

871. *The Hydrolysis of Metal Ions. Part III.*¹ Zinc.

By D. D. PERRIN.

A potentiometric study has been made of the hydrolysis of zinc ion. Values of the acid dissociation constant, $*K_1$, corresponding to the formation of the complex ion, $ZnOH^+$, have been obtained for the range 15—42° at various ionic strengths (adjusted by addition of potassium nitrate). There was no evidence of formation of polynuclear complexes.

THE recorded values of the acid dissociation constant ² of the zinc cation range (at room temperature) from $10^{-5.08}$ to $10^{-10.48}$, calculated on the assumption that $ZnOH^+$ is formed. Hence it was decided to study the hydrolysis of the zinc cation over a range of concentration, ionic strength, pH, and temperature. For concentrations of zinc ranging from $5 \times 10^{-4}M$ to 0.1M, results now indicate that hydrolysis proceeds according to the equilibrium, $Zn_{aq}^{2+} \rightleftharpoons ZnOH^+ + H^+$, and, up to the onset of precipitation, $ZnOH^+$ is the major hydrolysed species.

EXPERIMENTAL

Crystalline zinc perchlorate, obtained by dissolving zinc oxide in excess of hot 60% perchloric acid and cooling, was rinsed with cold water and dried at 80°; the preparation contained free perchloric acid. Stock solutions of zinc perchlorate were standardised by complexometric titration against ethylenediaminetetra-acetic acid, Eriochrome Black T being used as indicator,³ and the perchloric acid content was determined by potentiometric titration against potassium hydroxide.

The apparatus, method, and experimental procedure were as described for manganese(II)⁴ (except that zinc perchlorate and perchloric acid solutions were used): zinc perchlorate solutions of known concentration were titrated potentiometrically against potassium hydroxide up to the onset of precipitation. The solutions contained known (low) concentrations of perchloric acid to ensure that initially no hydrolysed zinc species were present, and varying amounts of potassium nitrate to alter the ionic strength. As with copper⁵ and manganese,⁴ attainment of pH constancy after each addition of alkali was slow, averaging 15 to 20 min. at 20°. In the limited ranges of Z (the average number of hydroxyl ions bound per zinc atom) which could be studied, results could be interpreted quantitatively by assuming that the only complex formed by hydrolysis was $ZnOH^+$, so that $*K_1$ was given by

$$*K_1 = \frac{[ZnOH^+](a_{H^+})}{[Zn^{2+}]} = \frac{([H^+] + [KOH]_{added} - [OH^-] - [HClO_4])(a_{H^+})}{([Zn^{2+}]_T + [HClO_4] + [OH^-] - [H^+] - [KOH]_{added})} \quad (1)$$

Data from a typical experiment are presented in Table 1.

*Effect of Ionic Strength and Temperature on $*K_1$.*—The values of $-\log *K_1$ listed in Table 2 were calculated by using equation (1). They indicate that $-\log *K_1$ is relatively insensitive to ionic strength, changing by less than 0.3 logarithm unit as I varies from 0.0015 to 1.50. [Similar insensitivity is shown by $\log *K_1$ for manganese(II) ion⁴ and $\log *K_{22}$ for copper(II) ion.⁵] Also, the absence of significant formation of polynuclear complexes is indicated by the closeness of estimates of $-\log *K_1$ at $I = 1.503$ and $I = 1.600$ for concentrations of zinc ion which differ by a factor of 100.

To obtain $-\log *K_1^\circ$ at 20° from the results in Table 2 the arbitrary but reasonable values of $\alpha = 1.65$ and $\beta = 0.30$ were assigned to the constants in the Debye-Hückel equation:

$$-\log *K_1^\circ = -\log *K_1 - 1.506I^{\frac{1}{2}}/(1 + \alpha I^{\frac{1}{2}}) + \beta I. \quad (2)$$

¹ The papers, *J.*, 1960, 3189; 1962, 2197; are regarded as Parts I and II.

² Bjerrum, Schwarzenbach, and Sillén, "Stability Constants. Part II. Inorganic Ligands," The Chemical Society, London, Spec. Publ. No. 7, 1958.

³ Schwarzenbach, "Complexometric Titrations," Methuen and Co. Ltd., London, 1957, p. 83.

⁴ Perrin, *J.*, 1962, 2197.

⁵ Perrin, *J.*, 1960, 3189.

TABLE 1.

Evaluation of $*K_1$ from potentiometric titration.

$[\text{Zn}(\text{ClO}_4)_2] = 0.00100\text{M}$. $[\text{HClO}_4] = 8.83\mu\text{M}$. $[\text{KNO}_3] = 0.300\text{M}$. Temp. 20° . Titrated with 0.100M-KOH . $[\text{ZnOH}^+]$ assumed = $[\text{KOH}] + [\text{H}^+] - [\text{HClO}_4] - [\text{OH}^-]$.

[KOH] added (μM)	pH	[ZnOH ⁺] (μM)	[Zn ²⁺] (μM)	Z	$-\log *K_1$
0	5.220				
4	5.485				
8	6.085	(0.38)			
10	6.579	1.54	998		(9.38)
12	6.943	3.28	997	0.0033	9.42
14	7.171	5.19	995	0.0052	9.45
16	7.326	7.14	993	0.0072	9.47
18	7.439	9.05	991	0.0091	9.48
20	7.535	11.00	989	0.0111	9.49
24	7.671	14.90	985	0.0151	9.49
28	7.758	18.83	981	0.0192	9.48
34	7.823	24.75	975	0.0254	9.42
Average					9.46

TABLE 2.

Effect of ionic strength on $*K_1$ at 20° .

$\text{Zn}(\text{ClO}_4)_2$ solutions, containing low concentrations of HClO_4 and various concentrations of KNO_3 , titrated with 0.100M-KOH . Values of $-\log *K_1^\circ$ calculated from $-\log *K_1$ by using equation (2) with $\alpha = 1.65$ and $\beta = 0.30$.

pH range	$[\text{Zn}^{2+}]_T, \text{M}$	I	Z	$-\log *K_1 \pm \text{range}$ (no. of obs.)	$-\log *K_1^\circ$
7.239—7.870	0.00050	0.0015	0.013—0.056	$9.17 \pm 0.04(5)$	9.11
7.273—7.645	0.00100	0.0130	0.010—0.030	$9.32 \pm 0.05(5)$	9.18
7.072—7.765	0.00100	0.0430	0.006—0.026	$9.41 \pm 0.05(5)$	9.19
6.844—7.765	0.00100	0.0630	0.003—0.024	$9.43 \pm 0.03(5)$	9.18
7.235—7.778	0.00100	0.1030	0.007—0.024	$9.42 \pm 0.03(5)$	9.13
6.613—7.838	0.00100	0.2030	0.003—0.029	$9.45 \pm 0.05(10)$	9.12
6.943—7.823	0.00100	0.3030	0.003—0.025	$9.46 \pm 0.04(8)$	9.12
6.842—7.784	0.00100	0.603	0.003—0.025	$9.40 \pm 0.04(8)$	9.07
6.941—7.768	0.00100	1.003	0.004—0.026	$9.41 \pm 0.05(8)$	9.14
6.834—7.692	0.00100	1.503	0.004—0.026	$9.35 \pm 0.06(8)$	9.19
5.493—6.132	0.100 (ZnSO_4)	1.600	1.0×10^{-4} — 4.9×10^{-4}	$9.47 \pm 0.03(7)$	9.33

TABLE 3.

Thermodynamic acid dissociation constants for zinc ion from 15° to 42° .In all cases $[\text{Zn}(\text{ClO}_4)_2] = 0.0005\text{M}$ for $I = 0.00150$, and 0.001M for $I = 0.0130, 0.0430$.

I	$-\log *K_1^\circ$					
	15°	20°	25°	30°	36°	42°
0.00150	9.28		8.93	8.76	8.59	8.48
0.0130	9.32		8.97	8.81	8.62	8.43
0.0430	9.29		8.98	8.79	8.65	8.47
Average	9.30	9.15*	8.96	8.79	8.62	8.46
(\pm range)	± 0.02	± 0.04	± 0.03	± 0.03	± 0.03	± 0.03

* From Table 2.

For the range of ionic strength 0.0015 to 1.503 , values of $-\log *K_1^\circ$ at 20° lie within the limits 9.13 ± 0.06 . Theoretical uncertainties inherent in equation (2) and in the values of α and β become less important at lower ionic strengths, so that only results for $I \leq 0.303$ have been included in obtaining the final value, at 20° , of $-\log *K_1 = 9.15 \pm 0.04$. Similarly, by replacing the factor, 1.506 at 20° , by the corresponding theoretical values which range from 1.494 at 15° to 1.572 at 42° , equation (2) has been used to calculate $-\log *K_1^\circ$ at other temperatures from the experimental results for $-\log *K_1$ over the range 15 — 42° . The values in Table 3 have been obtained by taking $\alpha = 1.65$ and $\beta = 0.30$, as at 20° .

DISCUSSION

The extent to which hydrolysis of zinc salts can be studied by potentiometric titration is limited by the solubility of zinc hydroxide, onset of precipitation causing a rapid downward drift of pH readings. The break in the titration curve can be used to obtain a lower limit for the solubility product, S . Thus the break occurred at pH 7.90 in the titration at 20° and $I = 0.00150$, of a solution containing a concentration of free zinc ion of $4.63 \times 10^{-4}M$. pK_w being taken as 14.17, this gives $-\log S \geq 15.9$, in accord with values² of 16.0—16.7 at 18—20°.

Over the region (which, for millimolar zinc solutions, includes values of Z from 0 to about 0.025) where titration is possible, results can be interpreted quantitatively on the assumption that $ZnOH^+$ is the only hydrolysed zinc species. The values of $-\log {}^*K_1^\circ$ obtained in this way and listed in Table 3 can be reproduced with an average deviation of 0.01 logarithm unit by taking $A = 2923$ and $B = 0.84$ (obtained by the method of least squares) in the equation

$$-\log {}^*K_1^\circ = A/T - B, \quad (3)$$

where T is in °K. Equating A and $\Delta H^\circ/2.303R$ gives $\Delta H^\circ = 13.4$ kcal. for the reaction, $Zn_{aq}^{++} \rightleftharpoons ZnOH^+ + H^+$. This value is probably correct only to within about 1 kcal.; the simpler equation obtained by putting $A = 2673$ (corresponding to a ΔH° of 12.2 kcal.), $B = 0$, in equation (3), also fits the results within the experimental uncertainty of ± 0.03 . For the same reason, an accurate calculation of the entropy change for this reaction cannot be made by taking $B = \Delta S^\circ/2.303R$, but the values of B indicate that ΔS° must be small.

The present finding that hydrolysis of zinc ion does not give polynuclear complexes accords with similar conclusions for cadmium⁶ and mercury(II)⁷ ions, which it might be expected to resemble.

DEPARTMENT OF MEDICAL CHEMISTRY, INSTITUTE OF ADVANCED STUDIES,
AUSTRALIAN NATIONAL UNIVERSITY,
CANBERRA, A.C.T., AUSTRALIA.

[Received, April 24th, 1962.]

⁶ Marcus, *Acta Chem. Scand.*, 1957, **11**, 690.

⁷ Hietanen and Sillén, *Acta Chem. Scand.*, 1952, **6**, 747.