Solvent Friction Mechanism of an Elementary Charge-Transfer Step and Cation-Regulated Preequilibrium for a Pt/Fe(CN)$_6^{4-/3-}$ Electrode Process

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The apparent standard rate constant, k^0, for a Pt/hexacyanoferrate(II/III) electrode process, known to be strongly dependent on the nature and the concentration of supporting electrolyte (viz., of its cationic component), is proven to also display a lateral dependence on the solution viscosity (water/glucose mixtures, 0.24−2.0 M in KCl and LiCl). The viscosity performance is complementary to the catalytic effect of cations and seems to operate independently. The catalytic role of cations is discussed in terms of the preequilibrium concept, considering the influence of a double-layer potential on the effective concentration of reactant ions at the active site near the electrode. k^0 is inversely proportional to the solution viscosity, indicative of strong solute/ solvent and intersite electronic coupling, provided that the observed relationship is a manifestation of the solvent friction ("overdamped") mechanism for an elementary electron-transfer step.

1. Introduction

Profound studies of manifold electrode charge-transfer patterns have undoubtedly grown into one of the most intriguing topics of modern physical chemistry. In particular, the kinetics and mechanism of hexacyanoferrate(II/III) electron exchange at platinum and gold electrodes have long been the subjects of extensive studies (see refs 1−9). Initially this redox couple was considered to be a simple electrochemically reversible system, convenient for the testing of different formal models, unless some interesting features were disclosed incompatible with a simplified theoretical shape.

First of all, among established kinetic results, a clear dependence of the heterogeneous rate constant on the sort and concentration of the cationic component of the supporting electrolyte could be outlined,[4−6,9] exhibiting quasilinear (first-order) character in a surprisingly large range of electrolyte concentrations (e.g., up to 10 M for LiCl[5]). This behavior was explained by the inclusion of the additional stoichiometric cation into the activated complex formed in the course of the elementary electrochemical step, involving reactive species already associated with at least one cation[5,9] (see Discussion below). Another interesting kinetic manifestation of the hexacyanoferrate(II/III) electrode process was observed recently, as a specific dependence of the heterogeneous rate constant on the solution viscosity, varied by the addition of an electrochemically inert organic compound—glucose.[8] This kind of relationship, implying direct control of the charge-transfer step by slowly fluctuating relaxational degrees of freedom of the reactants' environment, was predicted theoretically[10−12] as a manifestation of so-called "strong electronic coupling" or a "solvent friction" mechanism of electron transfer and was disclosed also for some

other fast electrochemical[13−15] and homogeneous[16,17] charge-transfer processes.

In the meantime, along with the above-mentioned reliable results indicating rather complex but distinct electrochemical behavior, several reports revealed serious complications such as irreversible blocking of the electrode surface by hexacyanoferrate species or their products,[5,7,18] leading to the poor reproducibility of kinetic results. The latter circumstance may bring some skepticism to the possibility of further application of the hexacyanoferrate(II/III) couple as a model redox system. However, recent extensive studies of Fe(CN)$_6^{4-/3-}$ electrode kinetics on platinum using the techniques of chronoamperometry, square-wave voltammetry (SWV), and steady-state voltammetry[19] have made it obvious that the inhibition of the charge-transfer process, which appears to be more or less rapid depending on the nature and concentration of the electrolyte, can be readily eliminated by sufficient cleaning of the working electrode before each measurement. With a freshly polished electrode, we were able to obtain voltammograms exhibiting the theoretical aspect of SWV waves without any complication, even in the case of LiCl as supporting electrolyte, including the most "destabilizing" Li$^+$ ion.[5,7] Hence, we came to the conclusion that for all conventional electrolytes the redox reaction can be properly studied under appropriate experimental conditions and careful instrumental control. The results of the previous work[19] obtained for a wide spectrum of electrolytes (monovalent chloride salts) confirmed earlier observations of the quasilinear first-order dependence of the heterogeneous rate constant on the cation concentration and of the catalytic effect of cations changing in the order of NH$_4^+$ > Cs$^+$ > Rb$^+$ > K$^+$ > Na$^+$ > Li$^+$ ∼ N(CH$_3$)$_4^+$ > N(C$_2$H$_5$)$_4^+$.

In the present work, the dependence of the heterogeneous rate constant of the Pt/hexacyanoferrate(II/III) electrode process on the solution viscosity (varied by the addition of glucose)

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was rigorously investigated using different concentrations of two representative electrolytes, KCl and LiCl (exhibiting different catalytic effects), and the same experimental technique. The results obtained, together with the data on the catalytic effect of cations, are discussed in terms of the preequilibrium concept, considering the influence of the double-layer potential on the effective concentration of reactant ions at the electrode and invoking the solvent friction mechanism of the elementary electron-transfer step, within the framework of modern charge-transfer theory.

2. Methodology

The methodology exploited in the present work was the same as that described previously.[19] The standard apparent rate constants were determined in most cases by steady-state current measurements at a rotating platinum disk electrode.

Experiments were performed at 25 ± 1 °C with solutions of potassium hexacyanoferrate(III) 2×10^{-3} M in KCl and LiCl (0.24–2.0 M) in which the viscosity was varied by the addition of glucose (anhydrous (+)-D-glucose, Prolabo normapur). The reduction of the hexacyanoferrate(III) species by glucose is very slow and does not affect measurements when fresh solutions are used.

The relative viscosities for water/glucose mixtures are readily available in the literature,[20] while for water/electrolyte/glucose mixtures they are not. The KCl electrolyte does not affect the viscosity of aqueous solutions appreciably, while LiCl alters it significantly.[19] As was found in the previous work,[19] for hexacyanoferrate(II) and -(III) species in KCl and LiCl at concentrations higher than 0.1 M, the product of viscosity and diffusion coefficient, $\eta_r D$, is constant. The same relationship holds in water/electrolyte/glucose mixtures (see section 3 for details and also ref 8). Therefore, in the present work the parameter D is considered to be a variable equivalent to $1/\eta$.

Diffusion coefficients in water/electrolyte/glucose mixtures were determined by chronoamperometry at a static mercury drop electrode. The polarization was performed at potentials near the zero charge point (−0.5 V/SCE). We note that the reduction wave of the aldehyde group of glucose occurs at more negative potentials than −0.5 V/SCE (polarographic half-wave potential for the glucose = −1.56 V/SCE[21]).

3. Results

According to the Stokes−Einstein theory,[22−25] the diffusion coefficient of a diffusing particle is related to the solution viscosity by the following expression:

$$D = k_B T/\theta \pi r \eta \qquad (1)$$

where k_B is Boltzmann's constant, η is the viscosity, r is the hydrodynamic radius of the diffusing species, and θ is a constant which for the present case (for a particle of spherical symmetry which sticks to the solvent) could be set to 6.[25] The applicability of eq 1 was observed in a previous work[19] for electrolyte solutions with no viscous additives. It was also found to hold in the present work using water/electrolyte/glucose mixtures. The plots of D (our experimental data) versus $1/\eta_r$ (where the relative viscosity, η_r, was determined from ref 20) were straight lines in each case, intercepting the origin (Figure 1) as predicted by eq 1. Such a relation between D and $1/\eta_r$ shows that the conditions for validity of the Stokes−Einstein equation are fulfilled over the entire range of the glucose concentrations applied and that the degree of association of reactant species with specifically bound water molecules and counterions does
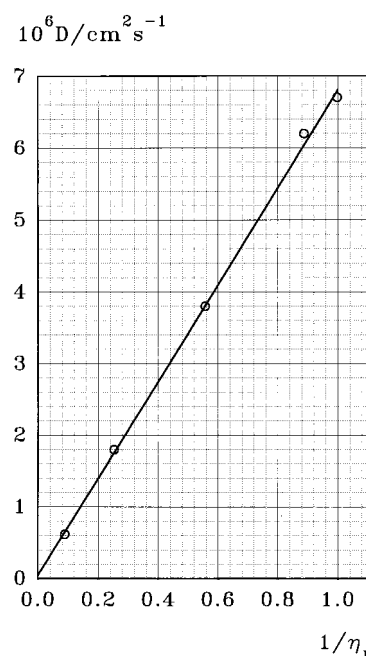

Figure 1. The typical Stokes−Einstein relationship for a hexacyano-ferrate(III) ion in 2 M KCl as supporting electrolyte.

not change with glucose concentration (see refs 8 and 24, and specifically ref 19 for a relevant discussion). The relationship expressed by eq 1 breaks down, e.g., for small solute particles weakly interacting with the solvent (see refs 25 and 26). In the present case, the validity of eq 1 is probably due to the relatively large size of the hexacyanoferrate species, as well as the strong solute/solvent coupling via the hydrogen-bonded network involving water molecules present in the first solvation sphere as a preferential solution component (see refs 25 and 27 and section 4 for further discussion).

Kinetic data on the effect of glucose concentration on the Pt/Fe(CN)$_6$$^{4-/3-}$ electrode process in the presence of 0.24, 1, and 2 M KCl (k^0 vs $1/\eta_r$) and 0.5, 1, and 2 M LiCl (k^0 vs D) are presented in Figures 2 and 3, respectively. In all cases, a linear dependence of k^0 versus $1/\eta_r$ or D was detected, in good agreement with the earlier results of Zhang et al.[8] obtained for 0.5 M K$_2$SO$_4$ as a supporting electrolyte. In Figure 4, kinetic data obtained with higher concentrations of KCl and LiCl (for which more experimental points were available), together with the data of Zhang et al.,[8] are presented using logarithmic coordinates (viscosities for the water/LiCl/glucose mixtures were calculated using the interpolated values of η_r and D for corresponding aqueous LiCl solutions[19] and eq 1). The slopes of these linear plots could be directly compared with the solute/solvent coupling parameters predicted theoretically (see the next section for further discussion). Interestingly, the quasilinear first-order dependence of the apparent rate constants on the cation concentration of the supporting electrolyte was preserved while going to the highest viscosities in the case of both electrolytes explored (Figures 2 and 3), indicating that the "catalytic" effect of cations and the "inhibiting" effect of the viscous additive are independent phenomena. Next, we discuss both effects within the unified formalistic approach.

4. Discussion

Catalytic Effect of Cations. In earlier papers,[5,9] an attempt to explain the catalytic effect of cations was made considering the kinetic pattern via incorporation of an extra cation into the activated complex of the redox process, in addition to those
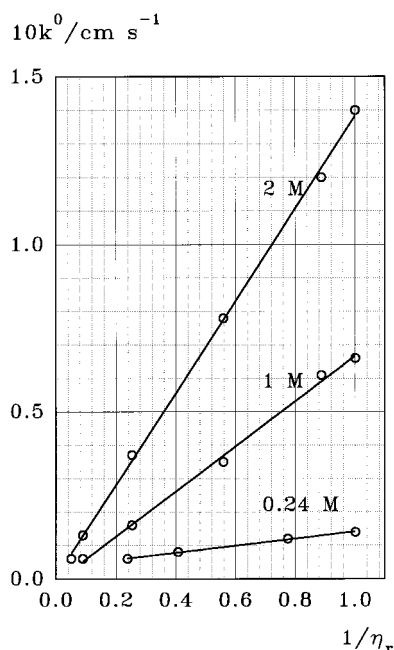
Figure 2. A plot of the apparent rate constant versus solution viscosity in the presence of KCl as supporting electrolyte.
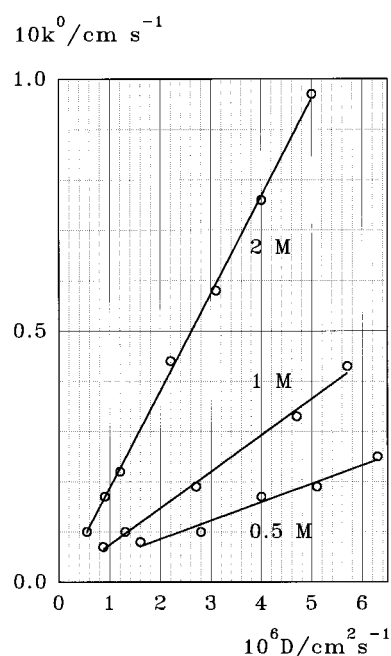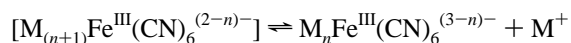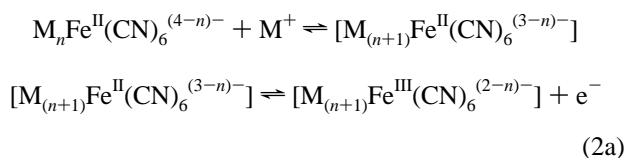

Figure 3. A plot of the apparent rate constant versus diffusion coefficient (variable equivalent to $1/\eta$) in the presence of LiCl as supporting electrolyte.

ions strongly associated with the reactant species (at least one counterion per Red and Ox states), by the following mechanism:

$$M_nFe^{II}(CN)_6^{(4-n)-} + M^+ \rightleftharpoons [M_{(n+1)}Fe^{II}(CN)_6^{(3-n)-}]$$

$$[M_{(n+1)}Fe^{II}(CN)_6^{(3-n)-}] \rightleftharpoons [M_{(n+1)}Fe^{III}(CN)_6^{(2-n)-}] + e^-$$

$$(2a)$$

$$[M_{(n+1)}Fe^{III}(CN)_6^{(2-n)-}] \rightleftharpoons M_nFe^{III}(CN)_6^{(3-n)-} + M^+$$

where M^+ is the cationic component of the supporting electrolyte. This mechanism implies that the species $M_nFe(CN)_6^{(4-n)-}$ and $M_nFe(CN)_6^{(3-n)-}$ are the predominant associates of the redox
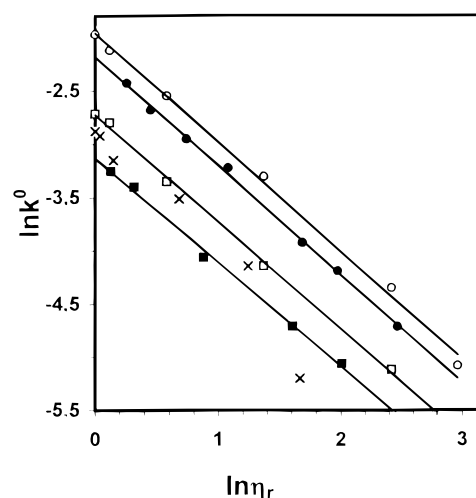

Figure 4. The data of Figures 2 and 3 plotted on logarithmic coordinates demonstrating the slope of 1. Supporting electrolytes: KCl, 2 M, open circles; KCl, 1 M, open squares; LiCl, 2 M, close circles; LiCl, 1 M, closed squares (data for LiCl are shifted downward for 0.1 units of *y* axes for clarity). The data of Zhang et al.[8] obtained under similar conditions are also presented for comparison (crosses).

species 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 dependence 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 eq 2a, to similar effective charges for both of them), namely,

$$M_nFe^{II}(CN)_6^{(4-n)-} - M^+ - e^- \rightleftharpoons M_{(n-1)}Fe^{III}(CN)_6^{(4-n)-}$$

$$(2b)$$
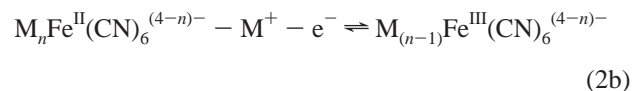
In particular, in the case of strong catalyst ions such as NH_4^+ or K^+, the data obtained for a wide range of electrolyte concentrations (NH_4Cl or KCl, 0.1–2.0 M;[19] KF, 0.2–7.0 M[5]) strongly suggest that predominant redox-active components would be $M_2Fe(CN)_6^{2-}$ and $MFe(CN)_6^{2-}$.[19] Takagi and Swaddle came to a similar conclusion when considering the effect of KCl on the homogeneous $Fe(CN)_6^{4-/3-}$ electron self-exchange reaction.[28] Thus, the stoichiometry of the mechanism given by eq 2a 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 counterions can be changed other than through the charge-transfer step itself, as is indicated by eq 2b (implying either preequilibrium or concerted mechanisms 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 concentrations[19] (see also further discussion below). We propose that the stoichiometric ion association effects reflected by standard potentials (contact ion association) should be distinguished from the ion association of hydrated ions in the spirit of Debye–Hückel theory, the electrochemical version of which is given by the Gouy–Chapman–Stern model of the diffusive part of an interfacial double layer (see refs 29 and 30). 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^0, and the standard apparent redox potential, $E°$, respectively.[19] Specifically, the effects of cations Li^+ and $N(CH_3)_4^+$ are similar for k^0 but very different for $E°$.

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At the same time, the effects of K$^+$ and NH$_4^+$ are similar for $E°$ but rather different for k^0.[19] Hence, we conclude that the mechanism given by eq 2a, though it explains formally the quasilinear first-order character of electrode kinetics with respect to cation concentration, is not consistent with our knowledge regarding ion association in the bulk and at the Pt/electrolyte interface. In contrast, the more realistic mechanism given by eq 2b, compatible with the equilibrium data, does not imply the catalytic role of cations, the origin of which is to be found elsewhere.

Bindra et al.[4] excluded interpretation of the catalytic effect of cations on the basis of a double-layer phenomenon, applying a widely accepted Frumkin expression[31] which in the context of the conventional preequilibrium concept could be presented as (see also refs 13, 32, and 33)

$$k^0 = \delta_r k^{et} \exp(-zF\Phi_r/RT) \tag{3}$$

where δ_r is the effective thickness in centimeters of a reaction zone at the reactive site within which the reactant should be located in order to contribute to k^0,[32] z is the effective charge of the reactant ion (as it was concluded above, probably $z_{Ox} = z_{Red} \cong -2 = $ const in most common cases, including our present interest[19]), Φ_r is the average potential at the active site near the outer Helmholtz plane (OHP, see below), and k^{et} is the rate constant for the intrinsic electron-transfer step near the equilibrium potential. The authors of ref 4 argued that, at the equilibrium potential positive of the point of zero charge in the absence of specific adsorption, Φ_r would be positive, and thus eq 3 predicts the decrease of the apparent rate constant with the increase of ionic strength. However, the same eq 3 can explain the catalytic (i.e., reverse) effect, provided that $\Phi_r < 0$ (and becomes more negative as the ionic strength increases), which for the present system in particular is possible only in the case of specific adsorption of the electrolyte anions.[29,30] The latter conjecture was rejected in ref 4 since the catalytic effect was observed in both Cl$^-$ and F$^-$ electrolyte solutions. It is well established that chloride ions adsorb specifically at the Pt/electrolyte interface in the potential region of our kinetic measurements (>0.3 V positive of the point of zero charge for pH-neutral electrolyte solutions).[34,35] Hence, at exceedingly high concentrations of corresponding electrolytes (total coverage of the metal surface by specifically adsorbed anions) the active sites for hexacyanoferrate species participating in the electron exchange process would be localized in the cation-enriched diffusive part of the double layer, near the OHP.[29,30] In contrast, the F$^-$ ions were known to be nonadsorbable, particularly on the mercury.[36] However, as it was shown recently by Hirota et al.[37] by in situ IR experiments, the ClO$_4^-$ ions (also assumed earlier to be nonadsorbable), present at 0.1 M, start to replace specifically adsorbed water at the Pt(111) surface at potentials more than 0.4 V (NHE). Presumably the F$^-$ ions do the same on Pt, as could be concluded from the similar trends in behavior of adsorbed water in both systems (mononuclear F$^-$ ions could not be detected directly at the surface or elsewhere by vibrational IR technique). Consequently, one can conclude that, for the case of the Pt electrode at moderate and high concentrations of conventionally employed electrolytes containing ClO$_4^-$, F$^-$, or SO$_4^{2-}$ anions, the structure of the double layer should be similar to the one in the presence of Cl$^-$. With this clue in mind, we shall try to show here that the observed catalytic effect of almost all conventional electrolyte cations on the Pt/hexacyanoferrate-(II/III) electrode process could be explained in a quantitative manner by the interfacial potential effects of the diffusive part of a double layer.

When the electrolyte concentration is high compared to one of the reactant species, the interfacial potential is formed exclusively by the charge distribution of electrolyte ions in the compact and diffusive parts of the double layer. Considering the equilibrium distribution of electrolyte components, including the cations, between the bulk and the proposed active site, from the equality of corresponding electrochemical potentials, one can derive the following equations (see ref 30)

$$\frac{\partial \Phi_r}{\partial \mu_o^+} = \frac{1}{zF}\left(1 - \frac{\partial \mu_r^+}{\partial \mu_o^+}\right) \tag{4}$$

$$\frac{\partial \Phi_r}{\partial \ln C_o^+} = \frac{RT}{zF}\left(1 - \frac{\partial \ln C_r^+}{\partial \ln C_o^+}\right) \tag{5}$$

where Φ_r is again the average potential at the active site near the electrode, μ_o^+ and μ_r^+ are the chemical potentials of cations in the bulk and the active site, respectively, and C_o^+ and C_r^+ are the corresponding concentrations. Assuming now that

$$(\partial \ln C_r^+)/(\partial \ln C_o^+) = \text{const} \geq 1,$$

i.e., the increase of cation concentration in the bulk should be accompanied by a corresponding exceeding increase of the concentration in the diffuse layer, we obtain that the potential at the active site is a function of the cation concentration in the bulk:

$$\Phi_r = \text{const} - \beta \ln C_o^+ \tag{6}$$

where $\beta > 0$, indicating that potential becomes more negative when the cation (electrolyte) concentration increases. Combining eqs 3 and 6, assuming also that δ_r and k^{et} are almost independent of electrolyte concentration, we obtain:

$$k^0 = (\text{const})C_o^+ \delta_r k^{et} \tag{7}$$

in which case the apparent standard rate constant should exhibit first-order dependence on the cation concentration via the potential modulation mechanism altering a cation-enriched region (reaction active site) of the diffuse part of the double layer. This in turn determines the concentration of reactant species at the active site in the same zone. We suppose 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 solvation shells) being more compact and better charge-screening agents. The Na$^+$ and Li$^+$ ions, preserving their solvation spheres to a larger degree (e.g., compared to K$^+$ or Cs$^+$) are less effective catalysts, probably due to larger effective radii comparable to those of tetraalkylammonium cations (which is reflected also by the ion-association characteristics[19]). This leads to less-compact packing of the diffuse layer and less-effective screening of the reactants' effective charges (for the effective radii of cations, see ref 38 and especially Figure 2 therein). We note that eqs 5 and 6 were derived first for the potential change in the compact part of the double layer and were valid in their original form for a relatively low electrolyte concentration (at a low degree of surface coverage). In contrast, in the present case these expressions are valid at any electrolyte concentration, significantly exceeding the concentrations of electrochemically active species. Indeed, in ref 9 it was demonstrated that the quasilinear first-order dependence of k^0 on [K$^+$] could be extended down to [K$^+$] $\approx 4.4 \times 10^{-3}$ M, after which some other mechanism seemingly starts to operate,

probably via direct adsorption of reactant ions on the electrode. In conclusion we propose the above-discussed conception as a reasonable alternative to the mechanism expressed by eq 2a, suggested by Peter et al.[5,9]

Viscosity-Dependent Rate Constant. In previous sections we have demonstrated that the catalytic effect of cations could be explained on the basis of eq 3 in the framework of preequilibrium formalism, considering the concentration effect of the double layer. As the observed kinetic viscosity effect (section 3) seems to be complementary to and formally independent of the above-discussed cation-regulated preequilibrium phenomenon, it is unlikely that it could be explained by the influence of added glucose on the preequilibrium static and dynamic characteristics connected with the ionic distribution in the diffuse part of double layer. Indeed, any kind of salting-out effects from the bulk would increase the effective concentration of the electrolyte at the Pt surface and, thus, the catalytic effect of cations, whereas we observe a decrease of the rate constant. The surface blocking effect by glucose is also unlikely, because according to refs 8 and 24, sugars are not active at the interfaces. Besides, the surface blocking effect hardly could initiate the very regular linear dependence of k^0 on $1/\eta_r$ or $\ln k^0$ on $\ln \eta_r$, as observed in previous papers[8,24] and in the present work (Figures 2−4).

According to the modern theory of charge-transfer processes,[10−12] in the case of strong electronic coupling between the electron donor and acceptor sites (the high solvent friction regime), the rate constant of the intrinsic electron-transfer step could be presented as

$$k^{\mathrm{et}} = \tau^{-1}(\Delta G^*/4\pi RT)^{1/2} \exp(-\Delta G^*/RT) \tag{8}$$

where ΔG^* is the activation (Gibbs) energy of the elementary charge-transfer step including inner- and outer-sphere contributions, $\Delta G^* = \Delta G^*_{\mathrm{in}} + \Delta G^*_{\mathrm{out}}$[39,40] (see discussion below), and τ is some relaxational characteristic of the solute/solvent system, representative of the slowest degree of freedom coupled with the electronic subsystem. In the simplest case, τ is connected with the solution viscosity via the equation[41]

$$\tau = 3V_{\mathrm{m}}\eta/RT \tag{9}$$

where V_{m} is the molar volume.

The dependence of k^0 on η according to eqs 8 and 9, in cases of variation of the latter parameter by the change of organic solvents, was proven earlier for some organic[14,17] and metal-locene[13,15] "low charged" redox couples. For redox species insoluble in organic solvents, such as the hexacyanoferrate(II/III) couple, the only way to vary the relaxational characteristics of the reactants' environment is the implication of different viscous additives (glucose, sucrose, etc.[8,24]). In a previous work,[8] the linear dependence of k^0 on $1/\eta$ (viscosity was varied by adding glucose) for the present redox system in 0.5 M K$_2$SO$_4$ was demonstrated to be in general accordance with eqs 8 and 9. Results of the present paper, obtained for two additional electrolyte solutions, are in a good agreement with the results of ref 8 (Figure 4) and with the ascription of the observed relationship to the solvent friction mechanism made there (see also Concluding Remarks below).

Kinetic manifestation of the heterogeneous rate constant of electron transfer via eqs 8 and 9 indicate that the intrinsic electron-transfer step is strongly coupled with the relaxational motion of the reactants' environment.[10−12] For previously studied electrochemical processes involving Fc$^{0/+}$ (ferrocene)[8] and Cr(EDTA)$^{−/0}$ [24] redox species, the modified dependence,

similar to eq 8, was observed:

$$k^0 = A\eta^{-\gamma} \exp(-\Delta G^*/RT) \tag{10}$$

(where A could be considered nearly constant in value). Applying eq 10 to the data of refs 8 and 24, the values of $\gamma \approx 0.7$ and 0.8 could be deduced, respectively, different from the theoretical value of 1, which corresponds to the strong coupling with the relaxational degree of freedom.[25,27] In our case, $\gamma = 1 \pm 0.03$ (Figure 4), pointing to the direct strong coupling. Observation of a strong coupling limit indicates that probably the first solvation sphere of the hexacyanoferrate reactant species (consisting of water molecules and counterions only, over the whole range of variation of glucose concentration, according to the above-discussed results for D) is directly coupled on one hand with the electronic subsystem in the electron-transfer step and on the other hand with the relaxational "bath" of the water/electrolyte/glucose medium (provided that the solvent friction mechanism is the case, see also Concluding Remarks below). In contrast, smaller values of γ may indicate that the first solvation sphere is less sensitive to the relaxational changes in the bulk solution. The latter situation is typical for biochemical transformations taking place in the environment of protein globules, for which the influence of viscous additives in most cases yields $0 < \gamma < 1$.[25,42]

For a limited range of temperatures, say 0−60 °C, the viscosity of pure water or water/electrolyte/glucose solutions could be presented as (see ref 27)

$$\eta = \eta_{\mathrm{o}} \exp(\Delta H_\eta/RT) \tag{11}$$

where η_{o} and ΔH_η can be considered to be independent of temperature. The equilibrium free energy to bring reactant particles to the active site, defined by eq 3, can be presented as

$$zF\Phi_{\mathrm{r}} = \Delta G_{\mathrm{r}} = \Delta H_{\mathrm{r}} - T\Delta S_{\mathrm{r}} \tag{12}$$

and, disregarding the weak temperature dependence of the preexponential term in eq 8, for the apparent standard (experimentally determined) rate constant one can write

$$k^0 = B \exp(-(\Delta H_\eta + \Delta H_{\mathrm{r}} + \Delta H^*)/RT) \tag{13}$$

where ΔH_η and ΔH_{r} are defined by eqs 11 and 12, respectively, and $\Delta H^* \cong \Delta G^*$ (as $\Delta S^* \approx 0$[40]). The preexponential term, B, is weakly dependent on the temperature and includes also the entropy contribution, arising mostly from the preequilibrium term (eqs 3 and 12, see further discussion below).

In the previous work[5] it was shown that the experimentally detected enthalpy of activation for the present electrochemical process, $\Delta H^{\ddagger} = \Delta H_\eta + \Delta H_{\mathrm{r}} + \Delta H^*$, determined within the temperature interval of 0−60 °C for a wide range of electrolyte concentrations (0.1−1.0 M KF and 0.5−4.5 M LiNO$_3$), is independent of the electrolyte nature and concentration and equals 20.0 ± 1 kJ/mol.[5] Hence, the features associated with a catalytic effect have a purely entropic origin, and thus $\Delta H_{\mathrm{r}} \approx 0$ (see also discussion in ref 5). The value of ΔH_η in the same temperature range could be determined from the published data[43] to be 14.5 ± 0.5 kJ/mol, constituting the larger part of the experimental value of the activation enthalpy. For the intrinsic enthalpy of activation we obtain $\Delta H^* = \Delta H^{\ddagger} - \Delta H_\eta = 5.5 \pm 1.5$ kJ/mol.

As was mentioned above, according to the theory of Marcus et al.[39,40] this value consists of inner-sphere (intramolecular) and outer-sphere (solution) contributions: $\Delta H^* = \Delta H^*_{\mathrm{in}} + \Delta H^*_{\mathrm{out}}$. The value of ΔH^*_{in} could be calculated on the basis of structural

and spectroscopic data[40,44] to be 1.5 ± 0.5 kJ/mol. Hence, $\Delta H^*_{\text{out(el)}} = 4.0 \pm 1.5$ kJ/mol. This value is too small and incomparable to one established for a homogeneous self-exchange process involving the same redox pair, $\Delta H^*_{\text{out(hom)}} = 27.7 \pm 0.5$ kJ/mol[45] (according to Marcus,[39] $\Delta H^*_{\text{out(hom)}} = 2\Delta H^*_{\text{out(el)}}$). Such a low value of $\Delta H^*_{\text{out(el)}}$ hardly could be explained by the lowering of a static dielectric constant in the double layer, on the basis of Marcus theory, or similar approaches;[39,40,46] hence, the estimated maximal effect can be of the order of 20%. Another more realistic reason may lie in the specific nature of the elementary electron-transfer mechanism itself. According to the theory of Zusman,[10,47] when the solution subsystem, undergoing reorganization in the course of electron transfer, consists of slower (relaxational) and fast (elastic) degrees of freedom, the solvent friction mechanism will be realized as a prevailing motion of the reactive system along the slower reaction coordinate. Therefore, the part of the activation barrier connected with fast variables is turned off.[47] In contrast, in the case of a nonadiabatic (weak coupling) regime, the contribution of fast (elastic) degrees of freedom should be much larger compared to slow (relaxational) variables.[46,47] It is not surprising to observe different mechanisms of the elementary electron-transfer step, viz., weak and strong coupling regimes, for homogeneous and electrochemical processes, respectively, since parallel electron transitions to or from a band of states near the Fermi level may result in the total probability of electron transfer near 1 and thus in much stronger intersite electron coupling in the case of electrode processes compared to analogous homogeneous electron self-exchange.[39] This conclusion is compatible also with the recent results on homogeneous and electrode electron exchange of ruthenium ammine complexes.[48] In the heterogeneous electron-transfer case, rapid-scan cyclic voltammetric studies showed a correlation of electron-transfer rate with solvent longitudinal relaxation time, τ_L, while deuterium NMR homogeneous self-exchange studies revealed no dependence of this kind, indicating a change to nonadiabatic from overdamped behavior upon going from the heterogeneous to the homogeneous process. This was also found to be the case in the present work and in recent NMR studies for homogeneous Fe(CN)$_6^{4-/3-}$ electron self-exchange (the extension of earlier ^{13}C NMR line-broadening studies[45] to water−glycerol mixtures[49] showed no change in the bandwidth due to the change of solution viscosity).

Concluding Remarks. The almost perfect inverse proportional character of the viscosity dependence ($\gamma = 1$, eq 10), demonstrated in the present work for the apparent standard rate constant of the representative electrode process, is a rare example of the manifestation of the limiting theoretically allowed case (eq 8) for an elementary charge-transfer mechanism. Analogous results were obtained in two different laboratories (described in ref 8 and the present work, respectively) by using different electrochemical techniques. Beforehand application of cycling voltammetry at different scan rates[26] to the same redox system revealed the same type of dependence for the rate constant (in the presence of glucose and 1M KCl as supporting electrolyte), with a somewhat larger experimental error[50] compared to the results of present work. There is a little doubt regarding the propriety of the determination of the viscosity-sensitive heterogeneous rate constant (k^0). However, the above-discussed ascription of the viscosity-controlled slow relaxational motion (contributing to k^0 via eq 8 or 10) to the specifically solvating water requires further justification. We consider below three additional possible mechanisms, including those with the direct involvement of quasidiffusional reactant motion as a slow (and viscosity-dependent) rate-determining process:

(a) The short-range motion of the reactant species directly coupled with the electron transfer, as it was considered for electrochemical proton[46] or heavy ion[51] transfer reactions. Obviously, involvement of this kind of motion is not likely, because the probability of electron hopping to/from any position near the OHP is already high enough[40,46] and the additional approach of reactant species to the electrode in this particular case is not required.

(b) "Dynamic diffuse layer effect" of the type considered by Levich[52] (see also ref 53 for a recent discussion on this topic), implying the rate-determining motion of the reactant species, without coupling of such a motion with the electron transfer. This mechanism can be excluded by taking into account the extremely high sensitivity of experimentally determined rate constants to the pretreatment procedure for a working electrode (also in the case of measurements in viscous media) and the observation of a specific Batler−Volmer relationship yielding transfer coefficients around 0.5,[2,19,54] as is expected for the rate-determining electrochemical steps involving electron transfer.

(c) The ion association/dissociation process as a slow relaxational motion coupled with the electron transfer expressed by eq 2b. Though such a coupling seems to be the plausible reason for the observed dependence, recent studies of the Fe(CN)$_6^{4-}$/DMV^{2+} (DMV^{2+} = dimethyl viologen) ion pair electrical field-induced short-range dissociation/association process in viscous media[55] indicated the stepwise rather than gradual change of the corresponding relaxation rate constant, while the heterogeneous rate constant determined in the present work revealed gradual change with the viscosity.

So we conclude that the reorientational motion of solvating water is most probably strongly coupled with the electron transfer within the rate-determining electrochemical step. As discussed recently by Agmon,[56] the slow relaxational motion in the solution, largely contributing to the macroscopic viscosity, should be connected to the reorientational mobility of water molecules along the librational degrees of freedom, with a characteristic time of $\tau \cong 0.5$ ps and an activation energy of $E_{\text{or}} = 14.5$ kJ/mol. It seems likely that the observed effect of macroscopic viscosity on k^0 is connected with the hinderance of the reorientational motion of water molecules, situated in the first solvation sphere of red and ox hexacyanoferrate reactant species, forming jointly fluctuating hydrogen-bonded networks with cyanoligands of reactant particles on one hand and with the bulk solution composed of water/glucose conglomerates on the other. The involvement of water molecules situated in the first solvation shells of hexacyanoferrate ions in the substantial rearrangement process accompanying the redox transformation was proven directly by using the difference near-infrared O−D overtone spectroscopy of heavy water as solvent.[57]

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