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INFLUENCE OF COMPLEX FORMATION AND SOLVATION ON THE ELECTRODE REACTIONS OF SOME METAL IONS AT AMALGAMS IN APROTIC SOLVENTS

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CONTENTS

A. INTRODUCTION

From investigations of the kinetics of electrode reactions at mercury or liquid amalgams with the participation of metal ions it is well known that different anions often have a considerable influence on the rate of reaction. This influence cannot be explained solely as a Frumkin effect, i.e. a coulombic attraction or repulsion of the reacting ions by the field of the electrode double-layer.

Heyrovský [1] was the first to suggest that catalysis by halide ions during the electroreduction of different metal ions, e.g. In(III), Sb(III) and Bi(III), is due to electron transfer through a halide bridge between the electrode and the metal ion. However, only in a few cases has it been possible to provide evidence that anions can function as electron mediators in electrode reactions (see ref. 2). For instance, in studies [3] of the influence of halide ions on the rate of oxidation of Cr(II) at electrodes and similar measurements [4] of the effect of thiocyanate, it was shown that specifically adsorbed anions function as ligand bridges. In an investigation [5] of the electroreduction of

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In(III) in the presence of thiocyanate ions, direct evidence was not obtained, but the mechanism most probably involves ligand bridging.

For other electrode reactions involving amalgams the explanations given for the rate-enhancing effect by complex-forming anions are more uncertain. Most authors have suggested that the increase in rate often found in halide and thiocyanate solutions is due to the specific adsorption of these anions, without explicitly mentioning ligand bridging at the amalgam as a possible mechanism.

However, it has been shown with some systems that the catalysed charge transfer at the amalgam is brought about by a single complex, e.g. the complex $BiCl_2^+$ in the Bi(III) chloride system [6]. The concentration of the electroactive complex can be very low compared with that of the predominant complex in the solution. In such a case it is not reasonable to ascribe the catalytic effect solely to specific adsorption of the ligand. Most probably the effect is also due to a change in the coordination geometry and the solvation when the electroactive complex is formed.

So far, most investigations of electrode reactions of metal complexes refer to water solutions or some other protic solvents (cf. ref. 7). However, during the last decade much information about thermodynamic properties and structures of metal complexes in aprotic solvents has become available. By selection of an aprotic solvent with suitable donor properties, sufficient solubility can often be obtained for metal halides that are sparingly soluble in aqueous solution. Furthermore, stronger solvation generally decreases the rate of charge transfer at the electrode and thus facilitates an accurate determination of the exchange current density. Therefore, electrode reactions which are very fast in aqueous solution can often be studied.

I discuss here some studies on halide and thiocyanate systems of Zn(II), Cd(II), Hg(II) and Cu(I) with dimethylsulphoxide (DMSO) or acetonitrile (AN) as solvents. The aim is to show how different factors, connected with complex formation and important for the rate of charge transfer at amalgams (am), can be elucidated.

B. THEORETICAL

(a) If the central ion is a monovalent metal ion M^+ forming mononuclear complexes with the ligand L^-, the overall electrode reaction might proceed by a set of parallel metal ion transfers according to reaction (1):

$$ML_j^{1-j} + e^-(am) \rightleftharpoons M(am) + jL^- \qquad (1)$$

The exchange current density, i_0, is a measure of the rate of the ion transfer in both directions of reaction (1) at the equilibrium electrode potential. If it is supposed that the complexes are in equilibrium during the measurements of i_0, the general theory for electrode kinetics (cf. refs. 8,9) and the introduction of stability constants, β_j, of the complexes yield eqn. (2):

$$i_0 = \sum_j k_j [\mathrm{M}^+]^{\alpha_j} [\mathrm{L}^-]^j \qquad (0 < \alpha_j < 1) \tag{2}$$

Here α_j is the anodic transfer coefficient and k_j a composite coefficient, for which expression (3) is valid:

$$k_j = Fk_j^{\ominus} \beta_j^{\alpha_j} [\mathrm{SV}]^{j(\alpha_j - 1)} [\mathrm{M(am)}]^{1-\alpha_j} \exp\{(j - \alpha_j)\phi_2 F/RT\} \tag{3}$$

In this expression $k_j^{\ominus}$ denotes the true rate constant, SV the solvent, and ϕ_2 the potential of the OHP. The exponential factor is the Frumkin factor. As solvent molecules must also be involved in reaction (1), the rate constant should be a function of [SV]. It is appropriate to separate the factor $[\mathrm{SV}]^{j(\alpha_j-1)}$ from the rate constant. In this way all $k_j^{\ominus}$ have the dimension length time^{-1}, and their ratios can be compared. From measurements of i_0 the quantities α_j (equal to about 0.5) and k_j can be obtained, and if β_j and ϕ_2 are known from separate investigations, $k_j^{\ominus}$ can be calculated.

(b) When dinuclear complexes also take part in ion transfer according to the reaction

$$\mathrm{M_2L}_j^{2-j} + \mathrm{e^-(am)} \rightleftharpoons \mathrm{M(am)} + \mathrm{ML}_j^{1-j} \tag{4}$$

terms of the type $k_j'' \, [\mathrm{M}^+]^{1+\alpha_j} \, [\mathrm{L}^-]^j$ also appear in eqn. (2).

(c) For a divalent metal ion M^{2+} it is probable for energetic reasons [10] that the charge transfer proceeds stepwise with the solvated M(I) as an intermediate. If the first step, the electron transfer

$$\mathrm{ML}_j^{2-j} + \mathrm{e^-(am)} \rightleftharpoons \mathrm{ML}_j^{1-j} \tag{5}$$

is rate determining, eqn. (6) should be valid:

$$i_0 = \sum_j k_j [\mathrm{M}^{2+}]^{(1+\alpha_j)/2} \, [\mathrm{L}^-]^j \tag{6}$$

The expression for k_j is in this case given by eqn. (7):

$$k_j = Fk_j^{\ominus} \beta_j^{\alpha_j} \gamma_j^{1-\alpha_j} K^{-(1-\alpha_j)/2} [\mathrm{M(am)}]^{(1-\alpha_j)/2} \exp\{(j - 1 - \alpha_j)\phi_2 F/RT\} \tag{7}$$

where γ_j is the stability constant of the intermediate ML_j^{1-j} and K the disproportionation constant of M^+. To obtain values of the ratios $k_j^{\ominus}/k_{j-1}^{\ominus}$, it is often necessary to make some approximation about the unknown quantities $\gamma_j^{1-\alpha_j}$. When $1 - \alpha_j$ is small (less than 0.5) and the values of γ_j can be supposed to be low, $(\gamma_j/\mathrm{M}^{-j})^{1-\alpha_j} \approx 1$ is a useful approximation.

If the second step, the ion transfer, is rate determining, $[\mathrm{M}^+]$ in eqn. (2) can be exchanged for $[\mathrm{M}^{2+}]^{1/2}$ because of the disproportionation equilibrium.

(d) A dinuclear complex $M_2L_j^{4-j}$, involved in reaction (5), gives an additional term k_j'' $[M^{2+}]^{(3+\alpha_j)/2}$ $[L^-]^j$ in eqn. (6).

An average value [11] of the exponents for $[M^+]$ and $[M^{2+}]$ in the expressions for $i_\circ$ is obtained from the function $\overline{\alpha} = (\partial \log i_\circ / \partial \log[M^{n+}])_{[L^-]}$. If $\overline{\alpha}$ is found to be independent of $[L^-]$, the value of the exponents is found directly.

The measurements of $i_\circ$ must be carried out in the presence of a supporting electrolyte, NH_4ClO_4 or Et_4NClO_4, of constant and fairly high ionic strength. In this way variations in the activity coefficients and in the ϕ_2 potential can be suppressed so that true rate constants are obtained.

C. THE ELECTRODE REACTIONS Zn(II)/Zn(Hg), Cd(II)/Cd(Hg) AND Hg(II)/Hg IN DIMETHYLSULPHOXIDE

The acceptors Zn^{2+}, Cd^{2+} and Hg^{2+} are strongly solvated by DMSO through coordination to these cations via the oxygen atom [12]. The enthalpies of transfer [13] of these ions from water to DMSO are −60, −68 and −76 kJ mol^{-1}. The stronger solvation in DMSO compared with that in water gives rise to a decrease in the rate of charge transfer and makes an accurate determination of the exchange current density from faradaic impedance measurements or by a cyclic current-step method [14,15] feasible.

(i) Cadmium(II) systems

When dealing with measurements in DMSO the results obtained for the cadmium systems prove to be the easiest to explain.

The electrode reaction in perchlorate solutions has been frequently studied, both in water [16] and in various non-aqueous solvents, including aqueous–non-aqueous mixtures [17]. In general, very low values, 0.15–0.20, for the apparent cathodic transfer coefficient, (the exponent for [Cd(am)] in eqn. (3) or (7)), were obtained. Such values have been accounted for by suggesting [18,19] a stepwise charge transfer with Cd^+ as an intermediate. Another mechanism discussed [17] a transition state with a partially discharged and specifically adsorbed Cd^{2+}.

In aqueous chloride solutions, the electrode reaction has such high exchange current densities that it has been impossible to arrive at a conclusive determination of the mechanism [20]. However, chloride ions have a catalytic effect.

In DMSO solutions, measurements [21] show that at a constant amalgam concentration, $i_\circ$ is a function solely of $[Cd^{2+}]$. Thus the chloride complexes [22], which are more stable in DMSO than in aqueous solution, do not contribute noticeably to $i_\circ$. This observation provides the opportunity to

TABLE 1

Composite coefficients k_j, k_0' and k_j'' in eqns. (8)–(10), (12), (13) and (16) at 25 °C when $i_\circ$ is expressed in milliamperes per square centimetre, and $[M^{2+}]$, $[M^+]$ and $[L^-]$ are molar concentrations. Medium: DMSO, 1 M NH_4ClO_4 or AN, 0.1 M Et_4NClO_4

	L^-					
	Cl^-	Br^-	I^-	SCN^-		Cl^-
Zn(II)/Zn(Hg), DMSO					Hg(II)/Hg, DMSO	
$\log k_0$	1.34	1.54	1.56	1.70	$\log(k_0 + k_0')$	3.61
$\log k_1$			1.26		$\log k_1$	11.63
					$\log k_2$	18.18
					$\log k_3$	22.54
Cd(II)/Cd(Hg), DMSO					$\log k_4$	24.95
$\log k_0$	3.45	3.46	3.45	3.08	$\log k_1''$	15.18
$\log k_1$	< 4.5	5.30	6.20	4.48		
$\log k_2$		8.00	8.75	4.18		
$\log k_0'$	0.85	1.08		0.54		
Cu(I)/Cu(Hg), DMSO					Cu(I)/Cu(Hg), AN	
$\log k_0$	6.78				$\log k_0$	3.11
$\log k_2''$	18.00				$\log k_1$	7.85
$\log k_3''$	18.65				$\log k_2$	11.18

study the dependence of $i_\circ$ on $[Cd^{2+}]$ within a broad concentration range, 10^{-7}–10^{-2} M. The function $\bar{\alpha}$ has very different values at high and low $[Cd^{2+}]$, and all measurements can be very well represented by eqn. (8):

$$i_\circ = k_0[Cd^{2+}]^{0.85} + k_0'[Cd^{2+}]^{0.20} \tag{8}$$

The values for the coefficients are given in Table 1. From the exponents for $[Cd^{2+}]$ the charge transfer most probably proceeds stepwise (case (c) above) with the electron transfer Cd(II)/Cd(I) predominating at high $[Cd^{2+}]$ and the ion transfer Cd(I)/Cd(Hg) being most important at very low $[Cd^{2+}]$. In this case, $i_\circ$ is the sum of the exchange current densities of the two steps and indicates that the steps are parallel (cf. ref. 11). This implies that the disproportionation of Cd(I) and the complex equilibria involved are very rapid compared with the charge transfer steps. A similar mechanism has been suggested earlier [19] for cadmium perchlorate in aqueous solution without any clear evidence. Furthermore, as the estimated value of the disproportionation constant is very high, probably weakly solvated Cd^+ is stabilized by specific adsorption on the amalgam.

For the bromide, iodide and thiocyanate systems, measurements [21,23] indicate that $i_\circ$ depends on both $[Cd^{2+}]$ and the free ligand concentration

[L$^-$]. All measurements can be represented by an equation of the following type:

$$i_\circ = [\mathrm{Cd}^{2+}]^{0.85} \sum_{j=0}^{2} k_j [\mathrm{L}^-]^j + k_0' [\mathrm{Cd}^{2+}]^{0.20} \tag{9}$$

The linear and quadratic terms in [L$^-$] show that besides the solvated Cd^{2+} the complexes CdL$^+$ and CdL$_2$ most probably take part in the Cd(II)/Cd(I) step. As a consequence, the contribution to $i_\circ$ from this step predominates within the whole range of measurements. In the bromide and thiocyanate systems $i_\circ$ decreases at increasing [L$^-$] for constant Cd(II) concentration. Thus there is no catalysis of the overall charge transfer. A difference between the two systems is that the influence of CdL$_2$ on $i_\circ$ is much smaller in the thiocyanate system than in the bromide system.

TABLE 2

Rate constants, $k_j^\ominus$ (cm s^{-1}), or their ratios, relating to the participation of metal complexes ML$_j$ in electrode reactions at M(Hg). Enthalpy changes ΔH_j° (kJ mol^{-1}) and entropy changes ΔS_j° (J K^{-1} mol^{-1}) in the reactions ML$_{j-1}$ + L $\rightleftharpoons$ ML$_j$ [a]

	L$^-$					
	Cl$^-$	Br$^-$	I$^-$	SCN$^-$		Cl$^-$
Zn(II)/Zn(Hg), DMSO					Hg(II)/Hg, DMSO	
$k_0^\ominus \times 10^5$	1.4	1.3	1.3	1.5	$k_1^\ominus/k_0^\ominus$	> 350
$k_1^\ominus/k_0^\ominus$		< 14	45	< 10	$k_2^\ominus/k_1^\ominus$	15
ΔH_1°	22.3	27.8	19.0	5.5	$k_3^\ominus/k_2^\ominus$	20
ΔH_2°	0.8	9.1	29.4	23.5	$k_4^\ominus/k_3^\ominus$	7
					ΔH_1°	−19.2
					ΔH_2°	−29.7
Cd(II)/Cd(Hg), DMSO					ΔH_3°	−20.1
$k_1^\ominus/k_0^\ominus$	< 0.6	7	180	17	ΔH_4°	−16.5
$k_2^\ominus/k_1^\ominus$		250	360	1.4		
ΔH_1°	−6.3	−3.9	2.4	−3.0		
ΔH_2°		17	27	−2.8		
Cu(I)/Cu(Hg), DMSO					Cu(I)/Cu(Hg), AN	
$k_0^\ominus$	55				$k_0^\ominus \times 10^3$	1.7
ΔH_1°	−6.4				$k_1^\ominus/k_0^\ominus$	2600
ΔH_2°	−7.8				$k_2^\ominus/k_1^\ominus$	9
ΔS_1°	62				ΔH_1°	16.8
ΔS_2°	60				ΔH_2°	4.4
					ΔS_1°	133
					ΔS_2°	121

[a] ΔH_j°, ΔS_j° values were taken from the following refs: for Zn(II) [31], Cd(II) [22], Hg(II) [34], Cu(I) in DMSO [42], Cu(I) in AN [43].

Finally, in the iodide system, the complexes CdI^+ and CdI_2 take part so effectively in the Cd(II)/Cd(I) step that the contribution to $i_\circ$ from Cd(I)/Cd(Hg) is negligible. Furthermore, at a constant Cd(II) concentration there is a pronounced catalysis of the total charge transfer on addition of iodide ions. Only at higher $[I^-]$, when anionic complexes are formed, does $i_\circ$ decrease again.

From the k_j coefficients (Table 1) the ratios of the rate constants $k_j^\ominus$ have been calculated (Table 2) according to eqn. (7). The change in the rate constant on formation of CdL^+ leads to the conclusion that ligand bridging at the electrode is not very probable, except for the iodide system. The enthalpy change ΔH_1° (Table 2) does not indicate any large change in solvation, and consequently these solvated complexes should be six-coordinate as in the octahedral $Cd(DMSO)_6^{2+}$ [12].

From the $k_2^\ominus/k_1^\ominus$ values the formation of CdL_2 in the bromide and iodide systems gives rise to a large increase in the rate constant. This effect can be correlated with the fairly large and positive values for the enthalpy change ΔH_2° in the second step of complex formation. These values indicate a pronounced decrease in the inner-sphere solvation, probably a change from octahedral to tetrahedral coordination [22]. As a result of this partial desolvation an increase in the rate constant should be expected. For the thiocyanate system the small and negative ΔH_2° does not indicate a corresponding change in solvation. Accordingly, no increase in the rate constant is obtained. Thus the correlation explains why in some cadmium systems a certain complex can be especially electroactive.

For the anionic complexes, no additional rate-increasing effect can be expected. In this case the negative ϕ_2 potential, -40 mV, makes their Frumkin factors so small that the participation of these complexes in the electrode reaction is not detectable.

(ii) Zinc(II) systems

It is well known that in water solution, halide and thiocyanate ions increase the rate of the electrode reaction at zinc amalgam. This effect parallels [24,25] the specific adsorbabilities [26] of these anions, i.e. $Cl^- < Br^- < SCN^- < I^-$. Accordingly, some authors [25,27] have concluded that the rate enhancement in the halide systems is due to specific adsorption, whereas others [28] have stressed the importance of complex formation.

The difficulty in distinguishing between the two effects is partly connected with the very weak complex formation in the zinc halide systems in aqueous solution [29]. However, in DMSO, complex formation is much stronger [30], especially with Cl^- and Br^-, and for this reason DMSO is a more suitable solvent for studies of electrode kinetics. Electrocapillary measurements [15,23] in DMSO show that the specific adsorbabilities of Cl^- and Br^- are stronger in DMSO than in water, whereas for I^- the values are very similar in both solvents. The sequence in DMSO is $Cl^- \approx SCN^- < Br^- < I^-$.

Kinetic measurements [15,22] on the chloride, bromide, iodide and thiocyanate systems in DMSO showed that at constant [Zn(Hg)] the $i_\circ$ function is represented by eqn. (10)

$$i_\circ = [Zn^{2+}]^{\alpha_0}(k_0 + k_1[L^-]) \tag{10}$$

For the ligands Cl^-, Br^- and SCN^-, α_0 has the values 0.50, 0.60 and 0.65, respectively, and $k_1 \approx 0$. Thus in all these systems the solvated Zn^{2+} dominates the charge transfer, even if its concentration in the bulk of the solution is only a few per cent of the total zinc concentration. For the iodide system, $\alpha_0 = 0.60$, and the term $k_1[L^-]$ is of importance in this case. Thus, most probably both Zn^{2+} and ZnI^+ contribute to the charge transfer.

The value $\alpha_0 = 0.50$ for the chloride system makes it likely that the charge transfer for Zn^{2+} proceeds as a one-step ion transfer in DMSO (case (a) above with M^+ exchanged for M^{2+}). For a two-step process with the electron transfer Zn(II)/Zn(I) as the rate-determining step, an unlikely low value (about zero) for the anodic transfer coefficient would be obtained. Even if α_0 and k_0 (Table 1) differ between the different zinc systems, they give the same value for the rate constant $k_0^\ominus$ (Table 2). This observation supports the conclusion that the mechanism is largely the same for all these systems. From the reproducibility of the measurements, upper limits can also be estimated for the ratio $k_1^\ominus/k_0^\ominus$. Only with I^- does the formation of ZnL^+ give a considerable increase in the rate constant. In these systems the ϕ_2 potential has a value of about −60 mV, making the contributions to $i_\circ$ from the complexes very small in the absence of any catalytic effect.

Thus with respect to the influence of the formation of the complex ML^+ on the rate of the charge transfer, the zinc systems in DMSO behave similarly to the corresponding cadmium systems. The only difference is that with I^- as ligand the effect is smaller for zinc than for cadmium.

The large positive ΔH_1° and/or ΔH_2° values (Table 2) certainly indicate changes in the coordination geometry [31] but the non-appearance of any catalysis of the charge transfer as a result of complex formation, except for ZnI^+, makes a transition from octahedral to tetrahedral coordination improbable as the main change. Instead, another interpretation is possible.

On heating the solid $Zn(DMSO)_6(ClO_4)_2$, one DMSO is lost before melting and a pentasolvate is formed [32], contrary to the situation with $Cd(DMSO)_6(ClO_4)_2$. This seems to be due to steric crowding in the octahedron around the small Zn^{2+}. In DMSO solution, charge compensation by complex formation might yield a similar effect, so that the first two complexes take part in equilibria between six- and five-coordinate zinc:

$$\mathrm{ZnL}_j(\mathrm{DMSO})_{6-j}^{2-j} \rightleftharpoons \mathrm{ZnL}_j(\mathrm{DMSO})_{5-j}^{2-j} + \mathrm{DMSO} \tag{11}$$

($j = 1$ and 2)

Thus in the chloride and bromide systems the decrease in effective charge on the central zinc atom should be sufficient already in the first complex to make it predominantly five-coordinate, whereas in the iodide and thiocyanate systems such a change in coordination will occur mainly at the second step of complex formation. Several solid complexes with five-coordinate zinc(II) are known (cf. ref. 33).

This interpretation implies that five-coordination in DMSO does not give more effective ligand bridging at the electrode than six-coordination.

(iii) The mercury(II) chloride system

This system cannot be studied in water solution because of the very slight solubility of $\mathrm{Hg_2Cl_2}$. In DMSO, however, the species are soluble, and with chloride ligands, Hg(II) is strongly stabilized compared with Hg(I) [34]. The strong solvation of $\mathrm{Hg^{2+}}$ and presumably also of $\mathrm{Hg_2^{2+}}$ makes an accurate determination of the exchange current density possible [35]. However, $i_\circ$ can be obtained only at ligand numbers $\bar{n} \leqslant 1.3$ or $\bar{n} \geqslant 2.3$. Measurements indicate that in the range between these limits there is a specific adsorption of a charge-transferring species, probably $\mathrm{HgCl_2}$, determining the rate of the overall electrode reaction. This uncharged complex might form an adsorbed two-dimensional network on the mercury surface with a slow exchange adsorption rate.

At a constant mercury concentration, pronounced catalysis of the charge transfer is obtained on addition of $\mathrm{Cl^-}$. $i_\circ$ is a function of both $[\mathrm{Hg^{2+}}]$ and $[\mathrm{Cl^-}]$, and the following rate law (eqn. (12)) describes all the measurements well:

$$i_\circ = [\mathrm{Hg^{2+}}]^{0.88}\left(k_0' + \sum_{j=0}^{4} k_j[\mathrm{Cl^-}]^j\right) + k_1''[\mathrm{Hg^{2+}}]^{1.7}[\mathrm{Cl^-}] \tag{12}$$

From this rate law the following oxidants take part in the charge transfer: $\mathrm{Hg_2^{2+}}$, HgCl_j^{2-j} ($j = 0$–4) and $\mathrm{Hg_2Cl^{3+}}$. In this system the ϕ_2 potential is small and positive, 4 mV at $\bar{n} \approx 3$. Therefore the contributions from all the mononuclear complexes to $i_\circ$ can be determined in more detail than is possible with the cadmium systems. The contribution from each complex is predominant within a certain $[\mathrm{Cl^-}]$ range [35]. It is also found that the dinuclear $\mathrm{Hg_2Cl^{3+}}$ has a noticeable influence on $i_\circ$ around $\bar{n} = 1$ even at low mercury concentrations.

The existence of this complex in DMSO solution has not been revealed previously, but formation of the corresponding iodide complex has been indicated by Raman measurements [36]. The main cause of the high electroactivity of Hg_2Cl^{3+} is probably a considerable decrease in inner-sphere solvation with the formation of this complex from $HgCl^+$ and the octahedral [12] solvated Hg^{2+}.

The high exponent 0.88 for $[Hg^{2+}]$ in the terms pertaining to the mononuclear species suggests a stepwise charge transfer with the electron transfer step Hg(II)/Hg(I) as rate determining (cases (c) and (d) above). A further indication of a two-step mechanism is the effective participation of the very strong $HgCl_j^{2-j}$ complexes. This observation would not be expected for a one-step ion transfer mechanism that would involve breaking of the strong Hg(II)–Cl bonds.

Values for the coefficients in eqn. (12) (Table 1) and for the ratios $k_j^{\ominus}/k_{j-1}^{\ominus}$ (Table 2) have been recalculated because of revised stability constants [34]. The estimated value of 350 for the ratio $k^{\ominus}(HgCl^+)/k^{\ominus}(Hg^{2+})$ is based on the assumption that $k^{\ominus}(Hg^{2+}) \approx k^{\ominus}(Hg_2^{2+})$. As most probably $k^{\ominus}(Hg^{2+}) < k^{\ominus}(Hg_2^{2+})$ owing to stronger solvation of Hg^{2+} than of Hg_2^{2+}, the approximation should yield a lower limit of the ratio. The large increase in the rate constant on formation of $HgCl^+$ can be explained by the change from octahedral to strongly distorted tetrahedral coordination that has been proven by extended X-ray absorption fine structure (EXAFS) measurements [37] to accompany the formation of halide complexes HgL^+ in DMSO. From Table 2 it is also evident that there is a steady increase in the rate constant with the number of Cl^- coordinated. This observation can be correlated with the simultaneous lengthening in the Hg(II)–Cl distance [36] that indicates a weakening of the bond.

As mentioned above, the specific adsorbabilities of Br^- and I^- are larger than that of Cl^- also in DMSO solution. From this fact we may conclude that the range, where the rate-determining adsorption step prohibits determination of i_0, should broaden in the mercury(II) bromide and iodide systems and make a close study of these electrode reactions impossible.

D. THE ELECTRODE REACTION Cu(I)/Cu(Hg) IN HALIDES-CONTAINING DIMETHYLSULPHOXIDE SOLUTION

The Cu^+ acceptor is strongly solvated in DMSO, and its disproportionation constant [38] is about 10^6 times smaller than that in water. In consequence, Cu^+ can exist in DMSO as the solvated ion. This species is four-coordinate, most probably tetrahedral, as has been found in EXAFS measurements [39]. Furthermore, the halides of Cu(I) are readily soluble in DMSO.

In studies [40] of the reduction of Cu(II) in aqueous ammonia solutions it was found that chloride ions have a catalytic effect on the Cu(I)/Cu(Hg) step, that cannot be explained as a Frumkin effect.

In DMSO chloride solutions, measurements of i_0 can be carried out [41] only at $[\mathrm{Cl}^-] > 15$ mM, where CuCl_2^- and CuCl_3^{2-} are the main complexes in solution [42]. At these chloride concentrations Cu(I) is strongly stabilized compared with Cu(II), and calculations on the disproportionation equilibrium show that the ratio [Cu(II)]/[Cu(I)] is extremely small. At lower $[\mathrm{Cl}^-]$, specific adsorption of a species, most probably CuCl forming a surface network, is rate controlling for the overall electrode reaction and prohibits determination of i_0.

Within the range of $[\mathrm{Cl}^-]$ available, the rate law

$$i_0 = k_0[\mathrm{Cu}^+]^{0.65} + [\mathrm{Cu}^+]^{1.65} \sum_{j=2}^{3} k_j''[\mathrm{Cl}^-]^j \qquad (13)$$

represents the measurements very well. The term with the exponent 0.65 indicates that the solvated Cu^+ takes part in the metal ion transfer (case (a) above). However, there is no indication that any of the mononuclear chloride complexes takes part as oxidant in the charge transfer. This result can be correlated with the negative ΔH_1° and ΔH_2° values (Table 2), as a participation of these complexes would involve breaking of fairly strong Cu(I)–Cl bonds.

The other two terms in eqn. (13) with the exponent 1.65 must pertain to participation of the dinuclear complexes $\mathrm{Cu_2Cl_2}$ and $\mathrm{Cu_2Cl_3^-}$ as oxidants (case (b) above). This charge transfer should be energetically more favourable, if it involves breaking of a weak Cl^- bridge between the two Cu(I) in the complexes. Furthermore, formation of such complexes should give rise to considerable partial desolvation.

From the k_0 value (Table 1) a very high rate constant, 55 ± 5 cm s^{-1}, for the electrode reaction with solvated Cu^+ is obtained according to eqn. (3) with $\phi_2 = -27$ mV. This suggests that bridging at the electrode by specifically adsorbed Cl^- catalyses the charge transfer. Electrocapillary measurements also show an approximately constant specific adsorption of Cl^- within the concentration range used, and this can explain the constant coefficient k_0. Then the following mechanism for charge transfer is deduced:

$$\mathrm{Cl}^-_{\mathrm{ads}}\text{–}\mathrm{Cu}^+ + \mathrm{e}^-(\mathrm{am}) \rightleftharpoons \mathrm{Cl}^-_{\mathrm{ads}} + \mathrm{Cu(am)} \qquad (14)$$

$$\mathrm{Cl}^-_{\mathrm{ads}}\text{–}\mathrm{Cu_2Cl}_j^{2-j} + \mathrm{e}^-(\mathrm{am}) \rightleftharpoons \mathrm{Cl}^-_{\mathrm{ads}} + \mathrm{Cu(am)} + \mathrm{CuCl}_j^{1-j} \qquad (15)$$

$(j = 2$ and $3)$

The rate-controlling adsorption step mentioned above is more pronounced in the copper(I) bromide and iodide systems [41] and precludes determination of $i_\circ$ over the whole ligand concentration range available.

E. THE ELECTRODE REACTION Cu(I)/Cu(Hg) IN CHLORIDE-CONTAINING ACETONITRILE SOLUTION

In acetonitrile (AN) the two mononuclear complexes formed in the copper(I) chloride system have stability constants with an order of magnitude [43] similar to that of the corresponding constants in DMSO. However, in AN, the ΔH° and ΔS° values are positive. Thus a study of the electrode kinetics provides the possibility to test further the correlation mentioned above between kinetic and thermodynamic quantities. In AN, Cu^+ is strongly solvated, and its disproportionation constant has an extremely low value, 10^{-21} M^{-1}, which means that Cu(I) is stable. The solvated Cu^+ is four-coordinate, most probably tetrahedral [39].

Measurements of $i_\circ$ in the presence of 0.1 M Et_4NClO_4 [44] can be carried out only in the range $1.3 < \bar{n} < 1.9$ and at $[Cu^+] < 1$ mM. Results from electrocapillary measurements indicate that at higher electrode potentials there is specific adsorption of Et_4N^+, which can inhibit charge transfer.

The rate law

$$i_\circ = [Cu^+]^{0.70} \sum_{j=0}^{2} k_j [Cl^-]^j \tag{16}$$

represents the experimental data fairly well. This rate law shows that the oxidants taking part in the charge transfer are $CuCl_j^{1-j}$ with $j = 0$–2 (case (a) above). From the k_j values (Table 1) the maximum contribution to $i_\circ$ from CuCl is more than 70%, though the maximum concentration of this complex in the bulk of the solution is only 8% [43].

With $\phi_2 = -65$ mV the rate constant $k_0^\ominus$ (Table 2) for the electrode reaction with the solvated Cu^+ is found to be much lower than that in DMSO. This is probably mainly because for AN the rate constant was obtained from measurements on pure perchlorate solutions, whereas DMSO solutions with free Cl^- present were used. Thus in the AN solution no influence from bridging at the electrode by specifically adsorbed Cl^- was possible.

The pronounced participation of the mononuclear complexes as oxidants in the charge transfer is contrary to what is true for DMSO solution. From Table 2 it is obvious that the formation of CuCl gives rise to a large increase in the rate constant. The effect can be correlated to the large and positive ΔH_1° and ΔS_1°, which should indicate a decrease in the inner-sphere solvation or a labilization of the solvation shell. Ligand bridging at the electrode via the coordinated Cl^- could also contribute to the large effect. Formation of $CuCl_2^-$, however, does not cause any additional large increase in the rate constant. This observation, combined with a small ΔH_2° and a large ΔS_2°, suggests a further weakening of the Cu(I)–AN bond and a simultaneous strengthening of the Cu(I)–Cl bond, probably by formation of a linear complex. The resulting effect of the two changes could be a fairly unaffected rate constant.

F. CONCLUSIONS

It is quite clear from the results obtained with Zn(II) and Cd(II) in DMSO solution with halide and thiocyanate ions that specific adsorption of the free anions on mercury and complex formation are not per se sufficient conditions for catalysis of the charge transfer at the corresponding amalgams. The different kinetic behaviour in DMSO and aqueous solutions can be explained by supposing that under certain conditions the large DMSO molecules cause the distance of closest approach of the central ion in a solvated complex to the amalgam surface to be too large to permit effective ligand bridging at the electrode by Cl^-, Br^- and SCN^-. It is true that SCN^- is linear, but as a bridge it is bent at S [45], resulting in a bridge "length" which does not exceed the Br^- diameter [23].

In fact, if the solvated complex ML^+ is octahedral or trigonal pyramidal, it cannot be contact-adsorbed on the amalgam surface via the coordinated ligand L^- without displacement of several adsorbed DMSO molecules or distortion of the coordination polyhedron. If the energy required for this process is larger than the energy of the bond between the amalgam and the coordinated ligand, substantial bridging at the electrode is inhibited.

The larger I^-, however, with its higher specific adsorbability should be able to act better as a bridging group even in an octahedral complex. With a tetrahedral complex the probability of ligand bridging can be expected to be larger for all these ligands. It is also obvious that in water solutions such a steric hindrance cannot exist for any of these anions.

At the low equilibrium electrode potentials in the Zn(II) and Cd(II) systems discussed above the charge density q on the amalgam is negative, approximately $-12\ \mu C\ cm^{-2}$ and approximately $-8\ \mu C\ cm^{-2}$ respectively [15,21,23]. The specific adsorbability of the free ligand L^- varies strongly [46] with q. For instance, $-\overline{\Delta G}^\circ$ of adsorption of I^- on mercury from aqueous solution at 25°C decreases [47] from 49 to 11 kJ mol^{-1} when q is changed from 10 to $-10\ \mu C\ cm^{-2}$. In the case of adsorption of ML^+ via the coordinated L^- the $-\overline{\Delta G}^\circ$ values can be expected to be lower but to show an analogous variation with q. This should make bridging in the Zn(II) and Cd(II) systems especially sensitive to the steric hindrance discussed. For this reason, comparisons with solvent influences on homogeneous self-exchange reactions $M^{(n-1)+}$–M^{n+} in halide or thiocyanate solutions cannot be used as a test of the model for electrode reactions given above.

In conclusion, for the complexes ZnL^+ and CdL^+ ($L = Cl^-$, Br^-, SCN^- and I^-) in DMSO an indication of effective ligand bridging at the electrode is found only for $L^- = I^-$. In the copper(I) chloride system in DMSO the high electroactivity found for the tetrahedral Cu^+ indicates bridging by specifically adsorbed Cl^-.

Another important result from the studies of the Cd(II) and Hg(II) systems in DMSO is that a change from octahedral to tetrahedral geometry with formation of a certain complex can result in a large increase in the charge transfer rate constant. There are different factors that might contribute to this catalytic effect. By the pronounced decrease in the inner-sphere solvation, inherent in the change in geometry, the difference in solvation between M(II) and the intermediate M(I) should decrease and lower the activation energy of the electron transfer step. The following complexes have a high electroactivity either because there is a change in geometry at their formation, or there is solely a pronounced decrease in their inner-sphere solvation energy.

$CdBr_2$, CdI_2, $HgCl_j^{2-j}$ ($j = 1$–4), Hg_2Cl^{3+}, $Cu_2Cl_j^{2-j}$ ($j = 2$ and 3) in DMSO; $CuCl$ and $CuCl_2^-$ in AN.

Formation of a tetrahedral complex can also be expected to improve the possibility of ligand bridging at the electrode. However, a necessary condition for obtaining an electron mediating bridge should be considerably covalent character in the metal–ligand bond. There are several indications that the bonding is more covalent in a tetrahedral than in an octahedral complex for a given complex system. This is shown, for instance, by the theory for the oscillator strengths of *d–d* absorption bands of transition metal complexes (cf. ref. 48) and by calculations of ionicities [49,50], i.e. fractional charges on the ligand, in halide complexes of transition metals. An IR investigation [51] on thiocyanate complexes in aqueous solutions should also be mentioned. Values for the integrated absorption of the C–N vibration indicate, for example, a low degree of electronic interaction between metal and ligand in $CoNCS^+$, most probably octahedral, whereas the tetrahedral $Co(NCS)_4^{2-}$ has predominantly covalent σ bonding. It is true that the examples given relate to transition metal ions, but the conclusions arrived at should also be valid for the divalent d^{10} acceptors discussed.

The mechanism of electron transfer through the probable ligand bridge at the electrode should conform to the same rules as those of bridged electron transfer in homogeneous exchange reactions and redox reactions (cf. refs. 52,53). Thus when the bridge is monoatomic it is likely that resonance transfer will be predominant. In this case the bridge might influence the electronic coupling between the electrode and the metal ion and increase the electron transfer probability. An alternative mechanism is the chemical mechanism, involving formation of an intermediate with the bridging ligand either oxidized or reduced. However, at least for $L^- = Cl^-$ or Br^- the formation of a true intermediate with L or L^{2-} as bridge in the systems discussed above does not seem possible for energetic reasons.

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