THE COORDINATION MODEL FOR NON-AQUEOUS SOLVENTS

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Abstract - The historical development of the coordination model is briefly discussed. The use of this approach to indicate that the essential solvent properties involve donor-acceptor interactions and solvation is presented. Various ways to estimate these solvent properties are critically discussed.

INTRODUCTION

The coordination model for non-aqueous solvent behavior now seems like such an obvious approach to this problem that I would like to begin this article by briefly reviewing the state of the art when it was first proposed in 1961. At that time many of the weaker organic bases that did not coordinate to metal ions in aqueous solution, for example acetonitrile, were considered non-coordinating polar solvents. The chemistry in non-aqueous solvents was being explained (1) in terms of the solvent systems concept; a model based on the autoionization of these solvents:

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]  
\[ \text{POCl}_3 \rightleftharpoons \text{POCl}_2^+ + \text{Cl}^- \]  
\[ \text{N}_2\text{O} \rightleftharpoons \text{NO}^+ + \text{NO}_3^- \]

In analogy to chemistry based on the ionization of water, \((\text{POCl}_3 \rightleftharpoons \text{POCl}_2^+ \text{H}^+ \text{Cl}^- \text{SO}_2\text{H}_2\text{O}, \text{POCl}_2^+ \text{H}^+ \text{Cl}^- \text{NO}_3^-)\) an acid in these solvents was defined as a substance that coordinates chloride ion (or in equation 3, nitrate ion) and increases the concentration of POCl_2^+. (or in equation 3, NO^+). Addition of the Lewis acid FeCl_3 reportedly gave rise to POCl_2^+ and FeCl_4^-. Titration of this iron solution with a source of chloride ion (the base in this solvent) involved conversion of the POCl_2^+ to POCl_3. The analogy to chemistry in water was pushed to the point of defining a pPOCl_2^+ scale analogous to pH. Though FeCl_4^- could be observed, all attempts to find comparable concentrations of POCl_2^+ failed. A base was defined in this solvent as a substance that coordinates to POCl_2^+ (or NO^+) and increases the concentration of the anion formed in the autoionization reaction. Some energetically unbelievable ionization schemes were proposed (2) for solvent species, for example:

\[ 2 \text{SO}_2 \rightleftharpoons \text{SO}_2^+ + \text{SO}_2^2^- \]  
\[ (\text{C}_2\text{H}_5)_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5^+ + \text{OC}_2\text{H}_5^- \]

In equation 4, thionyl compounds are considered acids and sulfites as bases. In equation 5, \(\text{C}_2\text{H}_5^+\) is the acid and \(\text{OC}_2\text{H}_5^-\) the base.

The solvent systems concept completely dominated the thinking in the area of non-aqueous solvents in the 1950's and its virtues were preached by some of the most powerful European chemists who worked in this area. In a courageous break with tradition, Groeneveld (3) proposed that in oxyhalide solvents coordination to an acid solute occurred through the solvents' oxygen atoms lone pair of electrons. Spectroscopic (4) and x-ray diffraction (5) studies soon showed that adducts formed by Lewis acids with many oxychloride molecules coordinated to the oxygen atom. A whole host of radiotracer experiments (6) were reported, many of which provided additional evidence regarding the inadequacy of the solvent system concept as applied to certain solvents. However, no new generalized approach for explaining all of the experimental results evolved.
In 1961, Meek and Drago (7) demonstrated that the solution properties of anhydrous iron(III) chloride in triethylphosphate are very similar to those in phosphorus oxychloride. Solution spectra as well as acid-base conductometric titration results were comparable in the two solvents. The tetrachloroferrate ion, FeCl₄⁻, was shown to be a prominent species. Since the solvent triethylphosphate cannot furnish chloride ion, the possibility that the solvent is the source of chloride ion for forming FeCl₄⁻ (as was produced for POCl₃ in equation 1) is excluded. The following set of equilibria were offered to account for the formation of FeCl₄⁻:

\[
\text{FeCl}_3 + Y_3\text{PO} \rightleftharpoons [\text{FeCl}_3\text{OPY}_3]_m \rightleftharpoons (1/x+1)\text{FeCl}_{3-x}(\text{OPY}_3)_n^{x^+} + (x/x+1)\text{FeCl}_4^- \\
\text{FeCl}_{3-x}(\text{OPY}_3)_n + x\text{Cl}^- 
\]

where Y can be Cl, OEt, etc.

This experiment showed that solvent ionization is not required to generate FeCl₄⁻. The equations proposed suggest that donor solvent coordination and halide ion displacement from the solute FeCl₃ could give rise to this species. This role of solvent behavior was referred to as the coordination model for non-aqueous solvent chemistry. The acid species in PO(OEt)₃ are the cationic iron complexes (8) and the acid-base titration with chloride ion involves converting all of these iron(III) cations to FeCl₄⁻. Since POCl₃⁺ has not been found to be present in concentrations equal to FeCl₄⁻ in POCl₃ and since the coordination model has been shown to be consistent with all the structural, spectral, conductometric and radiochemical results on the oxyhalide and oxide solvents, it was offered (9) as a viable alternative to the solvent system concept.

The extension of these findings in our laboratory proceeded along three lines:

1. A series of investigations (10) were carried out to establish that various weakly basic, non-aqueous solvents could function as ligands to transition metal ions. Octahedral and tetrahedral complexes, M₃⁻L₃⁻, where L = CH₃CN, \((\text{CH}_3)_2\text{SO}\), \(\text{RC(O)NR}_2\), \(\text{OP(NR}_2\)), and \(\text{CH}_3\text{OH}\) were synthesized and identified.

2. The behavior of FeCl₃ in a series of non-aqueous solvents was investigated (8) and shown to conform to the equilibria represented by equation 6.

3. Cationic complexes [FeS₃]⁺ClO₃⁻ were synthesized (where S refers to basic solvent molecules) titrated with chloride ion and the resulting iron-chloro complexes identified spectrally. These results were used (8,9) to establish the existence of the cationic species proposed in equation 6.

After much initial resistance, the aspects of the coordination model presented above have been accepted (11) by the solvent systems advocates. Much of the effort now being expended in the area of non-aqueous solvents involves obtaining fundamental information about the nature of the solvent and solute that enables one to understand the factors influencing the position of the equilibrium in equation 6.

ELUCIDATION OF THE ESSENTIAL SOLVENT PROPERTIES

One of the major contributions of the coordination model is that it focuses attention on the essential solvent properties for understanding the reactivity of solutes with solvents. Since details can be found in the original references and in review articles (9), a brief overview will be given here.

The next step in extending our understanding of the coordination model involves obtaining a quantitative expression of the factors that influence the position of the equilibrium in equation 6. This is most easily accomplished by focusing upon the displacement of a single halide ion. The essential aspects of the series of equilibria represented by equation 6 are summarized by the simpler general equations written below:

\[
pS(l) + MX(s) \rightleftharpoons MS_pX(sol)^{+n} \rightleftharpoons MS_q(sol)^+ + X(sol)^- 
\]

This equation represents the ionization of a solid substance of general formula MX in a basic solvent S. The first equilibrium represents the solution of MX to form a neutral adduct with p molecules of solvent coordinated. In the second equilibrium, the coordinated anion is displaced and q molecules of solvent are coordinated to the cation. The first equilibrium determines the extent to which MX dissolves. In the coordination model approach, the essen-
tial factors influencing the position of an equilibrium are determined by writing an energy cycle that connects the solution process to a gas phase reaction. This is illustrated for the first step of equation 7 in Fig. 1.

\[
\begin{align*}
MX(g) + pS(g) & \xrightarrow{\Delta G_{AB}(g)} MXS(g) \\
\uparrow \Delta G_{sub} & \uparrow \Delta G_V & \downarrow \Delta G_{sol} \\
MX(s) + pS(l) & \xrightarrow{\Delta G_{sol}} MXS(sol)
\end{align*}
\]

Fig. 1 An enthalpy cycle for the solubility of MX

The position of the equilibrium in solution is a free energy consideration and has contributions to it from the gas phase basicity of S and the gas phase acidity of MX (the step \( \Delta G_{AB}(g) \)), the free energy of sublimation of MX (\( \Delta G_{sub} \)), the free energy of vaporization of S (\( \Delta G_V \)) and the free energy of solvation of MXS (\( \Delta G_{sol} \)). Enthalpy and entropy terms are associated with all of these steps and contribute to our quantitative understanding of the solution process.

The second equilibrium in equation 7 can also be represented by an energy cycle as shown in Fig. 2.

\[
\begin{align*}
MXS(g) + nS(g) & \xrightarrow{\Delta G_{GSX}} MS_q^+(g) + X^-(g) \\
\uparrow \Delta G_{ds} & \uparrow \Delta G_V & \downarrow \Delta G_{sol} & \downarrow \Delta G_{sol} \\
MXS(sol) + nS & \xrightarrow{\Delta G_{sol}} MS_q^+(sol) + X^-(sol)
\end{align*}
\]

Fig. 2 An energy cycle for the ionization of a solute

The ionization process depends upon the free energy of desolvation of MXS (\( \Delta G_{ds} \)), the free energy of vaporization of S (\( \Delta G_V \)), the free energy of solvation of MSq^+ (\( \Delta G_{sol} \)) and X^- (\( \Delta G_{sol} \)) and the relative basicity of S and X^- (\( \Delta G_{GSX} \)). Again, there are entropy and enthalpy terms associated with each of the steps in this cycle that can influence the ionization process (12). Indeed, solubility and solvation are very complex processes. In view of this complexity, how can one arrive at a generalized working approach to the correlation and prediction of the nature of solutes in various solvents? The equation for ionization of a solute involves the relative coordinating abilities of S and X^- to the MSq^+ cation and the difference in the solvation of MSpX and MSq^+ + X^- by the solvent. Stronger donor solvents will be more effective in the displacement of X (all other factors being the same). Better solvating solvents will solvate the ionic species more extensively than MSpX resulting in solute ionization (13). Thus the coordination model as applied to solvent variation for a given solute focuses upon the solvent's coordinating ability and solvating ability. In this context, the solvating ability includes specific and non-specific interactions and excludes only those Lewis acid-base reactions involving the first coordination sphere of the Lewis acid.

When the solvent is held constant and the ionization of various solutes is compared, the basicity of X^- versus S toward MSq^+ is important, as is the difference in solvation of MSpX and MSq^+ + X^-.

Quantitative understanding of the general problem of solvation and solute ionization have been hampered by the difficulty of obtaining information about the gas phase thermodynamics of ion-molecule reactions. This problem is being rectified by recent advances in the area of ion-cyclotron resonance (ICR). Enthalpies for multiple coordination steps of ligands to metal ions are being probed in the gas phase (14). It is hoped that investigators in this area will design experiments that measure coordination processes in the gas phase that are relevant to the equilibria involved in the coordination model. A complete evaluation of all the steps involved in the reaction of several amines with aqueous hydronium ion provides an illustration of the coordination model and of the application of ICR data to processes in aqueous solvents (15).

Several important synthetic concepts can be understood by application of the
coordination model. Water is a very good ionizing solvent because it has a high dielectric constant and also because it is amphoteric. The water molecule can function as a Lewis base, coordinating to the cation, and it can behave as a Lewis acid by hydrogen bonding to the anion. For example $K^+OH^-$ is converted to $K^+(aq)$ and $OH^-(aq)$ when it is dissolved in water. When potassium hydroxide dissolves in $(CH_3)_2SO$, the $K^+$ coordinates to the solvent $K[(CH_3)_2SO]_n^+$ but the $OH^-$ is only weakly solvated relative to the situation in water. The result is a very strongly basic anion in dimethyl sulfoxide (16). In super acid solvents, solution of a solute occurs because the anion is solvated extensively by the solvent. The weakly solvated cation is a very acidic species (17,18). Carbonium ions have been made in this way (17). The cycle presented in Fig. 2 also suggests mixed solvents (one a good donor solvent toward the desired solute and the other a good solvating solvent) can be designed to dissolve and ionize solutes. As can be seen from the brief coverage and few examples given here, the coordination model is fundamental to the interpretation of reactions in solution. The general concepts find applicability in many areas of chemistry. Recognition of this fact has resulted in the coordination model becoming an integral part of the more modern textbooks on Inorganic Chemistry (19).

ESTIMATION OF THE ESSENTIAL SOLVENT PROPERTIES

Quantitative estimates of the essential solute properties enabling one to understand the position of the equilibrium in equation 6 for various materials would require the evaluation of enthalpies and entropies for every step in the cycles presented in Figs. 1 and 2. Quantitative estimates of the essential solution properties of solvents would be derived by similar studies involving representative solutes in many solvents. From the massive amount of data collected, one would hope to derive generalizations with predictive powers. Since a massive effort would be required to solve the problem in this manner, indirect methods have been sought. Two basic approaches to the problem have been attempted:

(1) Donor and acceptor numbers

(2) Fundamental studies of coordination and solvation

Donor numbers (11) are based upon the enthalpy of the reaction of a basic solvent with a 1,2-dichloroethane solution of $SbCl_5$. Acceptor numbers pertain to anion bonding and are based upon the relative $^31P$ chemical shifts of $(C_2H_5)PO$ in various solvents. The dissociation of the anion is claimed to depend upon the donor number and acceptor number. A high dielectric constant is claimed to be mainly responsible for breaking up the ion pair and not with dissociation of the anion from the metal (20). These claims (11) are not correct for they are in violation of the experimentally observed behavior of iron(III) chloride in dimethyl sulfoxide (DN = 29.8) and pyridine (DN = 33.1). Far more extensive displacement of chloride from the coordination sphere of the iron(III) occurs in dimethylsulfoxide. Later we shall return to the question, what do donor numbers mean?

The approach labeled fundamental studies of coordination and solvation recognizes that the equilibria in equation 7 have contributions from entropy and enthalpy terms. However, since fundamental understanding is the goal, a decision was made to begin with an evaluation of the enthalpy terms. Recall bond strengths are given by enthalpies. The solution process is also clearly broken up into parts -- coordination and solvating tendency. Coordination is to be evaluated under conditions where solvation is minimal (in solvents such as hexane and CCl$_4$). The solvating tendency toward an acidic solute is measured under conditions where coordination of the solute to the cation does not occur (cations such as R.N$^+$). In an acidic solvent, coordination of the anion to the solvent becomes important and the problem is reformulated accordingly. Once this fundamental information is obtained, one can look at qualitative trends in reactivity and determine if they are dominated by the understood effects. If not, more detailed study of the coordination process including entropy determination will have to be investigated and understood.

THE E AND C APPROACH

Ideally, gas phase enthalpies of adduct formation are desired in order to understand coordinate bond strengths. In view of the difficulty involved in accurately obtaining this data for neutral acid-base adducts, solvation minimized data (measured in CCl$_4$ or hexane) have been collected. These enthal-
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The empirical set of parameters given in Table 1 for a base, $E_B$ and $C_B$, and for an acid, $E_A$ and $C_A$, which when substituted into the following equation reproduce (21,22) enthalpies of adduct formation to within ± 0.2 kcal mol$^{-1}$:

$$\Delta H = E_A E_B + C_A C_B$$

(8)

The $E_A E_B$ products parallel our qualitative ideas about the trends in electrostatic bonding in the adducts and the $C_A C_B$ products parallel the trends in covalent bonding. The two-term equation accommodates the reversals in donor order that are known to occur when coordination to soft and charged acids (23) are compared.

TABLE 1. $E$ and $C$ numbers for various acids and bases

<table>
<thead>
<tr>
<th>Formula</th>
<th>$E_A$</th>
<th>$C_A$</th>
<th>$w^b$</th>
<th>C/E</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. I$_2$</td>
<td>1.00*</td>
<td>1.00*</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2. ICl</td>
<td>5.10</td>
<td>0.830</td>
<td></td>
<td>0.16</td>
</tr>
<tr>
<td>3. C$_2$H$_5$SH</td>
<td>0.99</td>
<td>0.198</td>
<td></td>
<td>0.20</td>
</tr>
<tr>
<td>4. C$_2$H$_5$OH</td>
<td>4.33</td>
<td>0.442</td>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>5. p-C$_6$H$_5$SH</td>
<td>4.18</td>
<td>0.404</td>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>6. p-FC$_6$H$_4$OH</td>
<td>4.17</td>
<td>0.446</td>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>7. m-FC$_6$H$_4$OH</td>
<td>4.42</td>
<td>0.506</td>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>8. p-CIC$_6$H$_5$OH</td>
<td>4.34</td>
<td>0.478</td>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>9. m-CF$_3$C$_6$H$_4$OH</td>
<td>4.48</td>
<td>0.530</td>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td>10. (CH$_3$)$_3$COH</td>
<td>2.04</td>
<td>0.300</td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>11. CF$_3$CH$_2$OH</td>
<td>3.88</td>
<td>0.451</td>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td>12. (CF$_3$)$_2$CHOH</td>
<td>5.93</td>
<td>0.623</td>
<td>1.10</td>
<td>0.11</td>
</tr>
<tr>
<td>13. C$_6$H$_6$NH</td>
<td>2.54</td>
<td>0.295</td>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td>14. CHCl$_3$</td>
<td>3.02</td>
<td>0.159</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>15. (CH$_3$)$_3$SnCl</td>
<td>5.76</td>
<td>0.03</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>16. BF$_3$(g)</td>
<td>9.88</td>
<td>1.62</td>
<td></td>
<td>0.16</td>
</tr>
<tr>
<td>17. B(CH$_3$)$_3$(g)</td>
<td>6.14</td>
<td>1.70</td>
<td></td>
<td>0.28</td>
</tr>
<tr>
<td>18. Al(CH$_3$)$_3$</td>
<td>16.9</td>
<td>1.43</td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>19. SO$_2$</td>
<td>0.920</td>
<td>0.808</td>
<td></td>
<td>0.88</td>
</tr>
<tr>
<td>20. Cu(hfac)$_2$</td>
<td>3.46</td>
<td>1.32</td>
<td></td>
<td>0.38</td>
</tr>
<tr>
<td>21. H$_2$O</td>
<td>1.64</td>
<td>0.571</td>
<td></td>
<td>0.35</td>
</tr>
<tr>
<td>22. CH$_3$Co(DMG)$_2$</td>
<td>9.14</td>
<td>1.53</td>
<td></td>
<td>0.17</td>
</tr>
<tr>
<td>23. Zn[N(Si(CH$_3$)$_3$)$_2$]$_2$</td>
<td>5.16</td>
<td>1.07</td>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td>24. Ni(TFACCAM)$_2$</td>
<td>3.38</td>
<td>0.640</td>
<td></td>
<td>0.19</td>
</tr>
<tr>
<td>25. NiMDPT</td>
<td>3.94</td>
<td>0.500</td>
<td></td>
<td>0.13</td>
</tr>
<tr>
<td>26. $\pi$-allyl PdCl</td>
<td>3.41</td>
<td>0.980</td>
<td>3.1</td>
<td>0.29</td>
</tr>
<tr>
<td>27. RhCODCl</td>
<td>4.93</td>
<td>1.25</td>
<td>6.3</td>
<td>0.25</td>
</tr>
<tr>
<td>28. Rh(CO)$_2$Cl</td>
<td>8.72</td>
<td>2.02</td>
<td>11.3</td>
<td>0.23</td>
</tr>
<tr>
<td>29. ZnTPP</td>
<td>5.15</td>
<td>0.620</td>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td>30. CoTPP</td>
<td>4.44</td>
<td>0.58</td>
<td></td>
<td>0.13</td>
</tr>
<tr>
<td><strong>Bases</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>31. NH$_3$</td>
<td>1.15</td>
<td>4.75</td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>32. CH$_3$NH$_2$</td>
<td>1.30</td>
<td>5.88</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>33. (CH$_3$)$_2$NH</td>
<td>1.09</td>
<td>8.73</td>
<td></td>
<td>8.0</td>
</tr>
</tbody>
</table>
34. \((\text{CH}_3)_2\text{N}\) & 0.808 & 11.54 & 14.2
35. \(\text{CH}_3\text{CN}\) & 0.886 & 1.34 & 1.5
36. \((\text{CH}_3)_2\text{NCN}\) & 1.10 & 1.81 & 1.7
37. \(\text{CH}_3\text{CON}(\text{CH}_3)_2\) & 1.32* & 2.58 & 2.0
38. \(\text{CH}_3\text{COOC}_2\text{H}_5\) & 0.975 & 1.74 & 1.8
39. \((\text{CH}_3)_2\text{CO}\) & 0.937 & 2.33 & 2.5
40. \((\text{C}_2\text{H}_5)_2\text{O}\) & 0.936 & 3.25 & 3.5
41. \(\text{O(\text{CH}_2)}_4\text{O}\) & 1.09 & 2.38 & 2.2
42. \((\text{CH}_2)_4\text{O}\) & 0.978 & 4.27 & 4.4
43. \(\text{HC(S)N(\text{CH}_3)}_2\) & 0.76 & 8.19 & 10.8
44. \((\text{CH}_3)_2\text{SO}\) & 1.34 & 2.85 & 2.1
45. \((\text{CH}_3)_4\text{O}\) & 1.38 & 3.16 & 2.3
46. \((\text{CH}_3)_2\text{S}\) & 0.343 & 7.46 & 21.8
47. \((\text{C}_2\text{H}_5)_2\text{S}\) & 0.339 & 7.40* & 21.8
48. \(\text{C}_5\text{H}_5\text{NO}\) & 1.34 & 4.52 & 3.4
49. \(\text{C}_5\text{H}_6\text{NO}\) & 1.36 & 4.99 & 3.7
50. \((\text{CH}_3)_3\text{P}\) & 0.838 & 6.55 & 7.8
51. \(\text{C}_6\text{H}_4\) & 0.280 & 0.590 & 2.1
52. \(\text{C}_9\text{H}_{18}\text{NO(TMPNO)}\) & 0.915 & 6.21 & 6.8
53. \(\text{HC(C}_2\text{H}_4)_3\text{N}\) & 0.700 & 13.2 & 18.9
54. \(\text{C}_6\text{H}_{15}\text{O}\) & 1.08 & 3.76 & 3.5
55. \((\text{CH}_3)_2\text{Se}\) & 0.217 & 8.33 & 38.4
56. \(\text{C}_5\text{H}_6\text{C(\text{CH}_2)}_3\text{P}\) & 0.548 & 6.41 & 11.7
57. \([\text{(CH}_3)_2\text{N)]_3\text{PO}\) & 1.52 & 3.55 & 2.3
58. \(\text{C}_5\text{H}_5\text{N}\) & 1.17 & 6.40 & 5.5
59. \(\text{CH}_3\text{C}_4\text{H}_4\text{N}\) & 1.26 & 6.47 & 5.1
60. \(\text{N-methyl Imidazole}\) & 0.934 & 8.96 & 9.6

aFor a more complete list see references 22 and 39. Error limits for the parameters are also given in these articles.

bSystems for which a \(W\) is reported should be used in the equation \(-\Delta H + W = E\text{E} + C\text{C}\), vide infra.

cFor acid 20 hfac is hexafluoroacetylacetone, for 22 DMG is dimethylyglyoximate, for 24 TFACCAM is trifluoroacetylcamphorato, for 29 and 30 TPP is tetraphenylporphine, for base 52 C9H19NO is the free radical 2,2,6,6-tetramethylpiperidine-N-oxyl, for 54 C6H10O is 7-oxabicyclo[2.2.2]heptane.

Structural formulae are readily written for the acids and bases from the information given.

The reversals in donor orders that can occur when an acid is varied is illustrated by plotting (24) the \(E\) and \(C\) parameters as shown in Fig. 3. One plots \(-\Delta H/(C\text{C} + E\text{E})\) on the vertical axis and \((C\text{C} - E\text{A})/(C\text{C} + E\text{A})\) on the horizontal. The order of increasing donor strength is given for a particular acid by calculating \((C\text{C} - E\text{A})/(C\text{C} + E\text{A})\), and reading the base sequence at that point. When two lines intersect in this figure, the donor order reverses on opposite sides of the intersection. Bases with similar \(C\text{C}/E\text{C}\) ratios give non-intersecting lines in Fig. 3. For these systems, the same order of donor strength is obtained for all acids studied (25).

The interactions incorporated by the \(E\) and \(C\) model are those which involve sigma bond formation. Systems in which steric effects exist cannot be incorporated into the scheme. A very important application of the model involves its use for the prediction of what a normal sigma bonding interaction is. When abnormal situations arise they can be readily recognized and probed.
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Fig. 3. Base donor orders toward different acids
with spectroscopic techniques to ascertain the cause of the deviation. The establishment of significant \( \pi \)-backbond stabilization in a metal cluster system illustrates this application (26). In a similar application, a free radical ligand complexed to a transition metal system and underwent a significant antiferromagnetic interaction. It could be shown that the spin-pairing made no contribution to the adduct bond strength (27) by using the E and C approach.

In addition to the correlative and predictive properties of the E and C model, a theoretical justification for its existence has been offered (28). Having obtained a fundamental understanding of coordination, we are now in a position to use this understanding to determine if more complex phenomena are dominated by coordinate bond strengths. This is the subject of a recent review (29).

Briefly, in an experiment in which the change in some property of an acid, \( \Delta X \), is measured as bases are varied, one can write:

\[
\Delta X = E_A' - E_B + C_A' - C_B
\]  

Selecting a series of bases in the correlation, a series of simultaneous equations can be written and solved for the two unknowns \( E_A' \) and \( C_A' \). If a reasonable fit is obtained, dominance of the chemistry by coordinate bond strengths is indicated. In this type of application, care must be taken to select bases with different \( C_B/E_B \) ratios. In a purely qualitative type of application where no measured value is available for \( \Delta X \), a base ordering for a qualitative sort of observation is made. By referring to a plot like Fig. 3, one can determine if the observed order corresponds to any point on the \( (C_A - E_A)/(C_A + E_A) \) axis. If it does, predictions about the influence of other bases in the E and C correlation can be made. If the order does not agree with any order found on the plot, some factor other than coordinate bond strength is dominating the chemistry in at least some of the systems. Though this discussion has been in terms of experiments in which an acid property is measured as bases are varied, it also applies to systems in which a base property is studied as acids coordinate. The acid counterpart of Fig. 3 is given in reference 24.

Using the approach described above, the E and C parameters have been offered (29) as a replacement of \( pK_B \) data as a criterion for coordinate bond strength. The \( pK_B \) has to be one of the worst quantities that one could use to estimate coordinating tendencies of bases to anything other than a proton in water.

One has to be impressed by the wide range of base functional groups and types of Lewis acids included in the E and C correlation. No other attempt to parameterize chemical reactivity has come close to the E and C model in versatility and accuracy. For more details about experimental procedures for determining E and C parameters the reader is referred to reference 22. For more details on the applications and uses of the parameters the reader is referred to reference 29.

There are many ionic systems for which a calorimetric determination of the enthalpy of binding cannot be carried out in a poorly coordinating medium. As mentioned earlier, ion cyclotron resonance is a powerful tool for obtaining coordinate bond strengths on these systems. A recent finding permits the correlation of all of this data along with that for neutral adducts to a single empirical equation (30).

**DONOR NUMBERS**

We note that donor numbers are in violation of two important points mentioned in the previous section. First, they provide a single scale basicity order. Second, they have not been measured in poorly solvating solvents. In the next section we shall see that enthalpies measured in 1,2-dichloroethane have extensive contributions from solvation. In view of the solvation problem one can question whether or not donor numbers are dominated by coordinate bond strengths. If one substitutes the donor number for \( \Delta X \) in equation 9 and uses known \( E_B \) and \( C_B \) numbers for the bases (Table 1), very poor fits are obtained in the solution for \( E_A \) and \( C_A \). However, the deviations are not random. The weak adducts (DN<22) all had positive deviations from the best fit values and the strong adducts (DN>25) all had negative deviations as can be seen by comparing column 1 of Table 2 with column 2. This suggests that in attempting to compensate for large solvation effects in the strong adducts, the parameters are overcompensating the predicted enthalpies of the weak adducts. A 1.0 kcal mole\(^{-1}\) solvation energy is reported when enthalpies for weak adduct formation are studied in 1,2-dichloroethane instead of \( \text{CCl}_4 \) (31). We are able to fit
(32) the donor numbers corrected by 1.0 kcal mole\(^{-1}\) of the weakly interacting systems to equation 9 "EA" = 14.4 and "CA" = 1.17. The bases selected for this E and C analysis and the fit obtained is shown in column 3 of Table 1. Since these E and C parameters fit the solvation-minimized data for ethyl acetate reported earlier and since the E, C, and W parameters fit the weak donors in 1,2-dichloroethane, we suggest that these EA and CA parameters for SbCl\(_5\) replace the tentative values reported earlier (22).

If one uses these new parameters (E, C, and W) for SbCl\(_5\) to predict the enthalpies of adduct formation for some of the stronger donors in the donor number correlation, the values in parentheses are obtained. A plot of these values versus the deviation of experimental and calculated results shows that as \(\Delta H\) increases solvation increases. We propose that as the base-antimony interaction increases, the antimony-chlorine bond becomes more ionic and the chlorines in the adduct are more extensively solvated by the solvent than is the case for weaker adducts. The abruptness of the onset of this extra stabilization is surprising. Triethyl phosphate (DN = 23.4) obeys equation 7 but DMA (DN = 27.8) does not. The data for DMF (DN = 26.6) does not fit this plot. Apparently, E and C predicted enthalpies in the 21-23 kcal mole\(^{-1}\) range may or may not have extensive solvation depending upon the solvating properties of the base.

<table>
<thead>
<tr>
<th>Lewis Base</th>
<th>E and C Calc. (-\Delta H) (1^a) (kcal mole(^{-1}))</th>
<th>Exptl. (-\Delta H) (1^b) (kcal mole(^{-1}))</th>
<th>E, C and W Calc. (-\Delta H) (2^b) (kcal mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)CN</td>
<td>16.5</td>
<td>14.1</td>
<td>15.3</td>
</tr>
<tr>
<td>O(-CH(_2)-CH(_2)-)(_2)O</td>
<td>21.9</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>CH(_3)COOCH(_3)</td>
<td>17.4</td>
<td>16.5</td>
<td>15.9</td>
</tr>
<tr>
<td>CH(_3)COOC(_2)H(_5)</td>
<td>18.8</td>
<td>17.1</td>
<td>17.1</td>
</tr>
<tr>
<td>(CH(_3))(_2)CO</td>
<td>20.1</td>
<td>17.0</td>
<td>17.9</td>
</tr>
<tr>
<td>(C(_2)H(_5))(_2)O</td>
<td>21.6</td>
<td>19.2</td>
<td>18.6</td>
</tr>
<tr>
<td>(-CH(_2)-CH(_2)-)(_2)O</td>
<td>23.9</td>
<td>20.0</td>
<td>20.1</td>
</tr>
<tr>
<td>(C(_2)H(_5))(_3)PO</td>
<td>24.9</td>
<td>23.4</td>
<td>22.7</td>
</tr>
<tr>
<td>CH(_3)CON(CH(_3))(_2)</td>
<td>25.9</td>
<td>27.8</td>
<td>(23.0)</td>
</tr>
<tr>
<td>(CH(_3))(_2)SO</td>
<td>26.7</td>
<td>29.8</td>
<td>(23.6)</td>
</tr>
<tr>
<td>C(_5)H(_5)N</td>
<td>31.2</td>
<td>33.1</td>
<td>(25.2)</td>
</tr>
<tr>
<td>[(CH(_3))(_2)N(_2)]PO</td>
<td>31.0</td>
<td>38.8</td>
<td>(27.0)</td>
</tr>
<tr>
<td>CH(_3)C(_5)H(_5)NO</td>
<td>36.3</td>
<td>36.3</td>
<td>(26.3)</td>
</tr>
</tbody>
</table>

\(^a\)This is the combined fit of strong and weak adducts to equation 9.

\(^b\)This is the fit of the weak adducts to equation 9 using a value of W = 1.0 kcal mole\(^{-1}\) to correct \(\Delta X\) for solvation. The values in parentheses were calculated using the EA and CA values obtained for the weak adducts (EA = 14.4, CA = 1.17, W = 1.0 kcal mole\(^{-1}\)) in the equation \(-\Delta H + W = E_A E_B + C_A C_B\).

Little data is available for systems in which the E and C equation predicted \(-\Delta H\) is above 27 kcal mole\(^{-1}\). Donor numbers for these bases have been determined by indirect methods and they are higher than those predicted by extrapolating the \(\Delta H\)-deviation plot. Either the indirect method overestimates the parameter or there is even more extensive solvation in these systems than that indicated by an extrapolation of the plot. Based on these results the following conclusions written in terms of a base variation experiment can be drawn about Donor number correlations:

1. For an acid with a CA/EA ratio of \(-0.1\), we expect a plot of DN versus any sigma bond strength related property to curve and scatter (depending on the base used) about the DMF donor number.
(2) If a straight line is obtained when DN is plotted against some measured property, some additional effect is involved in the measurement that enhances the response of the system for strong bases above that expected from their bond strength.

(3) For an acid with a CA/EA ratio other than ~0.1, scatter will result unless the bases employed all have similar CB/EB ratios. Note that the authors have carefully avoided sulfur donors from Donor Number analyses.

(4) If the CA/EA ratio of the measured property is ~0.1 or if bases with similar CB/EB ratios are employed, a straight line correlation will result if only weak bases are used (DN<24) or only strong bases are used (DN>26 to 38) or if bases are selected from a plot of ΔH_f and C vs. Δ such that a straight line can be drawn through them. (That is, extend Fig. 1 to include points to DN = 16 and pick bases that would fall on a line.) These conditions either are similar to those reported to give parallel lines in and E and C determination (22) or do not permit a separation of bond strength and solvation effects. Accordingly, no significance can be assigned to either the existence of or lack of a correlation of DN with a spectral or reactivity parameter.

SOLVATION EFFECTS

The question of estimating the solvating properties of a solvent is a much more complicated problem. Earlier (9) we proposed measuring the association constant K_a for an alkylammonium salt RN+X^- as the best criterion. The anion X^- should be that being displaced in the solutes of interest. The breakup of the ion pair is a result of non-specific solvation of the cation and specific (for example, hydrogen bonding) and non-specific solvation of the anion. These interactions and the coordination tendency cover the essential factors influencing solute ionization in most systems. If the solvent is amphoretic, for example H_2O, the coordinated ligand will undergo a simultaneous specific acid-base reaction with the bulk solvent molecule further complicating the problem. Determination of K_a leads to a semi-quantitative ordering of solvation energies. A log K_a criterion is recommended.

When K_a data are not available, less satisfactory solvent scales based upon solvatocromatic shifts of different indicators can be used. The agreement of various scales has recently been investigated and a composite scale of π* values reported (33). When "specific effects such as hydrogen bonding and other contributions from aromatic and polyhalogenated solvents" are eliminated, an excellent correlation of the composite solvation parameters and the molecular dipole moment of the solvent results. The authors conclude that aprotic polar solvent effects (in the absence of specific interactions) are mostly determined by solvent-solute dipolar interactions. When specific interactions exist, spectral scales provide uncertain estimates of solvation energies. For they depend upon how close the indicator approximates the specific solute.

In order to gain a fundamental appreciation for solvation effects, a series of experiments were carried out in our laboratory in which reactions in the E and C correlation

A + B ⇄ AB

were studied in polar solvents. An equation of the form of equation 10 can be subtracted from the equation

A + B' ⇄ AB'

to produce

AB + B' ⇄ AB' + B

Since there is no free acid in equation 12, the displacement reaction for a whole series of bases, B', can be investigated in a basic polar solvent without any contribution to the enthalpy from specific effects (Note a). Furthermore, with the products and reactants having the same molecular weight and similar geometries, dispersion forces should be about the same and cancel out. Some typical data (34,35) are presented in Table 3.

Note a. The bases should be selected so that they do not have acidic sites (as in CH_3OH) that could react with a basic solvent in the AB adduct.
The coordination model for non-aqueous solvents

We note in Table 3 that the same displacement enthalpy is obtained for a given reaction, regardless of the solvent used. For example, the reaction of Et₃N with o-Cl₂C₆H₅ requires cyclohexane for a poorly solvating solvent, while the acid reaction with DMSO, DMA, and EtOAc requires CCl₄. We note in Table 3 that the same displacement enthalpy is obtained for a given reaction, regardless of the solvent used. For example, the reaction of Et₃N with o-Cl₂C₆H₅ requires cyclohexane for a poorly solvating solvent, while the acid reaction with DMSO, DMA, and EtOAc requires CCl₄.

### Table 3: Summary of the enthalpy of the reactions for AB + B' + AB' + B type interactions (enthalpies in kcal mol⁻¹)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Compd</th>
<th>AB + B' → AB' + B</th>
<th>-ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>m-F-C₆H₄OH·EtOAc + DMSO → m-F-C₆H₄OH·EtOAc + EtOAc</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>m-F-C₆H₄OH·EtOAc + DMSO → m-F-C₆H₄OH·EtOAc + EtOAc</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>m-F-C₆H₄OH·EtOAc + Et₃N → m-F-C₆H₄OH·Et₃N + EtOAc</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>m-F-C₆H₄OH·EtOAc + Et₃N → m-F-C₆H₄OH·Et₃N + DMSO</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>m-F-C₆H₄OH·DMSO + Et₃N → m-F-C₆H₄OH·Et₃N + DMSO</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>CCl₄</td>
<td>Cu(hfac)₂·EtOAc + DMA → Cu(hfac)₂·DMA + EtOAc</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>Cu(hfac)₂·EtOAc + DMA → Cu(hfac)₂·DMA + EtOAc</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>CCl₄</td>
<td>Cu(hfac)₂·EtOAc + DMSO → Cu(hfac)₂·DMSO + EtOAc</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>Cu(hfac)₂·EtOAc + DMSO → Cu(hfac)₂·DMSO + DMA</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>Cu(hfac)₂·DMA + Et₃N → Cu(hfac)₂·Et₃N + DMA</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Inert</td>
<td>Cu(hfac)₂·DMA + Et₃N → Cu(hfac)₂·Et₃N + DMA</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>Cu(hfac)₂·DMA + Et₃N → Cu(hfac)₂·Et₃N + DMA</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>Inert</td>
<td>Cu(hfac)₂·DMA + Et₃N → Cu(hfac)₂·Et₃N + DMA</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>Cu(hfac)₂·DMA + Et₃N → Cu(hfac)₂·Et₃N + DMA</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>HFIP·DMA + 1-MeIm → HFIP·1-MeIm + DMA</td>
<td>-1.7</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>HFIP·DMA + 1-MeIm → HFIP·1-MeIm + DMA</td>
<td>-1.1</td>
<td></td>
</tr>
<tr>
<td>NO₂C₆H₅</td>
<td>HFIP·DMA + 1-MeIm → HFIP·1-MeIm + DMA</td>
<td>-1.1</td>
<td></td>
</tr>
<tr>
<td>CCl₄</td>
<td>HFIP·DMA + HMPA → HFIP·HMPA + DMA</td>
<td>-1.2</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>HFIP·DMA + HMPA → HFIP·HMPA + DMA</td>
<td>-1.1</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>HFIP·DMA + HMPA → HFIP·HMPA + DMA</td>
<td>-1.1</td>
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<tr>
<td>NO₂C₆H₅</td>
<td>HFIP·DMA + HMPA → HFIP·HMPA + DMA</td>
<td>-1.2</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>HFIP·1-MeIm + HMPA → HFIP·HMPA + 1-MeIm</td>
<td>-1.1</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>HFIP·1-MeIm + HMPA → HFIP·HMPA + 1-MeIm</td>
<td>-1.1</td>
<td></td>
</tr>
<tr>
<td>NO₂C₆H₅</td>
<td>HFIP·1-MeIm + HMPA → HFIP·HMPA + 1-MeIm</td>
<td>-0.7</td>
<td></td>
</tr>
<tr>
<td>CCl₄</td>
<td>HFIP·EtOAc + DMA → HFIP·DMA + EtOAc</td>
<td>-2.1</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>HFIP·EtOAc + DMA → HFIP·DMA + EtOAc</td>
<td>-2.6</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>HFIP·EtOAc + DMA → HFIP·DMA + EtOAc</td>
<td>-2.5</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>HFIP·EtOAc + 1-MeIm → HFIP·1-MeIm + EtOAc</td>
<td>-4.2</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>HFIP·EtOAc + 1-MeIm → HFIP·1-MeIm + EtOAc</td>
<td>-4.4</td>
<td></td>
</tr>
<tr>
<td>CCl₄</td>
<td>HFIP·EtOAc + HMPA → HFIP·HMPA + EtOAc</td>
<td>-3.5</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>HFIP·EtOAc + HMPA → HFIP·HMPA + EtOAc</td>
<td>-3.7</td>
<td></td>
</tr>
<tr>
<td>o-Cl₂C₆H₄</td>
<td>HFIP·EtOAc + HMPA → HFIP·HMPA + EtOAc</td>
<td>-3.6</td>
<td></td>
</tr>
</tbody>
</table>

*aReactions of Et₃N require cyclohexane for a poorly solvating solvent; that of the acid, with DMSO, DMA, and EtOAc require CCl₄.*
reaction in the solvent minimized solvent ("inert" in the table) and in benzene, ortho dichlorobenzene, and nitrobenzene. Since the enthalpy for equation 10 is not the same in these various solvents, the difference between the enthalpy for a whole series of bases toward a given acid in a given solvent must differ from that in a poorly solvating solvent by a constant amount, $S$. 

$$\Delta H(\text{poorly solvating media}) = \Delta H(\text{polar solvent}) - S$$  \hspace{1cm} (13)

where $S$ is a constant for a particular solvent and acid interacting with a whole series of bases. This conclusion forms the basis of so-called ESP (elimination of solvation procedure). By writing our enthalpy cycle that connects the enthalpy measured in the polar solvent to that in poorly solvating media one can determine that $S$, the constant difference between the enthalpy measured in a polar and solvent minimized solvent, has contributions to it from the difference in non-specific solvation of the adducts and the corresponding acids and bases in the polar solvent. It also includes the energy required to overcome the specific interactions of the acid with the solvent. Equation 13 is a direct consequence of obtaining constant enthalpies for equation 12 for a series of bases in a solvent. Thus, if the acid is held constant in a given polar basic solvent and a series of bases studied, the assumption that solvation contributions to the general equation 12 cancel is analogous to the assumption that the enthalpies measured in the polar basic solvent will differ by a constant amount from those measured in the poorly solvating media. In weakly basic solvents, the value of $S$ is dependent only on the acid and the solvent employed and is independent of the base if it does not interact specifically with the solvent. For 1,1,1,3,3,3-hexafluoro-2-propanol in benzene, o-dichlorobenzene, and nitrobenzene, the constant $S$ is $1.7 \pm 0.2$, $0.7 \pm 0.2$, and $3.5 \pm 0.1$ kcal mol$^{-1}$, respectively.

In several of the systems reported in Table 3, enthalpies have been determined for all of the steps in the thermodynamic cycle and the constancy of the solvation difference of $B$ and $BA$ is demonstrated. In the case of the solvent benzene, it has been shown that nearly all of the contribution to the magnitude of $S$ arises from the specific acid-base interaction with the basic benzene solvent (39). Non-specific solvation of the products and reactants by benzene cancel (Note a).

As a consequence of equation 13, a system in which the adduct or base is insoluble in CCl$_4$ or hexane can be studied in a basic polar solvent and its enthalpy corrected back to a poorly solvating medium. The value of $S$ can be readily determined for new acids or solvents by using the procedures outlined in the literature.

If one is interested in investigating the reaction of a series of acids toward a given base, acidic solvents (CH$_2$Cl$_2$, CHCl$_3$, etc.) should be selected and reactions of the form 

$$B + A \rightleftharpoons BA$$

$$B + A' \rightleftharpoons BA'$$

combined to produce the displacement reaction 

$$BA + A' \rightleftharpoons BA' + A$$

Each constant base in each acidic solvent will have a constant $S$ value for variation of a series of acids (36). In the case of CH$_2$Cl$_2$, the $S$ value for the equation 

$$\Delta H(\text{poorly solvating media}) = \Delta H(\text{polar acidic solvent}) - S_B$$  \hspace{1cm} (14)

is largely dominated by the specific hydrogen bonding interaction of the base with CH$_2$Cl$_2$. As a result, $S_B$ can be calculated with the E and C equation (equation 9 using $S_B$ for $\Delta x$) from the $E_B$ and $C_B$ parameters of the constant base using $C_A = 0.01$ and $E_A = 1.66$ for CH$_2$Cl$_2$ (37).

When one attempts to use 1,2-dichloroethane as a solvent for the systems reported in Table 3, an ESP type of correction of the data is not possible. This solvent is poorly behaved because gauche and trans isomers exist and

Note a. Note this is not the case for the base pyridine where a specific pyridine-benzene complex exists.
and they have different dipole moments. Various bases and adducts have different polarities and these induce varying amounts of the gauche isomer in the vicinity of the solute and thus varying solvation energies. These studies support the conclusion of the E and C analysis that indicated that donor numbers are a poor criterion of donor strength. The solvent 1,2-dichloroethane was selected because the SbCl₅ adducts are insoluble in CCl₄ or benzene. Solubility occurs because of solvation and unfortunately the solvation energy difference of a base and its SbCl₅ adduct is not constant for a wide range of base types. These solvation contributions greatly complicate the interpretation of donor numbers. When a set of data is found to parallel donor numbers, the interpretation of this data set is hampered by the same complications.

The approach described above for the estimation of solvation energies has expanded the range of systems for which solvation minimized enthalpies can be obtained. It has, however, only scratched the surface of the problem of understanding solvation effects. A remaining complication in the application of the procedures described above involves our poor understanding of the nature of weak intermolecular interactions. For example, the base pyridine does not produce solvation minimized enthalpies in CCl₄ or benzene solvent because of weak intermolecular interactions. Accordingly, the procedure described above for eliminating solvation effects has been referred to as ESP. Potential problems can be minimized by selecting two different solvents for study in order to provide a check on the corrections for obtaining solvation minimized data. The ESP approach provides an excellent way of detecting the existence of weak intermolecular interactions. These kinds of studies coupled with improved procedures for obtaining gas phase enthalpies are needed before solvation effects on chemical reactivity become understandable and predictable.

REFERENCES

13. Species such as MX₄²⁻ and MX₄⁴⁺ often have high stability in poorly basic low dielectric constant solvents. As the solvent becomes more effective in the dissociation of anions, anions are displaced and these species
are converted to MS$_p^{2+}$ and Cl$^-$. This equilibrium is covered by a cycle similar to Fig. 2 by adding, for example, steps MCl$_4^{2+}$ + S $\rightarrow$ Cl$^-$ + MCl$_3$S and MCl$_3$S $\rightarrow$ S + MS$^-$Cl$_2$ + Cl$^-$.  

13. The ionization step can be considered to involve MXS$_p$ + nS $\rightarrow$ [MS$^+X^-$](sol) $\leftrightarrow$ MS$_q^+$ (sol) + X$^-$(sol) where the brackets represent ion pairs. More effective solvents drive this equilibrium to the right.


23. For an explanation of why these terms are preferred to soft and hard see R. S. Drago, Inorg. Chem. 12, 2211 (1973).


$$\frac{-\Delta H}{C_A+E_A} = \frac{C_B+E_B}{2} + \frac{(C_B-E_B)^2}{(E_A+C_A)^2}$$

If one plots $-\Delta H/(C_A+E_A)$ vs $(C_A-E_A)/(E_A+C_A)$ after substituting $E_B$ and $C_B$ values for a base a straight line characteristic of that base reacting with any acid will result.


