The Hydrolysis of Metal Ions. Part 7.[1] Beryllium(II)

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The potentiometric titration technique has been used to study the hydrolytic behaviour of beryllium(II) ion in 0.10 mol dm^{-3} potassium nitrate at 25.0 °C. Treatment of the data obtained indicates the presence of the species $Be(OH)_2$, $[Be_2(OH)]^{3+}$, and $[Be_3(OH)_3]^{3+}$, the $-\log \beta_{pq}$ values being 11.320(0.008), 2.955(0.007), and 8.804(0.002) respectively, the estimated standard deviations being given in parentheses.

In recent years the hydrolysis of the beryllium(II) ion has been the subject of many investigations.[2-9] An examination of the various results reveals that the two polymeric species, $[Be_2(OH)]^{3+}$ and $[Be_3(OH)_3]^{3+}$, have been used to explain in part the data in all the studies. However, conflict has arisen as to which minor species may also fit the data.

In keeping with our previous work in this series, the hydrolysis of the metal ion was studied in 0.10 mol dm^{-3} potassium nitrate solutions at 25.0 °C.

Experimental

Reagents.—Unless otherwise stated, all reagents were Merck Suprapur. The source of beryllium was beryllium nitrate pentahydrate (Fluka Guarantie). Sodium hydroxide was used as the base. The beryllium(II) nitrate stock solution was analysed spectrophotometrically using Chrome Azurol S.

Procedure.—The titration equipment consisted of a Radiometer Research pH Meter (PHM 84), a Radiometer ABU 80 Autoburette (2.5-cm^3 burette, tolerance ± 0.0001 cm^3), and a conventional stirred, degassed, and thermostatted reaction vessel. A Radiometer GK 2401 C glass electrode was used and showed negligible drift over extended periods (*ca.* 0.003 pH units per 24 h); this was an important feature since each titration occupied 30—40 h. The titrant (nominally 0.01 mol dm^{-3} sodium hydroxide) was delivered *via* a Teflon needle (Hamilton, 0.25-mm bore) dipping about 1 cm below the surface of the test solution. All measurements were carried out at a total ionic strength of 0.10 mol dm^{-3} (potassium nitrate).

The titration equipment was controlled by a microprocessor (Intel 8085 A). Titrant was added in constant increments (for a given titration) every 20 min and the pH was recorded every minute. Communication with the system is achieved *via* a Clare R53/LTT keyboard and a Trendcom 100 thermal printer.

To characterise the equipment and approach, the pK_a of benzoic acid (Fluka Guarantie) was determined; this compound was used as a primary standard without further purification. The concentration range of benzoic acid was 2.538—10.150 mmol dm^{-3} and the pH ranged from 3.071 to 5.009. Three titrations were performed and λ for the system was found to be 0.905. The refined pK_a was 4.0068(0.0004), the estimated standard deviation being given in parentheses.

As the hydrogen-ion mass-balance equation was not of the same magnitude as that for beryllium(II), the correction factor λ (see ref. 10) in the expression $[H^+] = 10^{-pH}/\lambda$ could not be sensibly refined. A value of 0.850 was used in keeping with adopted policy,[11] and the log K_w value [10] was taken to be -13.80. A summary of the titrations is given in Table 1; full details are available on request.

Table 1. Summary of titrations of beryllium(II) at 25 °C and in 0.1 mol dm^{-3} KNO_3

Total initial beryllium concentration (10^{-3} mol dm^{-3})	pH range	Number of points
2.684	4.213—5.285	106
1.342	4.224—5.289	107
0.690	4.426—5.295	98
0.358	4.609—5.297	87

Results

The adopted convention [1,10-14] for the reactions (1) defines the stoicheiometric equilibrium constants as in equation (2). Each species will be represented by its formula or by a (*p*,*q*) pair.

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

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

The two polymeric species $[Be_2(OH)]^{3+}$ and $[Be_3(OH)_3]^{3+}$ have been documented in all recent studies.[2-9] These two species were therefore used in an attempt to explain the data, but the error-square sum was too high for this to be considered a ' best ' model.[10,12] It was thus assumed that one or more additional species were present. Our version [15] of MINIQUAD [16,17] was used to perform further calculations, with the (2,1) and (3,3) species as the base model, and the (1,1), (1,2), (2,2), (3,4), (4,4), (5,7), (6,8), and (6,9) species (previously postulated [2-9]) added in various combinations. The best fit was obtained when the (1,2) species was added. Indeed, this model meets the conditions of our acceptance criteria (*R* factor = 0.0014),[1] and is compared with some closely situated minima in Table 2. No other alternative explanation was acceptable as indicated by (*a*) the standard deviations and (*b*) the agreement factor. The agreement factor alone cannot be used as a criterion of acceptability as has been emphasised previously.[14]

In previous studies in this series,[1,10-14] equilibrium was obtained almost immediately ($\leqslant$ 1 min). In the present system, however, equilibrium was reached 3—7 min after addition of each aliquot of titrant, depending upon pH and the beryllium(II)-ion concentration. As a result of this slower attainment of equilibrium, the time between successive additions of titrant was set at 20 min instead of the usual 5 min.[1,10-14] For two reasons, we suggest that the slow reaction is the formation

Table 2. Comparison of some models of beryllium(II) hydrolysis

Model number	Model	$-\log \beta_{pq}$	Estimated standard deviation of $-\log \beta_{pq}$	Estimated relative standard deviation (%) of β_{pq}	R
1	(1,1)	5.33	0.01	2.87	
	(1,2)	11.12	0.01	3.10	0.002 513
	(3,3)	8.94	0.004	0.81	
2	(1,1)				
	(2,1)	model fails: (1,1) becomes negative			
	(3,3)				
3	(1,1)				
	(1,2)	model fails: (2,1) becomes negative			
	(2,1)				
4	(1,2)				
	(2,1)	model fails: (2,1) becomes negative			
	(2,2)				
5	(1,2)	11.12	0.01	2.68	
	(2,1)	2.46	0.007	1.59	0.002 880
	(4,4)	10.46	0.006	1.42	
6	(2,1)	2.95	0.02	5.02	
	(3,3)	8.76	0.008	1.85	0.003 470
	(5,7)	23.99	0.04	9.25	
7	(2,1)	2.97	0.02	5.65	
	(3,3)	8.75	0.009	2.02	0.003 691
	(6,8)	25.86	0.05	11.53	
8	(2,1)	3.36	0.03	7.35	0.004 575
	(3,3)	8.84	0.006	1.39	
9	(2,1)				
	(3,3)				
	(3,4)	model fails: (6,8), (6,9) become negative			
	(6,8)				
	(6,9)				
10	(1,2)	11.320	0.008	1.77	
	(2,1)	2.955	0.007	1.57	0.001 411
	(3,3)	8.804	0.002	0.50	

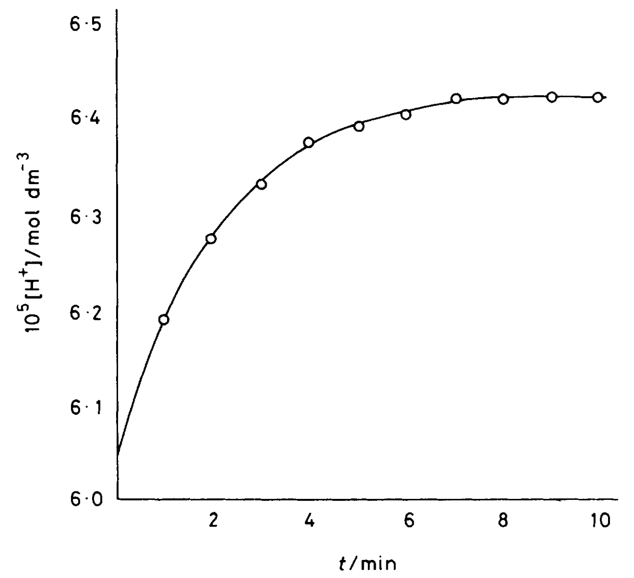

Figure 1. Plot of hydrogen-ion concentration *versus* time

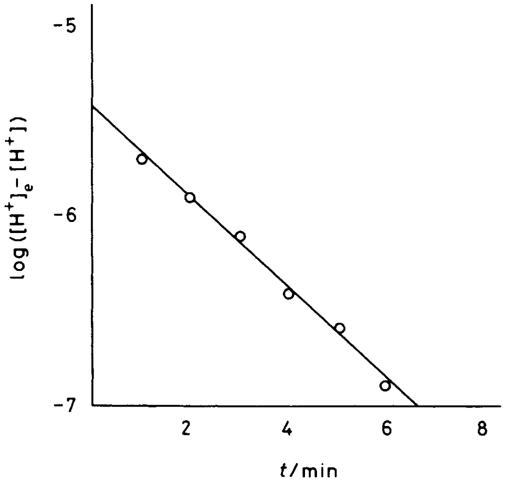

Figure 2. Plot of $\log([H^+]_e - [H^+])$ *versus* time, showing that the generation of hydrogen ions is first order

of the dimer $[Be_2(OH)]^{3+}$. First, the attainment of equilibrium is slower at high beryllium(II) concentrations and low pH where this species is more dominant. Secondly, when the base addition is made a rapid increase in pH is noted, followed by a slower decrease in pH until equilibrium is reached. Since this generation of protons can be shown to be first order, by plotting $\log([H^+]_e-[H^+])$ (where $[H^+]_e$ is the equilibrium hydrogen-ion concentration and $[H^+]$ the hydrogen-ion concentration at each time interval) against time,[18] there must be one hydroxide ion present in the hydrolysed species (see Figures 1 and 2).

Discussion

A survey of some previous studies of the hydrolysis of beryllium(II) ion is given in Table 3. An important feature of

Table 3. Survey of potentiometric investigations of the hydrolysis of beryllium(II)

Medium	Temp. (°C)	Total beryllium(II) concentration (10^{-3} mol dm^{-3})	$-\log \beta_{pq}$ (1,2)	(2,1)	(3,3)	(3,4)	(6,8)	(6,9)	Model number	Ref.
3 mol dm^{-3} ClO_4^-	25	40—1 000		3.22	8.66				8	3,6 *
3 mol dm^{-3} $NaClO_4$	25	1—49	10.9	3.24	8.66				10	2,6 *
3 mol dm^{-3} KCl	25	29—174		3.18	8.91				8	5
2 mol dm^{-3} KNO_3	25	8.3—1 100		3.28	8.90	16.00	27.50	34.50	9	7
1 mol dm^{-3} NaCl	0	3.42—94.11		4.64	10.081		31.15		7	8
1 mol dm^{-3} NaCl	25	1.930—45.43		3.42	8.907		27.46		7	8
1 mol dm^{-3} NaCl	60	1.739—18.00		2.91	7.664		23.73		7	8
0.5 mol dm^{-3} $NaClO_4$	25	1—50							10	9
0.1 mol dm^{-3} KNO_3	25	0.358—2.684	11.320	2.955	8.804				10	This work

* Recalculation in cited reference.

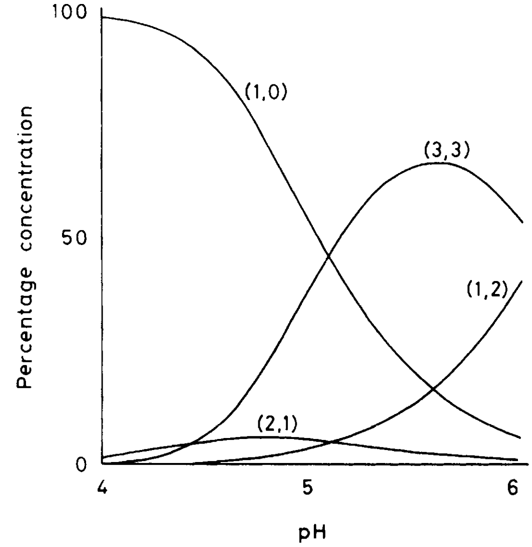

Figure 3. Percentage distribution of beryllium(II) in various species (p,q), for a total concentration of 0.7 mmol dm^{-3}

this table is the near invariance of the formation constants of each species (at 25 °C) with ionic strength and medium.

In the concentration ranges studied in the present work, the (3,3) species is an important species at all concentrations. The dimer is important at low pH values and high metal-ion concentrations, and the monomer at high pH values and low metal-ion concentrations. The relative percentage formation of each species for 0.7 mmol dm^{-3} metal ion is given in Figure 3.

The most extensive earlier work on beryllium(II) hydrolysis is that of Mesmer and Baes [8] in 1.0 mol dm^{-3} sodium chloride at 0, 25, and 60 °C. They found evidence for existence of the (2,1), (3,3), and (5,7) species. Even though replacing the (5,7) with the (6,8) species gave a slightly poorer fit, they expressed preference for the latter species in a later publication.[19] In the earlier report, the authors also gave evidence that the postulation of the monomer in another study [2] was incorrect. However, the present study has also found evidence for the existence of the (1,2) species. Indeed, the results of Ohtaki [4] show a convergence of all titration curves to a point at $\bar{n} = 1$ ($\bar{n}$ is the average number of hydroxide groups per metal ion) and pH *ca.* 5.3, which is consistent with the formation of the (1,2) species. This pH value is also consistent with the formation of solid beryllium hydroxide [20] as indicated by the concentrations of free beryllium and hydroxide ion, which suggests that pH measurements above this value are subject to systematic errors because of lack of equilibrium.

The Stockholm school reported [2,3,6] evidence for the (2,1) and (3,3) species and Kakihana and Sillén [2] found evidence for the existence of $Be(OH)_2$ at the lowest beryllium concentrations. These three species were also found by Bertin *et al.*[9] A probable explanation for the inability of Carell and Olin [3] to detect the (1,2) species is (*a*) the use of very high, total beryllium concentrations (see Table 3) and (*b*) the errors incurred by their use of the self-medium method.[19] The Stockholm data were later recalculated [6] using the LETAGROP program,[21] and the agreement between the present work and the recalculated work of Kakihana and Sillén is excellent when the differences in ionic strength and total beryllium concentrations used in the two studies are taken into consideration.

In all other studies in this series,[1,10-14] evidence has been presented for the formation of the monomer M(OH) (ignoring ionic charges). In the present study, however, $[Be(OH)]^+$ has not been detected (see Table 2). We believe this result is due to the stability of the dimer $[Be_2(OH)]^{3+}$ (relative to the stability of the monomer [22]), which is higher than that usually found for most metal ions.[19]

The present work again confirms [10-12] that it is prudent to avoid high metal-ion concentrations and to vary these within a relatively narrow range despite the inherently greater ease of numerical analysis that use of a large range permits.

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