

Is Lewis acidity in metal dications triggered by solvent shell fluctuations?

Anthony J. Stace

Department of Physical and Theoretical Chemistry, School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

Abstract

The ability of metal ions to generate protons in aqueous solution is of fundamental significance to many processes in chemistry and biochemistry. Numerous attempts have been made to categorise the event in a way that reflects the physical properties of the ions involved; however, several metal ions, including Pb(II) and Sn(II) frequently fail to conform. Here it is proposed that an intrinsic instability exhibited by metal ions associated with water molecules in the gas phase, can offer insight into the ability of the same ions to promote the release of protons in aqueous solution. It has already been shown that the gas phase results overlap with other methods that have traditionally been used to classify the behavior of metal ions in solution, e.g. HASB and the Irving-Williams series. To account for the Lewis acidity of metal ions in solution, a simple model based on fluctuations in solvent shell occupancy is proposed.

Introduction

In aqueous solution Lewis acidity is promoted via the hydrolysis reaction (1):



and for metal dications the hydrolysis constant associated with Eq. 1, K_h , is defined as (1)

$$K_h = \frac{[M^+OH][H^+]}{[M^{2+}]} \quad (2)$$

which provides a measure of the acidic strength of water when M^{2+} cations are present in aqueous solution. Numerous methods have been proposed in an attempt to correlate the physical properties of metal ions with the value of pK_h ($= -\log K_h$); for example plotting against various combination of charge to size ratio (2,3). For closed-shell cations, such as the alkaline earth metals, these correlations often work and suggest that pK_h reflects both the underlying electrostatic nature of the M-O bond and the contribution changes in charge density make to the M^{2+} - water interaction. However, there are some very notable exceptions to any of the methods that have been proposed, with the most obvious being Sn^{2+} , Pb^{2+} and Hg^{2+} . Some underlying anomalies are obvious; for example, ionic radius of Pb^{2+} is comparable to those of both Ca^{2+} and Sr^{2+} , in aqueous solution the former yields a proton concentration that is two orders of magnitude larger than either of the latter. Similarly, Mg^{2+} has a second ionisation energy that is comparable to Pb^{2+} , but this time there is almost four orders of magnitude difference in the proton concentrations they generate in aqueous solution. Suggestions as to why Sn^{2+} , Pb^{2+} and Hg^{2+} behave differently, have included: (i) their “softness” (4); (ii) changes in coordination number, particularly in the case of Sn^{2+} (5,6); and (iii) covalent contributions to the M-OH₂ bond (5). Some attempts to understand and/or quantify hydrolysis have actually omitted Sn^{2+} , Pb^{2+} and Hg^{2+} from the discussion. At a molecular (gas phase) level, there have now been numerous experimental studies demonstrating the ability of alkaline earth metal dications to promote proton release from water molecules. Theoretical interpretation of these (7) and similar events proposed for Sn^{2+} ,

Pb^{2+} and Hg^{2+} (8) has involved salt bridge structures which have been shown to lower barriers to proton transfer (7,8).

The purpose here is to develop this gas phase analogy of metal ion acidity by interpreting recent experimental data in terms of how shells of solvent molecules might behave when metal cations are in aqueous solution. In a recent series of papers results were present showing how stable gas phase metal dication complexes were with respect to the proton transfer reaction (9,10):



Where X is OH (water), OCH_3 (methanol) or NH_2 (ammonia). In the case of water, Eq. 3 is equivalent to the forward reaction in the hydrolysis step, Eq. 1. For each of the three molecular systems, a value for n , identified as n_s , was recorded that corresponded to the minimum number of solvent molecules required to stabilise a dication complex against spontaneous hydrolysis.

For water, measurements for a series of $[\text{M}(\text{H}_2\text{O})_n]^{2+}$ complexes were performed on the following metal dications: Sr^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Cr^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} or Sn^{2+} , and these results are summarised in Table 1 giving a data set that spans a significant fraction of the available $\text{p}K_h$ measurements. The metal dications show considerable variation in the values determined for n_s ; however, the results obtained for Sn^{2+} and Pb^{2+} are particularly interesting in that the latter needs at least 11 water molecules to stabilise the ion against gas phase hydrolysis and for Sn^{2+} an incredible 26 water molecules are required. Both of these numbers are far in excess of the conventional picture of a stable solvated dication surrounded by just a primary shell of water molecules (5,11), and the results for Sn^{2+} suggest that

secondary and quite possibly tertiary shells of water are implicated in the ion solvation/stabilisation process (12).

Through the data in Table 1 a link has been proposed between pK_h and the critical size at which hydrated gas phase dications undergo spontaneous charge separation (10). A plot of pK_h against n_s exhibited a correlation that is approximately linear and could quite clearly accommodate the (apparent) excessive acidities of both Sn^{2+} and Pb^{2+} (10). Attempts to categorise pK_h data on metal dications, have previously divided the metals into four groups (1,5): Group A – very resistant to hydrolysis (Mg^{2+} , Ca^{2+} , and Sr^{2+}); Group B – less resistant for their size and charge (Mn^{2+} , Cu^{2+} , and Zn^{2+}); Group C – low resistance to hydrolysis, ‘soft’ post-transition metals with filled d shells (Pb^{2+}); and Group D – anomalously low resistance to hydrolysis (Sn^{2+}). Two further connections can be made with established sequences: first, the overall trend in n_s matches the hard-soft acid-base (HSAB) assignment of metal ions, i.e soft Pb^{2+} (and possibly Sn^{2+}) > borderline Cu^{2+} and Zn^{2+} > hard Mg^{2+} , Ca^{2+} and Mn^{2+} (13-15). Secondly, there is also a more limited link between n_s and the Irving-Williams series, namely, Mg^{2+} and $\text{Ca}^{2+} < \text{Mn}^{2+} < \text{Cu}^{2+} \approx \text{Zn}^{2+}$ (15,16).

The relationship between n_s and pK_h works because it reflects instability within each gas phase M^{2+} /water unit; however, a more realistic view for the condensed phase might be to consider the numbers of water molecules involved as representing a critical set of solvation shells over which a metal cation has influence. Measurements of the binding energies of water molecules to Ca^{2+} have shown that the charge on the metal ion exerts an influence on binding out as far as the third solvation shell (17); however, Table (1) would suggest that the conditions necessary for promoting reaction (3) and those responsible for binding molecules to some of the metal ions have different requirements. Exceptions would appear to be Pb^{2+} and Sn^{2+} , where promoting instability clearly involves water molecules in the second and third solvation shells. Within an aqueous environment fluctuations in solvent shell occupation

in close proximity to a metal ion could cause transient fluctuations in charge density on or in the vicinity of the metal ion, which in turn, might promote proton transfer. This view could be considered as being derived from the Marcus theory of electron transfer, where solvent fluctuation drives the movement of charge (18). A similar approach has been used to describe the mechanism of autoionisation by liquid water, where computer simulations have shown that fluctuations in the concerted motion of atoms can promote charge separation (19). For a metal cation to undergo hydrolysis solvent shell coordination would have to drop below n_s , and in the case of Sn^{2+} , that could happen very frequently because it would be hard to maintain an extended array of 25 water molecules. At the other extreme, the coordination of Mg^{2+} in the first solvation shell would have to drop below four in order for proton release to occur, and because such events are going to be highly improbable, this may account for the very weak Lewis acidity of Mg^{2+} .

Many simulations have demonstrated the presence of transient (ps) fluctuations in solvent shell occupation (20-23) and quantitative evidence of the displacement of water molecules comes from experimental exchange rates recorded for molecules within the first coordination sphere (5,11,24). Using data available for the reaction $\text{H}_2\text{O} \Leftrightarrow \text{H}^+ + \text{OH}^-$ it can easily be shown that the half life of a water molecule in the liquid phase with respect to autoprotolysis is of the order of 10^4 s (25). Assuming this number scales (very approximately!) with $\text{p}K_h$ and for a salt concentration of 1 mol l^{-1} , then following an analysis given by Stillinger (25), estimates of the timescale (τ_f) over which fluctuations of the type discussed above need to occur in order to maintain a particular level of acidity, are summarised in Table 1. The assumption being made here is that the reverse reaction in (1) is diffusion-controlled ($\sim 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$) in the aqueous phase irrespective of the metal cation. This is significant assumption, because unlike water, the ions diffusing together are both

positively charged. However, recent kinetic energy releases measurements recorded for reaction (3) give some reflection of the magnitude of the reverse activation barrier as determined by the degree of repulsion between the two separating charges (10). As measured, the gas phase barriers at 1-2 eV are clearly too large to be surmounted under thermal conditions; however, for ion encounters taking place in water these values will drop by a factor of ~ 80 , which brings even the largest value down to $< 2 kT$. There is also a systematic decline in energy release as the complexes increase in size, and this can be attributed to a gradual increase in separation between the MOH^+ unit and the position from which the solvated proton is released (10). For every factor of 10 drop in the value of the association rate coefficient, τ_f will increase by the same amount. In effect, the equilibrium shifts to the right and therefore fewer fluctuations are needed to maintain a specific $\text{p}K_h$ value.

Also given in Table 1 are exchange times for water molecules in the first coordination sphere; these numbers are not used as part of the calculation, but give an approximate measure of residence time and can place the required timescale for solvent fluctuation in context (5,11,24). Taking, for example Cu^{2+} , the exchange time is $\sim 10^{-10}$ s, whereas for the reaction $\text{Cu}^{2+}\text{H}_2\text{O} \Leftrightarrow \text{Cu}^{2+}\text{OH}^- + \text{H}^+$ to maintain a $\text{p}K_h$ of ~ 7 would require solvation shell fluctuations on a timescale of $\sim 10^{-4}$ s. Similarly, to maintain a $\text{p}K_h$ of ~ 11 in an aqueous solution of Mg^{2+} would require solvent shell fluctuations every ~ 2.5 s that are sufficient to bring the water molecule occupancy below 4 (n_s); again this number is to be compared with an exchange time of $\sim 10^{-6}$ s. The only obvious discrepancy in Table 6 is Sn^{2+} ; however, recent computer simulations have given mean residence times for water of the order of 10^{-9} s (26,27), which would appear to be more appropriate. However, first-shell exchange times may not always be a good indication of behaviour, since our gas phase results show that the number of solvation shells over which an ion has influence can be sufficiently large that the

displacement of solvent molecules in the second and quite possibly the third shell is going to be sufficient to promote hydrolysis. Although solvent exchange times might have been expected to provide a measure of the timescales for the type of transient fluctuation required in solvent occupancy to affect charge density and, hence promote hydrolysis, there is no clear correlation between those quantities and pK_h . Probably what is most significant is the result that τ_f can be up to six orders of magnitude longer than the exchange or mean residence times for water molecules, which in turn, reflects the rare and rather extreme event required, for example, to displace 3 water molecules from the primary shell of Mg^{2+} .

Results presented previously showed evidence of a remarkable correlation between the behaviour of metal dications in the gas phase and properties they exhibit when in aqueous solution. The molecular perspective afforded by this study has made it possible to offer a model of Lewis acidity in terms of an assembly of solvent molecules over which a metal ion has influence when in solution, and that fluctuations in the number of molecules within this grouping can promote Lewis acidity.

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Table 1

Metal	pK_h	n_s	Exchange time / s [#]	τ_f / s
Sr ²⁺	> 13	0	< 10 ⁻⁹	> 10 ²
Ca ²⁺	13	3	10 ⁻⁸	10 ²
Mg ²⁺	11.4	4	10 ⁻⁶	2.5
Mn ²⁺	10.6	5	10 ⁻⁷ -10 ⁻⁸	0.4
Cr ²⁺	10	7	10 ⁻⁹	0.1
Zn ²⁺	9	8	10 ⁻⁷ -10 ⁻⁸	10 ⁻²
Pb ²⁺	8	11	10 ⁻⁹	10 ⁻³
Cu ²⁺	7	8	10 ⁻⁹	10 ⁻⁴
Sn ²⁺	3	26	<10 ⁻⁴ (10 ⁻¹⁰ - 10 ⁻⁹)*	10 ⁻⁸

compiled from ref. 5,11 and 24.

* taken from ref. 26 and 27.