

A Potentiometric Study of the Systems H^+ —Adipate and H^+ —Cd(II)—Adipate Ion in 3 M $Na(ClO_4)$ Medium at 25 °C

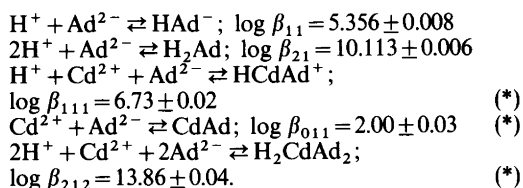
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The present work concerns studies by emf-titrations of complex formation with adipic acid (hexanedioic acid, $C_6H_{10}O_4=H_2AD$) in 3 M $NaClO_4$ medium. The protolysis of the acid in the concentration ranges: $3 < -\log h < 6.5$ and $10 \leq [H_2AD] \leq 50$ mM has been studied by measuring $[H^+] = h$ with a glass electrode.

The three component system H^+ —Cd(II)—Adipate (Ad^{2-}) has been studied by measurements of both the hydrogen ion and cadmium concentrations using glass and cadmium amalgam electrodes. The acidity range in this case was $3.4 < -\log h \approx 5$. A relatively high medium effect = $40.5[Cd^{2+}]$ mV was observed in the concentration range $5 < [Cd^{2+}] < 50$ mM studied.

The data can be explained by the species $HCdAd^+$, $CdAd$ and H_2CdAd_2 in addition to the species H_2Ad , HAd^- and Ad^{2-} . The equilibrium constants obtained are:



The limits of error are $\pm \log(3\sigma(\beta))$, where σ is the standard deviation, except in the case of constants marked with (*) where a graphically estimated maximum error limit is given.

The studies form part of an investigation of the complex formation equilibria of heavy metal ions like cadmium, copper *etc.* and ligands which are of interest in connection with attempts to find detergents which are biologically degradable.

The protolytic equilibria of adipic acid have been studied previously by several authors.^{1,2,3} The equilibrium constants¹ $\log \beta_{11} = 5.41$, $\log \beta_{21} = 9.83$ are extrapolated values for zero ionic strength (I) and 25 °C, calculated from data obtained with a hydrogen electrode. The measurements covered a relatively narrow range of concentration of adipic acid. The results² $\log \beta_{11} = 5.00$, $\log \beta_{21} = 9.28$ for $I = 0.1$ and 25 °C were obtained by emf measurements with glass electrodes. In 1 M $Na(ClO_4)$ the constants³ $\log \beta_{11} = 4.943$, $\log \beta_{21} = 9.244$ have been obtained with the help of a glass electrode.

For the formation of CdAd the equilibrium constant² $\log \beta_{011} = 2.1$, for $I = 0.1$, was obtained by potentiometric measurements using a glass electrode in solutions containing an excess of Cd^{2+} -ions.

SYMBOLS OFTEN USED IN THE TEXT

p, q, r = positive integers in the general formula for species containing cadmium, $H_pCd(II)_qAd_r$

$\beta_{p,r} = \beta_{p,0,r}$ = formation constants for the species H_pAd_r

$\beta_{p,q,r}$ = formation constant for the species $H_pCd(II)_qAd_r$

Ad = $[Ad^{2-}]$ = concentration of free adipate ion at equilibrium

AD = $[H_2AD]$ = total concentration of adipic acid

b = $[Cd^{2+}]$ = concentration of free cadmium ion at equilibrium

B = $[Cd(II)]$ = total concentration of cadmium

h = $[H^+]$ = concentration of free hydrogen ion at equilibrium

H = the total (analytical) concentration of hydrogen ion in excess of Ad^{2-} and H_2O for the

system $H^+ - Ad^{2-}$, and the total (analytical) hydrogen ion concentration in excess of Ad^{2-} , H_2O and Cd^{2+} for the system $H^+ - Cd(II) - Ad^{2-}$

$$Z = \frac{H-h}{AD} = \text{the average number of protons bound to one mol AD.}$$

All concentrations are expressed in mol/liter, M, if not otherwise stated.

H can be calculated as follows:

$$H = \frac{v_0(h_0 + 2AD) + \sum v_n(h_n + 2AD)}{v_0 + \sum v_n}$$

where

v_0 = the initial volume of the test solution S_0 , in ml;
 v_n = volume of the solution added from burette n , in ml;

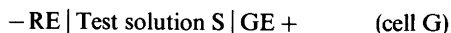
h_0 and h_n = respectively, the concentrations of free $[H^+]$ in S_0 and in the burette solution concerned, (in M).

PLAN OF INVESTIGATION

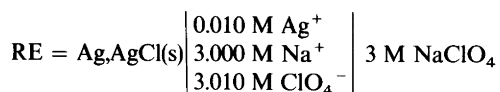
The acidity constants for adipic acid were determined by simple acid-base titrations in the chosen ionic medium. The complex formation between adipic acid and cadmium ion was studied by using both amalgam and glass electrodes (Table 1).

The work was completed with a relatively extensive investigation of the influence of various ions on the measured emf.

The concentrations of hydrogen and cadmium ions were determined by measuring the emf of the cells



where GE denotes a glass electrode and Cd, Hg represents the dilute amalgam electrodes used. The reference half-cell (RE) had the composition



The emf's in mV of the cells G and M at 25 °C can be written:

$$E_G = E_{OG} + 59.16 \log h + E_j \quad (1)$$

and,

$$E_M = E_{OM} + 29.58 \log b + E_j \quad (2)$$

The activity factors of the species involved are assumed to be constant. E_{OG} and E_{OM} are constants. E_j formally represents the liquid junction potential between the test solution S and 3 M $NaClO_4$, it includes several terms. For 3 M $NaClO_4$ medium – in the absence of Cd^{2+} ions – E_j can be estimated from the equation

$$E_j = -17 h \text{ mV} \quad (3)$$

This is valid as long as no great changes occur in the composition of the medium.⁴ For $NaClO_4$ ionic medium having a constant sodium ion concentration, $[Na^+] = 3 \text{ M}$, and containing Cd^{2+} and H^+ ions E_j is dependent on both the cadmium and hydrogen ion concentrations. The contribution of the H^+ ions to E_j can be neglected in the h range studied.

$$E_j = 40.5 [Cd^{2+}] \text{ mV} \quad (4)$$

This relationship, found by the author, is valid in the concentration range $5 < [Cd^{2+}] < 50 \text{ mM}$.

When the constants E_{OG} , E_{OM} and E_j are known the free concentrations b and h can be calculated using the appropriate equations, among (1)–(4). For solutions containing cadmium ions the method of successive approximations was used.

In order to ensure a reasonable constancy of the activity factors of the reacting species in all the solutions the sodium ion concentration was kept at 3 M by addition of $NaClO_4$ stock solution.

EXPERIMENTAL

The experimental conditions for each group of measurements are summarized in Table 1. This table indicates the initial composition of the test solutions S_0 , the composition of the reagents used in the burets (T_1 , T_2) and the other parameters.

The choice of experimental parameters was limited by the relatively low solubility of adipic acid in the ionic medium used ($\sim 0.14 \text{ M}$ in 3 M $NaClO_4$ at 25 °C), and of the cadmium adipate complexes. The composition of the solid phase was not analyzed. In solutions where $\log h < -5$ precipitates easily form, especially at the higher total concentrations of cadmium.

Table 1. Experimental parameters for the titrations. $[Na^+] = 3$ M and kept constant in all solutions. F, series with decreasing h ; R, series with increasing h .

Series	Test solution So			Reagent T1		Reagent T2	
	H mM	B mM	AD mM	h mM	B mM	H ₂ AD mM	Na ₂ AD ^b mM
Group 1. Variables kept constant: AD, measured: h							
3F ^a			9.88				
8F	53.73		24.98	-262.72		49.96	
13F	57.64		24.98	-262.72		49.96	
13R	2.54		24.98	181.36		49.96	
9F	102.55		49.83	-402.56		99.66	
9R	3.13		49.83	506.42		99.66	
Group 2. Variables kept constant: B,H, measured: b,h							
15*F	24.17	8.00	0	24.19	16.00	11.95	88.18
14F	24.18	16.00	0	24.19	32.00	11.95	88.18
29F	24.15	25.00	0	48.30	50.00	0	100.00
28F	24.20	32.00	0	24.20	64.00	11.95	88.18
Group 3. Variables kept constant: B > AD, measured: h							
21R	0.87	25.00	5.00	10.84	50.00	10.00	
21F	9.82	25.00	5.00	0.86	50.00	0.47	9.53
20R	1.43	50.00	5.00	11.72	100.00	10.00	
20F	9.27	50.00	5.00	1.75	100.00	0.47	9.53
22R	0.89	100.00	5.00	13.55	200.00	10.00	
22F	0.29	100.00	5.00	3.57	200.00	0.47	9.53
Group 4. Variables kept constant: AD > B, measured: b,h							
24F	102.10	5.00	50.00	10.17	10.00		100.00
24R	83.21	5.00	50.00	5.09(T2)	5.00(T2)	50.00(T2)	
25F	102.10	5.00	50.00	10.17	10.00	10.00	90.00

^a Coulometric titration. ^b Na₂AD stands for the stoichiometrically calculated concentration of neutralized adipic acid.

Reagents and solutions

Sodium perchlorate and dilute perchloric acid solutions were prepared and analyzed as usually in this laboratory.⁵

Sodium hydroxide. A carbonate free ~1 M NaOH stock solution was made according to Sørensen⁶ from an EKA Bohus *p.a.* product. This solution was stored and diluted under nitrogen, free CO₂. The concentration of sodium hydroxide in these solutions was determined by standardizing them against both recrystallized hydrazine sulfate and standardized HClO₄-solution. The results obtained by the two methods agreed to within ±0.1%.

Adipic acid, H₂Ad, (hexanedioic acid C₆H₁₀O₄). A crystalline product (purum, min. 99.5% H₂Ad) from KEBO was twice recrystallized from water and dried over CaCl₂ (*sicc.*) in a desiccator. The formula weight of the material so obtained was

determined by titration with standardized NaOH. It was found to be 145.9±0.1. The theoretical value is 146.14. Solutions containing different concentrations of adipic acid were prepared by dissolving weighed amounts of the recrystallized material in the ionic medium.

The cadmium perchlorate stock solution was prepared and analyzed according to Ref. 7. The crystalline Cd(NO₃)₂·4H₂O, Merck *p.a.* quality, was recrystallized once from 0.01 M HNO₃. The product was tested for chloride and further purification was found to be unnecessary.

The results of the gravimetric determinations of cadmium agreed to within ±0.1%.

The hydrogen ion content of the cadmium perchlorate stock solution (~1 mmol per 100 g) was estimated by titration with NaOH.⁷

Solutions containing cadmium in the desired concentrations were always prepared by weighing.

In most of the experiments *partly neutralized adipic acid solutions* were used to change the hydrogen ion concentration. In this way high local alkalinity and precipitation of metal hydroxo complexes could be avoided.

The mercury used for the preparation of cadmium amalgam was twice distilled under reduced pressure and then filtered through a glass filter G3. In order to reuse the Hg, it was cleaned by washing it first with 1:1 HNO₃ and then with successively more dilute acid and finally with water, as described in Ref. 8.

Dilute solutions were prepared using calibrated burets.

THE EMF MEASUREMENTS

Electrodes. Ag,AgCl electrodes were prepared by electrolysis.⁹ The glass electrodes were Beckman type 40498 electrodes.

Cadmium amalgam was prepared by coulometric electrolysis using a constant current of 3 mA. The amalgam was made to contain 0.01 wt % cadmium.¹⁰ A special vessel provided with a capillary tube was used for the preparation and transfer of amalgam.¹¹ As they were required portions of the

amalgam were rapidly introduced through the capillary into the test solution under a vigorous stream of nitrogen.

A stable emf value was obtained in the cells M after they had been standing for a few hours (or overnight), and the homogenization of the amalgam was complete. It was noted¹² that in order to attain a quick and stable emf the platinum spirals used as contact electrodes to the cells M have to be immersed completely in the Hg,Cd pools and the amalgam has to be stirred by lifting the Pt electrodes a few times after each addition of reagents.

The constants E_{0G} , E_{0M} and E_j were determined by titrations at the beginning of the experiments, in an acid test solution of suitable composition.

E_{0G} or E_{0M} and E_j were evaluated graphically using eqns. (1) or (2) and (3) or (4) as shown in Fig. 1. The intercepts of the straight lines in Fig. 1 give E_{0G} or E_{0M} and the slope gives the dependence of E_j on $[Cd^{2+}]$ (40.5 mV/mol) at constant h .

For group 1 the constant E_{0G} was determined at constant adipic acid concentration in a range of $-\log h$ where the adipic acid protolysis can be neglected. Although the variation of $[H_2Ad]$ might have had a slight effect on E_G (see next sec-

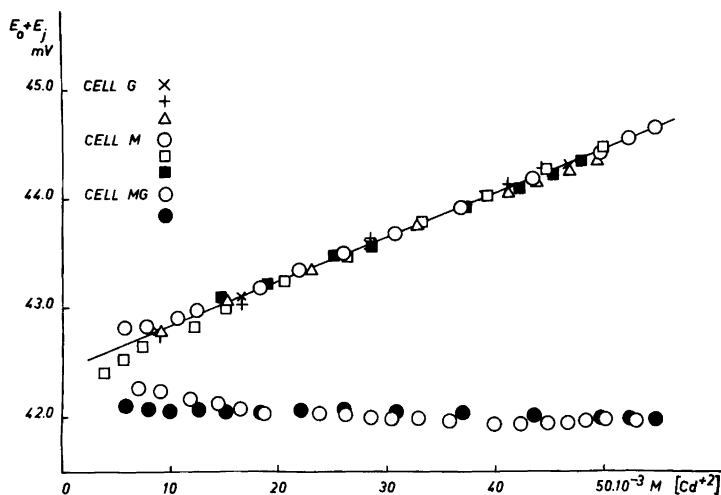


Fig. 1. Determination of E_{0G} , E_{0M} , E_{0MG} and E_j .

Cell G: $E_{0G} + E_j = E_G - 59.16 \log h$ as a function of b .

Cell M: $E_{0M} + E_j = E_M - 29.58 \log b$ as a function of b .

Cell MG: $E_{0MG} = E_{MG} - 59.16 \log h + 29.58 \log b$ against b .

Points with symbols Δ were shifted along the ordinate by 14.30, open circles \circ by 977.34 and the symbols \square \blacksquare by 987.76. Points belonging to cell MG were shifted along the ordinate by 99.70. Filled symbols correspond to points from reverse titrations.

tion, point e.) no correction was made for it in the calculations. In view of the low adipic acid concentrations used, it cannot be a large source of error.

For titrations belonging to group 3 the E_{0G} values, determined first in cadmium-free solutions, were corrected for the B levels used, according to eqns. (1) and (4), assuming that all adipic acid is bound to Cd(II) in species $H_pCd_1Ad_1$.

The liquid junction potential, E_j . As the effect of complex formation on the measured emf turned out to be very small, it was necessary to find out if cadmium ions and adipic acid or its ions have any influence on the emf of the cells G and M.

a. The influence of the cadmium ions on E_G was investigated using different glass electrodes in some experiments at constant h equal to 24.2 mM by varying the cadmium ion concentration in the range $8 < b < 50$ mM. The results obtained are plotted in Fig. 1.

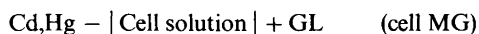
b. The influence of the cadmium ions on E_M was investigated in the same concentration range as for cell E_G using another cell arrangement with a new reference half cell. The results of a forward and reverse titration are shown in Fig. 1.

This figure indicates that the effect of the Cd^{2+} ions might be treated formally as a liquid junction phenomenon. The contribution of the cadmium ions to the liquid junction potential can then be estimated from

40.5b mV

This result was further checked by comparing E_M data obtained simultaneously in cells with and without liquid junction (cells M and MG) using the concentration conditions given for cell E_G above.

The cell without a liquid junction, formed using a glass electrode as the reference half cell:



had an emf described by:

$$E_{MG} = E_{0MG} + 59.16 \log h - 29.58 \log b$$

The results of a measurement with this cell are presented in Fig. 1. The constant E_{0MG} can be evaluated to ± 0.1 mV from the intercept in this figure.

c. The possibility that E_M might be effected by

H_2Ad was also investigated at constant h ($= 25.22$ mM) and constant b ($= 5$ mM) in the range $7 < AD < 25$ mM. No effect could be detected under these conditions.

d. However, a slight effect on E_M caused by the first addition of partly neutralized adipic acid reagents could be observed in test solutions where $h > 10^{-2.5}$ M. It appeared as a small positive shift in the emf of the amalgam half cells.

This phenomenon is perhaps due to the adsorption of the ions of the adipic acid on the amalgam surface. The effect of anions on the mercury electrode in polarographic measurements has been noticed by several authors.¹³

The E_{0M} values were corrected assuming that $b \cong B$.

e. The influence of the H_2Ad molecules on E_G was checked at constant h ($= 24.19$ mM) in the range $7 < AD < 50$ mM. A small effect could be observed but it could not be reproduced well because of the low concentrations of adipic acid. Changes of the medium effect ($=$ diffusion potential + activity coefficient contribution to the total cell emf) with the anion concentration have been observed by other authors.^{14,15}

The influence of the adipate ions (Ad^{2-}) on E_G was not investigated. Due to the low concentrations of adipic acid any error that might be introduced could not be large.

Anyhow the authors of Ref. 3 found that E_j is a function of $[H^+]$, $[H_2A]$, $[HAD^-]$ and $[Ad^{2-}]$ for the $H^+ - Ad^{2-}$ system in 1 M $Na(ClO_4)$.

Experimental details of the emf measurements

A cell arrangement usual in our laboratory¹⁶ was employed.

The test solutions were stirred and protected by purified¹⁷ nitrogen. The purification procedure was extended by using a wash bottle containing (0.5 M $CrCl_3$, ~ 1 M HCl , Hg , Zn).

The emf of cell M was measured with a Vernier compensator. The emf of cell G was measured with a Dynamco Ltd digital voltmeter, type DM 2022. Emf values stable to within 0.02 mV for cell M and (0.05–0.1) mV for cell G were reached a few minutes after each addition of reagent solution.

The solutions with acidity $-\log h > 5$ showed a tendency to become supersaturated.

TREATMENT OF THE DATA AND RESULTS

The primary data from this work are available from the author on request.

The system $H^+ - Adipate$ (Group 1). The experimental data are presented in Fig. 2 where some titration curves are plotted as $Z(\log h)_{AD}$. For clarity some randomly chosen titration points have been omitted. The range of Z covered is $0 \leq Z \leq 2$. As seen in Fig. 2 there is good agreement between the forward and reverse titrations. The good coincidence obtained for curves with different AD indicates that the main complexes are mononuclear.

The equilibrium process may thus be described by



The data were treated by the means of the generalized least squares program LETA-

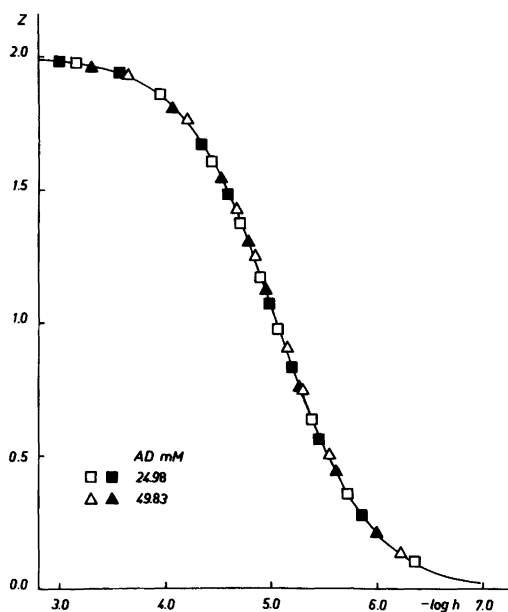


Fig. 2. Average number of H^+ bound per one mol adipic acid (Z) as a function of $-\log h$ for the $H^+ - Ad^{2-}$ system. The full drawn curves represent the theoretical Z functions calculated with the constants $\log \beta_{11} = 5.356$ and $\log \beta_{21} = 10.113$. Filled symbols represent points from reverse titrations.

GROPVRID.¹⁸ The computer calculated those β_{pr} values which minimized the function $U = \sum (Z_{calc} - Z_{exp})^2$.

The experimental data were introduced as pairs of values, $(\log h, Z)_{AD}$.

The best values found for the constants are $\log \beta_{11} = 5.356 \pm 0.008$; $\log \beta_{21} = 10.113 \pm 0.006$.

The system $H^+ - Cd(II) - Adipate$. The composition of the complexes considered to be the main species at the equilibrium in the system $H^+ - Cd(II) - Adipate$ investigated, were found for every titration group by graphical methods.

Graphical analysis of the data

(a) The function $F = (B - b)/b$. The titrations belonging to groups 2 and 4 were treated here in two separate sets. These titrations include the measurements of $[Cd^{2+}]$. For group 2 the condition $AD > B$ is valid and AD is varied within the range: $0.5 B < AD < 2B$.

The equilibria considered can be written as



For titrations with lower B (5, 8, 16 mM) the assumption that the cadmium adipate complexes $H Cd(II) Ad^+$ and $CdAd$ as well as the acid species are formed seems to be reasonable. Thus q may be considered to be equal to 1. The hydroxide ion and the hydrolysis products of $Cd(II)$ can be neglected in the range of h covered in this study: $3.4 < -\log h < 5$. We thus obtain

$$B = b + \beta_{111} h b Ad + \beta_{011} b Ad \quad (7)$$

$$AD = Ad + \beta_{101} h Ad + \beta_{201} h^2 Ad + \beta_{111} h b Ad + \beta_{011} b Ad \quad (8)$$

The free adipate concentration in equilibrium corresponding to monomer species alone (Ad_M) can be calculated using eqn. (7) and eqn. (8):

$$Ad_M = \frac{AD - (B - b)}{1 + \beta_{101} h + \beta_{201} h^2} \quad (9)$$

By means of eqns. (7) and (9) auxiliary variables can be defined as follows

$$F = \frac{B - b}{b} = \beta_{111} h Ad_M + \beta_{011} Ad_M \quad (10)$$

$$F / Ad_M = \beta_{111} h + \beta_{011} \quad (11)$$

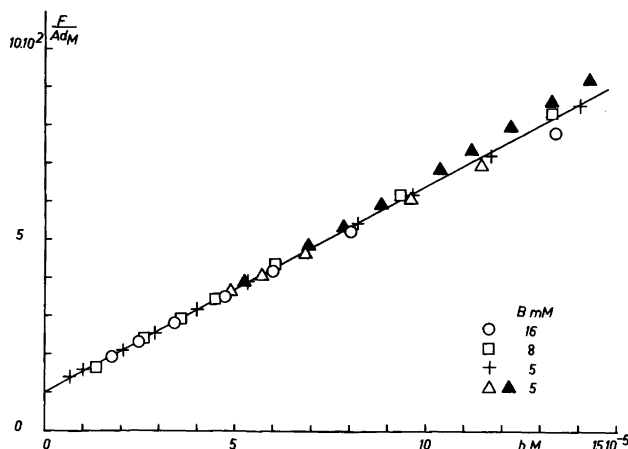
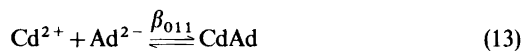


Fig. 3. Graphical determination of β_{111} and β_{011} . F/Ad_M as a function of h . Filled symbols represent points from reverse titrations.

If our assumption that the species formed are $H\text{Cd(II)Ad}^+$ and CdAd is correct, then a plot of F/Ad_M as a function of h should give a straight line with a slope of β_{111} and an intercept of β_{011} (Fig. 3).

As seen from Fig. 3 the plot F/Ad_M against h is well described by a straight line. This confirms the equilibrium model tested, namely



It leads to the following equilibrium constants: $\log \beta_{111} = 6.73 \pm 0.02$; $\log \beta_{011} = 2.00 \pm 0.03$. The error limits quoted for the constants are graphically estimated maximum errors.

The first points of every titration corresponding to acidity levels $-\log h < 3.4$ and expressed in the terms of eqn. (11), are uncertain due to the very low adipate concentration and the term $B - b \cong 0$. For this reason, points in this range have been excluded in the construction of Fig. 3.

The titrations with higher B (25, 32 mM) were used to test whether or not other cadmium adipate species were present. The free ligand concentration was estimated by using an integration procedure for titrations in group 2 (with acidity levels $-\log h > 3.4$) suggested by Österberg.¹⁹

In the present case this procedure gives the relation

$$\log Ad_{B_n} - \log Ad_{B_8} = \left[- \int_{B_8}^{B_n} \left(\frac{\partial \log B/b}{\partial AD} \right)_{H,B} dB \right]_{H,AD} \quad (14)$$

where the $\log Ad_{B_8}$ term is the integration constant. It is equal to the free adipate concentration for the particular Ad value chosen, at the lowest total metal concentration involved in the integration procedure (in our case at $B = 8$ mM), and can be calculated from eqn. 9. The $\log B/b$ against AD functions at constant H and B can be described by straight lines in the AD range involved, and reasonably accurate values of the derivative

$$\left(\frac{\partial \log B/b}{\partial AD} \right)_{H,B}$$

can be obtained in spite of the limited number of data available. The integral can then be evaluated by graphical integration.

In titrations of group 2, the condition $AD > B$ could make possible the formation of species such as H_2CdAd_2 , CdAd_2^- etc. The presence of H_2CdAd_2 was tested using the function B by calculating the function J

$$J \equiv \frac{B-b}{b} - Ad(\beta_{111}h + \beta_{011}) = \beta_{212}h^2Ad^2$$

and plotting the result as a function of h^2Ad^2 for the titrations $B = 25$ and 32 mM. The plot (Fig. 4) was linear within the experimental error. The slope

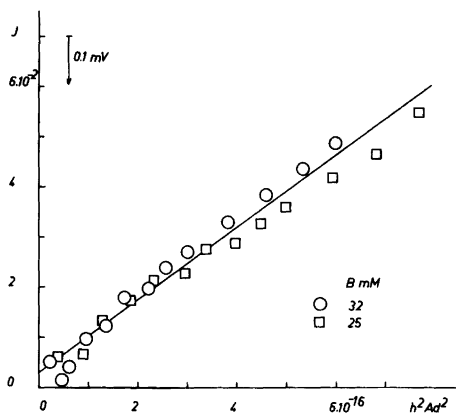
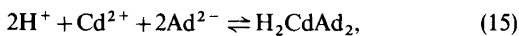


Fig. 4. Graphical estimation of β_{212} . The $J = \frac{B-b}{b} - Ad(\beta_{111}h + \beta_{011})$ term as a function of $h^2 Ad^2$.

of the line obtained gives the value of the formation constant of the species H_2CdAd_2 according to the reaction



$$\log \beta_{212} = 13.86 \pm 0.04.$$

The error limits of the constant are maximum errors, estimated graphically.

If any polynuclear complexes had also been present in a significant concentration, an intercept depending upon b respectively B would have been obtained. The fact that the intercept of the straight lines approaches zero indicates that such species are not present to any significant extent in the concentration range studied.

(b) *Normalized graphs of $Z(\log h)_{B,AD}$* . The principles of normalized curves have been described by Sillén.²⁰ Typical examples are given in Refs. 11, 17, 21, 22.

In the present work this method was applied to group 3 in order to examine which species are present under various experimental conditions. In the titrations of group 3 formation of polynuclear species is favoured. The family of the titration curves in Fig. 5 shows the data plotted as $Z(\log h)_{B,AD}$, where $Z = (H-h)/AD$. Again, there is good agreement between forward and reverse titrations.

The experimental Z curves could be explained by assuming the metal complexes $H Cd Ad^+$ and $Cd Ad$

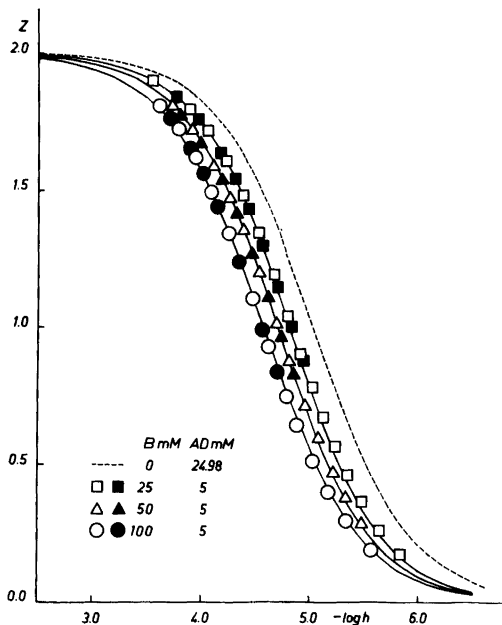


Fig. 5. Average number of H^+ bound per one mol adipic acid (Z) as a function of $-\log h$ for the $H^+ - Cd^{2+} - Ad^{2-}$ system. The full drawn curves represent the theoretical Z functions calculated with the constants $\log \beta_{11} = 5.356$, $\log \beta_{21} = 10.113$, $\log \beta_{111} = 6.68$ and $\log \beta_{011} = 1.905$. Filled symbols represent points from reverse titrations.

to be the main species besides H^+ , H_2Ad , $H Ad^-$ and Ad^{2-} . The following values for the equilibrium constants are obtained: $\log \beta_{111} = 6.71$; $\log \beta_{011} = 1.93$.

LETAGROP treatment of the data. The equilibrium models suggested by the graphical analysis has been refined by means of the generalized least squares program LETAGROP.^{23,24} The hydrolyzed species $CdOH^+$, Cd_2OH^{3+} and $Cd_4OH_4^{4+}$ found in Ref. 7 have also been introduced into the calculations.

All the data of titration groups 3 and 4 have been treated.

For the data of group 3 both the error square sums

$$U = \sum (H_{calc} - H_{exp})^2 \text{ and } U = \sum (E_{calc} - E_{obs})^2$$

were minimized supposing $H Cd Ad^+$ and $Cd Ad$ to be the cadmium-containing main species. The experimental data were introduced in the program

Table 2. Equilibrium constants estimated by graphical methods and LETAGROP.^a

Group	Graphical	LETAGROP
1		$\log \beta_{11} = 5.356 \pm 0.008$ $\log \beta_{21} = 10.113 \pm 0.006$
2	$\log \beta_{111} = 6.73 \pm 0.02$ $\log \beta_{011} = 2.00 \pm 0.03$ $\log \beta_{212} = 13.86 \pm 0.04$	
3	$\log \beta_{111} = 6.71$ $\log \beta_{011} = 1.93$	$\log \beta_{111} = 6.68 \pm 0.02$ $\log \beta_{011} = 1.905 \pm 0.008$
4	$\log \beta_{111} =$ see group 2 $\log \beta_{011} =$ see group 2	$\log \beta_{111} = 6.716 \pm 0.004$ $\log \beta_{011} = 2.01 \pm 0.01$

^a The limits of error are $\pm \log(3\sigma(\beta))$, where σ is the standard deviation. Suggested values: $\log \beta_{111} = 6.73 \pm 0.02$; $\log \beta_{011} = 2.00 \pm 0.03$.

as $(v, E_G)_{B,AD}$ pairs, where v denotes the number of the reagent solution added from one buret. A small analytical error in H , δH , was assumed. This assumption is rather likely due to the use of several solutions with different acidity levels in the adjustment of B and AD concentrations at the beginning of the titrations. The best fitting values of β_{111} and β_{011} obtained are given in Table 2. The method of calculation did not influence the values of equilibrium constants found.

A small systematic deviation can be observed in Fig. 5 between the experimental and theoretical curves which may be due to the presence of other, minor, species.

For the data pairs of $(v, E_M)_{B,AD}$ in group 4 the error square sum $U = \sum (B_{\text{calc}} - B_{\text{exp}})^2$ was minimized. A good fit was obtained by assuming HCdAd^+ and CdAd to be the cadmium adipate complexes. All errors were assumed to be random errors. The corresponding equilibrium constants can be found in Table 2.

CONCLUSIONS

As seen above the present data can be explained well by the formation of simple species: H_2Ad , HAD^- and Ad^{2-} in the H^+ -adipate system and of the metal-containing species HCdAd^+ , CdAd and H_2CdAd_2 in the H^+ - Cd(II) -adipate system. These complexes can be supposed to be the main species in the concentration ranges studied.

The present data indicate that polynuclear species like Cd_2HAD^+ , Cd_2Ad are not present to any significant extent in the solutions studied.

The ratio between the experimental consecutive dissociation constants of the adipic acid corresponds to the statistical ratio²⁵

$$\frac{K_n}{K_{n+1}} = \frac{(N-n+1)(n+1)}{(N-n)n} = 4$$

$$\frac{K_1}{K_2} = \frac{1.75 \times 10^{-5}}{0.440 \times 10^{-5}} = 3.98 \sim 4$$

indicating that electrostatic, ligand and rest effects (for terminology see Ref. 25) are small.

The adipate ion can form chelates by coordination of both carboxylate groups to the same metal ion. The identification of the type of bonding involved can be attempted by the following reasoning:

The HAD^- ion does not form chelates as it can only coordinate *via* one carboxylate group. The equilibrium constant K_1 for the reaction $\text{Cd}^{2+} + \text{HAD}^- \rightleftharpoons \text{CdHAD}$ is equal to $\log K_1 = 6.73 - 5.36 = 1.37$.

If the Ad^{2-} ion does not form chelates we expect the equilibrium constant β_{011}^{est} for the reaction $\text{Cd}^{2+} + \text{Ad}^{2-} \rightleftharpoons \text{CdAd}$ to be twice as large, *i.e.* $\beta_{011}^{\text{est}} = 2K_1 = 10^{1.67}$.

The factor two is a statistical factor caused by the equivalence of the two carboxylate groups in Ad^{2-} . The measured equilibrium constant is about twice as large as this figure. It is obvious that the supposed chelate complex CdAd would be only slightly stronger than the complex formed by the monodentate ligand. Taking into account the magnitude of β_{011} we can thus suppose that the

species CdAd to a large extent contains a *monodentate* ligand.

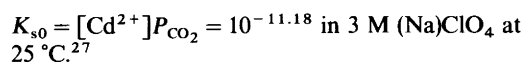
This might make possible the formation of dinuclear complexes. However, the presence of such species could not be confirmed.

The monodentate complex CdAd seems to be slightly stronger than the corresponding Cd-acetate compound.²⁶



In the final choice of values for the formation constants of the metal-containing species, the greatest weight has been given to data from groups for which measurements were made with cadmium amalgam half cells and several levels of *B* were used.

The accumulation of soluble cadmium-adipate species as pollutants in natural waters do not seem to be very probable, the weak complexations means that cadmium may be precipitated, *e.g.* by carbonate:



Comparison with the results of the previous investigations cited is made difficult by the great difference between the experimental conditions used^{1,2,3} and by the lack of detailed information on the experiments.²

The relatively high liquid junction effect observed in the present investigations at constant sodium ion concentration (3 M) is most probably due to changes in the activity factors of the H^+ and Cd^{2+} ions. Such changes might be caused either by a slight variation in the concentration of ClO_4^- or by specific ionic interactions, or possibly by both. This phenomena is under further investigation.²⁸

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