Anodically Generated Mercury(II) Ion as an Indicator for Metal–Ligand Formation Equilibria

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In the presence of solute species which complex with Hg^II ions, the polarographic anodic dissolution wave for mercury is displaced towards more negative potentials relative to the value shown in non-complexing media. Competition for a ligand between anodically generated Hg^II ions and other metal ions added to a solution may be used to calculate formation equilibrium data for mononuclear complexes of the latter species. These principles have been exemplified by investigation of the interaction between the cadmium ion and the analytical masking agents thiourea and thiosulphate ion.

Concentration-dependent anodic currents at a mercury electrode are shown especially by solutions of sulphur-containing ligands and this phenomenon has been used as the basis of analytical methods despite the fact that the signals are sometimes complicated by adsorption effects. At very low concentrations of many such species the observable diffusion-controlled currents are directly proportional to their concentration.[1] For the investigations reported here, however, the ligand concentrations were usually sufficiently high for the current plateaux to be unidentifiable.

Shifts of the position of the dissolution curves with increase in concentration of sulphur-containing solutes have served for the determination of the, usually very high, values of formation constants of mononuclear mercury complexes formed by the sequence in equations (1) and (2). Such equilibrium data have

$$\mathrm{Hg} \rightleftharpoons \mathrm{Hg}^{2+} + 2e \qquad (1)$$

$$\mathrm{Hg}^{2+} + j\mathrm{X} \rightleftharpoons \mathrm{HgX}_j \qquad (2)$$

been reported for the complexes of mercury(II) with thiourea,[2] thiocyanate,[3] and thiosulphate.[4] For each of these systems measurements were based upon shifts of potential observed at a constant low current on the anodic polarogram, since half-wave potentials were not obtainable.

The magnitudes of the shifts of the anodic curves are reduced if another metal ion is added which can also complex with the ligand and so provide a lower value of the latter's concentration to participate in equilibrium (2) at the electrode surface. Schematically the situation shown in Figure 1 is produced; curve I may serve as a calibration line and provide free-ligand concentration values, [X], at equal values of signals from curve II which corresponds to the presence of added metal ion, M. In practice it is necessary that the disturbance of the equilibrium is rapid, that the new position of equilibrium is established within the time of measurement of individual signals, and that only mononuclear complexes are formed.

At each value of total ligand concentration the corresponding potential on curve II derives from *two* sources: (*i*) the *free*-ligand concentration involving equilibrium (2) and (*ii*) the equilibrium involving Hg^{2+} and complexes of the added metal ion which may be expressed by equation (3), where $\bar{n}_{\mathrm{M}}$ and $\bar{n}_{\mathrm{Hg}}$

$$\left(\frac{\bar{n}_{\mathrm{M}}}{\bar{n}_{\mathrm{Hg}}}\right)\mathrm{Hg}^{2+} + \mathrm{MX}_{\bar{n}_{\mathrm{M}}} \rightleftharpoons \left(\frac{\bar{n}_{\mathrm{M}}}{\bar{n}_{\mathrm{Hg}}}\right)\mathrm{HgX}_{\bar{n}_{\mathrm{Hg}}} + \mathrm{M} \qquad (3)$$

are the *average* ligand numbers of the M–X and Hg–X systems respectively. The ligand number $\bar{n}_{\mathrm{M}}$ may then be expressed in the form in equation (4), where C_{X} and [X] are the total- and

$$\bar{n}_{\mathrm{M}} = \frac{C_{\mathrm{X}} - [\mathrm{X}] + C_{\mathrm{M}}(\bar{n}_{\mathrm{M}}/\bar{n}_{\mathrm{Hg}})}{C_{\mathrm{M}}} \qquad (4)$$

free-ligand concentrations respectively and C_{M} is the analytical concentration of M.

Superficially, equation (4) is of the same form as that of Ringbom and Eriksson,[5] equation (5). Here the term $C_{\mathrm{N}}\bar{n}'$,

$$\bar{n}_{\mathrm{M}} = \frac{C_{\mathrm{X}} - [\mathrm{X}] - (C_{\mathrm{N}}\bar{n}')}{C_{\mathrm{M}}} \approx \frac{C_{\mathrm{X}} - [\mathrm{X}]}{C_{\mathrm{M}}} \qquad (5)$$

referring to the chosen *solute* indicator system and representing the amount of X *not* available for interaction with M, is usually negligible compared with the quantity (C_{X} − [X]). In equation (4), however, the last term in the numerator represents the amount of X originally associated with M but abstracted from it during the operation of reaction (3). The magnitude of this quantity is *never* without significance relative to (C_{X} − [X]).

In terms of the quantity directly determinable from graphs of the form of Figure 1, equation (4) is best rearranged to give equation (6). If the formation constants of the $\mathrm{Hg^{II}}$ complexes

$$\frac{C_{\mathrm{X}} - [\mathrm{X}]}{C_{\mathrm{M}}} = \bar{n}_{\mathrm{M}}\left(1 - \frac{1}{\bar{n}_{\mathrm{Hg}}}\right) \qquad (6)$$

are several orders of magnitude higher than those of M, experimentally used ranges of ligand concentration are likely to correspond to $\bar{n}_{\mathrm{Hg}}$ realising its maximum value at each point of the range chosen. Thus equation (7) applies, so that, if $(n_{\mathrm{Hg}})_{\mathrm{max.}}$ is

$$\frac{C_{\mathrm{X}} - [\mathrm{X}]}{C_{\mathrm{M}}} = \bar{n}_{\mathrm{M}}\left[1 - \frac{1}{(n_{\mathrm{Hg}})_{\mathrm{max.}}}\right] \qquad (7)$$

3 or 4 the expressions for $\bar{n}_{\mathrm{M}}$ are given by equations (8a) and (8b) respectively.

$$\bar{n}_{\mathrm{M}} = \frac{C_{\mathrm{X}} - [\mathrm{X}]}{0.667\, C_{\mathrm{M}}} \qquad (8a)$$

$$\bar{n}_{\mathrm{M}} = \frac{C_{\mathrm{X}} - [\mathrm{X}]}{0.75\, C_{\mathrm{M}}} \qquad (8b)$$

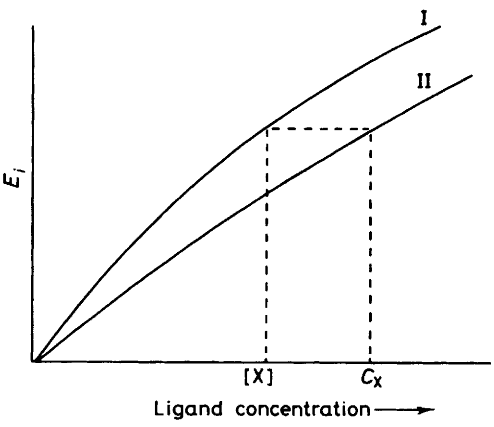

Figure 1. Schematic plot of potential, E_i, for fixed current *vs.* ligand concentration in the absence (I) and presence (II) of added metal ion, M

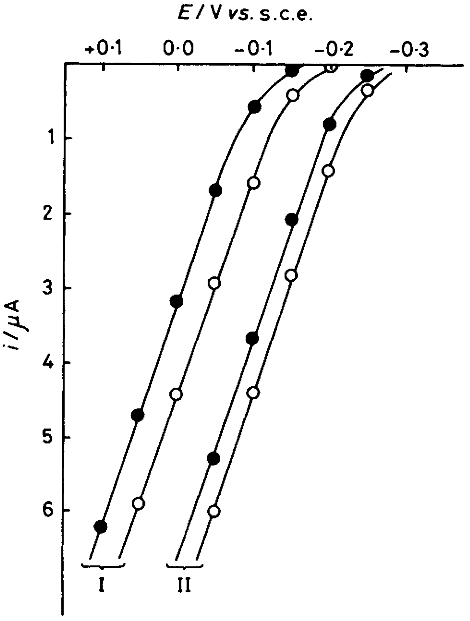

Figure 2. Mercury dissolution curves for 0.1 mol dm^{-3} thiourea (I) and 0.6 mol dm^{-3} thiourea (II) in the absence (○) and presence (●) of 0.1 mol dm^{-3} Cd^{2+}

Experimental

All chemicals were of analytical grade and all solutions were prepared in deionised water. For polarograms obtained manually a freely dropping mercury electrode of drop time 2.3 s was used together with a large low-resistance saturated calomel electrode (s.c.e.) as reference. Potentials were applied *via* a Pye potentiometer and currents measured using a calibrated Scalamp microammeter. A Princeton Applied Research model 174A polarograph operating in a three-electrode mode and with a controlled drop time of 1 s was employed for measurements of variation of diffusion current with ligand concentration at fixed potential.

Separate solutions containing varying amounts of thiourea or thiosulphate in the presence and absence of 0.1 mol dm^{-3} Cd^{2+} were prepared in volumetric flasks (100 cm^3) for the measurement of current and potential data as a function of ligand concentration. For measurement of the variation of diffusion currents of the cadmium–thiosulphate system, individual working concentrations were prepared *in situ* using the dilution technique described elsewhere.[6] A temperature of 298 ± 0.2 K was maintained throughout all measurements. Deoxygenation of working solutions was effected with 'white spot' nitrogen previously saturated with solvent by passage through a solution of the same composition as that to be analysed.

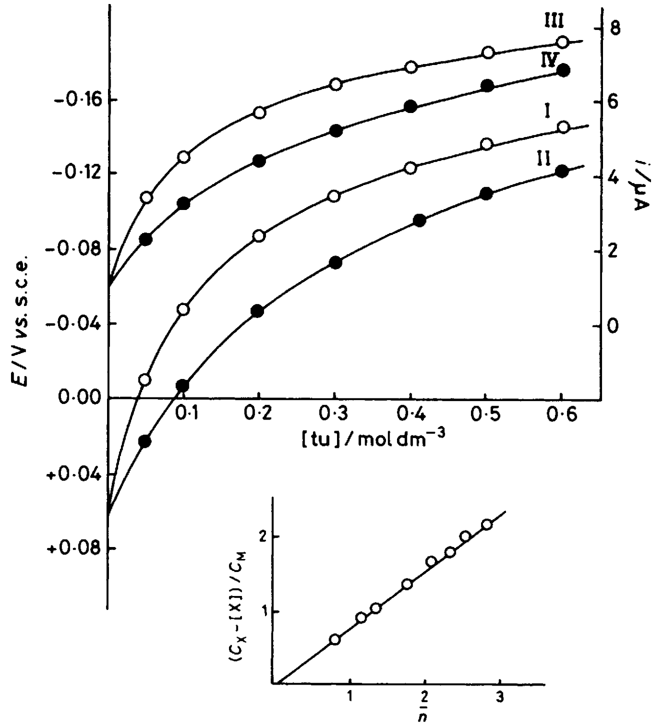

Figure 3. Variation in potential of anodic dissolution signal with thiourea concentration, at a current of 3 μA, for mercury in the absence (I) and presence (II) of 0.1 mol dm^{-3} Cd^{2+}. Corresponding variations in current (μA) at a constant potential of 0.0 V *vs.* s.c.e. in the absence (III) and presence (IV) of 0.1 mol dm^{-3} Cd^{2+}. Inset graph shows a plot of *observed* values of the function $(C_X - [X])C_M$ *vs.* theoretical $\bar{n}$ calculated from independent determinations of formation constants

Results and Discussion

(*i*) *The Cadmium–Thiourea System.*—The mercury dissolution curves produced for solutions containing 0.1 and 0.6 mol dm^{-3} thiourea in the absence and presence of 0.1 mol dm^{-3} Cd^{2+} are shown in Figure 2. After initial curvature from the baseline these are clearly parallel and uncomplicated by adsorption phenomena. Figure 3 shows the observed variations in potential *vs.* s.c.e., at a constant current of 3 μA, as well as variations in current at a constant potential of 0.0 V *vs.* s.c.e., for analytical concentrations of thiourea in the range 0.0—0.6 mol dm^{-3} in the absence (I, III) and presence (II, IV) of 0.1 mol dm^{-3} Cd^{2+}.

Formation constants of the mercury–thiourea system are very high, the extrapolated shift in potential, with respect to + 0.488 V *vs.* s.c.e.[2] for Hg^{2+}, in 1.0 mol dm^{-3} thiourea being 0.790 V. According to the Lingane equation[7] this is approximately equal to $(0.0591/2)\log_{10}\beta_j$, where β_j represents the overall formation constant at 298 K with a value of 5.4×10^{26}. In a detailed analysis of potential variations, Nyman and Parry[2] obtained a value of 6.3×10^{26} for β_4. Thus at all concentrations

Table. Estimates of mean ligand number, $\bar{n}$, for the system cadmium–thiourea at various values of free thiourea concentration

	Experimental $\bar{n}$			Theoretical $\bar{n}$		
[thiourea]/mol dm^{-3}	*a*	*b*	*c*	*d*	*e*	*f*
0.05	0.80 ± 0.07	0.80 ± 0.05	0.82 ± 0.05	0.81	0.81	0.66
0.10	1.33 ± 0.07	1.40 ± 0.05	1.39 ± 0.05	1.36	1.39	1.16
0.20	2.07 ± 0.10	2.21 ± 0.07	2.07 ± 0.07	2.08	2.22	2.36
0.30	2.53 ± 0.10	2.67 ± 0.10	2.51 ± 0.10	2.54	2.73	3.17
0.40	2.86 ± 0.15	2.86 ± 0.10	2.85 ± 0.10	2.84	3.06	3.53

[a] From application of equation (8b) using varying potentials at a constant current of 3 μA. Measurements made *via* recorded polarograms derived from the PAR polarograph. [b] Estimates made as in *a* but using manual measurements. [c] From application of equation (8b) using varying currents at a constant applied potential of 0.0 V *vs.* s.c.e. [d] Estimated from formation constants, derived from diffusion coefficients reported in ref. 8. [e] Estimated from the data in ref. 9. [f] Estimated from formation constants reported in ref. 10.

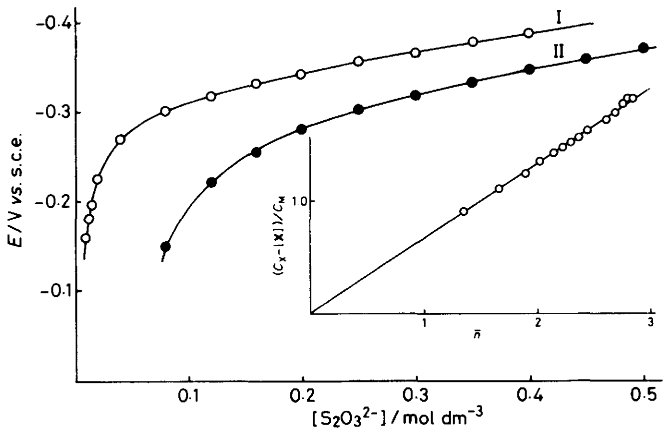

Figure 4. Variation in potential of anodic dissolution signal with thiosulphate concentration, at a constant current of 30 μA, in the absence (I) and presence (II) of 0.1 mol dm^{-3} Cd^{2+}. Inset graph shows a plot of *observed* values of $(C_X - [X])/C_M$ *vs.* corresponding values of $\bar{n}$ estimated from the formation constant data in ref. 11

of thiourea (tu) used here, $\bar{n}_{Hg}$ for the indicator system is virtually 4 and equilibrium (3) will involve $[Hg(tu)_4]^{2+}$ to the effective exclusion of all lower complexes and $\bar{n}_{Cd}$ will be given by equation (8b). Confirmation of this is provided by the inset graph in Figure 3 of the function $(C_X - [X])/C_M$ plotted *vs.* $\bar{n}$ values calculated from previously reported formation constant data.[8] The observed slope is 0.74.

Due to the proximity of the various curves it is possible for this system to employ an almost equally reliable alternative estimate of ligand concentrations based upon currents measured at fixed potentials (Figure 3, curves III and IV). Values of mean ligand number, estimated for a selection of values of free-ligand concentration are collected in the Table and compared with data calculated from previously reported values of formation constants (three sources).[8–10] Integration of the full formation curve provided by curves I and II in Figure 3 over the thiourea concentration range 0.0—0.6 mol dm^{-3} yielded the following log β_j data (those previously obtained from measurements of diffusion coefficients[8] are included for comparison): log β_1 = 1.34 ± 0.1, log β_2 = 2.48 ± 0.2, log β_3 = 2.85 ± 0.2, log β_4 = 3.11 ± 0.3 (present work); log β_1 = 1.30 ± 0.1, log β_2 = 2.20 ± 0.2, log β_3 = 2.66 ± 0.2, log β_4 = 3.07 ± 0.3 (from diffusion coefficients). The close agreement of these two sets of data contrasts with those reported by Lane *et al.*[10] and which were used to estimate one set of $\bar{n}$ data listed in the Table.

(*ii*) *The Cadmium–Thiosulphate System.*—Although some variation of ionic strength occurred for this case, so that a strict comparison with published data referred to constant ionic strength is less precise than for the system involving thiourea, the results obtained are within the limits to be expected.

Shifts of potential of the anodic signals were in this case very much larger than for thiourea. Clearly it was necessary for this system to make use of the variation of potential at constant current rather than the variation of current at fixed potential. The latter procedure, at whatever potential based, would only cover a fraction of the ligand concentration range required for a similar section of wave profile. This is reflected in varying $\bar{n}$ data obtained from current *vs.* concentration curves derived from measurements at various fixed applied potentials. Variation of potential at a constant current of 30 μA in the absence and presence of 0.1 mol dm^{-3} Cd^{2+} is shown in Figure 4 where the slope of the inset graph of 0.667 confirms the predominant formation of a mercury(II) species with maximum co-ordination number of 3 as reported by Nyman and Salazar.[4] Independent confirmation of the predominance of the three-co-ordinate species in the thiosulphate concentration range used, without resort to $\bar{n}$ data derived from published formation constants, is provided by the observation of a near-linear relationship between log $[i/(i_d - i)^3]$ and *E*, at least for lower values of *E*. A tendency to curvature at higher potentials may reflect the small influence of a fourth complex. For concentrations of thiosulphate $<10^{-3}$ mol dm^{-3} it has been shown that the two-co-ordinate species predominates as evidenced by the linear plot involving the function log $[i/(i_d - i)^2]$ reported by Kolthoff and Miller.[1] For the concentration range used *here*, distinct curves were obtained when plotting the latter function.

Shifts of potential shown by the anodic signal, at a constant current of 1 μA, measured with respect to a reference potential of +0.488 V for the Hg^0/Hg^{II} oxidation yielded formation constant data for the indicator system close to those reported previously, *viz.* log β_1 = 0, log β_2 = 28.90, log β_3 = 31.48, while Nyman and Salazar[4] reported (at zero ionic strength) log β_1 = 0, log β_2 = 29.27, log β_3 = 30.80.

Integration of the experimental formation curve derived from curves I and II in Figure 4 yielded the following values for the cadmium complexes: log β_1 = 3.10 ± 0.15, log β_2 = 4.78 ± 0.20, log β_3 = 5.93 ± 0.25. These compare favourably with those reported in 0.65 mol dm^{-3} KNO$_3$ by Pryszczewska[11] (3.20, 4.90, and 6.05 respectively).

Most of the reports of studies on the cadmium–thiosulphate system contain data for three complex species only; at least one early reference[12] as well as a more recent one[13] indicate the formation of the highly negatively charged four-co-ordinate species. Although this is not shown in terms of the anodic signals used here, there is some further evidence for the additional species from diffusion current measurements.

It may be shown that the change in diffusion current, Δi_d, of a metal aqua ion as it is progressively complexed by a species other than water may be expressed[14] by equation (9), where k

$$\bar{n} = k\,\Delta i_d \qquad (9)$$

is a constant characteristic of a given metal–ligand system. A graph of Δi_d *vs.* log [X], which has been designated the 'pseudo-formation curve,' may be integrated[15] to provide $F_0'[\mathrm{X}]$ data for each value of free-ligand concentration through the expression (10) ($F_0'[\mathrm{X}] = F_0[\mathrm{X}]/k$, where $F_0[\mathrm{X}] = 1 + \beta_1[\mathrm{X}] + \ldots + \beta_j[\mathrm{X}]^j$).

$$\frac{\mathrm{d}\log F_0[\mathrm{X}]}{k\,\mathrm{d}\log[\mathrm{X}]} = \Delta i_d = \frac{\mathrm{d}\log F_0'[\mathrm{X}]}{\mathrm{d}\log[\mathrm{X}]} = \frac{\bar{n}}{k} \qquad (10)$$

The pseudo-formation curve was integrated over the thiosulphate concentration range 0.0—0.14 mol dm^{-3}, the Δi_d data being observed for 10^{-3} mol dm^{-3} Cd^{2+} in the presence of 0.1 mol dm^{-3} $\mathrm{KNO_3}$ for very small increments of ligand concentration. $F_0'[\mathrm{X}]$ data obtained by the latter method should correlate simply with the $F_0[\mathrm{X}]$ data obtained by anodic signals described above. When the two sets of independently determined data were plotted, the clear linearity of the graph confirmed the essential validity of equation (10) and indicated a value for k of *ca.* 0.45. The fact that the line for this graph did not pass quite through the origin as expected is to be regarded as error introduced in assessment of the residual integral when estimating $F_0'[\mathrm{X}]$ values rather than indicating the presence of an additional term in equation (10). The above value of k accords with an estimate made from a plot of log $F_0'[\mathrm{X}]$ *vs.* log [X] whose limiting slope at log [X] = −0.8 yields $k = 0.472$, if it is assumed that a full co-ordination number of three is developed in the limiting linear region. There are a number of precedents for estimating k in this way, enabling $F_0[\mathrm{X}]$ data to be calculated from $F_0'[\mathrm{X}]$ data and so producing a set of formation constants. If no reasonable assumption regarding the maximum value of n may be made, more tedious methods are required to obtain the constants.[15]

For the $F_0[\mathrm{X}]$ data obtained by using $k = 0.472$, subsequent graphical analysis according to the Leden[16] method yields three constants agreeing quite closely with those obtained by other methods. However, the analysis strongly implies the presence of a less stable fourth complex whose formation constant is of the same order as values reported earlier,[12,13] *viz.*: $\log \beta_1 = 2.84 \pm 0.15$, $\log \beta_2 = 4.64 \pm 0.20$, $\log \beta_3 = 6.39 \pm 0.25$, $\log \beta_4 = 7.00 \pm 0.30$.

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