

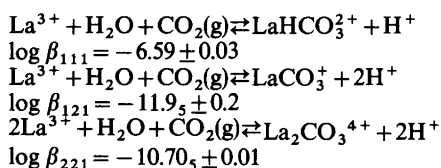
Studies on Metal Carbonate Equilibria. 3. The Lanthanum(III) Carbonate Complexes in Aqueous Perchlorate Media

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The complex formation equilibria were studied at 25 °C by measuring the hydrogen ion concentration of lanthanum perchlorate solutions saturated with CO₂–N₂ mixtures of known composition. The [La(III)] ranged from 0.1 to 1 M, while the partial pressure of CO₂ varied between 0.1 and 0.98 atm. All the test solutions were prepared to contain 3 M ClO₄⁻ by adding NaClO₄.

The emf data may be explained by assuming the equilibria



The effects on the constants of medium changes caused by the replacement of a large part of Na⁺ with La³⁺ were estimated by the specific interaction theory (SIT).¹

Only less than 1 % of the La³⁺ ion can be transformed into complexes without the formation of solid carbonates.

Our interest in metal carbonate chemistry has both fundamental and applied aspects. The fundamental problems probed are mainly the evaluation of the chemical composition and the equilibrium-constants of the species formed in metal–carbonate solutions, and the mode of bonding of the carbonate ion in solutions.

The applied aspects of main interest to us are related to metal migration in ground water. It is experimentally very difficult to determine the composition of the species formed in very dilute solu-

tions, as those obtained in most ground waters. Hence, our approach has been to determine the chemical composition of the species formed by using the ionic medium method. If we make the reasonable assumption that no other complexes are formed in solutions of low ionic strength, the results obtained in the presence of a concentrated ionic medium can be extended to such a system as ground water (*e.g.* by using the SIT¹ as shown in a following section of this work).

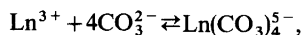
The study of complex formation in the system lanthanoid(III)–water–carbonate is complicated by the formation of a number of sparingly soluble phases and the possible occurrence of ternary complexes containing OH⁻, HCO₃⁻ or CO₃²⁻ as ligands. A review of some of the older literature in the field has been given by Krishnamurty *et al.*²

The experimental methods used include ion-exchange and spectrophotometry. The ion-exchange studies have been made at very low total concentrations of metal in order to avoid the formation of solid phases, while the spectrophotometric studies have been performed at very high concentrations of carbonate (0.2–5 M), where fairly large total concentrations of metal may be used. From these studies it was only possible to determine the stoichiometry of the limiting complex: Ln(CO₃)₄⁵⁻ was suggested by Poluektov and Kononenko.³

Sherry and Marinsky⁴ determined stability constants for a series of mononuclear lanthanoid bicarbonate complexes and some carbonate and mixed carbonate/hydroxide complexes using the ion exchange technique.

The more recent studies of the lanthanoid carbonate system include extraction studies by Dumon-

ceau *et al.*⁵ from which the overall stability constant for the reaction



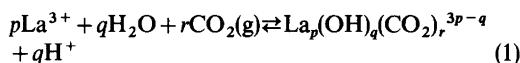
where $\text{Ln}^{3+} = \text{Sc}$ and all lanthanoids except Ce and Pm, was determined.

By using the experimental methods described above, it is difficult to obtain a unique chemical model for the complex formation, *i.e.* the stoichiometry of the complexes formed and their stability constants. This fact will, of course, impair any chemical discussion of the possible mode of bonding of the ligands and the geometry of the complexes.

This study has been undertaken in order to obtain precise information about the composition and stability constants in the lanthanoid(III) carbonate system at $\text{pH} < 4$. Lanthanum(III) was chosen as a model and was studied by the emf technique previously described in a study of the uranium(VI) carbonate system.⁶

NOTATIONS

The reacting species La^{3+} , H_2O and $\text{CO}_2(\text{g})$ form a series of complexes $\text{La}_p(\text{OH})_q(\text{CO}_2)_r$, $3p-q$. The equilibrium constant on the molar scale for eqn. (1) is β_{pqr} . The species $(\text{OH})\text{CO}_2^- (\equiv \text{HCO}_3^-)$



and $(\text{OH})_2\text{CO}_2^{2-} (\equiv \text{CO}_3^{2-})$ have the formation constants β_{011} and β_{021} , respectively.

Other symbols frequently used in the text are

- a = partial pressure of CO_2
- B = molar concentration of $\text{La}(\text{III})$
- b = molar concentration of La^{3+}
- β_{pqr} = equilibrium constant of (1) on the molal scale
- $\alpha(i,x)$ = interaction coefficient between the species i and x
- $f(i)$ = molar activity coefficient of i , defined so that $f(i) \rightarrow 1$ as $[i] \rightarrow 0$ in the solvent 3 M NaClO_4
- $\gamma(i)$ = molal activity coefficient of i , defined so that $\gamma(i) \rightarrow 1$ as $m_i \rightarrow 0$ in the solvent 3 M $\text{NaClO}_4 \equiv 3.489 \text{ mol/kg}$.
- h = molar concentration of H^+
- H = analytical excess of $\text{H}^+ = [\text{ClO}_4^-] - [\text{Na}^+] - 3B$
- $[i]$ = molar concentration of i

K_q = formation constant for all species containing q OH groups on the molar scale

${}^\circ K_q$ = as K_q , but expressed on the molal scale

m_i = molality of i

μ_c = number of micromoles of OH^- generated by electrolysis

μ_a = number of micromoles of H^+ generated by electrolysis

METHOD

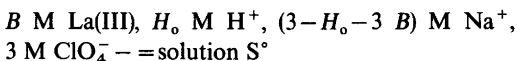
To study the equilibria, the hydrogen ion concentration of lanthanum(III) perchlorate solutions, saturated with N_2-CO_2 mixtures of accurately known composition, was measured with a glass electrode. The $[\text{La}(\text{III})]$ of the test solutions varied between 0.1 and 1 M, whereas the partial pressure of CO_2 ranged from 0.1 to 0.98 atm. At each $[\text{La}(\text{III})]$ and CO_2 pressure investigated, the acidity was decreased from a value where the complex formation is negligible, to low enough values for solid lanthanum carbonates to start to form. All the test solutions were prepared to contain 3 M ClO_4^- by adding NaClO_4 .

Preliminary experiments indicated that the complex formation is negligible at $\log h > -3$ and that less than 1 % of the $[\text{La}(\text{III})]$ can be transformed into reaction products before the appearance of a solid $\text{La}_2(\text{CO}_3)_3$ phase. Hence, clear, precipitate-free solutions are poorly buffered and considerable care had to be taken to keep protolytic contamination to a minimum.

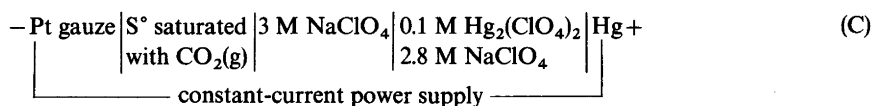
The experience, gained in previous studies⁷⁻⁹ of the hydrolysis of metal ions which behave as weak acids and form hydroxides of low solubility, was of great value. Test solutions in a state of high purity were obtained by generating OH^- or H^+ ions with constant-current coulometry. Stable and reproducible emf data could be measured even in solutions where the concentration of H^+ set free by reaction (1), $h-H$, had values as low as 20 μM .

Preparation of the test solutions

First, a solution of the composition



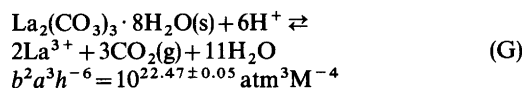
was prepared. H_0 was not precisely known at this moment, although the stock solutions from which S° was obtained were prepared so that H_0 should be about 1 mM or less. The accurate determination



of H_0 is obtained from the emf measurements described in the next section. V_0 cm³ of S° were then saturated with CO_2 of the chosen pressure, and its acidity was slowly decreased by electrolysis with the coulometric circuit (C).

To avoid local excess of OH^- on the Pt net, which might cause the premature precipitation of lanthanum carbonates or oxides, it was found advantageous to carry out the electrolysis at a rate not exceeding 10^{-3} $\mu\text{F/s}$ on Pt gauzes of 1 cm². Under these conditions, clear solutions with h values very close to the precipitation point could be obtained.

The electrolysis was continued until an h close to the value where solid lanthanum carbonate was formed. This h value was calculated from the equilibrium constant for the reaction



evaluated from unpublished experiments in 3 M NaClO_4 at 25 °C.

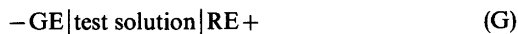
In the first stage of this study, the alkalification was performed in steps, and after each step, the equilibrium concentration of H^+ was measured. However, an experiment took more than 1 day by this procedure. Therefore, it proved more convenient to accomplish, firstly, an alkalification in one single step, usually overnight, until the solution had an $h-H$ close to the maximal value. The acidity of this solution was then increased by coulometric generation of H^+ in the circuit (C) with reversed polarities. The H values are given by

$$H = H_0 + (\mu_a - \mu_c) \times 10^{-3} V_0^{-1} \quad (2)$$

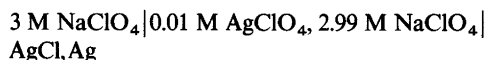
where μ_a and μ_c are, respectively, the micro mol of H^+ and OH^- generated coulometrically. After each increment of μ_c the equilibrium emf was measured.

Measurement of the hydrogen ion concentration

The hydrogen ion concentration of the test solutions was determined by measuring the emf of the cell



where GE denotes glass electrode and RE represents the reference half-cell



At 25 °C, the emf of cell (G) may be expressed by eqn. (3), where E_0 is a constant in each experiment,

$$E = E_0' - 59.16 \log h - 59.16 \log f(\text{H}^+) + E_j \quad (3)$$

E_j is the liquid junction potential arising at the boundary between the test solution and 3 M NaClO_4 .

Since at constant B the composition of the test solution changes only slightly when the complex formation takes place, we may, in each series of experiments, neglect the variation of $f(\text{H}^+)$ and calculate $\log h$ by the simplified form of (3): eqn. (4), where the $f(\text{H}^+)$ term is included in E_0 .

$$E = E_0 - 59.16 \log h + E_j \quad (4)$$

The junction potential is a function of both h and B . In a study of the hydrolysis of the La^{3+} ion in 3 M (Li^+ , La^{3+}) ClO_4^- media, Biedermann and Ciavatta⁷ found no appreciable difference between the potentials at the following boundaries: h M H^+ , $(3-h)$ M Li^+ , 3 M ClO_4^- | 3 M LiClO_4 and 0.967 M La^{3+} , h M H^+ , $(0.1-h)$ M Li^+ , 3 M ClO_4^- | 3 M LiClO_4 for solutions of $h < 10^{-2}$ M. We have here assumed a similar situation when Na^+ replaces Li^+ . For the estimation of E_j we have employed the relationship $E_j(0, h) = 16.9 h$ determined by Biedermann and Sillén.¹⁰ In the acidity range studied, $\log h \leq -3$, this is certainly a good approximation, since E_j attains a maximum value comparable to the uncertainty of the emf measurements ± 0.02 mV.

Each series of the emf measurements, which were performed as potentiometric titrations, was divided into two parts. In the first, measurements were made in the $\log h$ range from -4.3 to -3 in solutions saturated with CO_2-N_2 . In the second part, CO_2 was completely removed by pure N_2 and emf measurements in the $\log h$ range from -3 to -4.5

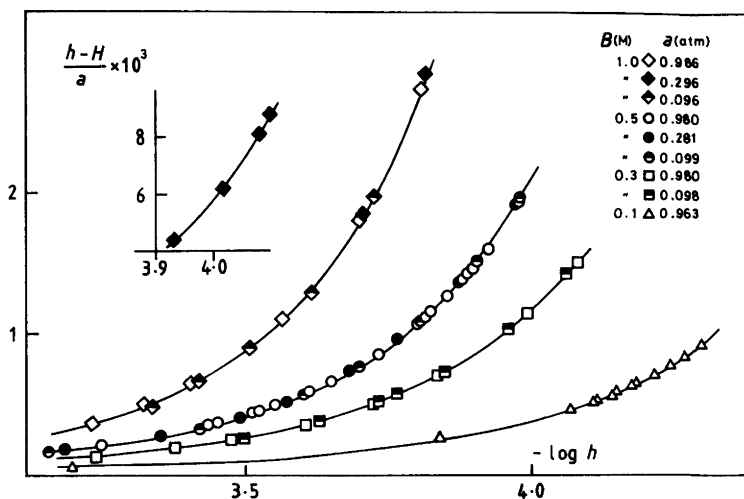


Fig. 1. The data $(h-H)/a$ as a function of $\log h$. The curves have been calculated using the expressions given in the eqns. (22)–(25).

were used to evaluate E_0 and H_0 in solution S_0 .

From the data of the second part, an accurate value of H_0 was calculated by extrapolating a Gran¹¹ plot of $10^{-E/59.16}$ vs. $\mu_c - \mu_a$. Then E_0 was evaluated for each point using (4) and $h = H_0$. E_0 values constant to 0.05 mV or better were found. As a check the E_0 and H_0 values were calculated on the basis of the principle of the least squares by minimizing the sum $\Sigma(E - E_{\text{calc}})^2$ where E_{calc} is a value estimated from a pair (E_0, H_0) . The results coincided with those deduced by the graphical procedure.

After determination of the E_0 and H_0 values, we could evaluate $\log h$ using (4) and H using (2), for each of the experimental points of the first part of the titration. Thus, we had all the information required to construct the $(h-H)(\log h)_{a,B}$ function which forms the basis of the following calculations.

It is important, at this point, to note the agreement between $(h-H)(\log h)$ data, obtained by increasing the acidity of the test solution with those measured during the alkalification of solution S_0 (c.f. Fig. 1). This may be invoked as proof of the attainment of true equilibria in our solutions.

EXPERIMENTAL

Materials and analysis

Lanthanum(III) perchlorate solutions were made from lanthanum(III) oxide of 99.995% optical grade

quality furnished by KEBO AB, Stockholm. This product was found to contain some carbonate which could be completely removed by bubbling pure nitrogen through the slightly acid solutions.

A series of 1.5 M stock solutions was prepared by dissolving the oxide in a slight excess of 5 M HClO_4 . The excess of perchloric acid was then adjusted to a value of about 2mM by adding either small amounts of lanthanum oxide or dilute HClO_4 . The exact value of the hydrogen ion concentration was determined by titrating a weighed amount of the stock solution with coulometrically generated OH^- ions, the end-point was obtained potentiometrically by using a glass electrode.

The $[\text{La(III)}]$ of the stock solutions was determined volumetrically by titrations with EDTA using xylenol orange as visual indicator. The analyses were performed by following the description given by Kolthoff and Elving.¹² The results were reproducible to within 0.1% or better. The EDTA solutions were standardized against lead(II) nitrate prepared by dissolving weighed amounts of 5 N quality lead metal in HNO_3 .

The nitrogen-carbon dioxide mixtures as well as the NaClO_4 , HClO_4 and AgClO_4 stock solutions were obtained and analyzed as described in a previous work.⁶ The equilibrium values of the partial pressure of CO_2 were evaluated by multiplying the CO_2 percentage by the atmospheric pressure corrected for the vapour pressure of water over 3 M NaClO_4 , 0.0276 atm at 25°C. This value was assumed unchanged when La^{3+} ions replace Na^+ of the medium.

Table 1. Survey of the $(h-H)$ $(\log h)_{B,a}$ data. $B=1\text{ M}$ $a=0.9862 \pm 0.0004\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 0.3561(3.230); 0.4981(3.334); 0.6391(3.413); 1.084(3.566); 1.793(3.704); 2.683(3.811). $a=0.2961 \pm 0.0001\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 2.608(4.100); 2.388(4.080); 1.841(4.018); 1.302(3.932); 0.833(3.820); 0.5420(3.707); $a=0.0959_1 \pm 0.00002\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 0.187₅(3.727); 0.1283(3.619); 0.0862(3.509) 0.0638(3.419); 0.0473(3.334). $B=0.5\text{ M}$ $a=0.9758 \pm 0.0004\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 1.863(3.979); 1.541(3.927); 1.331(3.880); 1.214(3.854); 1.110(3.825); 1.418(3.899); 1.072(3.816); 0.8233(3.735); 0.6377(3.653); 0.4720(3.552); 0.3569(3.453); 0.1980(3.247); 0.1174(3.066). $a=0.9836 \pm 0.0004\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 1.388(3.89₂); 1.043(3.806); 0.7496(3.702); 0.5710(3.613); 0.4391(3.5252); 0.3401(3.435). $a=0.2811 \pm 0.0001\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 0.5368(3.978); 0.3783(3.875); 0.2662(3.769); 0.2033(3.684); 0.1436(3.573); 0.1128(3.490); 0.0768(3.353); 0.0476(3.183). $a=0.0994 \pm 0.0001\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 0.1927(3.980); 0.1499(3.906); 0.1074(3.806); 0.0763(3.700); 0.0564(3.605); 0.0432(3.518); 0.0324(3.421); 0.0146(3.156). $B=0.3\text{ M}$ $a=0.9803 \pm 0.0002\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 1.457(4.083); 1.102(3.996); 0.6791(3.840); 0.4971(3.729); 0.3524(3.607); 0.2495(3.481); 0.1893(3.377); 0.1376(3.242). $a=0.0983 \pm 0.0001\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 0.0561(3.768); 0.1394(4.066); 0.1001(3.963); 0.070(3.850); 0.0511(3.735); 0.0379(3.632); 0.0252(3.503). $B=0.1\text{ M}$ $a=0.9644 \pm 0.0004\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 0.0551(3.199); 0.2637(3.842); 0.4738(4.071); 0.5244(4.109); 0.5796(4.147); 0.6325(4.178); 0.5739(4.143). $a=0.9625 \pm 0.0001\text{ atm}$ $(h-H) \times 10^3$ ($-\log h$): 0.5143(4.113); 0.6204(4.182); 0.6792(4.214); 0.7351(4.242); 0.7951(4.268); 0.8735(4.300).

Experimental details

All the emf measurements were carried out in a silicone oil thermostat at 25.00 ± 0.01 °C. The cell arrangement was similar to that described by

Forsling *et al.*¹³ The silver, silver chloride electrodes were prepared according to Brown.¹⁴ The glass electrodes Beckman were of the GP type. The E values were measured with a precision of 0.01 mV using a Dynamco Ltd. 2022 Digital Voltmeter.

After the generation of OH^- or H^+ ions, E became constant within 10 min and remained constant within 0.05 mV for at least 12 h. The reproducibility of $E - E_0$ was better than 0.1 mV.

In the coulometric circuit (C), a platinum gauze served as the working electrode, while the bridge solution and the auxiliary electrode (a mercury pool) were placed in a half-cell vessel of the "Wilhelm" type. The current source was a Metrohm E211A coulometer. The constancy and accuracy of the current was frequently checked by passing the current through a standard resistance and measuring the resulting potential with the digital voltmeter. Each of the current levels used, ranging between 0.1 and 3 mA, was found to be constant and accurate to within 0.02 %.

DATA AND CALCULATIONS

The experimental data $(h-H)_{a,B}$, which are collected in Table 1, are the starting point for the evaluation of the (pqr) coefficients in the reaction products and of the β_{pqr} constants. In the calculations, the concentration of CO_3^{2-} as well as of hydrolytic complexes $(pq0)$ were neglected. This is permissible in the acidity range investigated as estimated from the protolysis constants of carbonic acid, determined by Nilsson *et al.*¹⁵ and from Biedermann and Ciavatta's study⁷ on the hydrolysis of the La^{3+} ion.

Fig. 1 shows that the plots of $(h-H)/a$ vs. $\log h$ give points on the same curve for different a at $b \sim B = \text{constant}$. This implies the predominance of species with $r=1$, i.e. $\text{La}_p(\text{OH})_q\text{CO}_2^{3p-q}$.

The deduction of the principal (p,q) and β_{pqr} values was carried out in three steps. In the first step, each set of data obtained at a particular B level was evaluated by the self-medium approach suggested by Hietanen and Sillén.¹⁶ By this method, one obtains the number of OH^- groups in the reaction products, q , and the formation constants of species having a common $q, \kappa_q(B)$.

An estimate of the number of lanthanum atoms in the complexes, p , was obtained by analyzing the $\kappa_q(B)$ functions. In the first estimate, we disregarded the variation of the activity factors caused by the replacement of a large part of the inert cation (Na^+) with the reacting ion. κ_q is then a power series of the single variable B , and, provided the series contains no more than 2 or 3 terms, reasonable values of the exponents of B can easily be found.

More accurate conclusions concerning the existence of minor species and the refinement of the

equilibrium constants were obtained after estimation of the medium changes with the SIT^1 (the specific interaction theory).

I. Calculation of q . Treatment of the data by the self-medium method

In this section, each set of the $((h-H)/a) (\log h)_B$ data is examined separately.

At each B level studied, less than 1 % of the $\text{La}(\text{III})$ is present as reaction products. Consequently, in the general expression (5) the activity coefficients may be regarded as constant and in the first approximation

$$\frac{h-H}{a} = \sum_p \sum_q q \beta_{pq1} b^p h^{-q} f^{-1}(p,q) f^p(\text{La}^{3+}) f^{-q}(\text{H}^+) \quad (5)$$

$$b = B \quad (6)$$

Eqn. (5) can then be rewritten to eqn. (7), where κ_q is given in eqn. (8).

$$\frac{h-H}{a} = \sum_q q \kappa_q h^{-q} \quad (7)$$

$$\kappa_q = \sum_{p=0} \beta_{pq1} f^{-1}(p,q) f^p(\text{La}^{3+}) f^{-q}(\text{H}^+) B^p \quad (8)$$

Eqn. (7) is the basis for the model functions which compared with the experimental data furnish the most probable values of q and the formal constants κ_q .

First, we made an attempt to explain the data in the simplest way by assuming a single value of q .

In the entire $\frac{(h-H)}{a}$ range studied, no satisfactory agreement was found with any of the q values in the interval from 1 to 4. The shape of the $\frac{h-H}{a} (\log h)$ graphs was intermediate between those of the model curves calculated with $q=1$ and 2. Hence, the model function $y (\log u)$, cf. eqns (9) and (10), were calculated. These functions were obtained by assuming

$$y = \log \left[\frac{(h-H)}{a} h \right] - \log \kappa_1 = \log(1+u) \quad (9)$$

$$\log u = \log [2\kappa_2/(\kappa_1 h)] \quad (10)$$

Table 2. Survey of the κ_1 and κ_2 constants. The errors quoted are maximum deviations from the mean values.

B, M	$-\log \kappa_1^a$	$-\log \kappa_1^b$	$-\log \kappa_2^a$	$-\log \kappa_2^b$
1	6.86 ± 0.02	6.87 ± 0.02	10.66 ± 0.01	10.65 ± 0.01
0.5	7.02 ± 0.01	7.02 ± 0.01	11.25 ± 0.01	11.25 ± 0.01
0.3	7.14 ± 0.01	7.14 ± 0.01	11.68 ± 0.02	11.67 ± 0.02
0.1	7.47 ± 0.01	7.48 ± 0.01	12.54 ± 0.03	12.49 ± 0.03

^a Using the approximation $b=B$. ^b Using the approximation $b=B-(h-H)$.

that only species with $q=1$ and 2 are important, and they were found to agree satisfactorily with the experimental data. We may thus conclude that the data at the present level of accuracy may be explained by the presence of the species $(p',1,1)$ and $(p'',2,1)$.

The values of κ_1 and κ_2 were evaluated from the differences $y - \log [(h-H)h/a]$ and $\log u + \log h$ read off in the position of best fit. The results of the calculations are given in Table 2. The uncertainties of these constants and those in the following are maximum deviations from the mean value.

The calculations presented so far rest on the approximation $b=B$. In order to get an idea of the error introduced by this approximation, the calculations were repeated using eqn. (11) (*c.f.* the next

$$b = B - (h - H) \quad (11)$$

sections). From Table 2, it is evident that the constants evaluated using (6) or (11) were very similar. However, the values of κ_1 and κ_2 obtained from (11) are selected as the basis of the following treatment.

II. Estimation of the prevailing values of p

In order to evaluate the number of lanthanum atoms in the reaction products, the dependence of κ_1 and κ_2 on B was examined by using equation (8). Clearly, correct conclusions on the p and β_{pq} values may be reached only if we are able to estimate the changes of the activity factors obtained through the substitution of Na^+ with La^{3+} . However, since p is a small integer,^a the determination of the number of La^{3+} ions in the predominating complexes should not be affected appreciably by neglecting the activity factor variation. On the other hand, such

^a From structural considerations, it seems improbable the presence of more than 2La^{3+} per OH^- ion in each species, *i.e.* p values greater than 4.

changes cannot be ignored, if the evaluation of p for minor species and if more accurate values of the equilibrium constants are required. The calculations presented in this section have been made by assuming a constant activity factor ratio in equation (8). Medium effects are taken into account in the subsequent section as it was impossible to consider them simultaneously with the evaluation of p .

With these assumptions, eqn. (8) for $q=1$ may be written as eqn. (12).

$$\kappa_1 = \beta_{011} + \beta_{111}B + \beta_{211}B^2 + \dots \quad (12)$$

Fig. 2 shows the dependence of κ_1 on B . It is seen that for $B \leq 0.3$ M, the points lie within the limits of experimental errors, on a straight line. (The experimental point at $B=0$ $\beta_{011} = 1.03 \times 10^{-8} \text{ M}^2 \text{ atm}^{-1}$ has been determined separately.⁶) This means that at least one species LaOHCO_2^+ is present with $\beta_{111} = 10^{-6.7 \pm 0.1} \text{ M atm}^{-1}$ estimated from the slope of the straight line.

The deviations from the linear behaviour at $B > 0.3$ M cannot be accounted for in terms of additional $(p,1,1)$ complexes, because the points in Fig. 2 deviate in a direction opposite to that indicated by eqn (12). The variation of κ_1 with B can instead be explained in terms of medium effects on the equilibria, *c.f.* eqn. (8).

Eqn. (8) for $q=2$ can be rearranged to

$$\kappa_2 B^{-2} = \beta_{121} B^{-1} + \beta_{221} + \dots \quad (13)$$

From the plot of $\kappa_2 B^{-2}$ against B^{-1} , represented graphically in Fig. 3, the equilibrium constant β_{221} is obtained as the intercept and β_{121} as the slope. The error in the slope is fairly large and this is partly due to the fact that the complex $\text{La}(\text{OH})_2\text{CO}_2^+$ is a minor species. However, the present treatment is based on the hypothesis that the activity factors remain constant, and it is not suitable for the individuation of minor species. As shown in the next section, the variation of $\kappa_2 B^{-2}$ with B^{-1} cannot be entirely

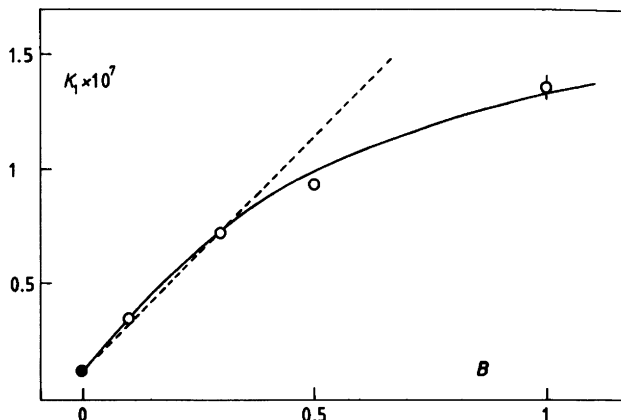


Fig. 2. κ_1 as a function of B (mol/l). The straight line represents $1.03 \times 10^{-8} + 2.1 \times 10^{-7} B$. The full drawn curve has been calculated with the expressions (22) and (23). The filled circle has been obtained in a separate study.⁶ The dashed curve is the expected functional behavior in the absence of medium effects due to the replacement of Na^+ by La^{3+} .

explained in terms of activity factor changes, thus indicating the presence of $\text{La}(\text{OH})_2\text{CO}_2^+$. We propose here

$$\log \beta_{221} = -10.67 \pm 0.03$$

$$\log \beta_{121} = -11.9 \pm 0.3$$

estimated from the slope and the intercept of the best straight line through the points of Fig. 3.

III. On the existence of minor species. Refinement of the equilibrium constants

The calculations presented in the preceding sections have indicated that the predominating complexes are LaOHCO_2^+ and $\text{La}_2(\text{OH})_2\text{CO}_2^+$, while no certain conclusions on the presence of $\text{La}(\text{OH})_2\text{CO}_2^+$ could be drawn because of the significant changes in the ionic medium. In this paragraph, the existence of the minor species is proved, and accurate values of the β_{pq1} constants are determined by introducing corrections for the medium changes on the basis of the SIT.¹

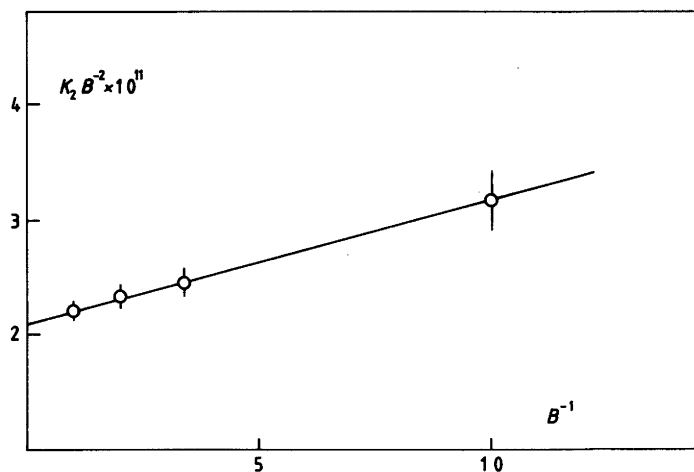


Fig. 3. $\kappa_2 B^{-2}$ as a function of B^{-1} (1/mol). The line represents $2.1 \times 10^{-11} + 1.26 \times 10^{-12} B^{-1}$.

In order to apply the SIT, quantities on the molal scale are required. The transformation from the molar to the molal scale is achieved through the densities of the solutions. We found experimentally the simple relationship

$$d = 1.2271 + 0.1014B$$

where d , the density, is expressed in g/cm^3 .

According to the theory, the activity coefficient, $\gamma(i)$, of the species i , defined so that $\gamma(i) \rightarrow 1$ as $m_i \rightarrow 0$ in the solvent 3 M $\text{NaClO}_4 \equiv 3.489$ mol/kg, may be expressed, in $\text{NaClO}_4 - \text{La}(\text{ClO}_4)_3$ mixtures of ionic strength 1 mol/kg, as

$$\log \gamma = -z_i^2(D - 0.2510) + \varepsilon(i, \text{Na}^+)(m_{\text{Na}^+} - 3.489) + \varepsilon(i, \text{ClO}_4^-)(m_{\text{ClO}_4^-} - 3.489) + \varepsilon(i, \text{La}^{3+})m_{\text{La}^{3+}} \quad (14)$$

in which z_i is the charge, $D = 0.5109\sqrt{I}/(1 + 1.5\sqrt{I})$ and ε is the symbol of the interaction coefficient.

The basic idea of the theory is that $\varepsilon(i, x) = 0$ for species i and x of the same charge sign. In the applications of (14), we make the additional assumption, amply verified for several (i, x) pairs, that the interaction coefficients are practically independent of the ionic strength in the investigated interval.

By assuming the presence of only $\text{La}_2(\text{OH})_2\text{CO}_3^{2+}$, we obtain eqn. (15) by combining (14) and (8);

$$[\kappa_2 \text{ antilog} \{ +0.09(m_{\text{ClO}_4^-} - 3.489) \}] m_{\text{La}^{3+}}^{-2} = \beta_{221} \quad (15)$$

we put $0.14 = \varepsilon(\text{H}^+, \text{ClO}_4^-)$, as evaluated from the osmotic coefficients given by Robinson and Stokes,¹⁷ $0.47 = \varepsilon(\text{La}^{3+}, \text{ClO}_4^-)$ as calculated from Pitzer and Mayorga's data.¹⁸ Furthermore, we assume $\varepsilon(\text{La}_2(\text{OH})_2\text{CO}_3^{2+}, \text{ClO}_4^-) = \varepsilon(\text{Fe}_2(\text{OH})_2^{4+}, \text{ClO}_4^-) = 0.75$ as estimated from the variation of the constant for $2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$ in perchlorate medium.¹⁹ The values of β_{221} deduced from (15) were found to increase systematically with B^{-1} beyond the experimental error. Hence, we assumed the presence of an additional species, $\text{La}(\text{OH})_2\text{CO}_3^+$.

The most probable β_{121} and β_{221} values were calculated by rewriting (8) for q and $p = 1$ and 2 , and by using (14) with $\varepsilon(\text{LaCO}_3^+, \text{ClO}_4^-) = \varepsilon(\text{HgCl}^+, \text{ClO}_4^-) = 0.20$, as reported by Biedermann.¹ After the rearrangement we have eqn (16).

$$[\kappa_2 \text{ antilog} \{ +0.09(m_{\text{ClO}_4^-} - 3.489) \}] m_{\text{La}^{3+}}^{-2} = \beta_{221} + \beta_{121} m_{\text{La}^{3+}}^{-1} + \text{antilog} \{ -6(D - 0.2510) + 0.09(m_{\text{ClO}_4^-} - 3.489) \} \quad (16)$$

The plot of the left-hand term of (16) against

$$m_{\text{La}^{3+}}^{-1} + \text{antilog} \{ -6(D - 0.2510) + 0.09(m_{\text{ClO}_4^-} - 3.489) \}$$

could be fitted very well with a straight line with intercept and slope, respectively

$$\log \beta_{221} = -10.64 \pm 0.01$$

$$\log \beta_{121} = -11.8 \pm 0.2$$

After conversion to the molar scale we get eqns. (17) and (18).

$$\log \beta_{221} = -10.70_5 \pm 0.01 \quad (17)$$

$$\log \beta_{121} = -11.9_5 \pm 0.2 \quad (18)$$

A comparison of these results with those obtained in the previous section indicates that medium changes have only a fairly small effect on the values of β_{221} and β_{121} .

By combining (14) with (8), written for (011) and (111) we have, after rearrangement

$$\phi = \{ \kappa_1 - \text{antilog} [-7.856 + 2(D - 0.2510) - 0.14(m_{\text{ClO}_4^-} - 3.489) - 0.22 m_{\text{La}^{3+}}] \} m_{\text{La}^{3+}}^{-1} = \beta_{111} \text{ antilog} [-4(D - 0.2510) + 0.33(m_{\text{ClO}_4^-} - 3.489) - \varepsilon_1(m_{\text{ClO}_4^-} - 3.489)] \quad (19)$$

where $\varepsilon(\text{H}^+, \text{ClO}_4^-) = 0.14$ and $\varepsilon(\text{La}^{3+}, \text{ClO}_4^-) = 0.47$, as above, $\varepsilon(\text{HCO}_3^-, \text{La}^{3+}) = \varepsilon(\text{Cl}^-, \text{La}^{3+}) = 0.22$, calculated from the osmotic coefficients given by Robinson and Stokes,¹⁷ and $\varepsilon(\text{HCO}_3^-, \text{Na}^+) = 0$ estimated from the variation of the constant for $\text{CO}_2(\text{g}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$ in NaClO_4 media.²⁰ Since we were not able to estimate a probable value for ε_1 , the interaction coefficient of $\text{La}(\text{OH})\text{CO}_3^+$ with ClO_4^- , we considered it as an unknown parameter to be determined simultaneously with β_{111} .

To obtain β_{111} and ε_1 , the left hand side of eqn. (20) was plotted as a function of $(m_{\text{ClO}_4^-} - 3.489)$.

$$\log \phi + 4(D - 0.2510) - 0.33(m_{\text{ClO}_4^-} - 3.489) = \log \beta_{111} - \varepsilon_1(m_{\text{ClO}_4^-} - 3.489) \quad (20)$$

As seen from Fig. 4, the experimental points fall on a straight line. From the slope and intercept we

$$\varepsilon_1 = -1.5 \pm 1$$

$$\log \beta_{111} = -6.52 \pm 0.03$$

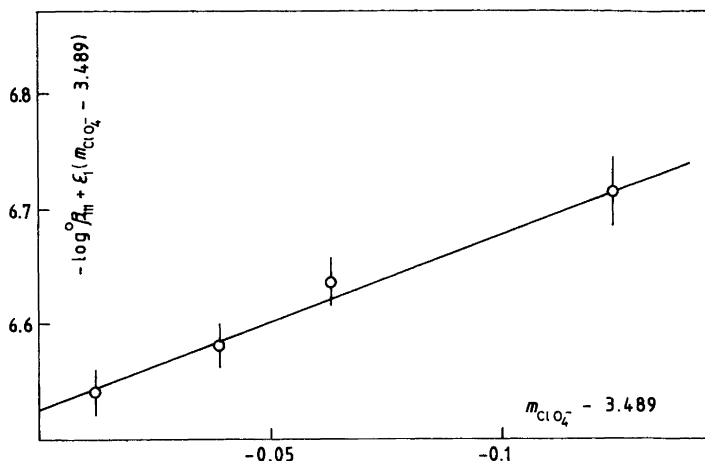


Fig. 4. $\log \beta_{111} - \varepsilon_1(m_{\text{ClO}_4^-} - 3.489)$, eqn. (20), as a function of $m_{\text{ClO}_4^-} - 3.489$. The line represents $-6.52 - 1.5(m_{\text{ClO}_4^-} - 3.489)$.

evaluated which after conversion into the molar scale becomes eqn. (21).

$$\log \beta_{111} = -6.59 \pm 0.03 \quad (21)$$

The large uncertainty of ε_1 depends on several sources of error. It also seems probable that the errors in the estimates of some $\varepsilon(i,x)$ used in the calculations and the approximations of the theory will influence the estimation of ε_1 appreciably. Nevertheless, the results are of the correct order of magnitude, thus indicating the essential soundness of the treatment.

CONCLUSIONS AND DISCUSSION

In the course of the mathematical treatment of the preceding section, we have replaced the interaction coefficients $\varepsilon(\text{La}(\text{OH})_2\text{CO}_2^{4+}, \text{ClO}_4^-)$ with $\varepsilon(\text{Fe}_2(\text{OH})_2^{4+}, \text{ClO}_4^-)$ and $\varepsilon(\text{LaCO}_3^+, \text{ClO}_4^-)$ with $\varepsilon(\text{HgCl}^+, \text{ClO}_4^-)$. We do not invoke any other argumentation to substantiate this arbitrary replacement except that substitution between species of similar composition and equal charge has proved plausible in a fair number of cases.¹ On the other hand, we have also allowed the interaction coefficients to vary as much as one unit from the assumed value in order to get an idea of how the magnitude of the equilibrium constants is influenced. We found that $\log \beta_{221}$ and $\log \beta_{121}$ did not change more than 0.1 and 0.2 units, respectively.

We may then summarize the results of this investigation by saying that the predominating carbonate complexes of lanthanum(III) formed in the concentration ranges investigated are $\text{La}_2(\text{OH})_2\text{CO}_2^{4+}$ ($\equiv \text{La}_2\text{CO}_3^{4+}$) and $\text{La}(\text{OH})\text{CO}_2^{2+}$ ($\equiv \text{LaHCO}_3^{2+}$), while $\text{La}(\text{OH})_2\text{CO}_2^+$ ($\equiv \text{LaCO}_3^+$) is a minor species.

Because of the influence of medium effects caused by substitution of Na^+ with La^{3+} , the experimental data could not be accurately described in terms of total concentrations and a medium independent set of equilibrium constants, β_{pq1} . Instead, we propose the expressions (22)–(25), which accurately describe β_{pq1} as a function of B , *i.e.* the changes of the ionic medium.

$$\log \beta_{111} = (-6.59 \pm 0.03) - (0.30 \pm 0.03) B \quad (22)$$

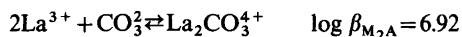
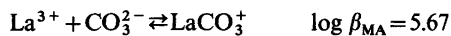
$$\log \beta_{011} = (-7.987 \pm 0.001) - (0.16 \pm 0.01) B \quad (23)$$

$$\log \beta_{221} = (-10.70_5 \pm 0.01) + (0.01_5 \pm 0.01) B \quad (24)$$

$$\log \beta_{121} = -11.9_5 \pm 0.2 \quad (25)$$

The full-drawn curves in Figs. 1 and 2 have been calculated using these equations. The agreement between the experimental data and those calculated by using the chemical model described above is excellent.

From the known equilibrium constants for the protonation of $\text{CO}_2(\text{g})$, one may calculate the equilibrium constants for the reactions



The value of $\log \beta_{\text{MA}}$ quoted above is of the same order of magnitude as the corresponding value for the $\text{Ce}^{3+} - \text{CO}_3^{2-}$ system studied by using the solubility method,²¹ $\log \beta_{\text{CeA}}$ is equal to 6.50 ± 0.01 .

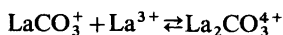
From the magnitude of the formation constants, one can conclude that the carbonate ion is chelated in LaCO_3^+ and bonded through only one oxygen donor atom in LaHCO_3^+ . The formation constant of LaHCO_3^+ is of the same order of magnitude as for ligands with a unidentate coordination, e.g. acetate ($\log \beta_{\text{LaAcetate}^{2-}} = 1.56$).²²

Marinsky *et al.*²³ found that the equilibrium constant for the reactions of the type

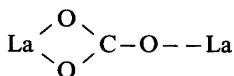


had values about 50. This result is not in agreement with our findings. Marinsky has neglected the formation of carbonate complexes and this has probably resulted in an erroneous interpretation of the experimental data.

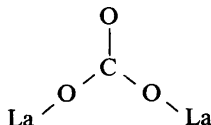
The logarithm of the equilibrium constant for the reaction



is 1.25 indicating that coordination of the second lanthanum ion occurs through one oxygen donor only. This information together with the bidentate coordination of the carbonate ion in LaCO_3^{4+} indicates that the bonding in the complex $\text{La}_2\text{CO}_3^{4+}$ is



rather than



Our experimental findings indicate that the dominating lanthanoid(III) and possibly also actinoid(III) complexes present in a typical granitic ground water (pH=8.2, $\text{pCO}_3^{2-}=3.85$), are LnCO_3^+ and $\text{Ln}(\text{CO}_3)_2^-$. The concentrations of LnHCO_3^+ and $\text{Ln}_2\text{CO}_3^{4+}$ are negligible.

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