Studies on the Hydrolysis of Metal Ions

45. The Hydrolysis of Magnesium in Chloride Self-Medium

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The hydrolysis of Mg(II) at 25°C, in solutions made to contain 3 M Cl⁻ by the addition of sodium chloride, has been studied by potentiometric titrations with barium hydroxide solution, using the hydrogen electrode or the glass electrode. The total concentrations of Mg(II), *B*, were 1.500, 1.250 and 1.000 M, so that the solutions corresponded to the self-medium principle. It is concluded that the results obtained with these solutions and for the range $8.5 < -\log [\text{H}^+] < 9.25$, are consistent with the formation of either MgOH⁺ or Mg₂OH³⁺ together with Mg₄(OH)₄⁴⁺. The equilibrium constants, $\beta_{p,q}$, found for the reactions

are:

for *B* = 1.500, $\log \beta_{1,1} = -12.21 \pm 0.12$, or $\log \beta_{1,2} = -12.38 \pm 0.12$,
and $\log \beta_{4,4} = -39.76 \pm 0.03$;

for *B* = 1.250, $\log \beta_{1,1} = -12.20 \pm 0.06$, or $\log \beta_{1,2} = -12.30 \pm 0.06$,
and $\log \beta_{4,4} = -39.80 \pm 0.02$;

and

for *B* = 1.000, $\log \beta_{1,1} = -12.33 \pm 0.06$, or $\log \beta_{1,2} = -12.33 \pm 0.06$,
and $\log \beta_{4,4} = -39.82 \pm 0.02$

Sources of error in the experiments are discussed.

A number of studies have been made of the hydrolysis of magnesium in dilute solution, the results of which are consistent with the formation of the first mononuclear species, MgOH⁺, alone. Thus, *e.g.*, Stock and Davies¹ titrated ca. 0.03 M magnesium chloride with barium hydroxide solution and obtained data with a glass electrode, from which they found $\log K_1^{25^\circ\text{C}} = 2.58$ (corrected to zero ionic strength) for the reaction

They made further measurements at higher concentrations of magnesium but did not report the results of them, because the ionic strengths of the solutions were too great for reliance to be placed on the empirical activity-coefficient

equation used. However, they found that, within the limits of this uncertainty, these measurements confirmed the results given above.

It has long been known that magnesia is very soluble in concentrated solutions of magnesium chloride (see *e.g.* Lukens²). This phenomenon suggests that magnesium forms polynuclear, basic species in concentrated solutions, and prompted the study, reported here, of the hydrolysis of magnesium, by the "self-medium" method developed in this laboratory.^{3,4}

A chloride medium was selected for this investigation because, in contrast to the perchlorate which would usually be preferred, magnesium chloride may be purified fairly easily by recrystallization from water. The total concentration of chloride ion in the solutions studied was kept constant at 3 M: sodium chloride was added when the concentration of magnesium was less than 1.5 M. At this concentration of chloride ion, the range of the total concentration of magnesium which was accessible to experiment was limited, by the solubility of sodium chloride in solutions of magnesium chloride and by the experimental design, to that above about 0.75 M.

EXPERIMENTAL

Reagents. Magnesium chloride solutions were prepared from a good commercial reagent (this and all other chemicals were Merck *p.a.* grade materials) which had been recrystallized from water; a concentrated solution of the reagent was evaporated until its boiling point reached 125°C, and it was then cooled in an icebath whilst being vigorously stirred. A primary solution of magnesium chloride was prepared by dissolving the recrystallized material in the minimum of doubly distilled water at 25°C. The concentration of magnesium in this solution was determined by evaporating aliquot portions of it with a 25 % excess of sulfuric acid, igniting the residue to 350°C and weighing it as MgSO₄, and also by the precipitation of magnesium oxinate. The results of the two methods agreed to within 0.1 %.

Sodium chloride solutions were prepared from *p.a.* reagent "as received": this material had previously been found in this laboratory to be of satisfactory purity. The primary solution of sodium chloride was analysed by evaporating aliquot portions of it, igniting the residue to 450°C and weighing it as NaCl.

Secondary solutions for use in the titrations, were prepared by diluting to standard volume, the appropriate, weighed aliquot portions of the primary solutions of magnesium chloride and of sodium chloride.

Barium hydroxide solutions were also prepared directly from *p.a.* reagent, no attempt at further purification being made, other than the removal of carbonate. A saturated solution of the hydroxide in doubly distilled water was prepared at 25°C. The bulk of the insoluble carbonate was eliminated by decantation and the last traces were removed by filtration through a G4 sintered glass filter in an atmosphere of nitrogen, free from carbon dioxide. The dilute solutions of the hydroxide which were used in the titrations were prepared by volume from this filtered solution.

Hydrochloric acid solutions were prepared by diluting *p.a.* reagent, and were standardized against recrystallized thallium(I) carbonate.

Carbon dioxide was expelled from the secondary solutions by bubbling nitrogen through them for several hours; a stream of nitrogen was also used to stir the solution in the titration cell. The guard-tubes which were used, were filled with "Ascarite" carbon-dioxide absorbent.

Apparatus. The titration cell was of the "Wilhelm" type.⁵ It was kept at $25.0 \pm 0.1^\circ\text{C}$ in a paraffin oil thermostat placed in a room which was thermostated at about 25°C.

The silver reference electrodes were prepared by the procedure recommended by Brown⁶ and were coated with silver chloride by electrolysis in 0.1 M HCl for 30 min with a current of 0.3 mA per electrode. Hydrogen electrodes were prepared by the method described by Bates.⁷ A Beckman, type 1190-80, glass electrode was used.

The emf's of cells with the glass electrode were determined to ± 0.2 mV, using a Radiometer, PHM4, valve potentiometer. Those of cells with the hydrogen electrode were measured to ± 0.01 mV, by means of a Cambridge, Vernier, potentiometer.

Procedure. The experimental investigation consisted of a series of potentiometric titrations at 25°C, in which the concentration, h , of free hydrogen ion in a magnesium chloride solution, S, was varied by the addition of aliquot portions of a barium hydroxide solution, T₁. The total concentration of magnesium in S, B molar, was kept constant by the addition of equal volumes of T₁ and of a solution, T₂, containing $2B$ molar magnesium chloride. In a few instances the experiment was continued with a back titration in which equal volumes of a hydrochloric acid solution, T₃, and of a $2B$ molar magnesium chloride solution, T₄, were added to S. The various solutions had the following general, analytical compositions: —

S: B M Mg(II), H M H⁺, $(3.01 - 2B - H)$ M Na⁺, 3.01 M Cl⁻

T₁: $\frac{1}{2}A_T$ (~ 0.025) M Ba(OH)₂, 0.02 M NaCl

T₂: $2B$ M MgCl₂, $(6 - 4B)$ M NaCl

T₃: H_T ~ 0.1 M HCl

T₄: $2B$ M MgCl₂, $(6.02 - 4B - H_T)$ M NaCl

Three values of B were used: 1.500, 1.250 and 1.000 M. The analytical excess concentration of hydrogen ion, H , was $+0.01$ molar at the start of every titration; it had negative values in the range where significant hydrolysis occurred.

The equilibrium value of h corresponding to each value of H , was determined by measuring the emf of the cell

$$\begin{array}{l} \text{Pt, H}_2 \mid \text{S} \mid \text{Ref.} \\ E_I = E_I^\circ - 59.15 \log h + E_j \end{array} \quad \begin{array}{l} \text{(I)} \\ \text{(1)} \end{array}$$

where Ref., denotes

$\mid B$ M MgCl₂, $(3 - 2B)$ M NaCl $\mid B$ M MgCl₂, $(3 - 2B)$ M NaCl, satd. AgCl $\mid$ AgCl, Ag

Because measurements with the hydrogen electrode are very time-consuming, it was convenient to make a more extended, concurrent series of measurements with the cell

$$\begin{array}{l} \text{Ref.} \mid \text{S} \mid \text{Glass electrode} \\ E_{II} = E_{II}^\circ + 59.15 \log h + \delta + E_j \end{array} \quad \begin{array}{l} \text{(II)} \\ \text{(2)} \end{array}$$

The results of the measurements that were made with the hydrogen electrode were used to calibrate the glass electrode, with which the greater number of measurements were made. The liquid junction potential, E_j , in cells I and II, is negligible over the range of $\log h$ which was encountered in this study.

The normality, A_T , of T₁ and E_I° and E_{II}° , were determined, in each titration, from the first few points ($H > 0$): the data being treated by Gran's method.⁸ In those experiments in which a reverse titration was performed, this was continued until $H \sim +0.01$ molar, to test whether E_I° or E_{II}° had changed significantly during the course of the titration. It was found, in a preliminary experiment with $B = 1.5$ M, that a visible precipitate was formed when the average number of hydroxyl groups bound per metal ion, Z , exceeded about 0.01. When H was increased by a small amount, this precipitate redissolved only very slowly. For this reason, in all subsequent experiments, the forward titration was terminated when $Z < 0.01$. In these experiments, the

potential of the glass electrode did not change significantly after ten minutes from the start of an addition of titrant. The time taken for the potential of the hydrogen electrode to reach a stable value, varied somewhat from one electrode to another: a fresh electrode was prepared for each titration. There was usually no significant change in potential (± 0.02 mV) after 20 min from the start of an addition, except in the immediate vicinity of the equivalence point where the potential was unstable. In occasional tests, no significant change in the final potential was found after periods of up to 3 h.

RESULTS

The primary data from the various titrations consisted of the sets of corresponding values of B , H , E_I and E_{II} that are summarised in Table 1. They were first used in the calculation of the correction term for the glass electrode, δ , from:

$$\delta = (E_I + E_{II}) - (E_I^\circ + E_{II}^\circ)$$

and in the construction of calibration curves, $\delta (E_{II}^\circ - E_{II})_B$. It was found that, over the range of $\log h$ where the hydrolytic equilibria were investigated, δ varied slightly with both $\log h$ and B . Where measurements had been made

Table 1. Primary data from the titration of B M MgCl_2 with *ca.* 0.025 M $\text{Ba}(\text{OH})_2$.

$B = 1.500$ M

Titration 1. H mM, E_I mV, E_{II} mV 8.777, 299.68, 510.3; 6.841, 306.39, 504.1; 5.132, 313.77, 496.5; 3.614, 322.81, 487.4; 2.255, 334.89, 475.2; 1.022, 355.23, 455.2; -0.597 , 688.80, 120.3; -1.088 , 697.53, 112.1; -1.557 , 701.58, 108.2; -2.435 , 705.73, 104.2; -3.627 , 709.11, 100.9; -5.002 , 711.57, 98.2; -7.691 , 714.48, 95.1.

Titration 2. H mM, E_{II} mV; 8.777, 501.5; 6.754, 494.5; 4.971, 486.6; 3.387, 476.6; 1.970, 462.8; -0.469 , 114.4; -1.517 , 99.2; -2.474 , 94.9; -4.166 , 90.5; -5.600 , 88.2; -6.836 , 86.8; -4.856 , 89.5; -2.986 , 93.5; -1.249 , 102.1; -0.420 , 118.0.

$B = 1.250$ M Titration 1. H mM, E_I mV, E_{II} mV, 10.55, 294.06, 518.6; 8.038, 301.00, 511.7; 5.826, 308.24, 503.5; 3.858, 319.84, 492.7; 2.100, 335.65, 476.7; 0.501, 372.13, 440.4; -0.931 , 699.48, 114.1; -2.231 , 709.09, 104.6; -3.420 , 712.72, 100.9; -4.509 , 715.07, 98.4; -5.522 , 716.56, 96.8; -4.381 , 714.60, 98.8; -3.286 , 712.26, 101.3; -2.230 , 708.69, 104.8; -1.216 , 701.93, 111.3; 4.184, 317.44, 494.7; 7.210, 303.44; 509.1; 9.881, 295.44, 517.1; 12.26, 289.53, 522.4.

Titration 2. H mM, E_{II} mV; 10.55, 513.5; 7.969, 506.4; 5.694, 497.7; 3.669, 483.6; 1.861, 468.9; 0.215, 413.5; -0.539 , 115.3; -0.903 , 108.5; -1.257 , 104.9; -1.941 , 100.9; -2.594 , 98.2; -3.818 , 95.0; -4.938 , 93.1; -5.979 , 91.8; -7.809 , 90.0.

Titration 3. H mM, E_I mV, E_{II} mV; 10.54, 296.27, 518.2; 6.106, 310.20; 504.3; 4.261, 319.43, 494.8; 2.609, 332.13, 482.2; 1.104, 354.05, 460.3; 0.417, 378.95, 435.6; -0.865 , 701.42, 111.5; -1.461 , 707.39, 108.0; -2.577 , 712.59, 102.9; -3.601 , 715.24, 100.0; -4.500 , 717.01, 98.3; -5.419 , 718.40, 96.9; -6.223 , 719.41, 95.9; -5.153 , 717.85, 97.6; -4.122 , 716.09, 99.2; -3.126 , 713.70, 101.8; -2.166 , 710.24, 105.1; -1.236 , 704.19, 110.9; -0.340 , 677.27, 136.2; 1.368, 348.04, 466.0; 2.986, 328.23, 485.7; 4.490, 317.81, 496.3; 7.238, 305.49, 508.9; 9.703, 297.96, 516.4.

$B = 1.000$ M Titration 1. H mM, E_I mV, E_{II} mV; 7.523, 306.53, 502.2; 5.889, 312.84, 495.7; 4.423, 320.17, 488.3; 3.100, 329.62, 478.9; 1.900, 341.98, 466.4; 0.795, 364.19, 444.4; -1.122 , 713.09, 96.5; -1.968 , 718.48, 91.2; -3.481 , 722.97, 87.0; -4.783 , $-$, 84.5; -5.920 , 726.99, 83.1; -6.927 , 728.12, 82.1.

Titration 2. H mM, E_I mV, E_{II} mV; 10.39, 298.20, 513.1; 7.951, 305.07, 506.3; 5.790, 313.20, 498.1; 3.850, 323.62, 487.7; 2.119, 338.64, 472.3; 0.547, 374.22, 437.2; -0.179 , 683.17, 128.3; -0.529 , 704.62, 108.0; -0.872 , 710.86, 102.1; -1.533 , 716.47, 96.4; -2.164 , 719.38, 93.5; -3.354 , 722.85, 90.2; -4.440 , 724.99, 88.1; -5.443 , 726.38, 86.8; -7.229 , 728.39, 85.0.

with cell II only, the appropriate values of δ were then obtained by interpolation on the calibration curves.

The values of $\log h$ and of Z corresponding to each value of H in the various titrations, were then calculated using eqn. 1, or 2, and the relations

$$BZ = -H + [\text{OH}^-]$$

and

$$-\log [\text{OH}^-] = \text{p}K_w + \log h$$

Since the value of the ionic product, $\text{p}K_w$, in concentrated solutions of magnesium chloride cannot be determined without a prior knowledge of the hydrolytic equilibria of the magnesium ion, and conversely, it was necessary to estimate this quantity from data for similar solutions of a comparable but unhydrolysed, metal ion. For this purpose, published data⁹ for solutions of barium chloride and of sodium chloride were combined to give the following estimates of $\text{p}K_w$

B	1.50	1.25	1.00
$\text{p}K_w$ 25°C	14.469	14.377	14.371

The errors in Z introduced by this approximation are small since $[\text{OH}^-]$ was always less than about $10^{-3}H$.

The data, $Z(\log h)_B$, obtained from the results of the various titrations are summarised in Fig. 1. Given the assumption that the magnitudes of the activity factors, involved in the formation constants of the hydrolysed species, do not change greatly over the range of values of B which was investigated, the non-coincidence of the curves indicates that at least one polynuclear species must be formed.

Fig. 1. Data, $Z(\log h)_B$, on the hydrolysis of magnesium in 3 M Cl^- medium. Circles: experimental points. Curves: calculated with $\beta_{1,2}$ and $\beta_{4,4}$ given in Table 3.

Fig. 2. Graphs of Zh versus $(10^9 h)^{1-p}$, relating to 1.500 M MgCl_2 , for $p = 3, 4$ (dots) and 5.

In the preliminary treatment of these data they were first analysed with regard to the number, p , of hydroxyl groups contained in the hydrolysed species, each set of data being treated separately. The sets of data for the different values of B were then combined, in order that an estimate might be formed of the number, q , of magnesium atoms present in each hydrolysed species.

The formation of any one hydrolysed species, $\text{Mg}_q(\text{OH})_p^{2q-p}$, may be represented by the reaction scheme

for which the equilibrium constant, β_{pq} , which includes activity factors that are assumed to be constant at constant B , is defined by

$$\beta_{p,q} = [\text{Mg}_q(\text{OH})_p^{2q-p}][\text{Mg}^{2+}]^{-q}[\text{H}^+]^p = [\text{Mg}_q(\text{OH})_p^{2q-p}]b^{-q}h^p$$

Thus the total concentration of hydrogen ion set free by hydrolysis, BZ , may be written

$$BZ = \sum_p \sum_q p\beta_{p,q}b^qh^{-p}$$

and, if Z is so small that $b \approx B$,

$$Zh = \sum_p \sum_q p\beta_{p,q}B^{q-1}h^{1-p}$$

In an analysis for homoligandic species, *i.e.* those containing the same number of hydroxyl groups, it may be first supposed that p assumes only two discrete values, 1 and P . Then,

$$Zh = \sum_q \beta_{1,q}B^{q-1} + P \sum_q \beta_{P,q}B^{q-1}h^{1-P} \quad (3)$$

Thus, if this hypothesis were valid, a plot of Zh versus h^{1-P} for a constant value of B and a unique value of p , would describe a straight line.

The sets of data, $Z(\log h)_B$, were treated on this basis by the construction of graphs of Zh versus h^{1-P} , for several different values of p . A good fit to a straight line was found when, and only when, $p = 4$. This, which is true for each value of B , is illustrated by the graphs, for $B = 1.500 \text{ M}$, shown in Fig. 2. It was concluded, therefore, that the data are consistent with the formation of complexes of the types $\text{Mg}_q\text{OH}^{2q-1}$ and $\text{Mg}_q(\text{OH})_4^{2q-4}$, alone.

In a further analysis of the data, with regard to the values assumed by q , it may be first supposed, as the simplest hypothesis, that only a single monoligandic species, $\text{Mg}_1\text{OH}^{2-1}$, and a single tetraligandic species, $\text{Mg}_4(\text{OH})_4^{2-4}$, are formed. Then,

$$Zh = \beta_{1,Q}B^{Q-1} + 4 \beta_{4,Q'}B^{Q'-1}h^{-3}$$

Thus, if this hypothesis were valid and if the changes in the activity factors on going from one value of B to another are not large, estimates of Q and of Q' , respectively, might be formed from the variations with B of the Zh -intercepts and of the gradients of the lines $Zh(h^{-3})_B$.

The intercepts of the best (least squares) lines defined by the data lead to the first estimates, $\beta_{1,Q}$, given in Table 2, of formation constants for the most probable, alternative, monoligandic species, MgOH^+ and $\text{Mg}_2\text{OH}^{3+}$. It is seen that $\beta_{1,1}$ and $\beta_{1,2}$ vary with B , and in opposite senses. The rate of change

Table 2. First estimates of formation constants for hydrolysed magnesium species, obtained by graphical analysis.

B	1.500	1.250	1.000
$10^{13} \beta_{1,1}$	6.9 ± 2.2	6.5 ± 1.4	5.1 ± 0.9
or $10^{13} \beta_{1,2}$	4.6 ± 1.5	5.2 ± 1.1	5.1 ± 0.9
and $10^{40} \beta_{4,4}$	1.68 ± 0.02	1.55 ± 0.02	1.48 ± 0.03

Table 3. Final, best estimates of formation constants for hydrolysed magnesium species, obtained using LETAGROP.

B	1.500	1.250	1.000
$10^{13} \beta_{1,1}$	6.2 ± 2.1	6.3 ± 1.0	4.7 ± 0.7
or $10^{13} \beta_{1,2}$	4.1 ± 1.4	5.0 ± 0.8	4.7 ± 0.7
and $10^{40} \beta_{4,4}$	1.75 ± 0.14	1.60 ± 0.07	1.53 ± 0.04

of $\beta_{1,2}$ is smaller than that of $\beta_{1,1}$ and, for this reason, the formation of $\text{Mg}_2\text{OH}^{3+}$ might be regarded as being more probable than that of MgOH^+ , but the latter cannot be excluded on the basis of the present data. With regard to other alternative monoligandic species, *e.g.*, $\text{Mg}_3\text{OH}^{5+}$, estimates of formation constants for such species vary more rapidly with B than does either $\beta_{1,1}$ or $\beta_{1,2}$ and it may be concluded that their formation is less probable.

The gradients of the best lines, $Zh(h^{-3})_B$, for $B = 1.500$ M and $B = 1.250$ M, taken with an estimate of $4 \beta_{4,Q}$ obtained from that of the best line for $B = 1.000$ M, lead to the results $Q' = 4.3$ and $Q' = 4.2$, respectively, indicating that the most probable tetraligandic species is $\text{Mg}_4(\text{OH})_4^{4+}$. First estimates of formation constants for this species, appropriate to each value of B , calculated from the gradients of these lines, are given in Table 2. The most probable alternative tetraligandic species are $\text{Mg}_3(\text{OH})_4^{2+}$ and $\text{Mg}_5(\text{OH})_4^{6+}$. Estimates of formation constants for these species, similarly calculated, vary more rapidly with B than does $\beta_{4,4}$, and each in a different sense, and it may be concluded that the formation of these species is less probable.

Thus it might be concluded that the data are consistent with the formation of either MgOH^+ or $\text{Mg}_2\text{OH}^{3+}$, together with $\text{Mg}_4(\text{OH})_4^{4+}$. No other hypothesis involving the formation of only two species explains the data more satisfactorily.

The variation with B of the formation constants in Table 2 might be attributable to changes in the corresponding quotients of activity factors; at present there appears to be no means of estimating the magnitudes of these quotients or their rate of change with B . However, it is desirable to consider these changes in relation to alternative hypotheses, involving the coexistence of more than two hydrolysed magnesium species, which might be supposed to explain the data.

The term, in eqn. 3, for monoligandic species is

$$\lim_{h^{-3} \rightarrow 0} Zh(h^{-3})_B = \sum_q \beta_{1,q} B^{q-1} = \beta_{1,1} + \beta_{1,2} B + \dots$$

Suppose that the first two monoligandic species are present, then

$$\lim_{h^{-3} \rightarrow 0} Zh(h^{-3})_B = \beta_{1,1} + \beta_{1,2} B$$

Thus, a linear increase with B of the intercepts of the lines, $Zh(h^{-3})_B$, might be interpreted as being consistent with the formation of both MgOH^+ and $\text{Mg}_2\text{OH}^{3+}$, together with tetraligandic species. On this basis, the best line that can be fitted to the mean values of these intercepts ($\beta_{1,1}$ in Table 2) would lead to the constants

$$10^{13} \beta'_{1,1} = 1.8 \pm 1.3, \text{ and } 10^{13} \beta_{1,2} = 3.6 \pm 1.8$$

However, the correlation between these intercepts and B is barely significant, and when weights are introduced, inversely proportional to the variances in the intercepts, no significant correlation is found. It may be concluded, therefore, that the coexistence of the species MgOH^+ and $\text{Mg}_2\text{OH}^{3+}$ cannot be demonstrated with the present data.

The term, in eqn. 3, for tetraligandic species is

$$(\partial(Zh)/\partial h^{-3})_B = P \sum \beta_{P,q} B^{q-1} = P(\beta_{P,1} + \beta_{P,2} B + \dots)$$

Suppose that only the fourth and the fifth tetraligandic species are present. Then,

$$(\partial(Zh)/\partial h^{-3})_B = 4 B^3(\beta_{4,4} + \beta_{4,5} B)$$

Thus, a linear increase with B of $0.25B^{-3}$ times the gradients of the lines, $Zh(h^{-3})_B$, might be interpreted as being consistent with the formation of the species $\text{Mg}_4(\text{OH})_4^{4+}$ and $\text{Mg}_5(\text{OH})_4^{6+}$, together with monoligandic species. This argument, applied to the best line fitted to mean values ($\beta_{4,4}$ in Table 2) would lead to the constants

$$10^{40} \beta'_{4,4} = 1.1 \pm 0.1, \text{ and } 10^{40} \beta'_{4,5} = 0.4 \pm 0.1$$

In this case the correlation is more probably significant, but, because of the relatively large errors in the gradients of the lines, $Zh(h^{-3})_B$ and of the limited number of values of B used, the formation of the species $\text{Mg}_5(\text{OH})_4^{6+}$ cannot be inferred with any assurance from the present data.

Thus it may be concluded that the best interpretation of the present data is in terms of the formation of the species MgOH^+ or Mg_2OH^+ , and $\text{Mg}_4(\text{OH})_4^{4+}$. The first estimates of the formation constants for these species, obtained by the preliminary, graphical treatment, have been refined using the "pit-mapping" method of LETAGROP program for the Ferranti, Mercury, computer.^{10,11} The final, "best" values obtained by this method are given in Table 3. The fit of the data to these constants is illustrated in Fig. 1, in which the full lines describe the curves, $Z(\log h)_B$, computed from the constants by means of the KUSKA loop of the program.

Fig. 3. An illustration of the hysteresis in data, $Z(\log h)_B$, from titrations in which B was 1.250 M: titration 1, $\circ$ -forward, $\bullet$ -back, and titration 3, $\blacktriangle$ -forward, $\blacksquare$ -back.

DISCUSSION

It can be seen from Fig. 1 and from the arguments above, that the experimental data are in good agreement with the conclusion that, when $8.5 < -\log h < 9.25$, the hydrolysis of the ion Mg^{2+} , in solutions containing from 1.0 M to 1.5 M magnesium and 3.0 M chloride ion, leads to the formation of a monoligandic species and a tetraligandic species. More than two hydrolysed magnesium species may be formed but this cannot be demonstrated from these data, with any high degree of assurance, partly because of the relatively high errors in them.

When the data are expressed in the form of the curves $Z(\log h)_B$, these errors, which are especially evident in the results of the titrations where $B = 1.250$ M, appear as small but significant differences between the shapes of the curves obtained from different replicate titrations. If it is assumed that the hydrogen electrode functions ideally in the solutions that were studied, such differences must be associated with systematic errors in H . For, since $[\text{OH}^-] \ll H$, errors in E° result only in the displacement of the curves along the $\log h$ -axis, without significant change in their shape.

Biedermann and Ciavatta¹² have discussed the errors arising in studies of hydrolysis equilibria, from the practically unavoidable presence of hydrolysable impurities. They point out that these will be important when Z is limited to small values and $5 < -\log h < 11$, especially when titrations with a solution of a strong base are involved, as in the present case.

There can be no doubt that systematic errors arising from the presence of foreign protolytes in the titration solutions, occur in the values of H given in Table 1. The normality of the barium hydroxide solution, T_1 , changed from titration to titration and, in consequence, so also did the volumes of T_1 and of T_2 which were added to attain any given value of H . Thus the systematic

error in H , arising from these foreign protolytes, varied somewhat between replicate titrations. However, the differences between the shapes of the experimental curves, $Z(\log h)_B$, for different replicate titrations cannot be attributed with confidence entirely to this cause, because of features of the data, not hitherto considered.

As indicated in the description of the experimental procedure, some experiments were continued with a back titration. This was concluded when H again reached about 0.01 M. Such, customary, back titrations are primarily intended to test that equilibrium has been attained at each point of the forward titration, and especially when a glass electrode has been employed, that the E° of the cell has not significantly changed during the course of the experiment. Neither of these conditions has been completely satisfied in this investigation.

Some data, $Z(\log h)_B$, obtained from the measurements with cell I in the forward and in the back titrations where $B = 1.250$ M (2 and 3 in Table 1), are illustrated in Fig. 3. A significant, though small, hysteretic effect is evident in them. A similar effect appears to have been observed by Gjalbaek¹³ during the course of an investigation of equilibria involving magnesium hydroxide, which he carried out using the hydrogen electrode. In addition to this hysteresis, the experimental data for both of these titrations show that E_I° decreased by about 0.3 mV during the course of the experiments: a change of this order in either E_I° or E_{II}° may be inferred from the sums, $(E_I + E_{II})$, of the emf's at each of the points where $H > 0$.

In experiments such as those reported here, involving the addition of a solution of a strong base, some difficulty may arise from the occurrence, during the addition, of locally high concentrations of base leading to the transient formation of a visible precipitate. In favourable cases this precipitate will rapidly redissolve, but in some cases, *e.g.*, that of iron, it may redissolve only slowly and, in consequence, the emf of a cell involving the solution will only slowly become steady. In an extreme case, the redissolution of the precipitate may take so long a time that the system may reach a spurious equilibrium, so that a virtually stable emf may be observed. Moreover, provided that only a small proportion of the metal were bound in this way, this spurious equilibrium might be reproducible within narrow limits and, insofar as this were true, the emf corresponding to it would be close to that corresponding to true equilibrium.

Although in this investigation, no visible precipitate was observed, it was found in some subsidiary turbidimetric experiments that appreciable amounts of colloidal material were formed during the titrations. It was not possible to make precise measurements of this effect but it was estimated that the concentration of colloidal material increased linearly with the volume of base solution added.

If the formation of colloidal particles is an intermediate stage between the formation of polynuclear species and the formation of a precipitate, it is likely to be accompanied by the elimination of protons and hence to give rise to small errors in H . Thus it seems probable that this phenomenon was the primary cause of the small differences between the shapes of the experimental curves, $Z(\log h)_B$, for different replicate titrations, and of the observed hysteretic effects.

The unsatisfactory performance of the hydrogen electrode in some solutions containing polyvalent ions, has been reported by Biedermann and Ciavatta¹² who consider that it may be caused by poisoning of the catalytic surface by adsorbed material. It is not unlikely that such an adsorption effect occurred, in the present investigation, and that this might cause or contribute to small changes in E_1° , like those observed. However, other potentially causative or contributory effects may be supposed, e.g., slow diffusion of solution from the interstices of the catalytic surface, and, at present, the most probable cause of these changes cannot be determined.

To some extent, the errors in the experimental data obtained in the present investigation, and the consequent uncertainties in the interpretation of the data, are concomitants of the problem. Thus, at present, it seems to be necessary to use the self-medium method, or some modification of it, if weak complexes for which the ratio $q:p$ is high are to be studied. This inevitably increases the uncertainties in quantities related to those coexisting complexes for which the ratio $q:p$ is relatively low: the variance in $\beta'_{1,1}$ above, for example, is inversely proportional to the average value of B which was, necessarily, high. However, the greater part of these errors arose from the experimental method employed. This adds point to Biedermann and Ciavatta's inference¹² that, when only low values of Z can be attained, titrations involving the addition of a solution of a strong base are an unsuitable means for the investigation of hydrolysis equilibria. Recently a coulometric method has been developed¹⁴ which is more appropriate to such a case, and a better understanding of the hydrolysis of magnesium might be obtained by using this method.

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