

A STUDY OF THE RATE OF SIMPLE ELECTRODE REACTIONS AS A FUNCTION OF THE SOLVENT

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The rate of the $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ reaction has been studied in several pure and mixed solvents by the faradaic impedance method. Low values of the cathodic transfer coefficient are obtained in all solvents. The mechanism of this reaction is discussed and it is concluded that the formation of a specifically adsorbed, partially charged ion is the most probable rate determining step although no mechanism can account for all the observed facts. Some qualitative suggestions are made to account for the solvent effect. It is concluded that the study of the solvent effect does not provide clear evidence for the mechanism of this type of electrode reaction.

Modern theories¹⁻⁵ of fast electrode reactions have shown that the energetics of these reactions are determined principally by the polarization of the surrounding medium in the field due to the electrostatic charge on the reacting ion. In view of the importance of the role played by the solvation shell in the activation process, it is surprising that the dependence of the rate of such reactions on the nature of the solvent has been studied so little. One reason is probably the lack of general electrochemical data about solutions in non-aqueous solvents. A systematic study of the $\text{Zn}^{2+} : \text{Zn}(\text{Hg})$ reaction was recently carried out by Jaenicke and Schweitzer⁶ using the galvanostatic pulse method. They measured the rate of this reaction in the complete range of mixtures of water and each of the solvents: tetrahydrofuran, acetonitrile, ethanol, ethylenediamine and acetone as well as mixtures of ethanol and acetone and some aqueous dioxane solutions. They explained the striking minima found in each of the aqueous systems in a qualitative way in terms of potential energy curves.

The present work was undertaken to investigate the solvent effect using the $\text{Cd}^{2+} : \text{Cd}(\text{Hg})$ reaction. In particular a series of solvent mixtures of almost constant permittivity (methanol + acetonitrile) and one of widely varying permittivity (N-methylformamide + N,N-dimethylformamide) were studied.

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EXPERIMENTAL

Measurements of the impedance of the dropping mercury electrode were made with the aid of the a.c. bridge described previously⁷. It was modified in the detection circuit by the use of a General Radio type 1232A tuned amplifier and a Telequipment type D43R oscilloscope. Results were obtained with a signal of 5 mV amplitude at six frequencies in the range 0.2 to 2 kHz. For the determination of the transfer coefficient such a series of measurements was repeated at four potentials on the ascending part of the polarographic wave. The counter electrode was a sheet of platinum in the form of a cylinder. Its area and capacity were very much larger than those of the mercury drop so that its contribution to the impedance was negligible.

Cadmium perchlorate was prepared from cadmium nitrate (Kahlbaum). The latter was recrystallized from twice distilled water. Cadmium hydroxide was then precipitated from an aqueous solution of the nitrate with sodium hydroxide solution. After the precipitate was filtered and washed it was dissolved in perchloric acid. The solution was concentrated by evaporation and the cadmium perchlorate precipitated by cooling. The salt was finally dried in vacuum at 80°C. AnalaR sodium perchlorate was recrystallized from twice distilled water and dried in vacuum at 80°C.

AnalaR methanol was dried by the method of Lund and Bjerrum⁸. The solvent was transferred to the cell without coming in contact with the atmosphere. BDH acetonitrile was distilled once from P₂O₅ and then twice from K₂CO₃. BDH dimethyl formamide was left for a week over NaOH and CaO with occasional shaking. It was finally distilled twice under reduced pressure. BDH N-methylformamide was left over Na₂SO₄ for two weeks and then distilled twice under reduced pressure. Propylene carbonate was purified as described previously⁹. Sulphamic acid was recrystallized from water and dried in vacuum. The vanadium ions were produced by electro-reduction from dried ammonium vanadate.

In methanol and acetonitrile and their mixtures the reference electrode was a silver sheet with additional silver electrodeposited on it. The electrode dipped into a solution containing 0.1 mol l⁻¹ AgNO₃ and 0.9 mol l⁻¹ NaClO₄ in the solvent being used. In the formamides a cadmium ion electrode prepared in a similar way was used. In the study of the vanadium reaction, a hydrogen electrode was used as reference.

RESULTS

The measured impedance was analysed in the usual way^{10,11} assuming that the double layer capacity was unaffected by the reactants. A typical Randles plot is shown in Fig. 1. The results in Table I are based on three or four determinations at different concentrations of cadmium in the range 0.3–0.8 mmol l⁻¹. The rate constants found were sufficiently high to satisfy the conditions under which this method may be used¹², except for those obtained in the pure solvents methanol, and propylene carbonate and the acetonitrile – water mixture. Nevertheless the mixture appeared to give reliable results, whereas the behaviour in pure methanol solution seemed less satisfactory. The quoted results for the latter were obtained from an extensive study of a.c. and d.c. behaviour. The supporting electrolyte was 0.9 mol l⁻¹ NaClO₄ in each case. Temperature coefficients were measured at four temperatures in the range 15°C–50°C. Transfer coefficients determined by the method described by Biegler and Laitinen¹² (see Fig. 2) were found independent of temperature.

The results for the vanadium reaction shown in Table I were obtained by classical polarography and analysed using Koutecký's method¹³. Again these results are mean values from three or four determinations at four temperatures between 15°C and 50°C.

DISCUSSION

The Cadmium Reaction

The mechanism of a reaction like the V^{3+}/V^{2+} reaction is now fairly well understood¹⁻⁵. In contrast there is no clear understanding as to why a reaction like cadmium deposition on an amalgam should be so fast. This reaction has been quite thoroughly studied from the point of view of the marked effect of anions on the kinetics^{14,15} and of the unusual value of the transfer coefficient^{16,17}, but these studies have not led to a definite conclusion about the mechanism. The low value of the cathodic transfer coefficient has led to the suggestion¹⁸ that the rate determining step is the reduction of Cd^{2+} to Cd^+ . Galvanostatic studies¹⁹ have been interpreted assuming the existence of this species together with the chemical reaction of disproportionation of the intermediate. However, the rate found in this study is only

TABLE I
Rate Parameters for the Reaction $Cd^{2+} + 2e \rightarrow Cd(Hg)$ in Various Solvents at 25°C; Base Electrolyte $0.9 \text{ mol l}^{-1} \text{ NaClO}_4$

Solvent	$k/cm \text{ s}^{-1}$	α	$\Delta H/kJ \text{ mol}^{-1}$
H ₂ O	0.45	0.15	
0.5 mol H ₂ O + 0.5 mol CH ₃ CN	0.0145		
CH ₃ CN	0.19	0.15	22.
0.8 mol CH ₃ CN + 0.2 mol CH ₃ OH	0.080	0.14	
0.5 mol CH ₃ CN + 0.2 mol CH ₃ OH	0.028	0.14	
CH ₃ OH	0.013	0.27	46.
DMF	0.15	0.24	17.
0.8 mol DMF + 0.2 mol NMF	0.081	0.14	
0.5 mol DMF + 0.5 mol NMF	0.089	0.20	22.
0.2 mol DMF + 0.8 mol NMF	0.108	0.18	
NMF	0.12	0.40	30
Propylene carbonate	≈ 0.01		

about 1% of that found in the present and other recent work^{20,21}. This suggests that the data of ref.¹⁹ may have been obtained with a contaminated electrode. Low rate constants were also obtained in potential step experiments²² but here the suggestion of unknown chemical complications was offered as an explanation. More recently²³ deviations from simple faradaic impedance behaviour were interpreted in terms of a Cd^+ intermediate. These deviations from a Randles circuit were found at reactant concentrations much higher than those used in the present work.

The existence of Cd^+ as a transient species in radiolysis experiments²⁴ is now established. The standard potential of the $\text{Cd}^{2+}/\text{Cd}^+$ couple has been estimated²⁵ as -1.9 to -2.5 V. The more negative values are consistent with the observation that Cd^+ is formed by reduction of Cd^{2+} only by the solvated electron and not by hydrogen atoms. If these values are accepted it follows that the minimum standard free energy of activation for the cadmium reaction with Cd^+ in solution as an intermediate would be about 200 kJ mol^{-1} . This is obviously inconsistent with the observed rate, hence it must be concluded that for Cd^+ to occur as an intermediate there must be considerable stabilization by adsorption. It is difficult to estimate whether this amount of stabilization could be achieved. It seems likely that an adsorption coefficient of the order of $10^{-7} \exp(+180/8.3 \times 0.3) = 10^{+3} \text{ cm}$ would be required; values of this magnitude are unknown in other systems involving the adsorption of ions on mercury¹⁷. Comparably strong adsorption occurs when strong chemisorbed species exist.

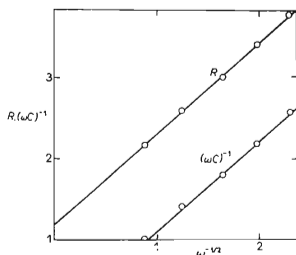


FIG. 1

Randles Plot of Data for $7.37 \cdot 10^{-4} \text{ mol l}^{-1} \text{ Cd}(\text{ClO}_4)_2$ in $0.9 \text{ mol l}^{-1} \text{ NaClO}_4$ in Acetonitrile at 25°C

R and $(\omega C)^{-1}$ in $\Omega \text{ cm}^2$, $\omega^{-1/2}$ in $10^2 \text{ s}^{1/2}$.

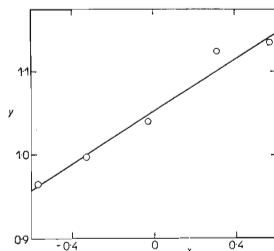


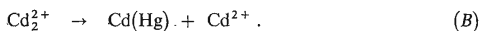
FIG. 2

Determination of Transfer Coefficient from Data for $4.01 \cdot 10^{-4} \text{ mol l}^{-1} \text{ Cd}(\text{ClO}_4)_2$ in $0.9 \text{ mol l}^{-1} \text{ NaClO}_4$ in Acetonitrile at 25°C

$Y = \log [i_a^0 i_d (i_d - i)^{-1}]$ in mA cm^{-2} , $X = \log [i(i_d - i)^{-1}]$.

An alternative possibility is the formation of the dimeric intermediate Cd_2^{2+} , the analogue of the mercurous ion. This is now well established in molten aluminochlorides^{26,27} as a stable species. It is difficult to predict from such data the stability of Cd_2^{2+} in aqueous solution but it does suggest that such a species is likely to be more stable than the monomeric ion. There is also a suggestion from radiolysis experiments²⁴ that Cd^+ is removed by dimerization and subsequent disproportionation. It therefore seems worth considering the effect on the analysis of assuming a dimeric intermediate

A possible reaction scheme involving Cd_2^{2+} is:



If double layer effects are ignored the rates of these reactions may be written

$$\vec{i}_A = 2F\vec{k}_0[\text{Cd}^{2+}]^2 \exp(-\beta Ef), \quad (1)$$

$$\overleftarrow{i}_A = 2F\overleftarrow{k}_0[\text{Cd}_2^{2+}] \exp(1 - \beta) Ef \quad (2)$$

where β is the cathodic transfer coefficient for the elementary step (A) and $f = F/RT$. If reaction (B) is assumed to be fast compared with reaction (A), the equilibrium condition

$$[\text{Cd}][\text{Cd}^{2+}]/[\text{Cd}_2^{2+}] = K \quad (3)$$

may be used. Hence equation (2) becomes

$$\overleftarrow{i}_A = 2F(\overleftarrow{k}_0/K)[\text{Cd}][\text{Cd}^{2+}] \exp(1 - \beta) Ef. \quad (4)$$

At equilibrium

$$\vec{i}_A = \overleftarrow{i}_A = \vec{i}; \quad E = E_r, \quad (5)$$

so that

$$\exp(E_r f) = (\vec{k}_0 K / \overleftarrow{k}_0) [\text{Cd}^{2+}][\text{Cd}]^{-1} \quad (6)$$

and

$$\vec{i} = 2F(\vec{k}_0)^{1-\beta} (\overleftarrow{k}_0)^\beta K^{-\beta} [\text{Cd}^{2+}]^{2-\beta} [\text{Cd}]^\beta. \quad (7)$$

This expression differs from the form

$$\vec{i} = 2F\vec{k}[\text{Cd}^{2+}]^{1-\alpha} [\text{Cd}]^\alpha \quad (8)$$

derived assuming that the reaction is first order in each direction, on which the analysis of the results of relaxation methods is based.

The assumption of a second order reaction could resolve one anomaly which exists in the published work on the Cd reaction in perchlorate solutions. Although most work^{12,17,20,28} yields a cathodic transfer coefficient of less than $\frac{1}{2}$, the work of Hampson and Larkin²¹ yields a value of 0.68. This was obtained as the coefficient $\{\partial \log \bar{i} / \partial \log [\text{Cd}(\text{Hg})]\}_{[\text{Cd}^{2+}]}$ which could therefore be interpreted as β in equation (7) or α in equation (8). It is possible that re-interpretation of the other results would yield a transfer coefficient in agreement with this. For example if it is assumed that the impedance data obtained with polarographic generation gives the correct exchange current then equation (5) of ref.¹²:

$$\log [(I_a^0)_i i_d / (i_d - i)] = \log [nFk_a^0 C_B (D_{Ox} / D_R)^{\alpha/2}] + \alpha \log [i / (i_d - i)] \quad (9)$$

which corresponds to (8), would be replaced by

$$\log [(I_a^0)_i \{i_d / (i_d - i)\}^2] = \log [nFk^0 C_B^2 (D_{Ox} / D_R)^{\beta/2}] + \beta \log [i / (i_d - i)] \quad (10)$$

which is derived by exactly analogous methods from equation (7). If the present results are plotted according to equation (10), the slight downward curvature of Fig. 2 is replaced by the slight upward curvature of Fig. 3 and the transfer coefficient has a value of about 0.6 in reasonable agreement with that obtained by Hampson and Larkin²¹.

There is, however, a difficulty with this mechanism. The rate constant obtained is in the region of $10^6 \text{ cm}^4 \text{ mol}^{-1} \text{ s}^{-1}$ which would correspond to a frequency factor of about $10^{10} \text{ cm}^4 \text{ mol}^{-1} \text{ s}^{-1}$ assuming¹⁶ a heat of activation of 20 kJ mol^{-1} . It is difficult to account for this high frequency factor and a simple model (see Appendix) gives a value a factor of 10^6 smaller. Consequently it appears that for either intermediate a simple mechanism with the intermediate in solution cannot be brought into full accord with the facts. On the other hand evidence for the existence of an adsorbed intermediate is almost non-existent. Impedance and rectification measurements seem to be explicable in terms of a Randles circuit although there is evidence

TABLE II
Rate Parameter for the Reaction $\text{V}^{3+} + e \rightleftharpoons \text{V}^{2+}$, Base, Electrolyte $1 \text{ mol l}^{-1} \text{ NH}_2\text{SO}_3\text{H}$

Solvent	$\overleftrightarrow{k} / \text{cm s}^{-1}$	α	$\overleftrightarrow{\Delta H} / \text{kJ mol}^{-1}$
H ₂ O	0.00336	0.60	17
NMF	0.00116	0.20	19

for the adsorption of Cd in amalgams from the results of Frumkin and Cirves²⁹. It may be concluded that the most probable mechanism involves a transition state consisting of a specifically adsorbed Cd^{2+} ion which has lost a small fraction of its normal charge³⁰. Since such an activated complex must have lost some of its solvation shell this mechanism may be considered as identical with that proposed by Randles¹⁶ and Barker¹⁷. The transfer coefficient obtained by Hampson and Larkin²¹ is not explicable in terms of this hypothesis.

Solvent Effects in Electrode Kinetics

Electrode kinetic parameters are expected to be sensitive to many of the solution properties which are changed when the composition of the solvent is varied. Some of the more important of these properties relevant to ion reduction are as follows: 1. Interaction between the reactant ion and the solvent molecules. 2. Interaction between the reactant ion and supporting electrolyte ions. 3. Interaction between supporting electrolyte ions and solvent. 4. Position of the equilibrium potential on some absolute scale. 5. Composition and dielectric constant of the solvent layer adsorbed at the electrode. 6. Distribution of supporting electrolyte ions in the double layer. 7. Distribution of reactant ions in the double layer in the initial and activated state.

To give quantitative expression to such changes seems at present impossible. However, the most significant outcome of studies in pure solvents to date is the

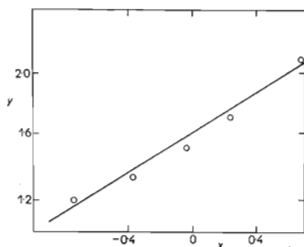


FIG. 3

Determination of Transfer Coefficient Assuming Second Order Reaction. $2.8 \cdot 10^{-4} \text{ mol l}^{-1} \text{ Cd}(\text{ClO}_4)_2$ in $1 \text{ mol l}^{-1} \text{ HClO}_4$ in Water at 25°C

$$Y = \log [i_0^0 i_d (i_d - i)^{-1}] \text{ in mA cm}^{-2},$$

$$X = \log [i(i_d - i)^{-1}].$$

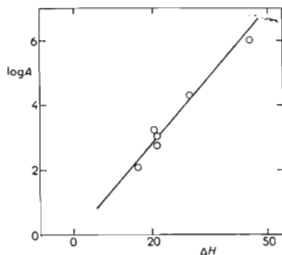


FIG. 4

Plot of Frequency Factor A (cm s^{-1}) (assuming first order reaction) Against Activation Energy ΔH^\ddagger (kJ mol^{-1}) for the $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ Reaction

remarkable *lack* of dependence of kinetic parameters on the nature of the solvent. The rate constant for the system $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ has been measured in this work for six solvents and ranges from 0.01 to 0.45 cm s^{-1} . This range of rate seems small in view of the large differences between other properties of such systems. Similarly, the exchange current for the $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$ varies by only a factor of 30 for solvents of very different properties⁶. The exchange currents for hydrogen evolution on mercury in water and methanol³¹ differ by a factor of only 2. Although not strictly relevant to the present discussion, one could point out for comparison purposes, that the introduction of only $6 \mu\text{C cm}^{-2}$ of I^- to the inner layer alters the rate constant for the $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$ system³² in aqueous solution by a factor of 20.

At first sight the main factor influencing the rate constant would seem to be the change in solvation energy. Such a model has been used by Salomon³³ in an attempt to account for the solvent effect on hydrogen evolution from HCl in water + methanol mixtures, but this calculation suffers from several oversimplifications such as the neglect of the potential due to solvent orientation at phase boundaries. It also equates the free energy of activation to a term $Ne^2/2\epsilon r$ where r is the ionic radius and ϵ the permittivity of the solvent. Such a term could be taken as the solvation energy of the initial or activated states but it does not seem valid to use it for the difference between them. In fact for the present reaction there seems to be no correlation between the rate and the available real free energies of solvation:

$$\begin{aligned}\alpha(\text{Cd}^{2+}, \text{H}_2\text{O}) &= -1805 \text{ kJ mol}^{-1}; & \alpha(\text{Cd}^{2+}, \text{CH}_3\text{OH}) &= -1850 \text{ kJ mol}^{-1}; \\ \alpha(\text{Cd}^{2+}, \text{CH}_3\text{CN}) &= -1790 \text{ kJ mol}^{-1}.\end{aligned}$$

However, such a relation could be obscured by the absence of a Frumkin or other type of double layer correction.

On the other hand the importance of solvation could be indicated by the existence of the compensation between the pre-exponential factor and the heat of activation shown in Fig. 4. The line as drawn has a slope close to 300 K, but it must be noted that it depends to a large extent on the value for methanol which is the most uncertain of these results. One indication that this result may be unreliable is the exceptionally large frequency factor which is difficult to account for. If this result is excluded from consideration, the remainder exhibit the normal variation round the value to be expected for a simple first order reaction. In particular they suggest that the mechanism is probably similar for the different solvents. If this is so then the low value of the transfer coefficient which is also found in all the solvents probably has a common origin. In general terms this process can be regarded as similar to that illustrated in Fig. 5 which is taken from the work of Conway and Bockris³⁴. It is evident from their work that the energy required to reach state (b) from state (a) is about the magnitude of the experimental energies of activation. Since it is very much smaller than the total solvation energy (about 1%) it is likely to be relatively independent of the latter.

A striking effect is found in many solvent mixtures, particularly those containing water. As the composition is varied, the rate constant passes through a minimum value typically one to two orders of magnitude smaller than in the pure solvents. This phenomenon was first observed for hydrogen evolution from water-methanol mixtures³¹. The main factor responsible seems to be the difference in compositions of the solvation sheaths of ion and electrode⁶. It is possible that the most significant consequence of this difference is an increase in distance between the electrode surface and the reactant ion in the pre-electrode layer compared with the distance in either of the pure solvents. This distance is determined by the radii of the solvation sheaths and the extent to which they can be shared. When electrode and ion solvations differ, solvent sharing is an energetically unfavourable process and the ion-electrode distance increases, thereby increasing the energy barrier for ion discharge. The constancy of α suggests that the mechanism of the process and the geometry of the energy barrier remain unchanged. This proposed mechanism is similar to the mechanism suggested to account for the inhibition of cadmium discharge by uncharged surfactants³⁵. The latter systems can be considered as extreme examples of the mixed solvent case in which a minor bulk species produces a large difference between ion and electrode environments.

This type of behaviour is particularly marked in mixtures of water with another solvent when the electrode reaction occurs at a potential not too far from the point of zero charge because under these conditions the non-aqueous solvent is preferen-

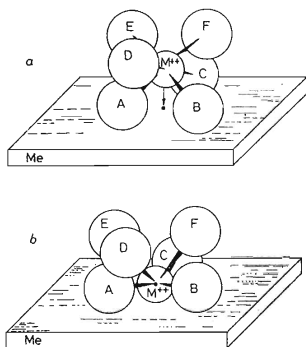


FIG. 5

Model of Symmetrical Transfer of a Divalent Ion to a Metal (Me) Surface (a) Initial State, (b) After Displacement (outer primary hydration layer is not shown). From Conway and Bockris ref.³⁴.

tially adsorbed at the interface while water preferentially solvates the reacting ion. The methanol-water system is the only one for which detailed data on electrode and ion solvation are available and these are consistent with the above proposals. In such mixtures, hydration of the proton is heavily favoured³⁶ and in solutions containing only a small proportion of water the hydronium ion is the major species. In the electrode-solution interphase the opposite situation prevails^{37,38}, and the mole fraction of methanol exceeds that in the bulk for all solution compositions. These are the conditions which can cause lowering of the charge transfer rate in solutions of intermediate composition.

In certain of the solvent mixtures ($\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$, $\text{NMF}-\text{DMF}$, $\text{CH}_3\text{OH}-\text{(CH}_3)_2\text{CO}$) the minimum discussed above is either very shallow or absent. It is probable that this finding indicates that in such mixtures the distributions of solvent around ion and electrode are similar.

An alternative explanation of this effect can be found in the framework of the theory of electron transfer reactions¹⁻⁴ if the formation of a charged intermediate like Cd^+ or Cd_2^{2+} is assumed. In this case the free energy of activation can be obtained from Marcus's theory³⁹ as:

$$\Delta G = \frac{1}{2}\alpha\lambda, \quad (11)$$

where

$$\lambda = (ne)^2 (a^{-1} - r^{-1})(\epsilon_0^{-1} - \epsilon^{-1}) \quad (12)$$

if a very simple model of the solvation shell is used. a is the radius of the ion with its primary solvation sheath; r is the distance between the reactant and its image in the electrode, ϵ_0 is the optical and ϵ the static permittivity. Since $\epsilon \gg \epsilon_0$ and ϵ_0 is relatively independent of the nature of the solvent, the main solvent dependence arise from the factor $(a^{-1} - r^{-1})$. This will be particularly marked for aqueous-non-aqueous mixtures because of the small size of the water molecule compared with other solvent molecules and the preferential adsorption of the non-aqueous solvent at the electrode while the ions tends to be preferentially aquated. Thus as the non-aqueous component of the mixture increases a remains constant while r increases causing an increase in $(a^{-1} - r^{-1})$ and hence the activation energy. As the mixture becomes completely non-aqueous r remains more nearly constant while a increases more rapidly leading to a decrease in the activation energy.

Thus the general behaviour of the rate in aqueous + non-aqueous mixtures is likely to be similar for either mechanism. Unfortunately the present results on the V^{2+} and V^{3+} reaction are insufficient to verify that a system likely to obey Marcus's theory does in fact show this behaviour. The striking decrease in the transfer coefficient for this reaction going from water to N-methylformamide is at present an isolated example. Further investigation is clearly required.

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APPENDIX

Approximate Calculation of the Pre-exponential Factor for the Reaction Following Equations (1) and (2)

The standard rate constant is obtained directly from equation (7) as

$$\vec{k} = (\vec{k}_0)^{1-\beta} (\vec{k}_0)^\beta K^{-\beta} \quad (13)$$

The corresponding pre-exponential factor is then

$$\vec{A} = (\vec{A})^{1-\beta} (\vec{A})^\beta \exp[-\beta \Delta S^+ / R] \quad (14)$$

where ΔS^+ is the standard entropy change in reaction (B).

The order of magnitude of \vec{A} the pre-exponential factor for the forward direction of reaction (A) can be obtained from a simple kinetic argument (cf. Randles⁴⁰). It is assumed that the reaction occurs by collision of two Cd^{2+} moving parallel to the interface. The rate of reaction is then

$$V = Nn^2 \sigma (8RT/\pi M)^{1/2} \exp(-E/RT) \quad (15)$$

where N is Avogadro's number, n is the surface concentration, σ the collision diameter and M the molecular weight of the colliding particles. The surface concentration may be obtained by assuming that the particles move in a thin layer of thickness equal to the molecular diameter; then $n = cl$ where c is the bulk concentration.

Thus the pre-exponential factor can be expressed as

$$\vec{A} = Nl^2 \sigma (8RT/M)^{1/2} \quad (16)$$

or

$$\vec{A} = V_m (8RT/\pi M)^{1/2} \quad (17)$$

where V_m is the molar volume, since $l^2 \sigma$ is approximately the volume of one particle. If V_m is taken as $10 \text{ cm}^3 \text{ mol}^{-1}$ and M as 112 g mol^{-1} , \vec{A} is found to be $2.4 \cdot 10^5 \text{ cm}^4 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C .

The pre-exponential factor for the reverse direction of (A) can be taken as the same as that estimated for a simple first order electrode reaction, i.e. $A \approx 10^3 \text{ cm s}^{-1}$

The standard entropy change in reaction (B) is likely to be not too different from that for the reaction



From tabulated values of standard entropies this can be calculated as $-19.2 \text{ J K}^{-1} \text{ mol}^{-1}$ the standard state for the metal being the pure liquid. This must be corrected to a standard state of 1 mol cm^{-3} to conform with the standard states used in the kinetics. The correction is approximately $+RT \ln V_m$ or $21.4 \text{ J K}^{-1} \text{ mol}^{-1}$ if the molar volume of cadmium ($13 \text{ cm}^3 \text{ mol}^{-1}$) is used. Thus $\Delta S^+ = +2.2 \text{ J K}^{-1} \text{ mol}^{-1}$.

With these values the apparent pre-exponential factor can be calculated from equation (14). If $\beta = 0.5$ the value obtained is $1.4 \cdot 10^4 \text{ cm}^4 \text{ mol}^{-1} \text{ s}^{-1}$. It is evident that the maximum variation of β cannot alter this value by more than a factor of 10.

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