4-}$ IONS, D_o AND D_R IN 0.05 M KCl AND HETEROGENEOUS ELECTRON EXCHANGE RATE CONSTANTS, k^0, Ψ AND ΔE AT DIFFERENT CONCENTRATIONS OF ADDED GLUCOSE AND RELATIVE VISCOSITY

Glucose (g/L)	D_o (cm^2/s)	D_R (cm^2/s)	ΔE_{obs}	ΔE_{corr}	Ψ	k^0 (cm/s)
0	7.23×10^{-6}	6.75×10^{-6}	80.01	76.17	1.50	0.0134
200	5.10×10^{-6}	3.88×10^{-6}	86.00	80.63	1.30	0.0083
402	4.09×10^{-6}	2.37×10^{-6}	90.03	86.71	0.92	0.0042
602	3.46×10^{-6}	1.75×10^{-6}	94.00	90.20	0.75	0.0028

TABLE-4

DIFFUSION COEFFICIENT OF THE $Fe(CN)_6^{3-}$ AND $Fe(CN)_6^{4-}$ IONS, D_o AND D_R IN 0.05 M NaCl AND HETEROGENEOUS ELECTRON EXCHANGE RATE CONSTANTS, k^0, Ψ AND ΔE AT DIFFERENT CONCENTRATIONS OF ADDED GLUCOSE AND RELATIVE VISCOSITY

Glucose (g/L)	D_o (cm^2/s)	D_R (cm^2/s)	ΔE_{obs}	ΔE_{corr}	Ψ	k^0 (cm/s)
0	7.16×10^{-6}	6.58×10^{-6}	90.21	84.54	1.15	0.0100
200	4.89×10^{-6}	3.67×10^{-6}	93.21	87.10	0.90	0.0055
402	3.95×10^{-6}	2.26×10^{-6}	101.25	98.40	0.60	0.0026
602	3.38×10^{-6}	1.52×10^{-6}	108.80	102.83	0.58	0.0020

According to the results shown in Tables 2-4, increasing the viscosity of solutions would cause the diffusion coefficients of the redoxed system to be decreased.

Based on experimental results, the rate constant, k^0, was found to be strongly dependent on the nature of supporting electrolyte, is proven to display inversely dependence on the solution viscosity (water/glucose mixtures in NaCl, KCl and CsCl).

It is supposed that the average effective volume of cations might play the key role in this effect.

Fig. 3. displays the cyclic voltammograms recorded at the scan rate of 100 mV/s for the $Fe(CN)_6^{3-/4-}$ redox system at different glucose concentrations. At higher scan rates, the cyclic voltammetry peak to peak separation is increased gradually, indicating onset of the kinetic factor.

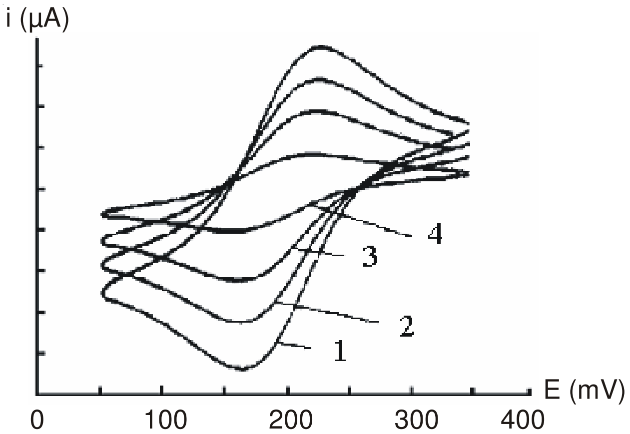

Fig. 3. Cyclic voltammograms recorded at the scan rate of 100 mv/s for the $Fe(CN)_6^{3-/4-}$ redox system at different concentrations of glucose peak current which decreases with the increase of the solution viscosity at the relative

In fact, the dependency of measured standard rate constant on the solution viscosity is depicted in the Fig. 4.

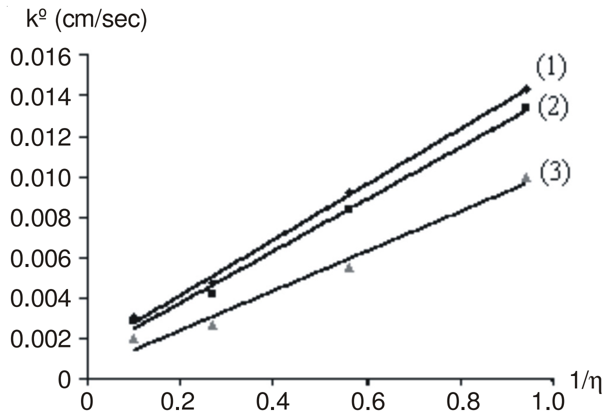

Fig. 4. Heterogeneous electron exchange rate constants, k°, for the $Fe(CN)_6^{3-/4-}$ couple in (1)- CsCl, (2)-KCl and (3)- NaCl aqueous solutions as functions of the relative viscosity obtained by different concentrations of added glucose

In previous studies attempts have been made to explain the catalytic effect of the cations by considering the kinetic pattern *via* incorporation of an extra cation into the activated complex of the redox process. In addition to those ions strongly associated with the reactant species (at least one counterion per Red and Ox states) by the following mechanism:

$$\begin{aligned} &M_n\,Fe^{II}(CN)_6^{(4-n)-} + M^+ \rightarrow [M_{(n+1)}\,Fe^{II}(CN)_6^{(3-n)-}] \\ &[M_{(n+1)}Fe^{II}\,(CN)_6^{(3-n)-}] \rightarrow [M_{(n+1)}\,Fe^{III}(CN)_6^{(2-n)-}] + e^- \\ &[M_{(n+1)}Fe^{III}\,(CN)_6^{(2-n)-}] \rightarrow M_n\,Fe^{III}(CN)_6^{(3-n)-} + M^+ \end{aligned} \tag{6a}$$

where M^+ is the cationic component of supporting electrolyte. This mechanism implies that the species M_n Fe $(CN)_6^{(4-n)-}$ and M_n $Fe(CN)_6^{(3-n)-}$ are the predominant associates of the redox species that present in the solution . In other words, the directly reacting Red and Ox species are each considered to be associated with an equal number of counterions. At the same time, our recent analysis of the dependency of the apparent standard potentials on the electrolytes concentrations points to the asymmetric character of ion association with respect to Red and Ox species (and in contrast to the mechanism expressed by eqn. 6a, to similar effective charges for both of them), namely,

$$Mn\,Fe^{II}(CN)_6^{(4-n)-} - M^+ -e^- \rightarrow M_{(n-1)}\,Fe^{III}(CN)_6^{(4-n)-} \tag{6b}$$

In particular, in the case of strong catalyst ions such as K^+, strongly suggest that predominant redox-active components would be $M_2Fe(CN)_6^{2-}$ and $MFe(CN)_6^{2-}$. Thus, the stoichiometry of the mechanism given by eqn. 6a is not compatible with the equilibrium data on standard potentials. Also there is no reason to think that the degree of stoichiometric ion association of reactant species with counter ions can be changed other than through the charge-transfer step itself, as is indicated by eqn. 6b (implying either pre-equilibrium or concerted mechanism of the addition of an extra cation). This is because, according to the standard potential data, the degree of ion association seems to be constant over a wide range of cation concentration[12]. It is supposed that the stoichiometry ion association effects reflected by standard potentials (contact ion associated) should be distinguished from the ion association of hydrated ions in the spirit of Debye-Hukel theory[13,14]. This becomes obvious with the comparison of the catalytic (kinetic) and equilibrium (thermodynamic) effects of different electrolytes on the corresponding parameters, the standard apparent rate constant, k^o, and the standard apparent redox potential, E^o, respectively[12].

It is presumed that the average effective volume of cations present in this zone should play the key role in this effect, with bigger cations (easily losing their salvation shells) being more compact and better charge-screening agent.

The Na^+ ions, preserving their salvation sphere to a larger degree (compact to K^+ or Cs^+) are less effective catalysts. This lead to a less.compact diffuse layer and less-effective screening of the reactants effective charges (for the effective radii of cations).

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