Hydrolysis of Magnesium(II) in 1.0 mol dm^{-3} Aqueous $(Na,H)NO_3$ Solution

By **Hisahiko Einaga**, National Institute for Researches in Inorganic Materials, Sakura, Niihari, Ibaraki, 300-31, Japan

Hydrolysis of magnesium(II) has been studied in 1.0 mol dm^{-3} $(Na,H)NO_3$ aqueous solution at 25.0 °C by means of e.m.f. measurements of a cell containing suitable test solutions. Magnesium(II) is hydrolyzed to form polynuclear complexes $[Mg_2(OH)_2]^{2+}$ (log β_{22} -22.0_7) and $[Mg_3(OH)_4]^{2+}$ (log β_{34} -39.0_6). The formation of these species can be accounted for by the ' truncated-core-plus-links ' expression.

HYDROLYSIS of magnesium(II) in aqueous solution has been widely studied and the formation constants of hydrolyzed species have been compiled.[1,2] Close inspection of these data reveals that there are some inconsistencies both in the formulae and in the stability (or formation) constants of the hydrolyzed species. A detailed study was made by Lewis,[3] who investigated the hydrolysis of Mg^{II} in a solution (3 mol dm^{-3} in chloride) of magnesium chloride and sodium chloride. However, complex formation between Mg^{II} and chloride ions (at this high concentration) may affect the extent of hydrolysis, and it would be preferable to reduce the possibility of such complex formation by using an anion which has little tendency to complex with Mg^{II}. Nitrate

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[1] L. G. Sillén and A. E. Martell, 'Stability Constants of Metal–Ion Complexes,' The Chemical Society (London), *Special Publ.*, no. 17, 1964, p. 41; no. 25, 1971, p. 16.

[2] W. Feitknecht and P. Schindler, *Pure Appl. Chem.*, 1963, **6**, 160.

[3] D. Lewis, *Acta Chem. Scand.*, 1963, **17**, 1891.

ions are suitable from this standpoint and in this study I have used a solution (1 mol dm^{-3} in nitrate) of magnesium nitrate and sodium nitrate.

EXPERIMENTAL

Reagents.—Magnesium nitrate solution was prepared from the recrystallized hexahydrate salt and was standardized by an ethylenediaminetetra-acetic acid (H_4edta) titration method against Eriochrome Black T as a metallochromic indicator.[4] Sodium nitrate solution was prepared from the recrystallized salt. Its concentration was determined by evaporating an aliquot portion to dryness at *ca.* 120 °C and weighing the residue. Nitric acid (s. g. 1.38) was standardized (after the appropriate dilution) with sodium carbonate as the primary standard by the conventional procedure. Sodium hydroxide was dissolved in small volumes of water (*e.g.* to give a 3 mol dm^{-3} solution) and a small amount of barium hydroxide (in the mol ratio $Ba[OH]_2 : Na[OH] = 1 : 100$) was then added. After standing for a few days, the supernatant was carefully removed and was preserved in a polyethylene bottle as a stock solution. It was appropriately diluted and standardized potentiometrically with the standard nitric acid solution.

Chemicals used were of analytical reagent grade as supplied by Wako Pure Chemicals Ind., Ltd., Osaka, Japan, unless otherwise stated. Preliminary experimental checks on elements and salts which are liable to cause hydrolytic reaction, such as Si^{IV}, Ti^{IV}, Al^{III}, Fe^{II}, Fe^{III}, *etc.*, and to react with Mg^{II}, such as phosphate, *etc.*, revealed that they were mostly absent or present in such concentrations (parts per million) as to exhibit negligible effects. Twice-distilled fresh water was used throughout the experiments.

Apparatus.—An Orion model 801 digital pH meter was used for potentiometric measurements. A Horiba no. 1326 glass electrode with a no. 2310 saturated calomel reference electrode was used for the detection of the e.m.f. in conjunction with an appropriate salt bridge as described later. A cell for measurements of the e.m.f. was constructed from a polyethylene bottle (100 cm^3), to which both the glass and the reference electrodes with the salt bridge were attached. The cell was kept at 25.0 ± 0.1 °C by circulation of water from a water-bath the temperature of which varied by less than 0.05 °C. The same water-bath was used for equilibration of the test solution.

Procedure.—Potentiometric measurements were made on several series of solutions which constituted a part of the following cell:

$$\text{Hg, Hg}_2\text{Cl}_2|3.33\ \text{mol dm}^{-3}\ \text{KCl}||1.0\ \text{mol dm}^{-3}\ \text{KCl}||1.0\ \text{mol dm}^{-3}\ \text{Na[NO}_3]||\text{test solution}|\text{glass electrode}$$

The test solution had the following composition: B mol dm^{-3} Mg^{II}, H mol dm^{-3} H^+, $(1.0 - 2B - H)$ mol dm^{-3} Na^+, and 1.0 mol dm^{-3} $[NO_3]^-$. The e.m.f. of the cell containing the test solution was measured after standing for 6 h at 25.0 °C, which was sufficient to attain equilibrium. Variations in e.m.f. were less than ±0.2 mV. The hydrogen-ion concentration at equilibrium was calculated from the measured e.m.f. according to the relation (1) where $E^{\ominus}$

$$E/\text{mV} = E^{\ominus} + 59.15\log h + E_j(h) \qquad (1)$$

is the standard electrode potential of the cell, $E_j(h)$ the liquid junction potential, and $h = [H^+]$. The ionic product of water K_w ($= [H^+][OH^-]$) in 1.0 mol dm^{-3} (Na,H)NO_3 aqueous solution at 25.0 °C was estimated by combination of published data for solutions of potassium nitrate and sodium perchlorate[5] to be $\log K_w = -13.80$.

RESULTS

Experimental data obtained for the relation between Z, the average number of hydrogen ions released from each hydrated Mg^{II}, and log h, the logarithm of the free hydrogen-ion concentration at equilibrium, for the specified value of B are presented in Figure 1. Here, the value of Z was calculated according to relation (2). It may be seen from

$$Z = ([OH^-] - H)/B \text{ and } \log [OH^-] = \log K_w - \log h \qquad (2)$$

Figure 1 that polynuclear hydrolyzed complexes of Mg^{II} are present in the solution because the relation between Z and log h is dependent on B. The hydrolysis of magnesium(II), $[Mg(OH_2)_n]^{2+}$, is represented as in (3) and (4).

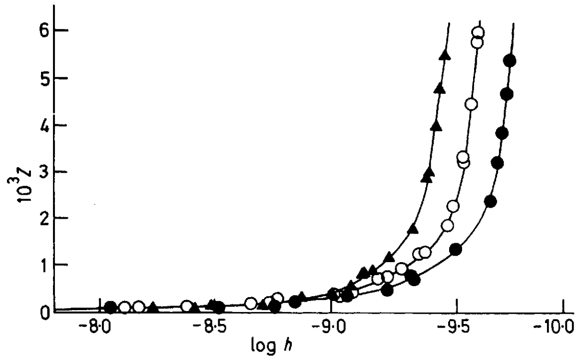

FIGURE 1 Relation between Z and log h for 0.049 6_4 (●), 0.096 2_4 (○), and 0.192_5 mol dm^{-3} Mg^{II} (▲)

$$q[Mg(OH_2)_n]^{2+} \overset{\beta_{qp}}{\rightleftharpoons} [Mg_q(OH)_p(OH_2)_{n-p}]^{(2q-p)+} + pH^+ \qquad (3)$$

The formulae $[Mg_q(OH)_p(OH_2)_{n-p}]^{(2q-p)+}$ will be simplified hereafter as $[Mg_q(OH)_p]^{(2q-p)+}$. Here p is the number of

$$\beta_{qp} = [Mg_q(OH)_p{}^{(2q-p)+}]h^p/[Mg(OH_2)_n{}^{2+}]^q \qquad (4)$$

hydroxo-groups and q the number of magnesium(II) atoms present in the hydrolyzed species, respectively. The terms Z and B are given by equations (5) and (6). Expression (7)

$$Z = \frac{\sum_1^q \sum_1^p p\beta_{qp}[Mg(OH_2)_n{}^{2+}]^q h^{-p}}{[Mg(OH_2)_n{}^{2+}] + \sum_1^q \sum_1^p q\beta_{qp}[Mg(OH_2)_n{}^{2+}]^q h^{-p}} \qquad (5)$$

$$B = [Mg(OH_2)_n{}^{2+}] + \sum_1^q \sum_1^p q\beta_{qp}[Mg(OH_2)_n{}^{2+}]^q h^{-p} \qquad (6)$$

then follows where BZ corresponds to the total concentration of hydrogen ion released by the hydrolysis.

$$BZ = \sum_1^q \sum_1^p p\beta_{qp}[Mg(OH_2)_n{}^{2+}]^q h^{-p} \qquad (7)$$

To simplify these equations, it was assumed that the complexes can be represented by the 'core-plus-links' expression,[6] $[Mg\{(OH)_tMg\}_m]^{[(2-t)m+2]+}$, where t is the

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[4] K. Ueno, 'Method of Chelatometric Titrations (Kireito Tekiteiho),' Nankodo, Tokyo, 1962, p. 274.

[5] Ref. 1, no. 17, p. 40; no. 25, p. 14.

[6] L. G. Sillén, *Acta Chem. Scand.*, 1954, **8**, 299, 318; S. Hietanen and L. G. Sillén, *ibid.*, p. 1607.

spacing for the specified value of Z of a set of parallel curves $Z(\log h)_B$ along the h axis as formulated in (8) and m

$$t = -(\partial \log B / \partial \log h)_Z \qquad (8)$$

is an integer starting from zero. In this case, the relations (9) hold. Hence, Z and B can be rewritten as follows:

$$t = p/(q - 1) \text{ and } m = q - 1 \qquad (9)$$

$$Z = \frac{\sum_{1}^{m} tm\beta_{m+1,tm}[\mathrm{Mg(OH_2)}_n{}^{2+}]^m h^{-tm}}{1 + \sum_{1}^{m} (m + 1)\beta_{m+1,tm}[\mathrm{Mg(OH_2)}_n{}^{2+}]^m h^{-tm}} \qquad (5')$$

$$B = [\mathrm{Mg(OH_2)}_n{}^{2+}]$$
$$\{1 + \sum_{1}^{m} (m + 1)\beta_{m+1,tm}[\mathrm{Mg(OH_2)}_n{}^{2+}]^m h^{-tm}\} \qquad (6')$$

If $Z \leqslant 1$, equations (5′) and (6′) can be combined into (10). Equation (10) may be analysed by a well known

$$Z = \sum_{1}^{m} tm\beta_{m+1,tm}B^m h^{-tm} \qquad (10)$$

curve-fitting method.[7] When $Y = Z/t$ and $X = Bh^{-t}$, equation (10) reduces to (11). Equation (11) clearly shows

$$Y = \sum_{1}^{m} m\beta_{m+1,tm}X^m \qquad (11)$$

that introduction of the new parameters X and Y instead of B, h, and Z relates all the experimental data on the curves $Z = \mathrm{f}(B,h)$ to $Y = \mathrm{g}(X)$ by the parameter t. The normalized curve is then expressed as (11′) and the stability

$$Y_0 = \sum_{i=1}^{m-1} p_{i0}X_0{}^i + X_0{}^m \qquad (11')$$

constants $\beta_{m+1,tm}$ can be obtained from the relations (12)

$$\log \beta_{m+1,tm} = -\log m + m(\log X_0 - \log X) \qquad (12)$$

and (13) where i is an integer starting from zero and ending

$$\log \beta_{i+1,ti} = \log (p_{i0}/i) + (i/m) \log m\beta_{m+1,tm} \qquad (13)$$

at $m - 1$ and p_{i0} is a parameter determined experimentally. On treating the data presented in Figure 2, it was concluded that the experimental data can be best fitted by the normalized curve (14) by taking the value of $t = 2$ determined from Figure 1.

$$Y_0 = 3.81 \times 10^{-2}X_0 + X_0{}^2 \qquad (14)$$

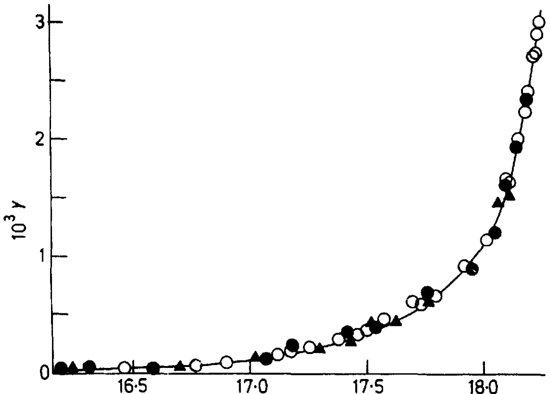

FIGURE 2 Relation between $Y(= Z/2)$ and $\log X$ $(= Bh^{-2})$. Conditions as in Figure 1. The full line is a theoretical curve drawn from the values of $\log \beta_{22}$ -21.0_7 and $\log \beta_{34}$ -39.0_6

Formulae of the hydrolyzed species of $\mathrm{Mg^{II}}$ and their stability constants are summarized in the Table. In Figure 2, the full line is a theoretical curve drawn from the data in the Table, and is in good agreement with the experimental data.

Formulae and stability constants of hydrolyzed species of magnesium(II) [25.0 °C, 1.0 mol dm^{-3} $\mathrm{(Na,H)NO_3}$]

Species	$\log \beta_{m+1,2m}$	m	p	q	Remarks
$[\mathrm{Mg_2(OH)_2}]^{2+}$	-21.0_7	1	2	2	$[\mathrm{Mg\{(OH)_2Mg\}}]^{2+}$
$[\mathrm{Mg_3(OH)_4}]^{2+}$	-39.0_6	2	4	3	$[\mathrm{Mg\{(OH)_2Mg\}_2}]^{2+}$

DISCUSSION

In this study a ' batch ' system was chosen for the preparation of test solutions and measurements of $\log h$, instead of a ' titration ' system which may give more accurate measurements of $\log h$. This stems from the fact that the surface of a glass electrode may be susceptible to change on its repeated immersion in and extraction from separated solutions. However, the batch system was chosen because the formation and attainment of equilibrium for the hydrolysis of $\mathrm{Mg^{II}}$ was so slow that it was necessary to allow the test solution to stand for more than *ca.* 4 h. Measurements of the e.m.f. were made 6 h after the preparation of the solution.

Hydrolysis of $\mathrm{Mg^{II}}$ to form polycationic species has been studied by Lewis,[3] who concluded that in aqueous solutions (3 mol dm^{-3} in chloride) at 25 °C there exist $[\mathrm{Mg(OH)}]^+$ ($\log \beta_{11}$ -12.20 to *ca.* -12.33) {or $[\mathrm{Mg_2(OH)}]^{3+}$ ($\log \beta_{21}$ -12.30 to *ca.* -12.38)} and $[\mathrm{Mg_4(OH)_4}]^{4+}$ ($\log \beta_{44}$ -39.76 to *ca.* -39.82), although he regarded the formation of $[\mathrm{Mg_2(OH)}]^{3+}$ as being more probable than that of $[\mathrm{Mg(OH)}]^+$. It may not be appropriate to compare these results directly with the present results because the nature of the solvent medium used was different, but some inconsistencies can be pointed out, especially in the form of the hydrolyzed species of $\mathrm{Mg^{II}}$. The cause of these inconsistencies cannot easily be clarified because the experimental conditions were rather different. The cause may be due in part to the difference in solvent composition, and perhaps to the difference in experimental procedure, because slow attainment of hydrolytic equilibria may cause some error in the analysis of the potentiometric titration data. The role of solvent anions in the hydrolysis of $\mathrm{Mg^{II}}$ should be studied in future.

As far as the present work is concerned, the formation of polynuclear cationic species of $\mathrm{Mg^{II}}$ is expressed by the ' truncated-core-plus-links ' system of Sillén and his co-workers[6] as $[\mathrm{Mg\{(OH)_2Mg\}}_n]^{2+}$ ($n = 1$, 2, *etc.*). According to these findings, there are possibilities for the existence of other higher polycationic hydrolyzed species, such as $[\mathrm{Mg_4(OH)_6}]^{2+}$. It was difficult to ascertain the presence of these species by the experimental procedure adopted in this work.

[6/1726 *Received, 13th September,* 1976]

[7] L. G. Sillén, *Acta Chem. Scand.*, 1956, **10**, 186.