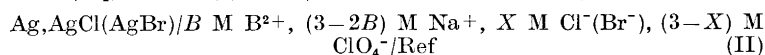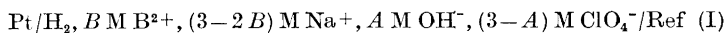# Studies on the Hydrolysis of Metal Ions

Part 36. An Estimate of the Formation Constants of CaOH$^+$, SrOH$^+$ and BaOH$^+$ in 3 M NaClO$_4$

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The formation constants of CaOH$^+$, SrOH$^+$ and BaOH$^+$ have been estimated from measurements, at 25°C, of the emf, E, of the cells
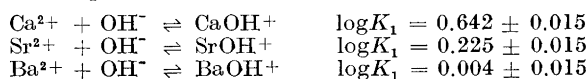
$$Pt/H_2, B \text{ M } B^{2+}, (3-2B) \text{ M } Na^+, A \text{ M } OH^-, (3-A) \text{ M } ClO_4^-/Ref \quad (I)$$

$$Ag,AgCl(AgBr)/B \text{ M } B^{2+}, (3-2B) \text{ M } Na^+, X \text{ M } Cl^-(Br^-), (3-X) \text{ M } ClO_4^-/Ref \quad (II)$$

where B^{2+} stands for Ca^{2+}, Sr^{2+} or Ba^{2+} and the reference half-cell (Ref) was

$$/3 \text{ M } NaClO_4/2.99 \text{ M } Na^+, 0.01 \text{ M } Ag^+, 3 \text{ M } ClO_4^-/Ag, AgCl. \quad (III)$$

From the measured values of E, [OH$^-$] was calculated using the relationship $E = E° + 59.15\log[OH^-] - 9.3B - 8[OH^-]$.

The following formation constants were obtained.

$$Ca^{2+} + OH^- \rightleftharpoons CaOH^+ \qquad \log K_1 = 0.642 \pm 0.015$$
$$Sr^{2+} + OH^- \rightleftharpoons SrOH^+ \qquad \log K_1 = 0.225 \pm 0.015$$
$$Ba^{2+} + OH^- \rightleftharpoons BaOH^+ \qquad \log K_1 = 0.004 \pm 0.015$$

The determination of the equilibrium constants (K_1) for the association between the alkaline earth metal ions and OH$^-$ has been the subject of a great number of investigations [1]. Since these constants are small the numerical values obtained are very sensitive to the assumptions made in deriving them. The difficulties met with when results from emf measurements are to be interpreted, are illustrated by the work of Bates, Bower, Canham and Prue [2]. From measurements with the cell Pt/H$_2$, Ca(OH)$_2$, KCl or CaCl$_2$/AgCl, Ag they found K_1 to be strongly dependent on the value chosen for f_{Cl}-/f_{OH}- and used in calculating [OH$^-$].

SYMBOLS

A total concentration of OH$^-$
a [OH$^-$], concentration of free OH$^-$

B total concentration of B^{2+}
b concentration of free B^{2+}
B^{2+} used to denote Ca^{2+}, Sr^{2+} or Ba^{2+}
K_1 equilibrium constant of the reaction $B^{2+} + OH^- \rightleftharpoons BOH^+$
$y(x)_v$, 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.

EXPERIMENTAL

$HClO_4$, $NaOH$ and $NaClO_4$ were prepared and analysed by the methods described in Refs. [3,4]

$Ca(ClO_4)_2$, $Sr(ClO_4)_2$ and $Ba(ClO_4)_2$ were prepared from the carbonates by the method described by Biedermann [5] for $NaClO_4$. The product was twice recrystallized from water and analysed by adding H_2SO_4, fuming off the $HClO_4$, and weighing as the sulphate.

Silver chloride and bromide electrodes were prepared according to Brown [6].

Hydrogen electrodes were prepared according to Bates [7].

ACTIVITY FACTOR OF OH^-, Cl^-, Br^-

In 1953 Biedermann and Sillén [8] published measurements on the cells
Ref/B M Me^{z+}, H M H^+, $(3-H-zB)$ M Na^+, 3 M ClO_4^-/electrode reversible to Me^{z+}

Ref/H M H^+, $(3-H)$ M Na^+, X M $Cl^-(Br^-)$, $(3-X)$ M ClO_4^-/AgCl(AgBr), Ag

Their main conclusion was that as long as the anionic composition of the solution is kept constant, the activity factor of the cation is practically constant when its concentration is low compared to that of the added inert salt $(NaClO_4)$.

The results from the second cell showed that when Na^+ was exchanged for H^+, log f_{Cl^-} or log f_{Br^-} varied linearly with $[H^+]$. Apparently a change in the composition of the counterions leads to changes in the activity factors. However, the interesting fact appears that the ratio $f_{Cl^-}/f_{Br^-} \simeq 1$, which suggests that in 3 M $NaClO_4$ it is a good approximation to set $f_{OH^-}/f_{Cl^-} = 1$.

In order to test this, measurements were made on the cell

$$Ag, AgCl(AgBr)/3 \text{ M } Na^+, X \text{ M } Cl^-(Br^-), (3-X) \text{ M } ClO_4^-/Ref \qquad (IV)$$
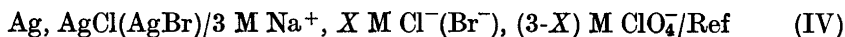
$$E = E^\circ_{IV} + 59.15\log[X] + 59.15\log f_X + E_j \qquad (1)$$

where Ref $= /3$ M $NaClO_4/$ 2.99 M Na^+, 0.01 M Ag^+, 3 M ClO_4^-/Ag, AgCl (III) and on the cell

$$Pt/H_2, A \text{ M } OH^-, X \text{ M } Cl^-, (3-A-X) \text{ M } ClO_4^-, 3 \text{ M } Na^+/Ag, AgCl \qquad (V)$$
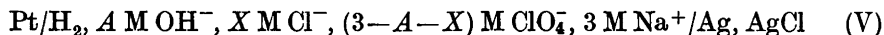
$$E = E^\circ_V + 59.15\log A/[X] + 59.15\log f_{OH^-}/f_{Cl^-} \qquad (2)$$

From these measurements, quantities E' were calculated, where for cell (IV)

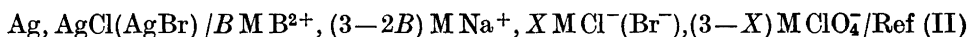$$E'_{IV} = E - 59.15\log[X] = E^\circ_{IV} + 59.15\log f_X + E_j \qquad (3)$$

and for cell (V)

$$E'_V = E - 59.15 \log A/[\text{X}] = E^\circ_V + 59.15\log f_{\text{OH}^-}/f_{\text{Cl}^-} \quad (4)$$

In the concentration range studied $0.005 < [\text{X}]$, $A < 0.025$ M, these quantities came out as constants. The simplest form of expression of these results is that, in 3 M $NaClO_4$, $f_{\text{Cl}^-} = f_{\text{Br}^-} = f_{\text{OH}^-} = 1$, and that E_j in cell (IV) is negligible.

Since a titration technique was used, cells involving liquid junctions were employed. They were

$$\text{Pt/H}_2, B \text{ M } B^{2+}, (3-2B) \text{ M Na}^+, A \text{ M OH}^-, (3-A) \text{ M ClO}_4^-/\text{Ref} \quad (\text{I})$$

$$E = E^\circ_I + 59.15\log a + 59.15\log f_{\text{OH}^-} + E_j \quad (5)$$

$$\text{Ag, AgCl(AgBr)} /B \text{ M } B^{2+}, (3-2B) \text{ M Na}^+, X \text{ M Cl}^-(\text{Br}^-),(3-X) \text{ M ClO}_4^-/\text{Ref} \quad (\text{II})$$

$$E = E^\circ_{II} + 59.15\log[\text{X}] + 59.15\log f_X + E_{jB} \quad (6)$$

and Ref = half-cell (III)

The important step in the evaluation of the formation constants (K_1) is the calculation of a from the emf of cell (I). To do this we shall make use of the following assumptions.

1. The liquid junction potential in cell (I), E_j, consists of two terms E_{jA} and E_{jB}.

$$E_j = E_{jA} + E_{jB} \quad (7)$$

E_{jB} is the liquid junction potential arising from the exchange of Na^+ for B^{2+}, and it is assumed to have the same value as in cell (II). E_{jA} is the liquid junction potential arising from the exchange of ClO_4^- for OH^- at constant B. It is assumed to have the value $E_{jA} = -8a$, which is the value in 3 M $NaClO_4$[9].

2. f_{OH^-} equals f_X. On this assumption we obtain from cell (II) $(59.15 \log f_{\text{OH}^-} + E_{jB})$ as a function of B.

Once numerical values for $(59.15\log f_{\text{OH}^-} + E_{jB})$ have been obtained, a can be calculated from eqn. (5).

B-DEPENDENT TERMS

Measurements on cell (II) were made with [X] ranging from 0.01 M to 0.025 M and B from 0 to 0.2 M. The results were plotted as

$$E - 59.15\log[\text{X}] (= E^\circ_{II} + 59.15\log f_X + E_{jB}) \quad (8)$$

as a function of B. In all cases, straight lines were obtained. The slopes of these lines, surprisingly enough, were the same $(= -9.3 \pm 0.3 \text{ mV/M})$ for all the B—X pairs studied, viz. Ba—Cl, Ba—Br, Ca—Cl, Ca—Br and Sr—Cl.

The plot of (8) versus B reflects the variation of f_X with B. We shall assume then, that the same result would have been obtained for the hydroxides, had these been completely dissociated. On this assumption we have

$$59.15\log f_{\text{OH}^-} + E_{jB} = -(9.3 \pm 0.3)B \quad (9)$$

CHOICE OF A AND B RANGE

The values of the concentration of B^{2+} and OH^- used in cell (I) were chosen from the following reasons. If we assume that BOH^+ is the only complex formed (which leads to no contradiction of the data), then

$$A = a + [BOH^+] \tag{10}$$

$$B = b + [BOH^+] \tag{11}$$

$$K_1 = [BOH^+] f_{BOH^+}/ab f_{OH^-} f_B{}^{2+} = [BOH^+]/abf \tag{12}$$

$$f = f_B{}^{2+} f_{OH^-}/f_{BOH^+} \tag{13}$$

which together with eqn. (5) give

$$E = E_I^\circ + 59.15\log A - 59.15\log(1 + K_1 f B/(1 + K_1 f a)) + 59.15\log f_{OH^-} + E_j \tag{14}$$

Choosing

$$Y = E - 59.15\log A \tag{15}$$

as the experimental variable and expanding the logarithm we get

$$Y \simeq E_I^\circ - 25.69 K_1 f B (1 - K_1 f a) + 59.15\log f_{OH^-} + E_j \tag{16}$$

$$Y' = Y - E_j - E_I^\circ - 59.15\log f_{OH^-} \simeq -25.69 K_1 f B (1 - K_1 f a) \tag{16a}$$

$$(\delta Y'/\delta B)_A \simeq -25.69 K_1 f (1 - K_1 a f) \tag{17}$$

$$(\delta Y'/\delta A)_B \simeq 25.69 K_1^2 f^2 B \tag{18}$$

Y' is a measure of the association. K_1 is small, therefore it is necessary to use fairly large concentrations of B^{2+} and OH^- to get Y' values large enough for the value of K_1, subsequently calculated from Y', not to be seriously affected by errors in the measured emf. Large changes in the medium are unwanted even if allowance is made by the term $(59.15\log f_{OH^-} + E_j)$. We may therefore ask which of B^{2+} or OH^- leads to the largest change in Y', for the same change in concentration. From eqns. (17) and (18) we find

$$l = |(\delta Y'/\delta B)_A/(\delta Y'/\delta A)_B| \simeq 1/K_1 f B \tag{19}$$

Using provisional values of K_1 (M^{-1}) (4.39, Ca^{2+}; 1.68, Sr^{2+}; 1.01, Ba^{2+}) we find that $l > 1$ for moderate values of B. The titrations were therefore arranged so that B was varied (at the most to 0.2 M) whereas A was kept low.

PRELIMINARY MEASUREMENTS ON CELL (I) AND THE CORRECTION FOR THE LIQUID JUNCTION POTENTIAL

The preliminary titrations were carried out with $Ba(ClO_4)_2$ solutions. Initially cell (I) contained ca 0.025 M OH^- and no Ba^{2+}. A was then gradually decreased by the addition of $HClO_4$ and E_I° calculated from eqn. (5) with $E_j = -8A$. After E_I° had been determined, $Ba(ClO_4)_2$ in 3 M ($NaClO_4$) was added to attain the desired value of B, then A was increased gradually whilst B was kept constant by further additions of $Ba(ClO_4)_2$. The results were plotted in the form $Y(A)_B$ where $Y = E - 59.15 \log A$. (15) The curves

were extrapolated to $A = 0$ in order to eliminate the liquid junction potential arising from the OH⁻ ions. On the basis of our assumptions (eqns. (7) and (9)) Y is given by

$$Y = E_I^\circ - 59.15\log(1 + K_1 fB/(1 + K_1 fa)) - 9.3B - 8a \qquad (20)$$

and the extrapolated value of Y (= Y_0), is given by

$$Y_0 = E_I^\circ - 59.15\log(1 + K_1 fB) - 9.3B \qquad (21)$$

It would have been more correct to plot $Y(a)_B$, however, the difference between A and a is small and the error introduced is negligible.

Support for the assumptions underlying eqn. (20) comes from the following results.

1. The lines $Y(A)_B$ were straight and, for $B < 0.1$ M, had slopes close to -8 mV/M, which is the value obtained with 3 M NaClO₄[9].

2. The points $(Y_0 - E_I^\circ)$ (B) fell on a straight line passing through the origin, as required by eqn. (21).

FINAL EXPERIMENTS AND CALCULATIONS

The simple relationship between $(Y_0 - E_I^\circ)$ and [Ba²⁺], led us to change the titration procedure. The measurements were started on a mixture of Ba(OH)₂ and NaClO₄, and [Ba²⁺] was then gradually increased by addition of Ba(ClO₄)₂ in 3 M NaClO₄. The initial values of A were between 0.015 M and 0.025 M. No OH⁻ was added during the titration so that A varied with the dilution only.

Y_0 was calculated from

$$Y_0 = E + 8A - 59.15\log A \qquad (21a)$$

and plotted as a function of $B = [Ba^{2+}]_{tot}$, and E_I° was found by fitting the data to a straight line by the method of least squares. With E_I° known, a was calculated from eqn. (5) using

$$59.15\log f_{OH^-} + E_{jB} = -9.3B; \quad E_{jA} = -8A \qquad (9), (22)$$

The terms [BaOH⁺] and [Ba²⁺] were found from eqns. (10) and (11) and inserted into

$$K_1 = \frac{[BaOH^+]}{[Ba^{2+}][OH^-]} \qquad (12a)$$

When K_1 had been determined a was calculated from eqns. (10), (11) and (12a) using the analytical data. E_I° was redetermined with the new value for E_{jA} ($-8a$) and K_1 calculated for the new value of E_I° if the change exceeded 0.02 mV.

With Sr²⁺ the technique described above was used. For Ca²⁺, however, the initial OH⁻ was provided by Ba(OH)₂ and $[Ba^{2+}]_{tot}$ was kept constant by adding Ba(ClO₄)₂ together with the Ca(ClO₄)₂. The additions of Ba²⁺ ranged between 0.007 and 0.012 M. Since we wanted to work with well buffer-
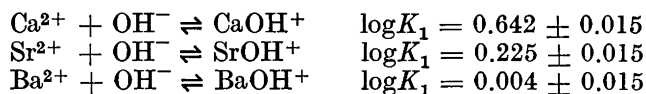
Table 1.

Ca²+

E mV observed	A M × 10³	B M × 10³	K_1 M⁻¹	E° mV calculated
1 390.46	15.21	3.092	4.15	1 498.74
1 388.91	14.52	5.092	4.44	1 498.70
1 387.47	13.88	8.475	4.57	1 498.68
1 386.12	13.29	10.84	4.39	1 498.71
1 384.83	12.76	13.01	4.41	1 498.72
1 383.61	12.26	15.00	4.33	1 498.73
1 382.44	11.80	16.86	4.33	1 498.75
1 381.31	11.38	18.58	4.33	1 498.74
1 380.19	10.98	20.19	4.37	1 498.71
1 379.22	10.61	21.68	4.37	1 498.75

Sr²+

E mV observed	A M × 10³	B M × 10³	K_1 M⁻¹	E° mV calculated
1 402.07	23.73	11.87	1.69	1 498.95
1 401.58	23.47	16.12	1.66	1 498.95
1 400.62	22.96	24.37	1.66	1 498.97
1 399.69	22.48	32.30	1.65	1 498.96
1 398.78	22.01	39.88	1.66	1 498.96
1 397.90	21.57	47.18	1.67	1 498.95
1 397.05	21.14	54.15	1.67	1 498.94
1 396.22	20.73	60.86	1.67	1 498.94
1 395.42	20.34	67.34	1.68	1 498.93
1 394.62	19.96	73.55	1.69	1 498.90
1 393.86	19.59	79.56	1.69	1 498.91
1 393.48	19.41	82.47	1.69	1 498.89

Ba²+

E mV observed	A M × 10³	B M × 10³	K_1 M⁻¹	E° mV calculated
1 403.90	25.59	18.83	0.940	1 498.90
1 402.94	25.04	30.24	1.003	1 498.87
1 402.01	24.51	41.23	1.017	1 498.87
1 401.13	24.01	51.71	1.020	1 498.85
1 400.30	23 52	61 81	0.988	1 498.89
1 399.47	23.06	71.47	1.003	1 498.87
1 398.65	22.61	80.75	1.009	1 498.85
1 397.93	22.18	89.72	0.978	1 498.90
1 397.13	21.76	98.31	0.996	1 498.87
1 396.38	21.36	100.6	1.000	1 498.86
1 396.00	21.17	110.7	1.004	1 498.83

ed solutions, the extrapolation of E_I° would have been quite long, had $Ca(OH)_2$ been used as the base. The ranges of B studied were:

$$Ca^{2+}, 0 \langle B \langle 0.025 \text{ M}; \ Sr^{2+}, \ 0 \langle B \langle 0.1 \text{ M}; \ Ba^{2+}, \ 0 \langle B \langle 0.125 \text{ M}.$$

The calculations with the data from the Sr^{2+} and Ca^{2+} titrations were carried out as described for Ba^{2+}; in the latter case this is permissible because $[Ba^{2+}]$ was kept constant.

Table 1 contains results typical of those obtained. One would expect the values of K_1 to show a trend since they relate to solutions in which Na^+ is increasingly replaced by B^{2+}. However, with Ca^{2+} and Ba^{2+} no such trend is observed; with Sr^{2+}, on the other hand, there is a small trend. As can be seen from the table the trend is only present at the highest Sr^{2+} concentrations. These values were excluded when taking the mean value of K_1. The following results were obtained:

$$Ca^{2+} + OH^- \rightleftharpoons CaOH^+ \qquad \log K_1 = 0.642 \pm 0.015$$
$$Sr^{2+} + OH^- \rightleftharpoons SrOH^+ \qquad \log K_1 = 0.225 \pm 0.015$$
$$Ba^{2+} + OH^- \rightleftharpoons BaOH^+ \qquad \log K_1 = 0.004 \pm 0.015$$

The last column in Table 1 shows the self-consistency of the treatment of the data. E_I° has been calculated from

$$E_I^{\circ} = E - 59.15 \log a + 9.3B + 8a \qquad (23)$$

with a found from the analytical data and the mean value of K_1 proper. For Ca^{2+} and Ba^{2+} E_I° comes out as a constant, as it should, whereas for Sr^{2+} there is a slight trend at the highest concentrations.

It is interesting to note that the ratios between K_1 (in 3 M $NaClO_4$) and K_1(in H_2O) for the different metals, are roughly the same, thus, Ca^{2+} $4.39/22.2 = 0.20$; Sr^{2+} $1.68/6.67 = 0.25$; Ba^{2+} $1.01/4.35 = 0.23$.

It is hard to say anything definite as to the physical significance of the formation constants. There is no theory which affords a means of calculating the properties of fully dissociated salts in solutions such as these. The simple results obtained with NaOH, NaBr, NaCl and the chlorides and bromides of Ca^{2+}, Sr^{2+} and Ba^{2+} in 3 M $NaClO_4$ seem to indicate that the thermodynamic properties of ions in an inert salt medium are, to a large extent, determined by the charge, and that size is of less importance. We may therefore have some confidence in taking the halides as "models" for the completely dissociated hydroxide. However, the formation constants obtained on this basis may be expected to give the upper limits for the true constants.

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