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# Parametric Correlation of Formation Constants in Aqueous Solution. 1. Ligands with Small Donor Atoms

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It is shown that four-parameter equations proposed by previous authors have poor predictive powers for data of formation constants in aqueous solution. This relates partly to the paucity of data on complexes of ligands such as ammonia which, with most metal ions, cannot exist in water because of hydrolysis. Equations previously proposed that relate the formation constants of polyamine and poly(aminocarboxylate) complexes to those of the ammonia and acetate complexes are used to calculate formation constants for these hydrolysis-prone ammonia complexes. An equation of the type $\log K_1 = E_A E_B + C_A C_B$, where $E$ and $C$ are identified with the tendencies of the Lewis acid A and base B to undergo ionic and covalent bonding, was used to correlate the $F^-$, $OH^-$, and $NH_3$ formation constants of 27 Lewis acids to a standard deviation of 0.24 log unit. Hardness parameters $H_A$ and $H_B$ were defined as $E_A/C_A$ and $E_B/C_B$ for acids and bases, respectively, and gave reasonable orders of hardness. It was found that for ligands with large donor atoms, such as $Cl^-$, and for sulfur or phosphorus donor atoms, deviations from the predictions of this equation were observed that appeared to be related to the size of the acid, so that no deviations were observed for large cations such as $Ag^+$ and $Pb^{2+}$, with occurrence of large deviations for smaller cations such as $Cu^{2+}$ or $Ni^{2+}$, with the very largest occurring for the proton. These deviations were attributed to steric hindrance between the large donor atom and adjacent coordinated water molecules.

The important contribution of the Edwards equation[1] lies in illustrating that formation constant data for complexes of unidentate ligands in aqueous solution need at least a dual-basicity scale for any kind of correlation to be obtained at all. There have been several other multiparameter equations[2-4] proposed for correlating formation constant data. The need for at least a dual-basicity equation has manifested itself in the classification of metal ions into Schwartzenbach's[5] and Ahrland and Chatt's[6] A- and B-type metal ions and Pearson's more general classification[7] of Lewis acids and bases into hard and soft acids and bases (HSAB). Drago and co-workers[8] have had considerable success with a more generalized form of a four-parameter equation similar to eq 1 for the correlation of enthalpy changes on adduct formation in solvents of low dielectric constant. In eq 1, which resembles Drago's expression, except that $-\Delta H^\circ$ has been replaced with $\log K_1$, $C$ and $E$ are identified with the tendency of each Lewis acid A or base B to undergo covalent or ionic bonding. This interpretation of the significance of the $C$ and $E$ parameters seems most reasonable in the light of the work of Klopman[9] on the origin of hardness and softness in acids and bases. Klopman[9] found softness to be associated with "frontier-controlled" (covalent) and hardness with "charge-controlled" (ionic) bonding in calculations based upon polyelectronic pertubation theory. We have therefore adopted the $E$ and $C$ formalism of Drago and co-workers[8] in this paper as probably being the best interpretation of the parameters in a four-parameter equation such as (1).

$$\log K_1 = C_A C_B + E_A E_B \tag{1}$$

One serious problem encountered in attempting to fit multiparameter equations[1-4] to formation constant data is that these data are rather limited in type. Most metal ions are hard, so that complexes are limited to those of the fluoride ion and oxygen-donor ligands. Close examination reveals that the predictive powers of most of the above equations[1-4] are limited outside of the set of formation constants used in the determination of the adjustable parameters. Thus, the equation proposed by Yamada and Tanaka,[2] which is a modification of the Edwards equation, predicts $\log K_1(NH_3) = 13$ for $Zr^{4+}$ which suggests that amine complexes of Zr(IV) might be resistant to hydrolysis in aqueous solution according to eq 2,

$$M(NH_3)^{n+} + H_2O \rightleftharpoons M(OH)^{(n-1)+} + NH_4^+ \tag{2}$$

taking $\log K_1(OH^-) = 14.6$ for $Zr^{4+}$ and the $pK_a$ of water and ammonia as 14 and 9.2, respectively. The Edwards equation itself predicts $\log K_1(NH_3) = 6.5$ for $Pb^{2+}$, which, with $\log K_1(OH^-) = 6.3$, suggests that Pb(II)–$NH_3$ complexes should also be stable to hydrolysis as in eq 2. The chemical evidence, however, suggests that neither the zirconium(IV)– nor lead(II)–ammine complexes can be formed in appreciable quantities in water. If it were possible to estimate the formation constants of these hydrolysis-prone ammine complexes in an independent way, these additional constants would provide a considerably improved test of the correlative ability of equations such as (1).

## Polydentate Ligands Containing Nitrogen Donor Atoms

Although no complexes of most hard metal ions with ammonia exist in water, most of these metal ions still form many complexes in which metal-to-nitrogen bonds exist, as in the complexes with EDTA (ethylenediaminetetraacetate). In recent publications[10,11] it was proposed that equations which relate the formation constants of complexes of polydentate ligands such as EDTA to those of their unidentate constituents ammonia and acetate could be used to generate formation constants for the hydrolysis-prone ammine complexes. Thus, eq 3 relates $\log K_1$(polyamine), where polyamines are of the

$$\log K_1(\text{polyamine}) = 1.152n \log K_1(NH_3) - \left(\sum_{i=1}^{n-1} i\right)\lambda_N + (n-1)\log 55.5 \tag{3}$$

type $H(NHCH_2CH_2)_{n-1}NH_2$ ($n = 2$, en; $n = 3$, dien; $n = 4$, trien; $n = 5$, tetren), to $\log K_1(NH_3)$ for any one metal ion. The factor of 1.152 in eq 3 is $pK_a(CH_3NH_2)/pK_a(NH_3)$, which takes into account the inductive effect of the ethylene bridges in the polyamine complexes, and the $(n - 1) \log 55.5$ term corrects for the asymmetry of the standard reference state.[12] $\lambda_N$, the logarithm of the ratio of successive ammonia formation constants, i.e., $\log K_n - \log K_{n+1}$, is equal to 0.5 for all complexes of polyamines forming five-membered chelate rings. Thus, from $\log K_1(\text{trien}) = 10.4$ and $\log K_1(\text{tetren}) = 10.9$, it follows that $\log K_1(NH_3) = 1.6$ for Pb(II) may be estimated. Of more use for the majority of metal ions, which do not even form complexes with polyamines in aqueous solution, is eq 4,

$$\log K_1(\text{aminocarboxylate}) = 1.152n \log K_1(NH_3) - \left(\sum_{i=1}^{n-1} i\right)\lambda_N + m \log K_1(CH_3COO^-) - \left(\sum_{i=1}^{m} i\right)\lambda_O + (m + n - 1)\log 55.5 \tag{4}$$

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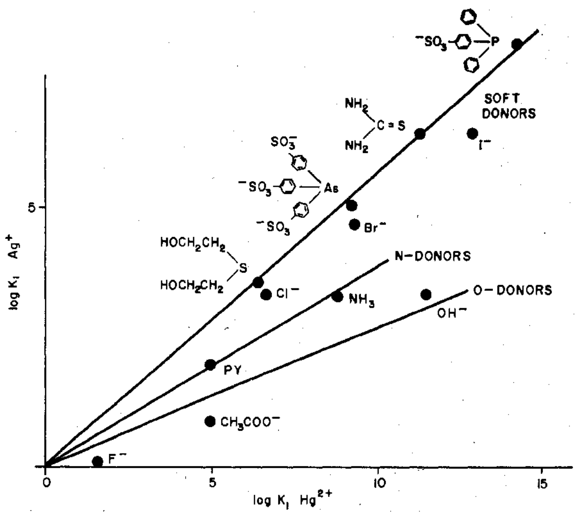

Figure 1. LFER diagram for $Ag^+$ vs. $Hg^{2+}$.

which relates the formation constants of the ammonia and acetate complexes to those of poly(aminocarboxylate) ligands containing $n$ aliphatic nitrogen-donor and $m$ carboxylate groups. $\lambda_O$ is $\lambda$ appropriate to carboxylate groups and is empirically set equal to 0.26 log $K_1(CH_3COO^-)$ – 0.19.

The predictive powers of eq 4 have already been discussed,[10,11] but as an example, for Co(II), log $K_1(NH_3)$ = 2.1 and log $K_1(CH_3COO^-)$ = 1.33 may be used in eq 4 to calculate log $K_1$ values of poly(aminocarboxylate) ligands (observed values follow in parentheses): log $K_1$(glycine) = 5.18 (5.23), log $K_1$(NTA) = 10.70 (10.46), log $K_1$(EDDA) = 11.75 (11.78), log $K_1$(DTMA) = 12.15 (12.11), log $K_1$ (HEDTRA) = 14.35 (14.40), log $K_1$(EDTA) = 16.81 (16.26) (NTA, $n$ = 1, $m$ = 3; EDDA, $n$ = 2, $m$ = 2; DTMA, $n$ = 3, $m$ = 1; HEDTRA, $n$ = 2, $m$ = 3; EDTA, $n$ = 2, $m$ = 4).

## The Linear Free-Energy Relation (LFER) Diagram

In several publication[13-15] it was shown that for any pair of Lewis acids, if all the formation constant data with monodentate bases in aqueous solution were plotted against each other, a diagram which would be readily interpretable in terms of Pearson's[7] ideas on hard and soft acids and bases (HSAB) could be obtained. Thus, in Figures 1–3 are plotted the LFER diagrams for $Ag^+$, $Bi^{3+}$, and $Fe^{3+}$ against $Hg^{2+}$ as a standard reference acid. It can be seen that for the $Ag^+/Hg^{2+}$ diagram, the ligands are arranged so that the hardest ligands ($F^-$, $RO^-$) form relatively stronger complexes with $Hg^{2+}$ than do the softer ligands (As, P, S, donors), with the LFER that contains the N donors occupying an intermediate position. Figure 1 suggests, in contrast to most other proposed orders of hardness, that $Ag^+$ is softer than $Hg^{2+}$, in terms of the definition[7] that hard acids prefer hard bases and soft acids prefer soft bases. Prefer must mean *relative* preference; otherwise one would confuse intrinsic strength of complex formation with preference, since $Hg^{2+}$ forms stronger complexes with all ligands than does $Ag^+$. However, Figure 1 shows clearly that $Hg^{2+}$ does prefer the harder ligands relative to $Ag^+$ and so must be regarded as harder.

Figure 2 is very similar to Figure 1, except that the relative stability order of the ligands has been reversed, indicating that $Bi^{3+}$ is harder than $Hg^{2+}$. With the very hard $Fe^{3+}$ ion (Figure 3), a similar diagram is obtained, except that the relative strength of the hardest ligands has increased still further and the very soft ligands now appear to have become so weak as to fall below the $x$ axis. The log $K_1(NH_3)$ values estimated as above, as seen for $Fe^{3+}$ and $Bi^{3+}$, fit in where expected on these diagrams (i.e., between the soft and $RO^-$-type ligands). The rather simple pattern observed in these diagrams appears to be general across the periodic table. The form of these diagrams suggests that one might be able to quantify this behavior by using, say, the ratio log $K_1(F^-)$/log $K_1(OH^-)$ or log $K_1(OH^-)$/log $K_1(NH_3)$ as a measure of hardness of the metal ion. The appropriateness of this approach is shown in that almost exactly the same order of hardness is given by both ratios.

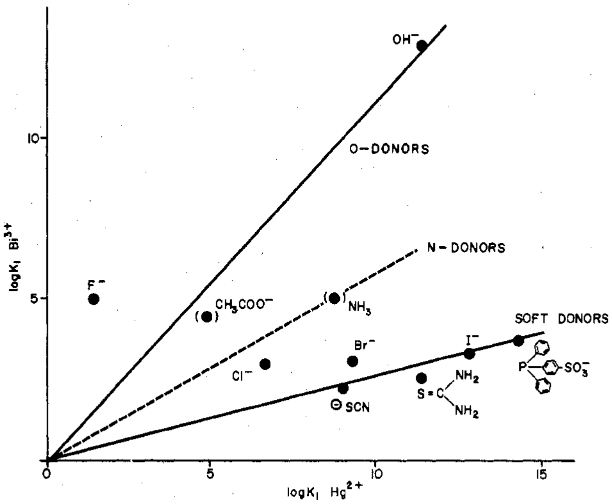

Figure 2. LFER diagram for $Bi^{3+}$ vs. $Hg^{2+}$.

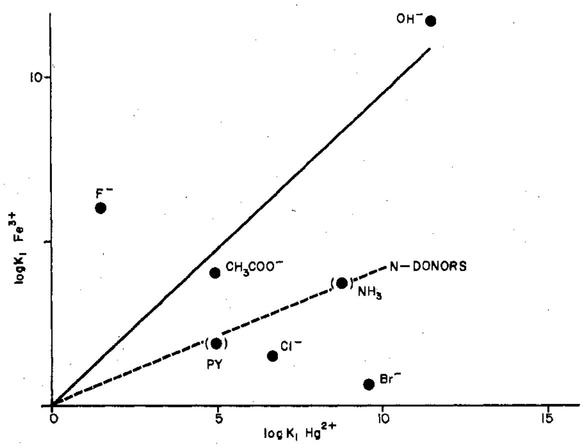

Figure 3. LFER diagram for $Fe^{3+}$ vs. $Hg^{2+}$.

This approach to the quantification of hardness of acids in aqueous solution can be incorporated into eq 1. As has been pointed out,[8] this equation is underdetermined and allows two parameters to be set arbitrarily for each metal ion. Thus one can define initial values of $E_A$ and $C_A$ as

$$E_A = \log K_1(F^-) \tag{5}$$

$$C_A = \log K_1(OH^-)/14.00 \tag{6}$$

$C_A$ was defined as in eq 6, where 14.00 is the ionic product of water, mainly because this gives numbers of a more convenient size. We have, in effect, set $E_B$ = 0 and $C_B$ = 14.00 for hydroxide. $H_A$, the measure of the ionic nature of the metal-to-ligand bond, or hardness of the metal ion, is given by the ratio $E_A/C_A$ and, for the ligand, $H_B$ by $E_B/C_B$.

For reasons which will become apparent later, eq 1 will be fitted to data for complexes of the ligands $F^-$, $OH^-$, and $NH_3$ only. Equation 1 can be rewritten as eq 7, so that plotting log

$$(\log K_1)/C_A = (E_A E_B/C_A) + C_B \tag{7}$$

$K_1(NH_3)/C_A$ against $E_A/C_A$ should give a linear relation of slope $E_B$ and intercept $C_B$ for ammonia. $E_B$ and $C_B$ for ammonia were obtained from this plot by means of a least-squares procedure. A weighting scheme was used to take into

**Table I.** Values of log $K_1$ Observed and Calculated Using Eq 1 for Fluoride, Hydroxide, and Ammonia Complexes of Aquo Ions[a]

| Metal ion | $H_A = E_A/C_A$ | $C_A$ | log $K_1$(MF) | | log $K_1$(MOH) | | log $K_1$(MNH$_3$) | |
|---|---|---|---|---|---|---|---|---|
| | | | Calcd | Obsd | Calcd | Obsd | Calcd | Obsd |
| $Ag^+$ | −1.21 | 0.240 | 0.36 | 0.37 | 3.36 | 3.32 | 3.27 | 3.31 |
| $Hg^{2+}$ | 1.63 | 0.826 | 1.45 | 1.50 | 11.57 | 11.51 | 8.74 | 8.8 |
| $Pd^{2+}$ | 1.73 | 0.910 | 1.63 | 1.6[e] | 12.74 | 12.7 | 9.56 | 9.6 |
| $CH_3Hg^+$ | 1.92 | 0.708 | 1.40 | 1.70 | 9.91 | 9.59 | 7.28 | 7.6 |
| $Tl^{3+}$ | 2.12 | 0.914 | 1.94 | <4 | 12.8 | 12.8 | 9.2 | 9.2[b] |
| $Cu^{2+}$ | 2.68 | 0.466 | 1.37 | 1.27 | 6.52 | 6.66 | 4.41 | 4.27 |
| $H^+$ | 3.04 | 1.009 | 3.07 | 3.19 | 14.12 | 14.00[f] | 9.14 | 9.26 |
| $Cd^{2+}$ | 3.31 | 0.344 | 1.29 | 1.06 | 4.82 | 5.2 | 3.03 | 2.65 |
| $Ni^{2+}$ | 3.37 | 0.300 | 1.20 | 1.26 | 4.20 | 4.11 | 2.62 | 2.71 |
| $Co^{3+}$ | 3.77 | 0.875 | 3.30 | | 12.25 | 12.20 | 7.25 | 7.30 |
| $Zn^{2+}$ | 4.26 | 0.312 | 1.43 | 1.26 | 4.37 | 4.60 | 2.41 | 2.18 |
| $Co^{2+}$ | 4.34 | 0.276 | 1.33 | 1.33[d] | 3.87 | 3.90 | 2.13 | 2.10 |
| $Fe^{2+}$ | 5.94 | 0.256 | 1.59 | 1.40 | 3.58 | 3.70 | 1.53 | 1.4[c] |
| $In^{3+}$ | 6.30 | 0.818 | 5.15 | 4.6 | 11.45 | 12.0 | 4.55 | 4.0[b] |
| $Bi^{3+}$ | 6.39 | 0.904 | 5.78 | 5.84 | 12.66 | 12.6 | 4.94 | 5.0[b] |
| $Pb^{2+}$ | 6.69 | 0.413 | 2.76 | 2.08 | 5.78 | 6.3 | 2.11 | 1.6[b] |
| $Mn^{2+}$ | 7.09 | 0.223 | 1.64 | 1.40 | 3.12 | 3.41 | 1.07 | 0.8[c] |
| $Cr^{3+}$ | 7.14 | 0.721 | 5.15 | 5.20 | 10.10 | 10.05 | 3.35 | 3.4[b] |
| $Fe^{3+}$ | 7.22 | 0.841 | 6.07 | 6.04 | 11.77 | 11.80 | 3.83 | 3.8[b] |
| $UO_2^{2+}$ | 7.36 | 0.646 | 4.76 | 4.51 | 9.05 | 9.3 | 2.85 | 2.6[b] |
| $Ga^{3+}$ | 7.69 | 0.788 | 6.06 | 5.86 | 11.03 | 11.23 | 3.20 | 3.0[b] |
| $U^{4+}$ | 7.80 | 0.968 | 7.55 | 7.9 | 13.55 | 13.2 | 3.80 | 4.15[b] |
| $Zr^{4+}$ | 8.61 | 1.079 | 9.29 | 9.80 | 15.11 | 14.6 | 3.29 | 3.8[b] |
| $Y^{3+}$ | 9.37 | 0.475 | 4.45 | 4.8 | 6.65 | 6.3 | 1.07 | 1.4[b] |
| $La^{3+}$ | 9.50 | 0.396 | 3.76 | 3.6 | 5.54 | 5.7 | 0.87 | 0.7[b] |
| $Sc^{3+}$ | 9.80 | 0.691 | 6.77 | 7.04 | 9.67 | 9.4 | 1.23 | 1.5[b] |
| $Mg^{2+}$ | 10.46 | 0.178 | 1.86 | 1.82 | 2.50 | 2.58 | 0.32 | 0.26 |
| $Al^{3+}$ | 10.50 | 0.657 | 6.90 | 7.00 | 9.20 | 9.1 | 0.71 | 0.8[b] |
| $Ca^{2+}$ | 12.16 | 0.081 | 1.19 | 1.1 | 1.29 | 1.4 | −0.05 | −0.2 |

[a] Values obtained at 25 °C and infinite dilution. The aquo ions are arranged in order of increasing $H_A$, the hardness parameter derived as described in the text. [b] Estimated from the chelate-effect equation as described in text. [c] Estimated by other authors. [d] Estimated by interpolation from $Fe^{2+}$ and $Ni^{2+}$ values. [e] Estimated from LFER. [f] Used instead of 15.74 for reasons discussed in a future paper.

account the error limits assigned to the data used for the fit. Having obtained $E_B$ and $C_B$, the initial values of $E_A$ and $C_A$ for each acid were then adjusted to give an overall best fit. This produced better values of $E_A$ and $C_A$, since they were adjusted to a fit on three rather than on two ligands. A very useful suggestion by Yamada and Tanaka[2] was followed in fitting the parameters, in that the Fuoss equation[16] was used to remove contributions to the overall formation constant from outer-sphere complexes, since these have no bearing on metal-to-ligand bonds. However, instead of modeling log $K_{is}$ (which is $ML_{is}/ML_{os}$ where "is" refers to the inner-sphere and "os" to the outer-sphere complex), we have used log $K_{in}$ = log $(K - K_{os})$ (where $K_{in}$ is the formation constant corrected for outer-sphere complex formation), since it seems more appropriate to us to model the free energy of formation of the complex from the free metal ion and ligand than from the outer-sphere complex.

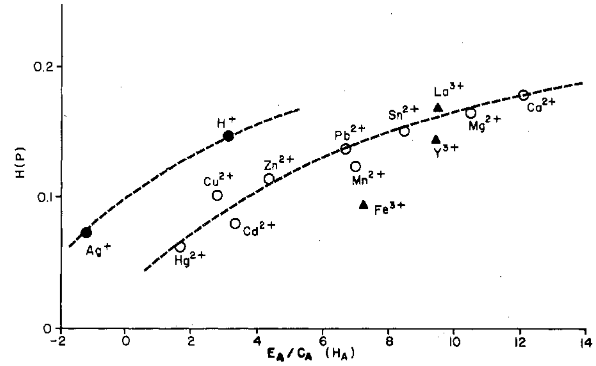

**Figure 4.** Plot of Pearon's[6] hardness parameter, $H$(P), against $H_A$ derived as described in text: ●, monovalent Lewis acids; ○, divalent Lewis acids; ▲, trivalent Lewis acids.

With $E_A$ and $C_A$ values as shown in Table I, and $E_B = -1.08$ and $C_B = 12.36$ for ammonia, log $K_1$ values for the $F^-$, $OH^-$, and $NH_3$ complexes of the acids shown in Table I can be calculated. The standard deviation between calculated and observed values is 0.24 log unit. The acids are arranged in order of increasing $H_A$. This order is similar to most other orders of hardness, e.g., Klopman,[9] Ahrland,[17] and Yamada and Tanaka,[2] but differs radically from the order of Yingst and McDaniel[18] in the position of the proton. Of particular interest is the relation of $H_A$ to the hardness parameter, which we shall call $H$(P), obtained by Pearson[19] using an approach very similar to ours from heats of formation of the halides in the gas phase. $H$(P) was defined as $[\Delta H°(F^-) - \Delta H°(I^-)]/\Delta H°(F^-)$, where $\Delta H°(F^-)$ or $\Delta H°(I^-)$ is the enthalpy change on formation of the metal–halide complex from its constituent ions in the gas phase. Plotting this parameter against $H_A$ (Figure 4), it can be seen that for the same charge very nearly the same order of hardness is obtained. The displacement in the order of hardness as a function of cationic charge can be readily understood from Figure 3 in Klopman's paper,[9] where it can be seen that ions of higher charge become relatively harder than those of lower charge as the dielectric constant of the medium is increased.

An important consideration in relation to goodness of fit in Table I is change of coordination number. It must be stressed that the $H_A$ values in Table I apply to the aquo ions only and not the same acid in some other environment. From Jørgensen's ideas on *symbiosis*,[20] we would expect that if the number of water molecules attached to the ion were to differ from one complex to another, the predictive powers of eq 1 would become somewhat poorer. Thus, it seems possible that the poorer than usual fit observed for $Cd^{2+}$ in Table I is associated with variation in coordination number, since the $Cd^{2+}$ ion can show coordination numbers from 2 to 6 and might, for example, be six-coordinate in the fluoride complex but four-coordinate in the ammonia complex. The poor fit for $Pb^{2+}$, which is also observed for $Sn^{2+}$ and $Tl^+$ (not included in Table I because the small values of log $K_1$ render $E_A$ and

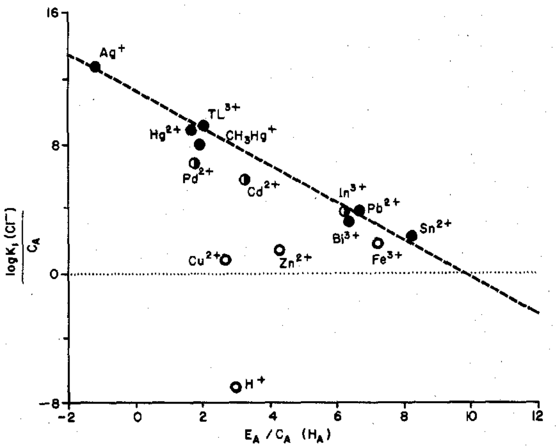

**Figure 5.** Plot of $[\log K_1(Cl^-)]/C_A$ vs. the hardness parameter $H_A$, which is $E_A/C_A$, for Lewis acids with ionic radius greater than 1.0 Å (●), between 0.8 and 1.0 Å (◑), and less than 0.8 Å (○).

$C_A$ somewhat indeterminate) may be due to the same effect, but "inert pair" ions have been observed by Williams[21] to have anomalous affinities for oxygen-donor ligands, so that this deviation may also have an electronic component to it.

Once eq 1 has been used to generate unknown formation constants for $OH^-$ and $NH_3$ complexes, as in Figures 1–3, it should be a simple matter to calculate formation constants for the complexes of other $RO^-$- and $NR_3$-type ligands, e.g., $CH_3COO^-$ or aniline. This must be approached with some caution, however. From the high $pK_a$ of $N(CH_3)_3$, it might be imagined that it would be a strong base for other Lewis acids, whereas for the majority of acids in aqueous solution, it is a very weak base because of steric hindrance. The importance of considerations of steric hindrance will become apparent.

It is found that eq 1 is unable to predict formation constants of any ligands other than those already discussed. A very convenient method of analyzing this failure is to plot $(\log K_1)/C_A$ vs. $E_A/C_A$ (eq 6), in which $E_B$ should be the slope and $C_B$ the intercept of a linear relation. This type of plot, shown for chloride ion in Figure 5, is typical of the plots obtained for other ligands with large donor atoms, e.g., $I^-$, $Br^-$, $RS^-$, $(C_6H_5)_2PC_6H_4SO_2OH$, and $R_2S$ (thiodiglycol). Large deviations from the dotted line occur for the proton and first-row divalent metal ions, with lesser deviations for $Pd^{2+}$ and $Cd^{2+}$. Drago[8] has pointed out that the number of sets of $E_A$, $C_A$, $E_B$, and $C_B$ which could be used to generate data such as in Table I is infinite and that they are related to each other by a transformation matrix and its inverse. They will, however, give exactly the same values of $\log K_1$ and so would all fail in the same way as in Figure 5. It therefore does not seem likely that a set of $E$ and $C$ parameters can exist which could simultaneously correlate the data in Table I and also formation constant data for ligands with second- or third-row donor atoms, such as $Cl^-$ in Figure 5.

The interest in Figure 5 and other such plots for ligands with large donor atoms is the cause of the observed deviations. The most attractive explanation for the failure, to our minds, is that advanced by Drago and co-workers[22] to account for the failure of their equation to predict correctly the heats of adduct formation of $Cu(hfac)_2$ (hfac = hexafluoroacetylacetonate anion) with bases such as $P(CH_3)_3$ and $S(CH_2)_4$ in solvents of low dielectric constant. It was proposed that the smaller than expected heats of adduct formation with such ligands was due to steric interaction between the large donor atom and adjacent coordinated groups, in this case the oxygens of hfac. All of the acids displaced from the line in Figure 5 are small, while most of those upon the line are large. The softness of $Zn^{2+}$ relative to $Pb^{2+}$ is indicated by both Table I and Pearson's[19] studies of gas-phase enthalpy changes on complex formation, although from the formation constants of the halide complexes in water $Pb^{2+}$ would be judged to be the softer. Steric hindrance in a complex such as that between $Zn(H_2O)_5^{2+}$ and $Cl^-$ or $PPh_3$ (i.e., octahedrally coordinated $Zn^{2+}$ with five waters and one ligand) can be visualized by construction of space-filling models. The role of steric hindrance has already been well established in organometallic chemistry by Tolman,[23] who found that steric effects can far outweigh electronic effects. The extent of the deviation from the dotted line shown by the proton in plots such as Figure 5 is related to the extent of deviation shown by the other Lewis acids that display deviations. This suggests that the cause of the deviation for the proton is the same as for the other Lewis acids, namely, steric hindrance between the chloride ion and the structured water around the proton. Support for the idea that steric hindrance may play an important part in rendering ligands with second- and third-row donor atoms much less basic than their first-row donor analogues comes from the observation[24] that it is likely in the gas-phase $PH_3$ is as strong a base as $NH_3$ but in water is almost nonbasic. The small deviation for such a small metal ion as $Fe^{3+}$ in Figure 5 represents a difficulty for the steric-hindrance interpretation of such deviations. It seems likely, however, that as the metal-to-ligand bonding becomes more ionic, sensitivity to bond deformation might become lower, so that deviations for metal ions of similar size might become smaller as $H_A$ increases.

**Table II.** $E_B$, $C_B$, and $H_B$ Parameters Calculated as Described for a Variety of Ligands[a]

| Ligand | $H_B$ | $E_B$ | $C_B$ |
|---|---|---|---|
| $F^-$ | ∞ | 1.00 | 0 |
| $OH^-$ | 0 | 0 | 14.00 |
| $NH_3$ | −0.088 | −1.08 | 12.34 |
| $Cl^-$ | −0.103 | −1.14 | 11.1 |
| $Br^-$ | −0.115 | −1.79 | 15.6 |
| $I^-$ | −0.122 | −2.81 | 23.1 |
| $S{=}C(NH_2)_2$ | −0.135 | −2.76 | 20.4 |
| $PPh_3$ | −0.118 | −2.96 | 25.0 |
| $CN^-$ | −0.189 | −6.79 | 36 |

[a] $H_B$, the ligand-hardness parameter, has a value of infinity for $F^-$ solely as a result of the initial choice of $E_B$ and $C_B$ parameters, so that no significance should be attached to this other than that $F^-$ is harder than $OH^-$.

If one accepts that the deviations in plots such as Figure 5 are not electronic in origin, the broken line can be used to calculate $E_B$ and $C_B$ values, and hence an estimate can be made of the hardness of the ligand from its $H_B$ value, which is $E_B/C_B$. $H_B$, $E_B$, and $C_B$ values for a selection of ligands are seen in Table II. Unlike other orders of hardness, the $H_A$ and $H_B$ values proposed here have very considerable predictive powers, except for the metal ions which show large deviations in Figure 5, but even these deviations are systematic. At the same time, these $H_A$ and $H_B$ values are specific to aqueous solution. Parametric correlation of thermodynamic data should come to have usefully accurate powers of prediction if its limitations are recognized, in that one cannot expect a simple correlation based upon electronic effects simultaneously to take into account additional effects such as steric strain.

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**Registry No.** $Ag^+$, 14701-21-4; $Hg^{2+}$, 14302-87-5; $Pd^{2+}$, 16065-88-6; $CH_3Hg^+$, 22967-92-6; $Tl^{3+}$, 14627-67-9; $Cu^{2+}$, 15158-11-9; $H^+$, 12408-02-5; $Cd^{2+}$, 22537-48-0; $Ni^{2+}$, 14701-22-5; $Co^{3+}$, 22541-63-5; $Zn^{2+}$, 23713-49-7; $Co^{2+}$, 22541-53-3; $Fe^{2+}$, 15438-31-0; $In^{3+}$, 22537-49-1; $Bi^{3+}$, 23713-46-4; $Pb^{2+}$, 14280-50-3; $Mn^{2+}$, 16397-91-4; $Cr^{3+}$, 16065-83-1; $Fe^{3+}$, 20074-52-6; $UO_2^{2+}$, 16637-16-4; $Ga^{3+}$, 22537-33-3; $Sn^{2+}$, 22541-90-8; $U^{4+}$, 16089-60-4; $Zr^{4+}$, 15543-40-5; $Y^{3+}$, 22537-40-2; $La^{3+}$, 16096-89-2; $Sc^{3+}$,

22537-29-7; $Mg^{2+}$, 22537-22-0; $Al^{3+}$, 22537-23-1; $Ca^{2+}$, 14127-61-8; $F^-$, 16984-48-8; $OH^-$, 14280-30-9; $NH_3$, 7664-41-7; $Cl^-$, 16887-00-6; $Br^-$, 24959-67-9; $I^-$, 20461-54-5; $S{=}C(NH_2)_2$, 62-56-6; $PPh_3$, 603-35-0; $CN^-$, 57-12-5; $(C_6H_5)_2P(C_6H_4\text{-}SO_3^-)$, 65355-51-3; $As(C_6H_4\text{-}SO_3^-)_3$, 65355-50-2; $HO(CH_2)_2S(CH_2)_2OH$, 111-48-8; py, 110-86-1; $CH_3COO^-$, 71-50-1; $SCN^-$, 1111-68-8; glycine, 56-40-6; NTA, 139-13-9; EDDA, 5657-17-0; DTMA, 55682-22-9; HEDTRA, 150-39-0; EDTA, 60-00-4.

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# Anation of Aquopentaamminerhodium(III) Cation by Chloride in Aqueous Solution. A Low, Variable Ionic Strength Approach for Studying Anation Reactions

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The high, constant ionic strength conditions conventionally employed in studying the kinetics of anation reactions yield data which have inherent interpretational shortcomings. Notably, pure rate and equilibrium constants cannot be extracted from such data. This paper reports the study of the $Cl^-$ anation of $Rh(NH_3)_5H_2O^{3+}$ by a low, variable ionic strength approach which overcomes these shortcomings. The kinetics of the anation reaction were studied at 40–70 °C with $\mu \leq 0.3$ M, $0.01 < [Cl^-] < 0.3$ M, and $[H^+] = 0.01$ M. The ion pairing of the reactants was also studied spectrophotometrically at 15–40 °C and potentiometrically at 25 °C under similar concentration conditions. The data from these three types of experiments were fitted to various models using the Davies equation with an adjustable parameter $b$ to correct for activity coefficient variations. The results confirm an interchange mechanism for the anation reaction. The zero ionic strength ion-pair association constant $K^\circ_{Cl^-}$ as well as the $b$ parameter are temperature independent. The interchange rate $k^\circ_I$ has $\Delta H^\ddagger = 26.2$ kcal/mol and $\Delta S^\ddagger = 3.3$ cal/(deg mol). Experiments with significant amounts of $ClO_4^-$ present show that it also pairs to the complex to such an extent that $K^\circ_{ClO_4^-} \approx K^\circ_{Cl^-}$. All three types of data can be fitted to a model having $K^\circ_{Cl^-} = 26.5 \pm 0.8$ $M^{-1}$ and $b = 0.91 \pm 0.05$. Comparisons of $k^\circ_I$ values with rates of water exchange suggest that bond making is less important with this Rh(III) complex than with other presumably associatively activated metal complexes. Remaining ambiguities regarding the mechanism of the reaction are discussed.

## Introduction

The conventional approach for studying the anation kinetics of octahedral transition-metal complexes in aqueous solution is to maintain the medium at a high constant ionic strength by the addition of substitutionally inert salts such as $NaClO_4$.[1,2] It has been pointed out, however, that data obtained under such conditions have two serious interpretational shortcomings when used to obtain mechanistic information.[1,3,4] This paper reports the study of the anation reaction

$$Rh(NH_3)_5H_2O^{3+} + Cl^- \rightarrow Rh(NH_3)_5Cl^{2+} + H_2O \qquad (1)$$

by a low, variable ionic strength approach which appears to overcome these problems to a substantial degree.

The high, constant ionic strength condition is usually employed in order to maintain a constant value for the activity coefficients of the reactants. However, it is almost certain that activity coefficients are not constant in such studies. There are abundant data on simple salt mixtures that show that the activity coefficients do vary as the relative amounts of two salts are varied at constant ionic strengths above about 0.3 M.[5] Thus the common practice of interpreting rate data from constant ionic strength studies of anation reactions solely in terms of a stoichiometric mechanism is seriously open to question. A part or all of the rate characteristics used to support a certain mechanism could be due simply to activity coefficient variations. Unfortunately, there are no reliable methods for estimating the magnitude of such variations for these anating systems.[3]

The second interpretational problelm is that pure rate and equilibrium constants cannot be extracted from such data if a component of the inert salt (i.e., $ClO_4^-$) ion pairs to the complex ion. As an example consider a reaction judged to proceed by an ion-pair interchange mechanism.[2] If $ClO_4^-$ ion pairs to an extent comparable to that of the attacking anion $X^-$, kinetic and thermodynamic data can only yield the composite constants[1,3]

$$k_{\text{calcd}} = k_I K_X/(K_X - K_P)$$
$$K_{\text{calcd}} = (K_X - K_P)/(1 + K_P \mu)$$

($K_X$ and $K_P$ are the concentration quotients for the ion pairing of $X^-$ and $ClO_4^-$, respectively, to the complex, $\mu$ is the ionic strength and $k_I$ is the rate constant for the interchange of the $X^-$ ion-paired complex.) It can be seen that insight into the factors controlling reactivity cannot be gained from such parameters. Comparing $k_{\text{calcd}}$ and/or $K_{\text{calcd}}$ values for a series of systems is a fruitless exercise since one cannot determine

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