

Studies on Metal Carbonate Equilibria 24. The Hydrogen Carbonate and Carbonate Complexes of the Lead(II) and Cadmium(II) Ions in Acid Solutions and a 3 M (Na)ClO₄ Ionic Medium at 25 °C

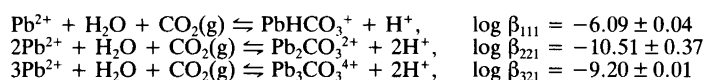
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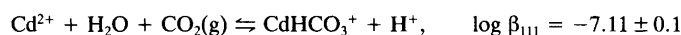
Neumann-Néher, E., 1992. Studies on Metal Carbonate Equilibria 24. The Hydrogen Carbonate and Carbonate Complexes of the Lead(II) and Cadmium(II) Ions in Acid Solutions and a 3 M (Na)ClO₄ Ionic Medium at 25 °C. – Acta Chem. Scand. 46: 231–239.

The complex formation of the systems Pb(II)–H₂O–CO₂(g) and Cd(II)–H₂O–CO₂(g) has been studied in a 3 M ClO₄[–] medium and at a temperature of 25 °C using an EMF method. The equilibrium concentration of the H⁺ ions, [H⁺] ≡ *h*, was measured using a glass electrode. The data could be explained by the chemical models given below.

In the concentration range [Pb(II)] = 0.2–0.7 M



Moreover, in the concentration range [Cd(II)] = 0.1–0.7 M



The equilibrium constants β_{ppq} refer to 3 M NaClO₄ as solvent. The errors quoted are maximum deviations evaluated graphically.

The Pb(II) and Cd(II) systems were studied in the range $3.0 < -\log h < 4.3$ and $3.0 < -\log h < 4.8$, respectively. The partial pressure of CO₂ was kept constant and had values within the range 0.1–1 atm. The procedures of liquid junction estimation and extrapolation to zero ionic strength are briefly discussed.

The magnitude of the stability constants indicates unidentate coordination of the HCO₃[–] ions, in analogy with metal acetate complexes. In the polynuclear carbonate species at least one bidentate bonding of the CO₃^{2–} ions appears.

Chemical speciation of trace heavy metals (Pb, Zn, Cd, Cu, Co, Fe, Mn and Hg) in natural waters is important in many cases, e.g. for the geochemical cycles of the elements and in problems connected with water pollution (metal uptake by plants and animals, toxicity and metal transport). The present investigation is part of a general study of metal carbonates and their relevance to the abovementioned problems.

The carbonate and the hydrogen carbonate ions are two of the most important ligands in natural waters, and they strongly affect the concentration, speciation and migration of several of the metal ions present in ground and surface water systems.

The concentration of lead in natural waters may be controlled by different processes depending on the environment. Some of these (as given in some references given in Ref. 1), such as the equilibrium solubility of some solid phases of lead, the kinetics of precipitation reactions,

cation exchange mechanisms and adsorption processes, are among those processes which take place continuously in nature.

There is a large amount of published literature on the solubility products of various carbonate-containing species.² However, information on soluble carbonates, and especially hydrogen carbonate complexes, in acidic solutions is much more limited.^{2,3}

Some authors^{3–5} reviewed in Ref. 3 tried to satisfy this need by an estimation of stability constants, for the hydrogen carbonate and carbonate complexes of some heavy metals, on the basis of different models and correlations. The information available about the soluble complexes of Pb²⁺ and Cd²⁺ ions with HCO₃[–] and CO₃^{2–} ligands can be found in Refs. 3–11. These investigations were generally carried out in the alkaline range at very low total concentrations of the metal ions: 10^{–7}–10^{–4} M. In these studies the formation of PbCO₃, Pb(CO₃)₂^{2–} and CdCO₃ was reported.

The existence of the complex PbHCO_3^+ was considered to be questionable. Moreover, hydroxy and mixed carbonate-hydroxo complexes were also found in the alkaline range.

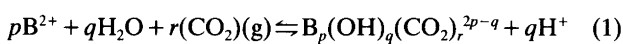
In the acid range, studied in the present paper, only the species PbHCO_3^+ , $\text{Pb}_2\text{CO}_3^{2+}$, $\text{Pb}_3\text{CO}_3^{4+}$ and CdHCO_3^+ were found.

Methodological information will also be introduced in this study. New functions will be used for the estimation of the liquid junction potential and the change of the activity factor of the potential-determining ion (H^+), defined as the liquid junction EMF. It will be proved that the technique used in this study, the so-called self-medium method,^{12,13} is free from those systematic errors¹⁴ which generally appear when other titration techniques are used.

It can be mentioned that within this series, for example, the following metal carbonate complexes were studied in this laboratory: La(III) carbonates,¹⁵ Hg(I) and Hg(II) carbonates,¹⁶ Zn(II) carbonates,^{17,18} Pb(II) carbonates in the alkaline range,¹⁰ Be(II) carbonates,¹⁹ and U(VI) and Th(IV) carbonates.²⁰

Definitions and notations

The reacting species B^{2+} , H_2O and $\text{CO}_2(\text{g})$ can form a series of (pqr) complexes with the general composition $\text{B}_p(\text{OH})_q(\text{CO}_2)_r^{2p-q}$ according to the formation reaction (1),



where $\text{OHCO}_2^- \equiv \text{HCO}_3^-$ and $(\text{OH})_2\text{CO}_2^{2-} \equiv \text{CO}_3^{2-}$. In the following, the ionic charges in subscripts will be omitted for simplicity.

B^{2+} denotes the central metal ion in the complexes studied.

β_{pqr}^{TD} denotes the formation constant of reaction (1), expressed on the activity scale (thermodynamic constant), defined by eqn. (2). The magnitude of β_{pqr}^{TD} depends on the choice of the reference or standard state for the activity coefficients.

$$\begin{aligned} \beta_{pqr}^{\text{TD}} &= [pqr][\text{H}^+]^q[\text{B}^{2+}]^{-p} a^{-r} f(pqr) f(\text{H})^q f(\text{B})^{-p} a_{\text{H}_2\text{O}}^{-q} \\ &\equiv \beta_{pqr}^{\text{B}} f(pqr) f(\text{H})^q f(\text{B})^{-p} a_{\text{H}_2\text{O}}^{-q} \end{aligned} \quad (2)$$

β_{pqr}^{B} [the conditional (so-called concentration) constant] is valid at a constant level of B(II) and at the ionic strength $I = C$ M, defined by eqn. (3). The ratio of the activity coefficients involved in eqn. (3) is generally considered to be constant.

$$\begin{aligned} \beta_{pqr}^{\text{B}} &= [pqr][\text{H}^+]^q[\text{B}^{2+}]^{-p} a^{-r} \\ &= \beta_{pqr}^{\text{TD}} f(\text{B})^p a_{\text{H}_2\text{O}}^q f(pqr)^{-1} f(\text{H})^{-q} \end{aligned} \quad (3)$$

a is the partial pressure of $\text{CO}_2(\text{g})$, in atm.

$a_{\text{H}_2\text{O}}$ is the activity of water. It can be calculated in an electrolyte mixture from the osmotic coefficient of the mixture, as described in Ref. 15. It is equal to 1 in C M NaClO_4 , according to the definition.

β_{pqr} is valid at trace levels of the species $i(c_i)$ in C M NaClO_4 as reference state. It can be determined on the basis of eqn. (3), which now takes the form of eqn. (4). Here, $\log f(i)$ values defined by eqn. (6) should be inserted.

$$\log \beta_{pqr}^{\text{B}} = \log \beta_{pqr} + p \log f(\text{B}) - \log f(pqr) - q \log f(\text{H}) \quad (4)$$

β_{pqr}^0 is the equilibrium constant in pure water as standard state for the activity factors. This can be determined through extrapolation of a suitable function to $I = 0$, using β_{pqr} values belonging to different C levels. This procedure is based upon eqn. (3), which now takes the form of eqn. (5), where $\log f(i)$ values defined by eqn. (7) should be inserted.

$$\log \beta_{pqr} = \log \beta_{pqr}^0 + p \log f(\text{B}) - \log f(pqr) - q \log f(\text{H}) \quad (5)$$

K_q are formal equilibrium constants which include the sums $\sum_{p,q} \beta_{pqr}^{\text{B}} B_T^p$ with $q = 1$ and 2 , respectively. The index T denotes total, analytical concentration.

$f(i)$ is the molar activity coefficient of ion i .

(a) If we choose C M NaClO_4 as reference state, $f(i)$ is defined so that as trace activity coefficient it goes to 1 at trace levels of c_i in C M NaClO_4 . These can be estimated on the basis of the simple specific ionic interaction theory (SIT).^{15,21-25} Therefore, we have eqn. (6) for the experimental condition $[\text{ClO}_4^-] = C$ M, constant, where the ionic interactions between i and the ClO_4^- ions, $\bar{\epsilon}(i, \text{ClO}_4)$ $\{[\text{ClO}_4^-] - C\}$, are zero and those with the HCO_3^- ions are negligible in the pH range studied.

$$\begin{aligned} \log f(i) &= -z_i^2 [D(I) - D(C)] + \bar{\epsilon}(i, \text{Na}) \{[\text{Na}^+] - C\} \\ &\quad + \bar{\epsilon}(i, \text{B}) [\text{B}^{2+}] \end{aligned} \quad (6)$$

(b) If we choose pure water as standard state, $f(i)$ is defined so that $f(i) \rightarrow 1$ as $I \rightarrow 0$. Hence we have eqn. (7). The terms $\{\dots\}_{\text{an}}$ are valid if i is an anion and $\{\dots\}_{\text{ca}}$ if i is a cation.

$$\begin{aligned} \log f(i) &= -z_i^2 [D(I) + \{\bar{\epsilon}(i, \text{Na}) [\text{Na}^+] + \bar{\epsilon}(i, \text{B}) [\text{B}^{2+}]\}_{\text{an}} \\ &\quad + \{\bar{\epsilon}(i, \text{ClO}_4) [\text{ClO}_4^-]\}_{\text{ca}}] \end{aligned} \quad (7)$$

z_i is the charge of the species i .

$D(I)$ is given by eqn. (8), and is valid on the molar concentration scale for water solvent at 25 °C. On the molal scale the coefficient is 0.5109. The term $-z_i^2 D$

(I) is the Debye–Hückel term,^{26,27} calculated with the ionic strength of the test solution, I .

$$D(I) = 0.5115 \sqrt{I}/(1 + 1.5\sqrt{I}) \quad (8)$$

$D(C)$ is the function $D(I)$ in the reference state, C M NaClO₄.

$\bar{\epsilon}(i, k)$ is the molar interaction coefficient between the ions i and k , in dm³ solution (mol solute)⁻¹.

$\epsilon(i, k)$ is the molal interaction coefficient between the ions i and k , in kg solution (mol solute)⁻¹.

I is the ionic strength, given by eqn. (9).

$$I = (1/2) \sum_i c_i z_i^2 \quad (9)$$

c_i is the molar concentration of ion i .

$b = [B^{2+}]$ is the free, equilibrium concentration of the metal ion B²⁺.

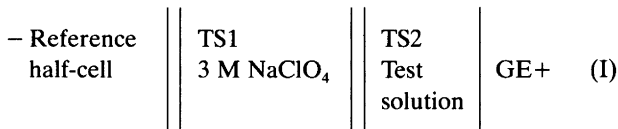
H_T is the total, analytical concentration of H⁺ ions.

Method of investigation

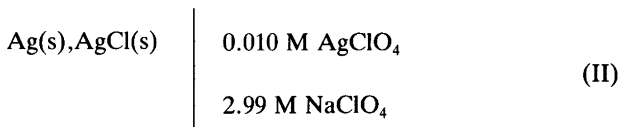
The investigation method used is similar to that described in Part 3¹² of this series.

For the determination of the formation constants in the Pb(II) or Cd(II)–H₂O–CO₂(g) systems, the self-medium method was used.^{12,13} This means that high and constant concentrations were used for the total, analytical concentration of the central metal ion: [Pb(II)] or [Cd(II)] $\equiv B_T$ ranged from 0.2 (or 0.1, respectively) to 0.7 M. The EMF measurements were carried out, for each B_T level, at two different partial pressures of CO₂(g) within the range 0.1–1 atm. The partial pressure of CO₂(g) was calculated as before.¹² All measurements were made at 25.00 \pm 0.02 °C by using the equipment described earlier.²⁸

The EMF cell used can be defined by cell (I), where GE



denotes a glass electrode. TS denotes terminal solution at the two ends of the junction studied. The composition of the reference half-cell is given by (II). The EMF of this cell



can be written as eqn. (10a), where E_{0H} is a constant,

$$E_H = E_{0H} + g \log [H^+] + g \log f(H)_{TS2} + E_D + E_{Df} \quad (10a)$$

E_D denotes the ideal diffusion potential (Henderson term), E_{Df} stands for the contribution of the changes of the activity factors to E_D and $g = (RT \ln 10/F) 10^3 = 59.16$ mV at 25 °C. The potential functions E_D and E_{Df} appear due to the presence of liquid junctions in the cell. The deduction of these terms, for cells containing mixtures of strong electrolytes and equilibrium systems, respectively, at different experimental conditions, is given in Ref. 14. It should be emphasized that all ions present in the mixture of the terminal solutions TS1 and TS2 contribute to the liquid junction EMF, defined¹⁴ by eqn. (10b). As seen, the term

$$lje_H = g \log f(H)_{TS2} + E_D + E_{Df} \quad (10b)$$

lje_H summarizes all potential anomalies appearing in EMF cells with a liquid junction. As the composition of the ionic medium is very much changed in the self-medium method, and the measured effect is very small in the present system, the contribution of lje_H to the cell EMF must be checked.

The determination of the constant E_{0H} . This was carried out in mixtures of the strong electrolytes HClO₄ + B(ClO₄)₂ + NaClO₄ in the concentration range $1 \leq [c_H \equiv \text{HClO}_4] \leq 30$ mM, using a constant level for B(ClO₄)₂. The pH of the test solution was increased by the use of X M NaOH + 3 M NaClO₄. The composition of the test solution is as follows.

$$[\text{ClO}_4^-] = C \text{ M, constant}$$

$$c_H = H_T = \text{HClO}_{4T} - \text{NaOH}_T \text{ M}$$

$$c_B = [\text{B(ClO}_4)_2] \equiv B_T \text{ M}$$

$$\begin{aligned} c_{\text{Na}} = [\text{Na}^+] &= C - \text{HClO}_{4T} - z_B B_T \\ &+ \text{NaOH}_T \equiv C - C_H - z_B c_B \text{ M.} \end{aligned}$$

For this cell, the evaluation of the liquid junction EMF results in eqn. (11) (cf. Part 4 of Ref. 14) for the total cell

$$\begin{aligned} E_H &= E_{0H} + g \log [H^+] - g[D(I) - D(C)] \\ &+ g c_B d_3 + g c_H d_4 + \text{corr} \end{aligned} \quad (11)$$

EMF. Here, d_3 and d_4 denote potential functions with constant values, in terms of some ionic equivalent conductances and interaction coefficients. These functions describe the main part of the potential contribution of the B²⁺ and H⁺ ions to lje_H , respectively. The term ‘corr’ summarizes¹⁴ the Debye–Hückel terms of the contribution of the activity coefficients to E_{Df} and is negligible at $C = 3$ M.

At $[\text{ClO}_4^-] = C$ M, constant, the ionic strength in the test solution is given by eqn. (12). As $c_B \equiv B_T$ is kept constant,

$$I = C + c_B(z_B^2 - z_B)/2 \quad (12)$$

the terms $g[D(I) - D(C)]$ and $gc_B d_3$ have constant values during the determination of E_{OH} and the study of complex formation; therefore they can be incorporated into a constant denoted E_{OH}^B . The intercept of the plot $E_H - g \log c_H - \text{corr}$ versus c_H , at constant c_B , defines the conditional constant E_{OH}^B by eqn. (13). It can be mentioned that for the

$$E_{OH}^B = E_{OH} - g[D(I) - D(C)] + gc_B d_3 \quad (13)$$

slope of this plot we obtained $SL(H, c_H) \equiv gd_4 = -17.6$ mV/M H^+ at two constant concentrations of the Pb^{2+} ions: 0.1 and 0.7 M.

The EMF of the cell during the study of complex formation.

When the determination of the constant E_{OH} was completed (the pH of the test solution was ca. 3), the titration was continued in order to study the complex formation reactions between the metal ions B^{2+} and the HCO_3^- and CO_3^{2-} ions, respectively. Volumetric titrations were carried out by adding (a) solution (1) with the composition: $2B_T$ M $B(ClO_4)_2 + c_1$ M $HClO_4 + (3 - 4B_T - c_1)$ M $NaClO_4$ and (b) solution (2) with the composition: c_2 M $NaHCO_3 + 3$ M $NaClO_4$, to the test solution in equal volumes.

As at most 1 % of B_T is bound in metal carbonate complexes, the dominating species in the test solution are B^{2+} , Na^+ and ClO_4^- . The equilibrium concentrations of the complexes formed are negligible, as is that of the ligand, $[HCO_3^-]$. Hence, we have eqns. (14) and (15) in the test

$$b = [B^{2+}] \equiv c_B \equiv B_T M$$

$$c_{Na} = C + yL_T - HY_T - z_B c_B M \quad (14)$$

$$\Delta c_{Na} = c_{Na} - C = yL_T - HY_T - z_B c_B \equiv G - z_B c_B M \quad (15)$$

solution, where Δc_{Na} is the change of the composition of the ionic medium, L_T is the total, analytical concentration of the complexing agent added in a given titration point, $[Na, L]$, in the present case $NaHCO_3$, HY_T is the total, analytical concentration of the strong acid added in a given titration point by solution (1), in the present case $HClO_4$, and G is given by eqn. (16).

$$G = yL_T - HY_T \quad (16)$$

This cell has the same concentration conditions as cells in which weak complexes are formed when using Na, L as complexing agent and the ligand comes from a weak acid. This case is examined theoretically in Section 2.c of Ref. 29. According to the deductions presented there, for the total cell EMF we obtained eqn. (17) for solutions with

$$E_H \approx E_{OH} + g \log h - g[D(I) - D(C)] + Q(H, c_B)c_B + Q(H, G)G + \text{corr} \quad (17)$$

pH ≈ 3 , where the potential contribution of the H^+ ions is neglected. Here, $Q(H, c_B)$ denotes²⁹ a function with constant value, in terms of some ionic equivalent conductances and interaction coefficients. This term describes the main part of the potential contribution of the B^{2+} ions to E_H , valid in a cell with an equilibrium system. This is, in principle, not identical with d_3 . However, if $b = B_T$, this equality is valid. Moreover, eqn. (18) holds, where λ_{Na} is

$$Q(H, G) = -g\lambda_{Na} / [2.303 C(\lambda_{Na} + \lambda_{ClO_4})] \quad (18)$$

the ionic equivalent conductance of the Na^+ ions in the test solution, and is approximated by $t_{Na}(C \text{ M } NaClO_4) \Lambda(C \text{ M } NaClO_4)$. For $C = 3$ M it has the following value: $0.43 \times 54.60 = 23.48 \text{ } \Omega^{-1} \text{ cm}^2 \text{ (g-equivalent)}^{-1}$. The term $\Lambda(C \text{ M } NaClO_4)$ denotes the equivalent conductance of $C \text{ M } NaClO_4$, and t_{Na} is the cationic transport number of $C \text{ M } NaClO_4$. The value for t_{Na} was taken from Ref. 30 and that for $\Lambda(3 \text{ M } NaClO_4)$ from Ref. 31. Hence, we have eqn. 19.

$$Q(H, G) = -3.68 \text{ mV/M } G \quad (19)$$

The magnitude of the term $Q(H, G)G$ was estimated in the last titration point of a titration where the highest B_T value (0.7 M) was used. We obtained $L_T = 12.30 \times 10^{-3} \text{ M}$, $HY_T = 5.36 \times 10^{-3} \text{ M}$ and $Q(H, G)G = -0.02 \text{ mV}$.

As seen, this potential contribution is negligible in every titration studied. For the ionic strength we have eqn. (20).

$$I \approx C + (1/2) \{h + c_B z_B^2 + yL_T - HY_T + [HCO_3^-] + \dots\} \quad (20)$$

Here, the maximum value of the term $yL_T - HY_T$ can reach $6.94 \times 10^{-3} \text{ M}$ in the present case, which is negligible. Hence, I can be described practically by the same function as during the determination of E_{OH}^B . Therefore, the use of eqn. (21) is verified for the total cell EMF during the study

$$E_H \approx E_{OH}^B + g \log h + \text{corr} \quad (21)$$

of complex formation.

As seen here, the use of the self-medium method results in a simple function for the total cell EMF, because the potential contribution of the metal ions to lje_H is constant and can be incorporated into the constant E_{OH}^B . Moreover, the contributions due to composition changes, when using a complexing agent and a strong acid, are negligible. However, this result, concerning the potential contribution of the complexing agent and the strong acid added, is not of general validity. Therefore, the magnitude of lje_H must be checked in each new system studied.

Experimental

Chemicals used.

Solutions of $NaClO_4$, $NaHCO_3$, $NaOH$, $AgClO_4$ and $HClO_4$ were prepared from reagents of analytical grade. They were analysed as described earlier.²⁸

$Pb(ClO_4)_2$ stock solutions were made by dissolving lead oxide in an excess of $HClO_4$, both Merck p.a. quality. The stock solutions were free from Cl^- impurities and were used without further purification. Their lead content was determined as $PbSO_4(s)$ by Winkler's method.³² The accuracy of the analysis was $\pm 0.1\%$.

$Cd(ClO_4)_2$ stock solution was made by dissolving CdO p.a. (Baker's Analysed Product) in a slight excess of hot $HClO_4$, Merck p.a. quality. The product was recrystallized twice. The stock solution was free from Cl^- impurities. Its cadmium content was determined as $CdNH_4PO_4 \cdot H_2O(s)$, according to Winkler's method.³² The results of the gravimetric determinations of cadmium agreed to within $\pm 0.1\%$. The hydrogen-ion concentration in the $Pb(ClO_4)_2$ and $Cd(ClO_4)_2$ stock solutions was determined potentiometrically, as described in Ref. 28, with the help of Gran plots.³³

Experimental details of the EMF measurements. As mentioned earlier, the self-medium method^{12,13} was used in the study. $B_T = 0.2\text{--}0.7\text{ M Pb}^{2+}$ and $B_T = 0.1\text{--}0.7\text{ M Cd}^{2+}$ were used in the investigations. Each potentiometric titration started with the determination of E_{0H}^B in the concentration range $[H^+] = 1\text{--}30\text{ mM}$ by using two burettes containing the solutions $X\text{ M NaOH} + 3\text{ M NaClO}_4$ and solution (1) defined in the previous section. Equal volumes were added from the burettes. These titrations were carried out in an atmosphere of $N_2(g)$ which had been passed through wash bottles containing (a) $0.1\text{ M Cr(NO}_3)_2 + c\text{ M HCl} + Zn, Hg$, (b) H_2O and (c) 3 M NaClO_4 . When the pH of the test solution was increased to ca. 3, the $N_2(g)$ was replaced by the mixture $Y\% CO_2(g) + W\% N_2(g)$, where Y was known. The titration was continued with two burettes containing solutions (1) and (2), defined previously, by adding equal volumes from the burettes. The titration was finished when a precipitate appeared. The equilibrium processes were fast: a constant EMF was obtained within 20–30 min. The EMF was measured with a Fluke multimeter, type 8840 A. A Metrohm pH glass electrode, type 6.0102.000, was used in the investigations. All measurements were carried out in a paraffin oil thermostat, at $25.00 \pm 0.02^\circ C$, in a thermostated room.

Calculations and results

The Pb(II)– H_2O – $CO_2(g)$ system. The calculation method was similar to that described in Ref. 12. Plots of $(h - H_T)/a$ versus $\log h$, shown in Fig. 1, turn out to be independent of a at a given value of B_T . Hence for the predominant species, $r = 1$.

Considering $[Pb^{2+}] = B_T$, we have eqn. (22). The data

$$(h - H_T)/a = \sum_p \sum_q q \beta_{pq1}^B B_T^p h^{-q} f(pq1)^{-1} f(Pb)^p f(H)^{-q} a_{H_2O}^2 \quad (22)$$

obtained are slightly affected by the hydrolysis of Pb^{2+} . The predominant hydrolysis products are $PbOH^+$ and $Pb_4(OH)_4^{4+}$. A correction was used for the presence of these species by using the values of $\log \beta_{110} = -7.9$ and $\log \beta_{440} = -19.25$ determined by Olin.³⁴

At constant B_T , the composition of the test solution is essentially constant. Hence, all activity factors are very near constant and we can use, first, the so-called conditional constants β_{pq1}^B . Plots of F , given by eqn. (23), versus

$$F \equiv (h - H_T - c_{110} - 4c_{440})h/a = \sum_p \sum_q q \beta_{pq1}^B B_T^p h^{-q+1} = \sum_q K_q h^{-q+1} \quad (23)$$

h^{-1} are linear, indicating the formation of complexes with $q = 1$ and $q = 2$. The definition of some of the terms appearing in eqn. (23) is given in eqns. (24)–(27) below.

$$c_{110} = (\beta_{110} B_T/h) f(Pb) f(110)^{-1} f(H)^{-1} \quad (24)$$

$$4c_{440} = (4\beta_{440} B_T^4/h^4) f(Pb)^4 f(440)^{-1} f(H)^{-4} \quad (25)$$

$$K_1 = \beta_{011} + \beta_{111}^B B_T + \beta_{211}^B B_T^2 + \dots \quad (26)$$

$$K_2 = \beta_{121}^B B_T + \beta_{221}^B B_T^2 + \dots \quad (27)$$

The intercept of the plot in question is K_1 and the slope $2K_2$. An estimation of the prevailing values of p and the equilibrium constants involved (β_{pq1}^B or β_{pq1} , respectively) was made through the study of the B_T -dependence of the formal constants K_1 and K_2 .

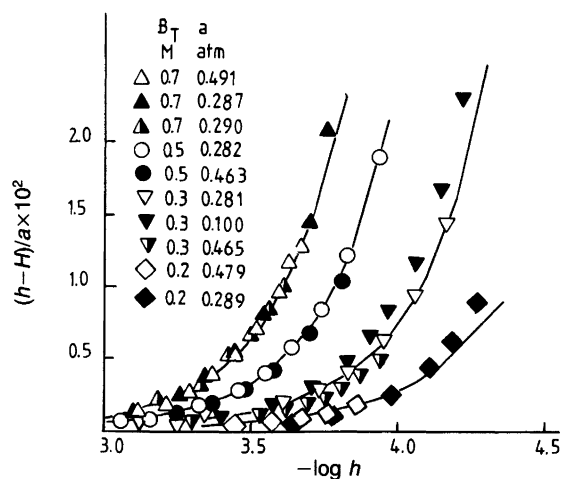


Fig. 1. The function $(h - H_T)/a$ versus $\log h$ for the $Pb(II)\text{--}H_2O\text{--}CO_2(g)$ system. Symbols are experimental points. The full drawn curves represent the theoretical functions calculated with the following formation constants: $\beta_{111}^B = 8.13 \times 10^{-7}$, $\beta_{221}^B = 3.0 \times 10^{-10}$, $\beta_{321}^B = 6.65 \times 10^{-10}$ and $\beta_{011} = 1.031 \times 10^{-8}$ (cf. Ref. 12).

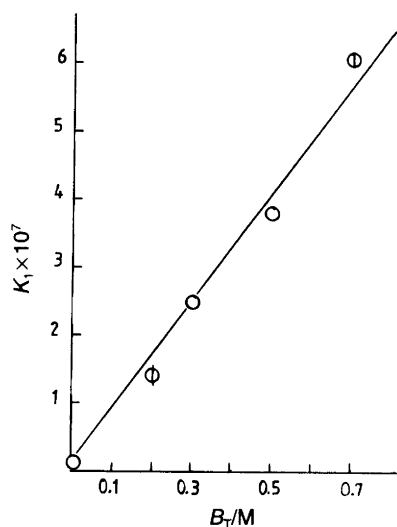


Fig. 2. Graphical determination of β_{111}^B . The formal equilibrium constant K_1 , defined by eqn. (26), is plotted as a function of B_T , for the $\text{Pb(II)}\text{-H}_2\text{O-CO}_2(\text{g})$ system. The vertical bars represent the experimental uncertainties. At $B_T = 0.3$ and 0.5 M this is smaller than the height of the symbol.

The estimation of β_{111} ($M \text{ atm}^{-1}$). A plot of K_1 versus B_T is given in Fig. 2, and is a straight line. This shows that the activity factors involved are quite constant. Moreover, the intercept of this plot is identical with β_{011} determined in 3 M NaClO_4 . This fact indicates that the activity factors are not far from unity. According to Fig. 2, the species HCO_3^- and $\text{Pb(OH)CO}_2^+ \equiv \text{PbHCO}_3^+$ exist over the whole B_T range studied, and the slope yields the constant $\log \beta_{111}^B = -6.09 \pm 0.04$. For the ratio of the activity factors involved [cf. eqn. (4)] we can calculate $1.0051 \leq f(111)f(\text{H})f(\text{Pb})^{-1} \leq 1.0328$ for the range $0.1 \leq B_T \leq 0.7$ M. These ratios are quite constant. Hence, we can consider the average value 1.0189, which results, for the equilibrium constant in a 3 M NaClO_4 reference state, in the value $\log \beta_{111} = -6.09 \pm 0.04$ on the basis of eqn. (4).

However, from the point of view of speciation of ions in surface and ground water systems, β_{pqr} values valid in the pure water standard state are important. It was proved earlier (e.g. in Ref. 15) that this extrapolation can be made on the basis of SIT. The best way to do it requires equilibrium constants measured at several C levels. In the present case, we have data only at the 3 M level of the ionic medium. However, an informative value for β_{111}^0 can nevertheless be calculated. The equilibrium constant β_{111}^B was also recalculated on the molal scale, at the different B_T levels used. However, the differences between the values belonging to the different B_T levels were less than the experimental uncertainty. Moreover, as the formula weight of 3 M NaClO_4 (367.92) is very similar to that of $\text{Pb(ClO}_4)_2$ (406.1012), their exchange results in a very small change in the molal concentration of the ClO_4^- ions. At $B_T = 0.2$ M, $m(\text{ClO}_4^-) = 3.4809$, and at $B_T = 0.8$ M, $m(\text{ClO}_4^-) = 3.4328$. Hence, an extrapolation to zero ionic strength was

not possible, from the present data, on the molal scale. Nevertheless, β_{111}^0 can be estimated from a single point, on the basis of eqn. (5), on the molar scale. Inserting the corresponding activity factor terms into eqn. (5) and after rearranging we have eqn. (28). Here, the interaction

$$\log \beta_{111}^0 = \log \beta_{111} + 2D(3) + [\bar{\epsilon}(\text{PbHCO}_3, \text{ClO}_4) + \bar{\epsilon}(\text{H}, \text{ClO}_4) - \bar{\epsilon}(\text{Pb}, \text{ClO}_4)] [\text{ClO}_4^-] \quad (28)$$

coefficient $\bar{\epsilon}(\text{PbHCO}_3, \text{ClO}_4)$ is not known. Therefore, the whole term, which includes the interaction coefficients, was taken from the $\text{Zn-H}_2\text{O-CO}_2(\text{g})$ system,¹⁷ as an approximation. Hence, we used the following interaction coefficients: $\bar{\epsilon}(\text{H}, \text{ClO}_4) = 0.18$,¹⁴ $\bar{\epsilon}(\text{Zn}, \text{ClO}_4) = 0.33$,²⁵ and $\bar{\epsilon}(\text{PbHCO}_3, \text{ClO}_4) \cong \bar{\epsilon}(\text{ZnHCO}_3, \text{ClO}_4) = 0.20$.¹⁷ Hence, we obtain $\log \beta_{111}^0 = -5.44 \pm 0.1$.

The estimation of β_{221} ($M \text{ atm}^{-1}$) and β_{321} (atm^{-1}). The investigation of the B_T -dependence of the function K_2 was made in the form of the plot $F_2 \equiv K_2/B_T^2$ versus B_T . The function F_2 is given by eqn. (29). This plot is presented

$$F_2 = \beta_{121}^B B_T^{-1} + \beta_{221}^B + \beta_{321}^B B_T + \dots \quad (29)$$

in Fig. 3. As seen, the plot can be described by a straight line. This can happen only if the species PbCO_3 ($pqr = 121$) does not exist in the solutions studied. This plot results in the conditional constant β_{221}^B as intercept and β_{321}^B as the slope of the plot in question. Hence, we obtained $\log \beta_{221}^B = -10.52 \pm 0.37$ and $\log \beta_{321}^B = -9.18 \pm 0.01$.

The ratio of the activity coefficients involved in the function describing β_{221}^B [cf. eqn. (4)] is $1.0107 \leq f(221)f(\text{H})^2 f(\text{Pb})^{-2} \leq 1.03281$ in the range $0.2 \leq B_T \leq 0.7$ M. These ratios are quite constant, and we can consider the average value = 1.0214. With this value the following equilibrium constant can be calculated, valid in 3 M NaClO_4 : $\log \beta_{221} = -10.51 \pm 0.37$.

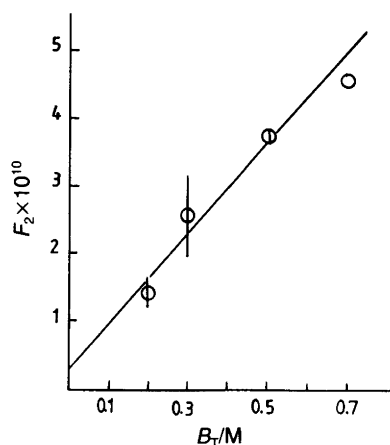


Fig. 3. The estimation of the equilibrium constants β_{221}^B and β_{321}^B . The function $F_2 \equiv K_2/B_T^2$ is plotted versus B_T , for the $\text{Pb(II)}\text{-H}_2\text{O-CO}_2(\text{g})$ system. The experimental uncertainties are given by the vertical bars. At $B_T = 0.7$ M this is smaller than the height of the symbol.

The estimation of this equilibrium constant in the pure water standard state can be made from a single point, on the molar scale, as eqn. (30) on the basis of eqn. (5). Here,

$$\log \beta_{221}^{\circ} = \log \beta_{221} + 2D(3) + [\bar{\epsilon}(\text{Pb}_2\text{CO}_3, \text{ClO}_4) + 2\bar{\epsilon}(\text{H}, \text{ClO}_4) - 2\bar{\epsilon}(\text{Pb}, \text{ClO}_4)] [\text{ClO}_4^-] \quad (30)$$

the interaction coefficient $\bar{\epsilon}(\text{Pb}_2\text{CO}_3, \text{ClO}_4)$ is not known. Therefore, the whole term, which includes the interaction coefficients, was taken from the Zn-H₂O-CO₂(g) system, as an approximation. Here we used $\bar{\epsilon}(\text{Pb}_2\text{CO}_3, \text{ClO}_4) \approx \epsilon(\text{Zn}_2\text{CO}_3, \text{ClO}_4)^{17} = 0.35$. Hence, the following value can be calculated: $\log \beta_{221}^{\circ} = -9.87 \pm 0.37$.

Concerning the equilibrium constant β_{321}^{B} , the following ratio of the activity factors is involved in the definition [cf. eqn. (4)]: $0.970 \leq f(\text{B})^{-3} f(321) f(\text{H})^2 \leq 0.907$ in the range $0.2 \leq B_T \leq 0.7$ M. These ratios are quite constant and we can consider the average value = 0.938 955. With this value the following equilibrium constant can be calculated, valid in 3 M NaClO₄: $\log \beta_{321} = -9.20 \pm 0.01$.

The estimation of this equilibrium constant in the pure water standard state can be done from a single point, on the molar scale, as eqn. (31) on the basis of eqn. (5). Here,

$$\log \beta_{321}^{\circ} = \log \beta_{321} - 6D(3) + [\bar{\epsilon}(\text{Pb}_3\text{CO}_3, \text{ClO}_4) + 2\bar{\epsilon}(\text{H}, \text{ClO}_4) - 3\bar{\epsilon}(\text{Pb}, \text{ClO}_4)] [\text{ClO}_4^-] \quad (31)$$

the interaction coefficient $\bar{\epsilon}(\text{Pb}_3\text{CO}_3, \text{ClO}_4)$ is not known. Therefore, the approximation $\bar{\epsilon}(\text{Pb}_3\text{CO}_3, \text{ClO}_4) \approx \epsilon(\text{Zn}_3\text{CO}_3, \text{ClO}_4) = 0.35$ was used, and the whole term, which includes the interaction coefficients, was taken from the Zn-H₂O-(CO₂)(g) system¹⁷ as an approximation. Hence, we obtained $\log \beta_{321}^{\circ} = -10.96 \pm 0.05$.

The Cd(II)-H₂O-CO₂(g) system. The calculation method is the same as that used for the Pb(II) system. Plots of $(h - H_T)/a$ versus $\log h$, as given in Fig. 4, turn out to be independent of a at a given value of B_T . Hence, for the predominant species, $r = 1$.

The hydrolysis of the Cd²⁺ ions is negligible in the entire $\log h$ range investigated. The plots of $(h - H_T)/a$ versus B_T turned out to be constant at constant B_T , indicating that only the species HCO₃⁻ and CdHCO₃⁺ were formed, because eqn. (32) holds. The plot of K_1 versus B_T is shown in

$$K_1 = h(h - H_T)/a = \beta_{011} + \beta_{111}^{\text{B}} B_T \quad (32)$$

Fig. 5, yielding the conditional constant β_{111}^{B} by the slope: $\log \beta_{111}^{\text{B}} = -7.12 \pm 0.1$. The intercept is again identical with β_{011} . The activity factor ratio in β_{111} is the same as that calculated for the same complex in the Pb(II)-H₂O-CO₂(g) system. Hence, we obtained $\log \beta_{111} = -7.11 \pm 0.1$. From this value, the following constant can be estimated for the

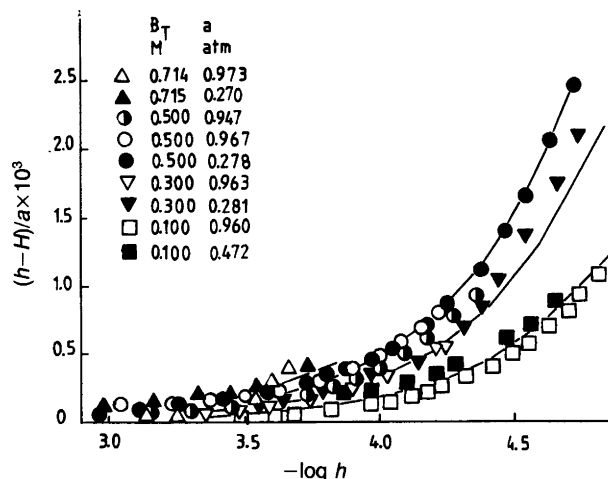


Fig. 4. The function $(h - H_T)/a$ versus $\log h$ for the Cd(II)-H₂O-CO₂(g) system. Symbols are experimental points. The full drawn curves represent the theoretical functions calculated with the formation constant $\beta_{011} = 1.031 \times 10^{-8}$ and $\beta_{111}^{\text{B}} = 7.6 \times 10^{-8}$.

pure water standard state, on the basis of eqn. (28): $\log \beta_{111}^{\circ} = -6.47 \pm 0.1$. Here, the approximation $\bar{\epsilon}(\text{CdHCO}_3, \text{ClO}_4) \approx \epsilon(\text{ZnHCO}_3, \text{ClO}_4) = 0.2$ was used,¹⁷ and the whole term, which includes the interaction coefficients, was taken from the system Zn-H₂O-(CO₂)(g).¹⁷

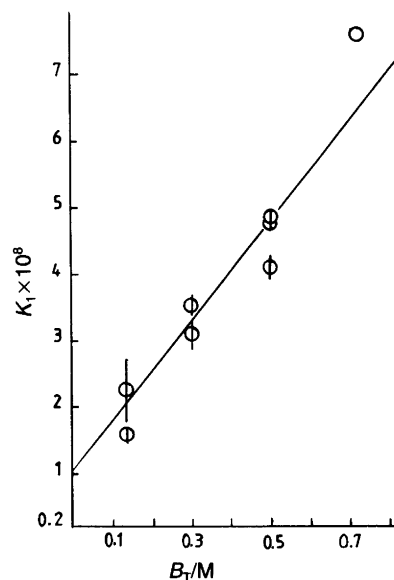
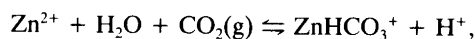


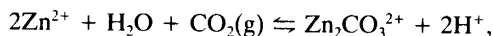
Fig. 5. Graphical determination of β_{111}^{B} for the Cd(II)-H₂O-CO₂(g) system. The function K_1 , defined by eqn. (32), is plotted against B_T . The experimental uncertainties are given by the vertical bars. At $B_T = 0.7$ M this is smaller than the height of the symbol.

Discussion

During this study, similar species were found as in the Zn-H₂O-CO₂(g) system:¹⁷



$$\log \beta_{111} = 7.70 \pm 0.05$$



$$\log \beta_{221} = -13.47 \pm 0.05$$

The charge and the composition of the ionic species formed in the Zn-containing system are similar to those found in the Pb²⁺-H₂O-CO₂(g) system. This similarity is the grounds for the estimation of unknown interaction coefficients. When using the specific ionic interaction theory for the estimation of the ionic activity factors, it is often supposed that ionic species of similar charge and composition produce similar ionic interactions. However, at present we do not have any theory which could relate the interaction coefficients to charge and structure, so the correlation is not always valid.

As the present study was proved to be free from systematic errors due to changes of the activity factors and liquid junction effects, the formation of the dimer species is verified. The formation constants found can be recalculated to the more convenient form given below, at zero ionic strength, by using the protolysis constants of H₂CO₃, valid at $I = 0$.¹⁵

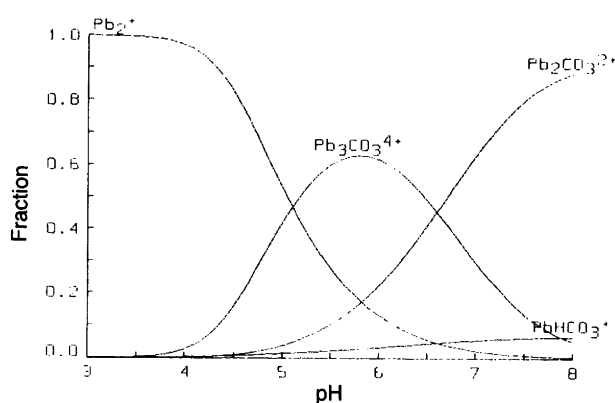
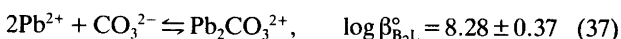
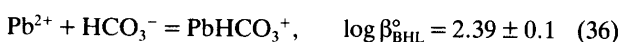
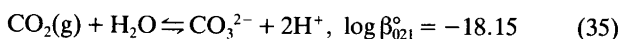
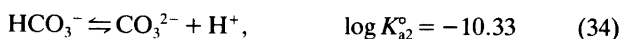
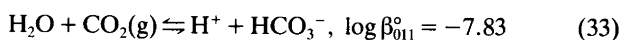


Fig. 6. The distribution of Pb²⁺ in metal-containing complexes, at the highest B_T value used. $[\text{Pb}^{2+}]_{\text{TOT}} = 700.00$ mM.

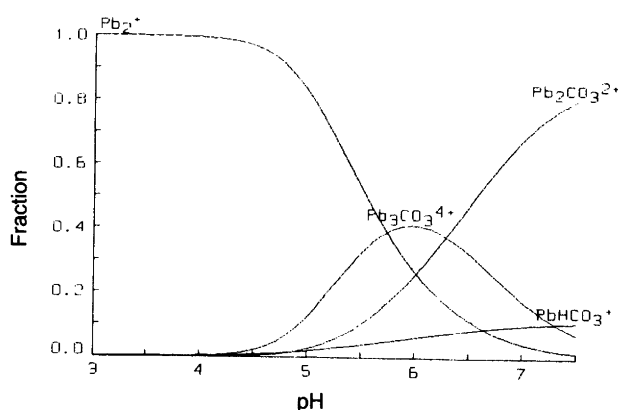
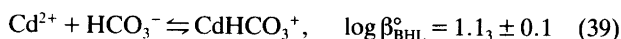
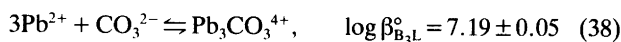


Fig. 7. The distribution of Pb²⁺ in metal-containing complexes, at the lowest B_T value used. $[\text{Pb}^{2+}]_{\text{TOT}} = 200.00$ mM.



The complex PbHCO₃⁺ is a weak one. It probably cannot be detected at concentrations of the central metal ion lower than those used in this study. It is stronger than the corresponding Zn complex¹⁷ ($\log \beta_{\text{BHL}}^\circ = 0.8 \pm 0.2$).

The formation of the species Pb₂CO₃²⁺ has not been reported in the literature until now. This complex is much stronger than the complex Zn₂CO₃²⁺, with a formation constant $\log \beta_{\text{B}_2\text{L}}^\circ = 5.1 \pm 0.2$.

The complex CdHCO₃⁺ is a very weak one. Obviously, it cannot be detected at low concentrations of Cd²⁺. This complex has not been reported in the literature.

The magnitude of the stability constants indicates unidentate coordination of HCO₃⁻ and bidentate coordination of the CO₃²⁻ ions. The value $\log \beta_{\text{BHL}}^\circ = 2.39 \pm 0.1$ of the complex PbHCO₃⁺ agrees quite well with that of the Cd(II) and Pb(II) acetate ($\equiv \text{ac}$) complexes:

Medium	$T/^\circ\text{C}$	$\log \beta_{\text{BHL}}$
Cdac ⁺ corrected to $I = 0$	25	1.928 ²
Pbac ⁺ corrected to $I = 0$	25	2.68 ²
0.1 M	25	2.1 ²

The complex Pb₂CO₃²⁺ seems to have bonding that is similar to the corresponding B(III)₂CO₃⁴⁺ complex previously studied.¹⁵ The calculated functions $(h - H_T)/a$ versus $\log h$ fit well to the experimental points.

The distribution of Pb²⁺ in metal-containing complexes at $[\text{Pb}^{2+}_T] = 0.7$ and 0.2 M, moreover at $a = 0.3$ atm, with all of these concentrations kept constant, is shown in Figs 6 and 7. These distribution curves were calculated with the computer program SOLGASWATER.³⁵ As seen, the fractions of the polynuclear species Pb₂CO₃²⁺ and Pb₃CO₃⁴⁺ are quite dominant.

The distribution of Cd²⁺ in metal-containing species at

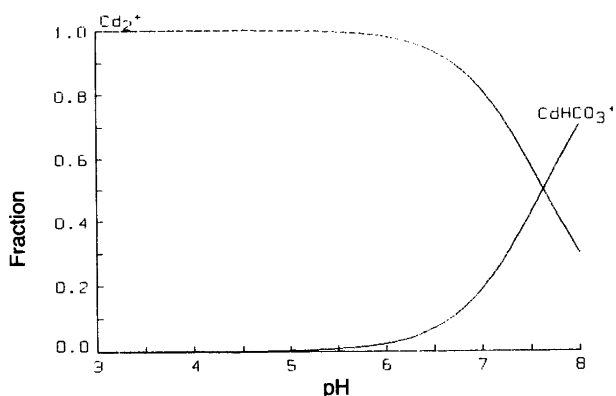


Fig. 8. The distribution of Cd^{2+} in metal-containing species, at the highest B_T value used. $[\text{Cd}^{2+}]_{\text{TOT}} = 700.00 \text{ mM}$.

$[\text{Cd}_T^{2+}] = 0.7 \text{ M}$ and $a = 0.3$ at m , is shown in Fig. 8.

The fractions of B^{2+} in metal-containing species was calculated from eqns. (40) and (41).

$$c_{pq1} = \beta_{pq1} [\text{B}^{2+}]^p a h^{-q} \quad (40)$$

$$\text{Fraction}_{pq1} = \frac{pc_{pq1}}{B_T} \quad (41)$$

The accuracy of the equilibrium constants obtained is quite satisfactory, in spite of the fact that the ligands HCO_3^- and CO_3^{2-} and the complex species are present in minor concentrations. This is due to the self-medium method used and the useful properties of the function studied: $(h - H_T)/a = f(\text{B}^{2+}, h)$. It may be pointed out that the variables of these functions: h , H_T , $[\text{B}_T^{2+}]$ and a , are known with good accuracy.

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