

# The Complex Formation of $H^+$ , $Cd^{2+}$ and $Pb^{2+}$ with the Benzoate, Phthalate and Isophthalate Ions

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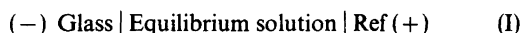
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By potentiometric measurements with an amalgam electrode the stability constants for the formation of  $H^+$ ,  $Cd^{2+}$  and  $Pb^{2+}$  complexes with benzoate, phthalate and isophthalate ions have been determined in 1 M  $Na(ClO_4)$  at 25 °C. Stability constants for the formation of BA,  $BA_2$ , BHA and B(HA)A are reported.

The complex formation of  $Cd^{2+}$  and  $Pb^{2+}$  (=B) with the phthalate and isophthalate ligands (=A) has been studied by Jain, Kumar and Gaur<sup>1,2</sup> using the polarographic technique. The formation of BA,  $BA_2$  and  $BA_3$  was reported. The numerical values of the stability constants are, however, somewhat unexpected. Thus the stabilities of the  $Pb^{2+}$  and  $Cd^{2+}$  complexes were found to be quite close, whereas in general Cd(II)–carboxylate complexes are substantially weaker than the lead(II) complexes.<sup>3</sup> Also the stabilities of the PbA complexes were reported to be smaller than the corresponding benzoate complex. It was therefore considered appropriate to re-investigate these systems and at the same time extend the pH range so that the formation of protonated complexes would be detected. Due to its low solubility it was not possible to include terephthalic acid in the measurements.

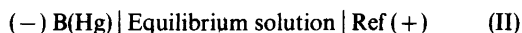
## EXPERIMENTAL

**Potentiometric measurements.** The experiments have been carried out as potentiometric titrations at 25.0 °C in a 1 M  $Na(ClO_4)$  medium using an automatic titrator. In general the ligand was added as a buffer with a constant quotient between the total concentration of  $H^+$ ,  $H$  and the total concentration of carboxylic acid,  $A$ . The free hydrogen ion concentration,  $h$ , was measured with the cell



$$E_g = E_g^\circ - 59.16 \text{ (mV)} \log (h/M) - E_j \quad (1)$$

and the concentration of the uncomplexed metal ion,  $b$ , with the cell



$$E_B = E_B^\circ - 29.58 \text{ (mV)} \log (b/M) - E_j \quad (2)$$

The liquid junction potential,  $E_j$ , can be expressed by

$$E_j = kh + l[H_2A] + m[HA^-] + na; (a = [A^{2-}]) \quad (3)$$

where  $k$ ,  $l$ ,  $m$  and  $n$  are constants.  $E_j$  was determined from titrations with buffers as described previously.<sup>4</sup> The quantity so determined will contain contributions from the "true" liquid junction potential, activity coefficient changes and dimerisation reactions in the buffer.<sup>5</sup>

**Chemicals and analysis.** Benzoic acid (Fluka p.a.) was recrystallized from water and the formula weight as determined by alkalimetric titration was 121.1 (calc. 121.1). Sodium benzoate (Merck zur Analyse) was used as received. 4-Hydroxybenzoic acid (Fluka puriss.), formula weight 138.3 (calc. 138.1) was used without further purification. Phthalic acid (Fluka p.a.). The formula weight was found to be 166.3 (calc. 166.1). Isophthalic acid (Fluka purum) was purified by repeated recrystallizations from water after treatment with charcoal. The formula weight of the final product was 166.5 (calc. 166.1).

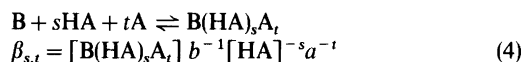
Cadmium perchlorate was prepared by dissolving CdO in a small excess of  $HClO_4$ . The oxide was prepared from the nitrate (Merck zur Analyse) as described by Biedermann and Ciavatta.<sup>6</sup> The cadmium content of the stock solution was determined gravimetrically as  $CdNH_4PO_4H_2O$ <sup>7</sup> and

as CdSO<sub>4</sub> after evaporation with H<sub>2</sub>SO<sub>4</sub>. The results agreed within 0.1%. The analytical hydrogen ion concentration was determined by potentiometric titrations with HClO<sub>4</sub> and the equivalence point was found from Gran plots.

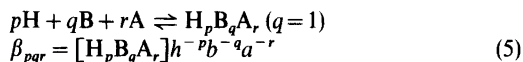
The cadmium amalgam electrode was prepared by dissolving cadmium metal in mercury (Kebo redist.). The cadmium metal, electrolytically prepared,<sup>8</sup> was a gift from Professor F. Nydahl. The cadmium concentration in the amalgam was 0.1% (weight) and the electrode was stable within ±0.02 mV for at least 12 h at a total metal ion concentration of 5 × 10<sup>-4</sup> M or more. The preparation and analysis of the other chemicals used have been described earlier.<sup>4</sup>

## RESULTS AND CALCULATIONS

In the complexation of the metal (B) HA<sup>-</sup> and A<sup>2-</sup> can be regarded as the ligands. The stability constants will then be defined by



since it will be shown that only mononuclear complexes are formed. It is sometimes more convenient to write the above reaction with H<sup>+</sup>, B, and A<sup>2-</sup> as components



With  $q=0$  eqn. (5) includes the proton complexes of A<sup>2-</sup>.

The preliminary analysis of the titration data was made graphically by studying  $(B/b-1)/a$  as a function of  $a$  at different values of the buffer quotient  $\theta = [HA]/a$ . The details of this treatment are presented in Ref. 9. For the final calculation of the stability constants the least-squares program Letagrop Vrid, version Etitr<sup>10</sup> was used.

The small solubilities of the lead(II) carboxylates did not allow studies of metal in concentrations higher than about 1 × 10<sup>-3</sup> M. A lower limit is set by the amalgam electrode which does not work satisfactorily for total metal ion concentrations below 2 × 10<sup>-4</sup> M. The lead(II) benzoate and phthalate systems were measured at 0.2 < B/mM < 0.5. Even then the solutions appear to be supersaturated. The exchange of the perchlorate ions of the medium by the ligands is generally less than 10%. When the solubility of H<sub>2</sub>A was sufficient the

measurements were, however, extended to  $[A^{2-}] = 0.1$  M.

## The proton carboxylate systems

*The proton-benzoate system.* This system was investigated in the range 0.01 <  $\bar{n}$  < 0.91 at a total benzoate concentration of 0.010 M.  $\bar{n}$  is the average number of protons bound per A. The liquid junction potential for the exchange of ClO<sub>4</sub><sup>-</sup> by A<sup>-</sup>,  $E_{j,A^-}$ , was determined in a buffer with  $[HA]/a = 0.05$  and found to be  $E_{j,A^-} = -25.4a$  mV M<sup>-1</sup>. This is a rather large value in comparison with  $E_j \approx -8a$  estimated from the Henderson equation. By the method of Farrer and Rossotti<sup>11</sup> the expression for  $E_j$  was found to be  $E_{j,FR} = 6.8[HA] - 9.5a$ . The coefficient for HA was found from measurements on 4-hydroxybenzoic acid, which has a higher solubility than benzoic acid.

Using  $E_{j,FR}$  as correction in eqn. (1), the large value of the coefficient in  $E_{j,A^-}$  can be accounted for by assuming an association between HA and A<sup>-</sup>. The least-squares treatment of the data yielded  $\beta_{101} = (1.068 \pm 0.001) \times 10^4$  M<sup>-1</sup>. The quoted error here and in the following is equal to three standard deviations. The value of  $\beta_{102} = 8.5 \times 10^3$  M<sup>-2</sup> should be regarded as an estimate since the constant is calculated from measurements on only one buffer.

*The proton-phthalate system.* The stability constants were determined from measurements at  $A = 0.010$  and  $0.020$  M in the range  $0.05 < \bar{n} < 1.75$ . The liquid junction potentials in buffers with  $H/A = 0.13, 0.33, 0.50, 0.67, 0.99$  and  $1.5$  could be expressed by  $E_j = 1.3[H_2A] - 25.5[HA^-] - 26.3a$ . The coefficient for  $[HA^-]$  is large and indicates association reactions. In order to find the stability constants for these reactions  $E_{j,FR} = 6.8[H_2A] - 9.5[HA^-] - 25a$  was used. The coefficients for  $[H_2A]$  and  $[HA^-]$  were taken from the benzoate system and the factor for  $a$  was determined with the phthalate ion. The following constants were obtained;  $\beta_{101} = (4.729 \pm 0.011) \times 10^4$  M<sup>-1</sup>;  $\beta_{201} = (2.303 \pm 0.007) \times 10^7$  M<sup>-2</sup>;  $\beta_{202} = (5.74 \pm 0.19) \times 10^8$  M<sup>-3</sup>;  $\beta_{302} = (1.31 \pm 0.08) \times 10^{12}$  M<sup>-4</sup>;  $\beta_{402} = (5.1 \pm 0.7) \times 10^{14}$  M<sup>-5</sup>. The  $\beta_{101}$  and  $\beta_{201}$  values are close to those reported by Lumme *et al.*<sup>12</sup>

*The proton-isophthalate system.* Due to the low solubility of isophthalic acid the  $\bar{n}$  range has been limited to values less than 0.6 at  $A = 6 \times 10^{-3}$  M. A solution of the acid was neutralized to  $\bar{n} = 0.05$  and then titrated with dilute HClO<sub>4</sub> until a per-

Table 1. Stability constants of Pb(II) and Cd(II) benzoate, phthalate and isophthalate complexes in 1 M NaClO<sub>4</sub> at 25 °C. The figures within parentheses are three times the estimated standard deviations.

System	$\beta_{011} \times 10^{-2}$ M <sup>-1</sup>	$\beta_{012} \times 10^{-3}$ M <sup>-2</sup>	$\beta_{111} \times 10^{-5}$ M <sup>-2</sup>	$\beta_{112} \times 10^{-7}$ M <sup>-3</sup>	$\beta_{1,0}$ M <sup>-1</sup>	$\beta_{1,1} \times 10^{-3}$ M <sup>-2</sup>
Pb(II)–benzoate	0.738(0.006)	0.778(0.011)				
Cd(II)–benzoate	0.102(0.001)	0.0449(0.0002)				
Pb(II)–phthalate (1)	5.95(0.03)	10.7(0.3)	8.32(0.09)	10.4(0.5)	17.6	2.2
Pb(II)–phthalate (2)	6.01(0.02)	10.2(0.2)	6.90(0.05)	6.0(0.3)	14.6	1.3
Cd(II)–phthalate (1)	0.722(0.003)	0.792(0.006)	2.31(0.02)	0.92(0.04)	4.9	0.2
Cd(II)–phthalate (2)	0.733(0.004)	0.755(0.008)	1.42(0.03)	0.30(0.05)	3.0	0.06
Pb(II)–isophthalate	1.464(0.007)	2.27(0.02)	8.8(0.4)	1.7(0.5)	60.3	1.2
Cd(II)–isophthalate	0.213(0.001)	0.149(0.001)	0.96(0.05)	–	6.6	–

manent precipitate was formed. The constants obtained were;  $\beta_{1,01} = (1.46 \pm 0.02) \times 10^4 \text{ M}^{-1}$ ;  $\beta_{2,01} = (3.7 \pm 0.2) \times 10^7 \text{ M}^{-2}$ . No attempt was made to identify dimeric species in this system.

#### The metal carboxylate systems

*The Cd<sup>2+</sup> – and Pb<sup>2+</sup> – benzoate systems.* The results from titrations to  $A=0.1 \text{ M}$  with a buffer having  $[HA]/a=0.05$  can be explained by the formation of BA and BA<sub>2</sub>. The discussion in Ref. 5, where the results are presented in more detail, suggests that the  $E_j$  correction proposed by Farrer and Rossotti leads to the best estimate of the stability constants. The  $\beta$  values so calculated are given in Table 1. The experimental data from the cadmium-benzoate system presented by Vartak and Shetiya<sup>13</sup> are in good agreement with our results. The numerical values of the equilibrium constants differ from our values since they have been calculated with  $E_j=0$ .

*The Pb<sup>2+</sup> – phthalate system.* The measurements were carried out with  $0.25 < B/\text{mM} < 0.5$  in the buffers ( $H/A, A_{\text{max}}/M$ ); 0.11, 0.017; 0.21, 0.023; 0.55, 0.022; 0.86, 0.022; 0.96, 0.067; 1.63, 0.041. The highest value of  $A$  reached during a titration is denoted by  $A_{\text{max}}$ . The concentration ranges are limited by the solubilities of phthalic acid and lead phthalate. The experimental data can be explained by the formation of PbA, PbA<sub>2</sub>, Pb(HA), and Pb(HA)A. In Table 1, two sets of stability constants are given (1) on the assumption that dimeric species are formed and thus  $E_{j,\text{FR}}$  is valid and (2) that the  $E_j$  coefficients found from buffers are measures of activity changes and “true” liquid junction potentials. In both cases  $\sigma(E_{\text{Pb}})$  is 0.02–0.04 mV.

*The Cd<sup>2+</sup> – phthalate system.* The experiments were carried out with  $B=1.0 \times 10^{-3} \text{ M}$  and the

buffers ( $H/A, A_{\text{max}}/M$ ); 0.14, 0.11; 0.51, 0.074; 0.99, 0.12; 1.35, 0.075. A model including the complexes CdA, CdA<sub>2</sub>, Cd(HA), and Cd(HA)A gave the smallest value of  $\sigma(E_{\text{Cd}})=0.03-0.04 \text{ mV}$  for both assumptions on  $E_j$  presented above. The constants are given in Table 1.

*The Pb<sup>2+</sup> – isophthalate system.* Titrations were performed with  $B=1.0 \times 10^{-3} \text{ M}$  and the buffers ( $H/A, A_{\text{max}}/M$ ); 0.05, 0.106; 0.25, 0.024; 0.35, 0.015. Again the data could be explained by the formation of PbA, PbA<sub>2</sub>, Pb(HA) and Pb(HA)A. The inclusion of Pb(HA)A lowers the value of  $\sigma(E_{\text{Pb}})$  from 0.05 mV to 0.02 mV. The constants are given in Table 1.

*The Cd<sup>2+</sup> – isophthalate system.* Measurements carried out at  $B=1.0 \times 10^{-3} \text{ M}$  in the buffers ( $H/A, A_{\text{max}}/M$ ); 0.05, 0.10; 0.31, 0.020 are well explained by the formation of the complexes CdA, CdA<sub>2</sub>, and Cd(HA).  $\sigma(E_{\text{Cd}})$  was 0.02 mV and the constants are given in Table 1.

#### DISCUSSION

The formation of the complexes BA and BA<sub>2</sub> is well established. No evidence for BA<sub>3</sub>, reported by Kumar *et al.*,<sup>2</sup> was found at the ligand concentrations ( $<0.1 \text{ M}$ ) studied here. The constants determined by them in 2 M NaClO<sub>4</sub> and 30 °C are in disagreement with our values, particularly for Pb<sup>2+</sup>.  $\beta_{011}=65$  and  $52.5 \text{ M}^{-1}$  for the phthalate and isophthalate complex, respectively, are remarkably small. They are even smaller than the constant for the benzoate complex,  $\beta_{011}=70 \text{ M}^{-1}$ , determined by the same authors.<sup>1</sup> This value is in agreement with our results.

The formation of protonated complexes in these systems has not been reported earlier but is in accordance with findings for other dicarboxylic

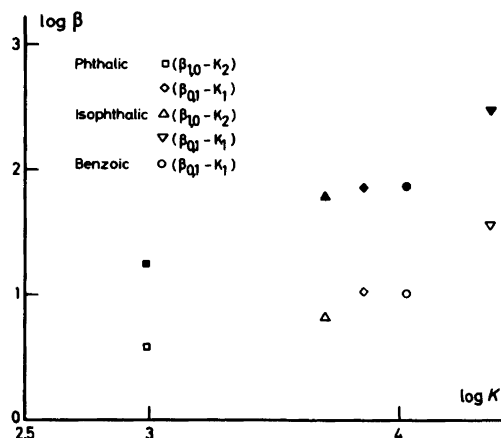


Fig. 1. Statistically corrected stability constants for the metal complexes (mean values from Table 1) plotted versus the corresponding constants for the proton complexes. Filled symbols are used for Pb(II). The data on which the points are based are indicated in the figure.

acids.<sup>9</sup> The variation of  $\beta_{1,1}$  with the nature of the complex forming system indicates that the evidence for B(HA)A is real and not caused by an erroneous  $E_j$ , since the same expression for  $E_j$  has been used in the two systems. The numerical values of  $\beta_{1,1}$  and  $\beta_{1,0}$  are, however, very sensitive to the choice of  $E_j$  as can be seen from Table 1.

Fig. 1 shows the correlation between  $\lg \beta_{1,0}$  and  $\lg (2K_2)$ , and  $\lg (\beta_{0,1}/2)$  and  $\lg (K_1/2)$ , i.e. statistically corrected constants have been used. For structurally related complexes such correlations are often found to be linear. Then it may be inferred that the phthalate complexes have an extra stability which indicates that this ligand acts bidentately forming a seven-membered ring. A ring of the same size can be formed by succinic acid, but a plot similar to that in Fig. 1 indicates that this ligand is essentially non-chelating. The difference in behaviour could be caused by the greater rigidity of the aromatic ligand.

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