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Acidic Nature of Metal Aquo Complexes: Proton-Transfer Equilibria in Concentrated Aqueous Media

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Optical-basicity arguments applied to hexaaquo- and tetraaquometal complexes predict pK_a values which are very much more negative than those determined experimentally. However, it is the predicted pK_a values which are in line with (i) the trend in Hammett acidity function as the water:metal ion ratio is reduced (measured for the $ZnCl_2$–H_2O system) and (ii) previously determined proton magnetic resonance shifts of concentrated aqueous solutions for a range of metal salts. The difference between predicted and experimental pK_a values probably illustrates the massive effect of outer-sphere hydration (hydrogen bonding) attenuating the true acidity of the "isolated" aquo complexes.

Introduction

Metal ions in aqueous solution interact strongly with water molecules to form aquo complexes, often the octahedral hexaaquo $[M(H_2O)_6]^{n+}$ species. For many metal ions, the metal ion–water interaction involves appreciable polarization of the water molecules and this results in the electron-charge clouds of the aquo ligands being attracted toward the central metal ion. In turn, there is impoverishment of electron density on the hydrogen atoms, and the metal aquo ion behaves as a Brønsted–Lowry acid (Table I gives pK_a values for some metal ions in aqueous solution). In effect, this acidity is a consequence of Pauling's electroneutrality principle,[1] but a long-standing problem is how to express these qualitative ideas numerically and to relate them to some parameter which quantifies the polarizing power of the metal ion.

Optical Basicity Scale. We propose to tackle this problem by regarding metal aquo complexes as no different from other oxidic acids and assuming that acidity depends upon the "state" of the oxygen atoms (or rather the oxide(–II) species) after dissociation of one or more protons.[2] The attraction that oxide(–II) has for regaining its proton depends upon its electron-donating ability, and this can be expressed in numerical terms as the *optical basicity*. (Optical basicity may be regarded as a means of quantifying Lewis basicity; it can be obtained either by experiment[3] or by calculation.[4]) Thus, we have earlier established that anions with a high optical basicity show a strong affinity for protons; hence the parent acid is weak, and vice versa.[2] The dissociation equilibrium of an oxyacid HB (which can be neutral or anionic) involves competition between the resulting anion and water molecules for protons:

$$HB + H_2O = H_3O^+ + B^- \qquad (1)$$

Therefore it should be expected that the difference between the optical basicity of the anion, λ_B, and that of water, λ_{H_2O}, is related to the strength of the acid. For many acids this is found to be the case.[2] Indeed, if pK_a is plotted against the optical basicity λ_B of the conjugate base, there is fairly good linearity. It is found that the data for oxyacids lie close to the line joining the points for the self-dissociation of water, that is, corresponding to (i) the protonation of OH^- ions and (ii) the protonation of H_2O molecules and given by eq 2. In

$$pK_a + 1.74 = 58.3(\lambda_B - 0.40) \qquad (2)$$

simple terms, for strong acids the values of λ_B are less than 0.40 (which is the λ value for H_2O) and for weak acids the λ_B value is greater—a result which appears to make good sense.

The optical basicity of an oxidic group depends upon the extent to which the electron-donor power of the oxide(–II) species is modified by the cations to which it is attached. For an oxyanion of an element Y (with oxidation number y) having the general formula $H_nYO_z^{m-}$ the "theoretical" λ_B is given by eq 3, where γ_H and γ_Y are the *basicity-moderating parameters*

$$\lambda_B = 1 - \left[\frac{n}{2z}\left(1 - \frac{1}{\gamma_H}\right) + \frac{y}{2z}\left(1 - \frac{1}{\gamma_Y}\right)\right] \qquad (3)$$

respectively of hydrogen and element Y.[3] (For several s- and p-block elements it has been shown that the γ values are closely related to Pauling electronegativity, x, by eq 4.) Thus, the

$$\gamma = 1.36(x - 0.26) \qquad (4)$$

dissociation of an oxidic acid is rationalized solely in terms of stoichiometry and basicity-moderating parameters.

Table I. Experimental and Predicted pK_a Values of Aquometal ions

metal ion	γ_M	exptl pK_a[a]	four-coordination λ[b]	four-coordination pK_a[c]	six-coordination λ[b]	six-coordination pK_a[c]
Ca^{2+}	1.00	12.85	0.475	2.6	0.45	1.2
Mg^{2+}	1.28	11.44	0.42	−0.6	0.41	−1.2
Zn^{2+}	1.82	8.96	0.36	−4.1	0.375	−3.2
Al^{3+}	1.65	4.97	0.33	−5.8	0.35	−4.7
Li^+	1.00		0.475	2.6	0.45	1.2
Na^+	0.87		0.49	3.7	0.46	1.9
HNO_3		−1.27[d]				

[a] Experimental value from data obtained for dilute aqueous solutions (C. F. Baes and R. E. Mesmer, "Hydrolysis of Cations", Wiley-Interscience, New York, N.Y., 1976). [b] λ is calculated for the conjugate base $[M(H_2O)_3(OH)]^{(n-1)+}$ or $[M(H_2O)_5(OH)]^{(n-1)+}$ from eq 3. [c] Predicted pK_a values are obtained from eq 2. [d] λ for NO_3^- is 0.39 and hence the predicted pK_a is −2.3.

Relationship 2 is especially successful when applied to successive ionization constants of polybasic acids. The possibility of applying the relationship to *positively charged* acids can be explored by extending the optical basicity argument to metal aquo ions. The acid dissociation of a metal hexaaquo ion is represented by

$$[M(H_2O)_6]^{n+} + H_2O = [M(H_2O)_5(OH)]^{(n-1)+} + H_3O^+ \qquad (5)$$

and it is necessary to obtain λ_B for the conjugate base $[M(H_2O)_5(OH)]^{(n-1)+}$ (or $[M(H_2O)_3(OH)]^{(n-1)+}$ if the initial aquo complex is four-coordinate). λ_B may then be substituted in eq 2 and we thus obtain the *predicted* value for K_a, the dissociation constant for the equilibrium eq 5. The results of such calculations (see Table I) indicate that the aquo complexes of metal ions such as Al^{3+} should be extremely acidic, comparable with mineral acids as strong as HNO_3 or even stronger. Experimentally, however, it is found that metal aquo ions in aqueous solution behave as rather weak acids, as can

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Table II. Lowest Energy Absorption Maxima of Organic Bases and Their Conjugate Acids

		λ_{max} of base, nm			λ_{max} of conjugate acid, nm	
base	$pK_a^{B\,a}$	ethanol	$ZnCl_2$ hydrate[b]	aq·$ZnCl_2$ (ca. 1 M)	9 M H_2SO_4	$ZnCl_2$ hydrate[b]
4-nitroaniline	0.99	376		380	258	259
		229		227	213	(c)
2-nitroaniline	−0.29	404	425[d]	420	267	287
		276		287		
4-chloro-2-nitroaniline	−1.03	415	430[d]	426	263	272
2,5-dichloro-4-nitroaniline	−1.82	362	382	376	312	259
4-nitrodiphenylamine	−2.38	394	434	412	260	
		260	262	266		
2,6-dichloro-4-nitroaniline	−3.24	357	383		260[e]	
benzalacetophenone	−5.61	312	323		439[e]	

[a] pK_a^B values taken from C. H. Rochester, "Acidity Functions", Academic Press, London and New York, 1970, and ref 8. [b] $[ZnCl_2]/H_2O]$ ratio = 1:4.43. [c] Maximum located beyond transparency of medium. [d] Approximate value owing to low absorption produced by the small proportion of unprotonated base. [e] In 98% H_2SO_4.

be seen from the experimental pK_a values given also in Table I.

The reason for this very large difference btween the predicted and experimental pK_a values, which amounts to 10–12 pK units, may arise from severe outer-sphere hydration which the metal aquo complexes suffer in aqueous solution. The question arises as to whether this effect is truly reflected in the difference between experimental and predicted pK_a values or whether the predicted pK_a values are simply in "error".

Molten Salt Hydrates. The conditions under which metal aquo complexes exist with little outer-sphere hydration are probably met in molten salt hydrates,[5] especially when the water:metal ion ratio is 6:1 or less. Molten salt hydrates have received attention in recent years largely because they form a bridge between anhydrous fused salts on the one hand and concentrated aqueous solutions on the other.[6] In many ways molten salt hydrates resemble anhydrous fused salts, and it would seem realistic to visualize "simple" hydrates, such as $Ca(NO)_3 \cdot 4H_2O$, as containing mainly $[Ca(H_2O)_4]^{2+}$ cations and NO_3^- anions[7,8] (although there is evidence[9,10] that the H_2O molecules are also influenced by the anions, which may also replace one or more water molecules in the coordination sphere).

On the basis of the above arguments, we might expect molten salt hydrates and concentrated solutions of salts to have interesting acid–base properties, although this aspect of their behavior has not so far received much attention. These ligands may also be model systems for exploring the relationship between protonating power and optical basicity. Elsewhere, in a preliminary note, we have reported that in the case of aqueous zinc chloride solutions approaching the composition $ZnCl_2 \cdot 4H_2O$, powerful Brønsted–Lowry acidity can be observed,[11] the trend in the Hammett acidity function resembling trends exhibited by the strongest mineral acids. Since the acidity of molten salt hydrates is of importance from both a theoretical and a practical point of view (bearing in mind projected use of the liquids in energy-storage devices, etc.), it would seem desirable to include in this paper details of the determination of the Hammett acidity function, as well as a discussion of the status of these liquids as protonic solvents.

Requirements for Measuring Acidity Functions. Experiments in our Laboratory have indicated that molten salt hydrates readily dissolve weak organic bases and that the protonating power is so great that the acidity is measurable only on the Hammett acidity scale. The Hammett acidity function, H_0, of a medium is defined[12] as

$$H_0 = -\log (a_{H^+} f_B / f_{BH^+}) \qquad (6)$$

where a_{H^+} is the activity of hydrogen ions and f_B and f_{BH^+} are respectively the activity coefficients of an added base B and its conjugate acid BH^+. The bases are often substituted aromatic amines, and the method of determining H_0 depends upon the spectrophotometric determination of the concentrations c_B and c_{BH^+}, since eq 6 can be rearranged as

$$H_0 = pK_a^B + \log (c_B/c_{BH^+}) \qquad (7)$$

where pK_a^B is the dissociation constant of the conjugate acid of the indicator base. If the activity coefficients, f_B and f_{BH^+}, are taken arbitrarily as unity (strictly true only in dilute aqueous solution), then H_0 can be identified with pH, and eq 7 is analogous to the well-known Henderson equation.

For measurements of H_0 to be made in a molten salt hydrate, it is desirable that the latter should (i) be fairly low melting so that there is no risk of thermally decomposing the organic base, (ii) have a low vapor pressure to avoid changes in composition, (iii) be fairly inert chemically to avoid side reactions such as nitration of the base, and (iv) have good ultraviolet transparency so that the lowest energy absorption band of the organic base and its conjugate acid can both be recorded. Of the various molten salt hydrates available, very few fulfill all of these requirements, transition-metal salt hydrates, e.g., $FeCl_3 \cdot 6H_2O$, being particularly troublesome as far as UV–visible transparency is concerned. One of the most convenient was found to be $ZnCl_2 \cdot 4H_2O$, especially since it is transparent to around 220 nm and also is a liquid at ambient temperature.

Experimental Section

Bulk quantities (100–200 g) of zinc chloride hydrate can be prepared from either (i) anhydrous $ZnCl_2$ and water or (ii) AnalaR ZnO and the equivalent quantity of concentrated hydrochloric acid. In both preparations, samples of the resultant liquids were analyzed for zinc (using EDTA solution, hexamine buffer, and Eriochrome Black T) and chloride (by Volhard's method of back-titrating excess added silver nitrate solution with potassium thiocyanate).

In the first method of preparation, the Cl:Zn ratio was always found to be less than 2:1, chloride having been evolved as HCl on initial contact of $ZnCl_2$ with water; in the case of commerically obtained $ZnCl_2$, the same ratio was found, owing to the presence of small quantities of ZnO. Therefore, it was necessary to adjust the stoichiometry by adding a small quantity of concentrated hydrochloric acid. In the second method (which was preferred) the Cl:Zn ratio was found to be almost exactly 2:1, but it was necessary to remove some water (by boiling) in order to achieve a H_2O:Zn ratio of around 4:1. Subsequent experiments showed that this particular ratio was not critical as far as any sudden changes in properties were concerned, and to avoid extra analytical work, salt hydrates approximating this ratio were used without final adjustment to exactly 4:1.

It was necessary to purify many of the organic bases and this was done by recrystallization or chromatography. The bases in Table II dissolved fairly readily in the salt hydrate, and the resulting solutions were scanned on a Unicam SP700C or SP800 spectrophotometer using 5-mm optical cells. The most comprehensive set of data was for $ZnCl_2 \cdot 4.43H_2O$, and Table II refers to this composition. It was evident that the absorption maximum of the base usually underwent a solvent

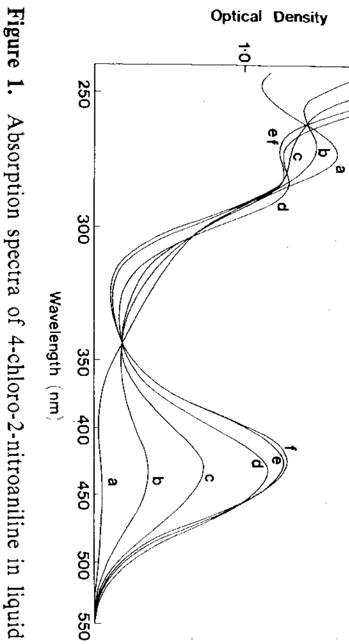

Figure 1. Absorption spectra of 4-chloro-2-nitroaniline in liquid $ZnCl_2{\cdot}4.43H_2O$: spectrum a, undiluted; spectra b–f, diluted with water to exactly compensate longer path lengths. (Path lengths: (a) 5 mm, (b) 6 mm, (c) 7 mm, (d) 10 mm, (e) 20 mm, (f) 40 mm.)

shift when the spectra were compared with those obtained for the base in ethanol (see Table II). Comparison with spectra of the bases in strong sulfuric acid indicated that, apart from extremely weak bases, protonation occurred in zinc chloride hydrate (again there was a solvent shift—see Table II).

Results

$ZnCl_2$ is known to form adducts with organic bases.[13] However, these are produced under aprotic conditions and it is doubtful if any were formed in the present work owing to the relatively high water content. Certainly in the case of 4-nitroaniline, spectroscopic results showed no adduct to be formed: the adduct with this particular base has an absorption maximum at 460 nm[13] but this characteristic absorption was never observed in zinc chloride hydrate.

Changes occurring on gradually diluting the salt hydrate solution with water were recorded spectrophotometrically by examining the diluted solutions with compensatingly increased path lengths (see Figure 1 for example). The final dilution was eightfold (40-mm cells), and at this stage virtually all of the conjugate acid was converted back into original base. The ratio of base to conjugate acid (c_B/c_{BH^+}) in the salt hydrate was taken as A_B/A_{BH^+} where A_B was the experimental absorbance of the base and A_{BH^+} was the difference between the experimental absorbance of the eightfold diluted solution (in 40-mm cells) and A_B. Determination of the ratio using the absorption band of the conjugate acid was not straightforward owing to the proximity of higher energy absorption bands arising from unprotonated base. For example, protonated 2,5-dichloro-4-nitroaniline in 98% sulfuric acid has its principal UV absorption band, with a maximum at 221 nm, lying very close to a strongly absorbing band, with a maximum at 214 nm, of the unprotonated base in ethanol.

4-Nitroaniline and 2-nitroaniline were almost completely protonated in zinc chloride hydrate, but some of the weaker bases in Table II had pK_a^B values suitable for obtaining the ratio c_B/c_{BH^+}; H_0 values were then calculated from eq 7 and the appropriate pK_a^B value. Three H_0 values were obtained for the hydrate melt $ZnCl_2{\cdot}4{\cdot}43H_2O$ (Table III), and the difference between them quite possibly arises from changes in the extinction coefficient of unprotonated base in going from the hydrate melt to aqueous solution. The absence of good isosbestic points supports this—see Figure 1 for example. Furthermore, the value of −2.35 obtained from data for 4-chloro-2-nitroaniline relies upon a very small c_B/c_{BH^+} ratio (owing to the ease with which the base is protonated) and is therefore only an approximate value; the H_0 values of −2.10 and −1.86 are probably more reliable since the c_B/c_{BH^+} ratios are closer to unity. Similarly for some of the diluted solutions, large differences between c_B and c_{BH^+} introduce error in obtaining H_0, and in Table III H_0 values are taken to be

Table III. Acidity Function Data for Zinc Chloride Solutions of Various Water Contents

				4-chloro-2-nitroaniline			4-nitrodiphenylamine			2,5-dichloro-4-nitroaniline			4-nitroaniline		
salt hydrate/ water ratio	sp gravity	molarity of Zn^{2+}	no. of H_2O's per $ZnCl_2$	c_B/c_{BH^+}	log (c_B/c_{BH^+})	H_0	c_B/c_{BH^+}	log (c_B/c_{BH^+})	H_0	c_B/c_{BH^+}	log (c_B/c_{BH^+})	H_0	c_B/c_{BH^+}	log (c_B/c_{BH^+})	H_0
1:0	1.81	8.36	4.43	0.047	−1.32	(−2.35)	1.89	0.28	−2.10	0.92	−0.04	−1.86			
1:0.20	1.66	6.97	5.66	0.37	−0.42	−1.45	28	1.45	−0.83	11	1.04	−0.78			
1:0.40	1.58	5.96	7.17	1.25	0.09	−0.93									
1:1.00	1.41	4.18	11.16	8.41	0.92	−0.11	67	1.83	−0.55						
1:2.00	1.22	2.08	25.00	55.4	1.74	(+0.71)							1.23	0.09	1.08
1:4.00	1.12	1.05	51.85										6.06	0.78	1.77
1:8.00	1.06	0.52	105.7										27.3	1.44	(2.43)

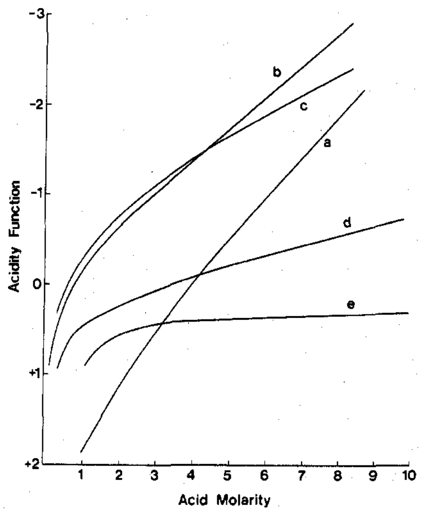

Figure 2. Trend in Hammett acidity function, H_0, with molarity for aqueous solutions of (a) $ZnCl_2$, (b) HCl, (c) HNO_3, (d) H_3PO_4, and (e) CH_3CO_2H. (Adapted from ref 8.)

meaningful only when c_B and c_{BH^+} are within a factor of 10 of each other.

Discussion

Typical strong acids such as HCl or H_2SO_4 increase enormously in protonating power as their aqueous solutions become more concentrated, and this is in contrast to weak acids, e.g., acetic acid, where there is little increase. Figure 2 has been adapted after Hammett[12] and shows the variation of H_0 with concentration for a number of acids in aqueous solution. Also included are the new data for zinc chloride, and it can be seen that in dilute solution the protonating power is very low indeed. It is not known what the aquo complex of zinc is in these solutions, though it may be $[Zn(H_2O)_4]^{2+}$ or $[Zn(H_2O)_6]^{2+}$. However, it is apparent from Figure 2 that at higher concentrations, i.e., as the aquo complex becomes less hydrated, protonating power increases. A $[H_2O]/[Zn^{2+}]$ ratio of 6 is reached at a $ZnCl_2$ concentration of around 7 M (see Table III), but well before this, e.g., at 4 M, the zinc chloride solution is more acidic than orthophosphoric acid. Moreover, the trend in acidity (compare line a with lines b (HCl) and c (HNO_3) in Figure 2) is that of a very *powerful* acid. Although there is no quantitative relationship between the H_0 values of concentrated aqueous solutions of acids and their pK_a values, in general, powerful Hammett acidity goes hand in hand with high Brønsted–Lowry acidity in dilute aqueous solution. The trend for $ZnCl_2$ therefore implies that hydrolytic dissociation of the zinc aquo complex should have a low pK_a value in dilute solution and that the experimentally obtained pK_a of 8.96 is the result of some mechanism occurring on dilution which severely dampens the acidity of the complex.

There is no reason to suppose that the $ZnCl_2$–H_2O system is in any way unique among salt–water systems. Indeed, strong Zn^{2+}–Cl^- interactions competing with the Zn^{2+}–H_2O interaction may actually *lower* the protonating power of these liquids as compared with, for example, nitrates and sulfates of equivalent $[H_2O]/[Zn^{2+}]$ ratios. There is indeed indirect evidence for very high acidity in mixed $AlCl_3$,$Al(NO_3)_3$ systems as seen from their exceptional reactivity (rapid dissolution of Au, Pt, etc.).[5]

NMR Studies. The proton magnetic resonance study by Angell and co-workers[5] is very relevant to the present study. These workers measured the downfield chemical shifts (relative to tetramethylammonium ion), as a function of temperature, for concentrated aqueous solutions of a large number of metal salts and correlated the shifts successfully with the basic properties of the various anions (oxyanions and nonoxyanions).

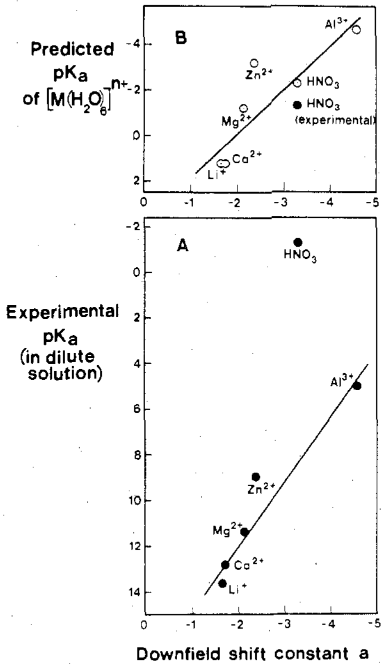

Figure 3. ^1H NMR shifts (ppm relative to tetramethylammonium ion) for salt hydrates $M(NO_3)_n \cdot 10H_2O$ and nitric acid vs. (A) experimental pK_a values and (B) predicted pK_a values. (^1H NMR shift constants, *a*, from ref 5.)

As far as the present discussion is concerned, it is possible to use some of their data to investigate the effect of changing from one cation to another but keeping the anion constant. The most suitable set of data is for nitrates where the water to salt ratio is 10, and furthermore this allows aqueous solutions for various salts to be compared with the corresponding nitric acid solution.

Figure 3A shows the plot of the downfield shift vs. the experimental pK_a value of the metal aquo ion. Since the downfield shifts represent the degree of proton deshielding in the water molecules, as a result of polarization by the metal ions, the observed sequence $Li^+ \sim Ca^{2+} < Mg^{2+}$ etc. in Figure 3A is consistent with expectation. Figure 3A also shows the experimental data point for nitric acid, and it is apparent that the deshielding effect caused by cations such as Mg^{2+} or Zn^{2+} is fairly similar to that suffered in nitric acid solution; in fact, in the case of Al^{3+} the effect is greater. However, the extent to which the point for nitric acid lies off the line in Figure 3A serves to indicate the inadequacy of pK_a values measured for metal ions in dilute solution. These pK_a values are far too positive and do little justice to the acidic properties of metal aquo ions in more concentrated solutions.

On the basis of their ^1H NMR data, Angell et al.[5] suggested that concentrated solutions of certain metal salts "must be regarded as forming an interesting class of strong protonic acids". It could well be that for these solutions the downfield shifts provide a good indication of the "true" acidity of the metal hexaaquo ions. As already suggested earlier in this paper, the pK_a values predicted from optical basicity (i.e., those in Table I) might also be a good indication of "true" acidity, and therefore it is a logical step to try to relate these pK_a values with the downfield shifts. The two sets of data are plotted in Figure 3B, and it can be seen that with these predicted pK_a values, nitric acid is no longer separated from the metal aquo ions. The predicted pK_a values show that the metal aquo ions *and* nitric acid constitute a set of powerful oxidic acids, just as Angell's ^1H NMR data also in effect showed.

Parenthetically, it is worth noting in Figure 3B that (i) the experimental point for nitric acid is quite close to that predicted (as it should be through the pK/λ relationship[2]) and (ii) the downfield shift for Zn^{2+} is less than expected from the predicted pK_a and that a similar pattern is observed for the experimental pK_a in Figure 3A.

General Conclusions

(1) The results presented in this paper seem to confirm the suggestion[5] (see above) that highly concentrated solutions of certain metal salts must be regarded as strong protonic acids.

(2) For highly concentrated aqueous solutions of metal salts the protonating power increases rapidly, and results such as those shown in Figure 2 indicate that when the metal aquo complex is rid of outer-sphere water molecules, it becomes a very powerful acid. Thus the pK_a values determined for metal ions in aqueous solution (i.e., the "experimental" values in Table I) do not represent the true acidity of the metal aquo complexes. On the other hand, the pK_a values predicted from optical-basicity theory seem much more informative. Furthermore, the previously obtained ^1H NMR data for concentrated aqueous solutions of metal salts[5] are explicable in terms of the predicted pK_a values but not with the experimental ones. The difference of 10–12 pK units between experimental and predicted values must reflect the enormous neutralizing effect of outer-sphere water molecules which severely attenuates the acidity of the metal aquo complexes.

(3) To avoid possible misunderstanding, it is worth pointing out that in comparing the acidity of a metal aquo complex, e.g., $[Zn(H_2O)_4]^{2+}$, with that of a conventional mineral acid, e.g., H_3PO_4, a comparison is *not* being made directly between the acidity of zinc(II) and phosphorus(V). To make such a comparison, it would be necessary to consider $[Zn(H_2O)_4]^{2+}$ alongside the (hypothetical) $[P(H_2O)_4]^{5+}$ species. The latter species would instantly lose five protons to yield H_3PO_4, and from this point of view, our present comparison is between the first dissociation of $[Zn(H_2O)_4]^{2+}$ and the *sixth* dissociation of $[P(H_2O)_4]^{5+}$.

(4) An important question arising from the present work is why solvation has such an enormously attenuating effect upon the acidity of the metal aquo complex. Bearing in mind that in terms of the pK–optical basicity argument, strong acids are those giving rise to conjugate bases with low λ values, it is necessary to consider how solvation affects the optical basicity of the conjugate base. Conjugate bases bearing a negative charge (i.e., those derived from oxyacids) will be solvated by the positive ends of the water dipoles, and thus the overall basicity will be reduced. On the other hand, conjugate bases bearing a positive charge (i.e., those derived from metal aquo complexes $[M(H_2O)_x]^{n+}$ and having the formula $[M(H_2O)_{x-1}(OH)]^{(n-1)+}$) will be solvated by the negative ends of the water dipoles. This can be viewed in terms of hydrogen bonding between the oxygen atoms of the outer-sphere H_2O molecules and the hydrogen atoms on the surface of the inner coordination sphere. In other words the basicity-moderating effect of these hydrogen atoms (expressed by γ_H) is no longer focused within the aquo complex but is dissipated throughout the solvent. This results in the basicity of the OH^- group in the coordination sphere being enhanced, and thus the original aquo complex behaves as a weaker acid.

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Registry No. $Ca(H_2O)_6^{2+}$, 17787-72-3; $Mg(H_2O)_6^{2+}$, 19592-06-4; $Zn(H_2O)_6^{2+}$, 15906-01-1; $Al(H_2O)_6^{3+}$, 15453-67-5; Li, 7439-93-2; Na, 7440-23-5; $ZnCl_2$, 7646-85-7.

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Reactions of Monomeric Silicon Difluoride and Silylene with Conjugated Pentadienes

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Monomeric $^{31}SiF_2$ formed in a nuclear recoil system reacts with 1,3-butadiene, *trans*-pentadiene, *cis*-pentadiene, and 2-methyl-1,3-butadiene to give equivalent amounts of difluorosilacyclopent-3-ene-^{31}Si and its methyl derivatives. The singlet to triplet $^{31}SiF_2$ ratios evaluated from these systems are all around 1:3. Similar equivalence in product yields is also observed for $^{31}SiH_2$ reactions with 1,3-butadiene and the pentadienes, and the evaluated singlet to triplet ratio from the pentadienes is about 1:6. For each of these two silylenes, the relative reactivities of the various dienes toward them have been measured. Minor steric hindrance exists in most cases to account for the smaller reactivities of the pentadienes. However, a large steric effect has been observed between *trans*- and *cis*-pentadienes for their reactivities toward a triplet $^{31}SiF_2$–donor, indicating a possible direct 1,4-addition process for such $^{31}SiF_2$–donor complexes.

Following the maturity of carbene chemistry, studies of silylene, silicon difluoride, and other substituted silylenes have drawn much interest during the past decade.[1-5] Silylenes are generally formed through the following three methods: (i) decomposition or reaction of silicon-containing compounds through pyrolysis or photolysis;[6-11] (ii) the reactions of silicon species formed by the thermal vaporization method;[4,5,12-16] and (iii) the reactions of silicon atoms formed by the nuclear recoil technique.[17-28] The last method has been proven to be very useful in studying the reactions of SiH_2 and monomeric SiF_2.

Gaspar and co-workers have employed the nuclear transmutation, $^{31}P(n,p)^{31}Si$, to produce ^{31}Si atoms which subsequently abstract H atoms to give $^{31}SiH_2$.[17,18] They have demonstrated that the $^{31}SiH_2$ being formed can insert into the Si–H bond of SiH_4 to give $^{31}SH_3–SiH_3$.[18] Later, we have shown in our laboratory that the $^{31}SiH_2$ thus formed can add

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