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Influence of the supporting electrolyte on standard electrode reaction rate constants on mercury

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Abstract The influence of the nature and the concentration of the supporting electrolyte on standard reaction rate constants in non-aqueous solvents is discussed. Reductions of the monoatomic cations Zn^{2+} , Cd^{2+} and Eu^{3+} as well as the reduction of bis(biphenyl)chromium(I) serve as models to evaluate the electrolyte contributions to standard reaction rate constants. The limitations of the Marcus theory and the Frumkin model to account for the effect of the electrolyte on standard reaction rate constants are described. The dependence of the apparent standard reaction rates on electrolyte properties such as the supporting electrolyte concentration, the viscosity and the resistivity are evaluated. Differences in the activities of the electroactive species at the reaction site and in the bulk of the solution are considered for qualitative descriptions of the electrolyte effect on standard reaction rates of Eu^{3+} on the one hand and of bis(biphenyl)chromium(I) on the other.

Keywords Supporting electrolyte · Standard reaction rate constants · Dimethylsulfoxide · Dimethylformamide

Introduction

Electrochemical studies of reversible or nearly reversible electrode reactions in non-aqueous solvents have provided considerable information on the nature of solute-solvent interactions [1, 2]. Solvent-independent redox scales have been established based on reference redox systems such as ferrocene [3] and bis(biphenyl)chromium [4, 5]. The assumption of a solvent-independent redox potential for the system bis(biphenyl)chromium(I)/(0) has allowed the calculation of single-ion Gibbs energies

of transfer of cations [6]. The data derived from electrochemical measurements compare well with the results derived from solubility measurements based on the reference electrolyte (tetraphenylarsonium tetraphenylborate) assumption [6].

However, efforts to investigate the effects of solvents on electrode kinetics have been less successful. One problem (which, in the view of the author, has not yet been solved) is the influence of the nature and of the concentration of the supporting electrolyte on standard reaction rate constants. It has been known for a long time that the nature and the concentration of the supporting electrolyte affect the reaction rate of inorganic and organic compounds. Examples in non aqueous systems are the effect of the nature and the concentration of the supporting electrolyte on the reduction of *t*-nitrobutane in acetonitrile [7] and the influence of the nature of the supporting electrolyte on the first heterogeneous electron transfer to cyclooctatetraene in dimethylsulfoxide on platinum [8, 9].

The standard reaction rate constant of *p*-benzoquinone to its anion radical in dimethylformamide on a gold electrode depends on whether tetraethylammonium or tetrabutylammonium perchlorate was used as supporting electrolyte [10]. It appears, however, that the reaction rate does not depend on the supporting electrolyte concentration.

The kinetics of the electroreduction of *N,N'*-bis(salicylidene)-ethylenediaminocobalt(II) in dimethylsulfoxide depends on the nature of the supporting electrolyte [11]. The standard reaction rate constants for 0.1 mol dm⁻³ solutions decreased in the order: tetramethylammonium, sodium, tetraethylammonium, tetrabutylammonium perchlorate.

Very few research groups have addressed this problem for a sustained period of time. Data for monoatomic cations are available from the research groups of Fawcett and Lasia, and from our own studies. Alkali metal cations [12], alkaline earth cations [13], Zn^{2+} [14], Cd^{2+} [14, 15], Pb^{2+} [16], Cr^{3+} [17], and Eu^{3+} [18] have been studied in dimethylformamide, Na^+ [12], Zn^{2+} [14, 19],

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Cd^{2+} [20, 21, 22], and Eu^{3+} [23, 24, 25] in dimethylsulfoxide. Data for the electrode kinetics of Li^+ , Na^+ , K^+ , Cs^+ [12] and of Cd^{2+} [22] are available in hexamethylphosphoric triamide, for Na^+ and K^+ [12] as well as for Cu^+ [26] and Zn^{2+} in acetonitrile [27], and for Zn^{2+} in propylene carbonate [27].

Tetraalkylammonium perchlorates, especially tetraethylammonium (TEA^+) and tetrabutylammonium (TBA^+) perchlorate, and occasionally tetrapropylammonium (TPA^+) and tetramethylammonium (TMA^+) perchlorate as well as sodium and lithium perchlorate have served as supporting electrolytes. The dependence of the standard electrode reaction rates on the electrolyte concentration is given either in numerical form or in figures for some of the alkali metal cations [12] and alkali-earth cations [13], for Zn^{2+} [14], Cd^{2+} [15], Pb^{2+} [16], Cr^{3+} [17], and Eu^{3+} [18] in *N,N*-dimethylformamide, and for Zn^{2+} [19], Cd^{2+} [21], and Eu^{3+} [23, 24, 25] in dimethylsulfoxide.

The influence of the tetrabutylammonium perchlorate concentration on the one electron reduction of bis(biphenyl)chromium(I) is available for the solvents *N,N*-dimethylformamide [28], *N*-methylpyrrolidone(2), and *N*-methylthiopyrrolidone(2) [29].

Critical evaluation of the experimental kinetic data available and discussion

A general view of the experimental data for electrolyte-dependent standard electrode reaction rates in non-aqueous solvents, employing mercury as the working electrode, yields the following groups of depolarizers:

- i. The apparent standard electrode reaction rate constants of the redox process decrease as the concentration of the supporting electrolyte increases. Examples are the alkali metal cations, and the alkaline earth metal cations, Cu^+ , Zn^{2+} , Cd^{2+} , Pb^{2+} , Cr^{3+} , and Eu^{3+} . This group splits into two subgroups. The standard reaction rate constants of the alkali metal cations and the alkaline earth metal cations in tetraalkylammonium perchlorate solutions increase for a given concentration of the supporting electrolyte in the order TMA^+ , TEA^+ , TPA^+ , and TBA^+ , while the standard reaction rates of Cu^+ , Zn^{2+} , Cd^{2+} , Pb^{2+} , Cr^{3+} , and Eu^{3+} decrease in this order.
- ii. The standard electrode reaction rate constant increases with increasing supporting electrolyte concentrations, as observed for the reduction of bis(biphenyl)chromium(I) and for some supporting electrolytes for the reduction of *t*-nitrobutane.
- iii. No influence of the concentration of the supporting electrolyte on the standard electron rate constants was observed, but the reaction rate depends on the nature of the supporting electrolyte.

Two different approaches have been used in the literature to account for the standard reaction rate constants. The Frumkin correction was applied [30, 31, 32]

to correct the experimental data for the influence of the double layer, and efforts to describe the influence of solvents on the k_s^{app} values in terms of the Marcus theory [33, 34, 35] have been undertaken.

Both the Frumkin and the Marcus model will be evaluated here in respect to their ability to account for electrolyte effects on standard reaction rate constants.

The Frumkin equation

$$\ln k_s^{\text{app}} = \ln k_s^{\text{true}} + (\alpha_c^{\text{true}} n - z) \frac{F\phi_2}{RT} \quad (1)$$

where n is the number of electrons in a single-step electrode process, α_c the corrected transfer coefficient, z the charge of the depolarizer and ϕ_2 the potential drop across the double layer, does not specifically refer to the nature of the solvent.

The calculation of the ϕ_2 potentials according to Eq. 2 is based on the diffuse layer theory [36, 37, 38]:

$$\begin{aligned} q^{2-s} &= -(q^m + q^i) \\ &= (2 \varepsilon_0 \varepsilon_r RT)^{1/2} \left(\sum_j c_j (\exp(-z_j \phi_2 F/RT) - 1) \right)^{1/2} \end{aligned} \quad (2)$$

where q^{2-s} is the charge density of the diffuse double layer, q^m is the charge density at the electrode and q^i the charge density of the specifically adsorbed ions in the inner layer. The only explicit solvent property included in this equation is the macroscopic dielectric constant, although q^{2-s} is affected by the supporting electrolyte and therefore also by the solvent through the experimentally-derived potential of zero charge as the reference potential and the double layer capacitance.

The Frumkin corrected standard reaction rate constants (k_s^{Frumkin}) should be independent of the concentration and the nature of the supporting electrolyte. Papers in which the Frumkin correction was applied to account for the concentration dependence of the standard reaction rate constants (k_s^{app}) of cations, however, reported that k_s^{Frumkin} depended on the electrolyte concentration and also on the nature of the electrolyte [12, 14, 15, 17, 21, 23, 24, 25].

The Marcus equation, modified for an electrode reaction, assumes that the electron transfer is the rate limiting step in the overall electrochemical process [33, 34, 35].

$$k = Z\kappa\rho e^{\left(\frac{-\Delta G^*}{RT}\right)} \quad (3)$$

Here Z is the collision number, while k_{el} is an averaged probability of remaining on the lowest surface on the passage through the intersect region. k_{el} for adiabatic reactions is 1. ρ , a ratio of mean displacement, is usually taken to be unity.

ΔG^* for an electrode reaction is assumed to be

$$\begin{aligned} \Delta G^* &= \frac{w^r + w^p}{2} + \frac{\lambda_{\text{el}}}{4} + \frac{nF(E - E'_0)}{2} \\ &+ \frac{[nF(E - E'_0) + w^p - w^r]^2}{4\lambda_{\text{el}}} \end{aligned} \quad (4)$$

w^r is the work required to bring the reactants together up to their separation distance, w^p is the corresponding term for the products for the same separation distance. E_0' is the formal standard potential. λ_{el} is the intrinsic "reorganization factor", describing the reorganization of the coordinates in energy terms. This rather complex equation, containing several unknown and experimentally not accessible parameters, is usually reduced to:

$$k_s^{corr} = Z\kappa_{el}e^{\left(\frac{-\lambda_{el}}{4RT}\right)} \quad (5)$$

This simplification of the Marcus equation pertains to electrode reaction rate constants at the formal potential. The conditions for neglecting the w^r and w^p terms have been discussed [39, 40].

The reorganization energy λ_{el} is usually separated into an inner term λ_i and an outer term λ_o . The inner reorganization energy is calculated by summing over the normal vibrational modes of the reactant. It is difficult to envision any effect of the supporting electrolyte concentration on this term. λ_o is based on the Born model of ion solvation and the Franck-Condon principle. λ_o for a single electron electrode reaction is given as

$$\lambda_o = \frac{e_0^2}{8\pi\epsilon_0} \left(\frac{1}{a_0} - \frac{1}{R} \right) \left(\frac{1}{n_D^2} - \frac{1}{\epsilon_s} \right) \quad (6)$$

a_0 is the radius of the reactant treated as a sphere, R is generally, but not always, taken as twice the distance from the center of the molecule to the electrode, n_D^2 (square of the refractive index, considered to be ϵ_{op}) and ϵ_s are the optical and the static relative permeability. This term may include solvent and possibly electrolyte contributions to the standard reaction rate constant.

However, the description of the ion (solute)–solvent interaction within the Born model is not in agreement with the current state of solution chemistry. Even for salts, it can be shown that the Gibbs energies and enthalpies of hydration calculated from the Born model do not agree with the experimental data. Even if one insisted on using the Born model it is difficult to obtain data for the relative permittivity of electrolytes. A few data for LiCl, NaI, LiNO₃ and NaNO₃ are available for dimethylsulfoxide and for NaI and NaClO₄ in dimethylformamide. The relative permittivity decreases with the electrolyte concentration and depends on the nature of the electrolyte [41]. Refractive indices of electrolytes are usually not available for the supporting electrolytes used in electrochemistry. Data measured for various sodium perchlorate solutions in dimethylsulfoxide did not show any change in the refractive index with the sodium perchlorate concentration within the precision of the experiment [25]. A comparison of the $\left(\frac{1}{n_D^2} - \frac{1}{\epsilon_s}\right)$ term for 0.1 mol dm⁻³ NaI (ϵ_s : 46.1 [41]) and 1.0 mol dm⁻³ NaI (ϵ_s : 35.4 [41]) solution in dimethylsulfoxide (ϵ_s : 46.40; n_D : 1.4773) yields 0.437 and 0.430. The data for 0.13 mol dm⁻³ NaClO₄ (ϵ_s : 36.32 [41]) and 1.02 mol dm⁻³ NaClO₄ (ϵ_s : 26.86 [41]) solutions in dimethylformamide (ϵ_s : 37.24; n_D : 1.4282) are 0.463 and 0.453. It is

hard to envision that such a modest change in the $\left(\frac{1}{n_D^2} - \frac{1}{\epsilon_s}\right)$ term may be responsible for changes of the order of one magnitude in the k_s^{app} values observed for Cd²⁺ and Eu³⁺ in dimethylsulfoxide and dimethylformamide. The electrostatic term cannot account for an increase in the standard reaction rate constants for organic or metal-organic molecules and for a decrease in cations with increasing supporting electrolyte concentration. Another generally unsolved problem in the treatment of electrode reactions is the lack of knowledge about the distance from the center of the depolarizer to the electrode surface.

The pre-exponential factors were later expanded to include a "pre-equilibrium" [42, 43, 44], modifying the Marcus equation to:

$$k_s = \kappa K_p v_n e^{\left(\frac{-\Delta G^*}{RT}\right)} \quad (7)$$

where K_p is the equilibrium constant of the precursor complex formation and v_n is the nuclear frequency factor.

$$v_n = \tau_L^{-1} (\Delta G^*/4\pi RT)^{1/2} \quad (8)$$

Based on this equation, correlations between the standard reaction rate constants and the longitudinal relaxation time of the solvent [45, 46, 47, 48, 49, 50, 51, 52, 53, 54] were investigated. The longitudinal relaxation time of a solvent, however, is not an unambiguous property. It is derived from $\tau_L = \tau_D(\epsilon_\infty/\epsilon_s)$ where τ_D is the Debye relaxation time, ϵ_∞ the infinite frequency relative permittivity, and ϵ_s is the static relative permittivity. From the limited data available for non-aqueous solvents, it becomes clear that all of these properties depend on the concentration of the dissolved electrolyte [41]. With the absence of data for the electrolytes used in electrochemistry it is impossible to search for correlations.

Since neither the rather complex electrostatic parameters nor the proposed models for electron transfer reactions describe the electrolyte effect on standard reaction rate constants, experimentally accessible electrolyte properties will be evaluated in order to learn about the propensity which relates to the observed changes in the k_s^{app} values. Such a search is hindered by several problems. Properties of electrolytes are in most cases not available, even if the solvent properties have been published. Furthermore, standard reaction rate constants were obtained by different methods such as cyclic voltammetry, convolution techniques, AC polarography (Sluyters and Randles evaluation) or chronoamperometry. In several cases the k_s^{app} values for a given redox system in a given supporting electrolyte in the same solvent differs considerably. An example is the kinetic data for the reduction of Zn²⁺ in propylene carbonate and in acetonitrile obtained from cyclic voltammetry and from chronoamperometry. But a suitable set of data is available to try to hunt for relations between the standard reaction rate constants and electrolyte properties. In order to exclude any possible

contribution to the electrode reaction rate from the electrode material, only redox systems measured on mercury will be considered. One set of data is the reduction of the monoatomic cations Zn^{2+} and Cd^{2+} to the respective amalgam; another is the reduction of Eu^{3+} to Eu^{2+} in dimethylsulfoxide and dimethylformamide. The natural logarithm of the apparent standard reaction rate constant is – for the concentration range investigated – in all cases a linear function of the square root of the supporting electrolyte concentration, as shown for Cd^{2+} in dimethylformamide (Fig. 1) and for Zn^{2+} in dimethylsulfoxide (Fig. 2). Such a dependence has also been reported for Eu^{3+} in dimethylformamide [18] and in dimethylsulfoxide [23, 24, 25].

Several properties also depend – at least to a good approximation – on the square root of the supporting electrolyte concentration for the concentration ranges usually employed in electroanalytical chemistry. One such property is the diffusion coefficient of the cation. This dependence has been employed to calculate the diffusion coefficient of the solvated cations in the “supporting electrolyte free” solvent. [25]. Linear relations between the natural logarithm of the reaction rate constant and the diffusion coefficient of the cation were observed for the reduction of Cd^{2+} and Eu^{3+} in dimethylsulfoxide and dimethylformamide, systems for which diffusion coefficients have been published (Fig. 3).

Detailed information on electrolyte properties for various supporting electrolyte concentrations is more or less only available for dimethylsulfoxide. A linear dependence of the logarithm of the standard reduction rate constant of Eu^{3+} on the reciprocal of the viscosity was observed (Fig. 4). It should be noted that the ϕ_2 -potential also depends on the square root of the sup-

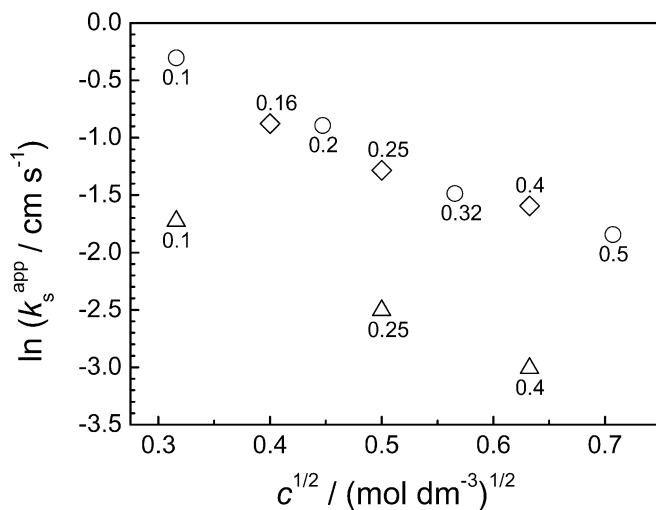


Fig. 1 Dependence of the natural logarithm of the apparent standard reaction rate constant for the reduction of Cd^{2+} in dimethylformamide on the square root of the concentration of the supporting electrolyte. Circles: tetraethylammonium perchlorate, diamonds: tetrapropylammonium perchlorate, triangles: tetrabutylammonium perchlorate

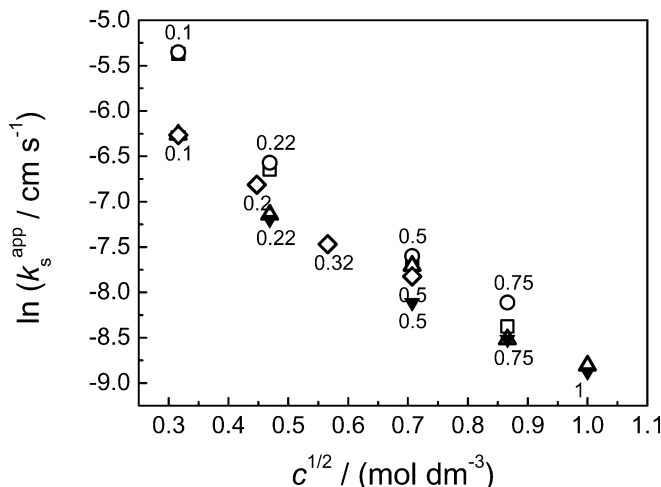


Fig. 2 Dependence of the natural logarithm of the apparent standard reaction rate constant for the reduction of Zn^{2+} in dimethylsulfoxide on the square root of the concentration of the supporting electrolyte obtained by different methods. Tetraethylammonium perchlorate, squares: cyclic voltammetry; circles: chronoamperometry. Tetrabutylammonium perchlorate, unfilled triangles: cyclic voltammetry; filled triangles: chronoamperometry; diamonds: average values from [14]

porting electrolyte concentration, as shown in Fig. 5 for the reduction of Eu^{3+} in dimethylsulfoxide.

The most striking relation, however, is the linear dependence of the standard reaction rate constant on the resistivity of the electrolyte. This relation was observed for the reduction of Zn^{2+} , Cd^{2+} and of Eu^{3+} in the solvents dimethylformamide and dimethylsulfoxide [25]. An example of this dependence is given in Fig. 6. Despite the completely different overall reaction schemes for Cd^{2+} , which is reduced to the amalgam, and Eu^{3+} ,

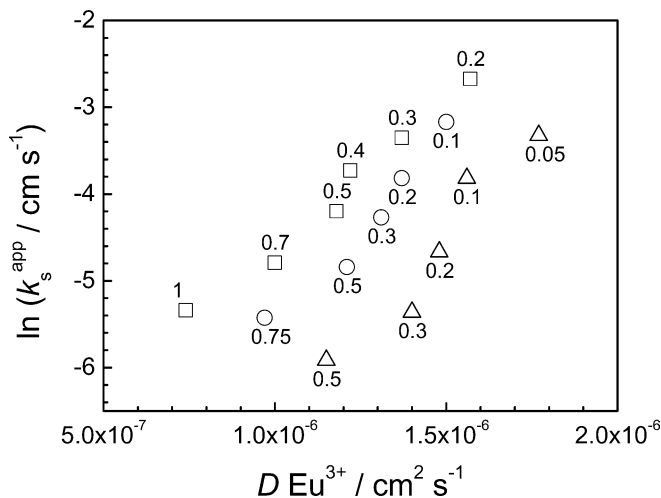


Fig. 3 Dependence of the natural logarithm of the standard reaction rate constant on the diffusion coefficient of Eu^{3+} in various concentrations of the supporting electrolytes in dimethylsulfoxide. Squares: sodium perchlorate; circles: tetraethylammonium perchlorate; triangles: tetrabutylammonium perchlorate

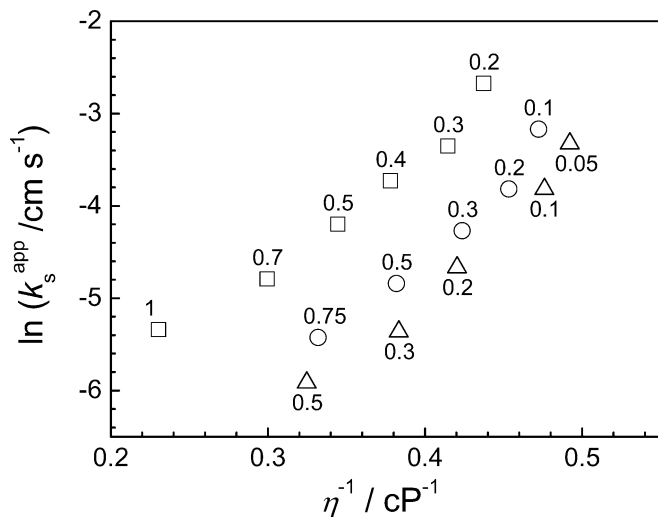


Fig. 4 Dependence of the natural logarithm of the apparent reaction rate constant for the reduction of Eu^{3+} on the reciprocal of the viscosity. Squares: sodium perchlorate; circles: tetraethylammonium perchlorate; triangles: tetrabutylammonium perchlorate

which converts to the solvated Eu^{2+} , it is striking how similar the reaction rate constants for these two processes are, especially for tetraethylammonium perchlorate.

Although several correlations of the standard reaction rate constants and electrolyte properties were observed, none of these properties led to an electrolyte-independent standard reaction rate constant. In all correlations tested so far, differences in the data for sodium, tetraethylammonium or tetrabutylammonium

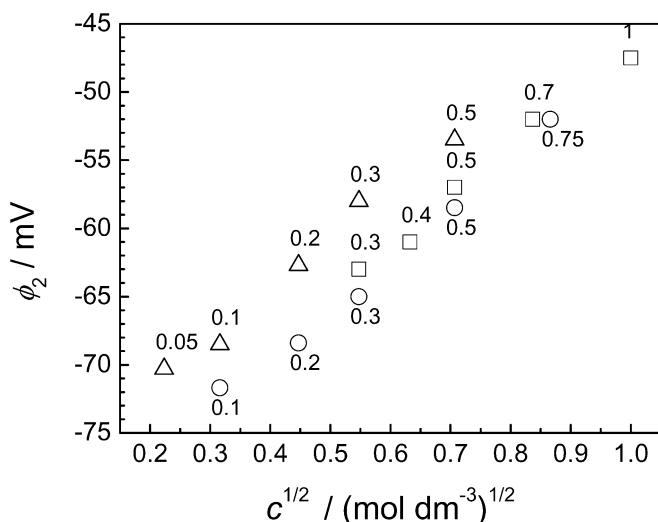


Fig. 5 Dependence of the ϕ_2 -potential on the square root of the supporting electrolyte concentration for the reduction of Eu^{3+} in dimethylsulfoxide. Squares: sodium perchlorate; circles: tetraethylammonium perchlorate; triangles: tetrabutylammonium perchlorate

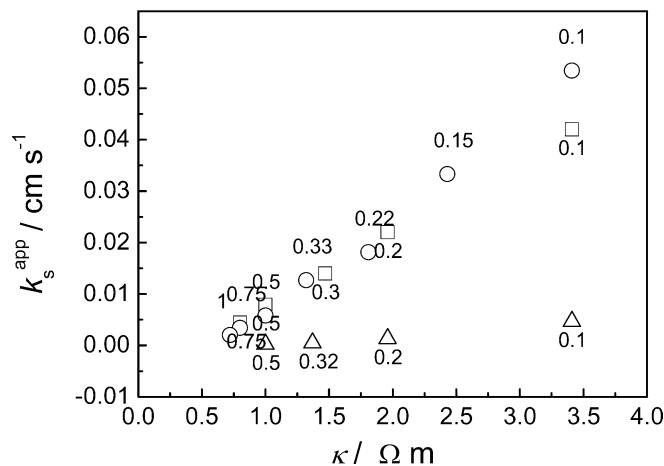


Fig. 6 Dependence of the standard reaction rate constants of (squares) Eu^{3+} , (circles) Cd^{2+} , and (triangles) Zn^{2+} on the resistivity of various concentrations of tetraethylammonium perchlorate in dimethylsulfoxide

perchlorate as supporting electrolytes were observed. This is somewhat surprising since all of the supporting electrolytes contained perchlorate as the anion. Ion pairing between the Eu^{3+} and the perchlorate ion has been reported, and association constants ranging from 11–15 have been given [23, 24, 25]. The association constants are practically the same.

Several possibilities for the rate limiting step in the reduction of monoatomic cations have been proposed, namely the transport through the double layer to the reaction site or the electron transfer itself. Another possibility is a “pre-equilibrium” between the depolarizer at the electrode surface (or the reaction site) and in the bulk of the electrolyte. The data set available at this time is quite limited and does not allow a clear distinction between these possibilities. A difference in the activity of the depolarizer at the electrode and in the bulk of the solution may be an explanation which comprises both the decrease in the reaction rate constants for Cd^{2+} , Zn^{2+} and Eu^{3+} with increasing supporting electrolyte concentrations, and the increase in the standard reaction rate constants of bis(biphenyl)chromium(I) (Fig. 7) and organic substances with an increase in the supporting electrolyte concentration. The mentioned monoatomic solvated cations must compete with the cations of the supporting electrolyte for positions in the reaction plane, while a “salting out effect” of the organic molecules may increase their concentration at the reaction site (Z. Galus, private communication). “Salting out” is mainly a solution effect and does not necessarily require specific adsorption of the reactant on the electrode surface.

This model is at present mainly of a qualitative nature. It should be a stimulus for further research into the effects of the electrolyte (nature and concentration) on standard reaction rate constants, and also for providing the respective electrolyte properties.

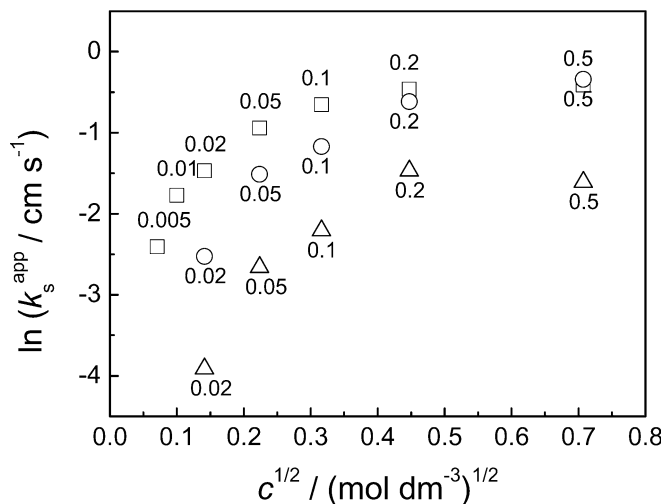


Fig. 7 Dependence of the natural logarithm of the apparent standard reaction rate constants of bis(biphenyl)chromium(I) on the square root of the tetrabutylammonium perchlorate concentration in (squares) *N,N*-dimethylformamide, (circles) *N*-methylpyrrolidone and (triangles) *N*-methyl-thio-pyrrolidone(2)

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