Studies on the Hydrolysis of Metal Ions

43. A Thermochemical Study of Hydrolysed Be(ClO₄)₂ Solutions

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Enthalpy titrations have been performed with hydrolysed Be(ClO₄)₂ solutions (25°C, 3 M (Na)ClO₄). The hydrolysis mechanism proposed by Kakihana and Sillén [1], viz.

$$2Be^{2+} + H_2O \rightleftharpoons Be_2OH^{3+} + H^+ \qquad (1)$$
$$3Be^{2+} + 3H_2O \rightleftharpoons Be_3(OH)_3^{3+} + 3H^+ \qquad (2)$$
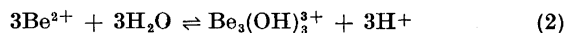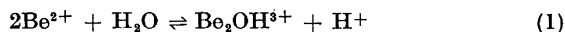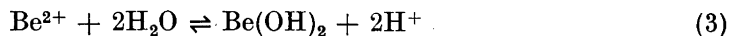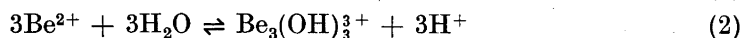
has been used as the basis for the interpretation of the heat data. These gave for reaction (1)

$\Delta H = 4.43 \pm 0.10$ kcal/mole; $\Delta S = 0.2 \pm 0.6$ e.u.

and for reaction (2)

$\Delta H = 15.18 \pm 0.05$ kcal/mole; $\Delta S = 11.3 \pm 0.3$ e.u.

No thermochemical data are available for hydrolysed beryllium salt solutions. This paper reports enthalpy titrations with hydrolysed Be(ClO₄)₂ solutions containing 3 M (Na)ClO₄ as supporting electrolyte. The interpretation of the experimental data in terms of ΔH values of the hydrolysis reactions has been based on the mechanism proposed by Kakihana and Sillén [1] from emf measurements, namely

$$2Be^{2+} + H_2O \rightleftharpoons Be_2OH^{3+} + H^+ \qquad (1)$$
$$3Be^{2+} + 3H_2O \rightleftharpoons Be_3(OH)_3^{3+} + 3H^+ \qquad (2)$$
$$Be^{2+} + 2H_2O \rightleftharpoons Be(OH)_2 + 2H^+ \qquad (3)$$

This mechanism has been confirmed by Carell and Olin [2] using a technique similar to that of Kakihana and Sillén, but with emphasis on concentrated Be(ClO₄)₂ solutions. The presence of Be²⁺ mainly as $Be_3(OH)_3^{3+}$ in dilute solution is also supported by solubility measurements of α-Be(OH)₂ in acids [3,4].

EXPERIMENTAL

The calorimeter constructed and described by Schlyter [5] has been used. The performance of the apparatus was tested by a determination of the heat of dilution of HCl. The results were compared with the values calculated from Sturtevant's data [6] and were found to agree to within 1 %.

The calorimeter was charged with a hydrolysed solution of $Be(ClO_4)_2$ and this solution was titrated with $HClO_4$ from a thermostated buret. The compositions of the two solutions were so chosen that in each experiment $[Be(II)]_{tot} = B$ and $[ClO_4^-] = 3$ M were constant. The additions of acid were continued till the heat evolved per addition had dropped practically to zero, *i.e.* when all the hydrolysed Be(II) had been converted to $Be^{2+}aq$.

The hydrolysed beryllium solutions were prepared by mixing stock solutions of $Be(ClO_4)_2$, $NaHCO_3$ and $NaClO_4$. The CO_2 formed was expelled by bubbling N_2 through the solutions for 2 h. The titrant was also made up from stock solutions. Kakihana and Sillén had observed that in solutions with a ratio OH^-/Be^{2+} $(= Z)$ greater than 0.8 the attainment of equilibrium was somewhat slow. Since slow reactions cannot be studied with the calorimeter we chose an initial value of $Z \simeq 0.6$ in our solutions. The values of B and the analytical hydrogen ion excess, H, in the various solutions used in the titrations are given in Table 1. The value of H, which is usually a negative number, at each point of a titration can be calculated from

$$H = (vH_T + V_0H_S)/(V_0 + v) \tag{4}$$

where $H_T = H$ of the buret solution; $H_S =$ initial value of H in the calorimeter solution; $V_0 =$ initial volume of the solution in the calorimeter vessel (always 224.08 ml); $v =$ volume of buret solution added.

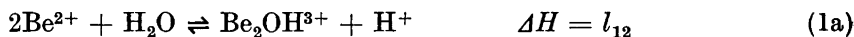As an example of the experimental results obtained the titration with $B = 0.04$ M is given in Table 2.

Table 1. Survey of titrations.

	$B = 0.32$ M	$B = 0.08$ M	$B = 0.04$ M	$B = 0.02$ M	$B = 0.01$ M
H_S, M	-0.0960	-0.0480	-0.0240	-0.0120	-0.00700
H_T, M	1.372	0.9037	0.4117	0.2740	0.1580

RESULTS AND CALCULATIONS

The heat evolved per addition of acid from the buret, Q, was calculated from the equations given by Schlyter [5].

If the heats of dilution are neglected Q is related to the enthalpy changes of the reactions

$$2Be^{2+} + H_2O \rightleftharpoons Be_2OH^{3+} + H^+ \qquad \Delta H = l_{12} \tag{1a}$$

$$3Be^{2+} + 3H_2O \rightleftharpoons Be_3(OH)_3^{3+} + 3H^+; \qquad \Delta H = l_{33} \tag{2a}$$

and the change in the number of moles of Be_2OH^{3+} and $Be_3(OH)_3^{3+}$ per addition of acid from the buret, δn_{12} and δn_{33}, by

$$Q = \delta n_{12}l_{12} + \delta n_{33}l_{33} \tag{5}$$

The concentration of $Be(OH)_2$ in the solutions studied is very small and has been neglected. The concentration changes have been calculated from the

Table 2. Data from titrations with $B = 0.04$ M.

v ml	Q cal	Q_{calc} cal	$Q - Q_{calc}$ cal	v ml	Q cal	Q_{calc} cal	$Q - Q_{calc}$ cal
1	2.100	2.083	0.017	2	4.103	4.177	−0.074
3	4.201	4.172	0.029	4	4.143	4.154	−0.011
5	4.151	4.141	0.010	6	4.140	4.130	0.010
7	4.166	4.118	0.048	8	4.085	4.097	−0.012
9	4.119	4.071	0.048	10	4.059	4.029	0.030
11	3.999	3.956	0.043	12	3.824	3.807	0.017
13	3.403	3.381	0.022	14	2.230	2.271	−0.041
15	0.976	0.963	0.013	16	0.401	0.310	0.091
17	0.162	0.133	0.029	18	0.075	0.073	0.002
19	0.065	0.046	0.019	20	0.043	0.032	0.011
21	0.025	0.023	0.002	22	0.031	0.017	0.014
23	0.004	0.014	−0.010	24	0.004	0.013	−0.009

analytical composition of the solutions and the equilibrium constants obtained from the emf work [2]. These calculations have been made with an electronic computer (Ferranti Mercury) and using a computer program whose essential part is the program HALTA described by Ingri and Sillén [7]. The computations were made on data with $B = 0.08$, 0.04, 0.02 and 0.01 M and with $\log \beta_{1,2} = -3.21$ and $\log \beta_{3,3} = -8.66$. Eqn. (5) was then solved for l_{12} and l_{33} according to the method of least squares.

The values of l_{12} and l_{33} thus found were

$$l_{12} = 4.43 \pm 0.10 \text{ kcal/mole}$$
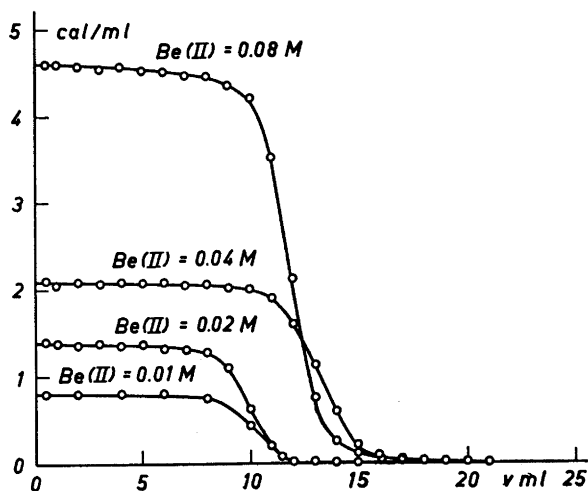$$l_{33} = 15.18 \pm 0.05 \text{ kcal/mole}$$

Fig. 1. Experimental Q and Q_{calc} (in cal per ml of acid added) as a function of v. The smooth curves have been drawn through the points for Q_{calc}, and the symbols represent Q for $B = 0.08$, 0.04, 0.02, 0.01 M.
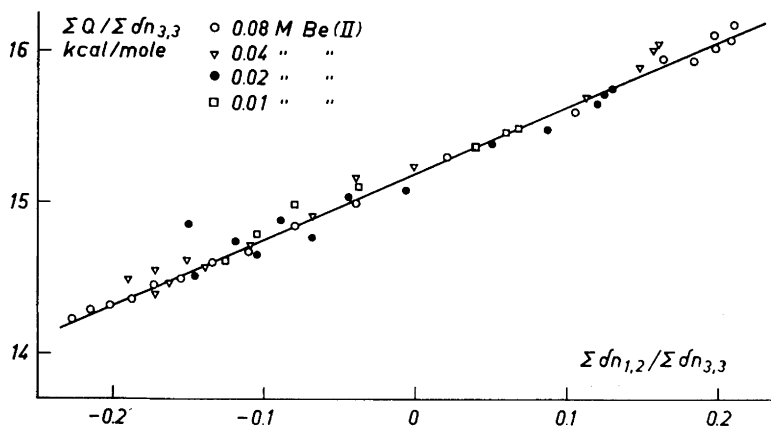
Fig. 2. Graphical determination of l_{12} and l_{33} according to eqn. (5a).

with these values of l_{12} and l_{33} the "expected" heat evolution per addition, Q_{calc}, has been calculated from eqn. (5) and is given in the second column of Table 2. In the third column of the same table the difference between Q and Q_{calc} can be found.

From Fig. 1, which is a graphical representation of Q and Q_{calc} for the various B values, it is seen that systematic deviations are absent. The estimated standard deviation in Q (for $Q > 0.5$ cal),

$$S = \pm \sqrt{\Sigma(Q - Q_{calc})^2/\nu} \tag{6}$$

where ν is the number of degrees of freedom, is found to be ± 0.034 cal. This is comparable with a value of ± 0.03 cal calculated (at the 95 % confidence level) from the calorimetric measurement uncertainties (Ref.[5]).

The values of l_{12} and l_{33} can also be found graphically. For that purpose eqn. (5) is written

$$\Sigma Q/\Sigma \delta n_{33} = l_{33} + (\Sigma \delta n_{12}/\Sigma \delta n_{33})l_{12} \tag{5a}$$

i.e. accumulated values of Q, δn_{12} and δn_{33} have been used. The plot of eqn. (5a) is shown in Fig. 2 together with the best straight line obtained from the least squares treatment above.

The results from the enthalpy titrations substantiate the hydrolysis mechanism suggested for Be^{2+} in so far as a reasonable interpretation of the heat data is obtained with this mechanism. At low values of B, however, the main part of the hydrolysed Be^{2+} is present as $Be_3(OH)_3^{3+}$ whereas $[Be_2OH^{3+}]$ is relatively small. It was therefore considered worthwhile to study a higher value of B also, since the proportion of Be_2OH^{3+} increases with B.

$B = 0.32$ M was chosen for this purpose and this concentration was studied in the range $0 < Z < 0.3$. These data were treated in the way described above. When the results were plotted as done in Fig. 1 small, systematic deviations
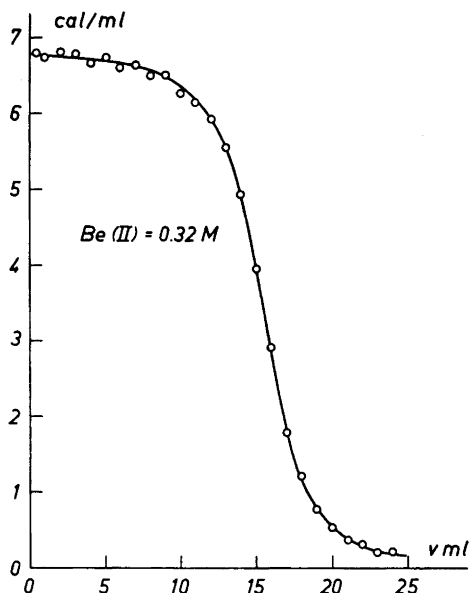
Fig. 3. Q and Q_{calc} (in cal per ml of acid added) as a function of v. The smooth curve has been drawn through the calculated points Q_{calc} and the symbols represent Q for $B = 0.32$ M.

were found. These deviations could be almost removed by an adjustment of the equilibrium constants. Values of β were sought which made the error square sum, $U = (Q-Q_{calc})^2$, a minimum. It was found that that variations in log $\beta_{3,3}$ of the order of 0.1 logarithmic units did not appreciably change U whereas log $\beta_{1,2} = -3.14$ gave U a pronounced minimum. This value of log $\beta_{1,2}$ thus differs from the value -3.21 found from the emf measurements by 0.07 logarithmic units. This is slightly larger than the estimated uncertainty of 0.05 in the latter value of log $\beta_{1,2}$. The values of the enthalpy changes found were
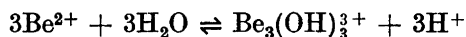
$$l_{12} = \quad 4.68 \pm 0.10 \text{ kcal/mole}$$
$$l_{33} = 14.95 \pm 0.05 \text{ kcal/mole}$$

They differ somewhat from the values obtained with $B \leq 0.08$ M. No calculations on the data with $B \leq 0.08$ M were done with log $\beta_{1,2} = -3.14$, since it is believed that log $\beta_{1,2} = -3.21$, found by emf methods (Ref.[1],[2]), is a better value of log $\beta_{1,2}$ for these values of B. Future experience with other systems will show if the significant difference of 1 % between the two values of l_{33} is reasonable or not. The results of the treatment of the data for $B = 0.32$ M is shown in Fig. 3 and we might conclude that these titrations again support the hydrolysis mechanism identified by emf methods.

Summary of the thermochemical data for $B \leq 0.8$ M

$$2Be^{2+} + H_2O \rightleftharpoons Be_2OH^{3+} + H^+$$
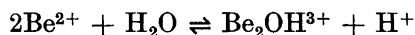
$\Delta G = 4.379 \pm 0.07$ kcal/mole; $\Delta H = 4.43 \pm 0.1$ kcal/mole; $\Delta S = 0.2 \pm 0.6$ e.u.

$$3Be^{2+} + 3H_2O \rightleftharpoons Be_3(OH)_3^{3+} + 3H^+$$

$\Delta G = 11.815 \pm 0.04$ kcal/mole; $\Delta H = 15.18 \pm 0.05$ kcal/mole; $\Delta S = 11.3 \pm 0.3$ e.u.

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