

# Potentiometric Studies on the Interaction of Bivalent Magnesium, Calcium, Strontium, Barium, Copper and Mercury Ions with Phthalate

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The interaction of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Cu^{2+}$  and  $Hg^{2+}$  ions with phthalic acid is followed by pH-metry. It is found that  $Mg^{2+}$  and  $Ba^{2+}$  do not form complexes whereas  $Ca^{2+}$  and  $Sr^{2+}$  form 1 : 1 complexes only at  $\mu \leq 0.02$ .  $Cu^{2+}$  and  $Hg^{2+}$  react with phthalate to give 1 : 1 complexes at  $\mu \leq 0.1$ . The stability constants and the thermodynamic functions are calculated.

$Ca^{2+}$  and  $Ba^{2+}$  ions form 1 : 1 metal to ligand complexes with phthalate as indicated from conductivity<sup>1</sup>, E.M.F.<sup>2</sup> and solubility measurements<sup>3</sup>.  $Cu^{2+}$  ion forms either 1 : 1<sup>4-6</sup> or 1 : 1 and 1 : 2<sup>6-8</sup> complexes as revealed from potentiometric<sup>4-6</sup>, solubility<sup>3</sup>, spectrophotometric<sup>7</sup> and polarographic<sup>8</sup> data. No report appeared in the literature describes the interaction of phthalate with  $Mg^{2+}$ ,  $Sr^{2+}$  and  $Hg^{2+}$ . This work was undertaken to investigate the complexation of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Hg^{2+}$  and  $Cu^{2+}$  by pH-metry with a view to determine the stoichiometry of the complexes formed, if any, their stability constants and the thermodynamic parameters.

## Experimental

Calvin-Bjerrum's technique as adopted by Irving and Rossotti<sup>9</sup> was used to determine the proton-association constants of the ligand (phthalate) and formation constants of its metal complexes at 25° in aqueous solutions.

pH measurements were carried out on a Corning 601A precision research ionalyzer digital pH meter. During the titrations, oxygen-free nitrogen was bubbled through the solution. The solutions of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Cu^{2+}$  (A.R., B.D.H.) and  $Hg^{2+}$  (Cambrian Chemicals) as chlorides were prepared and titrated complexometrically by EDTA. Perchloric acid (B.D.H.) and phthalic (Prolabo) were reagent grade.

The following solutions were titrated potentiometrically against standard carbonate-free sodium hydroxide (0.5 M) solution :

(i) 0.02 M  $HClO_4$

(ii) (i) + 0.02 M phthalic acid ( $H_2L$ )

(iii) (ii) +  $5 \times 10^{-3}$  M metal chloride solution. The total volume was adjusted to 50 ml by adding double-distilled water in each case.

The titrations were performed at different ionic strengths, viz. 0.02, 0.04, 0.06, 0.08 and 1.0 M by adding  $NaClO_4$  solution and at 30, 35, 40 and 45° ( $\mu=0.1$ ) in order to determine the thermodynamic functions.

## Results and Discussion

Representative titration curves are shown in Fig. 1. The values of  $\bar{n}_A$  as determined by the method of Irving and Rossotti<sup>9</sup> were compiled from the titration data using solutions (i) and (ii). Calculations of proton-ligand association constants were carried out by plotting a graph of  $\bar{n}_A$  against pH. The graphs are almost linear (Fig. 2). The values of  $\log K_1^H$  and  $\log K_2^H$  (the first and the second proton association constants of phthalate, respectively) are corresponding to  $\bar{n}_A=0.5$  and  $\bar{n}_A=1.5$ , respectively. The values of  $\log K_1^H$  and  $\log K_2^H$  (Table I) agree quite well with those previously reported<sup>10</sup>.

The titration curves of the metal-ligand solution (iii) is well separated from the ligand solution (ii) (Fig. 1). Thus, the replacement of  $H^+$  ions are due to complexation. However, in the case of  $Mg^{2+}$  and  $Ba^{2+}$  the separation of the curves were no longer observed under the present set of experimental conditions. Therefore, these metal ions are not capable of forming complexes with phthalate. The literature reveals that few reports have appeared describing the formation of 1 : 1 Ba-phthalate complexes with  $\log K_1=2.33$  ( $\mu=0$ )<sup>1</sup> and 0.92 ( $\mu=0.15$ )<sup>2</sup>. The titration curves of  $Ca^{2+}$  and  $Sr^{2+}$  were observed to be separated from the ligand titration curves only at low ionic strength, viz. 0.02 M.

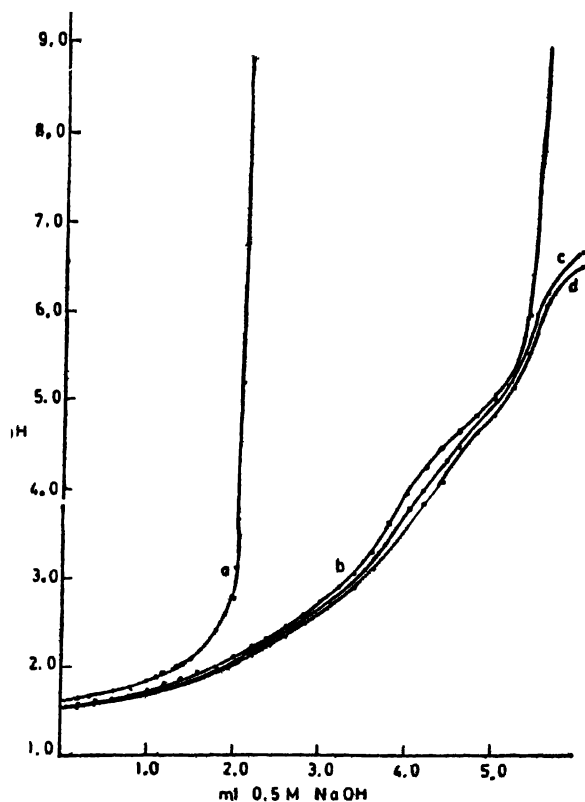


Fig. 1. Titration curves of (a) 0.02  $M$   $\text{HClO}_4$  + 0.08  $M$   $\text{NaClO}_4$ , (b) mixture (a) + 0.02  $M$  phthalic acid, (c) mixture (b) +  $5 \times 10^{-3} M$   $\text{HgCl}_2$ , and (d) mixture (b) +  $5 \times 10^{-3} M$   $\text{CuCl}_2$ , with 0.5  $M$   $\text{NaOH}$ ; total volume = 50 ml.

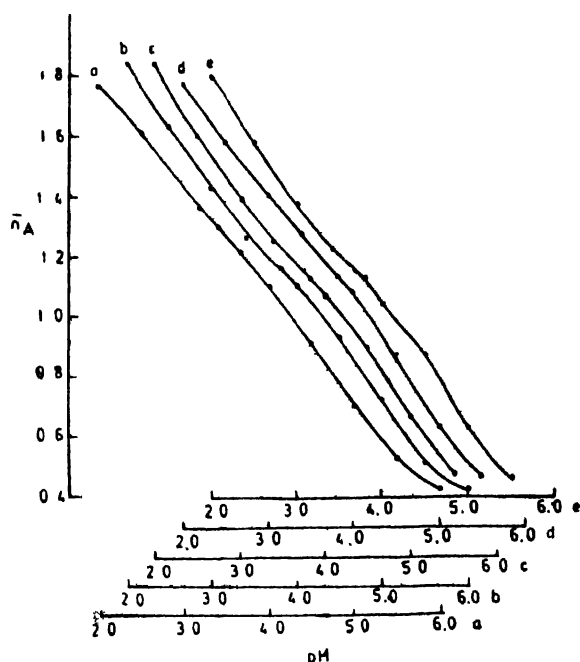


Fig. 2. Proton-phthalate formation curves at different ionic strengths: (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08, and (e) 0.10  $M$ .

TABLE 1—EFFECT OF IONIC STRENGTH ON PROTON ASSOCIATION CONSTANTS OF PHTHALATE AND FORMATION CONSTANTS OF ITS COMPLEXES (log  $K$ )

Temp. 25° $\mu$ $M$	H <sup>+</sup>		Ca <sup>++</sup>	Cu <sup>++</sup>	Hg <sup>++</sup>	Sr <sup>++</sup>
	$K_1$	$K_2$				
0.00	5.90	2.97	—	4.45	3.40	—
0.02	5.61	2.82	2.43	3.81	3.03	2.45
0.04	5.52	2.80	—	3.72	2.97	—
0.06	5.40	2.72	—	3.51	2.88	—
0.08	5.33	2.66	—	3.39	2.65	—
0.10	5.30	2.64	—	3.25	2.41	—

Above this ionic strength,  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$  ions seem to be inactive towards complexation with phthalate. However, solubility measurements carried out by Ghosh and Nair<sup>8</sup> indicate the formation of calcium phthalate complex with  $\log K_1 = 2.41$  at 25° and  $\mu = 0.1$ . On the other hand, the E.M.F. and conductivity data gave the values of  $\log K = 1.07$  ( $\mu = 1.15$ )<sup>9</sup> and 2.43 ( $\mu \rightarrow 0$ )<sup>1</sup>, respectively.

From the titration curves using solutions (ii) and (iii),  $\bar{n}$  (average number of ligand molecules attached per metal ion) and  $pL$  (free ligand exponent) values were calculated<sup>9</sup>. The  $\bar{n}$  values were plotted against the corresponding  $pL$  values to get the formation curves of the metal complexation equilibria. The formation curve of  $\text{Hg}^{++}$ -phthalate system is shown in Fig. 3. From these formation curves the values of stability constant listed in Table 1 were determined using the half-integral method<sup>9</sup>. Only 1 : 1

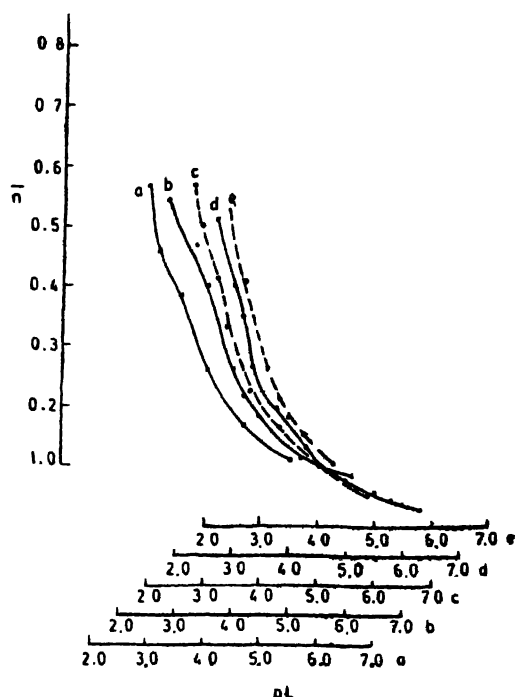


Fig. 3.  $\text{Hg}^{++}$ -phthalate formation curves at different ionic strengths: (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08 and (e) 0.1  $M$ .

metal to ligand complexes are formed between  $\text{Ca}^{II}$ ,  $\text{Sr}^{II}$ ,  $\text{Hg}^{II}$  and  $\text{Cu}^{II}$  ions and phthalate.

**Effect of ionic strengths :** The stability constants at different ionic strengths (0.02, 0.04, 0.06, 0.08 and 0.10  $M$ ) at  $25^\circ$  reveal that both the proton-ligand and the metal-ligand formation constants gradually decrease with increasing ionic strength. This shows that the ligand is interacting with metal ions both in undissociated and dissociated forms simultaneously. The thermodynamic stability constants were obtained by extrapolating the linear plots of  $\log K$  vs  $\sqrt{\mu}$  to zero ionic strength (Table 1). The corresponding values of  $\text{Ca}^{II}$  and  $\text{Sr}^{II}$  were not determined since the complexation was not observed at  $\mu > 0.02 M$ . The values of  $\log K_1$  of the  $\text{Cu}^{II}$  and  $\text{Ca}^{II}$  complexes are in accordance with those reported earlier<sup>1,3,5</sup>. No data are available in the literature concerning the phthalate complexes of Hg and Sr for comparison.

**Effect of temperature :** It is obvious from the data listed in Table 2 that  $\log K$  values of the metal ions phthalate formation constants gradually

TABLE 2—EFFECT OF TEMPERATURE ON PROTON ASSOCIATION AND COMPLEX FORMATION CONSTANTS ( $\log K$ )

$\mu = 0.1 M$

Temp. °C	$\text{H}^+$		$\text{Cu}^{II}$	$\text{Hg}^{II}$
	$K_1^H$	$K_2$		
25	5.30	2.64	3.25	2.41
30	5.26	2.62	3.45	2.94
35	5.21	2.60	3.79	3.09
40	5.13	2.58	4.07	3.20
45	5.05	2.56	4.36	3.29

TABLE 3—THERMODYNAMIC DATA FOR PHTHALIC ACID DISSOCIATION AND  $M^{II}$ -PHTHALIC ACID COMPLEX FORMATION

$\mu = 0.1 M$  at  $40^\circ$

Reaction	$-\Delta H^\circ$ kcal mol <sup>-1</sup>	$-\Delta G^\circ$ kcal mol <sup>-1</sup>	$+\Delta S^\circ$ cal mol <sup>-1</sup> deg <sup>-1</sup>
$\text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{HL}^-$	- 7.24	7.35	0.30
$\text{HL}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{L}$	- 1.69	3.68	6.35
$\text{Cu}^{2+} + \text{L}^{2-} \rightleftharpoons \text{CuL}$	+ 24.92	5.81	98.17
$\text{Hg}^{2+} + \text{L}^{2-} \rightleftharpoons \text{HgL}$	+ 9.52	4.57	45.01

increase on increasing the temperature. Endothermic heats are not uncommon in reactions where electrostatic interactions predominate<sup>11</sup>. The protonation constants seem to be slightly decreased on increasing the temperature. The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  have been determined and presented in Table 3. The positive values of  $\Delta S$  favour the complex formation.

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