

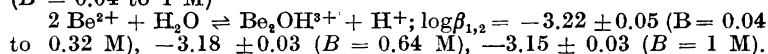
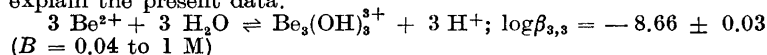
## Studies on the Hydrolysis of Metal Ions

## 37. Application of the Self-Medium Method to the Hydrolysis of Beryllium Perchlorate

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The hydrolysis of beryllium perchlorate has been studied in the concentration range  $B = 0.04-1$  M by measurements of  $\log h$  at 25°C. The same set of complexes as found by Kakihana and Sillén at low beryllium concentrations, namely  $\text{Be}_2\text{OH}^{3+}$  and  $\text{Be}_3(\text{OH})_3^{3+}$ , can also explain the present data.



In a recent study<sup>1</sup> on the hydrolysis of lead perchlorate in concentrated solutions, evidence was presented for the formation of  $\text{Pb}_2\text{OH}^{3+}$  and  $\text{Pb}_4(\text{OH})_4^{4+}$ . When the average number of  $\text{OH}^-$  per  $\text{Pb(II)}$ ,  $Z$ , exceeded about 0.1 however, deviations between the experimental data and the calculated curves  $Z(\log h)_B$  occurred. It was suspected then that the cause was variations in the activity factors.

From emf studies on the hydrolysis of  $\text{Be(II)}$ , Kakihana and Sillén<sup>2</sup> found evidence for the formation of  $\text{Be}_2\text{OH}^{3+}$ ,  $\text{Be}_3(\text{OH})_3^{3+}$  and in addition small amounts of  $\text{Be(OH)}_2$  at low concentrations. Although the case of beryllium is not strictly analogous to that of  $\text{Pb(II)}$  it was thought to be of interest to study concentrated  $\text{Be(ClO}_4)_2$  solutions to see if similar deviations were observed for this metal.

## SYMBOLS

$B$	total concentration of $\text{Be(II)}$
$b$	concentration of free $\text{Be}^{2+}$
$H$	analytical hydrogen ion concentration, often negative
$h$	actual hydrogen ion concentration
$Z$	average number of $\text{OH}^-$ split off by one $\text{Be(II)}$
$\beta_{p,q}$	equilibrium constant of the reaction

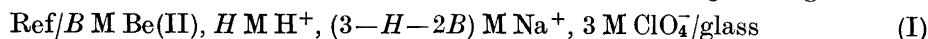


$y(x)$ ,  $y$  as a function of  $x$  at constant  $v$

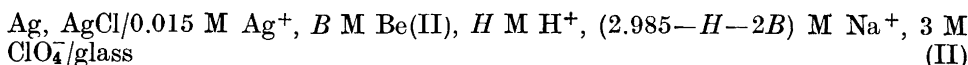
All concentrations are expressed in M (moles/l) and equilibrium constants are given on the M scale.

#### METHOD

The hydrolysis has been followed by measurements of  $\log h$  using the cells

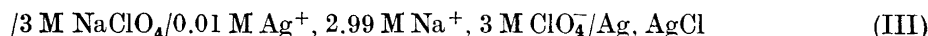


$$E = E_{\text{I}}^0 + 59.15 \log h + 59.15 \log f_{\text{H}^+} + E_j \quad (1)$$



$$E = E_{\text{II}}^0 + 59.15 \log h - 59.15 \log [\text{Ag}^+] + 59.15 \log f_{\text{H}^+}/f_{\text{Ag}^+} \quad (2)$$

The reference half-cell in (I) was



In some of the experiments with cell (I) the glass electrode was replaced by a quinhydrone electrode.

The experiments were carried out as potentiometric titrations and  $\log h$  was varied by addition of  $\text{HClO}_4$  or  $\text{NaHCO}_3$ .

#### EXPERIMENTAL

*Materials and analysis.*  $\text{HClO}_4$ ,  $\text{NaClO}_4$  and  $\text{AgClO}_4$  were prepared and analysed as described in Refs.<sup>3,4</sup>

$\text{NaHCO}_3$  solutions were prepared from  $\text{NaHCO}_3$  (Merck p.a.) and, after filtration, were used without further purification.

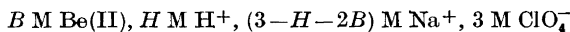
$\text{Be}(\text{ClO}_4)_2$  was prepared *via* the chloride. Beryllium metal (Pechiney) was dissolved in redistilled  $\text{HCl}$ , the chloride solution was evaporated to a thick syrup and finally the perchlorate was formed by the addition of  $\text{HClO}_4$  which completely displaced the  $\text{HCl}$ . The  $\text{Be}(\text{ClO}_4)_2$  was once recrystallised from  $\text{HClO}_4$ . Beryllium was determined as  $\text{BeO}$  by precipitating  $\text{Be}(\text{OH})_2$  with gaseous  $\text{NH}_3$  in a platinum vessel and igniting the precipitate at 1 000–1 100°C.

$[\text{ClO}_4^-]$  was found by ion exchange methods, and the analytical hydrogen ion concentration,  $H$ , was calculated as  $[\text{ClO}_4^-] - 2B$ . The value of  $H$  was checked by emf methods as described later.

*Glass electrodes.* Beckman glass electrodes (No. 1 190–808) were used. They were checked against the hydrogen electrode as described in Ref.<sup>4</sup>

*Experimental details.* In order to obtain an overlap between the measurements of Kaki-hana and Sillén and our own, we started the series of measurements with fairly dilute solutions. The values of  $B$  used were, 0.03973; 0.07944; 0.1589; 0.3178; 0.64 and 1 M.

The composition of the equilibrium solutions was



$H$  was often negative so that the solutions were deficient in hydrogen ions. The titrations were started either from slightly hydrolysed solutions ( $Z \simeq 0.01$ ), adding  $\text{NaHCO}_3$  solution, or from solutions with  $Z \simeq 0.4$ , adding  $\text{HClO}_4$ . The last procedure was found to be best suited for the highest values of  $B$ , since the bubbles of  $\text{CO}_2$  formed on the introduction of  $\text{HCO}_3^-$  sometimes adhered to the glass electrode, thereby causing erroneous emf's.

In all runs  $B$  and  $[\text{ClO}_4^-]$  ( $= 3 \text{ M}$ ) were kept constant. After each addition of acid or base the potential was followed till it reached a constant value. This seemed to be the

case after a few minutes. Since the sensitivity of the potentiometer used (Radiometer PHM 4a) is only 0.1 mV, we waited at least 15–20 min before the final reading was taken, to make sure that no slow drift in potential occurred. The agreement between the results obtained from titrations with increasing and decreasing  $Z$  seems to indicate that equilibrium was established in the  $Z$  range studied here.

The salt bridge was of the "Wilhelm" type and filled with 3 M NaClO<sub>4</sub>. In self-medium studies it has been customary (*cf.* cells (I) and (III) above) to have in the salt bridge a solution which also contains the metal ion being investigated and at the same concentration as in the test solution. At low values of  $B$  one would expect that the choice of solution for the salt bridge is of less importance. When, however,  $B$  has a high value the choice may become important. In the present study we have chosen instead to eliminate the liquid junction potential when studying the highest values of  $B$  and have added Ag<sup>+</sup> to the solutions and made use of the cell (II).

The evaluation of  $\log h$  from eqns. (1) and (2) necessitates a knowledge of  $E^\circ$ .  $E^\circ$  can be determined at low values of  $B$ , simply by adding enough acid to repress the hydrolysis sufficiently, so that it is permissible to set  $h = H$ . For the two highest values of  $B$  studied here, this is no longer feasible since the hydrolysis is so strong that  $h = H$  only at high acidities. This means that  $E^\circ$  is determined in a solution quite different from that where the main hydrolysis takes place and that for cell (I) the measured emf involves a large and unknown liquid junction potential. The  $E^\circ$  determined in these acid solutions was therefore regarded as only provisional and the final  $E^\circ$  was determined by the method described by Hietanen and Sillén<sup>2</sup>. The details of these calculations will be presented later.

## RESULTS AND CALCULATIONS

It will be convenient for the sake of presentation of the data to consider first the results obtained with the four lowest values of  $B$ . For these concentrations  $E^\circ$  was determined by suppressing the hydrolysis with HClO<sub>4</sub> till  $h = H$

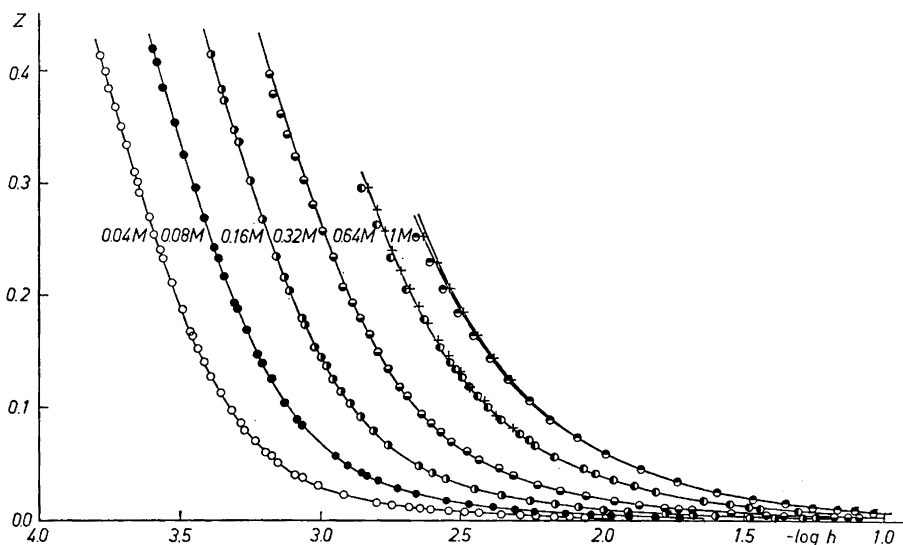


Fig. 1.  $Z$  as a function of  $\log h$ . Circles represent data from measurements with cell(I) and crosses data from cell(II). The curves are calculated with the equilibrium constants given in Table 3.

Table I. Corresponding values of  $-\log h$  and  $Z$  from Cell (I).

$B = 0.03972 \text{ M}; -\log h, Z;$									
2.115,	0.003;	2.167,	0.003;	2.232,	0.004;				
2.287,	0.004;	2.353,	0.005;	2.435,	0.006;	2.484,	0.007;	2.541,	0.008;
2.607,	0.009;	2.645,	0.010;	2.682,	0.011;	2.745,	0.013;	2.808,	0.015;
2.917,	0.022;	3.009,	0.030;	3.063,	0.038;	3.090,	0.040;	3.149,	0.050;
3.152,	0.051;	3.176,	0.057;	3.196,	0.060;	3.235,	0.070;	3.269,	0.082;
3.284,	0.086;	3.318,	0.097;	3.356,	0.113;	3.390,	0.127;	3.391,	0.129;
3.418,	0.140;	3.438,	0.152;	3.458,	0.163;	3.463,	0.167;	3.489,	0.185;
3.531,	0.211;	3.560,	0.233;	3.570,	0.241;	3.595,	0.254;	3.609,	0.270;
3.614,	0.274;	3.646,	0.292;	3.651,	0.301;	3.661,	0.310;	3.686,	0.331;
3.690,	0.334;	3.712,	0.350;	3.729,	0.367;	3.724,	0.371;	3.754,	0.384;
3.764,	0.399;	3.779,	0.410;						
$B = 0.07944 \text{ M}; -\log h, Z;$									
1.724,	0.002;	1.810,	0.002;	1.905,	0.003;				
1.968,	0.004;	2.040,	0.005;	2.128,	0.006;	2.240,	0.007;	2.307,	0.009;
2.385,	0.011;	2.469,	0.014;	2.555,	0.017;	2.643,	0.022;	2.658,	0.023;
2.724,	0.028;	2.795,	0.035;	2.836,	0.039;	2.855,	0.042;	2.905,	0.048;
2.945,	0.057;	3.068,	0.084;	3.085,	0.089;	3.127,	0.104;	3.176,	0.125;
3.208,	0.139;	3.223,	0.147;	3.265;	0.169;	3.296,	0.188;	3.308,	0.193;
3.345,	0.217;	3.364,	0.233;	3.379,	0.243;	3.416,	0.269;	3.446,	0.296;
3.487,	0.325;	3.519;	0.354;	3.564,	0.385;	3.583,	0.407;	3.605,	0.417;
$B = 0.1589 \text{ M}; -\log h, Z;$									
1.293,	0.002;	1.392,	0.002;	1.480,	0.003;				
1.599,	0.004;	1.678,	0.004;	1.777,	0.005;	1.907,	0.007;	1.987,	0.008;
2.084,	0.011;	2.165,	0.014;	2.253,	0.017;	2.354,	0.022;	2.447,	0.027;
2.552,	0.036;	2.598,	0.042;	2.631,	0.045;	2.648,	0.048;	2.748,	0.064;
2.753,	0.067;	2.812,	0.079;	2.853,	0.091;	2.897,	0.103;	2.926,	0.114;
2.934,	0.117;	2.958,	0.125;	2.980,	0.136;	3.000,	0.145;	3.022,	0.154;
3.058,	0.174;	3.066,	0.179;	3.112,	0.204;	3.130,	0.216;	3.161,	0.235;
3.198,	0.263;	3.208,	0.268;	3.250,	0.302;	3.293,	0.336;	3.308,	0.347;
3.345,	0.373;	3.353,	0.383;	3.392,	0.414;				
$B = 0.3178 \text{ M}; -\log h, Z;$									
1.086,	0.003;	1.127,	0.004;	1.177,	0.004;	1.177,	0.004;	1.243,	
0.003;	1.296,	0.004;	1.357,	0.005;	1.418,	0.005;	1.489,	0.006;	1.541,
0.007;	1.609,	0.007;	1.685,	0.009;	1.730,	0.010;	1.781,	0.011;	1.869,
0.013;	1.957,	0.017;	2.050,	0.019;	2.058,	0.021;	2.139,	0.024;	2.151,
0.026;	2.229,	0.031;	2.303,	0.037;	2.312,	0.040;	2.363,	0.046;	2.434,
0.053;	2.476,	0.061;	2.569,	0.078;	2.604,	0.086;	2.638,	0.094;	2.691,
0.110;	2.718,	0.118;	2.758,	0.134;	2.797,	0.149;	2.826,	0.165;	2.858,
0.179;	2.883,	0.193;	2.920,	0.207;	2.954,	0.233;	2.993,	0.257;	3.027,
0.280;	3.059,	0.302;	3.090,	0.323;	3.120,	0.343;	3.142,	0.361;	3.171,
0.379;	3.184,	0.396;							
$B = 0.64 \text{ M}; -\log h, Z;$									
1.177,	0.007;	1.248,	0.007;	1.306,	0.008;				
1.368,	0.009;	1.443,	0.011;	1.483,	0.012;	1.550,	0.015;	1.811,	0.025;
1.884,	0.030;	1.959,	0.035;	2.026,	0.041;	2.063,	0.046;	2.170,	0.056;
2.238,	0.066;	2.261,	0.072;	2.292,	0.076;	2.350,	0.088;	2.356,	0.090;
2.403,	0.100;	2.439,	0.110;	2.471,	0.119;	2.496,	0.127;	2.518,	0.134;
2.538,	0.140;	2.574,	0.154;	2.631,	0.179;	2.696,	0.205;	2.750,	0.233;
2.800,	0.263;	2.853,	0.295;						
$B = 1 \text{ M}; -\log h, Z;$									
0.988,	0.006;	1.038,	0.007;	1.104,	0.008;	1.168,	0.010;		
1.257,	0.011;	1.351,	0.015;	1.470,	0.018;	1.596,	0.025;	1.734,	0.034;
1.865,	0.045;	1.988,	0.058;	2.087,	0.073;	2.186,	0.089;	2.260,	0.106;
2.335,	0.125;	2.396,	0.144;	2.457,	0.164;	2.511,	0.184;	2.564,	0.206;
2.611,	0.229;	2.660,	0.252;						
Corresponding values of $-\log h$ and $Z$ from Cell (II). Data are given only for $Z > 0.1$ .									
$B = 0.64 \text{ M}; -\log h, Z;$									
2.417,	0.106;	2.467,	0.118;	2.501,	0.132;				
2.545,	0.147;	2.581,	0.160;	2.618,	0.175;	2.650,	0.190;	2.682,	0.206;
2.713,	0.222;	2.743,	0.240;	2.772,	0.257;	2.800,	0.276;	2.838,	0.295;
$B = 1 \text{ M}; -\log h, Z;$									
2.255,	0.106;	2.326,	0.125;	2.384,	0.144;	2.441,	0.164;		
2.489,	0.184;	2.541,	0.206;	2.629,	0.252;				

and calculating  $E^0$  from the emfs in these solutions with  $E_1$  values obtained from the calibration of the glass electrode. With  $E_0$  known,  $\log h$  was calculated from the emfs in hydrolysed solutions. The results are presented in Table 1 and as a set of curves  $Z(\log h)_B$ , where  $Z = (h-H)/B$ .

The set of curves  $Z(\log h)_B$  is shown in Fig. 1. It may be characterized as follows. For  $0.2 < Z < 0.4$  the curves are parallel with a spacing along the  $\log h$  axis at constant  $Z$

$$t = (\Delta \log B / \Delta \log h)_Z \simeq 1.5 \quad (3)$$

For  $Z < 0.2$  the value of  $t$  tends to decrease, this tendency being more pronounced the higher the value of  $B$ .  $Z$  apparently approaches 0 slowly, indicating that the last surviving complex contains only one or two  $\text{OH}^-$  groups. This characteristic was also shown by the set of  $Z(\log h)_B$  curves obtained by Kakihana and Sillén. At the outset therefore, it seemed likely that the same complexes, namely  $\text{Be}_2\text{OH}^{3+}$  and  $\text{Be}_3(\text{OH})_3^{4+}$ , proposed to explain their data, could also explain ours. We decided, however, not to make use of their findings and have started with our data, to determine what complexes are formed, although these data were obtained with solutions in which the activity factors may be expected to vary on account of the fairly large change in medium on going from 0.04 to 0.32 M Be(II). The computational methods have been deliberately chosen to be different from theirs.

*Complexes formed at low Z.* We shall start by considering the data for  $Z < 0.01$ . Putting  $b \simeq B$  we find for the formation of a set of complexes  $\text{Be}_q(\text{OH})_p^{(2q-p)+}$

$$Z = \Sigma p \beta_{p,q} B^{(q-1)} h^{-p} = \Sigma K_p h^{-p} \quad (4)$$

For each value of  $p$  we may construct a set of normalised curves  $Z(-\log X)$ , where  $X = K_p^{1/p}/h$ , and compare these with the experimental curves  $Z(\log h)_B$ . Only for  $p = 1$  a satisfactory agreement is found and the last surviving complex is thus  $\text{Be}_q\text{OH}^{(2q-1)+}$ . Information on the value of  $q$  can be obtained from the relative positions of the  $Z(\log h)_B$  curves. One way of doing this, which at the same time offers a check on  $H$ , will be given.

The analytical hydrogen ion concentration was calculated from the analysis of Be and  $\text{ClO}_4^-$  as  $H' = [\text{ClO}_4^-] - 2B$ . These analyses may be somewhat in error and we shall put the error so caused in  $H$  equal to  $\varepsilon B$ , corresponding to  $\varepsilon H^+$  per Be(II). For a given value of  $B$  we have

$$H = H' + \varepsilon B \quad (5)$$

$$h = H' + \varepsilon B + \beta_{1,q} B^q h^{-1} \quad (6)$$

where  $h$  is found from the measured emf.  $(h-H')$  is plotted as a function of  $h^{-1}$  and the intercept on the  $(h-H')$ -axis ( $\varepsilon B$ ) and the slope ( $\beta_{1,q} B^q$ ) of the line are determined. A similar method has been used by Hedström<sup>6</sup>.

In order to obtain sufficient accuracy  $\log h$  was measured with the quinhydrone electrode.  $\varepsilon$  was found to be  $0.0035 \pm 0.0005$ , which corresponds to an error in the beryllium analysis of 0.2 %.

$q$  was found to be 2, by plotting the logarithm of the numerical value of the slope against  $\log B$ . The complex is thus  $\text{Be}_2\text{OH}^{3+}$ .

$\text{Be}_2\text{OH}^{3+}$  can only account for the data at low  $Z$ , and larger complexes must be formed when  $Z$  increases. Information on these complexes has been obtained by calculating

$$\bar{p} = \frac{\Sigma p[\text{Be}_q(\text{OH})_p]}{\Sigma [\text{Be}_q(\text{OH})_p]} \quad ; \quad \bar{q} = \frac{\Sigma q[\text{Be}_q(\text{OH})_p]}{\Sigma [\text{Be}_q(\text{OH})_p]} \quad (7), (7a)$$

$\bar{p}$  and  $\bar{q}$  are thus average values of  $p$  and  $q$  for the complexes formed. A set of formulas for these calculations have been given by Sillén<sup>7</sup>. Of these the following have been used.

$$R = b/B + \Sigma [\text{Be}_q(\text{OH})_p]/B = 1 - \int_0^Z (\partial \log h / \partial \log B)_Z dZ \quad (8)$$

$$\ln b = R + \ln B - 1 - \int_{\ln h}^{\infty} Z d \ln h \quad (9)$$

The integral in (9) was calculated from the experimental data starting from  $Z = 0.005$  onwards. The residual integral was found on the assumption that  $\text{Be}_2\text{OH}^{3+}$  is the only complex present at  $Z < 0.005$ , and with a provisional value of  $\beta_{1,2}$  ( $5.75 \times 10^{-4}$ )

$$\int_{\ln h}^{\infty} Z d \ln h = \int_h^{\infty} \beta_{1,2} B h^{-2} dh = \beta_{1,2} B h^{-1} \quad (10)$$

$\bar{p}$  and  $\bar{q}$  was then obtained from

$$\bar{p} = BZ/(RB - b) \quad ; \quad \bar{q} = (B - b)/(RB - b) \quad (11), (11a)$$

A straight line drawn through the points  $(\bar{q}, \bar{p})$  passes close to (2,1) and (3,3). The complexes formed are thus shown to be  $\text{Be}_2\text{OH}^{3+}$  and  $\text{Be}_3(\text{OH})_3^{3+}$ , in agreement with the findings of Kakihana and Sillén.

Whereas there is no choice at the lower end of the line other than  $\text{Be}_2\text{OH}^{3+}$ , higher complexes than  $\text{Be}_3(\text{OH})_3^{3+}$  might also form at the other end of the line. In order to satisfy the equation of the line these would be  $\text{Be}_4(\text{OH})_5^{3+}$  ( $p/q = 1.25$ ),  $\text{Be}_5(\text{OH})_7^{3+}$  ( $p/q = 1.4$ ), etc. In order to test this possibility we have calculated the ratio  $\bar{p}/\bar{q}$  for the complexes other than  $\text{Be}_2\text{OH}^{3+}$ . [ $\text{Be}_2\text{OH}^{3+}$ ] was calculated using three provisional values of  $\log \beta_{1,2}$  for each  $B$  value ( $-3.20$ ,  $-3.25$ ,  $-3.30$ , obtained from curvefitting at low values of  $Z$ ). The results obtained for  $B = 0.03973$  M is shown in Table 2 and it may be concluded that complexes with  $p/q = 1$  predominate. The complexes present are thus  $\text{Be}_2\text{OH}^{3+}$  and  $\text{Be}_3(\text{OH})_3^{3+}$ . The formation constants  $\beta_{1,2}$  and  $\beta_{3,3}$  have been determined by curve-fitting.

*Method I.* Comparison of experimental curves  $Z(\log h)_B$  with normalized curves  $Z(-\log v)_i$ .

Normalized curves  $Z(-\log v)_i$  have been calculated from

$$Z = v^{-1}(\sqrt{1 + v(1-Z)} - 1)^2 + l(\sqrt{1 + v(1-Z)} - 1)^3 \quad (12)$$

Table 2.  $B = 0.03973$  M.

$Z$	$\bar{q}/\bar{p}$ for complexes other than $\text{Be}_2\text{OH}^{3+}$		
	$\log \beta_{1,2} = -3.20$	$-3.25$	$-3.20$
0.15	0.95	1.00	1.03
0.16	0.96	1.00	1.03
0.17	0.97	1.00	1.04
0.18	0.96	1.00	1.03
0.19	0.96	1.00	1.03
0.20	0.98	1.01	1.04
0.22	0.97	1.00	1.02
0.24	0.97	1.00	1.02
0.26	0.97	0.99	1.02
0.28	0.98	1.00	1.02
0.30	0.98	1.00	1.01
0.32	0.99	1.01	1.02
0.34	0.98	1.00	1.01
0.36	0.99	1.00	1.02
0.38	0.98	0.99	1.01
0.40	1.00	1.01	1.02

for a number of different values of  $l$ . Eqn. (12) may be derived from the two basic eqns. (13) and (14)

$$B = b + 2\beta_{1,2}b^2h^{-1} + 3\beta_{3,3}b^3h^{-3} \quad (13)$$

$$BZ = \beta_{1,2}b^2h^{-1} + 3\beta_{3,3}b^3h^{-3} \quad (14)$$

by elimination of  $b$  and introduction of

$$v = 4B\beta_{1,2}h^{-1} \text{ and } l = 3\beta_{3,3}/(8B\beta_{1,2}^3) \quad (15), (16)$$

By comparing the experimental  $Z(\log h)_B$  curve with the set of normalized curves  $Z(-\log v)_l$ , a best value of  $l$  is found and in the position of overlap between the two curves  $\log \beta_{1,2}$  and  $\log \beta_{3,3}$  are found from

$$\log \beta_{1,2} = \log v + \log h - \log (4B) \quad (15a)$$

and

$$\log \beta_{3,3} = \log l + 3\log \beta_{1,2} + \log (8B/3) \quad (16a)$$

This method has the great advantage that it involves a direct comparison of the experimental and normalized curves. From eqn. (16a) we see, however that when  $\beta_{3,3}$  is calculated 3 times the uncertainty in  $\log \beta_{1,2}$  is transferred to the value of  $\log \beta_{3,3}$ . But displacing the curves along the  $\log h$  axis often calls for a new value of  $l$ . In this way  $\log \beta_{3,3}$  stays more constant than would be expected from eqn. (16a).

*Method II.* Comparison of experimental curves  $y(x)_Z$ , ( $\log B - \log h = y$ ;  $\log B - 1.5 \log h = x$ ), with normalized  $Y(X)_Z$ . Method II provides a means of finding  $\log \beta_{3,3}$  and  $\log \beta_{1,2}$  independently and simultaneously. We have

$$B = b(1 + 3\beta_{3,3} b^2 h^{-3} + 2\beta_{1,2} b h^{-1}) \quad (17)$$

$$Bh^{-1} = bh^{-1}(1 + 3\beta_{3,3} b^2 h^{-3} + 2\beta_{1,2} b h^{-1}) \quad (18)$$

$$Bh^{-3/2} = bh^{-3/2} (1 + 3\beta_{3,3} b^2 h^{-3} + 2\beta_{1,2} b h^{-1}) \quad (19)$$

and

$$Z = \frac{\beta_{1,2} b h^{-1} + 3\beta_{3,3} b^2 h^{-3}}{1 + 2\beta_{1,2} b h^{-1} + 3\beta_{3,3} b^2 h^{-3}} \quad (20)$$

which can be normalized by the following substitutions

$$k^2 = 3\beta_{3,3}; \quad u = kbh^{-3/2}; \quad v = \beta_{1,2} b h^{-1} \quad (21)$$

to give

$$X = x + \log k = \log u + \log (1 + 2v + u^2) \quad (22)$$

$$Y = y + \log \beta_{1,2} = \log v + \log (1 + 2v + u^2) \quad (23)$$

$$Z = \frac{v + u^2}{1 + 2v + u^2} \quad (24)$$

where  $x$  and  $y$  are the corresponding experimental coordinates

$$x = \log B - 1.5 \log h \quad (25)$$

$$y = \log B - \log h \quad (26)$$

Normalized curves  $Y(X)_Z$  are calculated for a set of values of  $Z$  and compared with the experimental  $y(x)_Z$ . In position of best fit the equilibrium constants are found from eqns. (22) and (23).

*Treatment of data for B = 0.64 and 1 M.* For the highest values of  $B$ , the  $E^0$ 's in cells (I) and (II) were determined as described by Hietanen and Sillén<sup>5</sup>. From the analytical data ( $B$  and  $H$ ),  $h$  was calculated using provisional values of  $\log \beta_{1,2}$  and  $\log \beta_{3,3}$ .  $\log \beta_{1,2}$  was varied between  $-3.11$  and  $-3.23$  with a  $0.02$  unit interval, whereas  $\log \beta_{3,3}$  was kept constant at  $-8.66$ .

For cell (I) ( $E - 59.15 \log h$ ) was plotted as a function of  $h$ . A linear plot was taken as a criterion for a correct choice of  $\log \beta_{1,2}$ , and  $E_{\text{I}}^0$  was determined by extrapolation to  $h = 0$ . For cell (II) ( $E - 59.15 \log h$ ) was also calculated and the criterion would here be a constant value for this quantity.

With  $B = 1 \text{ M}$ ,  $\log \beta_{1,2} = -3.15$  gave values of ( $E - 59.15 \log h$ ) for cell (I) and cell (II) which fulfilled the above requirements. With  $B = 0.64 \text{ M}$   $\log \beta_{1,2} = -3.19$  gave best agreement for cell (I). For cell (II), however, no choice could be made since the determination of  $E_{\text{II}}^0$  in this case was done in so acid solution that variations in  $\log \beta_{1,2}$  did not produce a trend in  $E_{\text{II}}^0$ .

*Values of the equilibrium constants.* In Table 3 the values of the formation constants are given. They represent mean values of the results obtained by



Table 3.

<i>B M</i>	$\log \beta_{1,2}$	$\log \beta_{3,3}$	<i>Z</i>
0.03973	$-3.23 \pm 0.04$	$-8.67 \pm 0.03$	> 0.4
0.07944	$-3.23 \pm 0.04$	$-8.68 \pm 0.03$	> 0.4
0.1589	$-3.21 \pm 0.03$	$-8.64 \pm 0.03$	0.4
0.3178	$-3.21 \pm 0.03$	$-8.65 \pm 0.03$	0.3 (cell (I))
0.3178	$-3.21 \pm 0.03$	$-8.65 \pm 0.03$	0.4 (cell (II))
0.64	$-3.18 \pm 0.03$	$-8.64 \pm 0.03$	0.18 (cell (I))
0.64	$-3.18 \pm 0.03$	$-8.64 \pm 0.03$	0.25 (cell (II))
1	$-3.15 \pm 0.03$	$-8.66 \pm 0.03$	0.15 (cell (I))
1	$-3.15 \pm 0.03$	$-8.62 \pm 0.03$	0.2 (cell (II))

methods (I) and (II). The last column gives the highest value of *Z* at which these constants agree with our experimental results within 0.002–0.003 *Z*-units.

## DISCUSSION

From Table 3 we see that the values of the equilibrium constants stay constant despite the fairly large change in medium. The trend in  $\log \beta_{1,2}$  towards higher values with increasing *B* is probably real, whereas for  $\log \beta_{3,3}$  no trend is seen. At low *B* the values of the constants agree well with those of Kakihana and Sillén, who found  $\log \beta_{1,2} = -3.24$  and  $\log \beta_{3,3} = -8.66$ . An approximate constancy of the  $\beta$ 's has also been found for other cations<sup>1,5,8</sup>. This fact suggests that the relative positions of the curves  $Z(\log h)_B$  on the  $\log h$  axis at large *B*'s can be used to find the *q* values of the complexes formed.

The range in *Z* which can be accounted for is seen to diminish with increasing *B*. The calculated curves  $Z(\log h)_B$  are seen to lie above the experimental ones. The case of Be(II) is thus quite similar to that of Pb(II) and the deviations start at about the same values of *Z*. A definite increase in the range of validity seems to occur with the measurements from cell (II).

The variation of *E* of cell (II) is expressed by eqn. (2). If  $f_{H^+} = f_{Ag^+}$  in these solutions the measurements from this cell would give  $\log h$ . Evidence for this comes from the fact that constant  $E^0$ s were obtained when *h* was varied at constant *B*. Also the  $E^0$ s obtained at different values of *B* seemed to be the same, as is seen from the table below which gives the results for the two glass electrodes, "A" and "B", both used with cell II.

<i>B M</i>	$E_A^0$ mV	$E_B^0$ mV
0.3178	-105.7	-135.2
0.64	-105.7	-135.3
1	-106.0	-135.1

For cell (I) the variation of *E* is expressed by eqn. (1). " $E_I^0$ " is usually determined by plotting

$$(E - 59.15 \log h) = E_I^0 + 59.15 \log f_{H^+} + E_j \quad (27)$$

as a function of  $h$  and extrapolating to  $h = 0$ . Denoting the quantities relating to the solution with  $h = 0$  with primes, we have

$$E_I^{0'} = E_I^0 + 59.15 \log f_{H'} + E_j' \quad (28)$$

Inserting this into eqn. (1) we find

$$E = E_I^{0'} + 59.15 \log h + 59.15 \log f_{H+}/f_{H'+} + E_j - E_j' \quad (29)$$

The measurements will therefore give  $\log h$  only if  $f_{H+} = f_{H'+}$  and the difference between  $E_j$  and  $E_j'$  is negligible or can be corrected for. At a high value of  $B$  the change in the composition of the medium is considerable even at moderate values of  $Z$ . We need not therefore be surprised that somewhat different results are obtained from measurements of the two cells for  $Z > 0.1$ .

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