

ELECTRODE KINETICS AND DOUBLE LAYER STRUCTURE

IV. THE Eu(II)/Eu(III) ELECTRODE REACTION AT THE DME IN 1 M KSCN; INFLUENCE OF COMPLEX FORMATION

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INTRODUCTION

In a previous paper¹ we presented a study of the kinetic parameters of the Eu(II)/Eu(III) electrode reaction at the dropping mercury electrode (DME) in 1 M KCl and 1 M KI base electrolyte solutions. In this study it was shown that the influence of the anion on the apparent standard heterogeneous rate constant could be ascribed completely to the so-called Frumkin effect, contrary to the results found for example for the Zn(Hg)/Zn²⁺ electrode reaction^{2,3} where, besides the Frumkin effect, a relationship exists between rate constant and specific adsorbed amount of halide ions.

We stated that one can distinguish two classes of electrode reactions, *viz.* (a) where the electroactive species crosses the interface during oxidation or reduction, and (b) where both the oxidized and reduced species remain at the solution side of the interface, *i.e.* at or outside the Outer Helmholtz Plane (OHP), the electron tunnelling through the inner layer. The model of Parsons⁴ in which the activated complex is supposed to be situated in the inner layer, seems suitable to describe electrode reactions of class (a). It agrees very well with the experimental facts for the zinc system and for the hydrogen reduction.

Reactions of class (b) are likely to occur in systems where both the oxidized and the reduced component of the redox couple are present in the solution. Besides our study¹ on the Eu(II)/Eu(III) system, another example is provided by the results for the Cr(II)/Cr(III) reaction in various supporting electrolytes, recently published by Anson and coworkers⁵. Qualitative experiments of other authors on the europium reaction in other base electrolytes seem to give similar results. However, systems with thiocyanate ions⁷ and EDTA⁸ as the supporting electrolyte appear to be exceptions. In these media the reaction is found d.c. reversible, which indicates an exceptionally high rate constant. For 1 M KSCN this is confirmed by the measurements of Randles and Somerton⁹, who found an apparent rate constant of $8.0 \times 10^{-3} \text{ cm s}^{-1}$ (at 20°C) as compared to $1.6 \times 10^{-3} \text{ cm s}^{-1}$ (at 20°C) in 1 M KI. This is surprising, since SCN⁻ is less specifically adsorbed than I⁻ and therefore the Frumkin effect must be expected to be smaller.

As both EDTA and SCN⁻ form complexes with europium ions (SCN⁻ especially with Eu³⁺), it is worthwhile to investigate whether this may be an ex-

planation for the deviation of behaviour. In this paper we present a more detailed study of the europium reaction in 1 M KSCN, because the necessary double layer data are available¹⁰⁻¹². Moreover the stability of the europium thiocyanate complexes is such that at the OHP both the Ox- and Red-components are mainly present as uncomplexed, *i.e.* hydrated ions. This makes it reasonable to assume that the reaction takes place *via* the hydrated species and that thus it is useful to compare the kinetic parameters with those in 1 M KCl and 1 M KI. For this purpose an extension of the theory concerning the rate equation is necessary and this will be presented first. Furthermore the potential at the OHP in the presence of Eu(II) and Eu(III) will be calculated in the same way as was done in the KCl and KI case¹. On the basis of these concepts the experimental facts will be interpreted.

As the work of Anson and coworkers⁵, mentioned above, is closely related to our work, a short consideration will be dedicated to their data on the Cr(II)/Cr(III) reaction in the light of our own view on this subject.

THEORY

The meaning of the apparent rate constant in the case of partial complex formation

Thus far little attention has been paid to cases where the species participating in an electrode reaction form complexes with the supporting electrolyte. Well known in this field is early work by Gerischer¹³, studying the Zn(Hg)/Zn(II) reaction in various complexing media. The most important result was that he could indicate that in many cases the reaction proceeded *via* a complex which was present in a minor concentration, whereas most of the zinc was present as one dominating complex with a larger number of ligands.

Our case of Eu(III) and Eu(II) in 1 M KSCN is different from the systems Gerischer studied, as the different complexes have concentrations of the same order of magnitude. For example, from stability constants for Eu(III)-thiocyanate complexes measured by Choppin and Ketels¹⁴ it follows that Eu(III) is present as Eu^{3+} , $\text{Eu}(\text{SCN})^{2+}$ and $\text{Eu}(\text{SCN})_2^+$ in the ratio 7.8 : 39.2 : 53. For Eu(II)-thiocyanate complexes no data are available. In view of the work of Gerischer, the question arises as to which of the particles present is the actual reacting species. To resolve this difficulty, measurements of the exchange current density at varying SCN^- concentration and constant ionic strength are necessary, but, because complex formation is only partial, the analyses necessary for the interpretation of such measurements would be rather complicated.

For the purposes of the present paper it is convenient to consider the possibility that the charge transfer reaction takes place *via* the uncomplexed particles, *i.e.* *via* the hydrated Eu^{3+} and Eu^{2+} ions. As in our case it can be calculated (see DISCUSSION) that these ions are predominantly present at the reaction site (OHP), this seems to be a reasonable assumption.

We consider therefore the electron transfer reaction



where R denotes the Eu^{2+} and O the Eu^{3+} ion. The general current-voltage relation for this reaction may be written as

$$i = nFk_{\text{sh}}^f \{ \bar{c}_{\text{R}} \exp(\alpha\phi') - \bar{c}_{\text{O}} \exp(-\beta\phi') \} \exp [(\beta n - z_{\text{O}}) f\phi_2] \quad (1)$$

in which \bar{c}_R and \bar{c}_O are the surface concentrations just outside the double layer, and $f = F/RT$. The last exponential on the right-hand side of the equation is the well-known Frumkin correction containing the valency z_O of the ion O and the potential ϕ_2 at the outer Helmholtz plane¹⁵. Further k_{sh}^f is the true formal rate constant, including the activity coefficients of O and R, and $\alpha = 1 - \beta$ is the true anodic transfer coefficient. Finally one has

$$\varphi' = (nF/RT)(E - E'_0) \quad (2)$$

where E'_0 is the standard potential pertaining to the uncomplexed species, *i.e.* defined by

$$E_{eq} = E'_0 + (RT/nF) \ln [c_O^*/c_R^*] \quad (3)$$

in which E_{eq} is the equilibrium potential measured if both O and R are present, while c_O^* and c_R^* are the bulk concentrations of the uncomplexed species.

Especially in view of the impedance analysis to be followed in this paper, it is desirable to deal with a current-voltage relation in terms of the analytical concentrations c_{OT} and c_{RT} (inclusive all complexed and uncomplexed particles) and of the corresponding standard potential E_0 , defined by

$$E_{eq} = E_0 + (RT/nF) \ln [c_{OT}^*/c_{RT}^*] \quad (4)$$

The desired current-voltage relation therefore reads as:

$$i = nFk_{sh}^a \{ \bar{c}_{RT} \exp(\alpha\varphi) - \bar{c}_{OT} \exp(-\beta\varphi) \} \quad (5)$$

in which

$$\varphi = (nF/RT)(E - E_0)$$

while k_{sh}^a has to be specified further. Comparing eqns. (3) and (4) gives

$$E'_0 = E_0 - (RT/nF) \ln (r_O/r_R) \quad (7)$$

with

$$r_O = c_O^*/c_{OT}^* = \bar{c}_O/\bar{c}_{OT} \quad (8a)$$

$$r_R = c_R^*/c_{RT}^* = \bar{c}_R/\bar{c}_{RT} \quad (8b)$$

The equality of c^*/c_T^* (bulk concentrations) and \bar{c}/\bar{c}_T (surface concentrations just outside the double layer) indicates that the equilibria between the different complexes are supposed to be established infinitely fast.

With the aid of eqns. (6) and (7), eqn. (1) can be rewritten as:

$$i = nFk_{sh}^f r_O^\alpha r_R^\beta \{ \bar{c}_{RT} \exp(\alpha\varphi) - \bar{c}_{OT} \exp(-\beta\varphi) \} \exp [(\beta n - z_O) f \phi_2] \quad (9)$$

From eqns. (5) and (9) it is easily understood that one can write for the apparent rate constant k_{sh}^a :

$$k_{sh}^a = k_{sh}^f r_O^\alpha r_R^\beta \exp [(\beta n - z_O) f \phi_2] \quad (10)$$

Thus, besides the Frumkin correction term, there appears another term $r_O^\alpha r_R^\beta$ which accounts for the influence of complex formation on the apparent rate constant.

This term is, unlike the Frumkin term, not potential dependent, but it may have a large effect if one wishes to compare rate constants in different media. However, since r_O and r_R are always smaller than unity, we can conclude beforehand, that the correction term does not explain an exceptionally large value for the apparent rate constant eventually determined for the europium reaction in thiocyanate (see also DISCUSSION).

It may be noted that the theory given in this section is, only for the sake of simplicity but certainly not necessarily, limited to the assumption that charge transfer proceeds *via* the uncomplexed species. It is quite easily applicable to a case where charge transfer is thought to occur between two complexed species OL_m and RL_m with the same number m of ligands. In that case r_O and r_R in eqn. (10) are the ratios of the concentrations of the complexes concerned to the analytical concentration and z_O is the charge of the OL_m ion. However, k_{sh}^f is now the rate constant pertaining to standard circumstances concerning the complex species (*i.e.* the rate at the equilibrium potential if $c_{OL_m}^* = c_{RL_m}^* = 1$). This quantity cannot be compared with the rate constant measured in non-complexing media.

EXPERIMENTAL

Solutions of 2, 5 and 10 mM Eu(III) in 1 M KSCN at pH 2 were prepared by dissolving Eu_2O_3 (Fluka, puriss.) in a slight excess of HCl and adding the appropriate amount of KSCN. If necessary, Eu(II) was generated in these solutions by means of electrolysis as described elsewhere¹.

D.c. polarograms and impedance components at the DME in these solutions were determined at 25°C using the apparatus previously described¹. In order to increase its mechanical strength the DME was made of a fine-tapered capillary drawn from a normal polarographic capillary (internal diameter 0.04 cm). Impedance measurements in the absence of the redox couple still demonstrated some frequency dispersion—only of the ohmic component—caused by the shielding effect^{1,16}. Corrections for this effect were made by taking for the ohmic resistance the value found in the base electrolyte solution, at each frequency, instead of the high-frequency resistance (measured at *e.g.* 10 kHz) as is usual¹⁶.

RESULTS

(i) D.c. polarograms

In accordance with the results of other authors^{6,7} the slopes of the d.c. polarograms (or $\log [(i_g - i)/i]$ vs. E plots) indicate that the Eu(II)/Eu(III) reaction in 1 M KSCN is d.c. reversible. From a series of polarograms at different ratios $[Eu(III)]/[Eu(II)]$ the diffusion coefficients of the Ox and Red component were determined:

$$D_O = 5.6 \times 10^{-6} \text{ and } D_R = 7.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} .$$

These values are somewhat lower than the diffusion coefficients in 1 M KCl¹, KI¹ and NaClO₄^{6,17} reported earlier. This might be due to complex formation with SCN⁻ ions.

The standard potential was calculated from the equilibrium potentials. Its mean value is $E_0 = -640 \pm 3$ mV vs. SCE, which is in good agreement with the half-wave potential of -640 mV reported by Kinard and Philp⁷, from which, with our

diffusion coefficients, $E_0 = -643$ mV vs. SCE can be calculated.

The best value for the standard potential of the Eu(II)/Eu(III) system in non-complexing media appears to be^{6,17} -600 to -605 mV vs. SCE. If equality of the activity coefficients is assumed and differences in liquid junction potentials are neglected, this value can be identified with E'_0 , which is defined in eqn. (3). Consequently from eqn. (7) it can be derived that $r_O/r_R = \exp(nF/RT)(E_0 - E'_0)$ equals 0.23 ± 0.05 , indicating that Eu(III) is more strongly complexed by thiocyanate than Eu(II).

(ii) Impedance measurements

The measured impedance components for solutions with 2, 5 and 10 mM Eu(III) were converted to the components of the electrode admittance Y'_{el} and Y''_{el} in the usual way^{18,19}. Further analysis by means of the frequency variation method^{18,19} provided evidence that the data were in accordance with the Randles circuit, which means that Y'_{el} and Y''_{el} obey the equations:

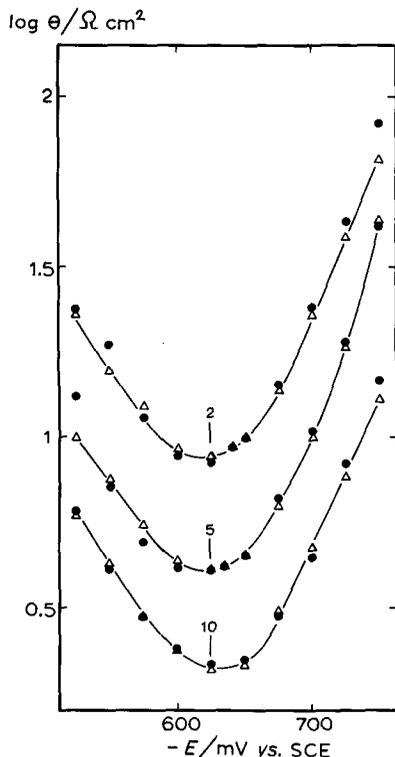


Fig. 1. Transfer resistance θ as a function of the electrode potential for the Eu(II)/Eu(III) reaction in 1 M KSCN for 2, 5 and 10 mM Eu(III) with d.c. polarization. (●) $\log \theta$ from frequency variation method, (Δ) $\log \theta$ from precalculated σ .

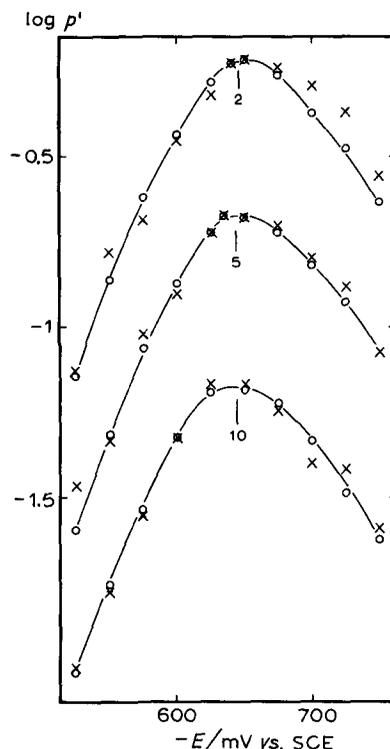


Fig. 2. $p' = \theta/\sigma$ as a function of the electrode potential for the Eu(II)/Eu(III) reaction in 1 M KSCN for 2, 5 and 10 mM Eu(III) with d.c. polarization. (×) $\log p'$ from frequency variation method, (○) $\log p'$ from precalculated σ . Curves for 2 and 5 mM are shifted respectively with 1.0 and 0.5.

$$Y'_{el} = \frac{\sqrt{\omega}}{\sigma} \frac{p+1}{p^2+2p+2} \quad (11a)$$

$$Y''_{el} = \frac{\sqrt{\omega}}{\sigma} \frac{1}{p^2+2p+2} + \omega C_d \quad (11b)$$

$$p = p'\omega^{\frac{1}{2}} = \theta/\sigma\omega^{-\frac{1}{2}} \quad (11c)$$

The values of C_d are identical to the double layer capacities in the supporting electrolyte alone, although, especially at potentials near the standard potential, a slight frequency dispersion was observed (maximal 4% in the solution with 10 mM Eu(III)). This might be due to experimental errors, *e.g.* caused by the shielding effect or by an error in the value of p inserted into eqn. (11b).

The analysis yields values for the Warburg coefficient σ and the irreversibility quotient p . From these quantities the transfer resistance θ can be determined *via* eqn. (11c). The accuracy was satisfactory over the potential region -525 to -750 mV *vs.* SCE.

Anticipating the values of the rate constant k_{sh}^a and the apparent and true transfer coefficient α^a and α (to be determined in the next section) these values can be used together with the diffusion coefficients D_O and D_R , to calculate theoretical σ values at each potential following the equation (eqn. 15) given in the next section under (ii). As the reaction is d.c. reversible, very rough estimates of k_{sh}^a , α^a and α are sufficient to calculate very accurate values of σ . The results can be compared with the values obtained experimentally and, where deviating, new values of p' and θ can be calculated after insertion of the theoretical σ value into eqn. (11a).

The results of both procedures are shown in Figs. 1 and 2. The agreement is evidently reasonable. Where differences occur, we prefer the results obtained with the precalculated σ (drawn lines) as they can be expected to be more accurate.

INTERPRETATION

(i) *The potential at the outer Helmholtz plane*

Several authors¹⁰⁻¹² have studied the structure of the electrical double layer on mercury in the presence of thiocyanate ions, which are found to be adsorbed specifically to an amount between that of bromide and iodide. Their results are in reasonable agreement, although exhibiting differences of 3-8 mV in the potential ϕ_2 at the OHP.

In this work we will use the most recent data of Parsons and Symons¹². As these do not cover the whole potential region of our measurements we extrapolated the ϕ_2 *vs.* E curve to more anodic potentials by a line parallel to the mean of the plots of the other authors.

As pointed out in our previous paper¹ it is necessary to recalculate the ϕ_2 potential for solutions containing Eu(III) and Eu(II), because of the high valency of the europium ions. This can be done with the aid of the equation of Joshi and Parsons²⁰,

$$q^{2-s} = -(q^m + q^i) = (2eRT)^{\frac{1}{2}} \left\{ \sum_j \bar{c}_j [\exp(-z_j f \phi_2) - 1] \right\}^{\frac{1}{2}} \quad (12)$$

where q^{2-s} , q^i and q^m are charge densities respectively in the diffuse double layer, in the inner layer and on the electrode surface; ϵ is the permittivity taken equal to that of pure water. The summation is made over all the ionic species with concentrations \bar{c}_j just outside the double layer and valency z_j .

Since our capacity values in the presence of europium are identical to those of the pure base electrolyte, we felt it permissible to take for q^{2-s} the values in the pure base electrolyte, reported by Parsons and Symons¹². With these premisses we calculated ϕ_2 potentials as a function of E for several cases. The results, summarized in Figs. 3 and 4, will be discussed briefly.

A. Pure base electrolyte at pH 2. The summation in eqn. (12) should include K^+ , SCN^- and the H^+ and Cl^- used to adjust the pH. The difference caused by the added HCl with respect to the case of 1 M KSCN is less than 0.2 mV (Figs. 3 and 4, curve a).

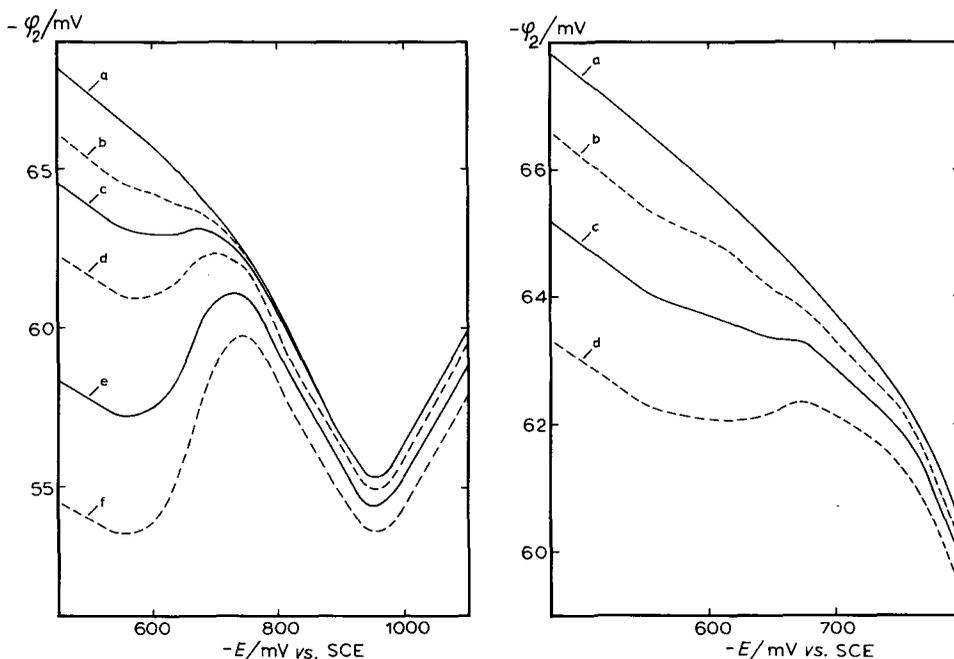


Fig. 3. Potentials ϕ_2 at the OHP as a function of the electrode potential for 1 M KSCN at pH 2, with (a) 0, (b) 0.5, (c) 1, (d) 2, (e) 5, (f) 10 mM Eu^{3+} with d.c. polarization (neglecting complex formation).

Fig. 4. Potentials ϕ_2 at the OHP as a function of the electrode potential for 1 M KSCN with (a) 0, (b) 2, (c) 5, (d) 10 mM $Eu(III)$ with d.c. polarization and complex formation.

B. Solutions of 0.5, 1, 2, 5 and 10 mM $Eu(III)$ with d.c. polarization. As a first approximation we will neglect complex formation. As was pointed out in our previous paper¹ one has to insert into eqn. (12) the concentrations \bar{c}_O and \bar{c}_R just outside the double layer. These concentrations vary with potential in the region of the polarographic wave and can be calculated from the polarographic current i at each potential according to

$$\bar{c}_O = c_O^* \left(1 - \frac{i}{i_{d,O}} \right) \quad (13a)$$

$$\bar{c}_O D_O^{\frac{1}{2}} + \bar{c}_R D_R^{\frac{1}{2}} = c_O^* D_O^{\frac{1}{2}} \quad (13b)$$

where $i_{d,O}$ is the limiting reduction current.

Since complex formation is ignored, \bar{c}_O and \bar{c}_R give the concentrations of Eu^{3+} and Eu^{2+} which must be inserted into eqn. (12) to give the ϕ_2 potentials represented by curves b–f in Fig. 3. Two remarkable conclusions have to be noted.

First, at all concentrations significant increases in ϕ_2 are observed. This will have its influence on the magnitude of the Frumkin correction, especially at the higher concentrations. Secondly, even at the lowest concentration, where the actual increase is only a few millivolts, the slope of the ϕ_2 vs. E plot is considerably different from that in the pure base electrolyte. At the higher concentrations the slope in the potential region of the polarographic wave has even changed sign. This is important for the determination of the transfer coefficient, as will be shown below.

C. Influence of complex formation. Complex formation of the europium ions with thiocyanate will diminish the amount of highly-charged particles and thus diminish the change in ϕ_2 potential.

Stability constants for thiocyanate complexes of Eu(III) at 25° and 1 M ionic strength have been reported by Choppin and Ketels¹⁴. From their data it can be calculated that $K_1^3 = 5.05 \pm 0.72$ and $K_2^3 = 6.8 \pm 1.4$ where

$$K_n^m = [\text{Eu}(\text{SCN})_n^{m-n}] / [\text{Eu}^m][\text{SCN}^-]^n \quad (14)$$

These data reveal that the total amount of Eu(III) is present as 7.8% Eu^{3+} , 39.3% $\text{Eu}(\text{SCN})^{2+}$ and 52.9% $\text{Eu}(\text{SCN})_2^+$.

For Eu(II) –thiocyanate complexes no data are available in the literature. Some information can be obtained from the standard potential E_0 in KSCN and E'_0 in non-complexing media, which are respectively –640 and –600 to –605 mV vs. SCE (*cf.* foregoing section). With these values we can calculate, following eqn. (7), that

$$r_O/r_R = \frac{[\text{Eu}^{3+}]}{[\text{Eu(III)}]} \frac{[\text{Eu(II)}]}{[\text{Eu}^{2+}]} = 0.23 \pm 0.05$$

and consequently from the total amount of Eu(II) we have $34 \pm 9\%$ present as Eu^{2+} .

Assuming that there are no Eu(II) complexes other than $\text{Eu}(\text{SCN})^+$ and $\text{Eu}(\text{SCN})_2$, this leaves the amounts of these species unknown. However, this is not important for the following reasons. The presence of the neutral species will have no influence on ϕ_2 . Under A it has been mentioned that the presence of a 10 mM concentration of a monovalent cation causes a difference of less than 0.2 mV in ϕ_2 . Therefore, even if the remaining 66% of the total amount of Eu(II) consists of $\text{Eu}(\text{SCN})^+$, this will have no significant influence on ϕ_2 if the concentration of Eu(II) is 10 mM or less.

On the basis of these considerations, all the necessary data are available to calculate the concentrations of the ionic species just outside the double layer, identifying \bar{c}_O and \bar{c}_R in eqn. (13) with Eu(III) and Eu(II) . The resulting ϕ_2 potentials for 2, 5 and 10 mM Eu(III) with d.c. polarization are represented by curves b, c and d

in Fig. 4. Although still significant, the increase in ϕ_2 is much less than in Fig. 3, owing to the complex formation. However, the slopes of the plots are still considerably different from that in curve a.

The ϕ_2 potentials calculated in case C will be used for the interpretation of our kinetic measurements.

(ii) "Apparent" and "true" rate constants and transfer coefficients

Analogously to the procedure followed for the europium reaction in KCl and KI, we will inspect in this section the potential dependence of the parameters σ , θ and p' in order to obtain information on the kinetic parameters describing the europium electrode reaction in thiocyanate.

Since eqn. (5) and (9) in the theoretical section are in principle identical (only with \bar{c}_{OT} and \bar{c}_{RT} instead of \bar{c}_O and \bar{c}_R) to the starting equation used by Timmer¹⁷ and Sluyters-Rehbach²¹ to derive expressions for this potential dependence, one can write analogously

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \times \frac{[D_R^{-\frac{1}{2}} \exp(\alpha\varphi) + D_O^{-\frac{1}{2}} \exp(-\beta\varphi)] [1 + a_O \exp(\beta\varphi) + (a_O/a_R) \exp(\varphi)]}{[(\alpha + g)a_O + \exp(-\beta\varphi)] c_{RT}^* \exp(\varphi) + [(\beta - g)a_O + (a_O/a_R) \exp(\alpha\varphi)] c_{OT}^*} \quad (15)$$

$$\theta = \frac{RT}{n^2 F^2 k_{sh}^a} \times \frac{1 + a_O \exp(\beta\varphi) + (a_O/a_R) \exp(\varphi)}{[(\alpha + g)a_O + \exp(-\beta\varphi)] c_{RT}^* \exp(\varphi) + [(\beta - g)a_O + (a_O/a_R) \exp(\alpha\varphi)] c_{OT}^*} \quad (16)$$

$$p' = \theta/\sigma = \frac{\sqrt{2} \exp(\beta\varphi)}{k_{sh}^a} [D_R^{-\frac{1}{2}} \exp(\varphi) + D_O^{-\frac{1}{2}}]^{-1} \quad (17)$$

with

$$a_i = (7/3\pi t)^{\frac{1}{2}} (D_i^{\frac{1}{2}}/k_{sh}^a), \quad (18)$$

t being the droptime of the DME, and

$$g = \frac{RT}{nF} \frac{d(\ln k_{sh}^a)}{dE} = \frac{RT}{nF} \frac{d(\ln k_{sh}^f)}{dE} + (\beta - z_O/n) \frac{d\phi_2}{dE} = g^i + g^d \quad (19)$$

In the case of d.c. reversible behaviour (in particular occurring at anodic potentials if $c_{RT}^* = 0$) eqns. (15) and (16) can be simplified to the so-called "reversible equations" which, with $c_{RT}^* = 0$, can be written as^{17,19}

$$\sigma = \sigma_{rev} = \frac{RT}{n^2 F^2 \sqrt{2} c_{OT}^* D_O^{\frac{1}{2}}} [(D_O/D_R)^{\frac{1}{2}} \exp(\varphi) + 2 + (D_R/D_O)^{\frac{1}{2}} \exp(-\varphi)] \quad (20)$$

$$\theta = \theta_{rev} = \frac{RT D_R^{\frac{1}{2}} \exp(-\alpha\varphi)}{n^2 F^2 c_{OT}^* k_{sh}^a} [D_R^{-\frac{1}{2}} \exp(\varphi) + D_O^{-\frac{1}{2}}] \quad (21)$$

(iii) *Transfer coefficient.* Attempts to determine the transfer coefficient always

lead to the apparent anodic or cathodic transfer coefficient, α^a or β^a , related to the true transfer coefficients α and β by ^{1,18}

$$\alpha^a = \alpha + g = 1 - \beta^a = 1 - (\beta - g) \quad (22)$$

in which g is given by eqn. (19).

Several procedures to determine α^a or β^a have been described previously³. In our case we can make use of the reversible eqn. (21) for θ , from which it appears that the slope of a plot of $\log(\theta/X)$, with $X = D_R^{-\frac{1}{2}} \exp(\varphi) + D_O^{-\frac{1}{2}}$, against E should give α^a . Similarly the slope of $\log(p'X)$ vs. E gives β^a .

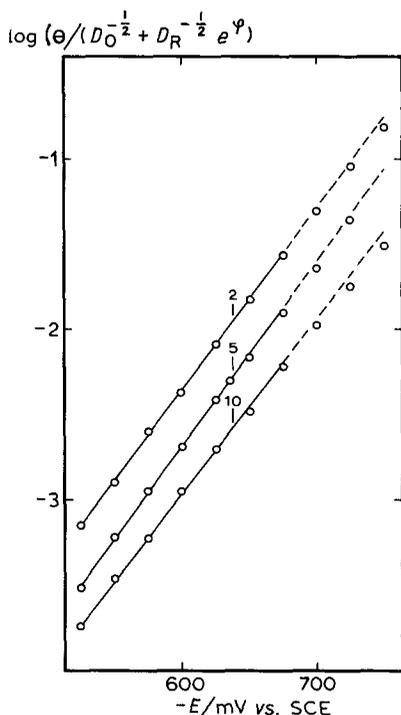


Fig. 5. Log of the function $\theta/(D_O^{-\frac{1}{2}} + D_R^{-\frac{1}{2}} e^\psi)$ for 2, 5 and 10 mM Eu(III) in 1 M KSCN.

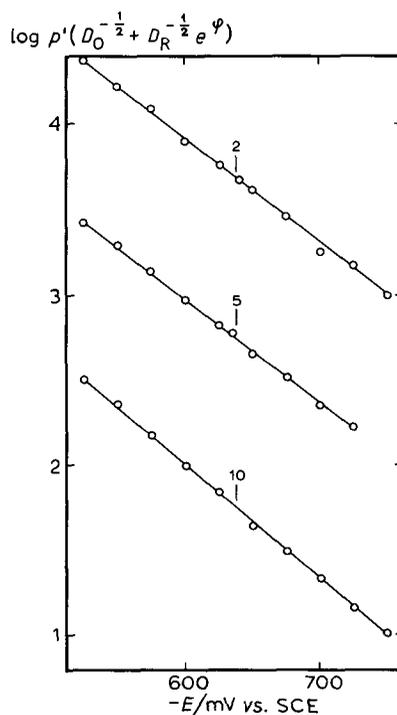


Fig. 6. Logarithm of the function $p'/(D_O^{-\frac{1}{2}} + D_R^{-\frac{1}{2}} e^\psi)$ for 2, 5 and 10 mM Eu(III) in 1 M KSCN. Lines for 2 and 5 mM are shifted respectively with 2.0 and 1.0.

The plots mentioned for p' , Fig. 6, are straight for all concentrations over the whole potential region of the measurements indicating that α^a is constant. The plots for θ , Fig. 5, are straight down to -700 mV vs. SCE. At more negative potentials slight deviations are due to non-validity of the reversible equation.

The resulting α^a values are tabulated in Table 1. They can be corrected for the Frumkin effect by calculating

$$\{\alpha^a - (1 - z_0/n)(d\phi_2/dE)\} / (1 - d\phi_2/dE) = \alpha + g / (1 - d\phi_2/dE) \quad (23)$$

In our previous study¹ of the europium reaction in KCl and KI the results were found

TABLE 1

VALUES OF THE APPARENT AND TRUE TRANSFER COEFFICIENT FOR THE Eu(II)/Eu(III) REACTION IN 1M KSCN (-575 to -650 mV vs. SCE)

Eu(III) concn./ mM l ⁻¹	α^a	α	From
2	0.63 ⁵	0.60 ± 0.02	θ_{rev}
2	0.64 ⁵	0.61 ± 0.02	p'
5	0.63 ⁵	0.61 ⁵ ± 0.02	θ_{rev}
5	0.64 ⁵	0.62 ⁵ ± 0.02	p'
10	0.61	0.61 ± 0.03	θ_{rev}
10	0.61	0.61 ± 0.03	p'

consistent with the assumption that $g^i=0$, in other words that k_{sh}^i is independent of potential. It seems reasonable to maintain this assumption also in the present case, unless it causes inconsistent results. Taking $d\phi_2/dE$ from Fig. 4 in the potential region -575 to -650 mV vs. SCE, where θ and p' appear to be most accurate, the left-hand side of eqn. (23), representing α , was calculated. The results are given in Table 1. Note that the slight concentration dependence of α^a disappears by means of the correction. The mean value for α , 0.61 ± 0.02 , is very close to the value 0.59 ± 0.02 found for the europium reaction in 1 M KCl¹.

(iib) Rate constant. Using this value for α we calculated k_{sh}^a as a function of potential from θ , eqn. (16), and from p' , eqn. (17). The two procedures give the same results, a survey of which is given in Table 2. At 2 and 5 mM concentration k_{sh}^a decreases significantly with decreasing potential, whereas at 10 mM concentration it is constant. Moreover there is a significant concentration dependence especially

TABLE 2

RATE CONSTANTS OF THE Eu(II)/Eu(III) REACTION IN 1 M KSCN

E/mV vs. SCE	I 10 ² k _{sh} ^a /cm s ⁻¹			II 10 ² k _{sh} ^a exp(3 - βn) fφ ₂ /cm s ⁻¹			III 10 ⁴ k _{sh} ^a exp(2 - βn) fφ ₂ /cm s ⁻¹		
	Eu concn./mM l ⁻¹			Europium concn./mM l ⁻¹			Europium concn./mM l ⁻¹		
	2	5	10	2	5	10	2	5	10
-525	3.3	3.0	2.5 ⁵	4.1	4.3 ⁵	4.4	5.2	5.2	4.9 ⁵
-550	3.3 ⁵	2.9	2.5	4.3 ⁵	4.3	4.4	5.4 ⁵	5.1 ⁵	4.9
-575	3.1	2.8	2.6	4.2	4.2 ⁵	4.7	5.1 ⁵	4.9 ⁵	5.1 ⁵
-600	3.3	2.8	2.5 ⁵	4.5	4.3	4.6 ⁵	5.5	5.0 ⁵	5.1
-625	3.1	2.7	2.6	4.4 ⁵	4.2 ⁵	4.7 ⁵	5.3 ⁵	4.9	5.2
-650	3.0	2.7	2.8	4.5	4.3 ⁵	5.1	5.3	5.0	5.5 ⁵
-675	2.9 ⁵	2.6 ⁵	2.7	4.5	4.3	4.8	5.3	4.9	5.3
-700	2.9	2.5 ⁵	2.6 ⁵	4.6 ⁵	4.3 ⁵	4.5	5.3 ⁵	4.9	5.2 ⁵
-725	2.7	2.3 ⁵	2.7	4.6	4.1 ⁵	5.0 ⁵	5.1 ⁵	4.7 ⁵	5.6
-750	2.6 ⁵		2.6	4.7 ⁵		5.1	5.2 ⁵		5.4
		mean value		4.4 ⁷	4.2 ⁸	4.7 ⁷	5.3 ⁰	4.9 ⁹	5.2 ⁵
				± 0.20	± 0.06	± 0.25	± 0.1	± 0.14	± 0.24
		10 ⁴ k _{sh} ^f /cm s ⁻¹		3.2 ± 0.15	3.1 ± 0.04	3.4 ± 0.2	12.5 ± 0.3	11.8 ± 0.3	12.4 ± 0.6
		with complex correction							

at more anodic potentials. Regarding eqn. (10) this behaviour corresponds qualitatively with the values of ϕ_2 at various concentrations and potentials (Fig. 4).

Application of the Frumkin correction, taking $z_O = 3$ and $\beta = 0.39$, produces corrected rate constants (Table 2, column II) which are completely potential independent at 5 mM concentration, but at 2 and 10 mM the original potential dependence appears to be overcompensated in view of the tendency toward increase with decreasing potential. However, the effect is rather small and may well be caused by experimental errors or errors in the calculation of ϕ_2 .

Taking $z_O = 3$ implies the assumption that the reaction proceeds *via* the non-complexed species. As pointed out in the theoretical section it is also possible to assume that complexed species with equal number of ligands for Ox and Red are involved, simply by taking z_O equal to the charge of the complexed species. In Table 2, column III, it can be seen that with $z_O = 2$ the potential dependence of the corrected rate constant is negligible for all concentrations, while in addition the variation with concentration is minimized (see also DISCUSSION).

The mean values under column II in Table 2 can be corrected for the complexation effect using the values $r_O = 0.078$ and $r_R = 0.34$ reported above. For a similar correction under column III the value of r_R is lacking. The reported results are obtained with $r_O = 0.39$ and $r_R = 0.5$ (estimated).

(iii) The Cr(II)/Cr(III) reaction in different supporting electrolytes

In their study of this reaction Anson and coworkers⁵ also considered the effect of the anion of the supporting electrolyte on the kinetic parameters. Because of the common features (both Ox and Red soluble in solution and fairly irreversible behaviour) it seems worthwhile to compare the chromium with the europium system. However, Anson's interpretation of results differs from our way of interpretation, thus preventing a direct comparison.

First, they tabulated apparent rate constants obtained by extrapolation of the parameter λ to the standard potential E'_0 (-650 mV vs. SCE) of the non-complexed couple. Since λ is obtained from $i/i_{d,0}$ in which of course $i_{d,0}$ is proportional to c_{OT}^* we can understand their definition of k_{sh} by writing eqn. (1) in the form

$$i = nFk_{sh}^f \{ \bar{c}_{RT} r_R \exp(\alpha\phi') - \bar{c}_{OT} r_O \exp(-\beta\phi') \} \exp[(\beta n - z_O) f \phi_2] \quad (24)$$

This equation does not allow incorporation of the complexation terms r_R and r_O directly in k_{sh}^a . Fortunately Anson *et al.* calculated the rate constants from i -values corrected for the back-reaction (*i.e.* Cr(II) oxidation) so that we have to deal with only the second term, $\bar{c}_{OT} r_O \exp(-\beta\phi')$, between the brackets. In this case we can define the apparent rate constant as

$$k_{sh}^a = k_{sh}^f r_O \exp[(\beta n - z_O) f \phi_2] \quad (25)$$

Second, as far as we can infer from their paper, Anson *et al.* ignored the presence of r_O in eqn. (25), but corrected for the occurrence of complex formation by taking for z_O the average charge of the Cr(III) in the bulk of the solution. In our opinion there is no sound reason for such an arbitrary treatment.

Finally, ϕ_2 potentials were taken equal to those of the supporting electrolytes. From Figs. 3 and 4 it can be deduced that this is not correct, especially in non-complexing media. As the Cr(III) concentration did not exceed 0.5 mM, the effect on the Frum-

TABLE 3

RATE CONSTANTS FOR THE $\text{Cr}^{2+}/\text{Cr}^{3+}$ REACTION AT -650 mV vs. SCE⁵

Electrolyte	$\log k_{\text{sh}}^{\text{a}}$	$\log k_{\text{sh}}^{\text{f}}$ (Anson)	$\log k_{\text{sh}}^{\text{f}}$ (complex correction)	
0.5 M NaClO ₄	-5.09	-6.89	-6.89	ϕ_2 from (10)
0.5 M NaClO ₄		-6.11	-6.11	ϕ_2 from (24)
1 M NaClO ₄	-5.10	-6.55	-6.55	ϕ_2 from (10)
1 M NaClO ₄		-6.14	-6.14	ϕ_2 from (24)
0.5 M KCl	-5.07	-5.67	(-5.03)	ϕ_2 from (22)
0.5 M KCl		(-6.12)	-5.66	ϕ_2 from (23)
1 M KBr	-4.87	-6.15	-5.76	
0.5 M KI	-4.01	(-6.86)	-7.15*	
0.5 M LiClO ₄	-5.19	-6.42	-6.42	ϕ_2 from (24)
1 M LiClO ₄	-5.44	-6.41	-6.41	ϕ_2 from (24)
0.083 M LaCl ₃	-5.19	-6.13	(-5.83)	ϕ_2 from (22)
0.083 M LaCl ₃		(-6.52)	-6.35	ϕ_2 from (23)
0.1666 M LaCl ₃	-5.58	-6.11	(-5.44)	ϕ_2 from (22)
0.1666 M LaCl ₃		(-6.63)	-6.17	ϕ_2 from (23)

* r_0 was estimated to be 0.4.

kin term itself will be negligibly small, but the change in $d\phi_2/dE$ can have a considerable influence on the value of the apparent transfer coefficient. Possibly the discrepancies in α (after Frumkin correction) among the various supporting electrolytes can be explained partly in this way.

In Table 3 a comparison is drawn between the apparent rate constants, rate constants corrected in Anson's way, and rate constants corrected in our way, using eqn. (25) (i.e. k_{sh}^{f} values). Special attention should be given to the chloride solutions for which Anson *et al.* used double layer data for NaF²² instead of the well-known data of Grahame and Parsons²³ for chloride itself. Moreover we also calculated the data for 0.5 M KI, which were omitted by Anson *et al.* because they thought that catalysis by the iodide ion would occur (k_{sh}^{a} is a factor of 10 larger than in the other media). However, our data show that, after correction, k_{sh}^{f} in KI is even smaller than the other values. This may be attributed to the fact that we used ϕ_2 values of the supporting electrolyte without accounting for the presence of Cr(III), which will introduce the largest error for KI (*cf.* ref. 1).

The overall data show a fairly constant k_{sh}^{f} , especially if we take into account only the values calculated with the most reliable ϕ_2 data (refs. 24 and 23). Only in the complexing media 0.5 M KCl and 1 M KBr do the values appear to be somewhat larger.

DISCUSSION

(i) Concentration dependence of k_{sh}^{a} and α^{a}

Especially at the more positive potentials is a significant concentration dependence of k_{sh}^{a} observed (Table 2). Though less impressive, the concentration dependence of α^{a} is also significant. To our knowledge such a behaviour has not been reported before. The effects can be explained by the difference in ϕ_2 potentials caused

by the contribution of the electroactive species to the double layer. As there is no significant concentration dependence after correcting for the Frumkin effect it appears that our method for calculating the contribution of the reacting species to the double layer, with q^{2-s} values equal to that in the pure base electrolyte solution, gives reliable results.

(ii) *Potential dependence of k_{sh}^f*

The significant potential dependence of k_{sh}^a can be ascribed entirely to the Frumkin effect, resulting in a potential independent true rate constant with a mean value,

$$k_{sh}^f = (3.2 \pm 0.2) \times 10^{-4} \text{ cm s}^{-1} \quad \text{if } z_O = 3 \text{ and}$$

$$k_{sh}^f \approx (12.2 \pm 0.4) \times 10^{-4} \text{ cm s}^{-1} \text{ (estimated with } r_R = 0.5) \text{ if } z_O = 2.$$

Thus, just as in the case of 1 M KCl and 1 M KI no influence of the specifically adsorbed amount of anions in the inner layer is observed. Regarding Parsons' model⁴, this means that the activated complex is not situated in the inner layer, and that the europium ions do not lose their hydration shell before or during the reaction and remain at their location in the diffuse double layer.

(iii) *Comparison with results in KCl and KI*

In our previous paper¹ we reported for the true rate constant of the Eu(II)/Eu(III) reaction in 1 M KCl and 1 M KI respectively $(1.4 \pm 0.2) \times 10^{-5}$ and $(0.6 \pm 0.1) \times 10^{-5} \text{ cm s}^{-1}$. These values are not corrected for the effect of complex formation. Thus before comparing them with the value in KSCN we will have to correct for this effect. Taking for the r_O ratios, respectively, 0.5 and 0.67, this results in a value of $(2.1 \pm 0.3) \times 10^{-5} \text{ cm s}^{-1}$ in 1 M KCl and $(0.75 \pm 0.1) \times 10^{-5} \text{ cm s}^{-1}$ in 1 M KI. Thus, the true rate constant in KSCN is more than one order of magnitude larger than in KCl and KI.

To explain the difference between the KCl and KI case we assumed tentatively that the reaction takes place somewhat outside the OHP, which would mean that instead of ϕ_2 a more positive value ϕ_x should be inserted into the Frumkin correction term. If we want to explain the results for KSCN in the same way, we have to assume that in this case a potential ϕ_x , which is more negative than the OHP potential, must be used. As it seems reasonable that in each case the reaction site is at the same distance from the electrode surface, this would mean that in KSCN the OHP is more remote from the electrode surface than in KCl and KI.

A rough estimate of the difference in distance could be made on the basis of our results. For the potential ϕ_x at a distance x from the OHP one can write²⁵

$$\phi_x = \phi_2 \exp(-\kappa x) \quad (26)$$

where $1/\kappa$ is the so-called thickness of the double layer (about $3 \times 10^{-8} \text{ cm}$ for 1 M 1-1 electrolyte solutions). Differentiation of eqn. (26) gives:

$$d\phi_x/dx = -\kappa\phi_2 \exp(-\kappa x) \quad (27)$$

As an approximation one can linearize this equation for small x -values to give:

$$\phi_x - \phi_2 = -\kappa\phi_2 x \quad (28)$$

Using this equation one can calculate the distance, x , between the reaction plane and the OHP by calculating the potential, ϕ_x , of the reaction plane from the equation:

$$(\beta n - z_0)(\phi_2 - \phi_x) = (RT/nF) \ln(k_{sh,x}^f/k_{sh,2}^f) \quad (29)$$

where $k_{sh,x}^f$ is the true rate constant, assuming that the reaction plane is situated at a distance x from the OHP, and $k_{sh,2}^f$ the rate constant we calculated inserting ϕ_2 into the Frumkin correction term.

Since in the KCl case ϕ_x will be least dependent on x , we put for this case $k_{sh,x}^f \approx k_{sh,2}^f$, *i.e.* $(2.1 \pm 0.3) \times 10^{-5} \text{ cm s}^{-1}$ (see above). If in KI and KSCN the true rate constant has the same value, one gets *via* eqns. (28) and (29):

$$\text{in } 1 \text{ M KI: } x = 0.16/\kappa \approx 0.5 \times 10^{-8} \text{ cm}$$

$$\text{in } 1 \text{ M KSCN: } x = -0.4/\kappa \approx -1 \times 10^{-8} \text{ cm}$$

The value for 1 M KSCN may be too large because eqn. (28), which is already an approximation, holds only for positive x , *i.e.* in the diffuse layer. For negative x , *i.e.* within the compact double layer, it is reasonable to assume that in our case ϕ_x decreases more rapidly, because there is a considerable amount of specifically adsorbed thiocyanate. With a value for the permittivity half of that of pure water, the capacity between inner and outer Helmholtz plane can be estimated to be $200 \mu\text{F cm}^{-2}$. With $q^i \approx 20 \mu\text{C cm}^{-2}$, this yields $\phi_1 - \phi_2 = -100 \text{ mV}$. Again assuming a linear relation between ϕ_x and x , this means that $x = 25/100$ times the distance between inner and outer Helmholtz plane. A reasonable estimate for the latter is the thickness of one water layer, *i.e.* $-2 \times 10^{-8} \text{ cm}$, so that x would be $-0.5 \times 10^{-8} \text{ cm}$.

The estimations above suggest that the distance of the OHP from the electrode surface increases in the order $\text{I}^- < \text{Cl}^- < \text{SCN}^-$. The relative distances of 0.5 \AA do not seem unrealistic.

Another explanation can be that the europium reaction is catalysed by adsorbed thiocyanate ions and possibly less by chloride and iodide ions. In that case, however, one should expect that the true rate constant is potential dependent. As we found that this is not the case to a significant extent, one must dismiss the possibility of catalysis by the anions.

A third explanation may be that the charge transfer reaction does not proceed *via* the non-complexed ions, but for example *via* the $\text{Eu}(\text{SCN})_2^{2+}$ or $\text{Eu}(\text{SCN})_2^+$ species and the corresponding Eu(II) complexes. Column III in Table 2 seems to provide an argument for this assumption, by the fact that the corrected rate constants with $z_0 = 2$ are slightly more consistent than with $z_0 = 3$. As in this case the ligand will play its particular role, it is of no use to compare the final true rate constant with those in chloride and iodide.

Since, in the OHP, the electroactive species is mainly present in the non-complexed form, (Eu(III) for about 70% as Eu^{3+} and Eu(II) for about 90% as Eu^{2+}) we prefer the explanation in terms of the reaction *via* the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ions, the OHP distances being dependent on the species of the base electrolyte. However, for a definitive choice between the two possibilities further investigations are necessary. Therefore one has to measure the rate constant at different thiocyanate concentrations. For a useful interpretation one needs accurate values for the stability constants of the Eu(III)- and Eu(II) complexes and for the ϕ_2 potentials in the different cases.

Moreover further investigations on the exact site of the reaction plane and the OHP seem to be necessary.

(iv) *Comparison with the Cr(II)/Cr(III) reaction*

The philosophy of the present paper and the previous paper on europium¹ is based to the idea that there is a class of electrode reactions of which the activated complex is situated outside the inner double layer, as shown by the lack of influence of specifically adsorbed anions on the true rate constant.

In the previous paper we had two arguments, *viz.* the potential independence of k_{sh}^f and the relatively small difference between k_{sh}^f in KCl and k_{sh}^f in KI, as opposed to the large difference in and potential dependence of specific adsorption of the anions. The data for the Cr(II)/Cr(III) couple in Table 3 show the second argument, *i.e.* the small anion effects, also for this reaction. Thus they provide additional confirmation of the idea postulated. It should be noted that the present list does not include data for the chromium reaction in thiocyanate media. It seems useful to investigate whether this supporting electrolyte produces also an exception in the chromium case.

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SUMMARY

A detailed study has been made of the kinetics of the Eu(III)/Eu(II) reaction at the DME in 1 M KSCN by means of impedance measurements. The data were analyzed according to the complex-plane method. Because of the considerable complexation of the europium ions in this medium, it appeared to be necessary to calculate the influence of complex formation on the apparent rate constant of the electrode reaction. Therefore an expression to correct for this effect was derived, assuming that the reaction takes place *via* the uncomplexed ions.

In order to apply Frumkin corrections, ϕ_2 potentials were calculated for the systems concerned, accounting for the presence of the electroactive species. It could be shown that even 0.5 mM concentrations of trivalent cations have a considerable effect.

The data are consistent with a "true" transfer coefficient $\alpha=0.61$. With this value the apparent rate constant was determined at different potentials and different europium concentrations. It was shown that the true rate constant was potential independent, with a mean value $k_{sh}^f = (3.2 \pm 0.2) \times 10^{-4} \text{ cm s}^{-1}$. As in the potential region studied the amount of specifically adsorbed SCN^- ions is strongly potential dependent, it can be concluded that, just as in KCl and KI, specific anion adsorption has no influence on the charge transfer of the europium couple. The rather large value of the rate constant in KSCN can be explained by assuming that the reaction plane is somewhat inside the outer Helmholtz plane. Another possibility is that the reaction takes place *via* the Eu(SCN) complex. In this case the true rate constant is also potential independent, with a mean value $k_{sh}^f = (12 \pm 0.4) \times 10^{-4} \text{ cm s}^{-1}$. Analysis of the

data of Anson *et al.*⁵ on the $\text{Cr}^{3+}/\text{Cr}^{2+}$ reaction with our way of correcting for complex formation shows that also in this case the amount of specifically adsorbed anions has no influence on the charge transfer of this reaction. This confirms our hypothesis that it holds for each electrode reaction where both the Ox and the Red components are present in the electrolyte solution.

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