# Structure and Stability of Carboxylate Complexes. Part 16.[1] Stability Constants of some Mercury(II) Carboxylates

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Complex formation between mercury(II) ions and a series of unsubstituted and substituted monocarboxylates (including some potentially bidentate ligands) has been studied by precise potentiometric titration at 25.00 °C in a 3 mol dm$^{-3}$ sodium perchlorate medium. A linear-free-energy plot indicates that unidentate complexes are formed in all of the systems studied, and that Hg$^{II}$ does not form five-, six-, or seven-membered chelate rings with appropriately *O*-substituted carboxylates.

DESPITE the environmental importance[2] of mercury, there is little information available on the complexes of mercury(II) ions with oxygen-donor ligands. Following extensive work in Oxford on the stability constants of copper(II) complexes of substituted alkanoates,[3] we have investigated the complexation of Hg$^{II}$ by several of these ligands.

A fundamental difficulty in this work arises from the competitive formation of hydroxomercury(II) species and of the conjugate acids of the ligands. Even at a hydrogen-ion concentration as high as $h = 10^{-2}$ mol dm$^{-3}$, *ca.* 4% of the free mercury(II) ion in solution is complexed by hydroxide, and yet at this hydrogen-ion concentration the ligands are at least 99% in the form of their conjugate acids. Measurements of high precision are therefore necessary in order to study the mercury alkanoates, and such precision has been made possible by improvements[4] in our potentiometric apparatus. Junction potentials also become increasingly important as the acidity of the solution is raised, and the 3 mol dm$^{-3}$ sodium perchlorate medium was chosen for this work so as to minimise the consequent corrections.

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[1] Part 15, *Acta Cryst.*, 1975, **B31**, 2047.

[2] 'Mercury in the Environment,' Chemical Rubber Company, Cleveland, Ohio, 1972.

[3] F. J. C. Rossotti and co-workers, unpublished work.

[4] R. P. Henry, J. E. Prue, F. J. C. Rossotti, and R. J. Whewell, *Chem. Comm.*, 1971, 868.

EXPERIMENTAL

*Reagents.*—Acetic acid (B.D.H. AnalaR), propanoic acid (B.D.H.), and methoxyacetic acid (Kodak) were purified by vacuum distillation, formic acid (B.D.H. AnalaR) by freezing, and hydroxyacetic acid (Koch-Light), cyanoacetic acid (Eastman), and chloroacetic acid (B.D.H. AnalaR) by recrystallisation from 50 vol.% AnalaR benzene–AnalaR acetone. 3-Methoxypropanoic acid was prepared by slow alkaline hydrolysis of the acid nitrile (Koch-Light) and purified by vacuum distillation. Sodium 3-hydroxybutanoate (B.D.H.) and sodium 4-hydroxybutanoate (prepared from the lactone) were purified by the method of Childers and Struthers.[5] Sodium perchlorate and hydroxide were prepared from B.D.H. AnalaR reagents as described elsewhere.[6] Mercury(II) perchlorate was prepared by repeated precipitation of mercury(II) oxide from AnalaR mercury(II) nitrate, and dissolution of the oxide in an excess of perchloric acid. The stock solution was analysed by precipitation of mercury(II) sulphide.[7]

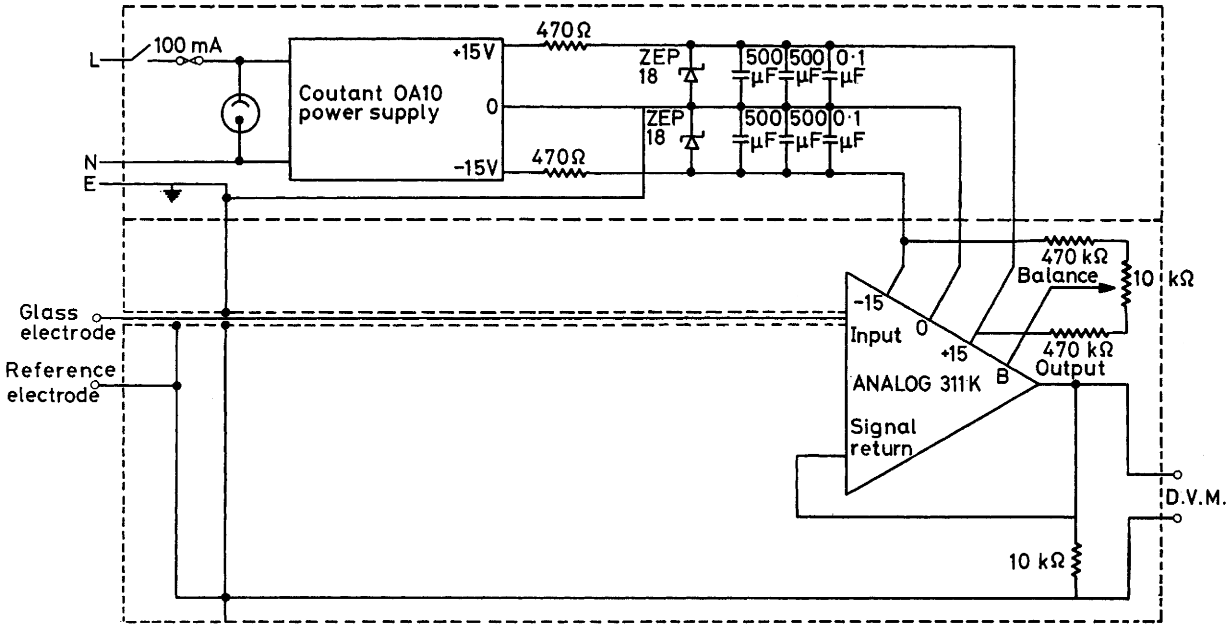

FIGURE 1 Circuit diagram of impedance converter unit; L = live, N = neutral, E = earth, D.V.M. = digital voltmeter

Working solutions contained (3 — 2$B$) mol dm$^{-3}$ sodium ion [where $B$ is the concentration of mercury(II) ions], and were made up in grade A volumetric flasks from weighed portions of stock solutions where possible.

*Apparatus.*—Titrations were performed in a room thermostatted at 24.5 ± 1 °C, using a water-bath to maintain a temperature of 25.00 ± 0.02 °C in the Metrohm titration vessel. Solutions were transferred to the vessel with a set of calibrated grade A pipettes and a Metrohm Multi-Dosimat piston burette. The titration solution was stirred with a stream of purified and presaturated nitrogen. The potential of cell (I) (which included a Wilhelm salt bridge [8]) was measured to ±0.01 mV as described previously [4] with a Solartron LM1867C digital voltmeter and an impedance converter. The impedance converter circuit was designed around a varactor bridge operational amplifier of high stability, and is shown in Figure 1.

| | | | | | |
|---|---|---|---|---|---|
| glass electrode (Activion 17SR) | titration solution | Na[ClO$_4$] 3 mol dm$^{-3}$ | Ag[ClO$_4$]0.01 mol dm$^{-3}$<br>Na[ClO$_4$]2.99 mol dm$^{-3}$ | Ag | (I) |

*Titration Procedure.*—*Calibration.* A value of $E_0$ for the cell (I) was obtained as the first part of every titration, from the titration of an aliquot portion of HClO$_4$ (3 × 10$^{-2}$ mol dm$^{-3}$) with sodium hydroxide (*ca.* 6 × 10$^{-2}$ mol dm$^{-3}$). Ten readings were treated by Gran's method [9,10] as described below.

*Ligand protonation.* The calibration titration was discontinued at a hydrogen-ion concentration $h \approx 10^{-3}$ mol dm$^{-3}$, and an aliquot portion of the weak acid was added. Titration with Na[OH] then gave *ca.* 15 readings from which the protonation constant was calculated, and a set of readings close to equivalence from which a suitable Gran plot gave the concentration of the weak acid. Sodium salts of weak acids were titrated with HClO$_4$, and their concentrations were deduced from the limiting concentration of bound protons. At least two protonation-constant determinations were carried out for each system, with weak-acid concentrations between 1.5 × 10$^{-2}$ and 6.0 × 10$^{-2}$ mol dm$^{-3}$.

*Mercury*(II) *complex formation.* The starting solution for the calibration titration contained a known concentration of

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[5] E. Childers and G. W. Struthers, *Analyt. Chem.*, 1955, **27**, 737.

[6] F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 1955, **9**, 1177.

[7] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961.

[8] W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, 1952, **6**, 901.

[9] G. Gran, *Analyst*, 1952, **77**, 661.

[10] F. J. C. Rossotti and H. S. Rossotti, *J. Chem. Educ.*, 1965, **42**, 375.

$Hg^{II}$, and the acid–base titration was discontinued at $h \approx 10^{-2}$ mol dm$^{-3}$. Titration with a solution of the conjugate acid of the ligand then followed, the measured free hydrogen-ion concentrations remaining in the range $10^{-1.5} \geqslant h \geqslant 10^{-2}$ mol dm$^{-3}$. Four titrations were generally carried out for each system, with variation of the metal ion ($3 \times 10^{-3}$–$1 \times 10^{-2}$ mol dm$^{-3}$) and titrant (up to 0.25 mol dm$^{-3}$) concentrations in the titration vessel. Stability constants for hydroxomercury(II) complexes were determined from slow titrations of mercury(II) perchlorate ($4 \times 10^{-3}$—$2 \times 10^{-2}$ mol dm$^{-3}$) in $HClO_4$ with Na[OH] to a free hydrogen-ion concentration of $10^{-3.5}$ mol dm$^{-3}$. The first part of the data was used for electrode calibration.

$$E = E^{\ominus} + E_j - \frac{RT}{F}\ln\gamma - \frac{RT}{F}\ln h \qquad (1)$$

$$= E_0 + E_j^* - \frac{RT}{F}\ln h$$

*Junction potentials.* Separate experiments with known concentrations of $HClO_4$ showed that the hydrogen-ion concentration-dependent term $E_j^*$ in the Nernst equation (1) is described by (2) where $0.1 \geqslant h$/mol dm$^{-3} \geqslant 0.01$ and $[Na^+] = 3$ mol dm$^{-3}$.

*Redox titrations.* Some confirmatory experiments were carried out on the mercury(II) acetate system, in which free mercury(II)-ion concentrations were measured in the presence of mercury(I) ions with a platinum flag electrode. Independent measurements of the stability of mercury(I) acetate are described elsewhere [11] together with the methods of preparation and analysis of mercury(I) perchlorate solutions.

$$E_j^*/\text{mV} = 6.7h/\text{mol dm}^{-3} \qquad (2)$$

The starting solution for the calibration titration contained both mercury(I) perchlorate ($2 \times 10^{-3}$—$3 \times 10^{-3}$ mol dm$^{-3}$) and mercury(II) perchlorate ($1.5 \times 10^{-2}$—$2.0 \times 10^{-2}$ mol dm$^{-3}$). The acid-base titration was discontinued at $h \approx 10^{-2}$ mol dm$^{-3}$, and values of $E_0$ for cell (I) and of the standard potential of the redox cell (II) were obtained. Titrations with acetic acid or sodium acetate then followed, additions of the latter being made rather slowly.

$$\text{Pt}\left|\begin{array}{c}\text{titration}\\ \text{solution}\end{array}\right|\begin{array}{c}\text{Na[ClO}_4]\\ 3\text{ mol dm}^{-3}\end{array}\left|\begin{array}{l}\text{Ag[ClO}_4]0.01\text{ mol dm}^{-3}\\ \text{Na[ClO}_4]2.99\text{ mol dm}^{-3}\end{array}\right|\text{Ag} \qquad \text{(II)}$$

CALCULATIONS

*Electrode Calibration.*—The Gran equation appropriate to a strong acid–strong base titration at 25.00 °C is (3) where $V_T$ is the total volume in the titration vessel, $V_B$ is the titre of base, $V_B = V_E$ at equivalence, $c_B$ is the concentration of base, and $\alpha$ an arbitrary number. A graph of the Gran function [left-hand side of equation (3)] against $V_B$ is a straight line; the program GRAN determines the 'best' line using procedure LINEFITTING [12] and calculates a value of $E_0$ from the gradient. Values of $\chi^2$ approximately equal to the number of degrees of freedom are obtained when the estimates of experimental error are $\sigma(E) = 0.01$ mV in the measured potential and $\sigma(V_B) = 0.001$ cm$^3$ in the volume of titrant. The hydrogen-ion concentration-dependent term $E_j^*$ in equation (3) necessitates an iterative calculation of the Gran function; a similar small term is also determined iteratively when mercury(II) ions are present in the solution, to allow for the formation of hydroxomercury(II) complexes.

$$V_T 10^{[\alpha-(E-E_j^*)]/59.157} = c_B(V_E - V_B)\,10^{(\alpha-E_0)/59.157} \qquad (3)$$

*Protonation Constants.*—Values of the protonation constants $K_1^H = [HA]h^{-1}a^{-1}$ were obtained from the data ($h$, $H$, $A$) by standard graphical and numerical methods.[13]

*Mercury*(II) *Complex Stability Constants.*—The constants quoted were calculated using the program MERCURY, although they were invariably checked graphically. The program consists of a series of interchangeable blocks to calculate the formation function $\bar{n}$ and the free-ligand concentration ($a$) for each experimental point, followed by common blocks for the calculation of the two stability constants $\beta_1$ and $\beta_2$ from the gradient and intercept of linear plots.

$$\bar{n} = (\sum^{N} n[BA_n])\,(b + \sum^{N}[BA_n])^{-1} \qquad (4)$$

$$\beta_n = [BA_n]b^{-1}a^{-n} \qquad (5)$$

*Calculation of $\bar{n}$.*—The details of the calculation of $\bar{n}$ as defined in equation (4) are dependent on the nature of the additional complex species considered. For a model involving only the complex species HA and $BA_n$, the mass-balance equations give (6) and (7) where $A$,$B$, and $H$ are the total ligand, mercury, and analysable proton concentrations respectively, and $a$, $b$, and $h$ are the free-ligand, mercury-ion, and proton concentrations. Data so calculated result in formation curves $\bar{n}$ (log $a$) which tend towards a maximum value of two, and yet are consistently asymmetric, and so cannot be interpreted by the stability constants $\beta_n$ [equation (5)].

$$a = (H - h)\,(hK_1^H)^{-1} \qquad (6)$$

$$\bar{n} = [(A - a) - (H - h)]B^{-1} \qquad (7)$$

It is therefore necessary to incorporate into the model other species present in the solution. Studies in Oxford [14,15] have shown that dimeric species of the conjugate acid of the ligand may exist in small concentrations at the high concentration levels used in these titrations. The published values of the stability constants $\beta_{22}^H = [H_2A_2]h^{-2}a^{-2}$ and $\beta_{12}^H = [HA_2]h^{-1}a^{-2}$ were used in the present work, although the species $HA_2$ is virtually absent. Since calculated concentrations of $H_2A_2$ never exceed 3% of the HA concentration in this work, there is negligible difference between this treatment and that of Farrer [16] who assigned

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[11] F. J. C. Rossotti and R. J. Whewell, following paper.

[12] G. L. Cumming, J. S. Rollett, F. J. C. Rossotti, and R. J. Whewell, *J.C.S. Dalton*, 1972, 2652.

[13] F. J. C. Rossotti and H. S. Rossotti, 'The Determination of Stability Constants,' McGraw-Hill, New York, 1961.

[14] D. L. Martin and F. J. C. Rossotti, *Proc. Chem. Soc.*, **1959**, 60.

[15] J. D. E. Carson and F. J. C. Rossotti in 'Advances in the Chemistry of the Coordination Compounds,' ed. S. Kirshner, Macmillan, New York, 1961, p. 180.

[16] H. N. Farrer and F. J. C. Rossotti, *Acta Chem. Scand.*, **1963**, **17**, 1824.

part of the apparent formation of dimeric species to activity-coefficient variation.

The formation of hydroxomercury(II) complexes was studied as a part of this work, and values of the constants $\beta_1^* = [B(OH)]hb^{-1}$ and $\beta_2^* = [B(OH)_2]h^2b^{-1}$ were obtained *via* $\bar{n}$ and $h$ by standard methods.[13] Such species undoubtedly exist in small concentrations under the conditions of the metal–ligand titrations.

There is therefore an added complication to the calculation

$$0 = (h - H) + ahK_1^{\mathrm{H}} + a^2h(\beta_{12}^{\mathrm{H}} + 2h\beta_{22}^{\mathrm{H}}) - Q \qquad (8)$$

of $\bar{n}$ and $a$. From the proton mass balance, we obtained (8) and (9). With $\beta_{12}^{\mathrm{H}} = \beta_{22}^{\mathrm{H}} = Q = 0$, equation (8) reduces

$$Q = b(\beta_1^*h^{-1} + 2\beta_2^*h^{-2}) \qquad (9)$$

to (6). With $Q = 0$ equation (8) is readily solved for $a$, preferably by Newton's method; since $Q$ is small by comparison with the first two terms of the equation, an iterative solution is appropriate in which values of $b$ are updated

$$b = B[(1 + \beta_1^*h^{-1} + \beta_2h^{-2}) + \sum_{n=1}^{N} a^n\beta_n]^{-1} \qquad (10)$$

on each cycle. Equation (7) can similarly be modified to give (11) and (12). Values of $\bar{n}$ were calculated in the same

$$n = [(A - a) - (H - h) - a^2h\beta_{12}^{\mathrm{H}} - Q](B - R)^{-1} \qquad (11)$$

iterative process as $a$; satisfactory values of both $\bar{n}$ and $a$ were obtained on the second iteration.

Formation curves calculated from our data using equations (8)—(12) and independently determined values of

$$R = b(\beta_1^*h^{-1} + \beta_2^*h^{-2}) \qquad (12)$$

$\beta_1^*$, $\beta_2^*$, $\beta_{12}^{\mathrm{H}}$, and $\beta_{22}^{\mathrm{H}}$ are readily fitted to a series of stability constants $\beta_n$ [equation (5)]. Comparison of these formation curves with the erroneous curves from equations (6) and (7) demonstrates the effect of hydroxomercury(II) species in the early part of the titrations (low $\bar{n}$ values) where $b$ is large, and of the dimeric species $H_2A_2$ in the later part (high $\bar{n}$ values) when $A$ is large.

*Higher Species.*—Two constants $\beta_n$ were generally sufficient to explain the formation curves obtained, but in two systems there is apparent evidence for the formation of a third complex $BA_3$. The calculation of the constants for these systems was carried out from $\bar{n}$, $a$ data generated as described above using HYPERPLANE,[17] a development of LINEFITTING to fit a hyperplane to co-ordinates in several dimensions.

The data $B/b = 1/\alpha_0$ and $a$ from the redox titrations were examined for evidence of $BA_3$ and BA(OH) species using HYPERPLANE, but the existence of neither was demonstrated. The calculation of $B/b$ and $a$ from the experimental readings included the species considered in the derivation of equations (8)—(12), and the change in the mercury(I)-ion concentration due to acetate formation was also corrected for. The strategy of the calculation (program BAOH) involved an iterative determination of $a$ within each cycle of the iterative determination of $\beta_n$.

## DISCUSSION

The measured stability constants are given in Table 1. The values of the protonation constants (log $K_1^{\mathrm{H}}$) agree in most cases with previous determinations [14,15] to better than 0.01 log units; the errors quoted are standard deviations. The errors for the mercury(II) constants are estimated from the range of values obtained from several titrations. The standard deviations of the constants from individual experiments (calculated by MERCURY) were uniformly below 0.01 log units and typically 0.005 log units.

TABLE 1

Stability constants of mercury(II) complexes at 25.00 °C in a 3 mol dm$^{-3}$ sodium perchlorate medium

| | Ligand | log$K_1^{\mathrm{H}}$ | log $\beta_1$ | log $\beta_2$ | log $\frac{K_1}{K_2}$ |
|---|---|---|---|---|---|
| (1) | Formate | 3.907 ± 0.002 | 3.66 ± 0.01 | 7.10 ± 0.01 | 0.22 |
| (2) | Acetate | 5.011 ± 0.002 | 4.22 ± 0.01 | 8.45 ± 0.03 | −0.01 |
| | | | 4.15 ± 0.01 [a] | 8.44 ± 0.02 [a] | −0.14 |
| (3) | Propanoate | 5.161 ± 0.002 | 4.33 ± 0.01 | 8.80 ± 0.03 | −0.14 |
| (4) | Chloroacetate | 3.028 ± 0.003 | 2.95 ± 0.02 | 5.61 ± 0.02 | 0.29 |
| (5) | Cyanoacetate | 2.654 ± 0.001 | precipitated | | |
| (6) | Hydroxyacetate | 3.923 ± 0.002 | 3.60 ± 0.01 | 7.05 ± 0.01 | 0.15 |
| (7) | 3-Hydroxybutanoate | 4.757 ± 0.004 | $4.25_5$ ± 0.01 | 8.36 ± 0.01 | 0.15 |
| (8) | 4-Hydroxybutanoate | 4.985 ± 0.005 | 4.34 ± 0.01 | 8.45 ± 0.01 | 0.23 |
| (9) | Methoxyacetate | 3.743 ± 0.002 | 3.54 ± 0.02 | 6.91 ± 0.03 | 0.17 |
| (10) | 3-Methoxypropanoate. | 4.707 ± 0.003 | 4.24 ± 0.02 | 8.45 ± 0.03 | 0.03 |
| | | | log $\beta_1^*$ | log $\beta_2^*$ | |
| | Hydroxide | 14.22 [b] | −3.44 ± 0.02 | −6.24 ± 0.03 | −0.64 |

[a] From redox titrations. [b] From ref. 18.

*The Precision of the Mercury*(II) *Complex Studies.*—The constancy of $E_0$ values for cell (I) throughout the calibration titrations justifies our claim [4] that cell potentials can be measured to 0.01 mV; this figure corresponds to a random error (one standard deviation) of 1 part in 2 000 in free-proton analyses. The titrations are also subject to random errors in the volumes of titrant added (*ca.* 1

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[17] J. S. Rollett, F. J. C. Rossotti, and R. J. Whewell, unpublished work.

[18] N. Ingri, G. Lagerström, M. Frydman, and L. G. Sillén, *Acta Chem. Scand.*, 1957, **11**, 1034.

part in 1 000) and to systematic errors in solution concentrations (*ca.* 1 part in 1 000) and in $K_1^H$. Following Cabani[19] it is pertinent to examine the effects of these errors on the formation curves; the simplified equations (6) and (7) are used for clarity.

$$\frac{(\Delta a)_{H,K_1^H}}{a} = \frac{-H\Delta h}{h(H-h)} = \frac{-H\Delta h}{[\mathrm{HA}]h} \qquad (13)$$

In the determination of *a*, by differentiation of equation (6), with $\Delta h = 0.000\,5h$, the relative error in *a* due to error in *h* is therefore $0.000\,5H/[\mathrm{HA}]$, $< 0.001$, but with $\Delta h = 0.023h$ as in ref. 19 and in many determinations of stability constants, the relative error becomes *ca.* 0.02 or 2%.

$$\frac{(\Delta a)_{H,h}}{a} = \frac{\Delta K_1^H}{K_1^H} \text{ or } (\Delta \log a)_{H,h} = -(\Delta \log K_1^H) \qquad (14)$$

Similarly, equation (14) may be written, so that a systematic error in log $K_1^H$ results in a constant displacement of log *a* values (and consequently of log β values). Again, we can write (15) if $\Delta H = 0.001H$.

$$\frac{(\Delta a)_{h,K_1^H}}{a} = \frac{\Delta H}{(H-h)} = \frac{0.001\,H}{(H-h)} \qquad (15)$$

Typical values give the relative error due to error in *H* as 0.001—0.002. It is noticeable that the effect of systematic errors in *H* is greater than that of the random errors in *h* in our titrations, although the converse would be true with poorer measurements of potential.

Turning to equation (7), it is the subtraction $(A - a) - (H - h)$ which gives rise to the most serious errors in the calculation. The concentration of ligand bound to mercury is calculated by this subtraction and is small in comparison with both *A* and *H*. In our titrations the errors in *A* and *H* are highly correlated since the conjugate acid of the ligand was used as the titrant. With errors in the small term *a* negligible, only errors in $(A - H)$ and *h* need therefore be considered; errors in $(A - H)$ arise from the hydrogen-ion concentration remaining after calibration (measured potentiometrically) and any excess of acid in the sodium perchlorate medium of the titrant (measured independently by titration).

$$\frac{(\Delta \bar{n})_{h,B}}{\bar{n}} = \frac{\Delta(A-H)}{(A-a)-(H-h)} \approx 0.003 \qquad (16)$$

Differentiating equation (7), we obtain (16) for typical values with $\Delta(A - H) = 0.001(A - H)$. Similarly we can write (17) with $\Delta h = 0.000\,5h$. The total error is therefore *ca.* 0.5%, and solution concentration errors are again more significant than potentiometric errors. However, with $\Delta h = 0.023h$, total errors of *ca.* 9% of $\bar{n}$ are predicted. Were the errors in *A* and *H* uncorrelated, a situation created by the independent addition of acetate and proton or hydroxide, then $\Delta(A - H)$ in equation (16) becomes $\Delta A + \Delta H$ $(=0.001A + 0.001H)$ and the relative error in $\bar{n}$ is increased by a factor of at least ten.

$$\frac{(\Delta \bar{n})_{A-H,B}}{\bar{n}} = \frac{\Delta h}{(A-a)-(H-h)} \approx 0.002 \qquad (17)$$

Thus titration design seriously influences the errors in the results.

A convincing demonstration of the effectiveness of these titrations is the comparison of the mercury(II) acetate constants derived from the titrations with those from the redox titrations (Table 1). The values of log $\beta_2$ differ by only 0.01; the 0.07 difference between the values of log $\beta_1$ is illustrative of the problem inherent in formation-curve work in determining the quotient of successive stepwise constants $K_2/K_1$ in cases where $K_1 \leqslant K_2$ and never more than one third of the metal ion is complexed as BA.

$$K_n = [\mathrm{BA}_n][\mathrm{BA}_{n-1}]^{-1}a^{-1} \qquad (18)$$

*Hydroxomercury*(II) *Complexes*.—The value of log $\beta_2^*$ determined for $\mathrm{Hg^{II}}$ is in good agreement with that of Ahlberg[20] (log $\beta_2^* = -6.21$) and of Dyrssen and Tyrrell[21] (log $\beta_2^* = -6.16$), but the values of log $\beta_1^*$ ($-3.55$ and $-3.23$ respectively) agree less well. This disagreement again stems from the difficulty in determining $K_2/K_1$ when $K_1 \leqslant K_2$. The formation of an oxo-complex $[\mathrm{HgO(OH_2)}_n]$ has been suggested[22] to explain the abnormally high value of $K_2/K_1$ for the hydroxide system.

*Mercury*(II) *Alkanoate Complexes*.—Side reactions are known to occur in these systems; mercuration of acetic acid to give $\mathrm{CH_2HgCO_2H}$ has been studied[23] and the reduction of $\mathrm{Hg^{II}}$ to $\mathrm{Hg^{I}}$ by formate and to a limited extent by acetate has been noted.[24] Both of these types of reaction, however, require longer times and higher temperatures than those of this work, and there was no evidence (such as drifting potentials) of these irreversible reactions.

The only system for which satisfactory constants were unobtainable was mercury(II) cyanoacetate, which proved so insoluble that only an approximate value of log $\beta_1 \approx 1.7$ could be inferred; the formation of a polymeric species would explain the lack of reproducibility of the formation curves as the mercury-ion concentration was varied.

The majority of the formation curves are fully consistent with the existence of two species BA and $\mathrm{BA_2}$. However, the formation curves of mercury(II) hydroxyacetate and of methoxyacetate do not level off at $\bar{n} = 2$;

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[19] S. Cabani, *J. Chem. Soc.*, 1962, 5271.

[20] I. Ahlberg, *Acta Chem. Scand.*, 1962, **16**, 887.

[21] D. Dyrssen and V. Tyrrell, *Acta Chem. Scand.*, 1961, **15**, 393, 1622.

[22] R. Arnek and W. Kakolowicz, *Acta Chem. Scand.*, 1967, **21**, 1449.

[23] W. Kitching and P. R. Wells, *Austral. J. Chem.*, 1963, **16**, 508; 1965, **18**, 305; 1967, **20**, 2029.

[24] N. V. Sidgwick, 'The Chemical Elements and their Compounds,' Oxford University Press, 1960, vol. 1.

the highest values of $\bar{n}$ achieved were 2.0 and 2.2 respectively, but the reproducibility at the upper end of the formation curves was less good than that generally obtained. A complex $BA_3$, with constants log $\beta_3 = 9.0 \pm 0.1$ for hydroxyacetate and $8.7 \pm 0.2$ for methoxyacetate, would explain these observations, but the existence of the $BA_3$ complexes cannot be regarded as proven.

TABLE 2

Stability constants of mercury(II) acetate complexes

| Ref. | Conditions | log $\beta_1$ | log $\beta_2$ | log $\beta_3$ | log $\beta_4$ | Method |
|---|---|---|---|---|---|---|
| 25 | 30 °C, 1 mol $dm^{-3}$ Na[$ClO_4$] | 5.56 | 9.30 | 13.28 | 17.06 | Batch measurements, glass electrode |
| *a* | 35 °C, Various media | | 8.43 | | | Solubility |
| 26 | 25 °C, 0.1 mol $dm^{-3}$ Na[$ClO_4$] | 5.89 | | | | Titration, glass and mercury electrodes |
| *b* | 25 °C, 3 mol $dm^{-3}$ Na[$ClO_4$] | 4.22<br>±0.01 | 8.45<br>±0.03 | | | Titration, glass electrode |
| *b* | 25 °C, 3 mol $dm^{-3}$ Na[$ClO_4$] | 4.15<br>±0.01 | 8.44<br>±0.02 | $\not> 8.5$ | | Titration, glass and redox electrodes |

[a] P. Mahapatra, S. Aditya, and B. Prasad, *J. Indian Chem. Soc.*, 1953, **30**, 509. [b] This work.

Further study of the mercury(II) acetate system included the use of both glass- and redox-electrode measurements, which enabled reliable results to be obtained down to hydrogen-ion concentrations of *ca.* $10^{-5}$ mol $dm^{-3}$. High concentrations (0.1 mol $dm^{-3}$) of free acetate could thus be achieved without the total ligand concentration exceeding 0.25 mol $dm^{-3}$. The curve $-\log\alpha_0$ (log *a*) from four experiments is shown in Figure 2. The fitted parameters $\beta_1$ and $\beta_2$ are in good agreement with those from glass-electrode measurements alone, and mixed species [BA(OH)] and higher species ($BA_3$) are not observed, despite a thousand-fold increase in *a*. Our results therefore bear no resemblence to those of Banerjea and Singh [25] (Table 2) who report four complexes.

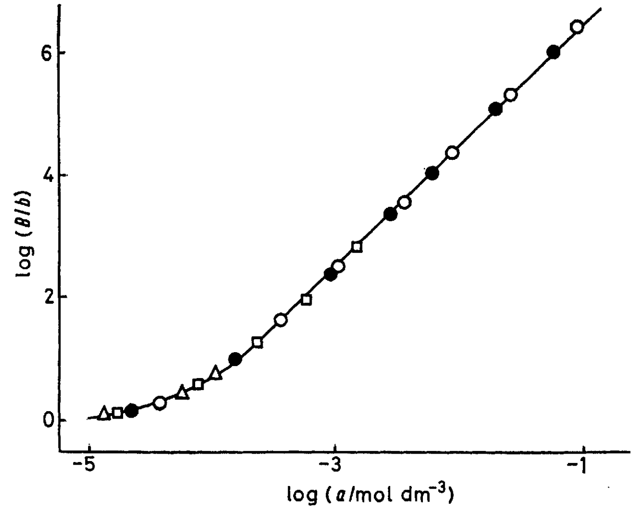

FIGURE 2 Redox titrations of mercury(II) acetate. Initial concentrations in $10^{-3}$ mol $dm^{-3}$: (● and ○) 12.0 $Hg^{II}$, 2.4 $Hg^{I}$ titrated with an acetic acid, sodium acetate buffer; (△) 12.0 $Hg^{II}$, 2.4 $Hg^{I}$, titrated with acetic acid then with sodium acetate; (□) 13.3 $Hg^{II}$, 1.3 $Hg^{I}$, titrated with sodium acetate. The curve was calculated from log $\beta_1$ 4.15 and log $\beta_2$ 8.44

Since the work described in this paper was completed, further studies of mercury(II) acetate (Table 2), chloroacetate, and formate (log $\beta_1$ 4.64 and 5.43 respectively) have appeared.[26] There is a greater difference between these results and ours than would be explained by the change in ionic strength, and close examination of Kumok's method of calculation shows that the discrepancy in the values of log $\beta_1$ obtained from mercury-

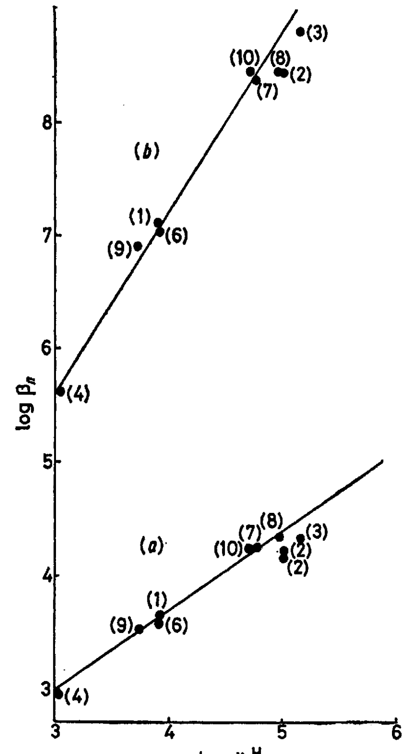

FIGURE 3 Linear-free-energy plots for complexes of mecury(II) ions with oxygen-donor ligands. The identification numbers correspond to those in Table 1. Line (*a*) is log $\beta_1 = 0.9 + 0.7 \log K_1^H$; (*b*) is log $\beta_2 = 0.8 + 1.6 \log K_1^H$

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[25] D. Banerjea and I. P. Singh, *Z. anorg. Chem.*, 1964, **311**, 225.

[26] L. P. Lisovaya, L. N. Usherenko, N. A. Skorik, and V. N. Kumok, *Zhur. neorg. Khim.*, 1973, **18**, 961.

electrode measurements is due to the invalid assumption that negligible amounts of mercury(I) alkanoates are formed. Substitution of our value [11] of log ${}^{I}\beta_1$ 3.57 for mercury(I) acetate into the calculation reduces the value of log $\beta_1$ from 5.89 to *ca.* 4.6, considerably closer to our value of log $\beta_1$ 4.22 for mercury(II) acetate. Further, there is very little variation in the free-ligand concentration among the four experiments quoted in ref. 26, so that a constant value of the single stability constant $\beta_1$ under these circumstances cannot be held to give evidence of the species present. It is inappropriate that we comment further on the glass-electrode results in ref. 26, other than to point out reservations described earlier in this paper concerning the results obtained when errors in $A$ and $H$ are uncorrelated and the errors in pH are as high as 0.01 log units.

Figure 3 shows linear-free-energy plots [27] in which log $\beta_1$ and log $\beta_2$ are plotted against log $K_1^{H}$. The straight line drawn, log $\beta_1 = 0.9 + 0.7$ log $K_1^{H}$, fits all the log $\beta_1$ values satisfactorily; further, the point (log $K_w$, log $K_w$ + log $\beta_1^*$) using the value [18] log $K_w$ 14.22 lies on the line. It can be concluded that all these ligands complex similarly with mercury(II) ions, and that unchelated complexes are formed despite the possibility with some of the ligands of five-, six-, or seven-membered chelate rings with two oxygen-donor atoms. These potentially chelating ligands include hydroxyacetate, methoxyacetate, methoxypropanoate, and the hydroxybutanoates. The gain in energy of forming a second Hg–O bond is thus insufficient to counterbalance the loss in distortion of the complex molecule. The second line, log $\beta_2 = 0.8 + 1.6$ log $K_1^{H}$, is also a satisfactory fit, but the theoretical basis is less clear.

Most of the systems shown in Table 1 have $K_1 \approx K_2$; this occurs in several silver(I) systems,[28] and is possibly a feature of linear co-ordination. Certainly, if the co-ordination number of the second complex is lower than

$$[\mathrm{HgA(OH_2)}_x]^+ + \mathrm{A}^- \rightleftharpoons [\mathrm{HgA_2}] + x\mathrm{H_2O} \qquad (19)$$

that of the first, the abnormal release of water on formation of the second complex [equation (19)] will stabilise it entropically. Further complex formation to $[\mathrm{HgA_3}]^-$ and $[\mathrm{HgA_4}]^{2-}$ will then be unfavourable, as illustrated by the cyanide [29] and chloride [30] systems in which $K_4 \approx K_3 \ll K_2 \approx K_1$.

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