Studies on Metal Carbonate Equilibria. 11. Yttrium(III) Carbonate Complex Formation in Aqueous Perchlorate Media of Various Ionic Strengths

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The complex formation equilibria in the system Y(III)—H₂O—CO₂(g) have been studied at 25 °C by emf measurements, using a coulometric alkaliification-acidiification technique. Measurements at the perchlorate concentration levels, C=0.3, 0.9, 1.5, and 3 M, were performed. For each perchlorate level, several Y(III) concentrations varying between 0.05 and C/3 M were studied. The acidity and the partial pressure of CO₂(g) ranged between 10⁻³ M≤h≤10⁻⁴.5 M and 0.09 atm ≤a≤0.99 atm, respectively.

All the emf data may be explained by assuming the equilibria:

\[
\begin{align*}
Y^{3+}+H_2O+CO_2(g) & \rightleftharpoons YHCO_3^{2+}+H^+ & \log \beta^{11} = -5.4 \pm 0.1 \\
Y^{3+}+H_2O+CO_3^2(g) & \rightleftharpoons YCO_3^{3-}+2H^+ & \log \beta^{21} = -10.0 \pm 0.2 \\
2Y^{3+}+H_2O+CO_3^2(g) & \rightleftharpoons Y_2CO_3^{4+}+2H^+ & \log \beta^{21} = -10.09 \pm 0.1
\end{align*}
\]

The equilibrium constant values at zero ionic strength (β_{pqr}^{0}) have been derived by using the Guggenheim-Scatchard specific interaction approach.¹ The same method has also been used to estimate the effect of ionic medium changes on the values of β_{pqr} constants at 0.3, 0.9, 1.5, and 3 M NaClO₄ (Table 3).

In two previous parts of this series we have reported the composition and the stability constants of the complexes formed in the La(III)² and Ce(III)³ carbonate systems. Two different methods were used, viz. emf and solubility technique. The emf study was made in solutions where the metal ion concentration was varied from 0.1 M to 1 M, while the perchlorate concentration was kept constant at 3 M. This large variation in the composition of the test solutions is expected to result in variations of the activity coefficient of the various species participating in the equilibria.

The observed variations of a measured quantity, e.g. the emf, may be due to variations in the activity factors of the various reactants and products and/or to the formation of new chemical species. It is important to be able to distinguish between these two factors. In the study of the La(III)—H₂O—CO₂(g) system this was done by using the specific interaction approach (S.I.T.). As described in Ref. 2, this method requires experimental information on some interaction coefficients. Some, e.g. ε(La^{3+}, ClO₄⁻), ε(Na⁺, HCO₃⁻), may be obtained

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by independent experimental methods such as activity coefficient determination of the corresponding electrolytes, while others, e.g. those involving the carbonate complexes, have to be estimated or determined experimentally. The latter procedure involves considerable experimental efforts because the measurements have to be made at several ionic strengths.

The previous study of the La\(^3+\)−H\(_2\)O−CO\(_2\)(g) system gave a satisfactory chemical model. However, the value reported for the interaction coefficient \(\varepsilon(\text{LaHCO}_3^{2+}, \text{ClO}_4^-) = -1.5\pm 1\) differed considerably from the values obtained for ions of the same charge type. This in turn implies that the variation of the equilibrium constant for the formation of LaHCO\(_3^{2+}\) with the ionic strength is quite different from that observed for similar ions.

In the present study we have tested the use of the specific interaction approach over a broader range of ionic strength. The yttrium carbonate system was chosen as a model and was studied in media where the perchlorate concentration ranged from 0.3 to 3 M. Our previous experience with the lanthanum carbonate system has shown that the precise data needed for this purpose can be obtained by using the emf method. These data may then be used to extrapolate constants to zero ionic strength by using the specific interaction approach. Calculations/extrapolations of this type are of considerable importance for many practical applications, e.g. modelling of ground water systems by using an equilibrium approach. In systems of this type equilibrium data at low ionic strengths are often needed. For some equilibria, e.g. protolysis constants of ordinary weak acids and bases, one may obtain experimental data at ionic strengths close to zero. For more complicated systems, e.g. those involving ions of high charge, this is not possible. In order to establish both a reliable chemical model and precise values of the various equilibrium constants, the experimental measurements must be made by using a medium of fairly high ionic strength. These data must then be recalculated if they are to be used at other ionic strengths, e.g. by using the specific interaction approach.

By studying the Y(III)−H\(_2\)O−CO\(_2\)(g) system and comparing the results with the previously studied La(III) and Ce(III) systems, we will also be able to obtain information on the variation of equilibrium constants with the size of the central ion.

**NOTATIONS**

The equilibrium constant for the reaction

\[
pY^{3+} + qH_2O + rCO_2(g) \leftrightarrow Y_r(\text{OH})_q(\text{CO}_2)_r^{3p-q} + qH^+
\]

(1)

is denoted \(\beta_{pq,r}\) and \(\beta_{pq,r}'\) at the reference states C M NaClO\(_4\) and pure water, respectively. The corresponding constants for the species (OH)\(_2\)CO\(_2=\)HCO\(_3^-\) and (OH)\(_2\)CO\(_2=\=\)CO\(_3^{2-}\)

**Table 1.** Experimental matrix for the Y(III)−CO\(_2\)(g)−H\(_2\)O system.

<table>
<thead>
<tr>
<th>Perchlorate concentration C (M)</th>
<th>Total metal ion concentration B (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1, 0.75, 0.5, 0.3, 0.1</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5, 0.3, 0.2, 0.1</td>
</tr>
<tr>
<td>0.9</td>
<td>0.3, 0.2, 0.1</td>
</tr>
<tr>
<td>0.3</td>
<td>0.1, 0.05</td>
</tr>
</tbody>
</table>

are denoted $\beta_{01}$ and $\beta_{02}$, respectively. The same symbols will be used for constants expressed on the molal scale, specifying the use of molal concentration scale in the text.

$$C=\text{molar concentration of } \text{ClO}_4^-$$

$$K_q=\text{formation constant for all species containing } q \text{ OH}^- \text{ groups}$$

$$f(i)=\text{molar activity coefficient of the species } i, \text{ defined so that } f(i)\rightarrow 1 \text{ as } [i]\rightarrow 0 \text{ in the solvent } C \text{ M } \text{NaClO}_4$$

$$\gamma(i)=\text{molal activity coefficient of } i, \text{ defined so that } \gamma(i)\rightarrow 1 \text{ as the ionic strength } I\rightarrow 0$$

$$D=0.51099\sqrt{I/(1+1.5\sqrt{I})} \text{ for a solution of ionic strength } I$$

$$D(I) \text{ represents the corresponding function when } I \text{ is expressed in the molar scale. } D(C) \text{ refers to } C \text{ M } \text{NaClO}_4 \text{ solutions.}$$

$$\varepsilon(i,x), \bar{\varepsilon}(i,x)=\text{interaction coefficient between the species } i \text{ and } x \text{ in the molal and molar scale, respectively.}$$

Other notations such as $b$, $B$, $h$, $H$, $m_i$ have their conventional meaning generally used in this laboratory (cf. Ref. 2).

EXPERIMENTAL

Chemicals and analysis

Yttrium perchlorate solutions were prepared from yttrium(III) oxide 99.99 % furnished by Alfa Products. The stock solutions were prepared$^4$ and analysed$^2$ as described elsewhere.

NaClO$_4$ and AgClO$_4$ stock solutions, as well as nitrogen carbon dioxide gas mixtures were obtained and analysed as before.$^5$ The partial pressure of carbon dioxide at equilibrium (denoted $a$) was calculated as:

$$a=(P_{\text{atm}}-P_{\text{H}_2\text{O}})X_{\text{CO}_2}$$

where $X_{\text{CO}_2}$ is the mole fraction of CO$_2$ in the gas mixture and $P_{\text{H}_2\text{O}}$ is the vapour pressure of water over the electrolyte mixture. $P_{\text{H}_2\text{O}}$ was estimated using the S.I.T. for the calculation of water activities from published data of the osmotic coefficients of NaClO$_4$,$^6$ and Ho(ClO$_4$)$_3$ solutions. The latter was considered to be a plausible model for Y(ClO$_4$)$_3$.

Method

The complex formation equilibria were studied at four different perchlorate concentrations. The set of Y(III) concentrations studied for every C level is given in Table 1. Measurements with CO$_2$-N$_2$ gas mixtures containing 10, 30 and 100 % CO$_2$ were performed for most B levels at C=3 M. Even though only species with $r=1$ were formed at this level, some measurements were made at two different partial pressures of CO$_2$ at the lower perchlorate levels, in order to verify that the chemical model was the same.

The measurements were performed as emf titrations, as described before.$^2$ The acidity of the test solutions was decreased by coulometric generation of OH$^-$ ions at current densities less than $5\cdot10^{-5}$ A/cm$^2$. Care was taken not to approach too close the $h$ values where solid yttrium carbonate may be formed. These values could be calculated from known data of the solubility product of yttrium carbonate, determined at different ionic strengths in a separate study.$^8$ The liquid junction potential arising at the boundary between the test solution and C M NaClO$_4$ was estimated as in Ref. 8.

In order to check that true equilibrium had been attained in the system, we made some experiments by increasing the hydrogen ion concentration stepwise. These data (denoted by double symbols in Fig. 1) always coincided with the data obtained in the reverse mode.

The measurements were made at 25.00 ±0.02 °C, using a microcomputer controlled system described elsewhere.$^7$ The potentials were read to 0.01 mV, using a preamplifier (Analog devices 311 K) and a Fluke 8810 digital voltmeter. The glass electrodes used were of

Fig. 1. The data \((h-H)/a\) as a function of \(\log h\) at the perchlorate levels \(C=3\) M, 1.5 M, 0.9 M, and 0.3 M, respectively. The curves have been calculated using eqns. (13)–(16) for \(C=3\) M (Fig. 1a) and similar expressions for the other perchlorate levels.

the type Metrohm EA 109. The constant current source in the coulometric circuit was an Electronic Measurement C633B Power Supply. The reader is referred to Ref. 2 for more details concerning the emf measurements.

CALCULATIONS AND RESULTS

The calculations are based on the experimental data recalculated to the form \((h-H)\), \((\log H)\) \(a_{b}\). For all \(C\) levels, the plots of \((h-H)a^{-1}\) vs \(\log h\) (cf. Fig. 1a–d) were found to show the same shape for different \(a\) at each \(Y(III)\) concentration studied. Hence only species with \(r=1\) (of general formula \(Y_p(OH)_qCO_2^{3-p-q}\)) exist in appreciable amounts in the acidity range investigated. Thus one may write:

\[
\frac{h-H}{a} = \sum_{p} \sum_{q} q\beta_{pq}b^{p}h^{-q}f_{1}^{(pq)}f_{1}^{(Y^{+})}f_{1}^{(H^{+})}a_{b}^{q} \quad (2)
\]

where \(a_{b}^{q}\) is the activity of water referred to the C M NaClO\(_{4}\) standard state. Estimation of \(\beta_{021}\) at all \(C\) levels studied, by interpolation of the data of Frydman et al.\(^{10}\), Mc Innes and Belcher\(^{11}\) as well as the data of Biedermann and Ciavatta on the hydrolysis of \(Y^{3+}\) ion,\(^{4}\) shows that the concentrations of \(CO_2^{2-}\) and of hydrolytic species \((p, q, 0)\) are negligible in the acidity range studied. Only a few percent of \(Y(III)\) could be transformed into reaction products before the precipitation of yttrium carbonate occurs. Hence \(b=B\) to a first approximation and also

\[
K_q = \sum_{p} \beta_{pq}B^{p}f_{1}^{(pq)}f_{1}^{(Y^{+})}f_{1}^{(H^{+})}a_{b}^{q} \quad (3)
\]

may be regarded as constant at each series of measurements with \(B=constant\). The data has shown the chemical model for the \(Y^{3+}-H_{2}O-CO_2(g)\) system to be identical with that of the previously studied \(La^{3+}\) system.\(^{2}\) Hence, the same procedure, cf. Ref. 2 pp. 408–410, could be used to determine the constants \(K_1\) and \(K_2\). These values are collected in Table 2.

Table 2. Survey of the $K_1$ and $K_2$ constants.

<table>
<thead>
<tr>
<th>C(M)</th>
<th>B(M)</th>
<th>$-\log K_1^a$</th>
<th>$-\log K_1^b$</th>
<th>$-\log K_2^a$</th>
<th>$-\log K_2^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
<td>6.86±0.01</td>
<td>6.86±0.01</td>
<td>10.70±0.01</td>
<td>10.70±0.01</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>6.91±0.01</td>
<td>6.92±0.01</td>
<td>10.89±0.01</td>
<td>10.88±0.01</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>7.03±0.02</td>
<td>7.03±0.02</td>
<td>11.16±0.02</td>
<td>11.16±0.02</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>7.17±0.02</td>
<td>7.17±0.02</td>
<td>11.55±0.02</td>
<td>11.55±0.02</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>7.51±0.02</td>
<td>7.51±0.02</td>
<td>12.40±0.03</td>
<td>12.39±0.03</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5</td>
<td>6.79±0.01</td>
<td>6.79±0.01</td>
<td>10.94±0.02</td>
<td>10.93±0.02</td>
</tr>
<tr>
<td>1.5</td>
<td>0.3</td>
<td>6.92±0.02</td>
<td>6.93±0.02</td>
<td>11.30±0.03</td>
<td>11.29±0.03</td>
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<td>1.5</td>
<td>0.2</td>
<td>7.04±0.02</td>
<td>7.05±0.02</td>
<td>11.59±0.03</td>
<td>11.58±0.03</td>
</tr>
<tr>
<td>1.5</td>
<td>0.1</td>
<td>7.22±0.02</td>
<td>7.22±0.02</td>
<td>12.10±0.03</td>
<td>12.07±0.03</td>
</tr>
<tr>
<td>0.9</td>
<td>0.3</td>
<td>6.82±0.01</td>
<td>6.82±0.01</td>
<td>11.21±0.02</td>
<td>11.20±0.02</td>
</tr>
<tr>
<td>0.9</td>
<td>0.2</td>
<td>6.95±0.02</td>
<td>6.95±0.02</td>
<td>11.49±0.03</td>
<td>11.47±0.03</td>
</tr>
<tr>
<td>0.9</td>
<td>0.1</td>
<td>7.14±0.02</td>
<td>7.14±0.02</td>
<td>11.98±0.03</td>
<td>11.95±0.03</td>
</tr>
<tr>
<td>0.3</td>
<td>0.1</td>
<td>7.01±0.02</td>
<td>7.01±0.02</td>
<td>11.84±0.02</td>
<td>11.81±0.02</td>
</tr>
<tr>
<td>0.3</td>
<td>0.05</td>
<td>7.19±0.03</td>
<td>7.20±0.03</td>
<td>11.26±0.03</td>
<td>12.19±0.03</td>
</tr>
</tbody>
</table>

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

The fact that plots of $(h - H)a^{-1}h$ vs. $h^{-1}$ are linear at all $B$ levels studied gives additional evidence for the formation of species with $q = 1$ and $q = 2$ only. The calculations were repeated by using $b = B - (h - H)$ instead of the approximation $b = B$. However, the set of $K_1$ and $K_2$ constants did not change significantly (cf. Table 2). Nevertheless these latter values were used in the following calculations.

The dependence of $K_1$ and $K_2$ on $B$ is shown in Figs. 2 and 3, respectively. The points at $B = 0$ in Fig. 2 represent the values of the constant $\beta_{011}$ in different C M NaClO$_4$ media. In 0.3 M NaClO$_4$ we obtained:

$$\beta_{011} = 10^{-7.578±0.005} \text{ M}^2 \text{ atm}^{-1}$$

The corresponding value at 3 M NaClO$_4$ was taken from Ciavatta et al.$^5$ From these data and data of Frydman et al.$^{10}$ Harned and Davis,$^{12}$ we could interpolate the values for $\beta_{011}$ at 0.9

![Fig. 2. $K_1$ and $K_2/B_1$ respectively, as a function of $B$ (mol/l). The dashed lines represent the expected functional behaviour in absence of medium effects due to the replacement of Na$^+$ by Y$^{3+}$. The full drawn curves have been calculated taking the change of activity factors into account [eqns. (6) and (7), respectively].](image)
and 1.5 M NaClO₄ using the S.I.T. Figs. 2 and 3 show that the points lie on straight lines for low values of $B$. This indicates that only complexes of the type $(p,1,1)$ with $p \leq 1$ and $(p,2,1)$ with $p \leq 2$ are formed in appreciable amounts. The bending of the curves towards the abscissa cannot be due to an incompleteness of the chemical model, since consideration of additional complexes would cause a deviation in the opposite direction from the one observed. Instead the deviations from the linear behaviour at the high levels of $B$ are mainly due to activity factor changes. This is to be expected in view of the large changes of the composition of the ionic medium (all NaClO₄ is replaced by Y(ClO₄)₃ at the highest level of $B$). These deviations cause an error of the order of 0.3 log units in the $\beta_{pq1}$ constants estimated from the slope and intercept of the linear parts of the curves.

The evaluation of medium effects on the equilibrium constants. The specific ion interaction approach as outlined by Brønsted and elaborated by Guggenheim and Scatchard will be used for the evaluation of activity factors. The reader is referred to Ref. 1 for an outline of the basic assumptions and examples of applications in the field of equilibrium analysis. The analysis of the experimental data with the S.I.T. will be performed in two steps:

First, we will calculate the equilibrium constants in NaClO₄ solvents of concentration 3, 1.5, 0.9 and 0.3 M at trace yttrium concentrations. This involves the evaluation of activity factor changes when part of NaClO₄ is replaced by Y(ClO₄)₃.

Second, we will estimate the activity factor variation when the solvent is changed from NaClO₄–H₂O to pure water. In this way we can evaluate the constants $\beta_{pq1}$ at zero ionic strength from the set of constants obtained in the first step.

Evaluation of medium effects in NaClO₄–Y(ClO₄)₃ mixtures. In this study all the reaction products formed, except HCO₃⁻, are positively charged species. A basic assumption of the S.I.T. used here is that $\varepsilon(i,x)$ is zero if $i$ and $x$ have the same charge sign. Hence, only their interactions with the perchlorate ion need to be considered, as [HCO₃⁻] is negligible compared to $C$. In activity coefficient calculations one usually employs the weight molarity (molality) scale. However, it is much more convenient to treat the data at a given $C$-level by using molar concentrations. The activity coefficient $f_i$ of a species $i$ can then be expressed as

$$\log f_i = -z_i^2 [D(I) - D(C)] + \varepsilon(i,\text{Na}^+) \quad ([\text{Na}^+] - C) + \varepsilon(i,\text{Y}^{3+}) [\text{Y}^{3+}]$$

(4)

where $z_i$ is the charge of $i$. The terms involving the interaction coefficients $\varepsilon(i,\text{ClO}_4^-)$ were neglected because the perchlorate concentration is constant, [ClO₄⁻] = $C$.

Fig. 4. $F=\beta_{111}[Y^{3+}]$ as a function of $[Y^{3+}]$ [eqn. (5)]. The straight lines have slopes corresponding to $\beta_{111}$ values in Table 3.

Equation (3) for $q=1$ can be written:

$$K_1=\beta_{111}f^{-1}(H+)f^{-1}(HCO_3^-)\delta(Y^{3+}, HCO_3^-)$$

The changes in water activities were evaluated and were found to be very small. Anyhow, they were included in the calculations.

Substitution of $f(i)$ from (4) in (5) gives after rearrangement:

$$F=(K_1-\beta_{111} \text{antilog } 2[D(I)-D(C)]-[\delta(Y^{3+}, HCO_3^-)-3\delta(Na^+, HCO_3^-)][Y^{3+}]) \text{antilog } 4[D(I)-D(C)] = \beta_{111}[Y^{3+}]$$

The interaction coefficient $\delta(Na^+, HCO_3^-)=0.01$ was calculated from data of Harned and Davis and the previously mentioned measurements of $\beta_{111}$ in different NaClO$_4$ concentrations. No experimental value is available for $\delta(Y^{3+}, HCO_3^-)$, instead we assume $\delta(Y^{3+}, HCO_3^-)=\delta(Y^{3+}, Cl^-)=0.30$ as calculated from data of Pitzer et al. and Spedding and co-workers. This analogy is based on the comparison of several $\delta(Me^+, HCO_3^-)$ and $\delta(Me^+, Cl^-)$ values. The densities of Y(ClO$_4$)$_3$–NaClO$_4$ electrolyte mixtures were found to vary almost linearly from one end member to the other for all C levels. The plot of the function $F$ versus $B$ at each C level could be fitted rather well with straight lines passing through the origin (cf. Fig. 4). The values of $\beta_{111}$ constants obtained from the slope of the lines at each C level are given in Table 3.

Medium effects on the constants $\beta_{121}$ and $\beta_{221}$ were estimated in a similar way. In this case we obtain:

$$Y=K_2 \text{antilog } 6[D(I)-D(C)]/[Y^{3+}] = \beta_{121} + \beta_{221} \text{antilog } 6[D(I)-D(C)]/[Y^{3+}]$$

<table>
<thead>
<tr>
<th>$C_{NaClO_4}$</th>
<th>$-\log \beta_{111}$</th>
<th>$-\log \beta_{121}$</th>
<th>$-\log \beta_{221}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>6.70±0.1</td>
<td>11.60±0.15</td>
<td>10.64±0.1</td>
</tr>
<tr>
<td>1.5</td>
<td>6.42±0.05</td>
<td>11.35±0.1</td>
<td>10.37±0.1</td>
</tr>
<tr>
<td>0.9</td>
<td>6.27±0.05</td>
<td>11.20±0.1</td>
<td>10.24±0.05</td>
</tr>
<tr>
<td>0.3</td>
<td>6.07±0.05</td>
<td>10.95±0.1</td>
<td>10.13±0.06</td>
</tr>
</tbody>
</table>

Table 3. Stability constants at trace levels of Y(III) in different NaClO$_4$ media, evaluated using S.I.T.

The plot of the left hand side against \( x = \text{antilog} \{6[D(I) - D(C)]/[Y^{3+}] \} \) was very near linear for \( B < 0.75 \). The values of the constants \( \beta_{121} \) and \( \beta_{221} \) collected in Table 3 were evaluated from the intercept and the slope of these straight lines. The points corresponding to \( B \geq 0.75 \) M at \( C = 3 \) M were taken into consideration only to estimate the errors as maximum deviations from the mean values, for reasons to be discussed later.

**Extrapolation of the equilibrium constants to zero ionic strength.** The equilibrium constants referring to the pure water standard state \( (\beta_{pq1}) \) can be calculated from the set of the constants collected in Table 3 by using the specific interaction approach. We have:

\[
\beta_{pq1} = \beta_{pq1}^{i=1} \gamma(i^{a})(\gamma(pq1)^{a} f_{H2O})
\]  

where \( \beta_{pq1} \) in the molal scale were calculated from values in Table 4 and published density data for NaClO₄ solutions. In this case we have for the molal activity coefficients \( \gamma_i \):

\[
\log \gamma_i = -z_i D + \sum_j \varepsilon(i,j) m_j
\]

Substitution in (10) gives after rearrangement:

\[
\log \beta_{111} + 4D - \log a_{H2O} = \log \beta_{111} + [\varepsilon(Y^{3+}, ClO_4^-) - \varepsilon(H^+, ClO_4^-) - \varepsilon(YHCO_3^+, ClO_4^-)] I
\]

\[
\log \beta_{121} + 6D - \log a_{H2O} = \log \beta_{121} + [\varepsilon(Y^{3+}, ClO_4^-) - 2\varepsilon(H^+, ClO_4^-) - \varepsilon(YCO_3^+, ClO_4^-)] I
\]

\[
\log \beta_{221} - \log a_{H2O} = \log \beta_{221} + [2\varepsilon(Y^{3+}, ClO_4^-) - 2\varepsilon(H^+, ClO_4^-) - \varepsilon(Y_2CO_4^{4+}, ClO_4^-)] I
\]

These equations represent straight lines (cf. Fig. 5 a–c) from which \( \beta_{pq1} \) values are determined as intercept while interaction coefficients for the complexes are estimated from the slopes.

The values of \( \beta_{pq1} \) thus obtained were

\[
\log \beta_{111} = -5.42 \pm 0.1 \quad \log \beta_{121} = -10.0 \pm 0.2 \quad \log \beta_{221} = -10.09 \pm 0.1
\]

**Fig. 5.** Variation of the equilibrium constants corresponding to the formation of \( YHCO_3^+, YCO_3^+, \) and \( Y_2CO_4^{4+}, \) respectively (Table 3) with the ionic strength. The straight lines represent eqns. (10), (11), (12), respectively.

Table 4. Survey of some interaction coefficients, \(\varepsilon(i,k)\), between the species \(i\) and \(k\). Unknown \(\varepsilon(i,k)\) values have been approximated with the interaction coefficients between the ions \(j\) and \(l\) in the second column. \(\varepsilon\) is assumed constant in the ionic strength range \(0.5 \text{ m} \leq l \leq 3.5 \text{ m}\).

<table>
<thead>
<tr>
<th>(i,k)</th>
<th>(j,l)</th>
<th>(\varepsilon)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ho}^{3+},\text{ClO}_4^-)</td>
<td></td>
<td>0.49</td>
<td>7</td>
</tr>
<tr>
<td>(\text{La}^{3+},\text{ClO}_4^-)</td>
<td></td>
<td>0.47–0.52</td>
<td>7</td>
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<tr>
<td>(\text{Lu}^{3+},\text{ClO}_4^-)</td>
<td></td>
<td>0.28</td>
<td>18</td>
</tr>
<tr>
<td>(\text{Y}^{3+})</td>
<td>(\text{Cl}^-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Y}^{3+},\text{HCO}_3^-)</td>
<td>(\text{Y}^{3+},\text{Cl}^-)</td>
<td></td>
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</tr>
<tr>
<td>(\text{Y}^{3+},\text{ClO}_2)</td>
<td>(\text{Ho}^{3+},\text{ClO}_4^-)</td>
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<td></td>
</tr>
<tr>
<td>(\text{Fe}^{3+},\text{ClO}_4^-)</td>
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<td>0.56</td>
<td>1</td>
</tr>
<tr>
<td>(\text{H}^+,\text{ClO}_4^-)</td>
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<td>0.14</td>
<td>6</td>
</tr>
<tr>
<td>(\text{YCO}_3^+,\text{ClO}_4^-)</td>
<td></td>
<td>0.17</td>
<td>This work</td>
</tr>
<tr>
<td>(\text{Hg}^{2+},\text{ClO}_2)</td>
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<td>0.20</td>
<td>1</td>
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<tr>
<td>(\text{Cd}^{2+},\text{ClO}_2)</td>
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<td>0.19</td>
<td>26</td>
</tr>
<tr>
<td>(\text{CdCl}^+,\text{ClO}_4^-)</td>
<td></td>
<td>0.24</td>
<td>27</td>
</tr>
<tr>
<td>(\text{CdSc}^+,\text{ClO}_4^-)</td>
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<td>0.23</td>
<td>27</td>
</tr>
<tr>
<td>(\text{Ca}^{2+},\text{ClO}_3^-) ([\text{Ca}^{2+},\text{Mg}^{2+},\text{Co}^{2+},\text{Cu}^{2+},\text{Zn}^{2+},\text{Hg}^{2+}],\text{ClO}_4^-)]</td>
<td></td>
<td>0.27–0.34</td>
<td>20</td>
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<tr>
<td>(\text{FeHCO}_3^+,\text{ClO}_4^-)</td>
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<td>This work</td>
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<tr>
<td>(\text{FeSCN}^+,\text{ClO}_4^-)</td>
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<td>(\text{FeOH}^{2+},\text{ClO}_2)</td>
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<tr>
<td>(\text{Y}_2\text{CO}_3^+,\text{ClO}_3^-)</td>
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<td>(\text{Fe}_2(\text{OH})_3^+,\text{ClO}_4^-)</td>
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<tr>
<td>(\text{Pb}_2(\text{OH})_4^+,\text{ClO}_2)</td>
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<tr>
<td>(\text{Pb}^{2+},\text{ClO}_2)</td>
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<td>0.16</td>
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</table>

The evaluation of \(\varepsilon\) values for the complexes involves the estimation of \(\varepsilon(\text{Y}^{3+},\text{ClO}_4^-)\), since no activity coefficient measurements of yttrium perchlorate solutions are available. Spedding and co-workers have measured the activity coefficients of rare earth chlorides and perchlorates, including yttrium chloride. We assumed \(\varepsilon(\text{Y}^{3+},\text{ClO}_4^-)=\varepsilon(\text{Ho}^{3+},\text{ClO}_4^-)\) = 0.49 based on the similar trends in the rare earth perchlorate and chloride series and the position of yttrium in the chloride series. Using this value and \(\varepsilon(\text{H}^+,\text{ClO}_4^-)=0.14\) as evaluated from mean activity coefficient data for HClO₄ solutions, we obtain

\[
\varepsilon(\text{YHCO}_3^+,\text{ClO}_4^-)=0.39, \quad \varepsilon(\text{YCO}_3^+,\text{ClO}_2)=0.17, \quad \varepsilon(\text{Y}_2\text{CO}_3^+,\text{ClO}_3^-)=0.83
\]

CONCLUSIONS AND DISCUSSION

This study has provided evidence that the predominant complexes formed in the concentration ranges studied are \(\text{YHCO}_3^{2+}\), \(\text{Y}_2\text{CO}_3^{4+}\) and \(\text{YCO}_3^+\). The corresponding constants are functions of \(B\) and \(C\). In the evaluation of the \(\beta_{pq1}\) constants at each \(C\) level we have replaced \(\varepsilon(\text{Y}^{3+},\text{HCO}_3^-)\) with \(\varepsilon(\text{Y}^{3+},\text{Cl}^-)\). By using the S.I.T. on the molar scale, no assumptions about the values of the interaction coefficients of the complexes (cf. Ref. 2) are needed. From the equations presented in the previous sections and the experimental values of \(\beta_{pq1}\) one can deduce the following expressions which describe the variation of equilibrium constants with \(B\) at \(C=3\) M:

log$\beta_{011}$ = $-7.987 - 0.23B$  \hspace{1cm} (13)
log$\beta_{111}$ = $-6.70 - 0.12B$  \hspace{1cm} (14)
log$\beta_{121}$ = $-11.61 - 0.18B$  \hspace{1cm} (15)
log$\beta_{221}$ = $-10.64$  \hspace{1cm} (16)

These equations explain that the bending of the curves towards abscissa in Figs. 2 and 3 is due to the decrease of the constants with $B$.

The quantitative predictions of the S.I.T. are demonstrated in Fig. 1. The full drawn curves in the figure were calculated using eqns. (13)-(16) and similar equations for the other C levels. The systematic deviations at $B\geq 0.75$ M are a result of the shortcomings of the S.I.T. at such high ionic strengths.

Anyway, the agreement between the experimental data (the symbols in Fig. 1 represent approximately the errors estimated for the constants $K_1$ and $K_2$) and the predictions of the S.I.T. over a large range of $B$ and $C$ values, may be regarded as a strong evidence for its practical utility in the area of solution chemistry. Another is the experimental observation that the interaction coefficients $e(YHCO_3^{2+}, ClO_4^-)$, $e(YCO_3^{4+}, ClO_4^-)$ and $e(Y_2CO_3^{4+}, ClO_4^-)$ have numerical values that closely agree with those of some other ions of the same charge, cf. Table 4. Observations of this kind have also been made by Biedermann and Ciavatta. The fact that it seems possible to predict interaction coefficients is of great practical advantage, if moderate precision in the equilibrium constants at infinite dilution is sufficient. Thus an error of 0.1 in the value of $e(i,x)$ for the complexes will cause an error of $\pm 0.1 I$ in log$\beta_{pq}$, where $I$ represents the ionic strength at which the constant is determined.

The value of the interaction coefficient $e(LaHCO_3^{2+}, ClO_4^-)$ = $-1.5 \pm 1$ evaluated in Ref. 2, differs considerably from the value obtained for the corresponding yttrium complex. One reason for this is that this interaction coefficient was determined as the slope of a linear function [Ref. 2, eqn. (20)] where the variable $(m_{ClO_4^-} - 3.489)$ represents the very small differences between the molality of ClO$_4^-$ in (La$^{3+}$, Na$^+$)ClO$_4^-$ mixtures and NaClO$_4$ solutions of the same (3 M) perchlorate concentration. The approximate character of S.I.T., especially in mixtures of electrolytes of such high ionic strength, is expected to result in much larger errors in the interaction coefficient thus evaluated than in the approach used in this communication. We have recalculated the data in the La(III) system with the interaction coefficients for complexes determined here and we found practically no change in the equilibrium constants. This can be understood from the close agreement of the assumed values for $e(La_2CO_3^{4+}, ClO_4^-)$, $e(LaCO_3^{3+}, ClO_4^-)$ and those evaluated in the present study.

There exist more elaborate and theoretically more firmly based varieties of the specific interaction approaches than the one used here. In a number of papers, Pitzer and co-workers have described equations which reproduce activity coefficients of electrolytes with a high precision over large concentration ranges. This method requires the determination of two or more parameters to be used in activity coefficient expressions. A great number of such determinations have been made from experimental activity coefficient data of pure electrolytes. In electrolyte mixtures containing ions of charge 3 and higher, Pitzer points out that even interactions between ions of the same charge become quite important. The fact that S.I.T. as used here neglects those interactions, may be a possible explanation for the deviations at the highest $C$ level. However, it is difficult to obtain any quantitative information about these effects in our case, since no data are available for the corresponding parameters of all the species studied. For that reason, the points at $B\geq 0.75$ M...
were taken into consideration only when estimating the errors in the $\beta_{pq}$ values at 3 M NaClO$_4$. The good agreement of the rest of the experimental data with the predictions of S.I.T. is possibly due to a cancellation of errors in the activity factor ratios appearing in the equilibrium constant expressions.

From the values of the constants in Table 4 and the protolysis constants for carbonic acid,$^{5,10}$ we may calculate the equilibrium constants at 3 M NaClO$_4$ for the reactions:

\[
\begin{align*}
Y^{3+} + CO_3^{2-} &\rightleftharpoons YCO_3^{+} & \log \beta_{MA} &= 6.02 \\
2Y^{3+} + CO_3^{2-} &\rightleftharpoons Y_2CO_3^{4+} & \log \beta_{M_A} &= 6.98 \\
Y^{3+} + HCO_3^- &\rightleftharpoons YHCO_3^{2+} & \log \beta_{MHA} &= 1.29
\end{align*}
\]

The values of $\log \beta_{MA}$ obtained in this study are quite close to the corresponding values for the Ce$^{3+}$ (6.32)$^3$ and Eu$^{3+}$ complexes (5.96 in 3 M NaClO$_4$, estimated from the value 5.93 in 1 M NaClO$_4$$^{25}$ using S.I.T.). The values of $\beta_{M_A}$ and $\beta_{MHA}$ are practically the same for the Y(III) and La(III) systems.

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