Factors Affecting the Hydrolysis and Dimerisation of Metal Ions

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A correlation of associated ion species in solution is at present hampered by uncertainties concerning the ability of the associating ligand to penetrate the hydration sheath of the metal ion. This is particularly evident where the association is predominantly electrostatic (see, *e.g.*, Williams¹). In metal-hydroxyl ion systems, however, the situation is probably rather simpler. As Davies² has pointed out, it is highly probable that in these complexes the hydroxyl ion is directly adjacent to the metal ion, such an arrangement being effected by a transition

It thus appears that correlation of the stabilities of these species may be possible.

THE FIRST MONOMER HYDROLYSIS PRODUCT, $\text{MOH}^{(z-1)+}$

The formation of this species by a mechanism such as the above would rule out application of the N. Bjerrum ion association theory³ to determine dissociation constants for purely electrostatic systems, for although the theory may apply to (I), the observed constant would relate to (II). Davies² has demonstrated the non-applicability of the Bjerrum theory in cases where electrostatic association is to be expected between the metal and hydroxyl ions.

The hydrolysis process may be pictured as a proton dissociation step:

The tendency of the hydrated ion to lose a proton should therefore be related to the strength of the metal ion-water linkage of the first coordination sphere.

Table 1. Data on

For definitions of symbols, see text. r = ionic radius * after Pauling except where marked x , these being experimental values. ΔH_s data are experimental values given by Bernal and Fowler †, except those in parentheses, which are estimates by these authors. ΔG values are calculated = $-RT \ln 55.5 \beta_1'$, using quoted values of β' or figures obtained from conversion of κ_1' to β_1' , assuming $K_w = 10^{-14.0}$. $\log \kappa_1'$ values given in parentheses are open to question on theoretical

Ion	r in Å	ΔH_s kcal.	N	$\log \kappa_1'$	Medium	Method employed	Ionic Strength
Na+	0.95	—114	3	~ 14.7	OH ⁻	(a) kinetic	
Li+	0.60	—136	3	~ 14.1	OH ⁻	(b) conductance	0
Ba ²⁺	1.35	—346	6	—13.36	OH ⁻	conductance	0
Sr ²⁺	1.13	—376	6	—13.05	OH ⁻	(8a) kinetic;	0
						E.M.F.	0
Ca ²⁺	0.99	—410	6	—12.70	OH ⁻	solubility	0
Mg ²⁺	0.65	—490	6	—11.41	Cl ⁻	(8a) kinetic;	0
Be ²⁺	0.31	—608	4	—6.52	ClO ₄ ⁻	E.M.F.	1.0
La ³⁺	1.15	—768	6	~ 10.7	(OH ⁻)	solubility	0
Ce ⁴⁺	1.01		6	+0.72	ClO ₄ ⁻	spectrophotometric	2.0
U ⁴⁺	0.97		6	—1.49	ClO ₄ ⁻	spectrophotometric	0.5
Pu ³⁺	1.01*		6	—6.95)	ClO ₄ ⁻	E.M.F.	0
Tl+	1.49	—107	2	—13.18	OH ⁻	solubility	0
Tl ³⁺	0.95		4	—1.14	ClO ₄ ⁻	E.M.F.	3.0
In ³⁺	0.81	—980	6	—3.85	Cl ⁻ , Br ⁻ I ⁻	E.M.F.	0
Ga ³⁺	0.62		6	(—3.43)	NO ₃ ⁻	E.M.F.	varied
Al ³⁺	0.50	—1 149	6	—4.89	ClO ₄ ⁻	kinetic	0
Pb ²⁺	1.21		4	—8.78	NO ₃ ⁻	E.M.F.	0
Sc ³⁺	0.81	($\sim$ —980)	6	—4.93	ClO ₄ ⁻	E.M.F.	1.0
V ³⁺	0.65*	($\sim$ —830)	6	(—2.92)	SO ₄ ²⁻	E.M.F.	small
Cr ³⁺	0.65*		6	—3.90	ClO ₄ ⁻	kinetic	0
Mn ²⁺	0.80*	—479	6	($\sim$ —9.5)	CH ₃ CO ₂ ⁻	distribution	varied
Fe ³⁺	0.67*	($\sim$ —1 185)	6	—3.05	ClO ₄ ⁻	E.M.F.	3.0
Fe ²⁺	0.75*	—500	6	—9.50	ClO ₄ ⁻	E.M.F.	1.0
Co ²⁺	0.72*	504	6	(—10.20)	Cl ⁻	E.M.F.	small
Ni ²⁺	0.69*	516	6	(—10.64)	Cl ⁻	E.M.F.	small
Ag ⁺	1.26	162	2	$\sim$ —11.7	(OH ⁻)	solubility	small
Cu ²⁺	0.70*	536	4	—7.97	NO ₃ ⁻	E.M.F.	0
Hg ²⁺	1.10	480	2	—3.70	ClO ₄ ⁻	E.M.F.	0.5
Cd ²⁺	0.97	462	4	($\sim$ —8.5)	CH ₃ CO ₂ ⁻	distribution	varied
Zn ²⁺	0.74	528	4	(—9.60)	SO ₄ ²⁻	E.M.F.	small
Th ⁴⁺	0.02 ($\sim$ 1 540)		6				

Only those ions whose radii are known are included in this Table. Other recent hydrolysis plutonium(IV) ⁴⁰,

Thus the heat of formation of this bond could be tried as a function of the logarithm of the acid dissociation constant of the aquo ion, $\log \kappa_1'$, where

$$\kappa_1' = \frac{[\text{MOH}^{(z-1)+}][\text{H}^+]}{[\text{M}^{z+}]}$$

(using the recent terminology of the Swedish schools ⁴). These heats are not known, but a useful average estimate that probably gives the correct relative

MOH(s-1) systems.

grounds, owing to neglect of factors such as possible polymerisation, complex formation with anions, etc.; these systems particularly merit fresh examination. ΔS values are calculated from Cobble's equations ⁴⁴, giving ΔH values from $\Delta H = \Delta G + T\Delta S$. p. = polymerisation.
e = electrostatic.

Temp. in °C	Reference No.	ΔS cal./ deg.(calc.)	ΔG kcal.	ΔH kcal. (calc.)	f_c (Fig. 2a)	f_c (Fig. 2b)	State of solution
	8(a),						
25	(b)	— 22	~ — 1.42	— 7.0	—		
25	8(b)	— 40	~ — 2.27	— 14.1	—		
	8(a),						
25	9	+ 27	— 3.26	+ 4.7	—		
25	10	+ 29	— 3.68	+ 5.1	—		
	8(a),						
25	11	+ 34	— 4.13	+ 5.9	—		
25	12	+ 43	— 5.92	+ 6.9	—		
25	13	+ 58	— 12.60	+ 4.7	0.35	.31	p. (ref. 13)
25	14	+ 22	~ — 6.89	— 0.3		.33	
25	15	+ 10	— 22.48	— 19.5			p. (ref. 15)
25	16	+ 12	— 19.48	— 15.9	.47		p. on ageing (ref. 16)
?	17	+ 22			.37		
25	11 (b)	— 3	— 3.52	— 4.4	.55	.51	
25	18	+ 23	— 19.98	— 13.0	.61		no p. (ref. 18)
25	19	+ 28	— 15.68	— 7.4	.48	.35	
25	20	+ 37	(— 16.80)	— 5.8	.43		p. (ref. 21)
15	22	+ 40	— 14.30	— 2.5	.29	.31	p. (ref. 23)
18	24	+ 29	— 9.27	— 0.9	.58		p. (ref. 24)
25	25	+ 28	— 14.79	— 6.4	.43	.35	p. (ref. 25)
25	26	+ 33	(— 17.53)	— 7.7	.46	.14	
15	22	+ 33	— 15.62	— 6.0	.42		p. on ageing (ref. 27)
20	28	+ 40	— 8.48	+ 3.2	.38		
25	29	+ 32	— 17.28	— 7.7	.48	.42	p. (ref. 29)
25	30	+ 40	— 8.53	+ 3.3	.39		no p. (ref. 30)
25	31	+ 41	(— 7.56)	+ 4.7	.26		
25	31	+ 42	(— 6.97)	+ 5.6	.22		
25	32	— 11	~ — 5.52	— 8.7	.65	.65	
18	33	+ 41	— 10.36	+ 1.7	.45	.50	p. (ref. 33)
25	34	+ 31	— 15.28	— 6.0	.71	.76	no p. (ref. 34)
20	28	+ 34	(~ — 9.72)	+ 0.2	.39	.53	
25	35	+ 40	(~ — 8.40)	+ 3.5	.35	.44	
	+ 10					.52	p. (ref. 36)

studies are those on tin(II) ³⁷, vanadium(IV) ²⁶, uranium(VI) ³⁸, neptunium(V) ³⁹, and (V) ⁴¹ and (VI) ⁴².

orders may be obtained by dividing the heat of hydration of the ion, ΔH_s , by the characteristic coordination number, N , of J. Bjerrum ⁵. This latter quantity indicates the number of energetically closely bound ligands found in a metal coordinate system, and is not necessarily the same as the maximum coordination number.

Figure 1 shows a plot of $\frac{\Delta H_s}{N}$ against $\log \kappa_1'$ for a number of metal ions, from the data of Table 1. It should be noted that the κ_1' values are not all comparable, owing to many of them having been obtained under different

Figure 1. Correlation of aquo ion acid dissociation constants with heats of hydration.

conditions of medium, temperature, and experimental accuracy, but nevertheless the plot is reasonably linear.

Assuming the correctness of this empirical relation, it is possible to predict the order of expected κ' values where these are uncertain. Mn^{2+} , Fe^{2+} , Co^{2+} , and Ni^{2+} should have $\log \kappa' \sim -11$. The reported values for these latter ions may be too high, for experimental difficulties are considerable (see also later comments). The indications are that Th^{4+} has a $\log \kappa'$ value ~ 1 , although not too much reliance may be placed on this, for the heat of hydration may be rather lower than that quoted. It is by no means certain that thorium is as strongly acid as this value of $\log \kappa'$ would imply (see, for example, the work of Kraus and Holmberg⁴³).

If, as suggested above, the OH^- ion in these hydrolysis complexes is adjacent to the cation, it should be possible to set up a simple coulomb expression to describe their behaviour where the association is purely electrostatic. Davies² has proposed an empirical expression equivalent to

$$\log \beta_1' = 0.607 \frac{z^2}{r} - 1.150$$

to correlate the association constant

$$\beta_1' = \frac{[\text{MOH}^{(z-1)+}]}{[\text{M}^{z+}][\text{OH}^-]}$$

with r , the ionic radius in Å, and the valence, z , in electrostatic cases. It would seem, however, that a term $\frac{z \cdot 1}{a}$, where a is the distance between the centres of charge on the metal ion and the hydroxyl ion, would emphasise the concept of coulombic attraction. To try this approach, the inter-charge distance was taken as $a = r + 0.74$, with satisfactory results. This presumes that although the metal ion could in principle approach quite close to the oxygen atom of OH^- along the O—H bond axis, it is highly probable that it could not come any closer to the centre of negative charge than the covalent radius of the oxygen atom, viz., 0.74 Å. Figure 2a shows a plot of $\log \beta_1'$ against $\frac{z}{r + 0.74}$ for the alkali and alkaline earth metals, where electrostatic association is to be expected. The linearity of the plot appears to justify the relation as an empirical criterion for solely electrostatic bonding forces.

Some support for this relation may be derived as follows. A theoretically more satisfactory quantity to correlate with $\frac{z}{a}$ would be the heat of formation of the M—OH bond (necessarily assuming that the effective dielectric constant for use in the coulomb expression does not vary too greatly from case to case). However, the thermodynamic quantities required for the evaluation of this heat, viz., the heat of removal of one water molecule from the hydration shell of the solvated M^{z+} ion and the heat of hydrolysis *, ΔH , for the reaction

are not known. Nevertheless, it is perhaps not unreasonable to expect that the heats of removal of one water molecule would follow the order of the heats of removal of one OH^- ion. The former quantity has been approximated to earlier in this paper as $\frac{\Delta H_s}{N}$, which itself is linearly related to $\log \kappa_1'$, and thus to $\log \beta_1'$ ($\kappa_1 = K_w \beta_1'$). Hence the use of $\log \beta_1'$ in the coulomb expression is somewhat justified. It is apparent that $\frac{\Delta H_s}{N}$ versus $\frac{z}{r + 0.74}$ may also be used as a criterion for electrostatic forces (Figure 2b).

Figures 2a and 2b include a number of systems which deviate markedly from the plot, and these may be considered to be 'covalent' to an extent measured by the deviation. Considering Figure 2a (the same type of definition would apply to Figure 2b), the electrostatic contribution, E , may be defined by

$$E = (\log \beta_1')_E - (\log \beta_1')_E^0$$

the difference between the 'electrostatic' $(\log \beta_1')_E$ given by the plot of Figure

* ΔH may be estimated from

$$\Delta H = \Delta G + T\Delta S,$$

using known ΔG values and calculated values of ΔS from Cobble's recent empirical equations ⁴⁴. Such estimates are included in Table 1, but it is difficult to assess their reliability until more accurate experimental data are forthcoming.

Figures 2a and 2b. Criteria for solely electrostatic association forces in metal hydrolysis species $\text{MOH}^{(s-1)+}$.

2a for a given r value and $(\log \beta_1')_E$ at $\frac{z}{r+0.74}=0$. The 'covalent' contribution, C , is expressed by

$$C = \log \beta_1' - (\log \beta_1')_E.$$

The covalent fraction, f_c , is then

$$f_c = \frac{C}{E + C} = \frac{\log \beta_1' - (\log \beta_1')_E}{\log \beta_1' - (\log \beta_1')_E^0}$$

Values of this function for various hydroxyl systems are included in Table 1. The differences in f_c from Figures 2a and 2b are not important in most cases, for the same qualitative trends are shown in both Figures, and f_c has only been defined to show relative characteristics. The observed trends are not unexpected: decreasing covalence accompanies the orders $\text{Ti}^{\text{III}} \rightarrow \text{In} \rightarrow \text{Ca} \rightarrow \text{Al}$, and $\text{Hg}^{\text{II}} \rightarrow \text{Cd} \rightarrow \text{Zn}$. A few differences are noticeable in the two sets of f_c values, however. The positions of V^{3+} and La^{3+} differ on the $\frac{\Delta H_s}{N}$ and $\log \beta_1'$ plots (they deviate from the relationship of Fig. 1). This may be due to inaccuracies in the ΔH_s estimate (Bernal and Fowler⁷ stress the approximate nature of their calculations for the +3- and +4-valent ions) and also, in the case of V^{3+} , possibly to the $\log \kappa_1'$ value (the calculations of Meites²⁶ neglect formation of anion complexes and polynuclear species). Behaviour comparable with Sc, Cr, and Fe^{III} is to be expected of V^{III} . Lanthanum, however, is probably highly polar. Differences are also apparent in the case of Fe^{2+} and Mn^{2+} . From other considerations (see below) it would appear that the $\frac{\Delta H_s}{N}$ plot is more reliable here, and that the Fe^{2+} , Co^{2+} , Ni^{2+} and Mn^{2+} hydroxyl systems are all highly polar, as Figure 2b suggests.

THE FIRST DIMER HYDROLYSIS PRODUCT, $\text{M}_2\text{OH}^{(2z-1)+}$

It is interesting to see how the tendency for the dimerisation reaction

to occur is related to the covalence of the M—OH bond. Figures 2a and 2b illustrate how the MOH systems may be broadly divided into three groups (though of course without implying discontinuity): (1) strongly electrostatic, (2) partly covalent, and (3) strongly covalent. Metals in groups (1) and (3) show no tendencies to dimerise, but there is marked polymerisation in group (2), containing partly covalent systems. Table 2 shows how the value of $\log K_1''$, defined by

$$K_1'' = \frac{[\text{M}^{z+}][\text{MOH}^{(z-1)+}]}{[\text{M}_2\text{OH}^{(2z-1)+}]}$$

appears to vary directly with $\frac{1-f_c}{r}$ for ions of a given valence ($1-f_c = E$, the electrostatic fraction). This observation may be discussed as to its possible causes. Two effects may govern the extent of dimer formation through —O— bridges:

(1). Where the M—OH linkage is electrostatic, the high dielectric constant of water will prevent significant triple ion formation⁴⁵ of the type $\text{M}^{z+} \text{OH}^- \text{M}^{z+}$, particularly where $z > 1$. The Fe^{2+} system may be mentioned again here.

Figure 2b indicates it to be electrostatic, implying no dimerisation possibilities, while the $\log \beta_1'$ plot suggests some covalence. Since Fe^{2+} does not form polynuclear complexes³⁰, this suggests that the system is electrostatic, and that the quoted value of $\log \beta_1'$ is too high, *i. e.* the aquo ion is a weaker acid than supposed.

It would seem, therefore, that dimerisation is only possible when some covalent forces are operating. On the other hand, increased participation of the oxygen bonding electrons in the metal-oxygen linkage as covalence increases would bring about a reduction in the electron density associated with the oxygen atom. This would have an effect of opposing dimerisation, for the tendency of a second metal atom to set up a similar bond with the oxygen atom would be diminished*. These two effects, acting in opposition, imply the existence of a maximum in dimerisation tendencies. The alkali and alkaline earth metals do not dimerise; while mercury(II) and thallium(III) do not dimerise either, presumably because of their relatively high covalence. In between these extremes, metals such as beryllium, aluminium, gallium, scandium, chromium(III), iron(III), etc. dimerise markedly.

(2). Professor J. Bjerrum has suggested to me that steric effects could also operate. With a highly polar M—OH linkage, the metal ion may be able to "move" to allow access to the oxygen atom by a second metal ion (for a triple ion, the configuration of minimum potential energy is a linear one). With increasing covalence, the angle MÔM probably decreases towards the value found in many strongly covalent oxygen compounds, *viz.*, ~ 100 — 110° , and the result of this would be to make dimerisation less likely for large ions than for small ones, other factors being equal. There would be insufficient room for two large ions to give a small MÔM angle. Ionic charge would also have some effect, it may be supposed, but there is insufficient data to test this.

This discussion indicates the basis of a working rule: that as the size of the metal ion and the covalence of the M—OH bond increase, the tendency to form dimers decreases. (This presumes, not unreasonably, that the M—OH bonds in the dimer partake of somewhat similar character to those in the monomer system). The properties of systems yet to be examined may thus be predicted. Within the series Cu^I , Ag^I , Au^I , the Ag—OH bond is quite covalent (Table 1), and this, together with the large radius of the Ag^+ ion (1.26 Å), can be expected to prevent significant dimer formation. The same would hold for

* Somewhat of interest here, and in agreement with the views expressed, are the recent comments of Hazel, McNabb and Santini⁴⁶ on the strong condensation tendencies of protomated vanadates. They point out that $\begin{array}{c} | \\ \text{—V—O—V—} \\ | \end{array}^{4-}$ should be favoured over $\begin{array}{c} | \\ \text{—V—O—H—} \\ | \end{array}^{3-}$, since vanadium is more electropositive than hydrogen; whereas with the corresponding phosphate ions, $\begin{array}{c} | \\ \text{—P—O—H—} \\ | \end{array}^{3-}$ and $\begin{array}{c} | \\ \text{—P—O—P—} \\ | \end{array}^{4-}$, the condensation process does not occur at room temperature, presumably because of the similar electronegativities of phosphorus and hydrogen. In the terms of the discussion given above, this is roughly the same as saying that the P—O bond is very much more covalent than the V—O bond, and hence in the former case polymerisation tendencies are considerably reduced.

Table 2. *Dimerisation of metal ions through hydroxyl bridging. All determinations made in perchlorate medium.*

Ion	$\log K_1''$	Ionic strength	Temperature in °C	Reference No.	f_c (Fig. 2a)	$\frac{1-f_c}{r}$
Hg ²⁺	too small for measurement	0.5	25	34	0.71	0.26
Pb ²⁺	0.48	0	18	24	0.58	0.35
Cu ²⁺	1.52	0	18	33	0.45	0.78
Be ²⁺	3.01	1.0	25	13	0.35	2.10
Tl ³⁺	too small for measurement	3.0	25	18	0.61	0.41
Sc ³⁺	3.87	1.0	25	25	0.43	0.70

Au^I. Similar considerations may possibly apply to Tl^I *. In Group IV b of the Periodic Table, Pb → Sn → Ge, the slight dimerisation of lead(II) proceeds to colloidal characteristics in germanium(II) ⁴⁸.

Interpolation of the data in Table 2 suggests that Cd²⁺ dimerises in the manner discussed to an extent between that of Cu²⁺ and Pb²⁺, while Zn²⁺ does so rather more strongly than copper. In³⁺ would show very similar characteristics to Sc³⁺.

SUMMARY

The state of solution of metal ions is discussed, and the acid dissociation constant of the aquo ion is correlated with the heat of hydration of the ion. The nature of the metal ion — hydroxyl ion bond is considered, and shown to be characterised in cases of electrostatic linking by a simple coulomb expression involving either the stability of the hydrolysis complex or the heat of hydration of the metal ion. Covalent contributions in other metal systems are estimated by their deviations from these empirical criteria, and later used in a discussion of the possible factors governing the formation of metal dimers through hydroxyl bridges. In this examination, the dimerisation characteristics of metal ions are related to the covalence of the metal-hydroxyl bond and the metal ionic radius. Some predictions of behaviour in systems yet to be examined are made.

I thank Professor J. Bjerrum for many helpful criticisms and his continued interest in this enquiry.

APPENDIX

The close correlation between the structures of solid hydroxides and the state of hydrolysed species in solution is of some interest. Thus it may be said in general that only those metals whose solid hydroxides have hydroxyl bonds linking the metal ion are able to polymerise in solution through hydroxyl bridging. (See Wells ⁴⁹ for a classification of

* George, Rolfe and Woodward ⁴⁷ have held that the Tl^I-OH system is electrostatic, but their evidence is not conclusive, as they acknowledged. Moreover, they did not consider the possibility of partial covalent character, discussed here.

solid hydroxides). Metals forming ionic lattices (*e. g.* alkali and alkaline earth metals excluding beryllium) show no dimerisation in the solution phase, while highly covalent systems would contain discrete molecules in their lattices, and here again there would be no polymerisation in solution. From this viewpoint, Mn(II), Fe(II), Co(II), Ni(II), and Cd should show no polymerisation tendencies, since the hydroxides of these metals have the CdI₂ ionic layer structure. (It should be remembered that the dimerisation expectations of cadmium mentioned above are based largely on a rather inaccurate determination of the first hydrolysis constant. Experimental studies are shortly to be undertaken to settle this point.)

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