

The Complex Formation between H^+ , Cd^{2+} and 1,2,4,5-Benzene-tetracarboxylic Acid

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The complex formation between Cd^{2+} , Pb^{2+} and aliphatic and aromatic carboxylate ligands has been extensively studied in this department. In this paper the results from an investigation of the Cd^{2+} –1,2,4,5-benzenetetracarboxylic acid system will be reported. Owing to the slight solubility of the compound formed between Pb^{2+} and the tetracarboxylate anion only the $Cd(II)$ system was amenable to a study by the potentiometric technique.

Experimental. The experiments have been carried out as potentiometric titrations at 25.0 °C in 1 M $Na(ClO_4)$ containing various total (analytical) concentrations of the constituents H^+ , cadmium(II), and tetracarboxylate ion, denoted H , B and A , respectively. The concentration of free H^+ , h , and the concentration of free Cd^{2+} , b , were measured with the cells

$$\begin{aligned} & - \text{glass} | \text{equilibrium solution S} | \text{ref} + \\ E_g &= E_{o,g} - 59.16(\text{mV}) \log(h/M) - E_j \\ & - \text{Cd(Hg)} | \text{equilibrium solution S} | \text{ref} + \\ E_{Cd} &= E_{o,Cd} - 29.58(\text{mV}) \log(b/M) - E_j \end{aligned}$$

E_j denotes the liquid junction potential. The general composition of solution S was: H H^+ , B $Cd(II)$, A A^{4-} , 1 M Na^+ , $(1M + 2B + H - 4A)$ ClO_4^- .

Apparatus. The titrations were performed with an automatic titrator. All potentials were measured with a digital voltmeter DATA PRECISION 2520 to ± 0.01 mV. The glass electrode used was an Ingold 201 which had been tested against the quinhydrone electrode.

Chemicals. 1,2,4,5-Benzenetetracarboxylic acid (Fluka, *purum*) was purified by recrystallization from water after treatment with charcoal. After filtration the stock solutions were standardized by titration with $NaOH$ to the fourth equivalence point with phenolphthalein as indicator. Various buffers were prepared by neutralization of stock solutions with $NaOH$.

Other chemicals and solutions were prepared as described in Refs. 1 and 2.

Calculations and results. Complexes and their corresponding stability constants are denoted according to Ref. 1.

Preliminary values for the stability constants of the proton complexes were determined with graphical methods. These values were then refined by the least-squares program Letagrop Vrid, version Etitr.³

Preliminary values of the stability constants for the metal complexes were obtained from graphs as described in Ref. 4. The constants were then refined with the same program as for the proton complexes.

The proton-tetracarboxylate system. The expression used for E_j was

$$E_j = -50 h - 9.5 [H_3A] - 25 [H_2A] - 31.8 [HA] - 38 [A]$$

where the coefficients for H_3A^- , H_2A^{2-} and HA^{3-} were assumed to be the same as for the benzoate,² phthalate² and tricarboxylate⁵ ions, respectively. The coefficient for H^+ was determined from a titration with A and $B=0$ in S and the coefficient for A^{4-} was found from a titration where H/A was 0.15.

Because of the low solubilities of the sodium salts, especially NaH_3A and Na_2H_2A , the stability constants were determined from titrations where the acid, neutralized to $\bar{n}_H=0.05$ was titrated with dilute $HClO_4$. The \bar{n}_H and A ranges covered were $0.05 < \bar{n}_H < 3.3$ and $2 < A < 5$ mM. The constants obtained were

$$\begin{aligned} \beta_{101} &= 5.15(\pm 0.05) \times 10^4 \text{ M}^{-1}, \\ \beta_{201} &= 3.15(\pm 0.03) \times 10^8 \text{ M}^{-2}, \\ \beta_{301} &= 9.19(\pm 0.11) \times 10^{10} \text{ M}^{-3}, \\ \beta_{401} &= 4.28(\pm 0.06) \times 10^{12} \text{ M}^{-4} \end{aligned}$$

The figures in the parentheses denote three times the estimated standard deviations.

The $Cd(II)$ -tetracarboxylate system. In the pH-range which could be studied, the acid was almost entirely in the forms HA^{3-} and A^{4-} . The concentrations of the other forms of the acid were so small that they could be neglected in the expression for E_j , which then became

$$E_j = -50 h - 31.8 [HA] - 38 [A]$$

Measurements were carried out with $B=0.1$ mM and the buffers (H/A , A_{\max}/M); 0.1, 0.008; 0.1, 0.01; 0.3, 0.01 and with $B=0.3$ mM and the buffer (H/A , A_{\max}/M); 0.1, 0.01. A_{\max} is the highest value of A reached in a titration. The data can be explained with the complexes BA , BA_2 and BHA . The constants obtained were

$$\begin{aligned} \beta_{011} &= 1.40(\pm 0.03) \times 10^2 \text{ M}^{-1}, \\ \beta_{012} &= 1.76(\pm 0.42) \times 10^3 \text{ M}^{-2}, \\ \beta_{111} &= 2.17(\pm 0.33) \times 10^6 \text{ M}^{-2} \end{aligned}$$

Including one more complex, B_2A_2 , lowered $\sigma(E_{Cd})$ from 0.09 mV to 0.03 mV. The constants then obtained were

$$\begin{aligned}\beta_{011} &= 1.34(\pm 0.01) \times 10^2 \text{ M}^{-1}, \\ \beta_{012} &= 1.44(\pm 0.14) \times 10^3 \text{ M}^{-2}, \\ \beta_{111} &= 2.75(\pm 0.12) \times 10^6 \text{ M}^{-2}, \\ \beta_{022} &= 8.96(\pm 0.82) \times 10^6 \text{ M}^{-3}\end{aligned}$$

Although the data indicate that polynuclear complexes are formed and the introduction of B_2A_2 substantially lowers $\sigma(E_{Cd})$, no definite conclusions can be drawn. It was not possible to vary the parameters B , H and A to an extent necessary for a positive identification of such complexes.

The value of β_{011} for the Cd(II)–1,2,4,5-benzenetetracarboxylate complex (140 M^{-1}) is about twice the value for the corresponding phthalate complex (72 M^{-1}).² From β_{111} and β_{101} one finds for the reaction $\text{Cd}^{2+} + \text{HA}^{3-} \rightleftharpoons \text{CdHA}^-$ a value of the equilibrium constant of about 50 M^{-1} . The results of our measurements on cadmium complexes with aromatic tri- and tetracarboxylate ions with not more than two adjacent carboxylate groups, indicate that reasonable estimates of the stability constants of complexes with these ligands can be obtained from the values of the constants for the benzoate and phthalate complexes.

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