280. *The Electrolytic Dissociation of Metal Hydroxides.*

By C. W. Davies.

The hydroxides of most metals are weaker electrolytes in water than their other compounds, and it is suggested that this is due to the absence of the hydration shell which normally protects the metal cation. As a result, the metal hydroxides may appear to be abnormally weak, either because of true covalent bonding or, in other cases, simply on account of small ionic size. A criterion for the occurrence of covalent forces in this class of compound is suggested.

A GENERAL understanding of the dissociation constants found for " strong " electrolytes is complicated by lack of a quantitative theory of ionic hydration. For instance, the association of magnesium, calcium, strontium, and barium with the nitrate or iodate ion increases, like the ionic mobility, with the atomic number, but with certain other anions the order is reversed, and incomplete dissociation is most evident with magnesium. The difference can, rather crudely, be explained by supposing that in the first case ion-pair formation does not involve the penetration of the hydration shell of the cation by the anion (the association thus being purely electrostatic) whereas in the second case it does (thus introducing the possibility of true co-ordinative bonding), but clearly a satisfactory treatment of electrolytic dissociation will require more detailed knowledge of the hydration energies of ions.

The metal hydroxides are particularly interesting in this respect. Although dilute salt solutions are frequently supposed, in the absence of information to the contrary, to be completely dissociated, yet it is common knowledge that most common salts, except those of sodium, potassium, calcium, and barium, show marked hydrolysis; the hydroxides of most metals are therefore much weaker electrolytes than their other compounds. There is no obvious property of the hydroxide ion, such as extreme polarisability or very small size, which would put it in quite a different category from other anions, and yet this apparent anomaly in the modern theory of solutions has received little attention.

A possible explanation is that with the hydroxides alone there is no likelihood of the cation being separated from its associated ion by water molecules. Thus for most anions the configuration M^+, H_2O, X^- may represent the closest approach of the metal ion to the anion X in aqueous solution; but for the hydroxides this configuration M^+, H_2O, OH^- would tend to pass over into M^+, OH^-, H_2O, and so the protective effect of ionic hydration is lost.

It is true that Harned (cf. Harned and Owen, " Physical Chemistry of Electrolytic Solutions," Reinhold, 2nd edn., 1950, p. 385) has suggested a formulation: $M^+ \,..\, OH^- \,..\, H^+ \,..\, OH^-$, with the proton regarded as oscillating between the hydroxyl groups, to account for the mean activity coefficients of the alkali-metal hydroxides; but even if such a complex were formed, its primary dissociation would be much more likely to give rise to $M^+ \,..\, OH^- + H_2O$ than to $M^+,H_2O + OH^-$.

The first three columns of the following table give a selection of the more reliable data at

			b	*a*				*b*	*a*
Metal.	*K.*	Ref.	(Pauling).	(Bjerrum).	Metal.	*K.*	Ref.	(Pauling).	(Bjerrum).
Li	1·2	a	2·00	2·35	La ...	$\sim 5 \times 10^{-4}$	f	2·55	$\sim$1·6
Na ...	(5)	a, b	2·35	3·31	Ag ...	0·005	g	2·66	<1
K	strong	a	2·73	>3·52	Tl^I^ ...	0·38	b	2·55	1·2
					Zn ...	4×10^{-5}	h, j	2·14	<1
Mg ...	0·0026	c	2·05	1·3	Cu^II^ ...	$3{\cdot}4 \times 10^{-7}$	h	2·22	<1
Ca ...	0·050	b, d	2·39	2·45					
Ba ...	0·23	b, e	2·75	5·55					

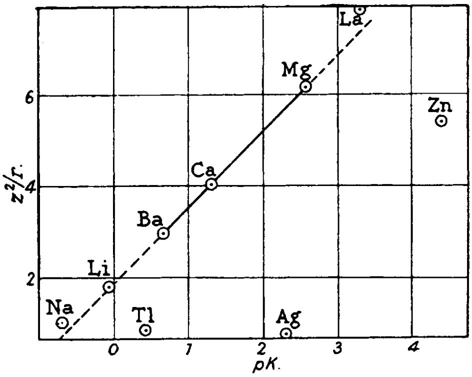
(a) Darken and Meirs, *J. Amer. Chem. Soc.*, 1942, **64**, 622 (conductivity). (b) Bell and Prue, *J.*, 1949, 362 (kinetic). (c) Stock and Davies, *Trans. Faraday Soc.*, 1948, **44**, 856 (potentiometric). (d) Davies and Hoyle, *J.*, 1950, (solubility). (e) Davies, *J.*, 1939, 349 (potentiometric). (f) Estimated from Kolthoff and Elmquist's pH measurements (*J. Amer. Chem. Soc.*, 1931, **53**, 1217). (g) J. Bjerrum, *Chem. Rev.*, 1950, **46**, 384 (potentiometric). (h) Calculated from Owen and Gurry's pH measurements (*J. Amer. Chem. Soc.*, 1938, **60**, 3074). (j) Kolthoff and Kameda, *ibid.*, 1931, **53**, 832 (potentiometric).

present available for the dissociation constants of metal hydroxides. The K values are thermodynamic constants for the process $(M, OH)^{(n-1)+} \rightleftharpoons M^{n+} + OH^-$.

That of sodium hydroxide is so high as to be subject to considerable experimental uncertainty, but nevertheless the same value has been reached independently by two entirely different methods. Col. 4 of the table shows the sum of the crystallographic radii (in A.) of the cation and the oxygen ion; a mean value of 1·40 is taken for the latter (Pauling, "Nature of the Chemical Bond," 2nd edn., Cornell Univ. Press, p. 346; Bernal and Megaw, *Proc. Roy. Soc.*, 1935, *A*, **151**, 388). Both for the alkali and the alkaline-earth metals, the strength of the hydroxide increases with the interionic distance, in agreement with the view that the radius of the bare cation is the governing factor.

If the complication of ionic hydration is absent with hydroxides, this group of electrolytes should be especially favourable for testing Bjerrum's theory of ion association (*Kgl. Danske Vid. Selsk., Mat.-fys. Medd.*, 1926, **7**, No. 9) which yields, for cases where the interaction is purely electrostatic, a relation between the dissociation constant of an ion pair and the closest distance of approach of the participating ions.

Values calculated for the latter quantity are given in cols. 5 and 10 of the table. Comparison with the figures in the preceding column shows that there are large differences between the calculated values and the crystallographic data. The Bjerrum value for $MgOH^+$ is too small whilst that for $BaOH^+$ is impossibly large, and systematic deviations of the same kind, though less pronounced, are evident in the data for the alkali metals. Of course Bjerrum's theory was intended as a simplified, and not as an exact, treatment of the problem; for instance, the normal dielectric constant of water is used in calculating the Coulomb interaction between two ions in contact. Bell and Prue (*loc. cit.*) have cited the impossibly low Bjerrum value for thallous hydroxide as evidence that an electrostatic explanation is inadequate, and that covalent forces must be involved in the formation of the undissociated molecule; but the table shows that this test is of doubtful value and might lead to false conclusions when applied, for instance, to lanthanum or magnesium.



It should nevertheless be possible to find an experimental criterion for the occurrence of covalent forces. If we assume that these are absent among the alkali and alkaline-earth metals, we have a limited body of data in which K should be a function only of ionic size (and valency). In the Figure, the negative logarithms of the K values collected in the table are plotted against z^2/r, where z is the valency of the cation and r its radius (Pauling, *op. cit.*). The points for the alkaline-earth metals fall accurately on a straight line, so that with this one valency group, where the relationship between radius and pK can be tested, it seems to be fully upheld. The empirical valency factor is more doubtful, but within the present limits of experimental error the points for Li, Na, and La are quite consistent with the same straight line, which may therefore serve as a useful criterion of ion-pair formation due wholly to electrostatic forces.

The equation of the line is $pK = 0{\cdot}607z/r^2 - 1{\cdot}150$, and if our criterion is correct this equation should express the behaviour of ideally strong metal hydroxides. Any deviations, such as those shown by zinc, copper, thallium, and silver, should be in the direction of lower dissociation constants, and the size of the deviation should indicate the extent to which covalent forces contribute in the formation of the hydroxide. The conclusion that specific chemical forces are involved with the metals named is supported by other arguments. These and other transitional metals form numerous co-ordination compounds, and their cations probably form definite chemical hydrates (cf. J. Bjerrum, *loc. cit.*); their formation of hydroxy-compounds is best written as

$$M,(H_2O)_n] + H_2O \rightleftharpoons [MOH,(H_2O)_{n-1}] + H_3O^+$$

If the ionic radius of beryllium is inserted in our equation the corresponding dissociation constant is 2 × 10^{-7}. The dissociation constant of beryllium hydroxide is not known, but it is interesting to see that the relationship now put forward would account for a very marked hydrolysis of beryllium salts without recourse to other explanations. The application to aluminium is more doubtful owing to the importance of the valency factor. The correctness of the valency-square relationship being assumed, the calculated dissociation constant of $AlOH^{++} \rightleftharpoons Al^{+++} + OH^-$ would be 2 × 10^{-10}, so that again the very weak basic constant appears as a logical outcome of the high valency and small ionic radius of the metal, and the hydroxy-compound may be 100% ionised, though only very slightly dissociated.

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