

A FARADAIC IMPEDANCE STUDY OF THE ELECTROCHEMICAL REDUCTION OF Cd(II) IONS FROM AQUEOUS 1 M (KF + KCl) MIXED ELECTROLYTE SOLUTIONS AT THE DROPPING MERCURY ELECTRODE

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ABSTRACT

It is shown that in the whole range of the composition of this base electrolyte the Cd(II) reduction can be explained on the assumption of a reaction mechanism that consists of a chemical step followed by two one-electron transfers, the transfer coefficients of which both appear to be 0.5. The rate constant of the chemical step is shown to increase rapidly with chloride ion concentration. The dependence of the electrochemical rate constants on the composition of the base electrolyte is also reported and discussed.

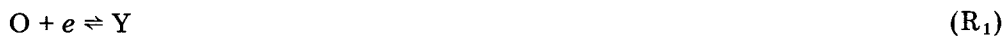
(I) INTRODUCTION

In a recent paper [1, this issue pp. 139–153] we have shown that the reduction of Cd(II) ions from an aqueous 1 M KF solution at the DME proceeds according to a two-step charge-transfer mechanism preceded by a heterogeneous chemical step, case B in ref. 1:



No information could be obtained on the exact nature of the reacting particles. However, it could be proved that the preceding chemical reaction should be first order with respect to the concentration of the reactant Cd(II).

The above mechanism is different from the mechanism found earlier in this laboratory [2] for the reduction of Cd(II) ions from aqueous 1 M KCl solutions, case G in ref. 1:



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in which the second step was assumed to be rate-determining.

From earlier observations it was known that both in fluoride and sulphate base electrolytes additions of small amounts of Cl^- ions accelerate the $\text{Cd(II)}/\text{Cd(Hg)}$ charge transfer appreciably and therefore we wondered at what chloride ion concentration the mechanism of the Cd(II) reduction would change from case B into case G, or whether in mixed $\text{KF} + \text{KCl}$ electrolytes yet another mechanism could be shown to occur.

Therefore, we decided to perform a number of impedance studies of the Cd(II) reduction in mixtures of KF and KCl as the base electrolyte at constant 1 M ionic strength. The choice of these base electrolytes is also attractive because double-layer data of the interface of these solutions with mercury are well known [3], possibly allowing Frumkin corrections to be applied.

(II) EXPERIMENTAL

Eight solutions made up of $x\text{M KCl} + (1 - x)\text{M KF}$, with $x = 0, 0.01, 0.04, 0.10, 0.25, 0.50, 0.75$ and 1 were freshly prepared from p.a. grade chemicals in twice-distilled water. After the double-layer capacitances were measured at 1000 Hz in the faradaic potential region a Cd(II) solution in the same base electrolyte was added in order to make the Cd(II) concentration 0.5 mM . Deaeration of the solutions was performed with argon freed from traces of oxygen with a B.T.S. catalyst.

The cell impedances and the dc polarograms were measured with the automatic network analyser system described earlier [4]. All experiments were performed at $25 \pm 0.1^\circ\text{C}$.

(III) RESULTS

In all supporting electrolytes and at all potentials the electrode impedance could be described according to Randles' simple equivalent circuit, i.e. in terms of a Warburg coefficient σ , a double-layer capacitance C_d and an irreversibility quotient p' . The details of this analysis and also a critical discussion on its reliability have been published elsewhere [5,6]. From the potential dependence of σ the reversible half-wave potential $E_{1/2}^r$ and the diffusion coefficient of the Cd(II) species were obtained in each base electrolyte. These values are reported in Table 1. As in an earlier publication [1] the diffusion coefficient of Cd in the mercury drop was taken equal to $10.7 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$.

In view of the fact that the potential dependence of σ was always found to be in perfect concordance with a dc reversible two-electron transfer behaviour it was concluded that a significant diffusional flux of any intermediate involved never occurred. Therefore, one of the mechanisms mentioned in Table 1 of ref. 1 could apply and an attempt could be made to find the proper rate equation describing the p' data. As pointed out in ref. 1 this can be done by examining the quantity

$$1/k_f = p' [1 + \exp(j)] (2 D_O)^{-1/2} \quad (1)$$

where p' is the experimentally obtained irreversibility quotient, D_O is the diffusion coefficient and $j = (nF/RT)(E - E_{1/2}^r)$; k_f can be considered as the poten-

TABLE 1

Reversible half-wave potentials $E_{1/2}^r$ and diffusion coefficients of Cd(II) in mixed $x M$ KCl + $(1 - x) M$ KF base electrolytes

x	$-E_{1/2}^r/V$ (vs. SCE)	$10^6 \times D_O/cm^2 s^{-1}$
0	0.6080	8.0
0.01	0.6097	8.0
0.04	0.6107	8.2
0.10	0.6133	8.4
0.25	0.6195	8.5
0.50	0.6270	8.8
0.75	0.6320	9.0
1 00	0.6375	9.0

tial dependent forward rate constant occurring in the overall rate equation.

In Fig. 1 we made plots of $\ln k_f$ vs. potential for the various base electrolyte solutions. A remarkable feature is that the curves tend to have a common asymptote at positive potentials, the slope of this asymptote being close to $-0.75 (nF/RT)$. The effect of the change in anion shows up most strongly in the extreme negative potential region.

The case of the KF supporting electrolyte ($x = 0$) was treated in detail in the earlier paper [1] and it was found that case B mentioned in the introduction was perfectly applicable. In view of the observations above we decided also to test the validity of this mechanism for the mixed electrolytes with KCl. This means that the following expression for $1/k_f$ should hold:

$$\frac{1}{k_f} = \frac{1}{k_c} + \frac{K_c}{k_1} + \frac{K_c K_1}{k_2} \quad (2a)$$

$$= \frac{1}{k_c} + \frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s1}K_c^{-1}} + \frac{\exp[\frac{1}{2}(1+\alpha_2)\phi]}{k_{s2}} \quad (2b)$$

Regarding this expression two items must be considered first: (1) The parameters k_1 and k_2 are the potential dependent forward rate constants of the charge-transfer reactions $O' + e \rightleftharpoons Y$ (R1) and $Y + e \rightleftharpoons R$ (R2) respectively. Via the definition of $\phi = (nF/RT)(E - E^0)$ in ref. 1 the potential was referred to the standard potential of the overall reaction $O + 2e \rightleftharpoons R$, and consequently k_{s1} is the value of k_1 at the particular potential $E = E^0$, k_{s2} is the value of $K_2 k_2$ (the backward rate constant of R2) at $E = E^0$. If it is desired to compare the results from the different KF + KCl mixtures it is preferable not to refer the potential to the E^0 pertaining to each solution, but to one and the same reference point, which of course may be chosen arbitrarily. In our analysis we chose the standard potential found in the 1 M KF solution, i.e. $E^0 = -0.610$ V vs. SCE.

(2) There are arguments in the literature [7,8] that for simple one-electron charge-transfer reactions the transfer coefficient should be equal to 0.5, or at least be close to this value. Adopting this idea we tried to verify eqn. (2b) with $\alpha_1 = \alpha_2 = 0.5$, thus restricting the number of degrees of freedom.

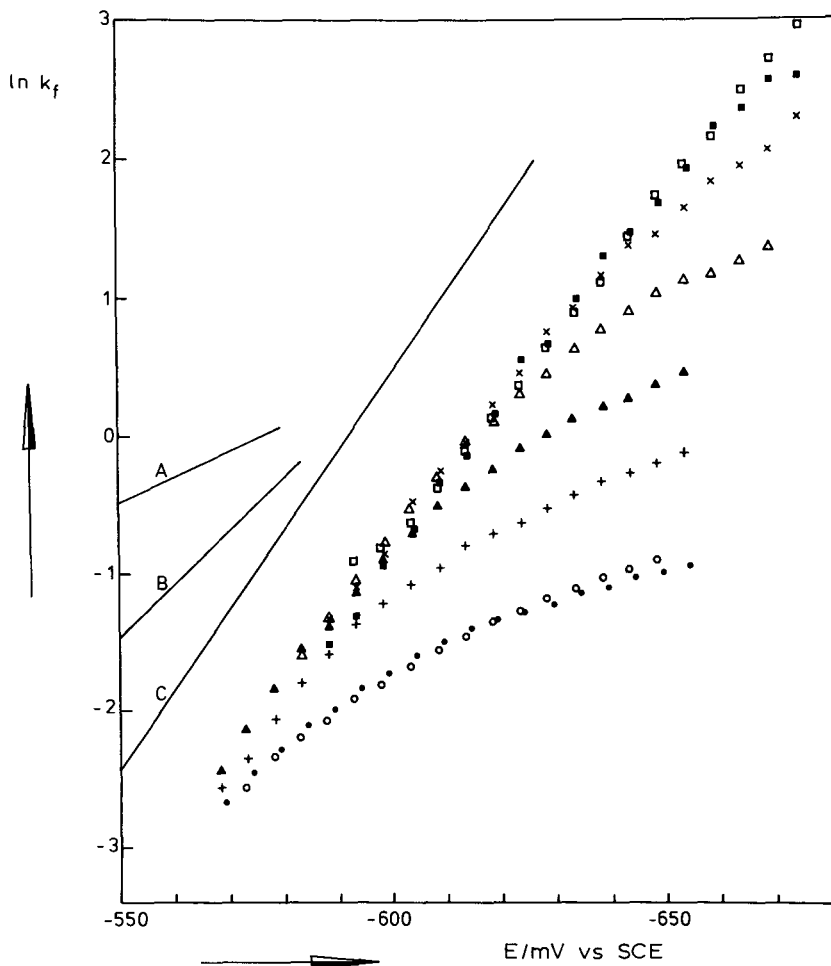


Fig. 1. Plot of $\ln k_f$ vs. potential for the Cd(II) reduction from xM KCl + $(1-x)M$ KF base electrolytes. (A), (B) and (C): lines with slopes respectively equal to 0.25, 0.50 and 0.75. (\bullet) $x = 0$, (\circ) $x = 0.01$, (+) $x = 0.04$, (\blacktriangle) $x = 0.1$, (\triangle) $x = 0.25$, (\times) $x = 0.5$, (\blacksquare) $x = 0.75$ and (\square) $x = 1$.

In Fig. 2 the function $1/k_f$, calculated with eqn. (1), has been plotted against $\exp[\frac{1}{4}\phi]$. Extrapolation of the curves to $\exp(\frac{1}{4}\phi) = 0$ should yield the reciprocal value of the rate constant of the preceding chemical step, $1/k_c$. It can be seen that for $x > 0.5$ the intercept does not differ significantly from zero, whereas for the lower chloride concentrations $1/k_c$ can be determined within certain ranges. Evidently k_c increases rapidly with increasing Cl^- concentration.

As the following step, plots were made of

$$\left[\frac{1}{k_f} - \frac{1}{k_c} \right] \exp[-\frac{1}{2}\alpha_1\phi] = \frac{1}{k_{s1}K_c^{-1}} + \frac{\exp[\frac{1}{2}(1 + \alpha_2 - \alpha_1)\phi]}{k_{s2}} \quad (3)$$

against $\exp[\frac{1}{2}\phi]$, tentatively taking $\alpha_1 = 0.5$.

Much to our surprise and satisfaction we obtained for all base electrolytes

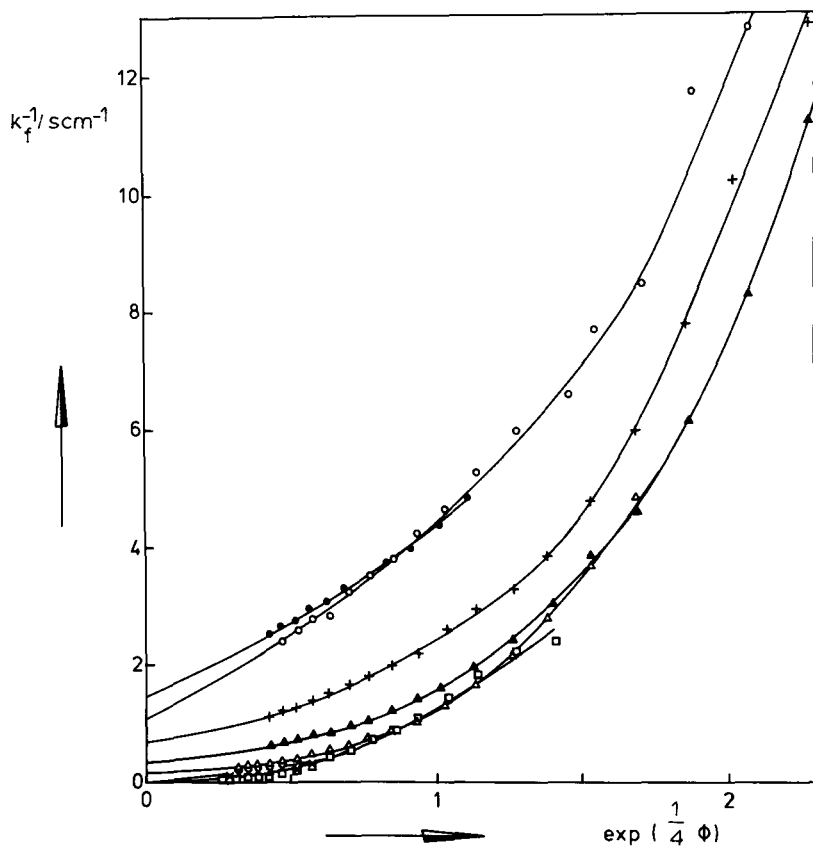


Fig. 2. Plot of k_f^{-1} vs. $\exp(\frac{1}{4}\phi)$. Symbols as in Fig. 1. For the sake of clarity $x = 0.75$ has been deleted.

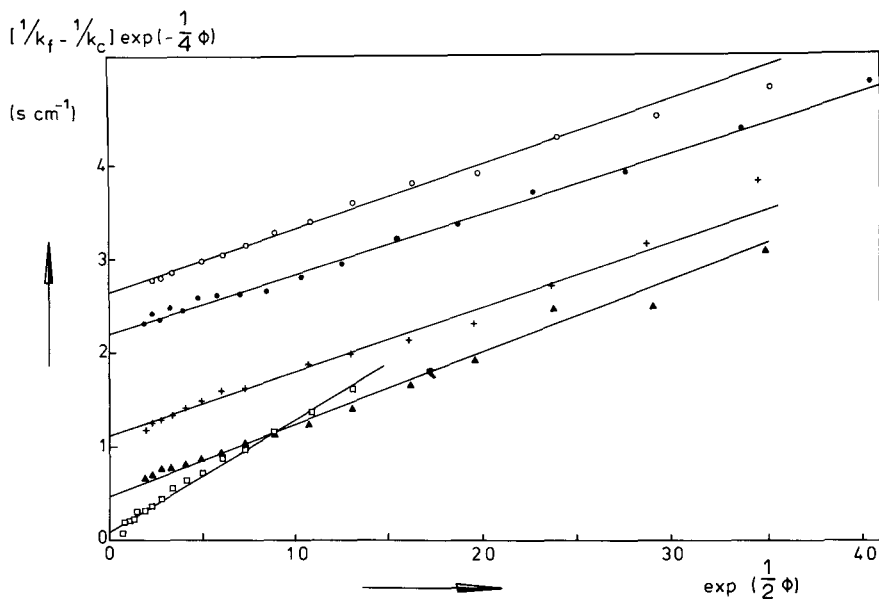


Fig. 3. Some examples of $[k_f^{-1} - k_c^{-1}] \exp(-\frac{1}{4}\phi)$ vs. $\exp(\frac{1}{2}\phi)$ obtained during the analysis. For explanation see text. Symbols as in Fig. 1.

TABLE 2

Rate constants of the chemical step and the two electrochemical steps at -610 mV for some compositions x M KCl + $(1 - x)$ M KF of the mixed electrolyte

x	$k_c/\text{cm s}^{-1}$	$k_{s_1}K_c^{-1}/\text{cm s}^{-1}$	$k_{s_2}/\text{cm s}^{-1}$
0	0.655	0.455	1.54
0.01	0.90	0.375	1.46
0.04	1.67	0.90	1.42
0.1	2.90	2.13	1.28
0.25	7.5	4.2	1.14
0.5	20	8	1.05
0.75	—	10	0.825
1.00	—	12	0.82

fairly straight lines, from which $1/k_{s_2}$ and $1/(k_{s_1}K_c^{-1})$ were derived as the slope and the intercept at $\exp[\frac{1}{2}\phi] = 0$ respectively. In some cases it was even possible to determine the value of $1/k_c$ more precisely (within the range initially indicated) by also demanding that the points close to the origin, which are most sensitive to $1/k_c$, should fall on the line. Some examples are shown in Fig. 3. The complete sets of rate parameters obtained in this way, are reported in Table 2 and Fig. 4.

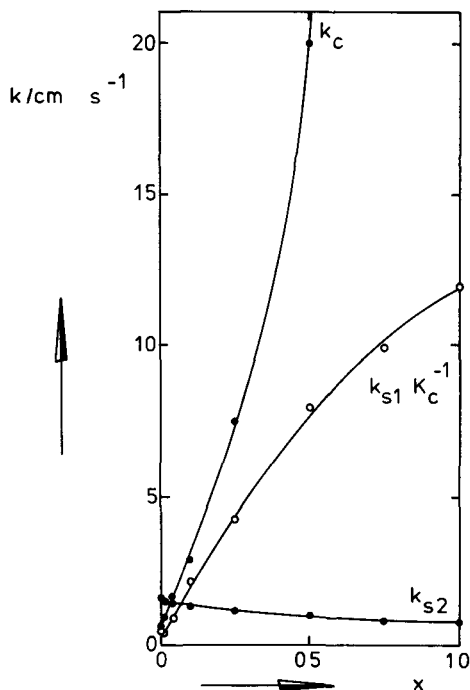


Fig. 4. Plot of the rate constants k_c , $k_{s_1}K_c^{-1}$ and k_{s_2} of the chemical and the two electrochemical steps in the Cd(II)/Cd(Hg) electrode reaction in aqueous x M KCl + $(1 - x)$ M KF as a function of the base electrolyte composition x .

(IV) DISCUSSION

Although the rate constants are obtained in a straightforward way and seem to describe the processes at the electrode surface quite well, some further remarks should be made.

Firstly it should be mentioned that the fit of the experimental data to eqn. (2) at $x = 0$ becomes slightly better, assuming $\alpha_2 = 0.6$ instead of 0.5 which is in accordance with our earlier observation reported in ref. 1. No further attention will be paid to this possible dependence of α_1 from the composition of the base electrolyte.

In order to exclude artefacts in the graphical analysis the original data were calculated back by substitution of these rate constants in eqn. (2b) and compared with the experimental values. The agreement with the data represented in Fig. 1 is within experimental error in all cases.

The nature of the reactants in the chemical step as yet being unknown, it is difficult to give an explanation of the increase of the rate constant k_c of the chemical step. Evidently, beyond $x = 0.5$ the influence of k_c on the overall rate becomes small so that at $x = 0.75$ and $x = 1$ mechanism A of ref. 1



might as well be adopted. If so the value of $k_{s_1}K_c^{-1}$ must be interpreted as the rate constant at $E = E^0$ of the first electron transfer.

If fluoro complexes are involved in the chemical step in 1 M KF, then the increase of k_c with increasing KCl concentration could mean that the chemical step is catalysed by chloride anions, or that another chemical reaction proceeds in parallel to the original one.

With a view to the experimental results obtained by Pospíšil and Kůta [9] in sulphate base electrolyte at varied pH it should not be excluded that the reaction proceeds via hydroxo-complexes that would make the rate constant of the chemical step pH dependent. We believe that further experiments along the lines developed in this paper could solve these questions and we hope to make further studies in the near future.

The question may arise, whether our experiments are sufficiently extensive to exclude the other mechanisms listed in Table 1 of ref. 1. In the case of 1 M KF it was already put forward that mechanism G, but extended with the preceding chemical step, could be fitted rather closely to the experimental results. If in the 1 M KCl and the 0.25 M KF + 0.75 M KCl solution the preceding step is not relevant (or absent), verification of Van der Pol's mechanism, case G1 in ref. 1, must be tried, with the expression for k_f :

$$\frac{1}{k_f} = 2 \left\{ \frac{\exp[\frac{1}{2}\alpha_1\phi]}{k_{s_1}} + \frac{\exp[\frac{1}{2}\phi]}{k'_c} \right\} \quad (4)$$

For this function the asymptote at positive potential in Fig. 1 should be 0.5 (nF/RT), whereas for both solutions the slope in the whole potential region is definitely larger. It must be concluded that our results are in disagreement with the disproportionation mechanism, deduced from Van der Pol's study using the

faradaic rectification method [2]. The reason for this discrepancy is not clear.

During the data analysis no indications were found that even slight reactant adsorption occurs. The capacitance of the double-layer was always found to be equal to the value in the absence of the electroactive species Cd(II) within the accuracy of the experiment. Finally, it should be realized that as yet no Frumkin corrections have been applied to the electrochemical rate constants. As we believe that for multistep mechanisms with intermediates that are not liable to be transported to and from the electrode surface, Frumkin corrections need special consideration, we prefer to communicate on this subject later, also because these corrections will be small in these particular cases. Possibly, however, the rather surprising significant minimum in $k_{s_1}K_c^{-1}$ at low values of x in Table 2 could disappear on applying Frumkin corrections.

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