The Adsorption of Metal–Halogeno-complexes at Metal–Molten Salt Interfaces

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INMAN and BOCKRIS[1] employed the chronopotentiometric technique to obtain the formation constants of the halogeno-complexes of cadmium in molten equimolar $NaNO_3$–KNO_3. Some other results at high cadmium-ion concentrations were interpreted in terms of the slow dissociation of a bromo-complex at the electrode surface.[2] These results exhibited some puzzling features; the interpretation of Bockris *et al.*[2] has been questioned by Laitinen and Osteryoung.[3] The results described in this Communication show that adsorption plays as important a role in molten salts as it does in aqueous solutions.

Solid micro-electrodes can be used for chronopotentiometric studies of metal ions such as Ni^{2+} and Co^{2+} in molten nitrates if the current-reversal modification is introduced.[4] This technique has now been extended to the study of Cd^{2+} ions at platinum and gold micro-electrodes. These were metal wires (~0·5 mm. diameter) sealed in glass to expose 2 mm. lengths. Transition times over the range 100—1500 milliseconds were recorded.

The transition times for the reduction of Cd^{2+} in molten $NaNO_3$–KNO_3 vary with applied current density according to Sand's equation. The addition of Br^- ions caused them to increase when a

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platinum electrode was employed. The transition times approached a limiting value as the Br^- concentration was increased. This depended on both the Cd^{2+} and Br^- concentrations. No increase was noted with gold electrodes. Similar behaviour was observed for Co^{2+} ions, but not for Ni^{2+} ions.

The plots shown in Figure 1 indicate that adsorption is involved. It is not possible, at present, to ascertain whether the reduction of the species diffusing from the bulk of the solution follows the reduction of the adsorbed species (AR, SR model) or whether these processes occur in parallel (SAR model).[5] The first model (AR, SR) requires that:—

$$I\tau = nFA\Gamma + \frac{D\pi(nFAC)^2}{4I}$$

the second (SAR) that:—

$$I\tau = nFA\Gamma + \frac{nFAC\,(\pi D\tau)^{\frac{1}{2}}}{2}$$

[τ is the observed transition time, Γ the adsorbed reactant surface excess (mole cm.$^{-2}$) and I the applied current. The other symbols have their usual meaning.] The appropriate plots give rise to the same intercepts in the present example (see Figure 1). (Because of the short transition times employed in this study, only the species originally adsorbed is expected to contribute to the transition times.[6])

These results also show that it is a halogeno-complex of the metal ion which is the adsorbed species. The adsorption behaviour apparently parallels the formation of complexes at the interface. It will depend on both the degree of adsorption of the anion and the extent of the interaction (that is complex formation) between the anion and the metal ion. Thus adsorption phenomena do not contribute to the electrode process in the case of Ni^{2+} ions because halogeno-complexes of Ni^{2+} are much weaker than those of Cd^{2+} and Co^{2+} (*e.g.*, see Gruen[7]). For these reasons, Cl^- ions are expected to have little effect, as has been observed experimentally. Small additions of iodide ions cause

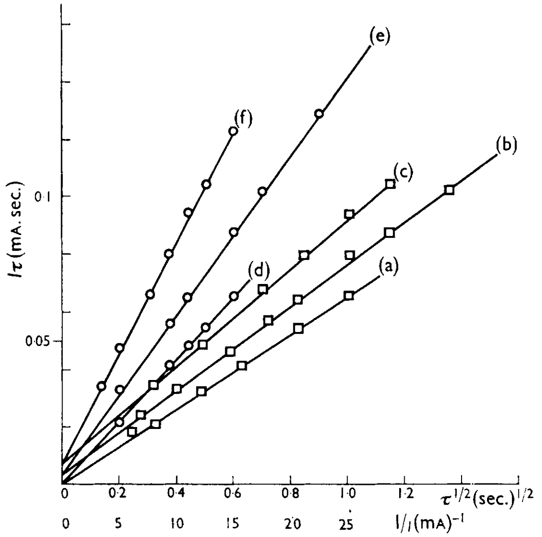

FIGURE 1. *Comparison of chronopotentiometric transition-time data for* $Cd(NO_3)_2$ ($1{\cdot}6 \times 10^{-3}$ *mole kg.*$^{-1}$) *in* $NaNO_3$–KNO_3 at 270°c, *according to the AR, SR, and SAR adsorption models*

(a), (d) $Cd(NO_3)_2$ ($1{\cdot}6 \times 10^{-3}$ *mole kg.*$^{-1}$)

(b), (e) $Cd(NO_3)_2$ ($1{\cdot}6 \times 10^{-3}$ *mole kg.*$^{-1}$) + KBr ($2{\cdot}28 \times 10^{-2}$ *mole kg.*$^{-1}$).

(c), (f) $Cd(NO_3)_2$ ($1{\cdot}6 \times 10^{-3}$ *mole kg.*$^{-1}$) + KBr ($4{\cdot}10 \times 10^{-2}$ *mole kg.*$^{-1}$).

Area of platinum electrode 0·017 *cm.*^{2}
○ *AR, SR model* ☐ *SAR model*

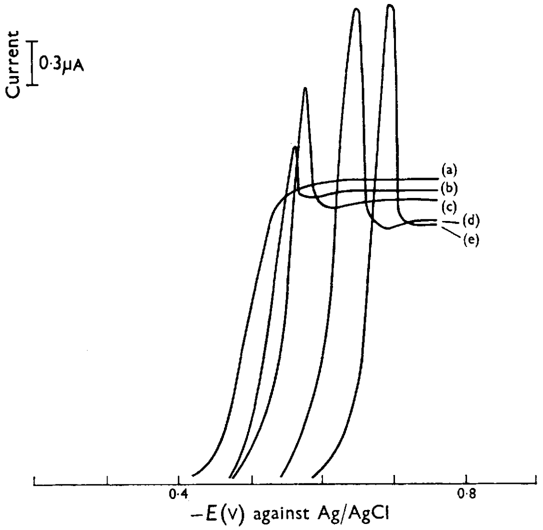

FIGURE 2. *Polarograms for* $Cd(NO_3)_2$ *in* $LiNO_3$–$NaNO_3$–KNO_3 *at* 140°c

(a) $Cd(NO_3)_2$ ($6{\cdot}4 \times 10^{-4}$ *mole kg.*$^{-1}$)

(b) $Cd(NO_3)_2$ ($6{\cdot}4 \times 10^{-4}$ *mole kg.*$^{-1}$) + KBr ($4{\cdot}6 \times 10^{-3}$ *mole kg.*$^{-1}$)

(c) $Cd(NO_3)_2$ ($6{\cdot}4 \times 10^{-4}$ *mole kg.*$^{-1}$) + KBr ($9{\cdot}3 \times 10^{-3}$ *mole kg.*$^{-1}$)

(d) $Cd(NO_3)_2$ ($6{\cdot}4 \times 10^{-4}$ *mole kg.*$^{-1}$) + KBr ($46{\cdot}0 \times 10^{-3}$ *mole kg.*$^{-1}$)

(e) $Cd(NO_3)_2$ ($6{\cdot}4 \times 10^{-4}$ *mole kg.*$^{-1}$) + KBr ($84{\cdot}4 \times 10^{-3}$ *mole kg.*$^{-1}$)

Droptime = 7·4 *sec. Rate of flow of mercury* = 0·838 *mg. sec.*$^{-1}$

large increases in the transition times for Cd^{2+}; these decrease with further I^- additions. Diffusion coefficient changes are probably significant in this case. These observations are in accord with those obtained by Inman and Bockris[2] at a hanging mercury-drop electrode.

The results described above also agree with those of a polarographic study using a dropping-mercury electrode in $LiNO_3$–$NaNO_3$–KNO_3 (Figure 2). The addition of Br^- ions leads to maxima in the polarograms for Cd^{2+} and Co^{2+} but not for Ni^{2+}. The magnitude of the peak current is a function of the concentrations of both the metal ions and halogen ions. No maxima were observed when Cl^- ions were added to the melts. The peak current was found to increase almost linearly with the area of the electrode. The limiting currents following the maxima were diffusion-controlled. For Cd^{2+} and Co^{2+} with added Br^- the maxima were sharp in spite of the difference in the reduction potentials. This observation supports the model suggested on the basis of the chronopotentiometric studies.

The polarographic technique allows the adsorption and diffusion behaviour to be separated. Thus it may prove to be the more useful technique in these studies. The interpretation of Bockris *et al.*[2] should be reviewed in the light of these results, because adsorption may also intervene if these electrode reactions are carried out on mercury in $NaNO_3$–KNO_3.

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