An Equation for Predicting the Formation Constants of Hydroxo-metal Complexes

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An equation has been developed to describe quantitatively the hydrolytic behaviour of most cations in the Periodic Table. This equation is a function only of the charge, ionic radius, and electronic structure, and takes the form shown below where log β_{pq} is the overall formation constant of the

$$\log \beta_{pq} = [(p-1)(\mathrm{Int}_2) - q(\mathrm{Int}_1)] + [(p-1)(\mathrm{Slp}_2) - q(\mathrm{Slp}_1)][g_1(z/r^2 + g_2)]$$

species $M_p(OH)_q$. Int_1 and Slp_1, and Int_2 and Slp_2, are least-squares intercept and slope values of linear equations for monomers and polymers (depending on the structure type), respectively; z is the cationic charge, r is the ionic radius, and g_1 and g_2 are functions of the electronic structure. Since both g_1 and g_2 are themselves functions of z, the log β_{pq} values are necessarily a function of z^2/r^2.

The strength of the chemical bond between a metal ion and a water molecule in aqueous solution and hence the magnitude of the formation constant for reaction (1) depends on many

$$[M(H_2O)_n]^{z+} + H_2O \rightleftharpoons [M(H_2O)_{n-1}(OH)]^{(z-1)+} + H_3O^+ \quad (1)$$

physical and chemical characteristics of the metal ion in solution.[1] It is well known that the stability of the first mononuclear species (and hence of all subsequent species, both mononuclear and polynuclear[2]) depends upon the charge and ionic radius of the metal ion. Thus, Davies[3] discusses the first hydrolysis constants of elements of Groups 1A and 2A, and some other metal ions, in terms of the ratio z^2/r, where z is the formal cationic charge and r is the ionic radius. (There is an error in the paper by Davies[3] where the text, as opposed to the Figure, refers to the ratio z/r^2.) Irving and Williams[4] and Williams[5] develop their argument concerning the stability of metal complexes in terms of the ratio z/r, the ionic potential, or the above function, z^2/r. Baes and Mesmer,[6] on the other hand, in discussing the hydrolysis constants of metal ions, consider the function z/d, where d is the interatomic distance, M–O, rather than the ionic radius of the metal ion. Palmer[7] refers to the ionic charge density, z/r^2, as the preferred parameter to quantify the 'effects of cations upon their anionic neighbours' and this he terms the 'superficial charge density'. Huheey[8] generalises the above approaches by stating that any function z^n/r^m can be used in this context with similar results.

In this paper we discuss the hydrolysis constants of metal ions and describe a model based upon the ratio z^2/r^2, together with terms related to the electronic structures of the ions.

Results and Discussion

The First Hydrolysis Constant: M(OH).—For the (hypothetical) general hydrolysis reaction (2) we define the (overall)

$$pM^{z+} + qH_2O \rightleftharpoons [M_p(OH)_q]^{(pz-q)+} + qH^+ \quad (2)$$

$$\beta_{pq} = \frac{[M_p(OH)_q{}^{(pz-q)+}][H^+]^q}{[M^{z+}]^p} \quad (3)$$

formation constant, β_{pq}, as in (3). We refer to any given species as a (p,q) pair. For the (1,1) species $p = q = 1$, and $\beta_{11} = K_1$, the step-wise formation constant; thus, K_2 refers to the step-wise formation constant of the second monomeric species, $M(OH)_2$ from M(OH), and then $\beta_{12} = K_1K_2$.

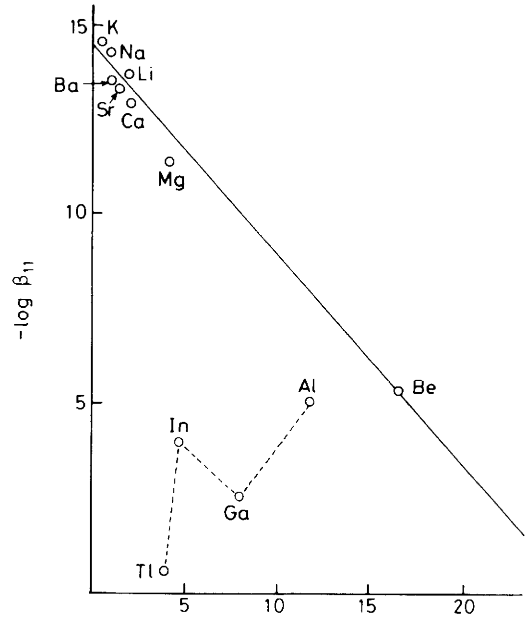

Figure 1. Plot of negative logarithm of formation constants for M(OH) against z/r^2 for the Group 1A, 2A, and 3B metal ions (25 °C)

In Figure 1 are plotted the presently available *thermodynamic* (zero ionic strength) β_{11} values (from Baes and Mesmer[6] and McGee and Hostetler[9]) of the Group 1A, 2A, and 3B cations against the z/r^2 values. For the alkali and alkaline-earth metal ions, taken together, a linear relationship is obeyed (solid line), namely equation (4), where the standard deviations are given in

$$-\log \beta_{11} = 14.40(0.15) - 0.556(0.025)z/r^2 \quad (4)$$

parentheses. Thus, for these ions a simple 'electrostatic model' can be said to apply. However, for the Group 3B cations such a simple model is obviously inapplicable since the hydrolysis constants both increase and decrease, step-wise, with increasing ionic radius for the same ionic charge. Obviously, other effects are present which completely eliminate the dominance of the simple ionic charge density argument.

At this stage, the notion of the *effective* (nuclear) charge $z_{\text{eff.}}$ can be introduced and this, in turn, must draw attention to the nature of the electrons (the orbitals) which screen the nucleus from neighbouring atoms or ions, here the oxygen atoms of the water molecules.

Slater[10] defined a screening constant which describes the screening of a single electron by the collection of other electrons, and formulated equation (5) where $z_{\text{eff.}}$ is the effective

$$z_{\text{eff.}} = A - \sigma \qquad (5)$$

ionic charge, A the nuclear charge, and σ the screening constant derived for the electrons r units distant (ionic radius) from the nuclear charge (considered a point charge). Slater's rules can be expressed as equation (6) where $g(n)$ is a function of the

$$z_{\text{eff.}} = z + 0.3 + 0.9g(n) + 0.15d \qquad (6)$$

principal quantum number, n, of the outermost shell of the *ion*: $g(n) = 0$ when $n = 1, g(n) = 1$ when $n > 1$; d is the number of d electrons present in the nth electron shell of the *ion*. These rules are generally considered to be approximately true for ions which do not contain f electrons; beyond this, however, it is not clear what the ordering of the subshells should be because of the spreading of the energy levels in these regions.[11] Since $5d$ and $4f$ electrons are energetically similar, the extent of screening from these groups might reasonably be considered to be similar, and equation (6) can be extended to equation (7) where f is the

$$z_{\text{eff.}} = z + 0.3 + 0.9g(n) + 0.15(d + f) \qquad (7)$$

number of f electrons in the $(n - 1)$th electron shell of the ion.

Bearing in mind the Slater approach and the failure of the simple 'electrostatic model', we then require an equation which describes the influence on z of electronic effects and which may then be regarded as an 'extended electrostatic model'. An examination of the highly variable hydrolysis behaviour of metal cations and the use of a Slater type approach lead to an equation of type (8) wherein the influence of the formal cationic

$$-\log \beta_{11} = \text{intercept} + \text{slope}[g_1(z/r^2 + g_2)] \qquad (8)$$

charge z is modified by the functions g_1 and g_2 which are, in turn, functions of only the charge and electronic structure of the metal ion. We find such a relationship is well obeyed if the g functions are defined as in equations (9) and (10). The presence of z in the expression for g_1 and g_2 indicates that the

$$g_1 = (1 + 2S + D)(z + 2) \qquad (9)$$

$$g_2 = g(n)(z - 1) + 0.1d(n - 3)^2(1 - S) \qquad (10)$$

expression for $-\log \beta_{11}$ is an indirect function of z^2/r^2, and not a function of z/r^2 as it might appear at first sight.

Here, $S = 0$ if no s electrons exist in the outermost shell of the *ion*, and $S = 1$ if s electrons are present; *e.g.*, $S = 0$ for ions such as Sn^{4+}, Cr^{3+}, and Ca^{2+} *etc.*, and $S = 1$ for Sn^{2+}, Bi^{3+}, and Tl^{+} *etc.* The value of D refers to the presence of d orbitals in the *metal atom* which may be vacant in the *ion*, but are still available. Thus, in the element scandium ($3d^1, 4s^2$), for example, the d orbital is vacant in the tripositive ion but is still available for bonding purposes. All elements to the right of Group 2A thus have $D = 1$ while elements in Groups 1A and 2A have $D = 0$. As before, z is the formal cationic charge of the metal ion. The function $g(n)$ is the same as defined by Slater[10] as in equation (6). The variables d and n refer, respectively, to the number of d electrons present in the ion, as in equations (6) or (7), and the principal quantum number of the outermost shell of the ion.

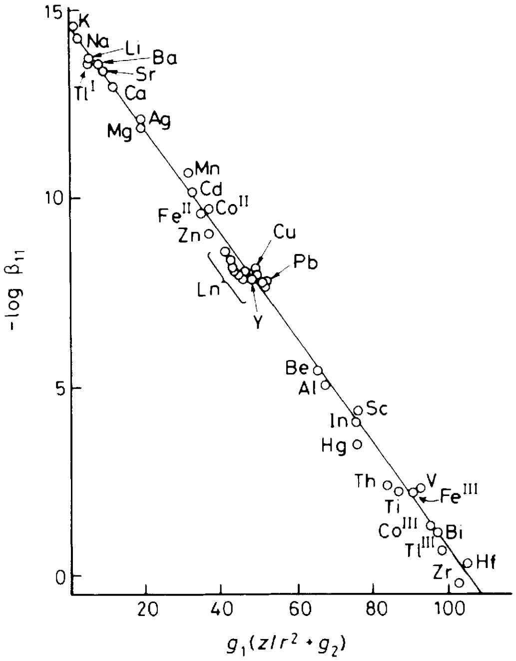

Figure 2. Plot of negative logarithm of formation constants for M(OH) against $g_1(z/r^2 + g_2)$ for some metal ions (25 °C); Ln = lanthanide ions

The problem of predicting the hydrolysis constants of metal cations is inseparable from that of determining the 'effective ionic radius' of the positively charged entity in solution. The notion of a discretely aquated cation is an idealised concept, and exchange studies and other investigations[12,13] show that this concept can be a poor approximation; some 'corrections' may well be applied to one or a small related group of cations but these can be quite inappropriate for other, different cations. Further to these limitations is that basis data will unavoidably derive mostly from the solid state and thus have a still more tenuous relationship to the situation in dilute aqueous solution. It might be said that the success with which such predictions can be made depends on how real these approximations are.

As a first step, the ionic radii of a collection of metal ions were chosen from Shannon and Prewitt.[14] Predicted $-\log \beta_{11}$ values are compared with those (25 °C) given by Baes and Mesmer[6] and some other sources. These results are given in Table 1. It is important to note that the $-\log \beta_{11}$ values being considered necessarily refer to thermodynamic constants (that is, at zero ionic strength) since medium effects are not relevant here. The results in Table 1 are plotted in Figure 2 [experimental $-\log \beta_{11}$ *versus* the function $g_1(z/r^2 + g_2)$] and the solid line is the least-squares line of best fit. This leads to the following values: slope = $-0.139(0.007)$, intercept = $14.52(0.10)$, correlation coefficient = 0.9971, with standard deviations in parentheses. Given that the calculations encompass 41 different metal ions, the goodness-of-fit is most satisfactory and demonstrates that the majority of the significant parameters have been taken into account. To our knowledge this is the first time that such an equation has been formulated. For convenience, we will refer collectively to equations (8)—(10) as the B.S.E. (Brown–Sylva–Ellis) equation.

The significance of the various terms in the B.S.E. equation is interesting and far-reaching. Metal ions can be divided into four distinct types as far as hydrolysis behaviour (and complex

Table 1. Experimental and predicted values (25 °C) of $-\log \beta_{11}$ for some metal ions

Metal ion	Ionic radius[a] (Å)	g_1	g_2	$g_1(z/r^2 + g_2)$	$-\log \beta_{11}$ Predicted	$-\log \beta_{11}$ Experimental	Ref.
Li^+	0.74 (6)	3	0	5.48	13.76	13.64	6
Na^+	1.02 (6)	3	0	2.88	14.12	14.2	6
K^+	1.38 (6)	3	0	1.56	14.31	14.5	6
Be^{2+}	0.35 (6)	4	0	65.32	5.45	5.4	6
Mg^{2+}	0.72 (6)	4	1	19.44	11.82	11.79	9
Ca^{2+}	1.00 (6)	4	1	12.00	12.86	12.9	6
Sr^{2+}	1.16 (6)	4	1	9.96	13.14	13.3	6
Ba^{2+}	1.36 (6)	4	1	8.32	13.37	13.5	6
Sc^{3+}	0.73 (6)	10	2	76.28	3.92	4.3	6
Y^{3+}	1.02 (6)	10	2	48.84	7.74	7.7	6
La^{3+}	1.18 (8)	10	2	41.56	8.75	8.5	6
Ce^{3+}	1.14 (8)	10	2	43.08	8.53	8.3	6
Pr^{3+}	1.14 (8)	10	2	43.08	8.53	8.1	6
Nd^{3+}	1.12 (8)	10	2	43.92	8.42	8.0	6
Sm^{3+}	1.09 (8)	10	2	45.24	8.23	7.9	6
Eu^{3+}	1.07 (8)	10	2	46.20	8.10	7.8	6
Gd^{3+}	1.06 (8)	10	2	46.68	8.03	8.0	6
Er^{3+}	1.00 (8)	10	2	50.00	7.57	7.9	6
Yb^{3+}	0.98 (8)	10	2	51.24	7.40	7.7	6
Lu^{3+}	0.97 (8)	10	2	51.88	7.31	7.6	6
Zr^{4+}	0.84 (8)	12	3	104.04	0.06	−0.3	6
Hf^{4+}	0.83 (8)	12	3	105.64	−0.17	0.3	6
Th^{4+}	1.00 (6)	12	3	84.00	2.85	2.35	23[b]
Al^{3+}	0.51 (6)	5	2	67.68	5.12	4.97	6
In^{3+}	0.81 (6)	10	3	75.72	4.00	4.0	6
Tl^{3+}	0.88 (6)	10	6	98.72	0.80	0.6	6
Tl^+	1.50 (6)	12	0	5.32	13.78	13.51	[c]
Pb^{2+}	0.94 (4)	16	1	52.20	7.27	7.7	6
Bi^{3+}	1.02 (6)	20	2	97.68	0.95	1.09	6
Zn^{2+}	0.74 (6)	8	1	37.20	9.35	8.96	6
Cd^{2+}	0.97 (6)	8	2	33.00	9.94	10.1	6
Hg^{2+}	0.69 (2)	8	5	76.00	4.29	3.4	6
Mn^{2+}	0.82 (6)	8	1	31.80	10.10	10.59	6
Fe^{2+}	0.77 (6)	8	1	35.00	9.66	9.5	6
Co^{2+}	0.74 (6)	8	1	37.20	9.35	9.65	6
Cu^{2+}	0.62 (4)	8	1	49.64	7.63	7.93	[d]
Ti^{3+}	0.67 (6)	10	2	86.84	2.45	2.2	6
V^{3+}	0.64 (6)	10	2	93.24	1.56	2.26	6
Fe^{3+}	0.65 (6)	10	2	91.00	1.87	2.19	6
Co^{3+}	0.63 (6)	10	2	95.60	1.24	1.25	[e]
Ag^+	0.67 (2)	6	1	19.36	11.83	12.0	6

[a] Co-ordination numbers given in parentheses; see ref. 14. [b] Estimated from ref. 23. [c] R. P. Bell and J. E. Prue, *J. Chem. Soc.*, 1949, 362. [d] A. J. Paulson and D. R. Kester, *J. Sol. Chem.*, 1980, **9**, 269. [e] L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, 1956, **52**, 1225.

formation, generally) is concerned because of such factors as, for example, electronegativity values, the inert pair effect, and covalent bonding effects, as follows.

(*i*) Metal ions for which $D = 0$ and hence $S = 0$ (n, any value). This involves such ions as the Group 1A, 2A, and aluminium ions. The form of the function is $f(az^2/r^2)$, where $a = 1$.

(*ii*) For all other metal ions, $D = 1$, since all have *d* orbitals available for bonding. Group (*ii*) ions have $S = 0$ and $n = 3$ (the minimum possible value, since $D = 1$) and invoke the ions of the elements of Group 3A, the lanthanides, the first-row transition metals, zinc, gallium, and possibly the actinides (depending on the distribution of the electrons in the 5*d* and 4*f* subshells of the ion). Here, $a = 2$.

(*iii*) For this group, $S = 0$ and $n \geqslant 3$ ($D = 1$). Members of this group are the second- and third-row transition metal ions, and Groups 2B, 3B, 4B, and 5B (second and third long Periods) in their Group valency states. These ions exhibit anomalously high electronegativity values[15,16] and, for example, hydrolyse to a greater extent than would be expected from simple charge/size arguments. This can be explained by the increasingly poorer shielding by the 4*d*, 5*d*, and 4*f* electrons. Thus, for example, Pb^{4+} hydrolyses more extensively than Sn^{4+}. The step-wise behaviour of the Group 3B ions (Figure 1) is explained by the functional behaviour of g_1 and g_2. In this group, $a = 2$ also.

(*iv*) This group contains metal ions which exhibit the inert pair effect[15,17,18] since $S = 1$ and $n \geqslant 3$ ($D = 1$), and includes Tl^+, Pb^{2+}, Sn^{2+}, and Bi^{3+}; anomalously high electronegativity effects are absent, as predicted by the B.S.E. equation; thus Pb^{2+} hydrolyses less readily than Sn^{2+}. Here, $a = 4$, because of the presence of the inert valence pair.

Despite the success of the B.S.E. equation it is perhaps significant that it seems not to apply, to a varying extent, for a number of cations, and these cations should be examined in more detail. They fall into three broad categories which, however, are not mutually exclusive: (*a*) metal ions for which ionic radii data are poor or inappropriate; and/or (*b*) metal ions for which experimental $-\log \beta_{11}$ data are absent or unreliable (because of widely different experimental difficulties); and (*c*) some of the first-row transition metal ions, namely Ni^{2+}, Cr^{3+}, and Mn^{3+}.

Table 2. Examples of apparent inapplicability of the B.S.E. equation.

Metal ion	Ionic radius[a] (Å)	g_1	g_2	$g_1(z/r^2 + g_2)$	$-\log \beta_{11}$		Ref.
					Predicted	Experimental	
Ce^{4+}	0.97 (8)	12	3	87.02	2.42	−1.52	*b*
Ac^{3+}	1.18 (6)	10	2	41.55	8.75	10.4	6
Sn^{2+}	0.93 (6)	16	1	53.00	7.15	3.4	6
Sn^{4+}	0.69 (6)	12	4	148.81	−6.17	−1.6	*c*
Pb^{4+}	0.78 (6)	12	7	162.90	−8.12	—	
Cr^{2+}	0.82 (6)	8	1	31.80	10.10	—	
Cr^{3+}	0.62 (6)	10	2	98.04	0.89	4.0	6
Mn^{3+}	0.65 (6)	10	2	91.01	1.87	−1.12	*d*
Ni^{2+}	0.70 (6)	8	1	40.65	8.87	9.86	6

[a] Co-ordination numbers given in parentheses; see ref. 14. [b] Estimated from T. J. Hardwick and E. Robertson, *Can. J. Chem.*, 1951, **29**, 818. [c] Estimated from V. A. Nazarenko, V. P. Antonovich, and E. M. Nevskaya, *Russ. J. Inorg. Chem.*, 1971, **16**, 980. [d] Estimated from C. F. Wells and G. Davies, *J. Chem. Soc. A*, 1967, 1858.

Table 3. Experimental and predicted values (25 °C) of $-\log K_2$ for some metal ions

Metal ion	Ionic radius[a] (Å)	g_1	g_2	$g_1(z/r^2 + g_2)$	$-\log K_2$		Ref.
					Predicted	Experimental	
Be^{2+}	0.35 (6)	4	0	65.32	6.30	5.7	*b*
Al^{3+}	0.51 (6)	5	2	67.68	6.00	5.23	*c*
Sc^{3+}	0.73 (6)	10	2	76.28	4.90	5.4	6
Y^{3+}	1.02 (6)	10	2	48.84	8.40	8.7	6
Nd^{3+}	1.12 (8)	10	2	43.92	9.02	8.9	6
Gd^{3+}	1.06 (8)	10	2	46.68	8.67	8.4	6
Dy^{3+}	1.03 (8)	10	2	48.28	8.47	8.2	6
Er^{3+}	1.00 (8)	10	2	50.00	8.25	8.0	6
Yb^{3+}	0.98 (8)	10	2	51.24	8.09	8.1	6
Mn^{2+}	0.82 (6)	8	1	31.80	10.57	11.61	6
Fe^{2+}	0.77 (6)	8	1	35.00	10.16	11.1	6
Fe^{3+}	0.65 (6)	10	2	91.00	3.03	3.48	6
Co^{2+}	0.74 (6)	8	1	37.20	9.88	9.15	6
Cu^{2+}	0.62 (4)	8	1	49.64	8.30	9.37	6
Ag^{+}	0.67 (2)	6	1	19.36	12.15	12.0	6
Zn^{2+}	0.74 (6)	8	1	37.20	9.88	7.94	6
Cd^{2+}	0.97 (6)	8	2	33.00	10.42	10.27	6
In^{3+}	0.81 (6)	10	3	75.72	4.97	4.84	*d*
Tl^{3+}	0.88 (6)	10	6	98.72	2.04	0.95	6
Pb^{2+}	0.94 (4)	16	1	52.20	7.97	9.41	6
Bi^{3+}	1.02 (6)	20	2	97.68	2.18	2.91	6

[a] Co-ordination number given in parentheses; see ref. 14. [b] Estimated from ref. 1. [c] Estimated from ref. 25. [d] Estimated from P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1982, 1911.

Some examples of the inapplicability of the B.S.E. equation are given in Table 2. The ions Ce^{4+}, Ac^{3+}, Pb^{4+}, and Cr^{2+} provide examples where experimental difficulties (radioactivity, redox properties, very extensive hydrolysis leading to great ease of precipitation) probably provide the main cause of discrepancies. For the ion Sn^{2+}, the value listed[14] for the ionic radius is probably not appropriate in solution since here it might be expected to be four-co-ordinate (tetrahedral); an estimate of 0.072 nm gives a predicted value of $-\log \beta_{11} = 3.72$ and this greatly improves the agreement, but such changes may be seen to be somewhat arbitrary. Comparison of predicted and experimental values of $-\log \beta_{11}$ for some first-row transition metal ions leads to some interesting differences. These involve the d^4 and d^9 ions, respectively, Mn^{3+} and Cu^{2+} (Table 1), which are found to hydrolyse more readily than expected, and the d^3 and d^8 ions, Cr^{3+} and Ni^{2+}, which hydrolyse less than might be expected. This is doubtless the result, at least in part, of the irregular effect[19] of filling the 3*d*-electron subshell of these ions, leading to uncertainties in the ionic radii in solution. In the case of Cu^{2+}, for example, not all $Cu{-}OH_2$ bonds of the aquated ion are equivalent.[12]

The example of the first hydrolysis constant of gallium(III) serves as an ideal one with which to illustrate some of the problems involved in assessing the predictive value of the B.S.E. equation. The literature[6,20] reveals a widely divergent series of values for $-\log \beta_{11}$ varying from 0.4 to > 4.3, depending on ionic strength (zero to 3 mol dm^{-3}, 25 °C). Such a dependence on ionic strength is not considered credible by us and the unavoidable conclusion is that many of these values are seriously in error. The value used in Figure 1 (2.6 at zero ionic strength, 25 °C) is taken from Baes and Mesmer[6] and wide variations in this value do not affect the purpose of Figure 1 (*i.e.*, to illustrate the inapplicability of the 'simple electrostatic model' to explain the first hydrolysis constant of the Group 3B metal ions). The value of the ionic radius of Ga^{3+}, 0.062 nm, given by Baes and Mesmer,[6] and presumably taken from Shannon and Prewitt,[14] however, leads to a predicted value of $-\log \beta_{11}$ of 0.89, using equations (8)—(10). The most recent values of $-\log \beta_{11}$ for gallium(III) known to us are 3.50 ± 0.01, 3.69 ± 0.01, 4.15 ± 0.04 (25.0 °C; 0.10, 0.50, and 1.50 mol dm^{-3} sodium perchlorate, respectively; errors are estimated standard deviations),[21] these having been determined by experimental

Table 4. Nature of polynuclear hydrolysis products

Stoicheiometry/ structure type, (i)	No. of hydroxo-bridges per metal cation	Stoicheiometry of polynuclear species	Examples
(I) Four-co-ordinate	3 (or more)	(3,3), (3,4), (3,5), (4,4), (6,8)	Mg^{2+}, Ni^{2+}, Pb^{2+}, Al^{3+}, Be^{2+}, Cd^{2+}
(II) Six-co-ordinate (sometimes seven)	2	(2,2), (3,4), (3,5) Possibly (4,6), (4,7)	UO_2^{2+}, Sc^{3+}, Cu^{2+}, Fe^{3+}, VO^{2+}, Cr^{3+}
(III)[a] Eight-co-ordinate or more	2 (or more)	(4,8), (4,12), (6,12), (6,15)	Zr^{4+}, Th^{4+}, Bi^{3+}, U^{4+}
(IV) Any co-ordination (?)	1	(2,1)	Be^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}[b]

[a] Oxo-bridges considered likely since $(q/p) \geqslant 2$. [b] Bivalent metal ions only.

and numerical techniques similar to our own.[1] These data provide an estimate of 2.93 at zero ionic strength as calculated by the method of Baes and Mesmer.[6] The only conclusion that can be drawn is that the reported[6,14] value of the ionic radius of Ga^{3+} is in error, it being approximately 0.005–0.007 nm too *small*. We note here that the B.S.E. equation can be used, through an independent experimental measurement of $-\log \beta_{11}$, to provide an estimate of the ionic radius and hence the hydration number of the ion in aqueous solution.

The Second (Monomeric) Hydrolysis Constant: $M(OH)_2$.—The Sylva–Davidson[22] empirical equation, namely (11), allows

$$\begin{aligned} A &= (r-1)(q+2-2p) - (p-1)(s+2-2r) \\ B &= (p-1)(u+2-2t) - (t-1)(q+2-2p) \\ C &= (r-1)(u+2-2t) - (t-1)(s+2-2r) \\ \log \beta_{pq} &= (A \log \beta_{tu} + B \log \beta_{rs})/C \qquad (11) \end{aligned}$$

the estimation of any constant, $\log \beta_{pq}$, from the known values of any other two constants (of the same metal ion) β_{rs} and β_{tu}. Consequently if a value of β_{11} (experimentally determined or estimated using the above) is used to determine β_{12}, the overall formation constant of the second, monomeric hydrolysis product, then $\log \beta_{12} \simeq 2 \log \beta_{11}$ and, obviously, for any monomeric species, $(1,q)$, $\log \beta_{1q} = q \log \beta_{11}$, approximately.

The B.S.E. equation, as written, corresponds to a step-wise process (since it is written for β_{11}). For the formation of (1,2) species, either the overall constant β_{12} can be considered or, preferably, for present purposes, the step-wise constant K_2 since the latter isolates the second step. Using 21 values of $-\log \beta_{12}$ from Baes and Mesmer[6] and other sources (at zero ionic strength), and converting to step-wise constants, K_2, a linear relationship is obtained within the limitations of experimental error with slope = −0.127(0.008), intercept = 14.62(0.49), and correlation coefficient = 0.9616; the standard deviations are given in parentheses. These values are not significantly different from the values obtained for K_1; however, *more precise experimental data* for K_2 would lead us to expect that, generally, $\log \beta_{1q} < q \log \beta_{11}$ $(q > 1)$ because removal of the first proton will decrease slightly the attraction of the metal ion for the water molecules, thus reducing the tendency further to deprotonate. In Table 3 is a comparison of the predicted and experimental values of $-\log K_2$.

For an infinitely large cation (of any charge), the intercept will be the same value (≈ 14.5) and it is only the product (slope)$g_1 g_2$, which will vary (slightly). This, of course, simply states that the hydrolysis constant cannot be determined for any step which has a value less than that of pure water under the same conditions.

Polynuclear Species: $M_p(OH)_q$.—In this section, all species are formulated as hydroxo-complexes, (p,q), as before, although in some instances oxo-bridges (equivalent to two hydroxo-bridges) may be present. At first sight what might appear to be a bewilderingly complex array of polynuclear species are claimed to exist but in fact, virtually all reliably documented cationic species are included in the eleven species (2,1), (2,2), (3,3), (3,4), (3,5), (4,4), (4,8), (4,12), (6,8), (6,12), and (6,15). Some of these stoicheiometries *e.g.* (6,15), may appear unlikely, but it is not too difficult experimentally and numerically (with adequate data) to distinguish between *e.g.* (6,14), (6,15), and (6,16), even in the presence of other species.[23] In addition, some of these species probably contain oxo- as well as hydroxo-bridges, which are, of course, indistinguishable by potentiometric measurements and, as written, their stoicheiometries can be misleading. As a general rule, considerations of geometry and preferred co-ordination number of a metal ion suggest that for $(q/p) \geqslant 2$, some oxo-bridges are present.

For $(q/p) < 2$, hydroxo-bridges alone are usually assumed to be present and, when so formulated, symmetrical structures can be realistically postulated;[6] however, with the notable exception of lead(II),[24] few structures have been determined in solution. The overriding property of the metal ion which determines the stoicheiometry of the hydrolytic species of a cation is thus the preferred stereochemistry; three 'types' of metal ions can be readily distinguished, namely those which have (I) four-co-ordination, (II) six- or seven-co-ordination, and (III) eight-co-ordination or higher. The stoicheiometries belonging to each of these groups, together with (2,1) species [type (IV)] form the four stereochemical types given in Table 4. The only significant overlap in Table 4 appears to involve the trimers (3,4) and (3,5) which are produced by both types (I) and (II). If we assume that any given metal ion belongs to only one structure type (but see below), it follows that these trimers can involve (at least) two preferred stereochemistries.

That which might be expected to be the most common polynuclear species, the (2,2) dimer, only occurs with type (II) cations (six-co-ordinate and octahedral, or seven-co-ordinate and pentagonal bipyramidal). Thus, metal ions such as Be^{2+}, Pb^{2+} (four-co-ordinate and tetrahedral), and Zr^{4+}, Th^{4+}, and

Table 5. Experimental and predicted values (25 °C) of $-\log \beta_{pq}$ of some metal ions

Metal ion type (i)	Intercept[a]	Slope[a]	Correlation coefficient	Metal ion	log C	Species	$-\log \beta_{pq}$ Predicted	Experimental	Ref.
(I)	2.11	0.019	0.7845	Co^{2+}	2.82	(4,4)	28.94	30.53	6
	(0.37)	(0.008)		Al^{3+}	3.41	(3,4)	13.66	13.94	6
				Be^{2+}	3.37	(3,3)	9.61	8.92	6
				Cd^{2+}	2.74	(4,4)	31.54	32.37	6
				Mg^{2+}	2.48	(4,4)	39.84	39.71	6
				Pb^{2+}	3.11	(3,4)	22.86	23.88	6
						(3,5)	30.13	31.41	22
						(4,4)	19.75	20.88	6
						(6,8)	42.61	43.61	6
(II)	11.57	−0.117	0.9408	Sc^{3+}	2.65	(2,2)	5.19	6.0	6
	(1.11)	(0.015)				(3,5)	14.30	16.34	6
				Ti^{3+}	1.41	(2,2)	3.49	3.6	6
				V^{3+}	0.67	(2,2)	2.45	3.8	6
				VO^{2+}	4.12	(2,2)	7.22	6.67	6
				Fe^{3+}	0.93	(2,2)	2.81	2.95	6
						(3,4)	5.62	6.3	6
				Cu^{2+}	5.76	(2,2)	9.50	10.36	6
						(3,4)	19.00	21.14	*b*
				In^{3+}	2.72	(2,2)	5.28	5.49	*c*
				UO_2^{2+}	4.23	(2,2)	6.37	5.62	6
						(3,5)	18.04	15.63	6
				NpO_2^{2+}	3.67	(2,2)	6.63	6.39	6
						(3,5)	18.41	17.49	6
				PuO_2^{2+}	4.07	(2,2)	7.13	8.36	6
						(3,5)	19.86	21.65	6
(III)	Insufficient data for analysis								
(IV)	−1.95	0.053	0.6337	Be^{2+}	1.51	(2,1)	3.94	3.97	6
	(1.49)	(0.023)		Mn^{2+}	−0.26	(2,1)	10.36	10.56	6
				Co^{2+}	0.02	(2,1)	9.33	11.2	6
				Zn^{2+}	0.02	(2,1)	9.33	9.0	6
				Cd^{2+}	−0.20	(2,1)	10.14	9.39	6
				Pb^{2+}	0.82	(2,1)	6.45	6.36	6

[a] Estimated standard deviations are given in parentheses. [b] Estimated from ref. 30. [c] Estimated from P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1982, 1911.

Bi^{3+} (co-ordination number of eight or more), though exhibiting extensive hydrolysis, do not form the (2,2) dimer. It is tempting to suggest that the known (2,2) species of all metal ions can only be octahedral and that this is the only energetically favourable stoicheiometry of a dimer since the (2,1) species is very poorly characterised (see below) and other stoicheiometries such as (2,3) and (2,4), for example, have never been substantiated.

A change in co-ordination number, however, might occur in the conversion of an aquated metal ion to a hydroxo-bridged polynuclear species; such has been said for the lanthanide ions.[6] A more pertinent example is the aluminium(III) ion.[25] The hydration number of the aquated aluminium(III) ion is six;[26,27] however, evidence can be given that the formation of low molecular weight hydrolytic polymers (25 °C) involves a reduction in co-ordination number: see below.

(*i*) Our investigation[25] of the hydrolysis of aluminium(III) clearly shows the absence of the (2,2) dimer even under conditions where the (1,1), (1,2), (3,4), and (13,32) species are appreciably formed (at 25 °C).

(*ii*) Earlier work[6,28] suggests that, at most, even under optimal conditions of metal ion concentration and pH (as defined by the results of the investigation) the (2,2) species is only a minor one; thus, the suggested value of *ca.* 8 for $-\log \beta_{22}$ corresponds to a maximum of *ca.* 1% of the total aluminium(III) concentration. We therefore conclude that the species does not exist under the conditions used.

(*iii*) If the (2,2) species did exist for Al^{3+}, the Sylva–Davidson equation predicts a value of 6.7 for $-\log \beta_{22}$ and, as such, the species should be readily detectable (*ca.* 15% under optimal conditions).

Thus, the absence of a (2,2) dimer for those metals whose aquated ions have a hydration number of six suggests that the ions undergo a reduction in co-ordination number during the formation of polynuclear species. Therefore, the same arguments exist for the metal ions Mg^{2+}, Ni^{2+}, Co^{2+}, and Cd^{2+}. Note that the same situation does not apply for the (3,4) species which is common to both types (I) and (II).

The (2,1) dimeric species presents a problem since its status is uncertain because it is always only a minor species usually produced at very high metal ion concentrations (an exception being the Be^{2+} ion[1,6]) where serious experimental difficulties exist owing to ionic medium effects. The most obvious difference between this species and all the others is the absence of a ring since the sharing of a corner rather than an edge (or edges) of metal ion moieties will be involved. Thus, it appears that an effect similar to the chelate effect[29] might be operative.

We now assume that the condensation processes involved in the formation of each of the four different structure types in Table 4 [type i, i = (I)–(IV)] are energetically different for each of the types, but the same within each type, irrespective of the stoicheiometry of the species. A simplified form of the Sylva–Davidson empirical equation[30] may be written as in (12), where p

$$\log \beta_{pq} = q \log \beta_{11} + [(p - 1)/(r - 1)](\log \beta_{rs} - s \log \beta_{11}) \tag{12}$$

and q refer to the stoicheiometry of the unknown species, and r and s are the stoicheiometry of any polynuclear species. Here, it is assumed that $\log \beta_{1q} = q \log \beta_{11}$ (the deprotonation step). The isolated condensation step ($\log C$) for the species (r,s) of a metal ion can then be expressed as equation (13). By analogy, then, with equation (8), we write equation (14). Thus, a single

$$\log C = [1/(r - 1)](\log \beta_{rs} - s \log \beta_{11}) \tag{13}$$

$$\log C = [\text{intercept, type (i)}] + [\text{slope, type (i)}][g_1(z/r^2 + g_2)] \tag{14}$$

value of each of the slope and intercept can be determined for every metal ion of type (i), allowing the calculation of $\log C$ for *each* metal ion of that type. Hence, the values of $\log \beta_{pq}$ can be calculated using equation (15); equation (16) follows from the

$$\log \beta_{pq} = q \log \beta_{11} + (p - 1) \log C \tag{15}$$

$$\log \beta_{pq} = [(p - 1)(\mathrm{Int}_2) - q(\mathrm{Int}_1)] + [(p - 1)(\mathrm{Slp}_2) - q(\mathrm{Slp}_1)][g_1(z/r^2 + g_2)] \tag{16}$$

expressions for $\log \beta_{11}$ and $\log C$ in equations (8) and (14), where Int_1 and Slp_1, and Int_2 and Slp_2, are the least-squares intercept and slope values of linear equations for the (1,1) species and the polymeric (p,q) species [type (i)], respectively.

In Table 5 are the results of such calculations for those metal ions for which data are available; thus, analysis cannot be given for type (III) ions. For the other metal ions, the agreement is satisfactory but still reflects the paucity of data available for the determination of the linear least-squares parameters and, hence, the predicted values of the formation constants of the various polynuclear species. Nevertheless, within these limitations, the approach is considered to be successful.

In using published experimental data for polynuclear species in order to verify or substantiate the present work, it is vitally important not to involve species whose existence is doubtful or which are 'self-evidently' undetectable. Indeed, three situations arise in this context which can be distinguished but which may, nevertheless, overlap.

(*a*) The first is those hydrolysis systems for which the data are inadequate (largely because of poor experimental design[22,23]). Good examples are furnished by a comparison of the studies of the hydrolysis of copper(II) by Berecki-Biedermann[31] with those of Perrin[32] and Sylva and Davidson[30] and also the majority of the studies of the lanthanide ion hydrolysis system (see, for example, Baes and Mesmer[6]).

(*b*) The second is the situation where, even with good experimental design, the species are self-evidently undetectable as indicated by the reported value of the formation constant of the species [see above for the (2,2) dimer of aluminium(III), and also the (2,1) and (3,3) species of mercury(II)[6,33]]. In such situations the extent of formation, as calculated from the stability constant and experimental conditions, is *ca.* 1% or less.

(*c*) The third situation involves studies in which the method of numerical analysis and/or the data are inadequate. An example here is that of scandium(III) for which two trimers are postulated by Aveston[34] and only one by Brown *et al.*[35] The significance here is the greater numerical discriminating power of our version of MINIQUAD[23,36–38] compared with LETAGROP[39] or ORGLS.[40]

An aditional problem is presented by the case of chromium(III) (and some other metal ions) where the B.S.E. equation apparently fails for the (1,1) monomer and thus, must necessarily fail for the polynuclear species [see equation (16)].

A distinction must be made between equations (16) and (11). Implicit in equation (11) is the assumption that all deprotonation and condensation steps in the formation of any species (p,q) from any precursors (one of which must, obviously, have $p > 1$) are equal and additive. For the formation of (2,1) species, constants cannot be predicted by equation (11) because this necessarily requires the use of data from two different *types* of metal ions (Table 4) since only the first member of the series $\mathrm{M[M(OH)]}_n$ is known to exist, and equation (11) involves the use of two *known* constants (one of which can be β_{11}) from the *one* type to predict an unknown constant from the *same* type. Equation (16), however, does not involve such prerequisites.

Conclusions

The B.S.E. equation describes quantitatively the hydrolytic behaviour of most metal cations of the Periodic Table as a function of the charge, ionic radius, and electronic structure of the metal ions. This approach is an advance on earlier work in this field[6,41–43] because a single form of the equation is used to predict the values of the formation constants of the first hydrolysis reaction, and a simple extension of this can be used to predict the formation constants of the polynuclear species, irrespective of their stoicheiometry.

The consequences of this equation could be important in the field of aqueous chemistry generally, and it may be possible to extend it to include other ligands, both unidentate and multidentate. This extension, which is expected to have an important bearing on stability sequences such as those of Mellor and Maley[44] and Irving and Williams,[4] is nearing completion.

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