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The solvent friction mechanism for outer-sphere electron exchange at bare metal electrodes. The case of $Au/Ru(NH_3)_6^{3+/2+}$ redox system

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Abstract

The heterogeneous rate constant for the $Ru(NH_3)_6^{3+/2+}$ electron exchange at the bare gold electrode displays a power-law dependence on the solution viscosity (varied by addition of glucose, 0–600 g l^{-1}) with a negative power index of $\delta = 1$, indicative of the "full" solvent friction (adiabatic) mechanism for the intrinsic charge-transfer step. Comparison with related processes suggests that this mechanism mainly occurs at bare metal electrodes irrespective of the reactants' charged state and the method of viscosity variation. The adiabatic regime operates notwithstanding the presence of at least one layer of solvating water, and/or specifically adsorbed ions, contributing to the charge-transfer distance.
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1. Introduction

In a great number of published work 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 has been observed [1–9]

$$k_{el} \propto \eta^{-\delta}, \tag{1}$$

where δ is an "empirical" parameter with the typical magnitudes within the range of $0 < \delta \leqslant 1$. These results were usually considered as validating the solvent friction (adiabatic) mechanism, since the adequate contemporary theoretical model for the corresponding intrinsic (unimolecular) rate constant reads [10–15] (see [13] for a present update)

$$k_{et(SF)} = \nu_{eff}\left(\frac{\Delta G_r^*}{\pi^3 RT}\right)^{1/2} \exp\left(-\frac{\Delta G_a^*}{RT}\right), \tag{2}$$

where ν_{eff} is a characteristic frequency for the relaxation of solvent molecules coupled to the electron transfer, ΔG_r^* and ΔG_a^* are the reorganization and activation free energy parameters, respectively (vide infra), R is the gas constant and T is the absolute temperature. According to [16,17]

$$\Delta G_a^* = \frac{(\Delta G_r^* - \Delta G_0^*)^2}{4\Delta G_r^*} - H_{if}, \tag{3}$$

where ΔG_0^* is the equilibrium free energy gap of the intrinsic charge transfer process, and H_{if} is the electronic coupling matrix element. It has been common to use a dielectric continuum approximation to express ν_{eff}. For a Debye-type solvent one finds that [10–15]

$$\nu_{eff} = \nu_L = \tau_L^{-1} = \left(\frac{\varepsilon_s}{\varepsilon_\infty}\right)\frac{RT}{3\eta V_m}, \tag{4}$$

where τ_L is the so-called longitudinal relaxation time of the solvent polarization, proportional to the Debye relaxation time and, thus, to the solvent (solution) viscosity, η; ϵ_s and ϵ_∞ are static and high-frequency

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dielectric constants, respectively, and V_m is the molar volume. From Eqs. (2) and (4) it follows that $k_{et} \propto \tau_L^{-1}$ ("full" solvent friction limit, $\delta \to 1$), or $k_{et} \propto \tau_L^{-\delta}$ (in the case of intermediate regime, see also [3,8,10–15]).

In the framework of encounter-preequilibrium model, for the experimentally measured electrochemical (heterogeneous) rate constant at zero overvoltage ($\Delta G_0^* = 0$) one can write [14,15]

$$k_{el}^0 = k_{et}^0 K_A = k_{et}^0 \delta R_e \exp\left(\frac{-Z_{ef} F \Phi_r}{RT}\right), \quad (5)$$

where K_A is the statistically averaged equilibrium constant proportional to the probability of finding the reactant species at the reactive site near the electrode usually considered as the outer Helmholtz plane (OHP), δR_e is the "effective thickness" of planar reaction zone (which is expected to have the value of the order of 10^{-8} cm [14,15]) reflecting the major portion of the space integral over the intrinsic charge transfer constant (k_{et}^0), z_{ef} is the effective charge of a reactant ion, and Φ_r is the effective potential at the average active site near the electrode (in the vicinity of OHP) [14,15].

However, the experimental conditions under which the solvent friction mechanism shows up and transforms into the intermediate and nonadiabatic (tunneling) regimes, are still not well understood. It is important to comprehend for this type of processes how general is the solvent friction mechanism regarding the method of viscosity variation and the reactants' charged state. In the present paper we offer data for the viscosity-dependent heterogeneous rate constant for the highly charged redox couple, $Ru(NH_3)_6^{3+/2+}$, capable of direct strong hydrogen bonding (HB) with solvating water (as a HB donor), in the presence of two different supporting electrolytes, $NaNO_3$ and KCl (both at 1 M), which differently affect the double layer structure [18–20] in the relevant potential range. The results are discussed in comparison with similar literature data.

2. Experimental

2.1. Cyclic voltammetry (CV)

A three electrode configuration cell with the platinum plate as an auxiliary electrode and the saturated calomel electrode (SCE) as reference was exploited throughout. The working electrodes were 1.6 mm diameter disc gold electrodes (99.99% Au wire sealed in plastic cylinders, Bioanalytical System Inc.). 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 μm alumina powder (Buehler) on a Buehler polishing cloth, washed with milliQ water with following sonification.

The solutions used contained either 1 M $NaNO_3$, or 1 M KCl (Fluka) as supporting electrolytes and 1 mM $Ru(NH_3)_6Cl_3$ (Aldrich). The viscosity of solutions was varied by addition of anhydrous (+)-glucose (Fluka). Glucose concentrations 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 °C), respectively [7,8,21]. Up to 4 disk electrodes were used for each experiment at different glucose concentrations in order to improve the statistics. Different disputable aspects of the application of sugars in electrochemical experiments were discussed elsewhere [2,7,8].

2.2. Rotating disk electrode (RDE)

The diffusion coefficients, D_O, of the reactant's oxidized form, $Ru(NH_3)_6^{3+}$ were determined in 1 M $NaNO_3$ solutions at different concentrations of (+)-glucose (0, 200, 402 and 602 g l^{-1}) from the slope of the $I_L/\omega^{1/2}$ characteristics (I_L = limiting current/A, ω = angular velocity = $2\pi f/s^{-1}$, f = rotating frequency/s^{-1}) [22] on a Pt RDE (2.0 mm diameter, Radiometer). The corresponding values, D_R, for the reduced form, $Ru(NH_3)_6^{2+}$, were derived from the difference between $E_{1/2}$ and the $E^{o\prime}$ [23].

All the measurements were performed on the AMEL 5000 instrument operated by the CorrWare software (Scribner Associates Inc.). The temperature of all the experiments was 25 ± 1 °C, An error in the determination of rate constants due to the temperature uncertainty (estimated through the Arrhenius equation) does not exceed 2%.

3. Results and discussion

The rate constants of heterogeneous electron exchange were determined from the CV fast scan peak-to-peak separation, ΔE_p, according to the method of Nicholson [22,24,25], by using the numerically evaluated relationship between ΔE_p and the Ψ function

$$\Psi = \frac{(D_O/D_R)^{\alpha/2}(RT)^{1/2} k_{el}^0}{(\pi n F D_O v)^{1/2}}, \quad (6)$$

where α is the transfer coefficient, for the present case known to be 0.5 (see e.g. [26]); D_O and D_R are the diffusion coefficients of $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$, respectively, v is the scan rate and n is the number of transferred electrons (here $n = 1$). At lower scan rates the CV peak-to-peak separation was 58 ± 2 mV, corresponding to the electrochemically reversible process as predicted theoretically [22,24,25]. Under this condition the peak current is entirely determined by the diffusion process (vide infra). Fig. 1 displays the cyclic voltammograms all recorded at the scan rate of 100 mV s^{-1} for

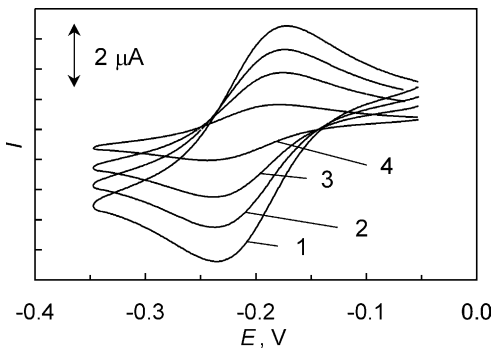

Fig. 1. Cyclic voltammograms for the $Au/Ru(NH_3)_6^{3+/2+}$ redox system at different concentrations of glucose, scan rate 100 mV s^{-1}. Peak current decreases with the increase of solution viscosity at the relative values of (1) 1.06, (2) 1.78, (3) 3.75 and (4) 9.92 (25 °C), respectively.

the $Au/Ru(NH_3)_6^{3+/2+}$ redox system at different concentrations of glucose.

At higher scan rates (above 0.5–2 V s^{-1}, depending on the glucose concentration), the CV peak to peak separation increased gradually, indicating onset of the kinetic factor [22,24,25]. Table 1 illustrates the procedure of the k_{el}^0 determination through the values of ΔE_p and Ψ. For a given η, several scans at different v were performed and the average values at each η were determined in order to improve the statistics.

The diffusion coefficients of reactant's oxidized and reduced forms, D_O and D_R, to be used in Eq. (6), were independently determined in RDE experiments (see Section 2). In the absence of glucose the optimized value of $D_O = 6.2 \times 10^{-6}$ cm^2 s^{-1} (25 °C, 1 M $NaNO_3$) is in good agreement with values reported by [27] ($D_O = 5.93 \times 10^{-6}$ cm^2 s^{-1} in 0.1 M phosphate buffer), [28] ($D_O = 6.2 \times 10^{-6}$ cm^2 s^{-1} in 0.8 M KCl + buffer, pH = 7.4) and [26] ($D_O = 5.43 \times 10^{-6}$ cm^2 s^{-1} at 20 °C, 1 M KF, after the correction for a temperature effect, implying changes of both T and η according to Eq. (7)). For the diffusion coefficient of reduced form, D_R, the optimized value of 5.0×10^{-6} cm^2 s^{-1} is smaller than expected, since the D_O/D_R ratio is expected to be lower than unity, as reported by [26,29], on the basis of a presumably larger solvation shell for the trivalent ion. However, recent calculations [30] of effective atomic charges for the present Ru(III)/(II) couple point to a positive charge evenly distributed over the central Ru atom and the 18 H atoms and to a small difference between the complex radii, as in agreement with [31,32]. This aspect allows for an essential insensitivity of the HB strength within the first solvation sphere on the complex charge state, as follows from the different near-infrared studies of O–D/N–D vibrational overtone spectra [33], and also the small variation of the electrostatic energies with the solvent [34]. It is then very likely that D_O/D_R is very close to, or even higher than, unity because, actually, geometric size of Ru(III) should be smaller than Ru(II), what follows as from our RDE experiments. Anyway, some variation of the values of these coefficients within any reasonable ranges does not affect significantly the values of heterogeneous rate constants (through Eq. (6)), which were the primary interest of this study. The optimized D_O and D_R values at different glucose concentration are collected in Table 2.

Table 1
Typical CV experimental series providing the average values of k_{el}^0 at fixed η according to Eq. (6)

v (V s^{-1})	ΔE_p (mV)	Ψ	k_{el}^0 (cm s^{-1})
3	71.6	2.12	0.0309
6	78.3	1.40	0.0289
10	82.5	1.10	0.0310
15	87.0	0.91	0.0294
Average	–	–	0.030

Experimental conditions for the given series: 1 M KCl; glucose 602 g l^{-1} ($\eta_r = 9.92$); $Ru(NH_3)_6^{3+}$ 1 mM; 25 °C.

The excellent linearity of the $\ln D$ vs. $\ln \eta$ dependence (not shown here) points to the validity of the viscous motion mechanism for both the $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ ions, provided that a variation of local viscosity is accounted for. In fact, as suggested also for the other kinds of solutes [35], the experimental data best fitting requires the use of a modified Stokes-Einstein equation [36], by introducing the corrective viscosity exponent a, according to

$$D = \frac{k_B T}{6\pi r \eta^a}, \tag{7}$$

where a spherical symmetry for the ruthenium complex is assumed. For both cations a resulted equal to 1.16 ± 0.02, to denote an increase of the local viscosity of the medium, which can be explained by the extensive HB of reactant ions with solvating water (which, in turn, is expected to interact strongly with the bulk glucose). From Eq. (7), the hydrodynamic radius of the $Ru(NH_3)_6^{3+}$ ion results $r = 3.7 \pm 0.1$ Å, a value which is higher than the geometric one (3.3 Å [31]) but lower than the estimated "rigid" hydrated radius (≈5 Å), which indicates that solvating water may contribute to the charge-transfer distance (vide infra). Due to equal or even lower diffusion coefficient, the same applies to the divalent $Ru(NH_3)_6^{2+}$ ion. The change of the solvating shell composition with the increase of the glucose concentration can be disregarded because the value of r remains unchanged throughout the viscosity variation.

Table 2 collects the standard rate constants for the rutheniumhexaamine complex for the two electrolyte solutions and at different glucose concentrations. There are only few reports on the heterogeneous rate constant for the electron exchange of $Ru(NH_3)_6^{3+/2+}$ couple at bare electrodes. Our values of 0.19 ± 0.02 and 0.29 ± 0.02 cm s^{-1} obtained in 1 M $NaNO_3$ and 1 M KCl, respectively, are close to the value of Gennett and

Table 2
Diffusion coefficients of the $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ ions, D_O and D_R, in 1 M $NaNO_3$ and heterogeneous electron exchange rate constants, k_{el}^0, for the $Ru(NH_3)_6^{3+/2+}$ couple in $NaNO_3$ and KCl aqueous solutions at different concentrations, c, of added (+)-glucose and related relative viscosities

c (g l^{-1})	η_{rw}	D_O (cm^2 s^{-1})	D_R (cm^2 s^{-1})	k_{el}^0 (cm s^{-1}) $NaNO_3$	k_{el}^0 (cm s^{-1}) KCl
0	1.06[a]	6.2E − 06	5.0E − 06	0.19	0.29
200	1.78	3.4E − 06	2.8E − 06	0.12	0.14
402	3.75	1.4E − 06	1.2E − 06	0.05	0.07
602	9.92	4.6E − 07	3.8E − 07	0.02	0.03

Experimental data are obtained at the $Ru(NH_3)_6^{3+}$ concentration of 1 mM.
[a] Value of relative viscosity in 1 M aqueous KCl is 0.995.

Weaver [37], 0.35 cm s^{-1} in 0.1 M KPF_6, and hence we concluded that the rate constant is much less sensitive to the electrolyte's composition and concentration as compared to the $Fe(CN)_6^{3-/4-}$ system, e.g. [7,8]. Winkler et al. [6] argued that the relative insensitivity of heterogeneous rate constant with the electrolyte type and concentration points to the location of the redox active site somewhat in distance from the OHP. Anyhow, in our cases the supposed distance from OHP (if any) is not large enough to deprive the observed fully adiabatic mechanism, vide infra.

In fact, the dependence of the measured standard rate constants on the solution viscosity, as depicted in Fig. 2 in logarithmic coordinates, results linear with a unity slope for both electrolytes. It is worthwhile to note that we can exclude any change of the rate constant as a result of the artefact due to the uncompensated resistance changes on the following grounds: (a) high concentrations of supporting electrolytes; (b) short distance between the Luggin capillary tip and the working electrode; (c) low concentrations of the reactant; (d) essential decrease of the (peak) current with the increase of resistance (viscosity), such that the product iR remains almost unchanged throughout; (e) the independence of k_{el}^0 determined through Eq. (6) on the CV scan rate (the essential basis for the application of the Nicholson method), Table 1. Consequently, the absolute error for

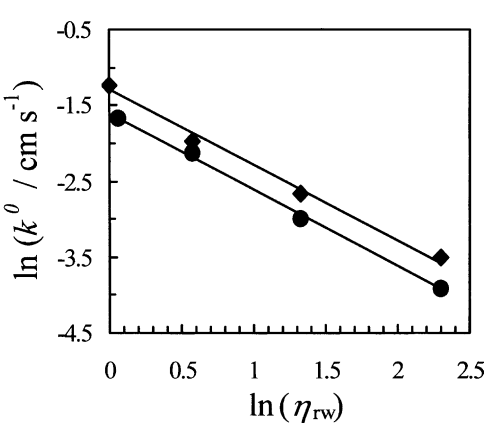

Fig. 2. Heterogeneous electron exchange rate constants, k_{el}^0, for the $Ru(NH_3)_6^{3+/2+}$ couple in $NaNO_3$ (circles) and KCl (rhombs) aqueous solutions as functions of the relative viscosity obtained by different concentrations of added (+)-glucose (in a double logarithmic scale).

the determination of ΔE_p (and hence, k_{el}^0) due to this effect is negligible (see also discussion in [8]), and in no case can be a reason for the observed viscosity pattern.

According to Eqs. (2) and (4), the slope of unity is theoretically predicted for the full solvent friction regime. Hence our values of $\delta = 1.00 \pm 0.04$ indicate that the electron transfer process follows the fully adiabatic regime, irrespective of the possible difference of the distance of the reacting site in the two different electrolytes (due to much stronger adsorption of Cl^- with respect to NO_3^- on bare Au [20]). For the $Fe(CN)_6^{3-/4-}$ system, in the case of bare metal electrode, along with the specifically adsorbed Cl^- ions, also the contribution to the charge-transfer distance of counter-ions, K^+, forming contact-type ion associates with the reactant $Fe(CN)_6^{3-/4-}$ ions, has been proposed [7,8]. Probably, this is not true for the case of $Ru(NH_3)_6^{3+}$ ion which instead, most likely, incorporates its solvating water into the charge-transfer distance. Essentially different behaviors (sensitivity) of two redox couples with respect to electrolytes' type and concentration probably is due to the completely different charge distribution (external vs. internal) for these complex compounds [32] (note also the opposite HB donor/acceptor character of these reactant ions). However, rather surprisingly, they demonstrate similar behavior with respect to the viscose additive – glucose, both exhibiting solvent friction (adiabatic) intrinsic charge-transfer mechanism. This phenomenon can be explained on the grounds of recent results for the $Fe(CN)_6^{3-/4-}$ redox process at SAM modified Au electrodes. The mechanism turnover to the nonadiabatic (tunneling) regime has been observed only at the reactant-electrode separations larger than 8.5 Å [8]. Nevertheless, the charge-transfer distance may affect the rate constant via the parameter H_{if} through Eq. (3).

Interestingly, research group of Curtis [38,39] studied the solvent dependence of a series of ruthenium pentaamines, $(NH_3)_5Ru^{II/III}(L)^{2+/3+}$ with L = 4-brompyridine, 4-picoline, etc., and found the correlation with solvent viscosity with slopes within the range of $\delta = 1.0 \pm 0.1$. The highest rate constants measured in organic solvents were about 1.5 cm s^{-1}. Notwithstanding the larger equivalent radii, it is highly probable that the substituted rutheniumpentaamine-L complexes may approach the electrode even closer than $Ru(NH_3)_6^{3+/2+}$,

via the π-conjugated ligand group, which provides more effective electron hopping pathway and increase of k_{el}^{0} via the increase of the parameter H_{if}, Eq. (3) (see e.g. [40]).

4. Conclusions

In conclusion, a comparison analysis of the present and literature data for the solvent (viscosity) effects on the outer-sphere heterogeneous electron exchange processes at bare metal electrodes shows that the solvent friction (adiabatic) mechanism can be considered as a preferable mechanism irrespective of reactants' charged state (including the mode of charge distribution) and the method of viscosity variation. Essentially different double-layer effects (leading to different reactant/counterion arrangement and preequilibrium properties at the active site near the OHP) are less important for the manifestation of intrinsic adiabatic mechanism exhibiting "universal" character at short electrode-reactant separations. The full solvent friction mechanism observed for the $Ru(NH_3)_6^{3+/2+}$ couple in two different electrolytes underlines a key role and advantage of this marker as a probe for the characterization of surface related processes.

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