

## Interaction of Mercury (II) with Organic Acids a Conductometric Study

By A. SALAHUDDIN<sup>1)</sup>

With 2 Figures

### Summary

Conductometric titrations of mercury (II) perchlorate in presence of glycolic acid, hippuric acid, malonic acid and succinic acid were carried out according to JOB's method of continuous variation. A reaction mixture contained X ml of the acid and (20 - X) ml of mercury (II) perchlorate, the two components being of equal molarity. The presence of only one but well-defined minimum in the plot of observed conductance versus X, for hippuric acid, oxalic acid, malonic acid and succinic acid showed that one complex of mercury (II) was formed in each case. The stoichiometry of the carboxylic acid complexes of mercury (II) was determined from the position of these minima and it was concluded that mercury (II) binds one hippurate, four oxalate and two malonate ions. The plot of observed conductance against X for glycolic acid, on the other hand, is characterized by the absence of any minimum and is in fact a straight line showing no interaction between mercury (II) and glycolate ion or an interaction too weak to be detectable by the present method.

Extending JOB's approach to conductometric data an attempt was made to derive quantitative expressions for the association constant of mercury (II) - carboxylic acid systems. The magnitude of association constants thus calculated showed that the carboxylic acids combined with mercury (II) with a decrease in free energy of about 5-6 kcalories/mole and that malonate is more effective than hippurate in binding mercuric ion.

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The electroanalytical methods generally employed in the study of ionic equilibria are potentiometry using a glass electrode, polarography and conductometry. The first is by far the most common technique currently available and has been used extensively in equilibrium investigations of a number of metal ion complexes of amino acids and other organic acids.<sup>2)</sup> Polaro-

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<sup>1)</sup> Present address: Department of Biochemistry, Duke University, Durham N.C. 27706, U.S.A.

<sup>2)</sup> "Stability Constants of Metal-ion Complexes, Section II: Organic Ligands", compiled by A. E. MARTELL, Special Publication No. 17 of The Chemical Society, London 1964.

graphy<sup>3)</sup>4)<sup>5)</sup> provides meaningful information only when a metal ion and its complex undergo reversible reduction at the dropping mercury electrode. The use of conductometry had been successfully demonstrated in the past by WERNER and later by LEVY but it has received very limited attention in recent years. This technique is much simpler than the other two and is fairly general although quantitative treatment of the results is not always possible because no satisfactory equation describing the dependence of conductivity of the mixed electrolyte on concentration has been hitherto obtained.<sup>6)</sup> It consists of determining the extent to which the course of conductometric titration of metal-ligand system in the presence of complex formation differs from that when no complex is formed. The most common effect of complex formation is the decrease in the conductivity of the system but in certain cases where complex ions carry more charge than the original metal ion, it might also cause an increase in conductance.

The conventional procedure for performing conductometric titration is to measure the conductivity of the pure component solutions separately and then the conductivity of the mixture containing the same concentration of the two components. A more convenient method might be to use conductometry according to JOB's method of continuous variation,<sup>7)</sup>8) where equimolar solutions of the reactants are mixed in varying proportions and a suitable extensive property is measured. In principle any one of the extensive properties like optical density, refractive index and specific conductivity can be used but the optical density has attracted the most attention so far and the latter two have been rarely used. It, therefore, seems quite appropriate to look for the possibility of using a property like conductivity which is simple and easily measurable.

With the above aim in mind a comparatively new and less familiar system, viz; mercury (II) — carboxylic acid was chosen primarily because of the significant role of mercuric compounds, both as toxic and therapeutic agents, in biological systems<sup>9)</sup>10)11) and also because such studies are

<sup>3)</sup> J. J. LINGANE, *Chem. Rev.* **29**, 1 (1941).

<sup>4)</sup> R. M. KEEFER, *J. Amer. chem. Soc.* **68**, 2329 (1946).

<sup>5)</sup> N. C. LI and B. DOODY, *ibid.* **72**, 1891 (1951); *idem.*, *ibid.* **76**, 221 (1954).

<sup>6)</sup> F. J. C. ROSSOTTI and H. ROSSOTTI, "The Determination of Stability Constants". New York, 1961, p. 314.

<sup>7)</sup> P. JOB, *Ann. Chim.* **9**, 113 (1928).

<sup>8)</sup> M. MUZAFFARUDDIN, A. SALAHUDDIN and W. U. MALIK, *J. Indian Chem. Soc.* **40**, 467 (1963).

<sup>9)</sup> P. L. BIDSTRUP, "Toxicity of Mercury and its Compounds". Amsterdam, 1964, p. 14.

<sup>10)</sup> M. C. BUTTIGELLI, *J. Occup. Med.* **2**, 337 (1960).

<sup>11)</sup> W. L. HUGHES, *Ann. N.Y. Acad. Sci.* **65**, 454 (1957).

extremely useful in X-ray structural studies of proteins in deciding whether or not the heavy metal ion is bound to carboxylic groups of the protein. Unlike this system, references on mercury (II) — nitrogen containing ligand system abounds and the general conclusion is that Hg (II) binds such ligands more strongly than the transition metals or even metal ions of  $d^{10}$  electronic configuration. The organic acids selected for the present studies were mainly glycolic, hippuric, malonic and succinic acids whose mercury (II) complexes have not been investigated so far. Some preliminary results on oxalic acid are also being communicated.

## Experimental

Chemically pure mercuric oxide was dissolved in requisite amount of perchloric acid and the mercury (II) concentration was determined gravimetrically<sup>12)</sup> as mercuric sulphide. Glycolic acid, hippuric acid, oxalic acid, malonic acid and succinic acid were of analytical reagent grade. Acid concentration was determined by pH titration against carbonate-free potassium hydroxide solution<sup>13)</sup> using BECKMAN model G pH meter. All-glass double distilled water with a conductance of about  $10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup> at 25°C was used in the preparation of solutions.

Measurement of Conductivity: Conductivity measurements were made at  $25 \pm 0.1^\circ\text{C}$  on W.T.W. Conductivity Bridge using dipping-type cell. The electrodes were freshly platinized and always stores in distilled water when not in use. This way the cell constant was found to remain constant within the limit of experimental error. The cell constant was determined by measuring the conductance of 0.2 M potassium chloride whose specific resistance at 25°C is known to be 0.002768 ohm<sup>-1</sup> cm<sup>-1</sup>. The resistance of the cell with this solution was found to be 312.5 ohm which will give a cell constant of 0.865 cm<sup>-1</sup> which did not change markedly during the course of these investigations.

In the concentration range of 0–0.05 M, conductivity of all acid (except hippuric acid where the maximum concentration was 0.018 M only) solutions and that of mercury perchlorate was determined. Then equimolar solutions of the acid and mercury perchlorate were mixed in such a way that 20 ml of the resulting solution contained X ml of the acid

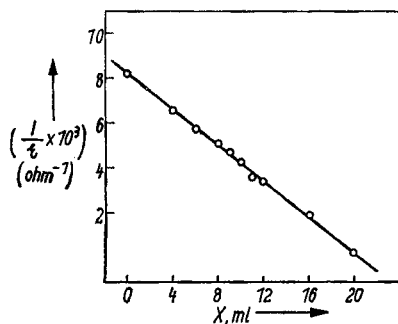


Fig. 1. Reciprocal of resistance for mixtures of X ml of 0.02 M glycolic acid and (20–X) ml of 0.02 M mercuric perchlorate

<sup>12)</sup> W. W. SCOTT, "Standard Methods of Chemical Analysis", Ed. H. FURMAN, New York 1945.

<sup>13)</sup> I. M. KOLTHOFF and E. B. SANDELL, "Text Book of Quantitative Inorganic Analysis" 3rd Ed. New York 1952, p. 526.

and  $(20 - X)$  ml of mercury perchlorate. Thus eleven solutions were prepared and their conductivities measured at  $25^\circ\text{C}$ . Experiments like this were performed at three different concentrations of the reactants namely 0.01, 0.02 M and 0.04 M. Except for glycolic acid (Fig. 1) the conductivity of the reactant mixture was found to be less than the sum of the conductivities of the reactants. This difference in conductance  $Y$ , was plotted against  $X$  in Fig. 2 for only one acid viz; malonic acid, curves for other acids being identical to that in Fig. 2, and, therefore, not shown for the sake of brevity.

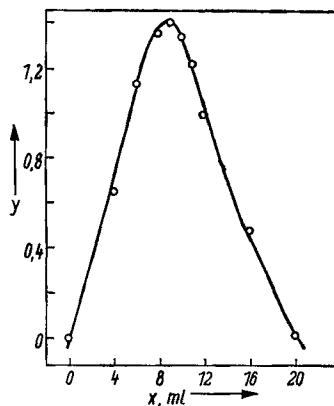


Fig. 2. Difference  $y$  for mixtures of  $X$  ml of 0.04 M malonic acid and  $(20 - X)$  ml of 0.04 M mercuric perchlorate

## Results

The ions which would contribute to the total conductance in the system under study are  $\text{H}^+$ ,  $\text{Hg}^{++}$ ,  $[\text{Hg}(\text{AH})]^+$ ,  $\text{HCO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{HA}^-$  and  $\text{A}^{=}$ , where  $\text{A}^{=}$  represents dicarboxylic anion. In case of monocarboxylic acid the cationic complex would be  $\text{Hg}(\text{R}-\text{COO}^-)^+$ , R being  $-\text{CH}_2-\text{OH}$  for glycolic acid and  $-\text{CH}_2-\text{NH}-\text{CO}-\text{C}_6\text{H}_5$  for hippuric acid. Since conductometric experiments were carried out below pH 5.0, the amount of  $\text{HCO}_3^-$  would be too small to have any detectable influence on conductivity. In order to find the contributions of acids the concentrations of their dissociated species were calculated from their initial concentrations and their known  $\text{pKs}^2$  and are listed in Table 1. The value of dissociation constant  $K$  for hippuric acid were taken from the Handbook of Chemistry and Physics.<sup>14</sup> Mercury perchlorate is also a weak electrolyte with  $K = 1 \times 10^{-3}$  as shown by DAVIES<sup>15</sup> and therefore free mercuric ion concentration at any given concentration of  $\text{Hg}(\text{ClO}_4)_2$  can be calculated. At two concentrations, 0.018 M and 0.00231 M, of mercury perchlorate the concentrations of mercuric ion were found to be  $2.76 \times 10^{-3}$  M and  $1.10 \times 10^{-3}$  M (Table 1,

<sup>14</sup> "Handbook of Chemistry and Physics", Cleveland, Ohio, 43rd Ed. 1961-1962, p. 1754.

<sup>15</sup> E. W. DAVIES, Thesis, University of Wales (1957), cited by C. B. MONK, in "Electrolytic Dissociation", London 1961, p. 240.

Table 1  
Stoichiometry of Mercury (II) Complexes From the Position of  
The Minimum in Conductometric Titration

Acid	[Acid] <sub>min</sub> (M/L) × 10 <sup>2</sup>	[Hg(ClO <sub>4</sub> ) <sub>2</sub> ] <sub>min</sub> (M/L) × 10 <sup>2</sup>	K <sub>1</sub> × 10 <sup>3</sup>	K <sub>2</sub> × 10 <sup>3</sup>	[HA <sup>-</sup> or A <sup>=</sup> ] (M/L) × 10 <sup>3</sup>	[Hg <sup>++</sup> ] × 10 <sup>3</sup>	$\frac{X}{(1-X)}$ = $\frac{[\text{Acid}]}{[\text{Hg}^{++}]}$
Hippuric	0.606	0.231	0.157 <sup>14)</sup>	—	0.90	1.10	0.82
Oxalic	0.48	0.231	59.0	64.0	4.46	1.10	4.05
Succinic	0.550	0.231	0.0689	2.47	0.582	1.10	0.53
Malonic	2.20	1.800	1.490	2.03	5.028	2.76	1.822

column 7). Since the second dissociation constant  $K_2$ , of malonic and succinic acid is very low ( $K_2 = 10^{-6}$ ), these acids would not furnish  $A^{=}$  to any measurable extent but in case of oxalic acid, ( $A^{=}$ ) will be about 11 per cent of ( $HA^{-}$ ) which is  $5.06 \times 10^{-3}$  M (Table 1). It, therefore, follows that the anion which might interact with mercuric ion is predominantly of the type  $HA^{-}$ . The calculated values of the concentrations of the organic acid and mercury perchlorate under columns (2) and (3) in Table 1 correspond to those at the maxima in the plot of Y versus X for each system. Not all the curves had as sharp maximum as that in Fig. 2, but the important feature common to all is the existence of only one maximum. At the position of maximum the first derivative of Y with respect to X will be zero and it can be seen that the value of  $\frac{(\text{Acid})}{(\text{Hg}^{++})}$  at this value of X would correspond to the stoichiometric ratio in the complex. The values of this ratio are listed in Table 1. It should, however, be noted here that (Acid) and ( $\text{Hg}^{++}$ ) represent free ionic concentrations which can be calculated from their pK values if we know how much acid or mercury perchlorate was taken initially in the total volume of 20 ml of the reaction mixture.

Calculation of the Apparent Association Constant. If x moles of the complex is formed in the reaction mixture containing a moles of  $\text{Hg}^{++}$  and b moles of  $HA^{-}$ , the apparent association constant K can be written as

$$K = \frac{x}{(a-x)(b-x)} \quad (1)$$

Further, if S and  $S^0$  are the total specific conductivities of the reactants in presence and absence of complex formation, and  $\Lambda_a$  and  $\Lambda_b$  represent the equivalent conductance for mercury perchlorate and the acid, the following equations hold good:

$$1000 kS^0 = {}^a\Lambda_a^0 + {}^b\Lambda_b^0 \quad (2)$$

$$1000 kS = (a-x)\Lambda_a^0 + (b-x)\Lambda_b^0 + x\Lambda_{ab} \quad (3)$$

where  $k$  is a constant by which  $a$ ,  $b$  and  $x$  has to be divided in order to convert molarity into normality. If the complex is uncharged,  $\Lambda_{ab} = 0$  and hence combination of equations (2) and (3) would give equation (4).

$$x = \frac{1000 k (S^0 - S)}{\Lambda_a^0 + \Lambda_b^0} \quad (4)$$

Here the tacit assumption is that  $\Lambda^0$  remains essentially unaltered on decreasing the concentration of the reactants by  $x$  moles. If the values of  $x$  do not exceed about 3 millimoles, the change in the equivalent conductance of the weak electrolytes under investigation would be insignificant (less than 0.1 per cent). This can be shown by actual calculation using equation (5)<sup>16</sup> which is valid for aqueous solution at 25 °C.

$$\Lambda_0 - \Lambda = (60.2 + 0.229 \Lambda_0) \sqrt{\alpha c}, \quad (5)$$

where  $\Lambda$  is the equivalent conductivity at the concentration  $c$ ;  $\Lambda_0$  is the conductivity in the limit of infinite dilution and  $\alpha$  is the degree of dissociation of the electrolyte. Values of  $\Lambda_b^0$  at a given concentration were computed from the plot of  $\Lambda \sqrt{S} / \sqrt{\alpha c}$  and were found to be nearly the same as the values of  $\Lambda_b^0$  in the limit of infinite dilution. The latter values were taken from a standard Table.<sup>17</sup> The conductivity of mercury perchlorate,  $\Lambda_a^0$  was found to be 129  $\text{ohm}^{-1} \text{cm}^{-1}$  at  $1.27 \times 10^{-3}$  M and 126  $\text{ohm}^{-1} \text{cm}^{-1}$  at 2.76 M. The measured difference in conductance ( $S^0 - S$ ) was multiplied by 1000  $k$  (where  $k$  is one for monovalent anion) and is given under column 2 in Table 2. The values of  $x$  calculated by equation (4) are listed in the third column. Knowing  $x$ ,  $a$  and  $b$  (from Table 1) the values of  $K$  and  $\Delta F$  for the association of mercury (II) with the carboxylic acids under study were determined and are given in the last two columns of Table 2. Equation (6) was used in the calculation of  $\Delta F$ .

$$\Delta F = -2.3026 RT \log K. \quad (6)$$

Table 2  
Apparent Association Constant For Mercury (II) Acid Complexes

Acid	1000 $k (S^0 - S)$ $\text{ohm}^{-1} \text{cm}^{-1}$ $\times 10^3$	$(\Lambda_a + \Lambda_b)$ $\text{ohm}^{-1} \text{cm}^{-1}$	$x$ (M/L) $\times 10^3$	$(a - x)$ $\times (b - x)$ $\times 10^{-7}$	log K	$-\Delta F$ kcal/mole
Hippuric	0.23	505	0.455	0.935	3.6871	5.0302
Oxalic	0.56	521	1.075	0.996	4.0331	5.5023
Succinic	0.30	511	0.587	0.215	4.4362	6.0522
Malonic	1.40	513	2.729	0.713	4.5829	6.2524

<sup>16</sup>) S. GLASSTONE, "Textbook of Physical Chemistry", New York 1946, p. 907.

<sup>17</sup>) "International Criticle Tables", Vol. VI., New York 1929, pp. 259-304.

## Discussion

The present conductometric results provide sufficient evidence for the interaction of mercury (II), from its perchlorate salt, with hippuric acid, malonic acid and succinic acid. Thus the course of conductometric titration of the reaction mixtures prepared according to JOB's method of continuous variation was found to be quite different from what it would have been if there were no interaction. This could not be simply due to the influence of one component on the conductivity of the other as found in case of mercury (II) — glycolic acid system, where the curve between the reciprocal of the observed resistance and  $X$ , the increasing concentration of the acid, is a straight line (see Fig. 1). Plots like this for the aforementioned acids, on the other hand, have definite minima which can be accounted for by the formation of uncharged complex (or complex with significantly lower ionic conductance). The fact that there is one and only one minimum in each case suggests strongly that only one mercury (II) complex of each acid (hippuric, malonic, succinic and oxalic) was formed.

**Composition of Mercury (II) Complexes:** From Fig. 2 it is clear that there is a well defined maximum in the curve  $Y$  versus  $X$  for malonic acid and this maximum corresponds to a composition of mercury:acid as 1:1.82 (Table 1). This would mean that one mercuric ion combines with nearly two malonate anions. Similar analysis of the conductometric results given in Table 1 indicates the binding of one hippurate, 4 oxalate and half succinate ions to one mercuric ion. The stoichiometry of mercury (II) — malonate complex is easy to understand in view of the general behavior of mercuric ion during complex formation since it is very likely that mercuric ion with a coordination number of four would form a complex of the type  $Hg(H_2O)_3(A^-)$  or  $Hg(H_2O)_2(HA^-)_2$ . That the latter is more probable is evident from the fact that only one carboxyl group of malonic acid would primarily offer sites for metal binding under experimental conditions because of the low second dissociation constant of the acid (Table 1). Simultaneous coordination of the mercuric ion with oxygen and nitrogen (or the carbonyl oxygen) atoms of the hippurate anion would satisfactorily account for the results obtained with mercury-hippurate system. Since the interaction of mercury (II) with oxalate anion gave precipitate the interpretation of the results obtained from JOB's method of continuous variation and hence the conclusions derived therefrom may be questionable. Nevertheless, if one can assume that equilibrium exists between the complex in the solid phase and ions in the solution one can conclude on the basis of the present data that one mercuric ion binds about four oxalate anions. Results on mercury-succinate system appear to be least definitive in providing in-

formation about the composition of the complex, perhaps because of the possible formation of a complex like  $(\text{OH})-\text{Hg}-\text{Hg}-(\text{succinate}^-)$ .

**Stability of the Mercury (II) — Carboxylic Acid Complex.** The values of the apparent association constants for the interaction of the above mentioned carboxylic acids with mercury (II) calculated from the present conductometric data and listed under column 6 of Table 2 appear to be invariably lower than that reported for mercury (II) — acetate complex.<sup>2)</sup> However, these results very well indicate that mercuric ion binds malonate ion more firmly than the hippurate ion, the decrease in free energy for mercury (II) — malonate complex being higher by about 2 kcalories/mole than for mercury (II) — hippurate complex (Table 2, column 6). It should be noted here that besides carboxyl oxygen hippurate ion also possess nitrogen and carbonyl oxygen atoms. The carbonyl oxygen atom of the hippurate is not very effective or at least much less effective than the carboxyl oxygen in interacting with the mercuric ion.

As stated above the values of  $\log K$  obtained in these investigations are lower than the literature value<sup>2)</sup> for mercury (II) — acetate system ( $\log K = 8.42$ ). The latter is far less than the value of  $\log K$  for mercury (II) — EDTA system ( $\log K = 22.64$ )<sup>2)</sup>, showing thereby that polydentate ligand fixes mercuric ion more strongly than the monodentate one. If this is true the malonate should have had stronger affinity for mercuric ion than acetate ion. One reason for this discrepancy could be the underestimation of  $(S^0 - S)$  in equation (4) and hence of  $x$  in equation (1). The former is quite possible if  $xA_{ab}$  in equation (3) is not zero. Furthermore, it may also be argued that the mercury (II) — acid interaction might have caused the formation of a hydrated complex of higher charge in concentration too low to affect the shape of the curve in Fig. 2 but sufficient enough to cause an increase in the value of  $S$ . This, however, seems very unlikely since formation of such a complex of mercury (II) would be more favoured in the absence of the carboxylic acid and this would also increase  $S^0$ .

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Aligarh (India), Department of Chemistry, Aligarh Muslim University.

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