

On the Mechanisms of the Zn(II)/Zn(Hg) and Cd(II)/Cd(Hg) Electrode Reactions in DMSO Solutions of the Thiocyanate Ion

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The electrode reactions Zn(II)/Zn(Hg) and Cd(II)/Cd(Hg) in complex thiocyanate solutions with DMSO as solvent have been studied at the equilibrium potentials by the faradaic impedance method and a cyclic current-step method. All the kinetic data refer to 25 °C and the ionic strength 1 M with ammonium perchlorate as supporting electrolyte. Double-layer data have been determined by electrocapillary measurements.

The results for the zinc system indicate that the solvated Zn^{2+} predominates in the electrode reaction, whereas the complexes do not take part noticeably. It is concluded that in DMSO ligand bridging by SCN^- at the electrode is hindered by the larger solvent molecules.

For the cadmium system it has been found that the solvated Cd^{2+} as well as the complexes $CdSCN^+$ and $Cd(SCN)_2$ take part in the rate-controlling charge transfer step Cd(II)/Cd(I). Furthermore the results confirm a suggestion that a decrease in or labilization of the inner sphere solvation of Cd(II) at the formation of a complex is of great importance for its contribution to the exchange current density.

The electrode reaction Zn(II)/Zn(Hg) in complex chloride, bromide, and iodide solutions with dimethyl sulfoxide (DMSO) as solvent was recently studied¹ in this laboratory. It was found that a rate-increasing effect on this electrode reaction by the halide ions, which is well-known for water solutions,^{2–4} does not exist for the DMSO solutions. On the contrary, the measurements proved that in DMSO the solvated zinc ion takes part in the electrode reaction, whereas the chloride and bromide complexes do not. However, in the iodide system also the first complex contributes to the

exchange current density. This solvent influence was explained with a model involving steric hindrance by the larger DMSO molecules to ligand bridging at the electrode by Cl^- and Br^- . The large and more polarizable I^- , on the other hand, could possibly act also in DMSO as an electron conducting bridge between the coordinated Zn^{2+} and the amalgam.

Then, it seemed interesting to supplement the studies of the halide systems by investigating the zinc thiocyanate system in DMSO, since for water solutions it is known² that the acceleration effect of the heavier halide ions and SCN^- on the electrode reaction increases in the order $Br^- < SN^- < I^-$. Furthermore, because of its linear shape⁵ also SCN^- could be expected to have a capability of ligand bridging at the electrode in DMSO solutions.

A recent investigation⁶ of the electrode reaction Cd(II)/Cd(Hg) in halide solutions in DMSO gave further support to the model given for the zinc systems. Furthermore, the complexes $CdBr_2$ and CdI_2 proved to give large contributions to the exchange current density which can be correlated to a pronounced change in the inner sphere solvation⁷ at this step of the complex formation. As there is no indication of such a sudden change in the solvation at the formation of $Cd(SCN)_2$ in DMSO solution, the cadmium thiocyanate system provides a valuable possibility to test the validity of the correlation suggested.

Stability constants relating to the complex formation in the zinc and cadmium thiocyanate systems in DMSO and necessary for the calculations of the

rate constants of the electrode reactions, have recently been determined in this laboratory.⁸ To be able to use these stability constants we carried out the present investigation with the same ammonium perchlorate medium.

For the two systems studied the rates of the electrode reactions, *i.e.* values of the exchange current density, i_0 , can be conveniently determined by alternating current methods. We used a square-wave method and in some measurements the faradaic impedance method.

As double-layer data for thiocyanate solutions in DMSO do not seem to be available in the literature, electrocapillary measurements have also been performed. In these measurements lithium salts were chosen as the most suitable ones for the ionic media.

EXPERIMENTAL

Chemicals. The hexasolvates $\text{Zn}(\text{DMSO})_6(\text{ClO}_4)_2$ and $\text{Cd}(\text{DMSO})_6(\text{ClO}_4)_2$ were the same preparations as used previously.^{1,6} They were analyzed with respect to zinc and cadmium by titration with EDTA.

Liquid zinc and cadmium amalgams of 0.3 and 0.1 % by weight, respectively, were also prepared as before^{6,9} and were kept in a nitrogen atmosphere. These amalgams were used throughout the kinetic measurements.

Analytical grade ammonium perchlorate and thiocyanate and lithium chloride were dried at 110 °C before use. The lithium perchlorate was dried at 185 °C.

Lithium thiocyanate was prepared by mixing equivalent amounts of lithium perchlorate and potassium thiocyanate in water solution. After cooling the solution it was separated from the crystallized potassium perchlorate and then evaporated at 130 °C. The salt is very hygroscopic. Its thiocyanate content was checked titrimetrically.

Stock solutions of the different salts were prepared with purified¹⁰ DMSO. The ionic strength of the cell solutions in the measurements of the electrode kinetics was 1 M with ammonium perchlorate as supporting electrolyte.

Experimental details. In the kinetic measurements two stationary small amalgam drops (*cf.* Ref. 11) of equal size were used as polarizable electrodes in the cell. By this arrangement the effect of some small dissolution of zinc and especially cadmium from the amalgams could be reduced. The surface area of a single drop was determined according to the drop weight method. Both drops were renewed before every new measurement.

In those measurements where the charge transfer resistance, R_t , was obtained from faradaic impedances the same a.c. bridge and procedure were used as in some earlier investigations (*cf.* Ref. 12).

However, the measurements in the main series were performed according to a cyclic current-step method.^{1,13} The bridge and procedure applied in this case for determining R_t were the same as described previously.¹

In both measurement methods the amplitude of the voltage response of the cell was kept smaller than 10 mV. Very reproducible R_t -values were obtained.

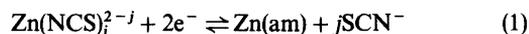
The electrocapillary measurements for determinations of double-layer data were made using the same apparatus and process as before.¹

All measurements were carried out at 25.0 ± 0.2 °C. Nitrogen gas that had been freed from oxygen was led through the complex solutions to protect the amalgam from oxidation and to ensure good mixing in the cell.

THE ELECTRODE KINETICS

The zinc thiocyanate system

Investigations⁸ of the complex formation have shown that SCN^- gives four mononuclear complexes with Zn^{2+} in DMSO. According to results from IR spectroscopy¹⁴ on water solutions Zn^{2+} coordinates the ligand *via* the N atom, and probably the same is valid for DMSO solutions. We then have to take into account the following set of parallel electrode reactions



The previous investigation¹ on the chloride system indicated that in DMSO the charge transfer process for the solvated Zn^{2+} is likely to be a simple one-step transfer. If this holds also for the electrode reactions (1) we should have eqn. (2) for the total exchange current density.

$$i_0 = \sum_j k_j [\text{Zn}^{2+}]^{\alpha_j} [\text{SCN}^-]^j \quad (2)$$

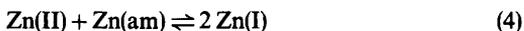
For the composite coefficients k_j the expression (3) holds.

$$k_j = 2Fk_j^\ominus \beta_j^{\alpha_j} [\text{Zn}(\text{am})]^{1-\alpha_j} \exp\{(j-2\alpha_j)F\phi_2/RT\} \quad (3)$$

Here k_j^\ominus denotes the true rate constant and α_j the anodic transfer coefficient of reaction (1). β_j is the stability constant of $\text{Zn}(\text{NCS})_j^{2-j}$ and the exponen-

tial factor represents the Frumkin correction for the influence of the ϕ_2 -potential. At a constant amalgam concentration k_j should be constant at varying $[\text{SCN}^-]$, if a supporting electrolyte in high and constant concentration is used, ensuring that variations in activity coefficients and in the ϕ_2 -potential are suppressed.

However, it could also be assumed that the charge transfer proceeds step-wise with Zn(I) as an intermediate. Then, if the step Zn(II)/Zn(I) is rate-controlling and furthermore the disproportionation equilibrium (4) is established at the amalgam,



the exponent for $[\text{Zn}^{2+}]$ in the equation for i_0 will be changed to $(1 + \alpha_{j,2})/2$, where $\alpha_{j,2}$ stands for the anodic transfer coefficient of the electrode reaction $\text{Zn(NCS)}_j^{2-j}/\text{Zn(NCS)}_j^{1-j}$. This is evident from the corresponding equation applied below for the cadmium system.

In both cases discussed i_0 is calculated in the same way¹⁵ from R_t .

An average of the different exponents for $[\text{Zn}^{2+}]$ in the equation for i_0 can be obtained from the

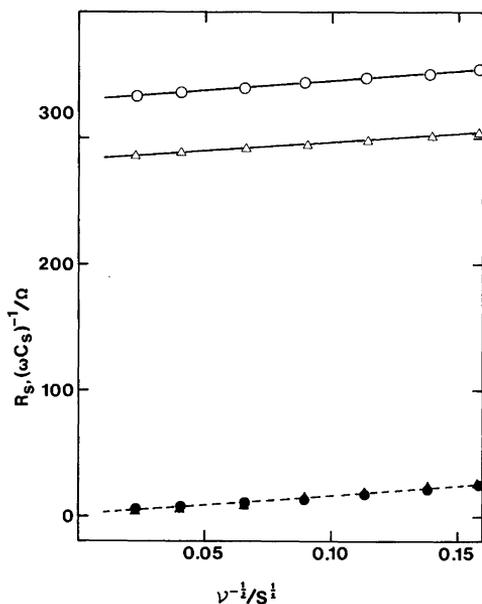


Fig. 1. The resistance R_s (—) and reactance $(\omega C_s)^{-1}$ (---) of the faradaic impedance as functions of $\nu^{-1/2}$ in the zinc thiocyanate system at $C_{\text{Zn}}/\text{mM} = 4.00$ and C_{SCN}/mM : 0 (\triangle); 7.90 (\circ).

Table 1. Measurements of i_0 in the zinc thiocyanate system. $C_{\text{Zn}} = 4.00$ mM.

C_{SCN}/mM , $[\text{SCN}^-]/\text{mM}$, $[\text{Zn}^{2+}]/\text{mM}$, $i_0/\text{mA cm}^{-2}$;
1.97, 1.78, 3.85, 1.45; 3.95, 3.50, 3.65, 1.35; 5.90, 5.10, 3.45, 1.30; 7.85, 6.55, 3.20, 1.20; 11.7, 9.2, 2.75, 1.05; 15.6, 11.6, 2.30, 0.92; 19.4, 13.9, 1.85, 0.75; 24.1, 16.8, 1.40, 0.62; 28.8, 19.8, 0.98, 0.49; 33.5, 23.0, 0.67, 0.38; 38.0, 26.5, 0.46, 0.30; 42.5, 30.2, 0.32, 0.25; 47.0, 34.0, 0.22, 0.21.

quantity $\bar{\alpha} = (\partial \lg i_0 / \partial \lg [\text{Zn}^{2+}])_{[\text{SCN}^-]}$ (cf. Ref. 16). It can be stated that if i_0 is controlled by the step Zn(II)/Zn(I) then $\bar{\alpha}$ -values between 0.5 and 1.0 should be found.

Measurements and calculations. The faradaic impedance, determined at different frequencies ν , proved to be in accordance with the expression $R_t + \text{const}(1-j)\nu^{-1/2}$, where j denotes the imaginary unit vector (Fig. 1). This Randles behaviour indicates that the electrode process is controlled by charge transfer and diffusion. Thus, a possible specific adsorption of charge transferring zinc species on the amalgam must be a rapid step and furthermore be weak. This means that the cyclic current-step method, used in the other kinetic measurements, should give true values of R_t .

In the main series given in Table 1 the total zinc(II) concentration, C_{Zn} , was kept constant while C_{SCN} was increased. Then i_0 decreased monotonically, and in order to obtain reliable R_t -values it was necessary to keep $C_{\text{SCN}} < 50$ mM. From the stability constants⁸ $\beta_1 = 24 \text{ M}^{-1}$, $\beta_2 = 600 \text{ M}^{-2}$, $\beta_3 = 1.6 \times 10^5 \text{ M}^{-3}$ and $\beta_4 = 7.2 \times 10^6 \text{ M}^{-4}$ $[\text{Zn}^{2+}]$ and $[\text{SCN}^-]$ were calculated as described for the halide systems.¹

In other series of measurements at selected fixed values of $[\text{SCN}^-]$, giving values of $\bar{\alpha}$, the compositions of the solutions to be used and $[\text{Zn}^{2+}]$ were also calculated by means of the constants. In these series, which are presented in Fig. 2, C_{Zn} was varied between about 1.5 and 15 mM.

From Fig. 2 it is evident that the $(\lg i_0 / \lg [\text{Zn}^{2+}])$ -data can be represented by a single straight line with the slope $\bar{\alpha} = 0.65 \pm 0.03$, independent of whether C_{Zn} or $[\text{SCN}^-]$ is chosen as a parameter. Thus, for all the measurements the very simple expression (5) is valid.

$$i_0 / [\text{Zn}^{2+}]^{0.65} = 50 \pm 5 \quad (5)$$

$(i_0 \text{ in } \text{mA cm}^{-2}, [\text{Zn}^{2+}] \text{ in } \text{M})$

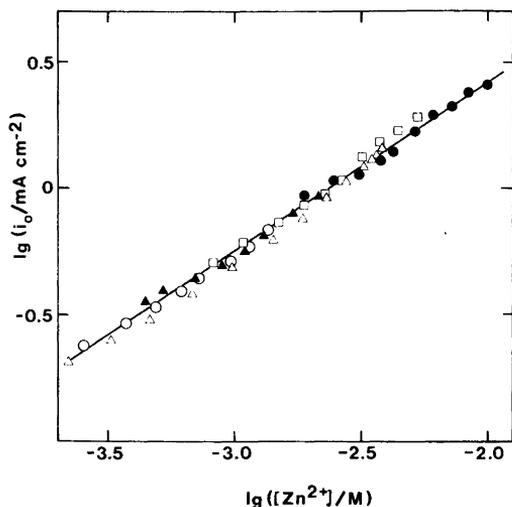
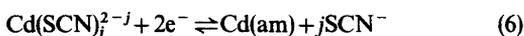


Fig. 2. $\lg i_0$ as a function of $\lg [Zn^{2+}]$ in the thiocyanate system at a constant C_{Zn} or $[SCN^-]$. $C_{Zn}/mM = 4.00$ (Δ); $[SCN^-]/mM$; 2.00 (\bullet); 12.0 (\square); 20.0 (\blacktriangle); 30.0 (\circ).

A comparison between eqns. (2) and (5) shows that at the $[SCN^-]$ used the solvated Zn^{2+} predominates in the electrode reaction, whereas the thiocyanate complexes do not take part noticeably, though in the bulk of the solution $[Zn^{2+}]/C_{Zn} < 0.1$ at $[SCN^-] = 30$ mM (Table 1).

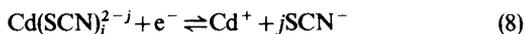
The cadmium thiocyanate system

From an investigation⁸ of the complex formation in DMSO it is known that SCN^- can give three mononuclear complexes with Cd^{2+} . It can be presumed that in these complexes Cd^{2+} , at least partly, coordinates the ligand *via* the S atom, in conformity with what has been found¹⁴ for water solutions. Then, we should have the following set of parallel electrode reactions

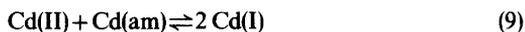


The studies⁶ of the cadmium halide systems in DMSO have shown that the charge transfer reactions most probably proceed step-wise with Cd(I) as an intermediate. Furthermore, there was no indication that any complexes of Cd(I) take part in the charge transfer step Cd(I)/Cd(am). Provided that these results are valid also for the thiocyanate

system, the following reaction scheme should be applicable.



In addition we have also the disproportionation equilibrium (9) to take into consideration.



Then the equations¹⁵ for the current densities i_{01} and i_{02} of the reactions (7) and (8) should be of the form

$$i_{01} = k_{0,1} [Cd^{2+}]^{\alpha_{0,1}/2} \quad (10)$$

$$i_{02} = \sum_j k_{j,2} [Cd^{2+}]^{(1+\alpha_{j,2})/2} [SCN^-]^j \quad (11)$$

$k_{0,1}$ and $k_{j,2}$ are composite coefficients,⁶ but only the complete expression (12) for $k_{j,2}$ will be of interest in the present study.

$$k_{j,2} = F k_{j,2}^{\ominus} \beta_j^{\alpha_{j,2}} (K^{\ddagger} [Cd(am)]^{\ddagger} [DMSO]^{-j})^{1-\alpha_{j,2}} \exp\{(j-1-\alpha_{j,2})F\phi_2/RT\} \quad (12)$$

Here $k_{j,2}^{\ominus}$ is the true rate constant and $\alpha_{j,2}$ the anodic transfer coefficient of reaction (8). K is the equilibrium constant of (9), applied to the free solvated ions Cd^{2+} and Cd^+ . Then, because of the formulation of the step Cd(II)/Cd(I) according to (8), we have found it convenient to separate in eqn. (12) a factor $[DMSO]^{j(\alpha_{j,2}-1)}$ from the rate constant. In this way all the rate constants $k_{j,2}^{\ominus}$ retain the usual dimension length/time. Of course the rate constants can still be functions of $[DMSO]$, since the number of DMSO molecules taking part in reaction (8) is not known.

For $i_0 \sim i_{01}$ and $i_0 \sim i_{02}$ the quantity $\bar{\alpha}$, which is analogous to that defined above for the zinc system, should have values of about 0.25 and 0.75, respectively.

In the investigation of the halide systems⁶ it was found that the electrochemically determined i_0 could be represented according to eqn. (13)

$$i_0 = 0.5 (i_{01} + i_{02}) \quad (13)$$

This means that the disproportionation of Cd(I) is so fast that the two charge transfer steps (7) and (8) are parallel instead of consecutive. It can be

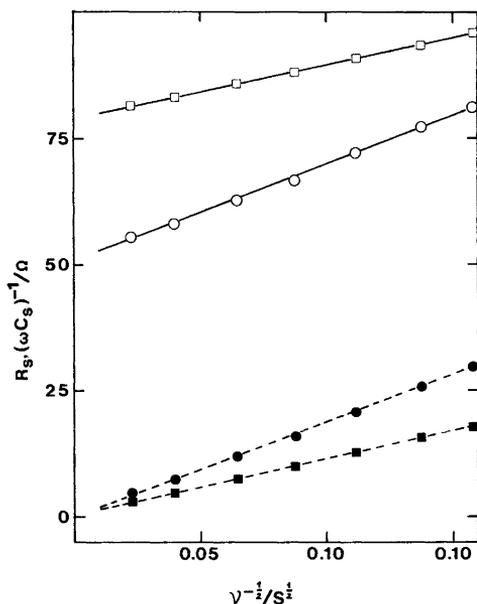


Fig. 3. The series resistance R_s (—) and reactance $(\omega C_s)^{-1}$ (---) of the faradaic impedance as functions of $v^{-1/2}$ in the cadmium thiocyanate system at different values of C_{Cd} and C_{SCN^-} . C_{Cd}/mM , C_{SCN^-}/mM : 2.00, 0 (○ ●); 4.00, 100 (□ ■).

presupposed that eqn. (13) is applicable also for the thiocyanate system.

Measurements and calculations. From Fig. 3 it is obvious that the faradaic impedance displays a Randles behaviour, and thus there is no slow adsorption of cadmium species influencing the determination of R_f -values. The main measurement series at a constant C_{Cd} is given in Table 2. Also in this system i_0 decreases on addition of thiocyanate ions. The stability constants⁸ used in the calculations of $[Cd^{2+}]$ and $[SCN^-]$ are $\beta_1=64 M^{-1}$, $\beta_2=520 M^{-2}$ and $\beta_3=850 M^{-3}$. The other

Table 2. Measurements of i_0 in the cadmium thiocyanate system. $C_{Cd}=2.00 mM$.

C_{SCN^-}/mM , $[SCN^-]/mM$, $[Cd^{2+}]/mM$, $i_0/mA cm^{-2}$;
3.95, 3.55, 1.60, 6.7; 7.90, 7.20, 1.35, 6.1; 15.7, 14.5, 0.98, 5.3; 23.5, 22.0, 0.75, 4.8; 38.0, 36.5, 0.49, 4.3; 56.5, 54.0, 0.33, 3.8; 73.5, 71.0, 0.235, 3.5; 107, 104, 0.140, 3.0; 137, 134, 0.095, 2.60; 192, 189, 0.053, 2.25; 250, 245, 0.033, 1.90; 330, 325, 0.0190, 1.60; 395, 390, 0.0125, 1.45; 495, 490, 0.0078, 1.20; 620, 615, 0.0046, 0.95.

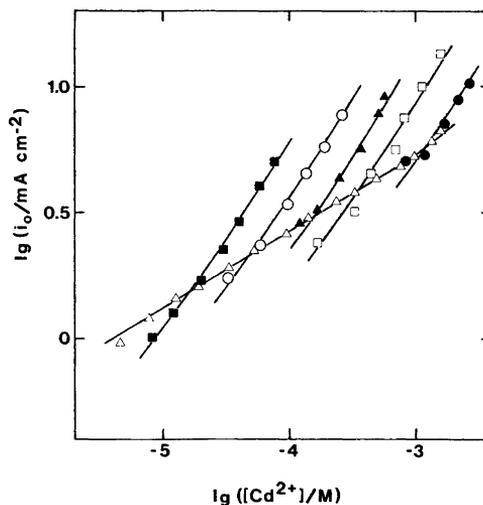


Fig. 4. $\lg i_0$ as a function of $\lg [Cd^{2+}]$ in the thiocyanate system at a constant C_{Cd} or $[SCN^-]$. $C_{Cd}/mM=2.00$ (Δ); $[SCN^-]/mM$: 10.0 (\bullet); 50.0 (\square); 100 (\blacktriangle); 200 (\circ); 350 (\blacksquare). The curves have been calculated from eqn. (14).

series of measurements, carried out at constant values of $[SCN^-]$ are given in Fig. 4. In these series C_{Cd} was varied between 1.0 and 11 mM.

From the plots in Fig. 4 it is seen that in this case i_0 is not a function of $[Cd^{2+}]$ solely but depends also upon $[SCN^-]$. From the last-mentioned series $\bar{\alpha} \approx 0.8$ is also found at different $[SCN^-]$. Thus it can be concluded that in eqn. (13) $i_{0,1}$ is of minor importance in the whole $[Cd^{2+}]$ -range used. It was presumed that $\alpha_{0,1}$ and $\alpha_{j,2}$ could be put equal to 0.40 and 0.70, respectively, as in the halide systems. Accordingly, $i_0/[Cd^{2+}]^{0.20}$ was plotted versus $[Cd^{2+}]^{0.65}$ at the different constant $[SCN^-]$. Straight lines with an approximate constant intercept, $0.5k_{0,1}$, on the ordinate axis were obtained, indicating that $i_{0,1}$ can be represented by the single term $k_{0,1}[Cd^{2+}]^{0.20}$ and thus confirming the validity of eqn. (10). Then in the function $(i_0 - 0.5i_{0,1})/[Cd^{2+}]^{0.85}$, which should be a polynomial in $[SCN^-]$, the coefficients $k_{j,2}$ were adjusted to the best fit with the measurements. From Fig. 4 it is seen that the i_0 -function calculated from eqn. (14) represents the measurement data very well.

$$i_0 = 3.5[Cd^{2+}]^{0.20} + [Cd^{2+}]^{0.85} (1.2 \times 10^3 + 3.0 \times 10^4 [SCN^-] + 1.5 \times 10^4 [SCN^-]^2) \quad (14)$$

(i_0 in mA cm^{-2} , $[\text{Cd}^{2+}]$ and $[\text{SCN}^-]$ in M)

Only at the lowest C_{Cd} are there in some cases differences that could be ascribed to a small dissolution of cadmium from the amalgam.

The results obtained confirm that no complexes of Cd(I) contribute noticeably to the charge transfer step Cd(I)/Cd(am). For the step Cd(II)/Cd(I), on the other hand, we arrive at the conclusion that the solvated Cd^{2+} as well as the complexes CdSCN^+ and $\text{Cd}(\text{SCN})_2$ take part.

THE DOUBLE-LAYER AND THE TRUE RATE CONSTANTS

Electrocapillary measurements were performed on pure mercury in contact with 1 M LiSCN in DMSO. From Fig. 5 it is seen that the electrocapillary curve obtained is very similar to that for 1 M LiCl. The charge density, q , on the mercury, the contribution, q_{SCN}^1 , from the specifically adsorbed SCN^- to the charge on the solution side and the ϕ_2 -potential were determined at the applied potential, E , versus a fixed reference electrode (see Fig. 5)

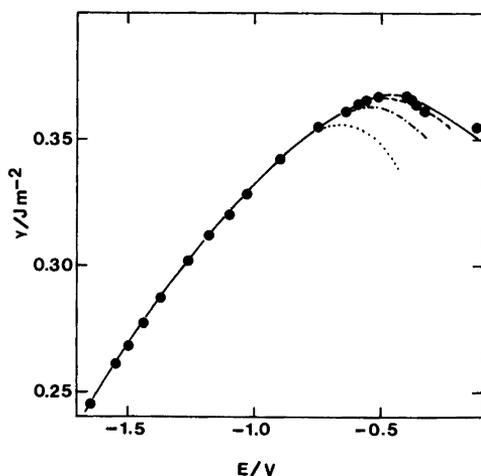


Fig. 5. The electrocapillary curve (●) for mercury and 1 M lithium thiocyanate in DMSO at 25 °C. The potentials are referred to the reference electrode Ag, AgCl in 10 mM LiCl+990 mM LiClO₄. The corresponding curves for lithium chloride (---), bromide (-·-), and iodide (· · ·) are also given (cf. Ref. 1).

as described previously.¹ For the sake of comparison the same potentials, $E = -1175$ and -785 mV, were used as in the studies of the halide systems.^{1,6} They are within the ranges of the equilibrium potentials of the zinc and cadmium amalgams, respectively, in the complex thiocyanate solutions. At $E = -1175$ mV the following values were obtained: $q = -12.1 \mu\text{C cm}^{-2}$, $q_{\text{SCN}}^1 = -1.0 \mu\text{C cm}^{-2}$ and $\phi_2 = -60$ mV. The q_{SCN}^1 -value confirms that in DMSO the specific adsorbability of SCN^- is approximately the same as that of Cl^- (cf. Ref. 1). At $E = -785$ mV we got $q = -7.9 \mu\text{C cm}^{-2}$ and $\phi_2 = -44$ mV. However, in this case it proved more difficult to obtain a reliable value of q_{SCN}^1 .

For $\alpha_j = 0.65$ and $\phi_2 = -60$ mV the Frumkin factor in eqn. (3) has the approximate value $10^{1.3-j}$. From the k_0 -value in eqn. (5), $[\text{Zn}(\text{am})] = 0.60$ M and the Frumkin factor for $j=0$, the true rate constant $k_0^\ominus = (1.5 \pm 0.2) \times 10^{-5} \text{ cm s}^{-1}$ of the electrode reaction (1) of the solvated Zn^{2+} is obtained.

The Frumkin factor in eqn. (12), for $\alpha_{j,2} = 0.70$ and $\phi_2 = -44$ mV, has the value $10^{1.3-0.75j}$. With $[\text{DMSO}] = 14$ M and using the values of the coefficients $k_{j,2}$, given by the expression (14), we finally calculated the ratios $k_{1,2}^\ominus/k_{0,2}^\ominus$ and $k_{2,2}^\ominus/k_{1,2}^\ominus$ of the true rate constants relating to the electrode reactions (8). For comparison these ratios have been put together (Table 3) with those of the cadmium halide systems.

DISCUSSION

The exponent $\alpha_0 = 0.65 \pm 0.03$ for $[\text{Zn}^{2+}]$ in eqn. (5) does not permit a distinction to be made between two possible mechanisms of the charge transfer for the solvated Zn^{2+} , either a one-step or a two-step transfer with Zn(II)/Zn(I) as the rate-

Table 3. Ratios of the rate constants $k_{j,2}^\ominus$ relating to the charge transfer step Cd(II)/Cd(I) in the thiocyanate, bromide and iodide systems, and enthalpy changes, ΔH_j^\ominus , in the reactions $\text{CdL}_{j-1}^{3-j} + \text{L}^- \rightleftharpoons \text{CdL}_j^{2-j}$. Medium: 1 M NH_4ClO_4 in DMSO.

L^-	$k_{1,2}^\ominus/k_{0,2}^\ominus$	$k_{2,2}^\ominus/k_{1,2}^\ominus$	$\Delta H_1^\ominus / \text{kJ mol}^{-1}$	$\Delta H_2^\ominus / \text{kJ mol}^{-1}$
SCN^-	17	1.4	-3.0	-2.8
Br^-	7	235	-3.9	17
I^-	180	360	2.4	27
Ref.			7	7

limiting step in the latter case and with the disproportionation equilibrium (4) established. However, the fact that the same k_0^\ominus -value has been obtained for the thiocyanate and chloride systems gives support to the conclusion that also the mechanism is the same. Now, the exponent $\alpha_0 = 0.50 \pm 0.03$ of the chloride system led to the presumption¹ that in DMSO the electrode reaction for Zn^{2+} is predominantly a one-step transfer, and thus the same should hold for the thiocyanate system. Furthermore, it is very improbable that the presence of SCN^- could change the mechanism, since according to the measurements i_0 is not a function of $[\text{SCN}^-]$. On the other hand, the difference found between the α_0 -values indicates that the different influences from SCN^- and Cl^- on the electrode double-layer are observable already at concentrations that are low compared with the ionic strength.

At the thiocyanate concentrations used in the kinetic measurements $[\text{ZnNCS}^+]/[\text{Zn}^{2+}] < 0.85$ and $[\text{Zn}(\text{NCS})_2]/[\text{Zn}^{2+}] < 0.70$ in the bulk of the solutions. Then, if there is no effect that catalyzes the charge transfer, the calculated Frumkin factor in eqn. (3), which decreases rapidly with increasing values of j , should give the result that the contributions from these complexes to i_0 are not observed. For the anionic complexes similar conclusions can be drawn.

The result that the electrode reaction $\text{Zn(II)}/\text{Zn(am)}$ in DMSO is not catalyzed by the presence of SCN^- as in water solutions would mean, according to the model given¹ for the solvent influence, that the DMSO molecules make the distance of closest approach of the zinc ion in the complexes to the amalgam surface too large to permit an effective ligand bridging at the electrode by SCN^- . Thus, in this respect SCN^- would be inferior to I^- in DMSO.

This conclusion could seem surprising in view of the linear shape of SCN^- . However, in crystalline AgSCN , containing bridging $-\text{SCN}-$ groups,⁵ the chains formed are bent at the S atoms with a bond angle $\text{Ag}-\text{S}-\text{C}$ of 104° . From this value and the bond lengths given an $\text{Ag}-\text{Ag}$ distance of about 6 Å can be calculated. If the ionic radii¹⁷ of the two Ag^+ are subtracted, the resulting "length" of the bridge is found to be not longer than the crystallographic diameter¹⁸ of Br^- . Thus, on the assumption that the bond angle at the S atom is of about the same magnitude for a specifically adsorbed SCN^- , which probably is bonded to the amalgam surface through the S atom, the con-

clusion about the low ligand bridging ability of SCN^- in DMSO seems reasonable.

The finding in the electrocapillary measurements that in DMSO the specific adsorbability increases in the order $\text{SCN}^- < \text{Br}^-$, whereas the reverse order¹⁹ is found for water solutions, could to some extent be explained by such a bond angle $\text{Hg}-\text{S}-\text{C}$. In this case the specifically adsorbed DMSO molecules should be expected to exert an extra large hindrance to adsorption of SCN^- .

For the cadmium thiocyanate system the calculated Frumkin factor in eqn. (12) does not decrease as rapidly at increasing values of j as for the zinc system, which helps to make the participation of CdSCN^+ and $\text{Cd}(\text{SCN})_2$ in the electrode reaction (8) observable. From the values of $k_{1,2}^\ominus/k_{0,2}^\ominus$ in Table 3 it is evident that on formation of the first complex CdL^+ the rate enhancing effect of L^- on the charge transfer step $\text{Cd(II)}/\text{Cd(I)}$ increases in the order $\text{Br}^- < \text{SCN}^- < \text{I}^-$. However, neither for Br^- nor for SCN^- do the values indicate an operative ligand bridging at the electrode, and this conclusion is in agreement with those arrived at for the zinc systems.

From the ratio $k_{2,2}^\ominus/k_{1,2}^\ominus$ in Table 3 it is seen that the increase in the rate constant at the formation of $\text{Cd}(\text{SCN})_2$ is very small compared with the corresponding effect for CdBr_2 and CdI_2 . The large increase for the last-mentioned complexes has been correlated⁶ to the large, positive enthalpy change, ΔH_2^\ominus , accompanying their formation in DMSO. These positive ΔH_2^\ominus -values indicate a pronounced decrease in the inner sphere solvation⁷ or a labilization of the solvation shell of the complex. In both cases a lowering of the energy of activation of the charge transfer step $\text{Cd(II)}/\text{Cd(I)}$ can be anticipated. Now, for the thiocyanate system the small and negative values of ΔH_1^\ominus and ΔH_2^\ominus do not indicate a strong change of the solvation in any of the corresponding steps of the complex formation. Accordingly, no large rate enhancement of the electrode reaction should be expected, and the results from the thiocyanate system give good support of the validity of the correlation suggested. Thus, we have a plausible explanation of why in some of the cadmium systems a certain complex can be especially electroactive.

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