THE FUNCTIONAL APPROACH TO IONIZATION PHENOMENA IN SOLUTIONS

U. MAYER and V. GUTMANN

Institut für Anorganische Chemie, Technische Hochschule Wien, Vienna, Austria

I. Introduction

Various approaches are in use to characterize properties of ions and molecules in solution.

Born (*1*) and later Bjerrum (*2*) developed a theoretical approach to ion–solvent interactions based on a rather simple electrostatic model. Ions are considered as rigid spheres of radius r and charge z in a solvent continuum of dielectric constant ε. Changes in enthalpy $\Delta H(\mathrm{sv})$ and in free energy $\Delta G(\mathrm{sv})$, respectively, associated with the transfer of the gaseous ions into the solvent are represented by the following equations:

$$\Delta G(\mathrm{sv}) = -\frac{N(ze)^2}{2r}\left(1 - \frac{1}{\varepsilon}\right) \tag{1}$$

$$\Delta H(\mathrm{sv}) = -\frac{N(ze)^2}{2r}\left\{1 - \frac{1}{\varepsilon} - \frac{T}{\varepsilon}\left(\frac{\partial \ln \varepsilon}{\partial T}\right)_p\right\} \tag{2}$$

According to this model cations and anions with the same radius and the same charge number should be equally solvated, and this is in contrast to experimental findings. Later Born's equation was modified by various authors, e.g., by using corrected ionic radii or by considering changes in the dielectric constant of the solvent in the vicinity of the ions (*3–5*). A more satisfactory explanation for the different behavior of cations and anions was given by Buckingham, who emphasized the importance of quadrupole interaction terms between ions and solvent molecules as well as between solvent molecules of the solvation sphere (*6*, *7*). The main difficulty in applying this model is lack of knowledge of quadrupole (or multipole) moments, solvation numbers, and the arrangement of solvent molecules in the solvation spheres, particularly in nonaqueous solvents. Furthermore absolute solvation energies are large, so that comparatively small errors in the parameters used introduce appreciable uncertainties in solvation energy differences for a given ion in different media. It may therefore be anticipated that successful calculations of solvation quantities by purely electrostatic models are not possible, both for experimental reasons and because of the inherent inadequacy of elementary electrostatic models in view of the actual charge distribution within the solvated ions.

Within the last 5 years a number of quantum mechanical calculations have been carried out, in particular for hydrogen-bonded systems such as H_2O, NH_3, and HF as solvents. Contrary to electrostatic models, MO calculations allow for the possibility of covalent bond formation and, consequently, constitute a fundamentally better approach to ion–molecule interactions. Some interesting results of recent model calculations, although qualitative in nature, are discussed in Section V.

It is well known that single-ion solvation quantities cannot be obtained by purely thermodynamic methods. Thermodynamic quantities obtained for neutral compounds may be split up into their ionic components by use of appropriate extrathermodynamic assumptions. These methods are based on the idea that changes in enthalpy or free energy associated with the transfer of a solute from one solvent to another will essentially be equal for structurally analogous ions or molecules. Examples include pairs of structural analogs such as $[As(C_6H_5)_4]^+$–$[B(C_6H_5)_4]^-$, $[As(C_6H_5)_4]^+$–$[Sn(C_6H_5)_4]$ or (less ideal) I_2–I_3^- (*8–11*).

A similar approach has been developed independently by Pleskov (*12*) and Strehlow *et al.* (*13*). They assume that redox potentials for certain redox systems such as ferrocene–ferricinium ion are essentially independent of the nature of the solvent. Recent investigations have shown that the ferrocene–ferricinium ion assumption works fairly well in nonaqueous solvents, but it cannot be applied to aqueous solutions (*14*).

Extrathermodynamic methods represent powerful tools for the evaluation of single-ion solvation quantities, but the available data are rather low in accuracy. Accurate knowledge of solubility and salt activity coefficients is highly desirable. Estimation of liquid–liquid junction potentials (particularly at nonaqueous–aqueous electrolyte interfaces) is another problem that has not been satisfactorily resolved. The use of extrathermodynamic data for a semiquantitative description of ionization equilibria is demonstrated in Section III.

In the following sections the functional approach (*15–17*) is used, according to which most chemical interactions in solution are considered as the result of electron pair donor (EPD)–electron pair acceptor (EPA) interactions between solute and solvent molecules. In the functional representation allowance is made for the charge transfer occurring in the course of a chemical interaction by taking into account all inductive and mesomeric effects both *between* and within the reacting molecules (*15–17*). This approach may be generally applied to all interactions involving the formation of more-or-less covalent bonds, provided the energy changes involved in covalent bonding *are high* as compared to any other energy contributions to the overall interaction energy.

II. Classification of Reactions Producing Ions in Solution

Two main groups of chemical interactions may be distinguished (*15–17*): (*1*) substitution reactions = displacement reactions = atom or group transfer reactions (EPD–EPA reactions); and (*2*) electron transfer reactions (ED–EA reactions). According to the functional approach to chemical interactions (*15–17*), substitution reactions may be initiated either by nucleophilic attack of an EPD or by electrophilic attack of an EPA. Characteristically, these reactions involve formation of a new coordinate bond between substrate and substituting agent with simultaneous cleavage of the substrate bond. Unlike substitution reactions, electron transfer reactions or ED–EA reactions proceed without mass transfer between the reacting particles. The ED–EA interactions probably involve formation of loose coordinate bonds between the reacting species which serve only as bridges for the electron transfer process, e.g.,

$$R + A\text{–}B \longrightarrow R^+ + (A\text{—}B)^-$$

Examples for displacement reactions are

$$\begin{aligned}
NH_3 + H\text{—}Cl &\longrightarrow NH_4^+ + Cl^- \\
H + Br\text{—}Br &\longrightarrow HBr + Br^* \\
Zn + 2H_2O &\longrightarrow Zn(OH)_2 + 2H \\
Zn + [S\text{—}S]^{2-} &\longrightarrow ZnS + S^{2-} \\
Au^+ + Cl\text{—}Cl &\longrightarrow [AuCl]^{2+} + Cl^- \\
Cr^{2+} + Br\text{—}Br &\longrightarrow [CrBr]^{2+} + Br
\end{aligned}$$

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[*] In solution, HBr undergoes a secondary displacement reaction, yielding H_3O^+ and Br^-.

It is apparent that both ions and radicals may be formed. Reactions between stable nonradicals will usually yield nonradical (ionic) products, whereas in substitution reactions between nonradical and radical species, radicals are produced (which will immediately recombine).

Ionization reactions in homogeneous liquid phase usually proceed as reactions between "closed-shell" molecules. According to the functional approach, these reactions are regarded as EPD–EPA reactions in the strict sense of the word. Owing to the inherently high stability of closed-shell molecules or ions, these reactions usually lead to heterolytic bond cleavage.

Heterolysis may be effected either by nucleophilic attack of an EPD or by electrophilic attack of an EPA at a given substrate A—B (*18*, *19*):

$$n\mathrm{EPD} \longrightarrow \mathrm{A}^{\delta+}\overset{\curvearrowright}{—}\mathrm{B}^{\delta-} \rightleftharpoons \underset{\substack{\text{stabilized}\\ \text{cation}}}{[\mathrm{A(EPD)}_n]^+} + \mathrm{B}^-$$

$$\mathrm{A}^{\delta+}\overset{\curvearrowright}{—}\mathrm{B}^{\delta-} \longrightarrow n\mathrm{EPA} \rightleftharpoons \mathrm{A}^+ + \underset{\substack{\text{stabilized}\\ \text{anion}}}{[\mathrm{B(EPA)}_n]^-}$$

Examples are given in Eqs. (3) and (4)

$$\text{pyridine} + \mathrm{Sn(CH_3)_3I} \rightleftharpoons [\mathrm{Sn(CH_3)_3}\cdot\text{pyridine}]^+ + \mathrm{I}^- \tag{3}$$

$$\mathrm{NOCl} + \mathrm{SbCl_5} \rightleftharpoons \mathrm{NO}^+ + \mathrm{SbCl_6}^- \tag{4}$$

There are also examples of combined EPD and EPA interactions, such as

$$\mathrm{HCl} + (n + m)\mathrm{H_2O} \rightleftharpoons [\mathrm{H(OH_2)}_n]^+ + [\mathrm{Cl(H_2O)}_m]^-$$

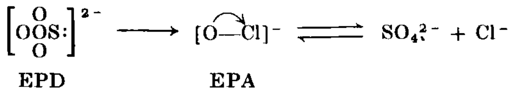
Usually attack of the EPD occurs at the more positive, and attack of the EPA at the more negative part of the molecule. In both cases, coordination leads to an increase in polarity of the bond $\mathrm{A}^{\delta+}—\mathrm{B}^{\delta-}$ and finally to heterolysis with formation of stabilized cations or of stabilized anions (*18*, *19*). It may be anticipated that a homolytic cleavage of $\mathrm{A}^{\delta+}—\mathrm{B}^{\delta-}$ is rather unlikely: A^+ acts as a much stronger EPA than $\mathrm{A}^{\delta+}$, and B^- acts as a stronger EPD than $\mathrm{B}^{\delta-}$, so that maximum stabilization is usually achieved by heterolytic cleavage of the $\mathrm{A}^{\delta+}—\mathrm{B}^{\delta-}$ bond.

Homolytic bond cleavage has been reported for the reaction between $\mathrm{CuCl_2}$ and thiourea (thu) which leads to formation of a Cu(I)–thiourea complex and chlorine radicals, which are converted into free chlorine (*20*):

$$\mathrm{CuCl_2} + n(\mathrm{thu}) \rightleftharpoons [\mathrm{CuCl(thu)}_n] + \mathrm{Cl}$$

This reaction has been explained by the back-bonding effect between thu and copper ion (*17*): thu acts both as σ-EPD and π-EPA; stabilization by back-bonding is particularly favorable for Cu^+ which is a stronger π-EPD than Cu^{2+} (*17*).

It has been stated that attack of an EPD usually occurs at the more positive part of the substrate and that this results in an electron shift from the more positive to the more negative part within the molecule. Exceptions to this rule are possible. In fact the nature of the reaction products formed depends on the relative thermodynamic stabilities of the individual species. An example is provided by the oxidation reaction of sulfite ions by hypochlorite ions [Eq. (5)].



$$\left[\mathrm{O}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}:\right]^{2-} \longrightarrow [\mathrm{O{-}Cl}]^- \rightleftharpoons \mathrm{SO_4^{2-}} + \mathrm{Cl^-} \qquad (5)$$

According to kinetic measurements (*21*), this reaction proceeds as a nucleophilic substitution reaction with sulfur acting as EPD and apparently involves an electron shift from the more negative to the more positive part of the hypochlorite ion. Formation of a coordinate bond between sulfur and oxygen has been demonstrated using ^{18}O-labeled OCl^-.

Traditionally reaction (5) is considered as a redox reaction. It is obvious that both from the functional point of view and from consideration of reaction mechanisms (*21, 22*), there is no basic difference between reaction (5) and "ordinary" substitution reactions such as Eq. (3).

The assignment of oxidation numbers to atoms within molecules is somewhat arbitrary and does not reflect the actual charge distribution within the molecules. For example, reaction (5) can equally well be formulated assuming an oxidation number of $-$II for sulfur and 0 for oxygen:

$$[\overset{-\mathrm{II}}{\mathrm{S}}\overset{0}{\mathrm{O}}_3]^{2-} + [\overset{0}{\mathrm{O}}\overset{-\mathrm{I}}{\mathrm{Cl}}]^- \longrightarrow [\overset{-\mathrm{II}}{\mathrm{S}}\overset{0}{\mathrm{O}}_4]^{2-} + \overset{-\mathrm{I}}{\mathrm{Cl}}$$

Then this reaction would not be considered a redox reaction since no change in oxidation numbers occurs during the reaction. Likewise the reaction

$$\mathrm{Cr^{2+} + Br_2 \longrightarrow [CrBr]^{2+} + Br}$$

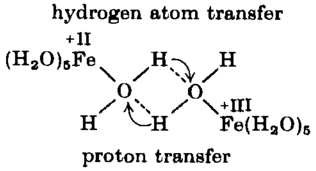
may be considered a coordinating rather than a redox reaction.

The distinction that is frequently made between redox reactions and "ordinary" displacement reactions is somewhat arbitrary and may be even misleading (see also Refs. *21–23*).

Unlike substitution reactions, electron transfer reactions proceed without mass transfer between the reacting species. Sometimes it is not possible to decide *a priori* whether a reaction is a true electron transfer reaction or rather a mass transfer (substitution) reaction (*21*). For example, evidence has been presented from kinetic studies that the reaction

$$[\overset{*}{\mathrm{Fe}}(\mathrm{H_2O})_6]^{2+} + [\mathrm{Fe}(\mathrm{H_2O})_6]^{3+} \rightleftharpoons [\overset{*}{\mathrm{Fe}}(\mathrm{H_2O})_6]^{3+} + [\mathrm{Fe}(\mathrm{H_2O})_6]^{2+}$$

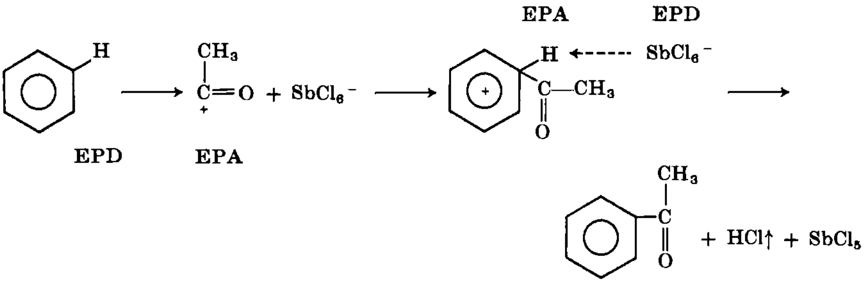
which formally is considered an electron transfer reaction, probably proceeds as a mass transfer reaction involving simultaneous transfer of a hydrogen atom and of a proton:



On the other hand, it has been shown that reactions between various substitution inert species, such as $[Fe(CN)_6]^{4-}$–$[Fe(CN)_6]^{3-}$, $[MnO_4]^{2-}$–$[MnO_4]^-$, $[Fe(phen)_3]^{3+}$–$[Fe(phen)_3]^{2+}$, clearly proceed as electron transfer reactions (*21*). Finally all electrochemical oxidation and reduction processes are to be considered as electron transfer reactions.

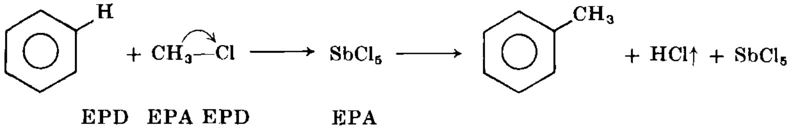
In numerous chemical reactions, ionic species are formed as intermediates which are subsequently converted into more stable, neutral, reaction products. Examples are provided by numerous well-known substitution reactions such as Friedel–Crafts acylations, nitration reactions, or chlorination reactions. The initial steps of these reactions are completely analogous to reactions of type (3) or (4).

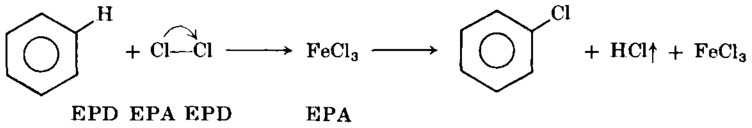
For example, acetylation of benzene by use of CH_3COCl with $SbCl_5$ as a catalyst is due to the intermediate formation of the acetylium ion, which has been shown to exist in stable ionic compounds such as $[CH_3CO]^+[SbCl_6]^-$ or $[CH_3CO]^+[BF_4]^-$.



Likewise the strong nitrating action of NO_2Cl–$SbCl_5$ mixtures is due to the formation of $[NO_2]^+[SbCl_6]^-$ acting as an electrophilic agent toward the aromatic ring.

In a number of cases substitution reactions appear not to involve the formation of true ionic intermediates but rather molecular complexes with strongly polarized bonds, e.g.,





It should perhaps be mentioned that Olah and co-workers (*24*) have been able to prove the existence of EPA-stabilized carbonium ions in highly acidic media, for example, in mixtures of HF and SbF_5:

$$RF + SbF_5 \longrightarrow [R^+SbF_6^-]$$

Similar considerations apply to various nucleophilic substitution reactions.

III. Ionizing Properties of Solvents

The relationship between thermodynamic properties, for example, ionization constants or solubility products of a compound AB, and the coordination chemical properties of solvents can be readily deduced from a consideration of the energy cycles shown in Eqs. (6)–(9).

$$\begin{tikzcd}
AB(g) \arrow[r, "\Delta G_{het}"] \arrow[d, "\boxed{\Delta G(sv)(AB)}"] & A^+(g) \arrow[d, "\boxed{\Delta G(sv)(A^+)}"] & + & B^-(g) \arrow[d, "\boxed{\Delta G(sv)(B^-)}"] \\
AB(sv) \arrow[r, "\Delta G"] & A^+(sv) & + & B^-(sv)
\end{tikzcd} \tag{6}$$

$$\Delta G = -RT \ln K \qquad K = \frac{[A^+][B^-]}{[AB]}$$

$$\Delta G = \Delta G_{het} - \Delta G(sv)(AB) + \Delta G(sv)(A^+) + \Delta G(sv)(B^-) \tag{7}$$

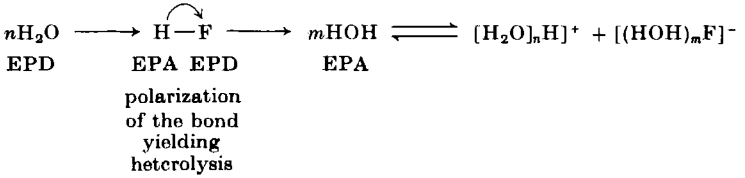
$$\begin{tikzcd}
\mathrm{AB(g)} \arrow[r, "\Delta G_{\mathrm{het}}"] \arrow[d, "\boxed{-\Delta G_{\mathrm{subl}}}"] & \mathrm{A^+(g)} \arrow[d, "\boxed{\Delta G(\mathrm{sv})(\mathrm{A}^+)}"] & + & \mathrm{B^-(g)} \arrow[d, "\boxed{\Delta G(\mathrm{sv})(\mathrm{B}^-)}"] \\
\mathrm{AB(c)} \arrow[r, "\Delta G"] & \mathrm{A^+(sv)} & + & \mathrm{B^-(sv)}
\end{tikzcd} \tag{8}$$

$$\Delta G = -RT \ln K_s \qquad K_s = [\mathrm{A}^+][\mathrm{B}^-]$$
$$\Delta G = \Delta G_{\mathrm{subl}} + \Delta G_{\mathrm{het}} + \Delta G(\mathrm{sv})(\mathrm{A}^+) + \Delta G(\mathrm{sv})(\mathrm{B}^-) \tag{9}$$

Cycle (6) shows the various free-energy contributions for the ionization of a covalent compound AB; cycle (8) applies to the heterogeneous equilibrium between a solid compound AB and its saturated solution containing ions A^+ and B^- (ΔG_{het} denotes the free enthalpy change for heterolysis). From Eqs. (7) and (9), it is obvious that both ionization constant and solubility of a given compound AB in different solvents are functions of the free energies of solvation of AB, A^+, and B^-, and these represent a measure of the solvating properties of the solvents. It should be noted that according to

$$\Delta G = \Delta H - T \cdot \Delta S \tag{10}$$

a direct relationship also exists between ionization constant or solubility and the enthalpies of solvation, $\Delta H(\mathrm{sv})$, of the species present in solution. The present approach considers the solvating properties of the solvents as a consequence of EPD–EPA interactions between solvent molecules and the various species present in solution, leading both to the formation of more-or-less covalent bonds between the reacting particles and to changes in bonding within the molecules (*15–19*, *25*). Consequently, this concept provides not only a generalized and unified description of chemical interactions, but it offers also the possibility of estimating and correlating thermodynamic properties of compounds in different solvent systems, provided that suitable quantities characteristic for EPD and (or) the EPA properties of the solvents can be defined. In principle, each solvent may function as EPD as well as EPA, but for most solvents either the EPD or the EPA functions prevail; the former are denoted as EPD solvents and the latter as EPA solvents (*25*). Examples of typical EPD solvents are pyridine, ethers, esters, dimethylsulfoxide, and hexamethylphosphoricamide; examples of typical EPA solvents are the liquid hydrogen halides, liquid sulfur dioxide, sulfuric acid, and trifluoroacetic acid. Several solvents are amphoteric as they are capable of exercising both EPD and EPA functions. For example, water owes its outstanding solvent properties to the fact that toward Lewis acids such as cations it functions as a fairly strong EPD (via the oxygen atom), whereas toward certain anions it functions as a fairly strong EPA (via the hydrogen atoms). Hence water can provide stabilization for both cationic and anionic species, e.g.,



$$\underset{\text{EPD}}{nH_2O} \longrightarrow \underset{\substack{\text{EPA EPD}\\ \text{polarization}\\ \text{of the bond}\\ \text{yielding}\\ \text{heterolysis}}}{\overset{\curvearrowright}{H{-}F}} \longrightarrow \underset{\text{EPA}}{mHOH} \rightleftharpoons [H_2O]_nH]^+ + [(HOH)_mF]^-$$

Simultaneous stabilization of both cations and anions may also be effected by combination of an EPD solvent (with poorly developed EPA properties) and a suitable EPA. For example, nitromethane (NM) as a solvent functions as a weak EPD and hence compounds such as $CoCl_2$ remain insoluble in this solvent. Addition of a strong EPA, such as $SbCl_5$, to this suspension leads to dissolution of $CoCl_2$ with simultaneous heterolysis of the Co—Cl bonds, owing to the stabilization of both cationic and anionic species:

$$CoCl_2 + 6NM + 2SbCl_5 \longrightarrow [Co(NM)_6]^{2+} + 2[SbCl_6]^-$$

On the other hand, $CoCl_2$ is insoluble in pure liquid $SbCl_5$ since cation stabilization cannot take place. The majority of solvents that are extensively used in solution chemistry (particularly in the field of organic chemistry) are typical EPD solvents. Gutmann (*25–28*) has introduced the so-called donor number or donicity (DN) as a measure of the EPD properties of donor solvents. This is defined as the negative ΔH values for formation of the 1:1 adduct of the EPD with $SbCl_5$ as reference standard EPA in a dilute solution of 1,2-dichloroethane. Donicities for various solvents are listed in Table I together with their dielectric constants ε.

The basic idea in defining the donicity is based on the work of Lindqvist (*29*), who obtained from calorimetric measurements an order of relative, solvent, EPD strengths toward $SbCl_5$. It was then supposed that the relative EPD properties toward different EPA units (neutral and cationic) could be predicted (at least qualitatively) from the trends observed toward $SbCl_5$. This is, indeed, true for a large number of both neutral and ionic substrates (*25–28*). Figure 1 shows the relationship between ^{19}F chemical shifts of CF_3I dissolved in various EPD solvents as a function of solvent donicity DN (*30*). Nucleophilic attack of an EPD at the iodine atom causes an electron shift from iodine to the

TABLE I

DONICITIES (DN) AND DIELECTRIC CONSTANTS (ε) FOR SEVERAL SOLVENTS

Solvent	DN	ε
1,2-Dichloroethane	—	10.1
Sulfuryl chloride	0.1	10.0
Benzene	0.1	2.3
Thionyl chloride	0.4	9.2
Acetyl chloride	0.7	15.8
Tetrachloroethylene carbonate	0.8	9.2
Benzoyl fluoride	2.0	22.7
Benzoyl chloride	2.3	23.0
Nitromethane	2.7	35.9
Dichloroethylene carbonate	3.2	31.6
Nitrobenzene	4.4	34.8
Acetic anhydride	10.5	20.7
Phosphorus oxychloride	11.7	14.0
Benzonitrile	11.9	25.2
Selenium oxychloride	12.2	46.0
Acetonitrile	14.1	38.0
Sulfolane	14.8	42.0
Propanediol-1,2-carbonate	15.1	69.0
Benzyl cyanide	15.1	18.4
Ethylene sulfite	15.3	41.0
Isobutyronitrile	15.4	20.4
Propionitrile	16.1	27.7
Ethylene carbonate	16.4	89.1
Phenylphosphonic difluoride	16.4	27.9
Methylacetate	16.5	6.7
n-Butyronitrile	16.6	20.3
Acetone	17.0	20.7
Ethyl acetate	17.1	6.0
Water	18.0[a]	81.0
Phenylphosphonic dichloride	18.5	26.0
Methanol	19.0	32.6
Diethyl ether	19.2	4.3
Tetrahydrofuran	20.0	7.6
Diphenylphosphonic chloride	22.4	—
Trimethyl phosphate	23.0	20.6
Tributyl phosphate	23.7	6.8
Dimethylformamide	26.6	36.1
N-Methyl-ε-caprolactame	27.1	—
N-Methyl-2-pyrrolidone	27.3	—
N,*N*-Dimethylacetamide	27.8	38.9
Dimethyl sulfoxide	29.8	45.0
N,*N*-Diethylformamide	30.9	—
N,*N*-Diethylacetamide	32.2	—
Pyridine (py)	33.1	12.3
Hexamethylphosphoric amide	38.8	30.0

[a] For water as a solvent, the bulk donicity $DN^B \sim 30$.

fluorine atoms the magnitude of which is proportional to the EPD properties (donicities) of the nucleophile:

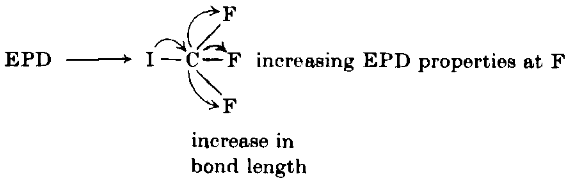


Figure 1 shows the linear correlation between ^{19}F chemical shift and solvent donicity. No relationship exists between chemical shifts and dipole moments or polarizabilities of the solvent molecules. This result is particularly significant in that it shows that the functional approach can be successfully applied even to weak chemical interactions, for example, to interactions that are usually considered as being due to Van der Waals forces or intermolecular forces in the sense of Mulliken's theory.

Essentially the same order of EPD strength as observed toward $SbCl_5$ was found for various EPA molecules such as $VO(acac)_2$ (see Table VII), $Sn(CH_3)_3Cl$, phenol, or $SbCl_3$ (*25*). Irregularities are

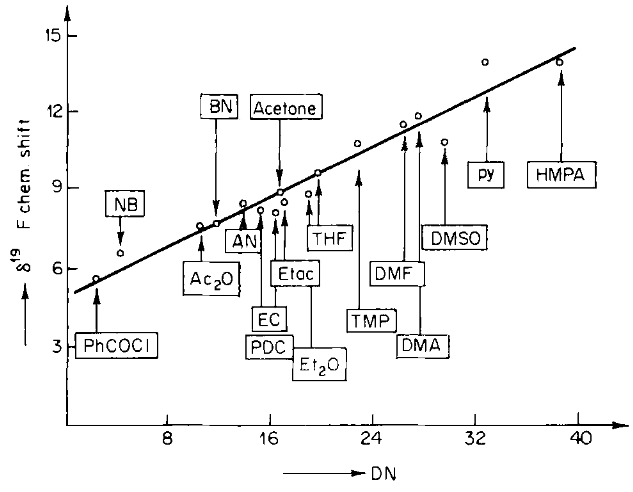


FIG. 1. Linear correlation between ^{19}F NMR chemical shifts at infinite dilution of CF_3I in various electron pair donor solvents and donicity (DN), referred to CCl_3F as external reference. NB, nitrobenzene; BN, benzonitrile; AN, acetonitrile; PDC, propanediol-1, 2-carbonate; THF, tetrahydrofuran; DMF, dimethylformamide; EC, ethylene carbonate; TMP, trimethyl phosphate; DMA, *N*,*N*-dimethylacetamide; DMSO, dimethylsulfoxide; HMPA, hexamethylphosphoric amide.

observed when relative EPD strengths for *both* hard *and* soft EPD are determined toward a hard EPA, on the one hand, and a soft reference EPA, on the other hand. For example sulfur donors (which are soft) behave as much stronger EPD toward soft EPA such as I_2, Ag^+, Cu^+ than analogous oxygen compounds (*31*, *32*), whereas reverse stabilities are found toward a hard EPA such as the proton, alkali metal ions, phenol, or an EPA unit with borderline behavior (Co^{2+}, Ni^{2+}, etc.) (*32*). Similarly, nitriles that behave as rather weak EPD molecules toward $SbCl_5$ show a much higher affinity toward a soft EPA such as Ag^+ and particularly Cu^+ (*33*). This suggests that nitriles may act toward soft acids both as σ donors and π acceptors. In practice these irregularities do not seriously restrict the applicability of the donicity concept since most of the solvents and solutes are rather hard.

Use of donicity values as a measure of cation solvation and cation stabilization has been demonstrated by polarographic measurements on alkali and alkaline earth metal ions, and various transition and rare earth metal ions (*17*, *16*, *34*). This is illustrated in Fig. 2 which shows the variation of half-wave potentials for the reduction of $Tl^+ \rightarrow Tl^0$, $Zn^{2+} \rightarrow Zn^0$, and $Eu^{3+} \rightarrow Eu^{2+}$ as a function of solvent donicities.

From the energy cycle,

$$\begin{tikzcd}
M^{z+}(g) \arrow[r, "-I"] \arrow[d, "\boxed{\Delta G(\mathrm{sv})(M^{z+})}"'] & M(g) \arrow[d, "\boxed{\Delta G_{\mathrm{amalg}}}"] \\
M^{z+}(\mathrm{sv}) \arrow[r, "\Delta G_{\mathrm{red}}"] & M_{\mathrm{amalg}}
\end{tikzcd}$$

$$\Delta G_{\mathrm{red}} = -zFE \qquad (E \approx E_{1/2} \text{ for reversible reductions})$$

and equation,

$$\Delta G_{\mathrm{red}} = -I + \Delta G_{\mathrm{amalg}} - \Delta G(\mathrm{sv})(M^{z+}) \tag{11}$$

it is apparent that standard redox potential and, consequently, the half-wave potential for the reduction of a given metal cation to the metal amalgam is only a function of the free energy of solvation. Increasing EPD strength of the solvent leads to an increased stabilization of the metal cation which is, therefore, less readily reduced and this results in a shift of $E_{1/2}$ toward more negative potential values (*16*, *17*). A similar consideration applies to redox reactions with both species solvated in solution: Eu^{3+} is a stronger EPA than Eu^{2+} so that with

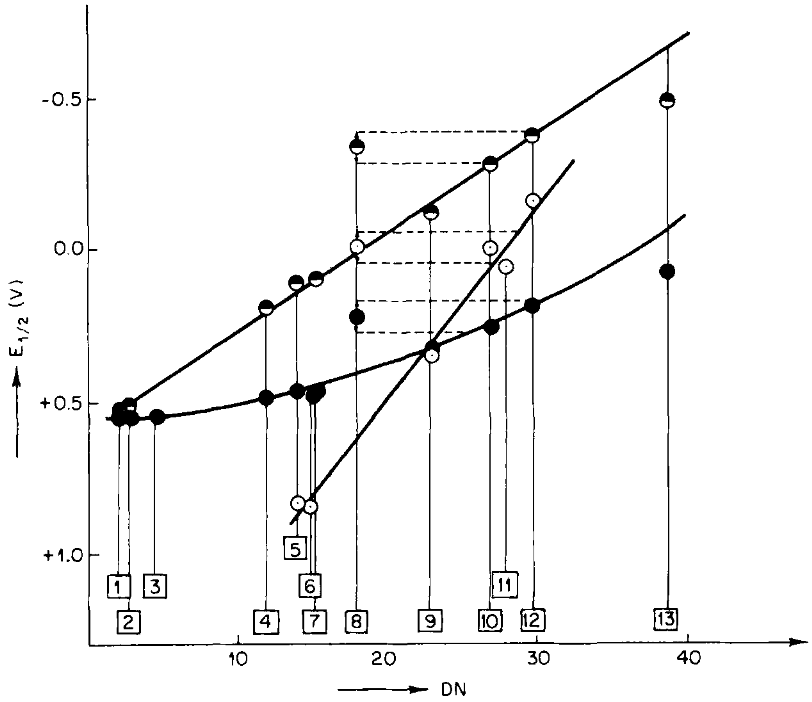


FIG. 2. Relationship between half-wave potential $E_{1/2}$ and solvent donicity (DN) for the polarographic reduction $Tl^+ \rightarrow Tl^0$ (●), $Zn^{2+} \rightarrow Zn^0$ (◓), $Eu^{3+} \rightarrow Eu^{2+}$ (○). 1—benzoyl fluoride; 2—nitromethane; 3—nitrobenzene; 4—benzonitrile; 5—acetonitrile; 6—propanediol-1, 2-carbonate; 7—ethylene sulfite; 8—Water; 9—trimethyl phosphate; 10—dimethylformamide; 11—*N*, *N*-dimethylacetamide; 12—dimethyl sulfoxide; 13—hexamethylphosphoric amide.

increasing solvent donicity the oxidized species will be more strongly stabilized. Figure 2 shows that with the exception of water, which behaves as a much stronger EPD than expected from its donicity, a good correlation between $E_{1/2}$ and DN exists for numerous redox pairs. The "anomalous" behavior of water is discussed in Section V.

In a solvent of more-or-less well-developed amphoteric properties the extent of ionization of a given compound $A^{\delta+}—B^{\delta-}$ [see Eq. (12)]

$$(A^{\delta+}—B^{\delta-})(sv) \rightleftharpoons A^{+}(sv) + B^{-}(sv) \qquad (12)$$

will depend both on the EPD and EPA properties of the solvents. Stabilization of A^+ and B^- by respective solvation will shift equilibrium (12) to the right side of the equation, whereas stabilization of the unionized substrate will shift the equilibrium to the opposite direction. Since

$A^{\delta+}$ (within $A^{\delta+}$—$B^{\delta-}$) is acting as a weaker EPA than A^+, and $B^{\delta-}$ is acting as a weaker EPD than B^-, increasing both EPD and EPA functions of a solvent will shift the equilibrium to the right side.

In order to gain a better insight into the basic relationships between ionizing power of solvents and their coordination chemical properties, it is necessary to study both the EPD effect at the cation A^+ and the EPA effect at the anion B^- separately. The role of the EPD effect has been successfully studied by the use of conductometric techniques for investigating the ionization equilibrium,

$$n\mathrm{EPD} + \mathrm{AB} \rightleftharpoons [\mathrm{A(EPD)}_n]^+ + \mathrm{B}^-$$

of suitable substrates AB in a weakly coordinating medium of sufficiently high dielectric constant (*35*) to which an EPD solvent is added in slight excess to the solute present. Under these conditions there will be no interference from anion solvation since B^- will be solvated only by the solvent molecules that are present in large excess. Furthermore, since the ions $[A(EPD)_n]^+$ and B^- are formed in a medium of invariable dielectric constant, the extent of ion pair formation (see Section IV) between $[A(EPD)_n]^+$ and B^- remains essentially constant* for different EPD units so that the conductivities are a direct measure of the EPD effect at cation A^+. Media that are particularly suitable for measurements of this type are nitrobenzene (DN = 4.4; ε = 34.8), nitromethane (DN = 2.7; ε = 35.9), and eventually dichloromethane (DN < 2; ε = 9.0). Figure 3 shows the increase in molar conductivities of

TABLE II

MOLAR CONDUCTIVITIES OF $(CH_3)_3SnI$ IN NITROBENZENE IN PRESENCE OF ELECTRON PAIR DONOR[a]

EPD[b]	Λ	DN	μ	ε
Nitrobenzene	0	2.7	3.54	35.9
Acetonitrile	0.1	14.1	3.2	38.8
Tetrahydrofuran	0.2	20.0	1.75	7.6
Diphenylphosphonic dichloride	0.45	22.4	—	—
Tributyl phosphate	0.95	23.7	3.06	6.8
Dimethylformamide	1.7	26.6	3.86	36.7
Pyridine	2.7	33.1	2.3	12.3
Dimethyl sulfoxide	3.7	29.8	3.9	48.9
Hexamethylphosphoric amide	17.5	38.8	5.54	33.5

[a] Molar ratio, EPD: $(CH_3)_3SnI$ = 8 at $c \approx 7 \times 10^{-2}$ (25°C).

[b] EPD, electron pair donor; DN, donicity.

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* This will only be true (see Section IV) if the coordinated cations $[A(EPD)_n]^+$ are sufficiently large and coordinatively saturated.

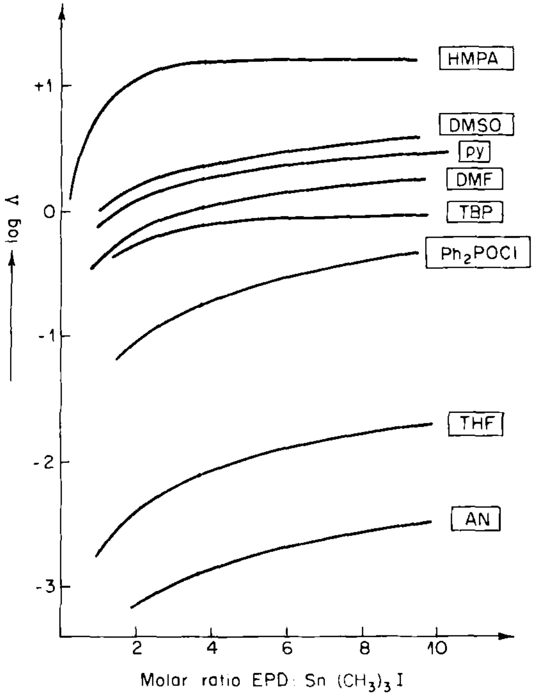

FIG. 3. Molar conductivities of $Sn(CH_3)_3I$ ($c = 7 \times 10^{-2}$ mole/liter) dissolved in nitrobenzene on addition of increasing amounts of various electron pair donor (EPD) solvents. HMPA, hexamethylphosphoric amide; DMSO, dimethyl sulfoxide; DMF, dimethylformamide; TBP, tributyl phosphate; THF, tetrahydrofuran; AN, acetonitrile.

$Sn(CH_3)_3I$ dissolved in nitrobenzene as a function of concentration of various EPD solvents added (*35*). In noncoordinating or weakly coordinating solvents, such as hexane, carbon tetrachloride, 1,2-dichloroethane, nitrobenzene, or nitromethane, $Sn(CH_3)_3I$ is present in an unionized state (tetrahedral molecules). Addition of a stronger EPD solvent to this solution provokes ionization, presumably with formation of trigonal bipyramidal cations $[Sn(CH_3)_3 \cdot (EPD)_2]^+$. Table II reveals that the molar conductivities at a given mole ratio EPD:$Sn(CH_3)_3I$ are (with the exception of pyridine) in accordance with the relative solvent donicities. No relationship appears to exist between conductivities and the dipole moments or the dielectric constants of the solvents.

The decreased EPD properties of pyridine may be due to steric hindrance between methyl groups and the α-hydrogens of the ring. Contrary to Fig. 3, conductivities measured for $Sn(CH_3)_3I$ in the pure

EPD solvents do not correctly reflect the ionizing properties of these solvents due to the differences in dielectric constants. Although $Sn(CH_3)_3I$ is considerably ionized in pure tributylphosphate, the solutions are essentially nonconducting because of the very low dielectric constant $\varepsilon = 6.8$ of this medium (see Section IV). Fuoss-Krauss analysis of conductance data for $Sn(CH_3)_3I$ in strong EPD solvents, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), pyridine, and hexamethylphosphoric amide (HMPA), reveal that the substrate is completely ionized and consequently behaves as a 1:1 electrolyte (*35*).

TABLE III

COUPLING CONSTANTS J (CH_3—^{119}Sn)

Solvent	DN	J_c(Hz)
Hexamethylphosphoric amide	38.8	72.0
Dimethyl sulfoxide	29.7	69.0
Dimethylformamide	26.6	68.5
Nitrobenzene	4.4	59.0

Nuclear magnetic resonance investigations demonstrate (Table III) the existence of an empirical relationship between the ionizing power of the EPD solvents and the coupling constants $J(CH_3\text{-}^{119}Sn)$ of the ionized substrate: the coupling constants are increased by increasing donicitiy of the EPD.

Conductometric investigations in nitrobenzene (NB) have recently been extended to trialkylsilicon and trialkylgermanium compounds (*36*). Again the extent of ionization increases with increasing donicity. In strong EPD solvents, iodo compounds are usually completely ionized, e.g., $Si(CH_3)_3I$ is completely ionized in HMPA, DMF, *N*, *N*-dimethylacetamide (DMA), pyridine, and tetramethylurea (DN = 29.8) with formation of stable pentacoordinated "siliconium" ions, $[Si(CH_3)_3 \cdot (EPD)_2]^+$ and I^-; this is particularly interesting, since evidence for the existence of *stable* siliconium ions *in solution* is rather scarce (*37*, *38*). All Group IV compounds exhibit hard acid behavior; consequently, sulfur compounds and phosphines behave as much weaker EPD ligands than the corresponding oxygen compounds and amines. In contrast, cacodylic iodide, $As(CH_3)_2I$, clearly behaves as a soft substrate and extensive ionization occurs on addition of phosphines and thioamides to the nonconducting solution of $As(CH_3)_2I$ in NB. On the other hand, amines and amides show only weak ionizing properties (*36*), the ionization increasing with increasing donicity.

In a similar manner, conductometric techniques may be applied to study the relationship between ionizing power and EPA properties of various solutes, for example, by conductometric titration of triphenylchloromethane dissolved in NB with EPA compounds:

$$(C_6H_5)_3CCl + SO_2 \rightleftharpoons (C_6H_5)_3C^+ + SO_2Cl^-$$

$$(C_6H_5)_3CCl + HCl \rightleftharpoons (C_6H_5)_3C^+ + HCl_2^-$$

$$(C_6H_5)_3CCl + AsCl_3 \rightleftharpoons (C_6H_5)_3C^+ + AsCl_4^- \quad \text{etc.}$$

Since the triphenylmethyl cation exhibits a strong absorption band in the visible region, these reactions may also be studied conveniently by the spectrophotometric method. The latter method has been used to determine relative EPA strength for numerous liquid and solid EPA compounds (*39*).

The situation becomes more complicated if a given ionization reaction is studied in solvents that differ both in their EPD and EPA properties. This may be illustrated for the complex formation between Co^{2+} and Cl^- ions. Qualitatively, stabilities of cobalt–chloro complexes usually decrease with increasing EPD strength of the solvent (*25*, *26*). Quantitative measurements reveal, however, a number of "irregularities" which cannot be understood by considering the differences in solvent donicities. Accurate thermodynamic data have recently been determined for the reaction

$$CoCl_3^- + Cl^- \rightleftharpoons CoCl_4^{2-} \tag{13}$$

$$K = \frac{[CoCl_4^{2-}]}{[CoCl_3^-]\cdot[Cl^-]} \qquad \Delta G = -RT \ln K$$

in various nonaqueous solvents (*40*) and are listed in Table IV. As expected, $[CoCl_4]^{2-}$ is most stable in NM, which is a poor EPD solvent, and it is least stable in strong EPD solvents such as DMF or DMA,

TABLE IV

Free Energies of Formation and Formation Constants for the Production of $[CoCl_4]^{2-}$ from $[CoCl_3]^-$ and Cl^- in Nonaqueous Solvents at Zero Ionic Strength and 25°C

Solvent	ΔG(kcal/mole)	K (liters mole^{-1})
Nitromethane	-6.59 ± 0.04	$(7.0 \pm 0.5) \times 10^4$
Benzonitrile	-4.82 ± 0.01	$(3.5 \pm 0.1) \times 10^3$
Acetonitrile	-3.92 ± 0.02	$(7.7 \pm 0.2) \times 10^2$
Acetone	-4.69 ± 0.04	$(2.8 \pm 0.2) \times 10^3$
Dimethylformamide	-1.64 ± 0.07	16 ± 2
N,*N*-Dimethylacetamide	-2.05 ± 0.07	32 ± 4

whereas intermediate stabilities are observed in solvents of medium EPD strength, namely, benzonitrile (BN), acetone, and acetonitrile (AN). On the other hand, stabilities in acetone and AN ($K_{\text{acetone}} \gg K_{\text{AN}}$) and DMA and DMF ($K_{\text{DMA}} > K_{\text{DMF}}$), respectively, apparently do not correspond to trends predicted from the consideration of the relative solvent donicities. Water in particular (not listed in Table IV) exhibits a strongly anomalous behavior in that $[CoCl_4]^{2-}$ is even less stable than in DMF and DMA.

These discrepancies are readily explained by taking into consideration the different EPA properties of the respective solvents (*42*, *34*, *41*).

TABLE V

FREE ENERGIES OF TRANSFER OF Cl^- FROM REFERENCE SOLVENT ACETONITRILE ($\Delta G°$) TO VARIOUS OTHER SOLVENTS

Solvent[a]	$\Delta G(sv)(Cl^-)$-$\Delta G(sv)°(Cl^-)$	Solvent[a]	$\Delta G(sv)(Cl^-)$-$\Delta G(sv)°(Cl^-)$
Water	−8.71	DMSO	0.00
Methanol	−5.98	DMF	1.22
Ethanol	−4.76	DMA	2.45
Nitro-methane	−3.13	Acetone	3.54
PDC	−0.14	HMPA	4.08
Acetonitrile	0.00		

[a] PDC, propanediol-1,2-carbonate; DMSO, dimethyl sulfoxide; DMF, dimethylformamide; DMA, *N*,*N*-dimethylacetamide; HMPA, hexamethylphosphoric amide.

No empirical quantity (analogous to donicity) is available to characterize relative EPA strength of solvents. Fortunately, it has been possible to obtain approximate values of free energies of solvation for individual ions by means of extrathermodynamic assumptions. Table V lists values of free energies of transfer for Cl^- (using AN as reference solvent), which have been calculated (*41*) from "solvent activity coefficient" data available in the literature (*11*). According to Table V, the following order of relative EPA strengths for EPD solvents is obtained:

$$H_2O \gg \text{methanol} > \text{ethanol} > \text{NM} \gg \text{PDC} \geq \text{AN} \approx \text{DMSO} > \text{DMF} > \text{DMA} > \text{acetone} > \text{HMPA}$$

The influence of anion solvation on equilibrium (*13*) can be derived from the energy cycle [Eq. (14)] which shows the relationship between the standard free energy ΔG of formation of $[\mathrm{CoCl_4}]^{2-}$ in a solvent L and in the gas phase $[\Delta G(\mathrm{g})]$.

$$\begin{tikzcd}
{[\mathrm{CoCl_3\cdot L}]^-(\mathrm{g})} \arrow[d, "\boxed{\Delta G(\mathrm{sv})(\mathrm{CoCl_3\cdot L^-})}"] & + & \mathrm{Cl^-(g)} \arrow[r, "\Delta G(\mathrm{g})"] \arrow[d, "\boxed{\Delta G(\mathrm{sv})(\mathrm{Cl^-})}"] & {[\mathrm{CoCl_4}]^{2-}(\mathrm{g})} \arrow[d, "\boxed{\Delta G(\mathrm{sv})(\mathrm{CoCl_4{}^{2-}})}"] & + & \mathrm{L(g)} \arrow[d, "\boxed{\Delta G(\mathrm{L})}"] \\
{[\mathrm{CoCl_3\cdot L}]^-(\mathrm{sv})} & + & \mathrm{Cl^-(sv)} \arrow[r, "\Delta G"] & {[\mathrm{CoCl_4}]^{2-}(\mathrm{sv})} & + & \mathrm{L}
\end{tikzcd} \tag{14}$$

$$\begin{aligned}\Delta G(\mathrm{g}) &= \Delta G + \Delta G(\mathrm{sv})(\mathrm{Cl^-}) + \Delta G(\mathrm{sv})(\mathrm{CoCl_3\cdot L^-}) \\ &\quad - \Delta G(\mathrm{sv})(\mathrm{CoCl_4{}^{2-}}) - \Delta G\,(\mathrm{L}) \qquad (15)\\ \Delta G &= -RT\ln K\end{aligned}$$

An analogous relationship also holds for the reference solvent $\mathrm{L^0}$ ($\mathrm{L^0}$ = acetonitrile):

$$\begin{aligned}\Delta G^0(\mathrm{g}) &= \Delta G^0 + \Delta G^0(\mathrm{sv})(\mathrm{Cl^-}) + \Delta G^0(\mathrm{sv})\,(\mathrm{CoCl_3\cdot L^{0-}}) \\ &\quad - \Delta G^0(\mathrm{sv})(\mathrm{CoCl_4{}^{2-}}) - \Delta G^0\,(\mathrm{L^0})\end{aligned} \tag{16}$$

Equations (15) and (16) reveal that a relationship between standard free energy (or stability constant) and EPD strengths of solvents can only be expected if the free energy for the gas phase reaction $\Delta G(\mathrm{g})$ (or the corresponding stability constant) is considered, since ΔG [in addition to $\Delta G(\mathrm{g})$] includes all contributions due to solvation of the reacting particles. Unfortunately, solvation energies of the complex anions are not known. Equation (15) can be simplified by assuming as a first approximation that contributions originating from groups $\mathrm{CoCl_3}$ and L to free energies of solvation of $[\mathrm{CoCl_3\cdot L}]^-$, on the one hand, and $[\mathrm{CoCl_3\cdot Cl}]^{2-}$ + L, on the other hand, will largely compensate each other and that $\mathrm{Cl^-}$ in $[\mathrm{CoCl_3\cdot Cl}]^{2-}$ will logically behave as a much weaker base than uncoordinated $\mathrm{Cl^-}$ By applying the same procedure to Eq. (16), one obtains by combination

$$\Delta G(\mathrm{g}) - \Delta G^0(\mathrm{g}) = \Delta G - \Delta G^0 + \alpha[\Delta G(\mathrm{sv})(\mathrm{Cl^-}) - \Delta G^0(\mathrm{sv})(\mathrm{Cl^-})] \tag{17}$$

where α is a constant that may take values between 0 and 1.*

Equation (17) allows calculation of standard free energies in the gas phase, [referred to the standard free energy of reaction (18)] from

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* Since Eq. (17) applies to free-energy differences for substitution reactions of the same type, it is plausible to assume that $\Delta H(\mathrm{DN})$–ΔG relationships are not too seriously influenced by variable entropy contributions. A more rigorous treatment of the energy cycle (14) will be discussed in a subsequent paper (*42*).

experimentally determined free-energy data and free energies of solvation listed in Table V.

$$[CoCl_3 \cdot AN]^-(g) + Cl^-(g) \longrightarrow [CoCl_4]^{2-}(g) + AN(g) \quad (18)$$

Values $\Delta G(g) - \Delta G^0(g)$ have been calculated for the solvents listed in Table IV assuming various values for α between 0 and 1. (Representative values, assuming $\alpha = 1$ and 0.5 are given in Table VI). Independent from the value of $\alpha (0.3 \leqq \alpha \leqq 1)$, the same relative stabilities are obtained. Contrary to stabilities observed in solution, the gas phase stabilities do correspond to stabilities predicted from the donicities of the EPD molecules:

TABLE VI

FREE ENERGY DIFFERENCES $\Delta G(g) - \Delta G(g)^\circ$ FOR VARIOUS ELECTRON PAIR DONORS[a]

EPD	$\Delta G(g) - \Delta G(g)^\circ$	
	$\alpha = 1$	$\alpha = 0.5$
Nitromethane	−5.80	−4.24
Acetonitrile	+0.00	+0.00
Acetone	+2.77	+1.00
Dimethylformamide	+3.50	+2.89
N,*N*-Dimethylacetamide	+4.37	+3.095

[a] Reference electron pair donor (EPD) is acetonitrile.

$$\text{DMA} > \text{DMF} \gg \text{acetone} > \text{AN} \gg \text{NM}$$

[Benzonitrile has not been included because $\Delta G(sv)(Cl^-)$ is not available for this solvent.]

Of course, it is impossible to determine α *a priori*. If Eq. (17) is physically reasonable, it should be possible to choose α in such a way that a plot of $\Delta G(g) - \Delta G^0(g)$ versus DN can be represented by a fairly smooth curve, as shown in Fig. 4 for $\alpha \approx 0.5$. This value appears reasonable: low α values are highly improbable since the free Cl^- ion is undoubtedly a much stronger base than the coordinated Cl^- ion in $[CoCl_4]^{2-}$; on the other hand, solvation enthalpies of the complex anions will compensate only in part, so that α is necessarily < 1. Equation (17) can be used to estimate free energies of formation or stability constants of $[CoCl_4]^{2-}$ in other solvents, provided that the donicities and the values $\Delta G(sv)(Cl^-)$ (Table V) are known. Values $\Delta G(g) - \Delta G^0(g)$ required for this purpose may be interpolated or extrapolated* from Fig. 4.

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* Long-range extrapolations should of course be avoided.

Application of Eq. (17) should be particularly instructive in the case of water as a solvent. According to its donicity, DN $\approx$ 18, one should expect a stability constant K_{water} for $[\mathrm{CoCl}_4]^{2-}$ that corresponds roughly to that observed in acetone, namely $K_{\mathrm{water}} \approx 10^{+3}$. Semiquantitative measurements show (*43*) that $[\mathrm{CoCl}_4]^{2-}$ is, in fact, extremely unstable in water—no appreciable amounts of $[\mathrm{CoCl}_4]^{2-}$ are formed even in the presence of a large excess of chloride ions ($[\mathrm{Cl}^-]$: $[\mathrm{Co}^{2+}] > 3000$; $(\mathrm{Co}^{2+}) \approx 10^{-3}$ mole/liter). This apparent anomalous behavior of water is easily explained by taking into consideration the strong EPA properties of water (*41*). By using values $\Delta G_{\mathrm{H_2O}}(\mathrm{g}) - \Delta G_{\mathrm{AN}}(\mathrm{g}) \approx +1.1$ from Fig. 4 and $\Delta G(\mathrm{sv})(\mathrm{Cl}^-) - \Delta G^0(\mathrm{sv})(\mathrm{Cl}^-) = -8.71$ from Table V, one obtains $\Delta G_{\mathrm{H_2O}}(\mathrm{solution}) \approx +1.54$, corresponding to a stability constant $K_{\mathrm{H_2O}}(\mathrm{solution}) \approx 7.4 \times 10^{-2}$. This predicted value is lower by more than 2 powers of ten than the stability constants measured for the strongest EPD solvents listed in Table IV and lower by more than 4 powers of ten than the expected value if anion solvation is ignored. This value is also in satisfactory agreement with experimental results.

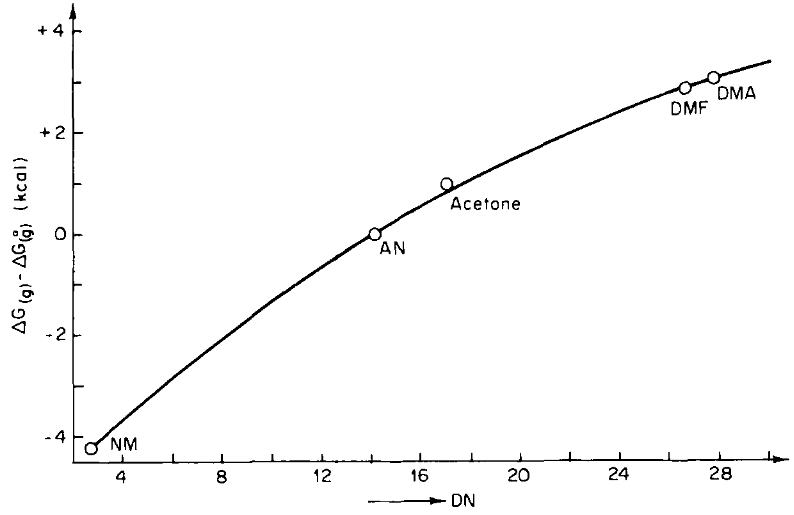

FIG. 4. Free-energy differences $\Delta G(\mathrm{g}) - \Delta G^{\circ}(\mathrm{g})$ for the gas phase reactions $[\mathrm{CoCl_3 \cdot L}]^- + \mathrm{X}^- \rightarrow \mathrm{CoCl_4}^{2-} + \mathrm{L}$ as a function of donicity (DN); superscript 0 refers to standard gas phase reaction with L^0 = acetonitrile (AN); $\alpha = 0.5$. DMF, dimethylformamide; DMA, *N*, *N*-dimethylacetamide.

It is highly probable that the "true" value of the stability constant in water K_{H_2O} (which has not yet been determined) is still lower, since the effective EPD strength of a highly associated liquid is considerably higher than that of the isolated molecules. This is regarded as a result of outer-sphere interactions between polarized solvent molecules of the inner and outer hydration spheres of the solvated cation (*34*). A more general and detailed discussion of outer-sphere effects is given in Section V.

Similar considerations may be applied to methanol as a solvent. Methanol has a donicity of DN = 19.1 so that, according to Table IV, a stability constant for $[CoCl_4]^{2-}$ of $K_{CH_3OH} \approx 5 \times 10^{+2}$ should be expected. Semiquantitative measurements carried out by Katzin (*44*) suggest, however, the stability of $[CoCl_4]^{2-}$ in methanol is lower than in DMF or DMA. This is readily explained by taking into account the strong anion-solvating properties of methanol: calculation of K(solution) by use of Fig. 4 ($\Delta G_{CH_3OH}(g) - \Delta G_{AN}(g) \approx +1.4$) and Table V gives values $\Delta G_{CH_3OH}(\text{solution}) \approx +0.48$ and $K_{CH_3OH}(\text{solution}) \approx 4.4 \times 10^{-1}$ in agreement with semiquantitative experimental results.

The strong anion-solvating power of water, methanol, and many other hydroxylic solvents is due to hydrogen bond formation.

Calculation of the stability constant of $[CoCl_4]^{2-}$ in DMSO may serve as a final test to Eq. (17); DMSO has nearly the same donicity as DMA but its EPA functions are much stronger. Consequently, K_{DMSO} (solution) is smaller than K_{DMA}(solution): $\Delta G_{DMSO}(\text{solution}) = -0.52$ and K_{DMSO} (solution) = 2.40 calculated from Fig. 4 and Table V. This is in excellent agreement with experimental values recently determined by Magnell and Reynolds (*45*) of $\Delta G_{DMSO} = -0.58$ and $K_{DMSO} = 2.66$.

It should be pointed out that the influence of anion solvation on equilibrium (*13*) cannot be explained by use of the Born-Bjerrum equations [Eqs. (1) and (2)]. Use of Eq. (2) generally gives negative ΔG values for the overall free-energy contribution to equilibrium (13) due to *anion* solvation. This means that formation of $[CoCl_4]^{2-}$ should be particularly favorable in solvents with high dielectric constants such as water in contrast to the experimental results.

Likewise the different behavior of $HClO_4$ and $(C_6H_5)_3COH$ in water and sulfuric acid cannot be explained by simple electrostatic models (*25*) as both solvents have nearly the same dielectric constant. Perchloric acid, which has pronounced EPA properties, is completely ionized in the EPD solvent, water, but it remains essentially unionized in the strong EPA solvent, sulfuric acid. Triphenylcarbinol, on the other hand, reacts quantitatively with the strong EPA solvent, H_2SO_4, but no interaction occurs with the strong EPD solvent, water.

In Section II it has been suggested that ionization reactions may be generally interpreted as substitution reactions:

$$\text{A—B} + \text{EPD} \rightleftharpoons [\text{A(EPD)}]^+ + \text{B}^-$$

In this reaction an anionic leaving group B^- is replaced by a neutral donor molecule. Consequently, if relative EPD strengths of *both* neutral *and* anionic EPD units are known, it should be possible to make at least qualitative predictions about the ionizability of substrates $A—B_1$, $A—B_2$, . . . in various EPD solvents. Approximate values of relative EPD strength of halide, pseudohalide, and neutral EPD units have been determined using vanadyl(IV)acetylacetonate, $VO(acac)_2$, as reference EPA (*46*) and are listed in Table VII. These values have proved useful for the interpretation of numerous reactions involving complex formation between transition metal ions and halide or pseudohalide ions (*18*, *46*, *28*). For example, complexes with very strong EPD ligands, such as N_3^-, NCS^-, CN^-, or F^- may exist even in solvents of high DN such as HMPA or DMSO. In solvents of weak or medium EPD properties, complex formation is essentially quantitative. On the other hand, bromo and iodo complexes usually exist only in weak EPD solvents, such as NM, PDC, or AN, and are completely ionized in solvents such as DMF, DMSO, or HMPA. The stabilities of chloro complexes are somewhat higher in the respective solvents. According to Table VII the chloride ion has an EPD strength similar to that of DMF or DMSO. Consequently chloro complexes in these solvents (compare Table IV) are ionized to some extent, sometimes with autocomplex formation.

TABLE VII

STANDARD FREE ENERGIES ΔG FOR THE 1:1 ADDUCT FORMATION OF $VO(acac)_2$ WITH NEUTRAL AND ANIONIC LIGANDS

Ligand[a]	ΔG (kcal/mole)	Ligand[a]	ΔG (kcal/mole)
N_3^-	−4.20	Cl^-	−0.83
CN^-	−4.20	DMF	−0.63
NCS^-	−2.69	TMP	−0.24
F^-	−2.69	Br^-	+0.65
HMPA	−2.50	Acetone	+1.30
Pyridine	−2.47	PDC	+1.75
$(C_6H_5)_3PO$	−2.11	I^-	+2.00
DMSO	−1.14		

[a] HMPA, hexamethylphosphoric amide, DMSO, dimethyl sulfoxide; DMF, dimethylformamide; TMP, trimethyl phosphate; PDC, propanediol-1,2-carbonate.

It should be emphasized that values given in Table VII as a measure of relative EPD strength are at best semiquantitative. The reasons for this situation will be analyzed briefly since they are of general importance to the understanding of ionization equilibria:

$$\mathrm{A_1 \cdot S_1} + L \rightleftharpoons \mathrm{A_1 \cdot L + S_1} \qquad \Delta G_{\mathrm{L}}{}^{\mathrm{A_1}}(\mathrm{S_1}) \tag{19}$$

$$\mathrm{A_1 \cdot S_1 + X^-} \rightleftharpoons \mathrm{[A_1 \cdot X]^- + S_1} \qquad \Delta G_{\mathrm{X^-}}^{\mathrm{A_1}}(\mathrm{S_1}) \tag{20}$$

$$\mathrm{A_1 \cdot S_2 + L} \rightleftharpoons \mathrm{A_1 \cdot L + S_2} \qquad \Delta G_{\mathrm{L}}{}^{\mathrm{A_1}}(\mathrm{S_2}) \tag{21}$$

$$\mathrm{A_1 \cdot S_2 + X^-} \rightleftharpoons \mathrm{[A_1 \cdot X]^- + S_2} \qquad \Delta G_{\mathrm{X^-}}^{\mathrm{A_1}}(\mathrm{S_2}) \tag{22}$$

$$\mathrm{A_2 \cdot S_1 + L} \rightleftharpoons \mathrm{A_2 \cdot L + S_1} \qquad \Delta G_{\mathrm{L}}{}^{\mathrm{A_2}}(\mathrm{S_1}) \tag{23}$$

$$\mathrm{A_2 \cdot S_1 + X^-} \rightleftharpoons \mathrm{[A_2 \cdot X]^- + S_1} \qquad \Delta G_{\mathrm{X^-}}^{\mathrm{A_2}}(\mathrm{S_1}) \tag{24}$$

In Eqs. (19)–(23), L denotes a neutral and $\mathrm{X^-}$ an anionic EPD, for which the relative EPD strength in solvents $\mathrm{S_1}$ and $\mathrm{S_2}$, respectively, toward an electron pair acceptor $\mathrm{A_1}$ are to be determined. Equations (23) and (24) are analogous to Eq. (19) and (20), except that $\mathrm{A_2}$ is used as reference EPA instead of $\mathrm{A_1}$. Using energy cycles similar to (14), the following equations can be derived, in which ΔG values refer to reactions (19)–(24) *in solution* and Δg values to the corresponding reactions *in the gas phase.* Symbols $\Delta G_{(\mathrm{sv})\mathrm{X^-}}(\mathrm{S_1})$ and $\Delta G_{(\mathrm{sv})\mathrm{X^-}}(\mathrm{S_2})$ are used for the free energies of solvation of $\mathrm{X^-}$ in the solvents $\mathrm{S_1}$ and $\mathrm{S_2}$, respectively, which are a measure of the EPA properties of these solvents; the constant α has the same meaning as previously.

$$\begin{aligned} \Delta G_{\mathrm{L}}{}^{\mathrm{A_1}}(\mathrm{S_1}) - \Delta G_{\mathrm{X^-}}^{\mathrm{A_1}}(\mathrm{S_1}) = {} & \Delta G_{\mathrm{L}}{}^{\mathrm{A_1}}(\mathrm{S_2}) - \Delta G_{\mathrm{X^-}}^{\mathrm{A_1}}(\mathrm{S_2}) \\ & + \alpha[\Delta G_{(\mathrm{sv})}{}_{\mathrm{X^-}}(\mathrm{S_1}) - \Delta G_{(\mathrm{sv})\mathrm{X^-}}(\mathrm{S_2})] \end{aligned} \tag{25}$$

$$\begin{aligned} & \Delta g_{\mathrm{L}}{}^{\mathrm{A_1}} - \Delta g_{\mathrm{X^-}}^{\mathrm{A_1}} - (\Delta g_{\mathrm{L}}{}^{\mathrm{A_2}} - \Delta g_{\mathrm{X^-}}^{\mathrm{A_2}}) = \\ & \qquad \Delta G_{\mathrm{L}}{}^{\mathrm{A_1}}(\mathrm{S_1}) - \Delta G_{\mathrm{X^-}}^{\mathrm{A_1}}(\mathrm{S_1}) - [\Delta G_{\mathrm{L}}{}^{\mathrm{A_2}}(\mathrm{S_1}) - \Delta G_{\mathrm{X^-}}^{\mathrm{A_2}}(\mathrm{S_1})] \end{aligned} \tag{26}$$

From Eq. (25) and (26) the following important conclusions may be drawn (*41*).

1. The relative EPD strengths* of anionic ligands $\mathrm{X^-}$ as compared to neutral ligands L determined toward a *given* reference EPA ($\mathrm{A_1}$) in different solvents ($\mathrm{S_1}$, $\mathrm{S_2}$), depend on the solvating properties of the solvents (i.e., the relative EPA properties) toward $\mathrm{X^-}$ and they are independent of the EPD properties of the solvents. Increasing EPA properties of the solvents causes a decrease in the EPD strength of $\mathrm{X^-}$. This may lead even to a reversal in relative EPD strength between $\mathrm{X^-}$ and L. Assume, that in a *poorly solvating solvent* a given anion $\mathrm{X^-}$

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* The relative EPD strengths are characterized by the sign and magnitude of the differences $\Delta g_{\mathrm{L}} - \Delta g_{\mathrm{X^-}}$ and $\Delta G_{\mathrm{L}} - \Delta G_{\mathrm{X^-}}$, respectively.

behaves as a slightly stronger EPD than L. When the same ligands (X^- and L) are considered in *a solvent with strong EPA properties,* then X^- may certainly behave as a weaker EPD than L, because its EPD properties are much more strongly reduced than those of L by the solvent functioning as strong EPA.

2. The relative EPD strengths of anions as determined in a *given solvent* [Eq. (26)] toward *different reference EPA units* depend on the EPA strengths of the (uncoordinated) EPA molecules. If X^- is a stronger EPD than L in the gas phase, $\Delta g_{L}^{A_1} - \Delta g_{X^-}^{A_1}$ will be positive. If the relative EPD strengths of X^- and L are determined in a solvating solvent S_1 toward a weak reference EPA (A_1), it may be possible that X^- behaves as a weaker EPD than L [$\Delta G_L(S_1) - \Delta G_{X^-}^{A_1}(S_1)$, negative], because the gas phase EPD strength of X^- will be reduced by anion solvation. If, however, the relative EPD strengths are determined (in the same solvent S_1) toward a very strong EPA (A_2), then X^- will probably behave as a stronger EPD than L *both in solution and in the gas phase*, since the free energy of solvation of X^- will only make a comparatively small contribution to the free-energy change of the overall reaction.

This is a very important effect because it readily explains, why $[CoCl_4]^{2-}$ dissolved in NB is easily ionized on addition of a strong EPD such as HMPA, whereas $Si(CH_3)_3Cl$ is not. The argument, that the strength of the Si—Cl bond is greater than that of the Co—Cl bond is insufficient. In fact, in the gas phase Cl^- is a stronger EPD than HMPA both toward (tetrahedral) $[CoCl_3]^-$ and $[Si(CH_3)_3]^+$. This means that relative EPD strengths in the gas phase are independent of EPA strengths of the acceptor groups and therefore, independent of the strength of the Co—Cl and Si—Cl bonds, respectively*. If, however,

$$[CoCl_3\cdot HMPA]^-(g) + Cl^-(g) \rightleftharpoons [CoCl_4]^{2-}(g) + HMPA(g) \qquad (27)$$

$$[Si(CH_3)_3\cdot HMPA]^+(g) + Cl^-(g) \rightleftharpoons Si(CH_3)_3Cl(g) + HMPA(g) \qquad (28)$$

the systems (27) and (28) are transferred from the gas phase to a solvent, then the Co—Cl bond will be more extensively ionized, because the free energy of solvation of Cl^- will make a comparatively larger contribution to the overall free-energy change in case of the weak EPA unit $[CoCl_3]^-$.

A simple approach, which is frequently used to estimate the ionizability of compounds is based on a comparison of bond energies. In thermochemistry the term *bond energy* usually refers to the dissociation energy of the gas phase reaction (29), which may be more precisely

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* This is valid only if both EPA units show the same [class (a) or class (b)] behavior, respectively.

termed *homolytic dissociation energy* (D_{hom}) since reaction (29) involves a homolytic cleavage of the bond A—B. It has been pointed out that,

$$\text{A—B(g)} \longrightarrow \text{A(g)} + \text{B(g)} \qquad D_{\text{hom}} \tag{29}$$

so far as ionization reactions are concerned, bond strength should be characterized by *heterolytic dissociation energies* (D_{het}) rather than by D_{hom} (*16*, *47*). Heterolytic dissociation refers to the gas phase reaction (30)

$$\text{A—B(g)} \longrightarrow \text{A}^+\text{(g)} + \text{B}^-\text{(g)} \qquad D_{\text{het}} \tag{30}$$

which involves a heterolytic cleavage of the bond A—B.*

The relationship between D_{hom} and D_{het} is given by Eq. (31) where I_A denotes the ionization energy of A and E_B the electron affinity of B.

$$D_{\text{het}} = D_{\text{hom}} + I_A + E_B \tag{31}$$

Although D_{het} is always greater than D_{hom},† EPD–EPA interactions in coordinating solvents usually lead to heterolytic bond cleavage. As has already been pointed out, this is owing to the fact that A^+ and B^- are considerably stronger coordinating, respectively, than the parent radicals, A and B. Consequently, stabilization of the reaction products by EPD or (and) EPA interactions with solvent molecules is more favorable for ionic reaction products than for radicals. In weakly coordinating or noncoordinating solvents, radical formation may sometimes be energetically favored, as in solutions of hexaphenylethane in benzene or in hexane.

From the foregoing considerations it is apparent that thermodynamic properties of compounds such as ionization constants or solubilities do not only depend on heterolytic dissociation energies but may be strongly influenced by free energies of solvation or free-energy contributions associated with changes in the state of aggregation.

An instructive example is the behavior of methylmercury halides, CH_3HgX. Thermochemical calculations (Table VIII) reveal that heterolytic dissociation energies for the reaction

$$CH_3HgX(g) \longrightarrow CH_3Hg^+(g) + X^-(g)$$

increase regularly in the series X = I < Br < Cl (*48*). Consequently, it may be expected that ionization constants in water increase in the order Cl < Br < I, as for the hydrogen halides (Table VIII). In fact, the

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* Since two modes of ionization are possible ($A - B \rightarrow A^- + B^+$), D_{het} always refers to the process that requires less energy.

† The lowest value of ionization potentials of neutral atoms or groups has been measured for cesium, $I_{Cs} = +3.89$ eV, the highest value of electron affinities of neutral atoms or groups is that of chlorine, $E_{Cl} = -3.61$ eV.

TABLE VIII

DISSOCIATION CONSTANTS (K), SOLUBILITY PRODUCTS (K_s), SOLUBILITIES, AND HETEROLYTIC DISSOCIATION ENERGIES (D_{het}) FOR VARIOUS COMPOUNDS

Compound	K (moles liter^{-1})	D_{het} (kcal)	Compound	K_s (moles^2 liter^{-2})	D_{het} (kcal)
HF	6.7×10^{-4}	368	AgCl	1.6×10^{-10}	166
HCl	$> 10^{+4}$	331	AgBr	6.3×10^{-13}	163
HBr	$> 10^{+6}$	321	AgI	1.0×10^{-16}	158
CH_3HgF	3.2×10^{-2}	—	TlCl	2.2×10^{-4}	144
CH_3HgCl	5.6×10^{-6}	188	TlBr	3.9×10^{-6}	140
CH_3HgBr	2.4×10^{-7}	184	TlI	3.1×10^{-8}	136
CH_3HgI	2.5×10^{-9}	180			
	Solubility[a] (moles/1000 gm H_2O)			Solubility[a] (moles/1000 gm H_2O)	
NaF	1.00	151	KCl	4.70	116
NaCl	6.16	131	KBr	5.71	112
NaBr	9.14	127	KI	8.84	107
NaI	12.40	116			

[a] Solubility products could not be calculated due to lack of activity coefficient data for saturated solutions.

reverse stability order is found in water and this has been considered as a consequence of typical "soft acid" behavior of the CH_3Hg^+ ion (*49*). This behavior is explained in the following qualitative way. The D_{het} values for CH_3HgX compounds are comparatively little differentiated. The increase in bond energies in the series I < Br < Cl is therefore overcompensated by the strong increase (numerical values) in solvation energies of the halide ions. This would suggest that methylmercury halides should show normal stabilities $K_{CH_3HgI} > K_{CH_3HgBr} > K_{CH_3HgCl} > K_{CH_3HgF}$,

$$K = \frac{[CH_3Hg^+][X^-]}{[CH_3HgX]}$$

in solvents of poor solvating properties for halide ions—a behavior that was actually found in preliminary conductometric studies in HMPA (*48*).

Obviously soft acid behavior of methylmercury *halides* is not an inherent property of the CH_3Hg^+ ion but actually a function of the solvating properties of the solvent toward the anionic ligands; this suggests a more critical interpretation of the basic principles of the Hard and Soft Acids and Bases (HASAB) concept (*50*).

However, ionization constants of the hydrogen halides increase in the sequence HF < HCl < HBr < HI corresponding to decreasing values of D_{het}.

Similar considerations apply to solubility equilibria [energy cycle (8)]. The D_{het} values for Ag(I) and Tl(I) halides (Table VIII) increase in the normal sequence I < Br < Cl < F, whereas solubilities are lowest for the iodides and highest for the fluorides. On the other hand, solubilities for some alkali metal halides show the same trends as may be expected from trends in D_{het} values because, for the alkali metal halides listed in Table VIII, the contributions to ΔG [see energy cycle (8)], arising from free energies of sublimation and free energies of solvation of the halide ions, are partly compensating. Compensation is incomplete for Ag(I) and Tl(I) halides so that solubilities are strongly influenced by anion solvation.

In practice, apart from the examples listed in Table VIII, there is a large number of compounds for which D_{het} values may serve as a qualitative measure of ionizability. For reasons previously discussed this will most probably be true for compounds characterized by high values of D_{het}. Examples are provided by many inorganic and organometallic halides, for instance, SiF_4 and $SiCl_4$ give only nonionic adducts with EPD molecules, even in the case of strong EPD units such as pyridine or ammonia. In contrast, iodo compounds, such as SiI_4, SnI_4, and BI_3, are easily ionized by strong EPD molecules (*51–54*), for example:

$$4py + SiI_4 \rightleftharpoons [py_4 \cdot SiI_2]^{2+} + 2I^-$$

$$2py + BI_3 \rightleftharpoons [py_2BI_2]^+ + I^-$$

IV. Ionization and Dissociation

It has been demonstrated that formation of ions from a covalent substrate is the result of EPD–EPA interactions.

So far the existence of ion pair equilibria has been excluded from our considerations. In fact, ion association is a common and characteristic phenomenon in nonaqueous solutions. Ionization of a covalent compound may be defined as the process leading to the formation of solvated ions independent of their presence as associated ions or as free entities.

Generally ionization of a covalent compound AB proceeds in two steps (*35*), which may be represented in the following way:

$$\underset{}{AB} \underset{\text{(step I)}}{\overset{K_{\text{form}}}{\rightleftharpoons}} [A^+ \cdot B^-] \underset{\text{(step II)}}{\overset{K_{\text{sep}}}{\rightleftharpoons}} A^+ + B^- \qquad (32)$$

Heterolysis of A—B due to EPD or EPA interactions with solvent molecules (not shown) results primarily in the formation of associated ions. This process (step I) may be characterized by the equilibrium constant K_{form} which may be termed "formation constant of the ion pair from the covalent substrate".

$$K_{\text{form}} = \frac{c_{A^+ . B^-}}{c_{AB}}$$

In a medium of reasonably high dielectric constant, the ion pair undergoes electrolytic dissociation into the free ions A^+ and B^-. This process (step II) may be characterized by the equilibrium constant K_{sep} which may be termed "ion pair separation constant":

$$K_{\text{sep}} = \frac{c_{A^+} \cdot c_{B^-}}{c_{A^+ . B^-}}$$

Step I is primarily dependent on the functional (coordinating) properties of the solvent; step II (according to the Coulomb law) is mainly a function of the dielectric constant of the medium (*35*)

The equilibrium constant K of the overall process.

$$\text{A—B} \rightleftharpoons \text{A}^+ + \text{B}^- \qquad K$$

is equal to the product of the equilibrium constants of the constituent equilibria.

$$K = K_{\text{form}} \cdot K_{\text{sep}}$$

Constant K is identical with the ionization or dissociation constant in the classical sense, also known as the acidity constant for Brönsted acids or the basicity constant for Brönsted bases.

In a medium of high dielectric constant, such as in water, the concentration of associated ions is negligibly small; K_{form} and K_{sep} cannot be measured separately and this is the reason why in water and in other solvents of high dielectric constant only the overall (classic) equilibrium constant K is meaningful. On the other hand, in solvents of low dielectric constant (e.g., tributylphosphate), there will be practically no electrolytic dissociation, so that the ionized substrate will be present nearly exclusively as associated ions. Consequently, the ionization process is best characterized by K_{form}.

In solvents of medium dielectric constant, K_{form} and K_{sep} may be determined separately by combination of appropriate experimental techniques. For example, spectrophotometric or NMR techniques may be applied to obtain the total concentration c_I of ionized substrate, that is,

$$c_I = c_{\text{A}^+.\text{B}^-} + c_{\text{A}^+} = c_{\text{A}^+.\text{B}^-} + c_{\text{B}^-}$$

whereas the concentration of free ions $c_{\text{A}^+} = c_{\text{B}^-}$ may be determined by conductometric measurements. With c_0 denoting the analytical concentration of the solute, one obtains:

$$c_0 = c_{\text{AB}} + c_{\text{A}^+.\text{B}^-} + c_{\text{A}^+} = c_{\text{AB}} + c_I$$

$$K_{\text{form}} = \frac{c_I - c_{\text{A}^+}}{c_0 - c_I} \qquad K_{\text{sep}} = \frac{c^2_{\text{A}^+}}{c_I - c_{\text{A}^+}}$$

If K_{form} and K_{sep} cannot be determined directly as shown in the preceding equations, approximate values of K_{sep} may be obtained by comparison with the electrolytic dissociation behavior of suitable model electrolytes such as quaternary ammonium salts.

Considering reaction (32), it is immediately realized that the ionization of a covalent substrate is a function of both the functional and the dielectric properties of the solvent. This may be illustrated by a simple model calculation as described in the following.

Consider two EPD solvents, S_1 and S_2, which have the same EPD properties and hence the same K_{form} values, e.g., $K_{\text{form}} = 1$. Solvent S_3 is assumed to be a stronger EPD solvent, characterized by $K_{\text{form}} = 3$. Solvents S_1 and S_3 may have similar dielectric constants of about 10, but S_2 is assumed to have a higher dielectric constant of about 30; this may correspond to values K_{sep} of approximately $K_{\text{sep}} \approx 10^{-4}$ (S_1, S_3) and $K_{\text{sep}} \approx 10^{-2}$ (S_2).

The extent of ionization, that is percentage of ionized substrate (ion pairs + free ions) of total solute concentration c_0 has been calculated and results are presented in Table IX. It is seen that AB is more strongly ionized in solvent S_2 which has the same EPD properties as S_1 but a considerably higher dielectric constant. On the other hand, AB is most strongly ionized in S_3 although its dielectric constant is low compared to S_2 and this is clearly due to its stronger EPD properties. However, solutions of AB are much better conductors in S_2 than in S_3 because in the latter solvent the ionized substrate is mainly present as ion pairs, which do not contribute to the conductivity of the solution.

TABLE IX

EXTENT OF IONIZATION OF A COVALENT SUBSTRATE A—B AT $c_0 = 10^{-2}$ MOLE/LITER UNDER ARBITRARILY ASSUMED CONDITIONS

Solvent	Assumed ε	Assumed K_{sep}	Assumed K_{form}	% Ionized
S_1	10	10^{-4}	1	53
S_2	30	10^{-2}	1	75
S_3	10	10^{-4}	3	77

Comparison of dissociation constants of acids and bases derived from electrochemical or conductivity measurements in solvents of different dielectric constants are meaningless (*25*, *28*) since equilibrium constants determined in this way always represent the overall equilibrium constant $K = K_{\text{form}} \cdot K_{\text{sep}}$.

Although liquid ammonia is known to have considerably stronger coordinating properties than water, the acidity constant of HCl is much smaller in liquid ammonia ($K_A \approx 10^{-4}$) than in water ($K_A \gg 10^4$). Ionization of HCl is essentially complete in both solvents, hence the observed large differences in dissociation constants are mainly due to differences in dielectric constants of the media (water, $\varepsilon = 81$; ammonia, $\varepsilon = 17$).

On the other hand, the acidity constant of acetic acid is higher in liquid ammonia ($K_A \approx 10^{-4}$) than in water ($K_A \approx 10^{-5}$). Acetic acid is moderately ionized in water, but in liquid ammonia, owing to its stronger EPD properties, ionization is nearly complete. Obviously the influence of K_{sep} in liquid ammonia is overcompensated by K_{form} (*25*, *28*).

Although comparison of classic dissociation constants for one compound in different solvents is meaningless, it remains useful to compare classic dissociation constants of different solutes in a given solvent.

The situation may be further illustrated by comparing the electrolytic dissociation behavior of lithium halides and tetrabutylammonium halides in the solvents PDC(DN $= 15.1$; $\varepsilon = 69.0$) and HMPA(DN $= 38.8$; $\varepsilon = 29.6$) (*55*). Lithium bromide and in particular LiCl are associated in PDC, but they are fully dissociated in HMPA. This cannot be explained by simple electrostatic considerations. The HMPA has a much lower dielectric constant, and the dipole moments of the two solvents are similar ($\mu_{\mathrm{HMPA}} = 5.37$; $\mu_{\mathrm{PDC}} = 4.98$). The behavior is, however, readily interpreted from the functional point of view. The HMPA acts as a very strong EPD and, consequently, lithium halides are completely ionized with formation of tightly solvated Li^+ ions. Due to the large effective radius of the HMPA-solvated lithium ion, the center-to-center distance in the ion pair $[Li(HMPA)_n{}^+ \cdot X^-]$ is so great that complete dissociation is easily effected in dilute solutions. In PDC, which is a considerably weaker EPD solvent, LiCl and LiBr exist as unionized molecules LiX ("contact" ion pairs)* in equilibrium with the free solvated ions Li^+ and X^-, the concentration of ion pairs $[Li(PDC)_n{}^+ \cdot X^-]$ being negligibly small due to the high dielectric constant of this solvent. The behavior of lithium halides in PDC is thus entirely analogous to the behavior of, for instance, acetic acid in water.*

The differing behavior of lithium halides in PDC and in HMPA is also in agreement with semiquantitative data for the relative EPD strengths of halide ions and EPD solvents (Table VII, Section III). The solvent HMPA is a stronger EPD than both Cl^- and Br^-, and hence these ligands are easily replaced by HMPA at the lithium ion; on the other hand, PDC is a weaker EPD than Cl^- and Br^-, and hence these ligands are only partly replaced despite the large excess of solvent molecules present.

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* From the functional point of view, there is no basic difference between an unionized CH_3COOH molecule and unionized LiX molecules. Consequently, it has been proposed (*16*) to consider "contact ion pairs" as unionized species rather than ionic associates. This appears particularly true in the case of lithium compounds, as lithium ion has a strong tendency for covalent bond formation. The term "ion pair" should therefore be restricted to interactions between tightly and fully solvated ions.

Unlike lithium halides, tetrabutylammonium halides are fully dissociated in PDC, but they are associated in HMPA, and this is in agreement with simple electrostatic considerations. Similar results have been found in DMF, where alkali metal halides are fully dissociated whereas tetraalkylammonium halides are associated (*56*, *57*).

It may be concluded that electrostatic models may be successfully applied only so far as interactions between weakly coordinating or noncoordinating species (such as tetraalkylammonium ions) are concerned. This is illustrated by Table X which shows that variations of association constants for tetrabutylammonium iodide as a function of dielectric constant roughly correspond to the trends predicted by the Bjerrum theory. When iodide, which is a comparatively weak base, is replaced by counterions with stronger EPD properties, such as bromide or chloride ions, anion solvation becomes increasingly effective and this is particularly true for hydrogen-bonded solvents. For example, in aprotic solvents, association constants of tetraalkylammonium halides usually increase in the series $Cl^- > Br^- > I^-$, whereas the opposite behavior is observed in hydroxylic solvents (e.g., CH_3OH and C_2H_5OH). Again, the elementary electrostatic theory cannot provide a *consistent* explanation for this behavior.

TABLE X

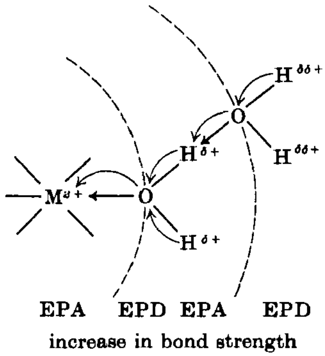
ASSOCIATION CONSTANTS K_{ass} OF TETRABUTYLAMMONIUM IODIDE AS A FUNCTION OF DIELECTRIC CONSTANT

Solvent[a]	ε	K_{ass}	Solvent[a]	ε	K_{ass}
Pyridine	12.3	2400	Methanol	32.6	16
1-Butanol	17.5	1200	DMF	36.7	8
1-Propanol	20.1	415	Acetonitrile	36.0	3
Methylethylketone	18.5	380	DMA	37.8	0
Acetone	20.7	143	DMSO	46.7	0
Ethanol	24.3	123	*N*-Methyl-acetamide	165.5	0
Nitrobenzene	34.8	27			

[a] DMF, dimethylformamide; DMA, *N*,*N*-dimethylacetamide; DMSO, dimethyl sulfoxide.

V. Outer-Sphere Interactions, Association and Self-ionization of Solvents

It has been mentioned in Section III that the polarographic reduction of metal cations occurs in water at much more negative potential values than would be expected from a donicity value of 18 for water. This has been explained in the following way (*34*). Water in the pure liquid state is a highly associated liquid. Coordination of water molecules to a metal cation (acting as EPA) causes polarization of the O—H bonds and hence an increase in acidity at the hydrogen atoms. Outer-sphere interactions between these acidic hydrogen atoms and additional water molecules lead to outer-sphere hydration. This coordination provokes at the already coordinated oxygen atoms of water molecules an increase in electron density and hence an increase in EPD strength. This transfer of negative charges toward the metal cation results in an increase in inner-sphere coordinate bond strength due to outer-sphere coordination. This has been called the *first outer-sphere effect* (*58*, *59*):



This effect may be further increased by further outer-sphere coordination, e.g., by attachment of additional hydration spheres or any other EPD ligands. As a consequence, water in the pure liquid state behaves as a stronger EPD as compared to single water molecules coordinated within *one* hydration sphere, for example, when a transition metal hydrate is dissolved in a weakly coordinating medium such as nitromethane or dichloromethane. A similar behavior may be expected for other associated liquids such as formic amide and acetic acid. In order to characterize the EPD properties of water (and other highly associated liquids), the term *bulk donicity* (DN^B) has been introduced (*34*). The bulk donicity is distinguished from donicity values (DN) determined toward (excess) $SbCl_5$ as reference acid in 1,2-dichloroethane which are a measure of the EPD strengths of the unassociated EPD molecules. Bulk donicity values of approximately 28 to 30 have been estimated for water from polarographic reductions of a number of divalent metal cations (*34*).

Outer-sphere effects occur also when an anion is acting as the coordination center: charge transfer from the anion via hydrogen bridges to the oxygen atoms leads to an increase in electron density at the oxygen atoms. Outer-sphere interactions with further water molecules (acting as EPA) in the second hydration sphere cause an increase in EPA properties of the hydrogens bonded to the anion and in this way the strength of the inner-sphere coordinate bonds is increased. This may be called the *second outer-sphere effect* because it arises from outer-sphere coordination of EPA units (*58*).

Outer-sphere interactions are by no means restricted to interactions between coordinated and uncoordinated solvent molecules (*58*, *59*). Generally, all interactions involving formation of coordinate bonds between coordinated (neutral or charged) ligands and neutral or charged reactants may be termed outer-sphere interactions. For instance, it has been shown by kinetic experiments that "coordinatively saturated" complex cations, such as $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, or $[Co(H_2O)_6]^{3+}$, are forming stable outer-sphere complexes with various anions (*60*); this has been confirmed by conductometric, spectrophotometric, and polarographic measurements (*61*, *62*). The high stability of these complexes is due to the existence of hydrogen bonds between the anions and the acidic hydrogen atoms. Similarly, it has been shown that exchange of NCS^- groups by solvent molecules S in the complex anion

$$[Cr(NH_3)_2(NCS)_4]^- + H_2O \longrightarrow Cr(NH_3)_2H_2O(NCS)_3 + NCS^-$$

proceeds much more rapidly in hydroxylic than in aprotic solvents (*63*). This is due to a weakening of the Cr—N bond by water coordinated to the NCS group of the complex ion with formation of hydrogen bridges (*59*). A similar explanation holds for the acid-catalyzed aquation of $[Cr(H_2O)_5Cl]^{2+}$ (*64*). The existence of outer-sphere interactions of this type has been clearly demonstrated by recent polarographic measurements (*65*). Half-wave potentials for the reduction of hexacyanoferrate(III) to hexacyanoferrate(II) in aprotic solvents are shifted to more positive values on addition of hydroxylic solvents. Since in the reduced state the nitrogen atoms of the coordinated ligands are more basic than in the oxidized state, the former will be more strongly stabilized by EPA outer-sphere coordination resulting in a shift to positive potentials values.

It has been mentioned in Section III that $[CoCl_4]^{2-}$ is unstable in water even in the presence of large amounts of alkali metal chlorides. In contrast $[CoCl_4]^{2-}$ is quantitatively formed in concentrated aqueous solutions of hydrochloric acid (*66*). Outer-sphere interactions between water molecules and hydronium ions will lead to the formation of highly aggregated clusters $[H(H_2O)_n]^+$. In this way the concentration of free water molecules available for outer-sphere coordination at Co^{2+} as well as for hydration of chloride ions is drastically decreased. Hence, in a concentrated HCl solution, both Co^{2+} and Cl^- are less strongly solvated than in alkali metal chloride solutions.

The existence of outer-sphere interactions in associated liquids as derived from experimental results and from functional considerations is supported by recent quantum mechanical calculations. Molecular orbital calculations (*67*, *68*) reveal that, contrary to elementary electrostatic models, hydration of ions is associated with a considerable charge transfer from the coordination center to the water molecules and a simultaneous increase (cation solvation) and decrease (anion solvation), respectively, of the terminal O—H bond distances. Addition of further water molecules in the second hydration sphere leads to an additional charge transfer and to a decrease in potential energy of the system. The extent of charge transfer by outer-sphere hydration is smaller than that by inner-sphere hydration. Mean hydrogen bond energies ΔE between water molecules of the first and the second hydration sphere are considerably greater than in pure water. In the case of lithium ion the polarizing influence of the coordination center is noticeable even in the third hydration shell, whereas only two coordination spheres appear to be involved in the hydration of the fluoride ion. The results of model calculations are listed in Table XI. It has been emphasized that the extent of charge transfer is exaggerated by the semiempirical CNDO/2 procedure compared to the results of *ab initio* calculations, but the qualitative trends, which are found identical for both methods (*67*, *68*), are significant.

It appears that outer-sphere effects are also responsible for the occurrence of self-ionization equilibria in pure amphoteric liquids. For instance, it has been recognized long ago that water and liquid ammonia undergo self-ionization to limited degrees. Jander (*69*) considered the existence of self-ionization equilibria as characteristic of so-called waterlike solvents. By analogy, self-ionization equilibria have been assumed for various nonaqueous solvents (usually because of low conductivities found in pure liquids) such as liquid sulfur dioxide or phosphorous oxychlorides (*70*). This concept has been widely used in a formal way on the basis of a generalized acid–base theory for the interpretation of reactions in these media. It is now generally recognized that a solvent may have good ionizing properties although there is no evidence for the existence of a self-ionization equilibrium. For example, isotopic exchange studies revealed that, in liquid sulfur dioxide, self-ionization is not detectable and that the low conductivities observed in the pure liquid are obviously due to trace impurities; on the other hand,

TABLE XI

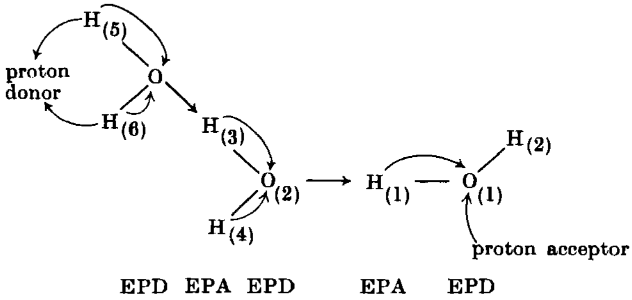
CHARGE DISTRIBUTION FOR HYDRATED LITHIUM AND FLUORIDE IONS (SINGLE HYDRATION SHELL)

Li⁺				F⁻			
Coordination No.	q_{Li}	$q_{\mathrm{H_2O}}$	ΔE(kcal)[a]	Coordination No.	q_{F}	$q_{\mathrm{H_2O}}$	ΔE(kcal)[a]
4	+0.444	+0.139	15.2	4	−0.549	−0.113	11.6
6	+0.311	+0.114	13.9	6	−0.560	−0.073	11.2
8	+0.245	+0.095	13.3	8	−0.052	−0.052	9.9

[a] Mean hydrogen bond energies ΔE for two hydration shells: each water molecule of the first hydration shell is coordinated to three water molecules of the second hydration sphere.

self-ionization is well supported for solvents such as liquid BrF_3, HF, ICl, H_2SO_4, or CH_3COOH.

A common feature of self-ionizing solvents are the amphoteric properties of the solvent molecules, since they may act both as EPD and as EPA (*27*). It appears therefore that outer-sphere effects, similar to those existing between polarized solvent molecules of solvated ions, occur in the pure liquids resulting in mutual polarization of solvent molecules within associated units. From the functional point of view this is described in the following way:



Nucleophilic attack of a water molecule [oxygen atom O(2)] at hydrogen atom (1) of another water molecule leads to an increase in acidity of hydrogen atoms (3) and (4) as well as to an increase in EPD strength of oxygen atom O(1). The EPD–EPA interactions between the hydrogen atoms (3) or (4) [which are more acidic than H(1)] will further increase both the acidity of the terminal hydrogen atoms H(5) and H(6) and the EPD strength of the terminal oxygen atom O(1). With increasing chain length this process may finally result in a proton transfer of an acidic hydrogen atom of one aggregate to the basic terminal oxygen atom of another aggregate. This process is known as autoprotolysis or self-ionization.

Recent quantum mechanical calculations strongly support this model. The CNDO/2 calculations on linear chains of H_2O and HF molecules reveal (Table XII) that the mean energy ΔE of the hydrogen bonds increases with increasing chain length (cooperative effect) (*68*). Even more significant is the energy $\Delta E_{(n-1)\rightarrow n}$ for addition of the "last" solvent molecule; it is always higher than ΔE and clearly reflects the increasing acidity (basicity) of the terminal hydrogen and oxygen atoms, respectively. Calculations for associates with tetrahedral geometry, which represent a more realistic model for the structure of liquid water, show similar trends although the effects are somewhat smaller (*71*). It should perhaps be mentioned that elementary electrostatic models

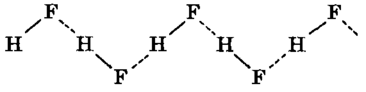
TABLE XII

MEAN HYDROGEN BOND ENERGIES FOR LINEAR CHAINS OF H_2O AND HF MOLECULES AS A FUNCTION OF CHAIN LENGTH

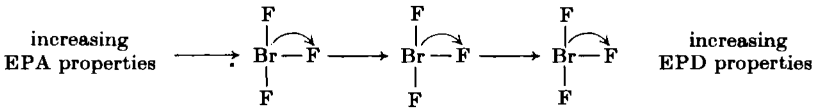
H_2O			HF		
No. of molecules	ΔE(kcal)	$\Delta E_{(n-1)\to n}$(kcal)	No. of molecules	ΔE(kcal)	$\Delta E_{(n-1)\to n}$(kcal)
2	8.68	8.68	2	9.50	9.50
3	9.63	10.59	3	10.88	12.25
4	10.12	11.11	4	11.62	13.12
5	10.43	11.34	5	12.08	13.45
6	10.61	11.44	6	12.38	13.60
7	10.78	11.50	7	12.60	13.68
8	10.98	11.54	8	12.76	13.72

cannot account for the structure of hydrogen-bonded associates: electrostatic theory predicts a linear arrangement of H—F molecules as the most stable structure of the HF dimer, in contrast to quantum-mechanical calculations (*68*) from which a bent structure is predicted in agreement with spectroscopic measurements.

The existence of hydrogen bonds is not a necessary condition for association and self-ionization of solvents. Association of liquid hydrogen fluoride, for example, can be explained equally well by hydrogen bridges between fluorine atoms and fluorine bridges between hydrogen atoms (*72*):

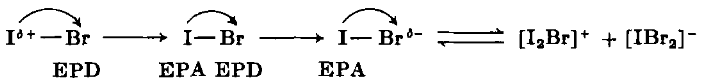


Fluorine bridges are responsible for the association of solvent molecules in liquid bromine(III)-fluoride (*73*):



$$(BrF_3)_m \cdot BrF_3 + (BrF_3)_n \cdot BrF_3 \rightleftharpoons [BrF_2 \cdot (BrF_3)_m]^+ + [BrF_4 \cdot (BrF_3)_n]^-$$

Analogous to water, increasing chain length results in increasing EPD properties of the terminal F atom and increasing EPA properties of the terminal Br atom. In this way fluoride ion transfer is promoted between two aggregates and this means self-ionization. Association in liquid ICl, IBr, $AsCl_3$, $SbCl_3$, $HgBr_2$, etc., may be explained similarly (*74–78*):



$$\underset{\text{EPD}}{\mathrm{I}^{\delta+}\text{—}\mathrm{Br}} \longrightarrow \underset{\text{EPA EPD}}{\mathrm{I}\text{—}\mathrm{Br}} \longrightarrow \underset{\text{EPA}}{\mathrm{I}\text{—}\mathrm{Br}^{\delta-}} \rightleftharpoons [\mathrm{I_2Br}]^+ + [\mathrm{IBr_2}]^-$$

Little is known about the thermodynamics of self-ionization equilibria. It appears that the extent of self-ionization is primarily related to the strength of the bridge bonds. For example, self-ionization constants for HF, H_2O, and NH_3 are decreasing in the order HF ($K \approx 10^{-12}$) > H_2O ($K \approx 10^{-14}$) ≫ NH_3 ($K \approx 10^{-33}$) which corresponds to the order of decreasing hydrogen bond strength. However, comparison of self-ionization constants is justified only so long as the dielectric constants of the solvents are about the same.

It is apparent that association between solvent molecules and self-ionization are interrelated phenomena in that both effects are increased by increase in extent of the amphoteric properties of the solvent molecules.

VI. Conclusion

Elementary electrostatic theory cannot account for the observed ionization equilibria in nonaqueous solvents. The functional approach provides a qualitative interpretation of all ionization phenomena, and this is in agreement with quantum mechanical results. This approach considers the coordinating properties of the solvents toward neutral solutes, cations, and anions and takes into account outer-sphere coordination occurring both in the pure solvents and in the solutions. The application of the donicity and of other phenomenological properties allows a number of semiquantitative predictions.

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