Influence of solvents on the rate of electrode reactions

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Abstract - The influence of single and mixed solvents on the rate of ele-
ctrode reactions is discussed.

INTRODUCTION

The thermodynamic and kinetic parameters of an electrochemical reaction are generally influ-
enced to a quite significant degree by a change in the medium in which it is taking place.
Let us consider the electroreduction of solvated metal ions which exist in the solution
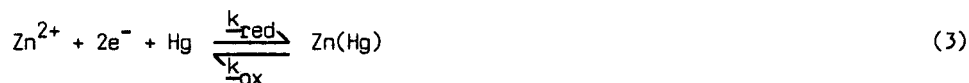
$$Ox + \underline{n} \ e^- \ \underset{\underline{k}_{ox}}{\overset{\underline{k}_{red}}{\rightleftharpoons}} \ R \tag{1}$$

where $\underline{k}_{red}$ and $\underline{k}_{ox}$ denote the rate constants at a given potential of electroreduction and
electrooxidation, respectively.
The product R of reaction (1) may be soluble either in solution as a metal ion of lower oxi-
dation state, or in mercury when mercury electrodes are used and electroreduction (1) pro-
ceeds to the metal.
An example of the first type of reaction may be represented for instance by the equation

$$Eu^{3+} + e^- \ \underset{\underline{k}_{ox}}{\overset{\underline{k}_{red}}{\rightleftharpoons}} \ Eu^{2+} \tag{2}$$

and the second by

$$Zn^{2+} + 2e^- + Hg \ \underset{\underline{k}_{ox}}{\overset{\underline{k}_{red}}{\rightleftharpoons}} \ Zn(Hg) \tag{3}$$

where zinc amalgam is the final product.
If we would assume that the reaction (1) is irreversible, the cathodic current of such a
reaction, $\underline{I}_c$, is given by the expression

$$\underline{I}_c = nFAc_{ox}^{\delta} \ \kappa_{el} \underline{Z}_{el} \exp\left[\frac{-\Delta\underline{G}^{\neq}}{RT}\right] \exp\left[\frac{-\alpha nF(E - \underline{E}_f^O)}{RT}\right] \exp\left[\frac{(\alpha\underline{n} - \underline{z})F \ \varphi_2}{RT}\right] \tag{4}$$

The change of solvent may influence the following parameters which appear in equation (4):
the formal potential, $\underline{E}_f^O$, the activation energy, $\Delta\underline{G}^{\neq}$, the concentration of reactant at the
reaction site, $\underline{c}_{ox}$, the transmission coefficient, κ_{el}, and the potential of the outer
Helmholtz plane, φ_2.
The heterogeneous collision frequency factor, $\underline{Z}_{el}$, and Tafel slopes, may also be dependent
to some extent on the nature of solvent.
When the reaction is quasireversible, a more complex equation than (4) should be used to
describe $\underline{I}_c$ as then the recorded current should be also a function of the solvent dependent
reactant diffusion coefficient.

An illustration of the influence of the solvent on both $\underline{E}_f^0$ and the kinetics of the Mn(II)/Mn(Hg) system is shown in Fig. 1.
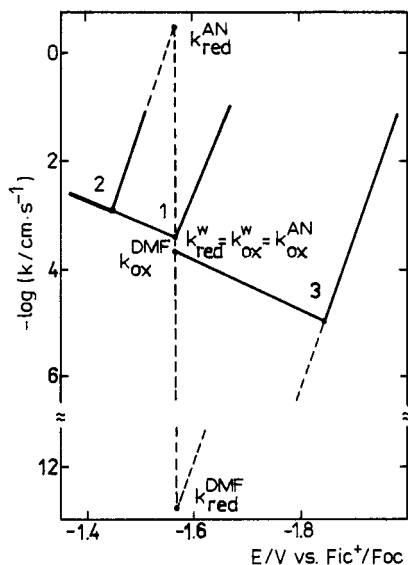

Fig. 1. Tafel plots for the Mn(II)/Mn(Hg) couple in (1) water, (2) acetonitrile, and (3) dimethylformamide.

Since, for a constant potential equation (4) may be written in a more concise form

$$\underline{I}_c = n F A \underline{c}_{ox}^0 \, \underline{k}_{red}^{ap} \tag{4a}$$

one sees, from Fig. 1 and equation (4a), that the change of solvent may influence the cathodic current of the electrode for several orders of magnitude. $\underline{k}_{red}^{ap}$ is the apparent cathodic rate constant.

So-called standard rate constants, determined by the intersection of the cathodic and anodic Tafel plots, as indicated in Fig. 1, are not so much dependent on solvent, since the change of anodic rate constant, $\underline{k}_{ox}$, at a constant potential for the Mn(II)/Mn(Hg) system is rather small.

To present the data obtained in several solvents in one plot, it is necessary to use one common potential scale. In Figure 1 the potentials are expressed with respect to the ferrocene electrode (ref. 1).

Inspection of Fig. 1 also reveals that formal potentials referred to the ferrocene scale are significantly dependent on the nature of the solvent. Such a dependence of formal or half wave potentials was studied and explained in numerous works of Gutmann and his school [see for instance (ref. 2)]. Later such dependences were analysed by Gritzner (ref. 3). Any error resulting from the use of the ferrocene electrode should have no influence on the standard rate constants determined at the formal potentials.

One should remember that in the case of more complex reactions, with participation of several electrons in the electrode process, the mechanism of the electrode reaction may be totally changed. For instance electroreduction of nitrobenzene in aqueous solutions proceeds directly in one step to phenylhydroxylamine, while in dimethylformamide this reaction occurs in a one-electron, followed by a three-electron step.

ELECTRODE REACTIONS IN SIMPLE SOLVENTS

The standard rate constant, corrected for the influence of the double layer structure, $\underline{k}_s^{cor}$, may be written in the form (ref. 4) [for reaction (2)]

$$\underline{k}_s^{cor} = \underline{B} \exp \left[\frac{-(\Delta \underline{G}_i^{\neq} + \Delta \underline{G}_0^{\neq})}{RT} \right] \tag{5}$$

where $\underline{B}$ is the preexponential factor; the Gibbs energy of activation involves two terms, one, $\Delta \underline{G}_i^{\neq}$, originating from intramolecular reorganization of the reactant and the second, $\Delta \underline{G}_0^{\neq}$, is due to reorganization of solvent around the reactant.

Both components of the energy of activation may be calculated using the following equations (ref. 4)

$$\Delta \underline{G}_i^{\neq} = 0.5 \sum_{\underline{i}}^{N} \underline{f}_{\underline{i}} [(\Delta \underline{a}_{\underline{i}})/2]^2 \tag{6}$$

and

$$\Delta \underline{G}_0^{\neq} = \frac{N e^2}{8} \left(\frac{1}{\underline{r}} - \frac{1}{\underline{R}} \right) \left(\frac{1}{\underline{D}_{op}} - \frac{1}{\underline{D}_s} \right) \tag{7}$$

$\Delta \underline{G}_i^{\neq}$ depends on the number of bonds, $\underline{N}$, undergoing distortions, the individual force constant of each bond, $\underline{f}_{\underline{i}}$, and change in equilibrium bond length, $\Delta \underline{a}_{\underline{i}}$, due to the change of the charge of reactant.

In equation (7) $\underline{D}_{op}$ and $\underline{D}_s$ represent the optic and static dielectric permittivities of the solvent, respectively, $\underline{r}$ is the reactant radius and $\underline{R}$ is twice the distance from the reactant in the transition state to the electrode surface.

Assuming that $\Delta \underline{G}_i^{\neq} \ll \Delta \underline{G}_0^{\neq}$, the influence of the solvent on the rate, according to equation (7), should be exerted by changes in $\underline{D}_{op}$, since $\underline{D}_{op} \ll \underline{D}_s$. Also the change of the radius of solvated reactant plays some role.

However, since the $(1/\underline{D}_{op} - 1/\underline{D}_s)$ term for different solvents changes only within narrow limits, 0.3 - 0.5, the significant changes of $\underline{k}_s$ cannot be explained solely by the change of the activation energy term.

It is also necessary to take into account the influence of the solvents on the preexponential factor, $\underline{B}$, though earlier it was assumed to be a solvent independent collision frequency parameter.

In the frame of an encounter preequilibrium model (ref. 5) the preexponential factor is given by the equation

$$\underline{B} = \underline{K}_p \kappa_{el} \nu_n \tag{8}$$

were $\underline{K}_p$ is the formation constant of a precursor state, κ_{el} (as before) stands for the electronic transmission coefficient and ν_n is the nuclear frequency factor.

In the case of simple reactions of large organic molecules and some complexes with very similar structure in the reduced and oxidized form $\Delta \underline{G}_0^{\neq} \gg \Delta \underline{G}_i^{\neq}$ and then ν_n and further $\underline{k}_s$ may be reciprocaly dependent on the solvent longitudinal relaxation time τ_L.

However when $\Delta \underline{G}_i^{\neq}$ increases it is expected (ref. 6) that $\nu_n \hookrightarrow \tau^{-\underline{p}}$, with $0 < \underline{p} < 1$. Nielson and Weaver (ref. 7) have confirmed these expectations in their studies of cobalt(III, II) clathrochelates.

Marcus (ref. 4) assumed that the equilibrium solvent dielectric polarization occurs simultaneously with the electron transfer. In the new approach it is assumed that when the frequency of changes of the electrical field exceeds the frequency of reorientation of solvent molecules, this reorientation determines the effective frequency of reorganization of the reacting systems.

The important role of the dynamics of solvent reorganization in the charge transfer reactions was pointed in several papers (refs 8 - 10).

When the Gibbs energy of reaction is equal to zero and reorientation of solvent molecules is

not limited by the thermic rotation (ref. 8) the effective frequency of rea-
ching the transition state is (ref. 9):

$$\nu_n = \tau_L^{-1} \left[\frac{\Delta G_o^{\neq}}{4 \pi \underline{RT}} \right]^{1/2} \tag{9}$$

By combining equation (4), (8) and (9) one obtains

$$\underline{k}_s^{cor} = \kappa_{el} \underline{K}_p \tau_L^{-1} \left[\frac{\Delta G_o^{\neq}}{4 \pi \underline{RT}} \right]^{1/2} \exp \left[\frac{-\Delta G^{\neq}}{\underline{RT}} \right] \tag{10}$$

Two limiting cases, corresponding either to limitation of the rate constant by the height of
the activation barier or by the change of frequency of reaching the transition state, are now
expected. In the intermediate cases both τ_L and $\Delta \underline{G}^{\neq}$ influence the rate of the electrode
reaction. Therefore experimental studies of different systems in various solvents have esta-
blished different dependences of the rate constant on the solvent properties.
An approximately linear dependence of $\underline{k}_s$ on τ_L^{-1} was observed for the electrode reaction of
salene complexes of transition metals in aprotic solvents (ref. 11).Also studies of the ele-
ctrode reactions of phenotiazine (ref. 12), p-phenylenediamine (ref. 13) and metallocenes
(refs 14, 15), as well as the electroreduction of acetylacetone complexes of cobalt(III)
(ref. 16) and chromium(III) (ref. 17), have revealed a linear relationship between $\underline{k}_s$ and τ_L^{-1}.
A different dependence was observed (refs 12, 13) for protolytic solvents which have hydrogen
bonds and in consequence exhibit several relaxation times.
Weaver and Gennett (ref. 18) studied the anodic oxidation of ferrocene in several solvents
with different $\underline{D}_s$, $\underline{D}_{op}$ and τ_L parameters. Since practically no dependence of $\underline{k}_s$ on these
parameters was found, the authors concluded that there is compensation of influences on $\Delta \underline{G}^{\neq}$
and frequency with regard to reaching the transition state.
Also the linear dependence of log $\underline{k}_s$ on $(\underline{D}_{op}^{-1} - \underline{D}_s^{-1})$ was found in the case of the electroredu-
ction of quinone (ref. 19) and the electrooxidation of diaminobenzenes (ref. 20), and for
various homogeneous charge transfer reactions.
Fawcett (ref. 21) analysed several processes using an equation involving two parameters.
Though he considered charge transfer and ion transfer reactions in the same fashion, such an
analysis is more valid for the former. Ion transfer reactions of solvated cations were stu-
died by a number of workers; such reactions need not be discussed here as they have been ci-
ted and referred in several other publications (refs 21 - 23). In the case of such reactions,
several equations which relate the rate constant (or energy of activation $\Delta \underline{G}^{\neq}$) of such pro-
cesses to different parameters, which depend either on the properties of the solvents used or
the reactant ion studied,were used in the analysis

$$\Delta \underline{G}^{\neq} = \underline{a} + \underline{b} \Delta \underline{G}_{tr} \quad (\Delta \underline{G}_{solv}) \qquad \text{(refs 21, 22)} \tag{11}$$

$$\log \underline{k}_s = \underline{c} + \underline{d} \, DN \qquad \text{(ref. 23)} \tag{12}$$

$$\ln(\underline{k}_s \tau_L) = \underline{e} + \underline{f} \, DN \qquad \text{(ref. 21)} \tag{13}$$

$$\ln \underline{k}_s = \underline{g} - \underline{h} \ln \tau_L + \underline{i} \, DN \qquad \text{(ref. 24)} \tag{14}$$

$$\underline{Y}_{red} = \underline{RT} (\ln \underline{k}_{red}^S - \ln \underline{k}_{red}^W) = \underline{S}_c \Delta \underline{G}_{tr} \quad \text{(ref. 23)} \tag{15}$$

$$\underline{Y}_{ox} = \underline{RT} (\ln \underline{k}_{ox}^S - \ln \underline{k}_{ox}^W) = \underline{S}_a \Delta \underline{G}_{tr} \quad \text{(ref. 23)} \tag{16}$$

where $\underline{a}$ - $\underline{i}$ are constants, DN is the Gutmann's donor number, $\Delta \underline{G}_{tr}$ - the Gibbs energy of tra-
nsfer, $\underline{S}_c = \bar{\alpha} + \alpha$ and $\underline{S}_a = \bar{\alpha} - \beta$, where α and β are the transfer coefficients of the
cathodic and anodic reaction,respectively. $\bar{\alpha}$ is defined by the equation

$$\underline{Y} = \underline{RT} (\ln \underline{k}_s^S - \underline{k}_s^W) = \bar{\alpha} \Delta \underline{G}_{tr} \qquad \text{(ref. 23)} \tag{17}$$

Superscripts s and w refer to the organic solvent and water, respectively; k_{red} and k_{ox} are the rate constants calculated at constant potential in the ferrocene electrode scale [other so-called solvent independent electrode may be used (ref. 25)].

Some other correlations were also attempted (ref. 24) and the results of the analyses according to equations (11) - (16) are given in Table 1.

TABLE 1. Results of analysis of ion transfer electrode reactions at mercury electrodes according to equations (11) - (16) (refs 21 - 24); n - number of solvents, r - the correlation coefficient

Deposited metal	Li	Na	K	Ca	Sr	Ba	Eu	Mn	Cd	Pb	Zn	Ni
Eq. (11) a	38.0					42.9	40.4			17.9		
b	-0.44	-0.1				-0.12	-0.16			-0.16	-0.10	-0.13
r	0.97					0.992	0.994			0.95	0.89	0.98
n	5					3	4			3	8	4
Eq. (15, 16) S_c	1.1	0.75	0.6	0.77	0.8	0.86	0.9	0.99		0.6	0.38	
S_a					-0.05	~0	~0	0.1	0.05			
r_{cat}	0.99	1.0	-	1.0	-	0.99	-	1.0		-	0.99	
n	5	4	2	3	2	4	2	3		2	8	
Eq. (12) c	1.9	0.63	2.5		-1.52	1.2	0.22	-0.02	poor cor-relation	3.4	2.7	2.9
d	-0.21	-0.061	-0.13		-0.16	-0.12	-0.21	-0.22		-0.17	-0.14	-0.15
r	0.97	0.99	0.93		-	0.96	-	0.96		0.997	0.90	0.993
n	5	5	3		2	3	2	4		3	7	4
Eq. (13) e	-29.3								-30			
f	-0.40								-0.11			
r	0.97								0.864			
n	6								6			
Eq. (14) h	1.4	0.95							1.13			
	$\bar{h}=0.35$	$\bar{h}=0.34$							$\bar{h}=0.62$			
i	-0.35	-0.03							0.092			
	$\bar{I}=0.65$	$\bar{I}=0.66$							$\bar{I}=0.38$			
r	0.986	0.996							0.967			
n	6	4							6			

Analysis of existing data for metal solvates reduced to corresponding amalgams, and treated according to equation (15), exibited linear behaviour with slopes S_c usually within the limits 0.5-1.0. Such linearity suggests a similar mechanism in the case of a given electrode system for the solvents involved. The only exceptions were for zinc, S_c was equal 0.38 (this reaction has quite low α), and lithium, S_c = 1.1. This last result is surprising since in simple terms it suggests that the change of the Gibbs energy of activation exceeds the change of the Gibbs energy of reaction.

For these reactions where S_c was found to be near to 1, S_a was near to zero. An example is the case illustrated by the reaction of the Mn(II)/Mn(Hg) system in Fig. 1.

For practical predictions the good linear dependence observed between log k_s and DN for all studied so far systems is very important (ref. 22).

Reaction is always slower when the reactant is reduced from a solvent of high Lewis basicity;
such behaviour is independent of the rate of the electrode reaction.

ELECTRODE REACTIONS IN MIXED SOLVENTS

The majority of studies in this area are concerned with solvent systems in which water is
one component of the mixture.

Now, in order to explain the behaviour of different electrode systems in such mixtures one
should take into account the interaction of the solvents both with the reactant and with
the electrode.

Frequently molecules of the organic solvent are strongly adsorbed on the electrode surface
even at low concentrations of this solvent where its interaction with the reactant at this
concentration range may be negligible. Under such conditions one may expect that the second
solvent at the lower concentration range will behave as a typical inhibitor.

One may easily distinguish such behaviour from that where either resolvation of reactant
occurs at higher organic solvent concentration, or when both processes occur simultaneously,
by studying the dependence of the rate constant at a given potential on the Gibbs energy of
transfer of the reactant under investigation from water to the mixture involved (ref. 26).
Examples of plots in this area are shown in Fig. 2 (ref. 26).

The behaviour of zinc(II) in mixtures of water with hexamethylphosphortriamide (HMPT)
(curve 1), and water with acetone (curve 2), show the significant decrease of the rate con-
stant in comparison with the rate in aqueous solutions. On the ordinate axis here the para-
meter involved, Y^m_{red}, is defined by the equation

$$Y^m_{red} = RT (\ln k^m_{red} - \ln k^w_{red}) \tag{18}$$

One sees that for these solutions there is significant decrease of Y^m_{red} as ΔG_{tr} approaches
zero. Such behaviour reveals that the zinc(II) ion is not interacting with the added solvent
and thus the decrease of the rate constant may be ascribed to the progressive coverage of
the electrode surface by the molecules of organic solvent.

Under such condition Y^m_{red} or k_{red} should be related to $(1 - \theta)$ by the equation given by
Parsons (ref. 27) for the inhibition of electrode reactions, viz.

$$\frac{k^m_{red}}{k^w_{red}} = (1 - \theta)^{r^{\neq}} \tag{19}$$

or, using Y^m_{red} notation,

$$Y^m_{red} = RT \ln (1 - \theta)^{r^{\neq}} \tag{20}$$

In equations (19) and (20) θ denotes the surface coverage and $r^{\neq}$ is the number of water mole-
cules removed from the surface to make the place for one reactant molecule.

For several systems the variation of $\log k^m_{red}$ vs $\log (1 - \theta)$ was linear; the slopes were
similar to those obtained in the case of other species reacting under conditions where the
processes were inhibited by higher aliphatic alcohols (ref. 28).

The increase of concentration of the organic solvent to such values that ΔG_{tr} starts to as-
sume value different from zero, makes a further change of the rate constant. If ΔG_{tr} is po-
sitive (reactant is less solvated) then Y^m_{red} increases to meet the straight line 4 which
gives the dependence of Y^m_{red} on ΔG_{tr} for zinc(II) in the case of the pure solvents. Such
behaviour is observed for zinc(II) in water-acetone mixtures (Fig. 2 curve 2). When ΔG_{tr}
assumes negative values in H_2O - HMPT mixtures (curve 1), Y^m_{red} further decreases, but with
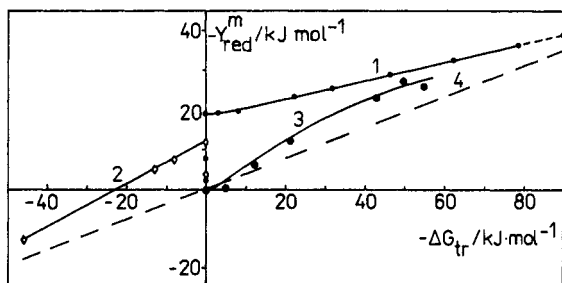considerably lower intensity.

Fig. 2. Dependence of Y^m_{red} on ΔG_{tr} for Zn(II)
reduction in (1) H_2O + HMPT, (2) H_2O + acetone,
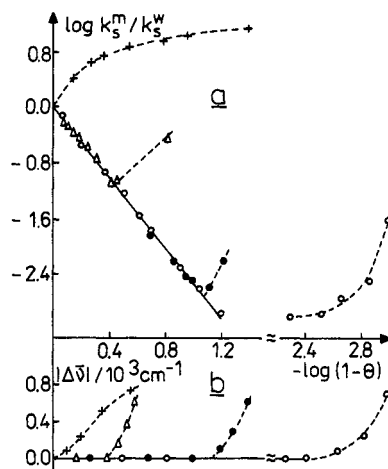(3) H_2O + DMF, (4) dependence in single solvents.

Fig. 3. Interrelations of the V(III)/V(II)
electrode reaction standard rate constant
(a) and resolvation of V(III) (b) in H_2O -
organic solvent mixtures: + - DMF, $\triangle$ - DMPU,
● - HMPT, o - AN, for details see (ref. 29).

This dependence should also coincide with line 4, when it approaches the pure organic sol-
vent.

Curve 3 in Fig. 2 represents the dependence for zinc(II) interacting with DMF in H_2O - DMF
mixtures at low concentrations of the organic solvent.

Such an explanation is clearly supported by the dependence given in Fig. 3 of log $\underline{k}^m_s/\underline{k}^w_s$, and
the difference in the wavenumbers $\Delta\bar{v}$ of the absorption maxima of V(III) in aqueous solution
and in water-organic solvent mixtures on log (1 - θ) (ref. 29).

One sees that there is very good correlation between the beginning of resolvation and the
change from inhibition to acceleration of the rate with further increase of the organic sol-
vent concentration [decrease of (1 - θ)].

The common straight line in Fig. 3, for different solvents (inhibitors), is a good illustra-
tion of the validity of equation (19).

There may also be a different type of behaviour: this is observed when even a small amount of
organic solvent changes both ΔG_{tr} and $\Delta\bar{v}$, and increases the rate constant of the reaction
(Figs 2 and 3). Inhibition of the electrode reaction is not observed in this case because
the reactant ion, solvated preferentially by the organic solvent, may easily approach the
electrode surface which is also preferentially populated by the organic solvent.

Line 4 in Fig. 2 represents the change of $\underline{k}_{red}$ on ΔG_{tr} for pure solvents (ref. 23) described
by equation (15). The deviations from this dependence are due to the composition difference
of the bulk and surface phases given by the relative surface excess of the organic component
Γ (ref. 26).

$$\underline{k}^m_{red} = \underline{k}^w_{red} \exp{(\underline{S}_c \, \Delta G_{tr}/\underline{RT})} \, \underline{P} \, (\Gamma) \tag{21}$$

where $\underline{P}$ (Γ) is a function of the surface excess Γ.

The relation between $\underline{P}$ (Γ) and Γ may be established by dividing the electrode reaction
into three steps consisting of (i) partial desolvation of the reactant in the solution, (ii)
removal of a solvent molecules (associates) from the electrode surface, or selective resol-
vation with surface organic molecules, and (iii) the formation of the activated complex fol-

lowed by ion transfer into the amalgam phase:

$$\underline{P}\ (\Gamma) = (1 - \Gamma/\Gamma_{\infty})\underline{a} + \underline{k}_{red}^{i}\ \underline{K}^{i}\ \Gamma\underline{b}/(\Gamma_{\infty}^{b}\ k_{red}^{w}) \tag{22}$$

By combining equations (21) and (22) one gets

$$\underline{k}_{red}^{m} = \left[\ \underline{k}_{red}^{w}\ (1 - \theta)\underline{a} + \underline{k}_{b}\theta\underline{b}\ \right]\ \exp\ (\underline{S}_{c}\ \Delta\underline{G}_{tr}/\underline{RT}) \tag{23}$$

When $\Delta\underline{G}_{tr}$ = 0 and surface coverage θ is not very large equation (23) simplifies to the equation given by Parsons (ref. 27).

One sees that for large θ the first term in the brackets in eq. (23) may be neglected in comparison with the second one, $\underline{k}_{b}\theta\underline{b}$. Since θ is then virtually equal to one, the shape of the log $\underline{k}_{red}$ - $\Delta\underline{G}_{tr}$ dependence is determined by the resolvation of the reactant, including resolvation at the electrode surface.

Recently we studied (ref. 30) the electrode kinetics of the V(III)/V(II) system in water and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) mixtures. The electrochemical experiments were accompanied by the study of the resolvation of the vanadium ions with DMPU molecules using visible spectroscopy. Also for that system one observes a dramatic decrease of the rate, as we discussed before, due to progressing coverage of the electrode by DMPU. At $x_{DMPU} \geqslant$ 0.1 when the degree of the surface coverage, θ, is in the range 0.9 - 1.0 the kinetics, as we discussed above, is determined largely by the solvation of the reactant. For $x_{DMPU} \geqslant$ 0.1 the values of δ both for V(III) and V(II) were found on the basis of spectrophotometric experiments, to be practically equal. Since δ may be simply related to the average number of organic molecules bound to the vanadium ions, one may assume that in mixtures of water with DMPU, the average compositions of the inner solvation shells of V(III) and V(II) are equal (Fig. 4).

Using equation (5) we may analyse more closely the reasons of the change of $\underline{k}_{s}$ observed for that system.

Expressing $\underline{B}$ by equation (8) one finds that $\underline{K}_{p}$ and also the transmission coefficient which is distance sensitive are only slightly dependent on the solvent (ref. 31).

In many solvents ν_{n} and in consequence $\underline{k}_{s}$ increases with a decrease of the solvent longitudinal relaxation time τ_{L}. But this model is not obeyed by the V(III)/V(II) system; this is well illustrated by the over one order of magnitude higher $\underline{k}_{s}$ in DMF than in aqueous solutions, though τ_{L} is equal 1.3 ps (ref. 31) and 0.19 ps (ref. 7) for DMF and $H_{2}O$, respectively. The reason of such behaviour may be the comparable magnitude of $\Delta\underline{G}_{i}^{\neq}$ and $\Delta\underline{G}_{0}^{\neq}$, as we observed earlier for the Eu(III)/Eu(II) couple in several solvents (ref. 32). Under such conditions the inner sphere bond vibrations ν_{i} contribute mostly to the preexponential factor.
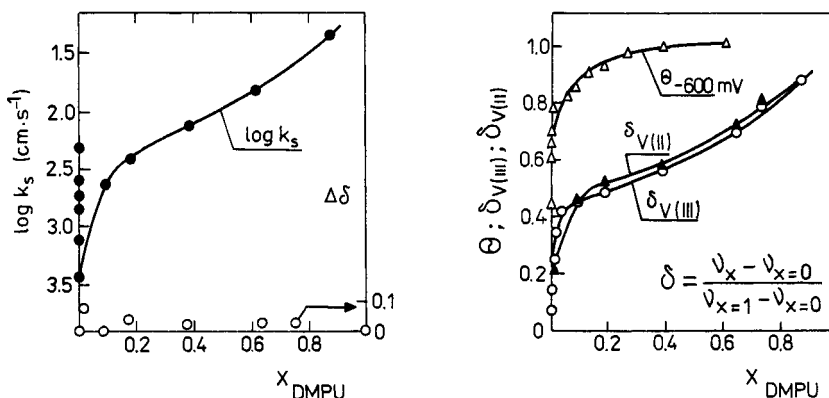

Fig. 4. Influence of DMPU concentration in $H_{2}O$ - DMPU mixtures on log $\underline{k}_{s}$, θ (at $\underline{E}$ = -600 mV $\underline{vs}$ SCE), $\delta_{V(III)}$, $\delta_{V(II)}$ and $\Delta\delta$.

Substitution of H_2O molecules by DMPU molecules, changes the inner shell bond vibrations v_i. Since V-DMPU vibrating group has larger effective mass than V-H_2O, one may suppose that $v_{V-DMPU} < v_{V-H_2O}$. This conclusion suggests, opposite to experimental observations, that the rate constant of the V(III)/V(II) system should decrease when resolvation with DMPU increases. However, the difference between v_{V-DMPU} and v_{V-H_2O} should be rather small.

In addition to dynamic effects, the changes in the coordination sphere may influence also the activation energy. It is difficult to calculate $\Delta G_i^{\neq}$ for the V(III)/V(II) + H_2O + DMPU system; however, it is reasonable to assume that it is easier to change the V-H_2O bond than V-DMPU, since water is less strongly coordinated by vanadium than DMPU. Such a dependence between rate constant and $\Delta G_i^{\neq}$ was earlier observed (ref. 32) for the Eu(III)/Eu(II) couple in several solvents. In consequence $\Delta G_i^{\neq}$ should increase on substitution of H_2O by DMPU according to the change of δ, but this disagrees with experimentally observed increase of k_s. As a result the observed behaviour should be explained by the change of $\Delta G_o^{\neq}$ given by equation (7). Using this equation we calculated values of $\Delta G_o^{\neq}$ and found that they decrease with the increase of DMPU content to reach finally a plateau for $x_{DMPU} > 0.5$.

The importance of the molecular aspects of solvent reorganization is shown in Fig. 4 where the shape of the log k_s on x_{DMPU} and $\delta_{V(III)}$ (or $\delta_{V(II)}$) on x_{DMPU} dependences are very similar.

Since such behaviour cannot be explained by inherent changes of the inner coordination sphere, one can suppose that the composition of the inner sphere influences the reorganization of the surrounding solvent. Such interdependence between inner and outer sphere may be due to hydrogen bonds. When H_2O molecules are substituted by DMPU the number of hydrogen bonds between the inner shell and the outer shell gradually diminishes, making the outer sphere more facile to the reorganization and accordingly to an increase in k_s of the V(III)/V(II) system.

Coordinated DMPU molecules do not contain any polar groups which could participate in hydrogen bonding with outer sphere water molecules. In pure DMPU the secondary solvation shell of the ion is ordered almost exclusively by nonspecific charge - dipole interactions. Such behaviour may occur also in other mixed solvent systems when water molecules are substituted in the first coordination sphere by molecules of solvents which are not hydrogen bond donors.

CONCLUSIONS

The influence of solvents on simple charge transfer reactions is relatively well described by the theory, if $\Delta G_i^{\neq} < \Delta G_o^{\neq}$ (ref. 21). The analysis of such reactions given by Fawcett (ref. 21) shows also that the Marcus expression (ref. 4) for $\Delta G_o^{\neq}$ is valid for such simple electrode reactions.

In the case of ion transfer (deposition type) reactions the situation is more complex, because these reactions may proceed in several charge transfer steps. Also the chemical step may control such reactions.

Therefore a poor fit of experimental data to model equations may result, among other things, from choice of unproper model or from change of the mechanism with the nature of solvent. However, also in the case of the correct choice of the model equation, the correlation may not be satisfactory.

One of the reasons, is a frequent use in correlations of the rate constants not corrected for the double layer effects.

This influence of the double layer on k_s described by the equation

$$k_s^{ap} = k_s^{cor} \exp \frac{(\alpha n - z) F \varphi_2}{RT} \tag{24}$$

may be significant and different in various solvents. In order to minimize this influence,

when the double layer data are not available, one should use rather high concentration of background electrolyte with non surface-active ions. The correction given by equation (24) may be not always effective, because the reaction site in different solvents may not coincide with the outer Helmholtz plane.

Also, when one uses solvents with low dielectric permittivity, the ion pair formation by background electrolyte and reactant ions may complicate the calculation of φ_2 potential and in consequence the use of equation (24).

To understand more properly the mechanism of the charge transfer and the ion transfer reactions, further work on various electrode systems in solvents with different properties should be carried out.

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