DALTON

Hydrolysis of magnesium(II) at elevated temperatures†

Paul L. Brown,[*,a] **Segal E. Drummond, jun.**[b] **and Donald A. Palmer**[*,b]

[a] *Environment Division, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234, Australia*

[b] *Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, Tennessee 37831-6110, USA*

A potentiometric titration technique utilising a hydrogen-electrode concentration cell was applied to study the hydrolytic behaviour of the magnesium(II) ion in 0.10 and 1.0 mol kg^{-1} sodium chloride at 60, 100, 150 and 200 °C. Data analysis indicates the presence of Mg^{2+} (aq) and the solid species $Mg(OH)_2$ (s), only. Independent measurements have confirmed that $[Mg(OH)]^+$ (aq) is a negligible ionic species under the prevailing experimental conditions. Experimental evidence indicated that the solid species formed both rapidly and reversibly. The equilibrium quotients for brucite formation were determined for each temperature and ionic strength investigated and the corresponding enthalpy and entropy of formation calculated. Formation constants have also been calculated at zero ionic strength using the Debye–Hückel equation, and these data, together with some other literature data, comply with the equation $\log \beta_{12s}{}^0 = 2.49 - (5847/T)$ where $\log \beta_{12s}{}^0$ is the logarithm of the formation constant of brucite at zero ionic strength and T is the temperature in Kelvin.

The hydrolysis of magnesium(II) has received little attention, particularly at elevated temperatures. The most extensive work, at temperatures below 100 °C, was performed by Hostetler,[2] McGee and Hostetler[3,4] and Lewis.[5] Only Lambert *et al.*[6] and Walther[7] have investigated the solubility of brucite [$Mg(OH)_2$ (s)] at temperatures in excess of 100 °C. The works of Hostetler[2] and Lewis[5] were consistent with the earlier work of Stock and Davies[8] in regard to the formation of the monomeric species $[Mg(OH)]^+$. Lewis[5] also chose the polymeric species $[Mg_4(OH)_4]^{4+}$ to explain his data, however he could not make an unequivocal choice as to the stoichiometry of this polymeric species. Later, McGee and Hostetler[3,4] performed experiments to determine the formation constants of both $[Mg(OH)]^+$ and $Mg(OH)_2$ (s) from 10 to 90 °C. Recently, Wesolowski and Palmer[9] performed potentiometric titrations with a modified version of the cell described here to determine the formation constant of $[Mg(OH)]^+$ from 25 to 250 °C at ionic strengths ranging from 0.1 to 5.0 mol kg^{-1} (NaCl).

The hydrolysis of magnesium(II) has an important role in both environmental and industrial processes.[3,4] In the environment, brucite is formed principally from the serpentisation process, where local ground-waters in the vicinity may have pH values in excess of 11, and the species $[Mg(OH)]^+$ is one of the dominant magnesium(II) aqueous species.[4] Magnesium hydrolysis is also important in industrial processes such as desalinisation and the production of magnesium from sea-water.[3] Since many of these processes often occur at elevated temperatures it appeared appropriate to reinvestigate the system and to use the advanced experimental and computational techniques developed at these laboratories[1,9–15] in an attempt to elucidate the magnesium(II) hydrolysis species which form. The current study was carried out at 60, 100, 150 and 200 °C in 0.10 and 1.0 mol kg^{-1} sodium chloride.

Experimental

Reagents

The source of magnesium was magnesium(II) chloride hexahydrate (Fisher Scientific A.S.C.). This was twice recrystallised, only about the first 10% being taken in each case. The final product was dried *in vacuo* over silica gel and used as a primary standard to prepare the stock solution. The magnesium stock solution was nominally 0.2 mol kg^{-1} (in 0.01 mol kg^{-1} acid). Other chemicals were either from Fisher Scientific A.S.C. (sodium chloride and 50% w/w sodium hydroxide) or A. Daigger and Co. (1 mol dm^{-3} hydrochloric acid). Hydrogen (99.999% purity) was supplied by Union Carbide Corporation. Water was purified by ultrafiltration and ion exchange, followed by distillation.

Procedure

The titration equipment consisted of two Teflon reaction vessels, one (containing the reference solution) housed inside the other (containing the test solution), with electrical contact being maintained between the vessels *via* a porous Teflon plug in the inner vessel.[16] These two vessels were contained in a conventional pressure vessel through which were passed two platinum electrodes (one into each reaction vessel), a titrant line and a hydrogen gas line. The solution in both reaction vessels was magnetically stirred, and the pressure vessel was submerged in a silicone oil-bath. The temperature of the latter was measured with a Rosemont platinum resistance thermometer and displayed on a Doric DS-100-T5 digital display unit. It was maintained *via* a Leeds and Northrup Speedomax recorder and calibrated Azar, which controlled two thermostats (steady and control heat sources). The heat for the thermostats was supplied by two Variac power units.

The platinum electrodes also served as thermocouples (type K chromel–alumel thermocouples) through which the temperature could be measured and displayed on a Doric Trendicator 412A thermometer digital display unit. The potential was measured with a Keithley 619 electrometer/multimeter and plotted on a Texas Instrument chart recorder (Denvo Niten II). The burette was a Ruska Instrument Corporation positive displacement pump (100 cm^3 capacity) the wetted surfaces of which were either Zircolly or Teflon. The pressure in the burette and the pressure vessel were monitored with conventional pressure gauges and displayed with a Precise Sensors Incorporated digital pressure indicator. All lines for hydrogen and titrant passage were made of platinum.

The electrodes, freshly coated with platinum black, dip into

---

† The Hydrolysis of Metal Ions. Part 12.[1]

Table 1 Summary of titrations of magnesium(II) hydrolysis in 0.10 and 1.0 mol kg^{-1} sodium chloride

Total initial magnesium(II) concentration/ mmol kg^{-1}	Ionic strength/ mol kg^{-1}	T/°C	$-\log[H^+]$ range	Number of titration points
5.00	1.0	60	8.979–9.530	10
1.00	1.0	100	8.358–8.648	7
5.00	1.0	100	8.006–8.178	10
9.90	1.0	100	7.904–8.070	8
5.00	1.0	150	7.119–7.394	13
1.00	1.0	200	6.717–6.950	9
5.00	1.0	200	6.401–6.816	13
9.90	1.0	200	6.290–6.381	11
5.00	0.10	60	8.896–9.455	10
5.00	0.10	100	7.956–8.190	9
5.00	0.10	150	6.998–7.365	10
5.00	0.10	200	6.321–6.839	17

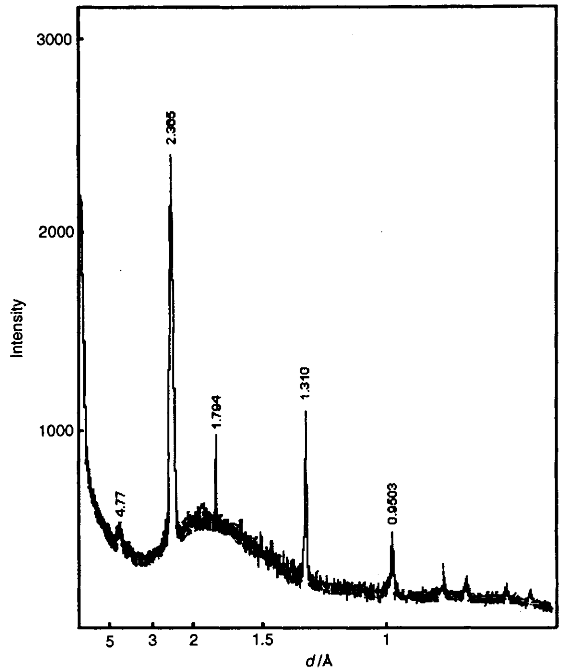

Fig. 1 X-Ray diffraction pattern of the solid taken from a titration experiment which corresponds to the pattern of brucite [$Mg(OH)_2$ (s)]

each vessel containing the inner reference solution and the outer test solution at the same initial composition, resulting eventually in a cell potential of close to zero (mV) at the commencement of each titration. The pressure vessel containing both solutions was immersed in the oil-bath and purged four times with hydrogen gas, with a final hydrogen pressure of 3.0–3.5 MPa. The temperature of the oil-bath was then raised to the desired level and an equilibrium potential established, after which the pressure in the burette was equalised with that in the pressure vessel. Titrant was then added incrementally to the test solution. The condition of equilibrium after each addition was indicated when a constant potential was achieved. Some 7–17 points were taken per titration. A summary of the titration details is given in Table 1; full details are available on request.

A solid product was formed in each titration. A number of these solids were characterised by X-ray diffraction, with Cu-Kα radiation, from 2θ 5 to 75° at a scan step of about 0.01° per 10 s, using a Norelco diffractometer with a diffracted-beam graphite monochromator.

Numerical analysis of the data was performed in the following manner. The NBAR program[17] was utilised to convert the data (pump reading, potential, solution composition, temperature, pressure) into hydrogen-ion and total metal concentrations and $\bar{n}$ data sets, prior to analysis with the ORGLS program.[18] The data treatment within the NBAR routine also included an algorithm for estimating the liquid-junction potential correction that must be applied to the measured potential in view of the differences in molalities of the constituent ions in the test and reference solutions.[18]

Table 2 Diffraction pattern of brucite using Cu-Kα radiation[19]

d/Å	I/I_0	hkl
4.77	90	001
2.365	100	101
1.794	55	102
1.573	35	110
1.494	18	103
1.310	12	201
1.183	10	202
1.034	6	203
1.0067	8	211
0.9503	6	114
0.9455	8	212

Results

The (hypothetical) hydrolysis reactions (1) can be used to define

$$p\mathrm{Mg}^{2+} + q\mathrm{H_2O} \rightleftharpoons [\mathrm{Mg}_p(\mathrm{OH})_q]^{(2p-q)+} + q\mathrm{H}^+ \quad (1)$$

the overall stoichiometric formation constants, β_{pq}, as in equation (2). Each species is represented by either its formula or by a (p,q) pair.

$$\beta_{pq} = [\mathrm{Mg}_p(\mathrm{OH})_q{}^{(2p-q)+}][\mathrm{H}^+]^q/[\mathrm{Mg}^{2+}]^p \quad (2)$$

The precipitates which were found at the end of each experiment were identified by X-ray diffraction as crystalline brucite. A typical pattern taken from one of the experiments is reproduced in Fig. 1 and can be compared to the literature pattern[19] given in Table 2. The experimental data, as illustrated in Fig. 2 (for 0.10 mol kg^{-1}), show a very steep increase in the plots of $\bar{n}$ *versus* $-\log[\mathrm{H}^+]$, consistent with the formation of a solid product. In the plot, $\bar{n}$, which is defined as the ratio of bound, or co-ordinated, hydroxide ion to the total magnesium(II) molality, was calculated according to equation (3),

$$\bar{n} = ([\mathrm{H}^+] - m_\mathrm{H} - [\mathrm{OH}^-])/m_{\Sigma\mathrm{Mg}} \quad (3)$$

where m_H and $m_{\Sigma\mathrm{Mg}}$ represent calculated stoichiometric molalities of hydrogen ion and total magnesium(II), respectively, and $[\mathrm{OH}^-]$ was derived from the measured hydrogen-ion molality and the dissociation constant of water in NaCl.[20]

For the formation of brucite, the equation representing the formation constant is redefined as equation (4), where β_{12s} is

$$\beta_{12s} = [\mathrm{H}^+]^2/[\mathrm{Mg}^{2+}] \quad (4)$$

the formation constant for brucite and is the inverse of the solubility product defined by reaction (5). Equation (4) can be

$$\mathrm{Mg(OH)_2\,(s)} + 2\mathrm{H}^+ \rightleftharpoons \mathrm{Mg}^{2+} + 2\mathrm{H_2O} \quad (5)$$

related to the usual definition of the solubility product of brucite, namely equation (6), through the dissociation constant

$$K_\mathrm{sp} = [\mathrm{Mg}^{2+}][\mathrm{OH}^-]^2 \quad (6)$$

of water; that is, $\beta_{12s} = K_\mathrm{w}{}^2/K_\mathrm{sp}$ where K_w is the dissociation constant of water.

Table 3 Comparison of some models of magnesium(II) hydrolysis

T/°C	Ionic strength/ mol kg^{-1}	log β_{12s}*	log β_{13}	Agreement factor, $\sigma(\bar{n})$
60	0.10	−15.29 (0.02)		0.1063
		−15.33 (0.009)	−27.85 (0.06)	0.0409
100	0.10	−13.45 (0.02)		0.1670
		−13.53 (0.02)	−24.94 (0.09)	0.0982
150	0.10	−11.62 (0.007)		0.0596
		−11.64 (0.002)	−22.23 (0.02)	0.0100
200	0.10	−10.21 (0.01)		0.0960
		−10.24 (0.006)	−20.12 (0.05)	0.0453
60	1.0	−15.52 (0.01)		0.0955
		−15.55 (0.01)	−28.26 (0.12)	0.0643
100	1.0	−13.64 (0.01)		0.2520
		−13.68 (0.005)	−25.49 (0.03)	0.0783
150	1.0	−11.88 (0.006)		0.0638
		−11.94 (0.004)	−22.46 (0.04)	0.0210
200	1.0	−10.44 (0.01)		0.2653
		−10.49 (0.006)	−20.60 (0.03)	0.0961

* Standard deviations in parentheses; β_{12s} is defined as the formation constant of solid magnesium(II) hydroxide.

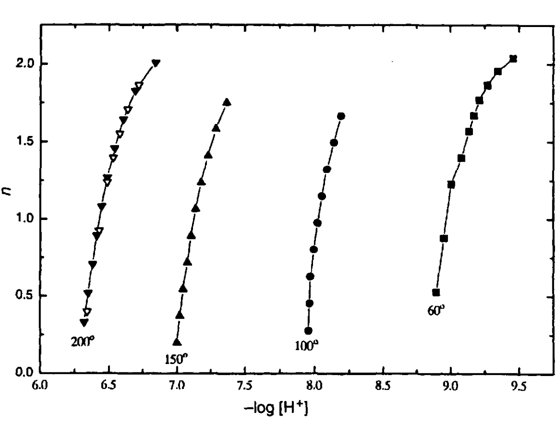

Fig. 2 Titration data for magnesium(II) hydrolysis in 0.10 mol kg^{-1} sodium chloride. The closed triangles for the 200 °C data represent a forward titration with NaOH and the open triangles a back titration with HCl

Initial weighted regression analysis involved models containing the solid species, $Mg(OH)_2$ (s), together with the aqueous species $[Mg(OH)]^+$, $Mg(OH)_2$ (aq) and $[Mg(OH)_3]^+$. However, visual inspection of the experimental data curves (for example, see Fig. 2) indicated that the amount of hydrolysis that occurred before precipitation was almost negligible. This qualitative judgement was substantiated by subsequent potentiometric titrations with the same apparatus,[9] which confirmed that precipitation of brucite occurred after less than 4% hydrolysis, with only $[Mg(OH)]^+$ forming before the onset of precipitation reactions. Table 3 contains the results of computations for models containing the solid species only and one containing the solid species together with the anionic species $[Mg(OH)_3]^-$. The information given indicates that the inclusion of the anionic species improves the fit to the data, as evidenced by the agreement factor, $\sigma(\bar{n})$. However, the inclusion of $[Mg(OH)_3]^-$ would not seem appropriate since its formation constant is inconsistent with that derived for $[Mg(OH)]^+$ by McGee and Hostetler.[3] Generally, it is found that $\beta_{13} < 3\beta_{11}$.[21] From the work of McGee and Hostetler[3] we calculate that, at 60 °C, the value of log β_{11} is -10.61 (at zero ionic strength), and therefore the value of log β_{13} should be less than -31.83. From the data presented in Table 3 the value of log β_{13} from the present study, under the same conditions, is calculated to be -27.80, which is at least four orders of magnitude too large. As such, it is concluded that the only species which forms under the experimental conditions used in the present study is $Mg(OH)_2$ (s).

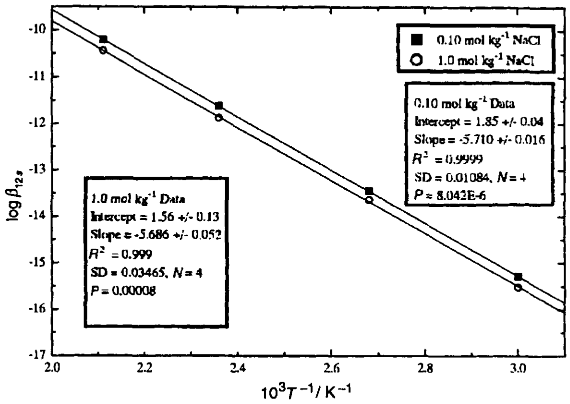

Fig. 3 Correlation of the logarithm of the formation constant, in both 0.10 and 1.0 mol kg^{-1} sodium chloride, of $Mg(OH)_2$ (s) with inverse of temperature

The enthalpy and entropy of formation of the species $Mg(OH)_2$ (s) were obtained by plotting log β_{12s} against the reciprocal of temperature, in Kelvin, as illustrated for both ionic strengths in Fig. 3, which shows that the formation constant is linearly dependent upon $10^3/T$. The slope of the line of best fit is $-\Delta H/2.303R$, where R is the universal gas constant, yielding a value of ΔH of 109 kJ mol^{-1} in both 0.10 and 1.0 mol kg^{-1} (NaCl), whereas ΔS was calculated to be 34.4 and 29.9 J K^{-1} mol^{-1} (25 °C), respectively. It is worth noting that the combined results[3,9] for the first hydrolysis constants of magnesium(II) according to equation (1) also showed a linear dependence of log β_{11} on reciprocal temperature (Kelvin), indicating very little change in solvation accompanying the hydrolysis of the small magnesium ion.

At 200 °C in 0.10 mol kg^{-1} NaCl an initial titration was performed with sodium hydroxide as in all the other titrations; however, this titration was followed immediately by a back-titration with hydrochloric acid (see Fig. 1), demonstrating the reversibility of the reaction.

Discussion

The results from some previous studies of the hydrolysis reactions of magnesium(II) are compared with those from the present study in Table 4. The table shows excellent agreement between the works of McGee and Hostetler[4] and Walther[7] and the present work, for the formation constant of $Mg(OH)_2$ (s), when the differences in ionic strength, temperature and pressure used in the studies are considered, as demonstrated below. Data presented by Walther[7] at higher temperatures have not been included in Table 4 since they would be supercritical at the low pressures used in the present study. Results from Lambert *et al.*[6] have also been excluded since (*a*) pH measurements were conducted at ambient temperature and then corrected to the experimental temperatures and (*b*) it is questionable whether appropriate corrections were made for chloride complexation.

The results presented in Table 4 have been utilised together with the Debye–Hückel equation[22] to calculate the formation constant of $Mg(OH)_2$ (s) at zero ionic strength. The Debye–Hückel equation can be represented by equation (7) where A is

$$\log \beta_{12s} = \log \beta_{12s}{}^0 + A\Delta z^2 I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) + bI \quad (7)$$

the Debye–Hückel constant,[23] I the ionic strength, $\beta_{12s}{}^0$ the formation constant of $Mg(OH)_2$ (s) at zero ionic strength, β_{12s} the same constant at I and Δz^2 is the charge of each species summed over the formation reaction of the complex (*i.e.* -2).

Table 4 Survey of some potentiometric investigations of the hydrolysis of magnesium(II)

Concentration (medium)	T/°C	Total magnesium concentration/ mmol dm^{-3}	$-\log \beta_{pq}$		Ref.
			(1,1)	$(1,2)_s$[a]	
0	25		11.44		8
0	25	2–45	11.44		2
1.6 mol dm^{-3} ($MgCl_2$)	25	1000–1500	12.29[b]		5
0	10	0.19–0.40	12.35		3
0	25	0.19–0.40	11.79		3
0	40	0.19–0.40	11.25		3
0	55	0.19–0.40	10.77		3
0	70	0.19–0.40	10.29		3
0	90	0.19–0.40	9.88		3
0	10	0.860–1.182		18.16	4
0	25	0.571–0.980		17.11	4
0	40	0.224–0.584		16.18	4
0	55	0.198–0.391		15.39	4
0	70	0.122–0.200		14.48	4
0	90	0.142–0.250		13.75	4
0	350			7.00[c]	7
0.10 mol kg^{-1} (NaCl)	60	5.00		15.29	This work
	100	5.00		13.47	This work
	150	5.00		11.62	This work
	200	5.00		10.21	This work
1.0 mol kg^{-1} (NaCl)	60	5.00		15.52	This work
	100	1.00–9.90		13.64	This work
	150	5.00		11.88	This work
	200	1.00–9.90		10.44	This work

[a] $(1,2)_s$ represents the (p,q) pair for the formation constant of solid magnesium(II) hydroxide. [b] $-\log \beta_{pq}$ (4,4) 39.75. [c] Extrapolated to saturation vapour pressure from tabulated values at 1 and 2 kbar.

Table 5 Calculated values of $\log \beta_{12s}{}^0$ at zero ionic strength

T/°C	$\log \beta_{12s}$
25	−17.13
50	−15.61
60	−15.07
100	−13.18
150	−11.33
200	−9.87
250	−8.69
300	−7.71
350	−6.90

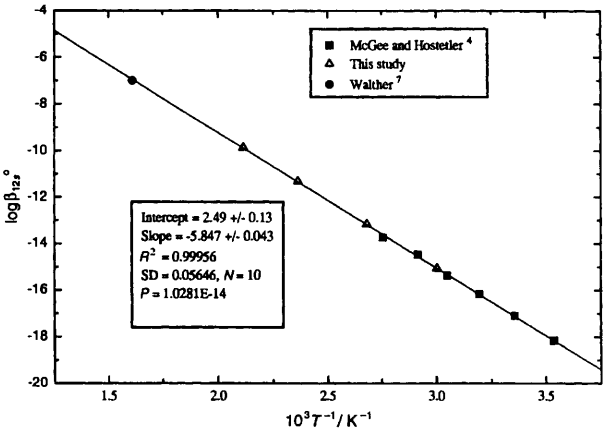

Fig. 4 Correlation of the logarithm of the formation constant, at zero ionic strength, of $Mg(OH)_2$ (s) with inverse of temperature from the present work, McGee and Hostetler,[4] and Walther[7]

The constant b was determined from a linear regression in I. The values for $\log \beta_{12s}{}^0$ are given in Table 5 for each temperature used in the present study together with a number of other temperatures.

Fig. 4 is a plot of $\log \beta_{12s}{}^0$ against $1000/T$ for the results of McGee and Hostetler[4] and the present study (at zero ionic strength). Also included on the plot is the calculated value from the work of Walther.[7] The plot indicates the excellent agreement of the results obtained between the studies and yields, at zero ionic strength, values for ΔH of 112 kJ mol^{-1} and ΔS of 47.7 J K^{-1} mol^{-1} (25 °C). These compare well with the predicted values of Baes and Mesmer,[24] namely 114 kJ mol^{-1} and 60.2 J K^{-1} mol^{-1}, respectively, where the latter values were calculated from linear free-energy relationships between the formation constant of $Mg(OH)_2$ (s) and that of $[Mg(OH)]^+$ [*cf.* the $-\log \beta_{12s}{}^0$ value of 17.13 (25 °C; this study, Table 5) with that of 16.84[24]].

An important feature of this system is the relatively rapid attainment of equilibrium after each titrant addition. It is often the case that equilibrium in the formation of a solid phase is reached slowly, since the reaction proceeds from a supersaturated condition and may involve the formation of an amorphous product which generally is slow to recrystallise. In the present study, however, crystalline magnesium hydroxide was formed relatively rapidly and reversibly (within *ca.* 1 h). Back titration with hydrochloric acid demonstrated the reversibility of the reaction. The data from the back titration coincided with the forward titration curve (see Fig. 2).

Finally, the effects of specific interactions, *viz.* ion association of Mg^{2+}(aq) and chloride ions from the supporting medium, have been ignored, and the linear dependence of $\log \beta_{12s}$ on the reciprocal temperature tends to indicate that the influence is indeed minor. Moreover, high temperature/pressure conductance measurements by Frantz and Marshall[25] give an approximate ion-pair association constant for $MgCl_2$ (aq) of less than 10^{-1} at 200 °C, decreasing sharply with decreasing temperature.

Conclusion

The data obtained in this study are consistent with the formation of solid magnesium(II) hydroxide. Although the fit to the data is improved by the inclusion of the anionic species $[Mg(OH)_3]^-$, this species is believed not to form since the calculated formation constant is inconsistent with previously determined formation constants for $[Mg(OH)]^+$.[3] Values of the formation constant of $Mg(OH)_2$ (s) determined in the study are in excellent agreement with previously determined values.[4,7]

Acknowledgements

P. L. B. thanks the Australian Institute of Nuclear Science and Engineering for the award of a post-graduate studentship and the Union Carbide Corporation for an exchange grant. Dr. Dave Wesolowski is thanked for reviewing the manuscript and providing many useful suggestions. Drs. Charles Baes, Bob Mesmer and Ron Sylva are thanked for the support they provided throughout the course of the study. Financial support was supplied, in part, by the Office of Basic Energy Sciences of the US Department of Energy under contract DE-AC05OR21400 with Lockhead Martin Energy Systems, Inc.

References

1 Part 11, P. L. Brown, *J. Chem. Soc., Dalton Trans.*, 1989, 399.
2 P. B. Hostetler, *Am. J. Sci.*, 1963, **261**, 238.
3 K. A. McGee and P. B. Hostetler, *Am. J. Sci.*, 1975, **275**, 304.
4 K. A. McGee and P. B. Hostetler, *J. Res. U. S. Geol. Surv.*, 1977, **5**, 227.
5 D. Lewis, *Acta Chem. Scand.*, 1963, **17**, 5.
6 I. Lambert, A. Lefèvre and J. Montel, 8th International CODATA Conference, Jachranka, October 1982, CEA-CONF. 6531.
7 J. V. Walther, *Geochim. Cosmochim. Acta*, 1986, **50**, 733.
8 D. I. Stock and C. W. Davies, *Trans. Faraday Soc.*, 1948, **44**, 856.
9 D. J. Wesolowski and D. A. Palmer, *J. Solution Chem.*, submitted for publication.
10 Part 10, P. L. Brown, M. E. Shying and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1987, 2149.
11 Part 9, G. H. Khoe, P. L. Brown, R. N. Sylva and R. G. Robins, *J. Chem. Soc., Dalton Trans.*, 1986, 1901.
12 Part 8, P. L. Brown, R. N. Sylva and J. Ellis, *J. Chem. Soc., Dalton Trans.*, 1985, 1967.
13 D. A. Palmer and S. E. Drummond, *J. Phys. Chem.*, 1988, **92**, 6795.
14 D. A. Palmer and D. Wesolowski, *J. Solution Chem.*, 1987, **16**, 571.
15 D. A. Palmer, D. Wesolowski and R. E. Mesmer, *J. Solution Chem.*, 1987, **16**, 443.
16 R. E. Mesmer, C. F. Baes and F. H. Sweeton, *J. Phys. Chem.*, 1970, **74**, 1987.
17 P. L. Brown, Ph.D. Dissertation, University of Wollongong, 1984.
18 C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, 1978.
19 Powder Diffraction File, Sets 6–10 (revised), Joint Committee on Powder Diffraction Standards, Philadelphia, 1967.
20 R. H. Busey and R. E. Mesmer, *J. Chem. Eng. Data*, 1978, **23**, 175.
21 P. L. Brown and R. N. Sylva, *J. Chem. Res.*, 1987, (*S*) 4; (*M*) 0110.
22 P. Debye and E. Hückel, *Z. Phys.*, 1923, **24**, 1985.
23 H. C. Helgeson, D. H. Kirkham and G. C. Flowers, *Am. J. Sci.*, 1981, **281**, 1249.
24 C. F. Baes and R. E. Mesmer, *Am. J. Sci.*, 1981, **281**, 935.
25 J. D. Frantz and W. L. Marshall, *Am. J. Sci.*, 1982, **282**, 1666.

Received 15*th December* 1995; *Paper* 5/08160B