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SUBSTITUENT EFFECTS ON THE STABILITY OF METAL CHELATES

and

FURTHER RELATIONSHIPS IN THE GRUNWALD TREATMENT OF ACID-BASE EQUILIBRIA IN HYDROXYLIC SOLVENTS

by

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Introduction

A considerable amount of work has been done in the study of metal chelate compounds. Such compounds appear in widely different fields from biochemistry to metallurgy, and any information obtained may have wide implications. A great deal of attention has been paid to the stability of these metal chelate compounds in both the thermodynamic sense and kinetically. Excellent reviews of the field are available in books by Martell and Calvin (1) and Bailar (2).

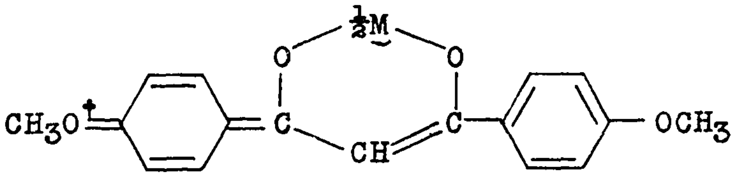
In this study attention will be centered in factors affecting the thermodynamic stability of metal chelate compounds. These factors, as in most cases, can be conveniently placed in one of two categories. First, steric factors are directly or indirectly related to non-bonding interactions between neighboring parts of a molecule or, more simply, factors which occur because two parts of a molecule cannot occupy the same space at the same time. Secondly, "electronic" factors are usually accounted for by electrostatic and electron delocalization considerations when steric effects may be counted as essentially negligible. The category of the present effort is that of "electronic" effects.

The most suitable way in which to study electronic effects is to carry out experiments in such a way that steric effects can be assumed essentially constant. In this case, metal chelates of a series of symetrically substituted dibenzoylmethanes were studied. Thus steric factors at the functional group of the molecule were kept essentially constant by keeping the substituents in the meta and para positions of the phenyl rings. Use of substituted aromatic compounds as a means of studying electronic factors has the further advantage of being amenable to treatment by Hammett's (3) relationship.

The Hammett correlation for substituted aromatic compounds is of the form

$$\log \frac{k}{k_0} = \rho\sigma$$

where k_0 is a rate or equilibrium constant of the unsubstituted compound, k is the rate or equilibrium constant of the substituted compound, σ is a constant which is characteristic of a given substituent, and ρ is a constant which is dependent on the type of reaction under investigation. The ρ values are chosen by assuming a ρ value of one for the acid dissociation constants of substituted benzoic acids in aqueous solution. The value of σ may be considered to be a measure of the sensitivity of a reaction to substituent effects. As a first approximation, it may be assumed that the sensitivity of a reaction to substituent effects can be interpreted electrostatically in terms of the interaction of the substituent dipoles with the change in the charge in the neighborhood of the functional group during a reaction. In the case of metal chelates of substituted dibenzoylmethanes, it would be expected that the value will reflect the charge distribution across the metal-oxygen bonds. It would be expected, for example, that metals forming more covalent bonds would have a smaller ρ value than those metals which form more ionic complexes. It is proposed, therefore, to measure the ρ values for some different divalent metals and compare them with our previous notions about their respective bonding characteristics. Of particular interest would be deviations of the p-methoxy substituents from a Hammett correlation. Such a deviation could be taken as indicating a significant degree of covalent character in the metal chelate bond because of possible contributions of structures such as



Experimental

The stability constants of the chelates of Be, Mg, Co, Ni, Cu, and Zn were measured using the method of Bjerrum (4). Because of the lack of solubility of the metal chelates in water, 75 per cent by volume dioxan-water was used as a solvent medium. This solvent, although greatly enhancing the solubility of the metal chelates, still allows suitably reproducible potentiometric measurements of hydrogen ion concentrations.

Materials

The preparation of the chelating agents, p-MeO, p-Me, m-MeO, m-Me, p-Cl, and the unsubstituted dibenzoylmethanes has been described previously.

The metal perchlorates were obtained from G. F. Smith Co. and were used without further purification. Beryllium nitrate was furnished by Dr. D. S. Martin. Potassium perchlorate was recrystallized from water to which a very small amount of potassium hydroxide was added.

Dioxan was purified according to the method of Fieser (6) and stored over sodium. Shortly before use the dioxan was refluxed until the sodium appeared bright, and the required amount of dioxan was distilled off. This procedure was used to eliminate noticeable amounts of acid which probably was formed by hydrolysis of an oxidation production of the dioxan.

Carbonate free 0.5 N potassium hydroxide solution was prepared by allowing a suitable amount of potassium to react with isopropyl alcohol under a nitrogen atmosphere and diluting with water to the proper volume.

Method and apparatus

The titration vessel used was a double walled beaker of about 250 ml. capacity fitted with an inlet and an outlet to the outer jacket. This outer jacket was connected with a pump which circulated water from a constant temperature bath of 25° C. through it. The top of the vessel was covered with a large rubber stopper fitted with Beckman glass and calomel electrodes, an air powered stirring motor, an inlet tube for nitrogen, and a tube for the addition of the titrant which was arranged so that it projected just below the surface of the solution in the vessel.

The potentials across the calomel and glass electrodes were measured with a Beckman model G pH meter. All parts of the apparatus were grounded to the same potential including the water in the water bath. At the time of a measurement, all electrical apparatus in the neighborhood of the titration vessel were shut off.

Calibration of the pH meter to measure log $[H^+]$

The pH scale of the pH meter was used for all measurements since it is necessary to go through zero milivolts during most titrations and this would require switching from the + to the - mv. scale, which apparently do not match up exactly on the meter used. An additional advantage of the pH scale is that with the temperature compensator set at 25° C. changes in potential are read directly in units of log $[H^+]$. All that need be determined is an additive constant which relates scale reading to log $[H^+]$. With the zero adjusting knob turned to the counter-clockwise limit the scale reading for an aqueous buffer of pH 7 was observed. This reading was recorded and any variation of it before and after a titration was taken to indicate a change in the condition of the electrodes.

The variation in this reading over a large period of time was negligible. The additive constant for the meter and electrodes used was determined by comparison of pH meter scale readings with known concentrations of perchloric acid in 75 per cent dioxan-water solutions. The range of perchloric acid concentration was between 0.0001 and 0.1 N. All solutions were 0.05 N in potassium perchlorate. The plot of log $[H^+]$ versus pH meter scale reading was essentially linear with a slope of one. The scale constant for the meter was found to be 1.25 ± 0.03. A similar process was carried out with solutions of known concentrations of potassium hydroxide. Using the scale constant of 1.25 the negative logarithm of the ion product of 75 per cent dioxan-water 0.05 N in $KClO_4$

was calculated to be about 16.9. This is a very reasonable value (7, p. 581). The reproducibility of this value was taken as indication of the purity of the dioxan.

Stability of the potentials

No great difficulty was involved in obtaining stable potentials in a fairly well buffered solution when suitable precautions were taken to ground the apparatus. The only time drifting potentials were observed was in the neighborhood of a sharp end point where buffering is slight. This introduces no great error since values of the potential at these points are not critical to the calculation of the equilibrium constants.

Measurements of stability constants

Suitable volumes of stock solutions of metal perchlorates in water and the chelating agent in dioxan were diluted with enough water and dioxan to form 98.5 ml. of a solution about 0.0005 M in metal ion and 0.002 M in chelating agent in 75 per cent by volume dioxan-water. Enough solid potassium perchlorate was added to make the solution 0.05 N in $KClO_4$. The volume 98.5 ml. is obtained when 25 ml. of water and 75 ml. of dioxan are combined. No measurable deviation from this value is observed in the presence of dissolved salts. The solution was titrated with approximately 0.05 N KOH in 75 per cent dioxan-water.

Calculation of stability constants

The method used to calculate the formation function is identical to that illustrated by Martell and Calvin (1, p. 87). The formation function values for a given titration are plotted *versus* the logarithm of the concentration of the chelating agent anion. A first approximation to the value of the pKs for the stability of the complexes is given by the value of the logarithm of the chelating agent anion which corresponds to a value of the formation function of 0.5 for the first step of chelation and a value of 1.5 for the second step. These approximate values are refined by means of the convergence relationship reported by Von Uitert, *et al.* (8). The refined values are given in Table 1.

The products of the first and second equilibrium constant were compared with the equilibrium constant of the overall reaction which is obtained from the value of the logarithm of the chelating agent anion concentration that corresponds to a value of the formation function of one. This comparison was used as a check on the internal consistency of the data. In any case in which the data did not check, and especially if it was not possible to experimentally observe all the constants as is the case of strong chelates, the formation of a species of KeMOH or the hydrolysis of the metal was suspected. In order to check the possibility of formation of KeMOH experiments were carried out in which the concentration of the chelating agent was varied while every-

Table 1. Stability constant of substituted metal dibenzoylmethane

	p-OCH_3	p-CH_3	H	m-OCH_3	p-Cl
pK_a	12.35	11.99	11.58	11.41	10.78
Be					
pK_1	11.81	11.36	10.55[a]	10.71	10.62
pK_2	10.59	10.46	9.93[a]	9.97	9.70
$\frac{1}{2}pK_1K_2$	11.20	10.91	10.30[a]	10.34	10.16
Co					
pK_1	8.43	8.33	8.28	8.10	7.82
pK_2	7.45	7.63	7.45	7.35	7.15
$\frac{1}{2}pK_1K_2$	7.94	7.98	7.86	7.72	7.49
Cu					
pK_1	12.42	---	12.02	11.42	---
pK_2	10.00	---	9.83	9.86	---
$\frac{1}{2}pK_1K_2$	11.03	---	10.92	10.64	---
Mg					
pK_1	6.54	6.48	6.39	6.27	6.06
pK_2	5.22	5.28	5.19	5.25	5.17
$\frac{1}{2}pK_1K_2$	5.89	5.88	5.79	5.76	5.62
Ni					
pK_1	8.90	8.91	8.76	8.99	8.33
pK_2	7.52	7.52	7.56	7.96	7.31
$\frac{1}{2}pK_1K_2$	8.21	8.21	8.15	8.48	7.82
Zn					
pK_1	8.39	8.20	8.05	8.01	7.62
pK_2	7.32	7.07	7.02	7.08	6.79
$\frac{1}{2}pK_1K_2$	7.82	7.64	7.54	7.54	7.21

[a] Equilibrium possibly not established.

thing else was kept constant. Any large variation in the calculated constants under these conditions was taken as indication of formation of a species other than those taken into consideration in the calculation of the formation function. On this basis, for instance, data for lead were not included.

Slow formation of the beryllium chelates

It was observed during the titration of the beryllium chelates that the pH meter reading drifted for a time after the solutions are mixed and also after some increments of base were added. This behavior was established as being due to the slow formation of the beryllium chelate by observation of a change with time in the ultraviolet spectra between 390 and 410 mμ. This experiment was carried out using a Beckman model DK-2 recording spectrophotometer. The difference in spectra between a 0.002 M solution of dibenzoylmethane in 75 per cent dioxan-water and a like concentration of chelating agent plus 0.0005 M beryllium perchlorate and a small amount of KOH was recorded. No attempt was made to obtain quantitative data because the evaporation of solvent from the 1 mm. cells used was quite rapid. It could be ascertained, however, that the changes in spectra with time were definitely due to the slow formation of beryllium chelate. The constant recorded for beryllium are based on data recorded when the pH meter reading became relatively stable. This required variable amounts of time depending on the extent of the titration and the chemical nature of the chelating agent used. The times ranged from several minutes to several hours.

Spectrometric determination of stability constants

It was hoped that a method could be developed for measuring stability constants in those cases in which hydrolysis occurred to give either some metal hydroxide or hydroxy chelate, KeMOH. The difficulty encountered in obtaining accurate stability constants when hydrolysis occurs arises from the fact that when suitable account is taken of the hydrolyzed species in Bjerrum's formation function, there is one more unknown than there are equations. Thus if it were possible to measure with sufficient accuracy one of the other species present in solution in addition to the hydrogen ion suitable account could be taken of the hydrolysis. Spectrometric methods were tried.

The change in the ultraviolet spectra of the chelating agent with the extent of chelation was observed. The concentration of the chelating agent in 75 per cent dioxan-water was kept the same as that for the potentiometric measurements in order that comparable results might be obtained. The concentration of metal ion was varied. The difference in the spectra between chelating agent and chelating agent plus metal ion was obtained by placing the chelating agent in the reference cell and the chelating agent plus metal in the sample cell of the Beckman model DK-2 recording spectrophotometer, and using the 0-200 scale. Cells of one mm. thickness had to be used because of the high absorbance of the chelating agent in the ultraviolet. The cell was capped to prevent excessive evaporation. Unfortunately the precision of this method was not as great as would be desired in order to utilize it in measuring the amount of hydrolysis which might occur. All that can be said is that the spectrometrically determined chelation equilibrium constants are of the same order of magnitude as the values determined potentiometrically.

A second spectrophotometric method was tried for the copper chelate of dibenzoylmethane based on the change with chelation in the visible spectra of copper ion in the region between 600 and 800 mμ. It was hoped that if the systems for the various copper chelates could be accurately analyzed, other metals could be observed by competition experiments.

The experiment was carried out by making up a solution similar to that utilized in the potentiometric experiments on the copper dibenzoylmethane chelate except that no chelating agent was present initially. The spectrum of this solution with increasing amount of added chelating agent was observed by pipetting a suitable amount of the solution into a 10 cm. spectrophotometer cell after each addition of chelating agent. The solution in the cell was poured back into the main body of the solution after observation of its spectra for the next addition of chelating agent. The small amounts of solution adhering to the sides of the cell were ignored. The concentration of chelating agent was varied from 0 to 0.002 M. The concentration of copper was kept constant at 0.0005 M. The pH meter reading of the solution was also recorded after each addition of chelating agent. When the addition of the chelating agent was completed, the solution was titrated with 0.05 N KOH and in a manner similar to the above, the spectra and the pH meter reading was observed.

Use of the pH meter data allows one to estimate from the earlier potentiometric data the degree of chelate formation and compare it with the spectra. It is observed that the absorption band of copper ion is shifted to shorter wavelengths as the degree of chelate formation increases to one. The extinction coefficient also increases in the monochelate species over that of the hydrated cupric ion. Addition of KOH increased the degree of chelate formation to about 1.5. The spectrum was shifted still further toward shorter wavelengths and the extinction coefficient still further increased. Unfortunately the changes in spectrum with chelating agent concentration were not large enough to allow accurate estimation of chelating constants directly from the spectral data. However, the value estimated from the data is of the right order of magnitude. Estimates were made of the extinction coefficients of the various species involved at 650 and 750 mμ, ignoring the possible hydrolysis products, by using equilibrium constants calculated from the potentiometric data. These data are shown in Table 2.

Discussion

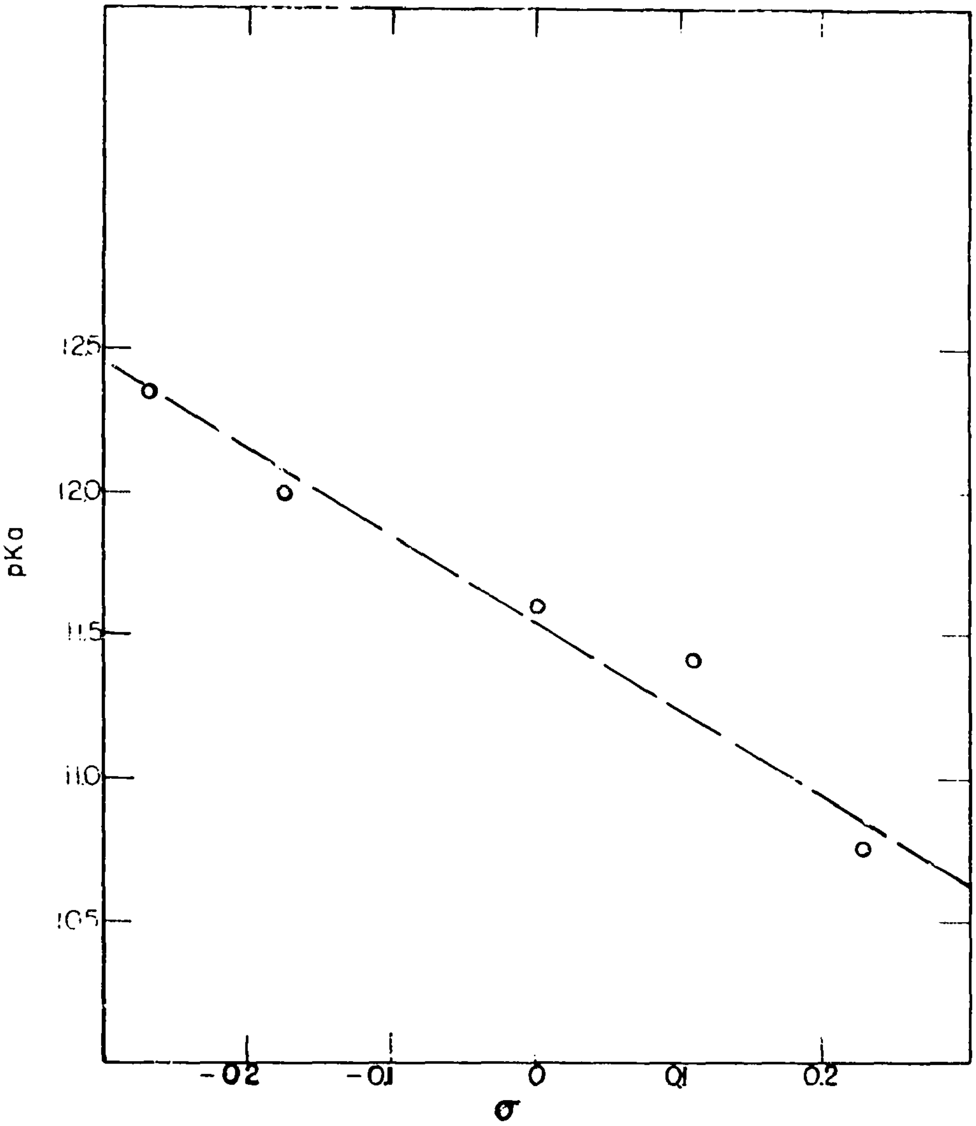
The variation in the sensitivity to substituent effects on the chelating molecule from metal to metal was not as large as might be desired, the observed variation in several cases being only on the borderline of experimental uncertainty.

Table 2. Extinction coefficients of the copper dibenzoylmethane

λ	650 mμ	750 mμ
MA	1.88×10^2	3.66×10^2
MA_2	6.12×10^2	3.89×10^2

In Figures 1 to 7 are plotted the stability constants for the various metal ions versus Hammett's sigma values. A best straight line is drawn. This line is drawn visually. No attempt was made to do a least squares treatment since several of the plots contain at least one point which deviates considerably and there are not enough points left to yield a more dependable value. The value of the slopes of these lines

Figure 1. Acid association constant of diaroylmethanes *versus* β .


12.5
12.0
11.5
11.0
10.5
pKa
-0.2
-0.1
0
0.1
0.2
σ

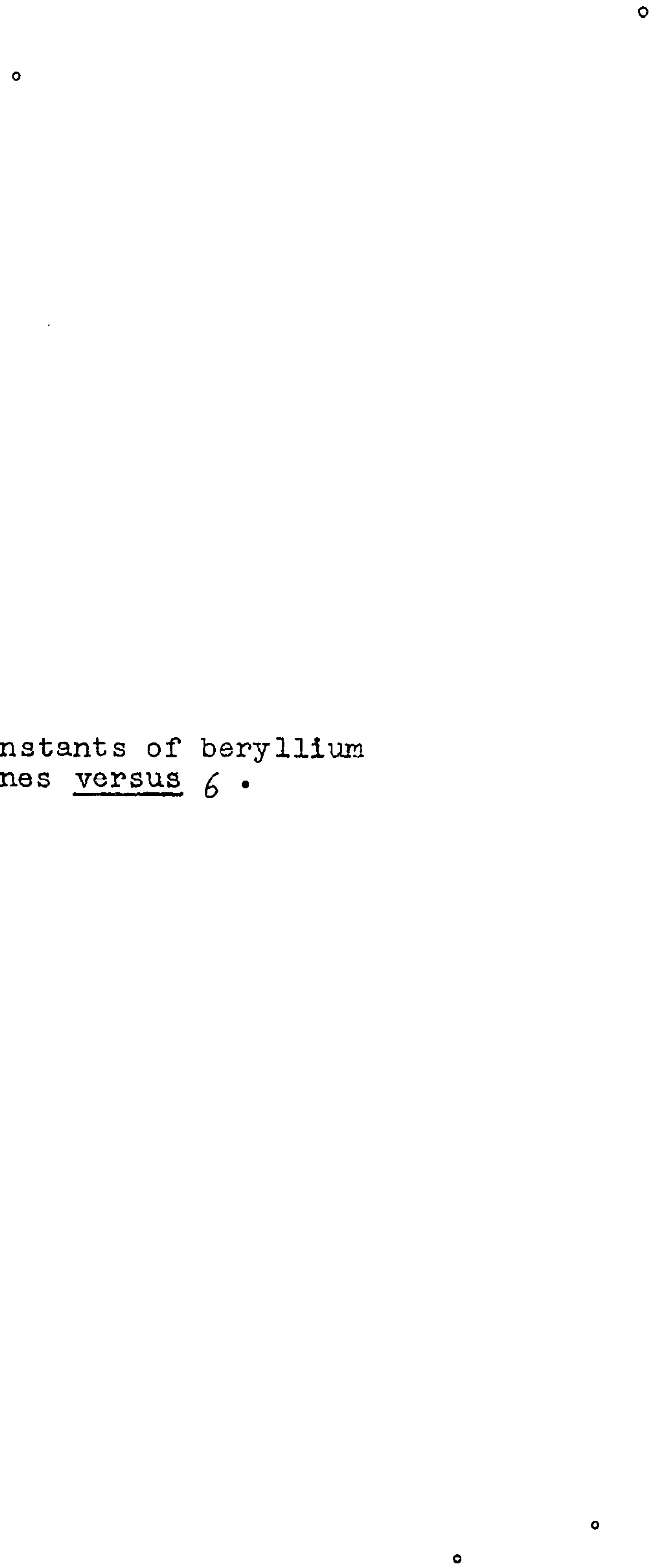


Figure 2. Stability constants of beryllium diaroylmethanes *versus* σ .

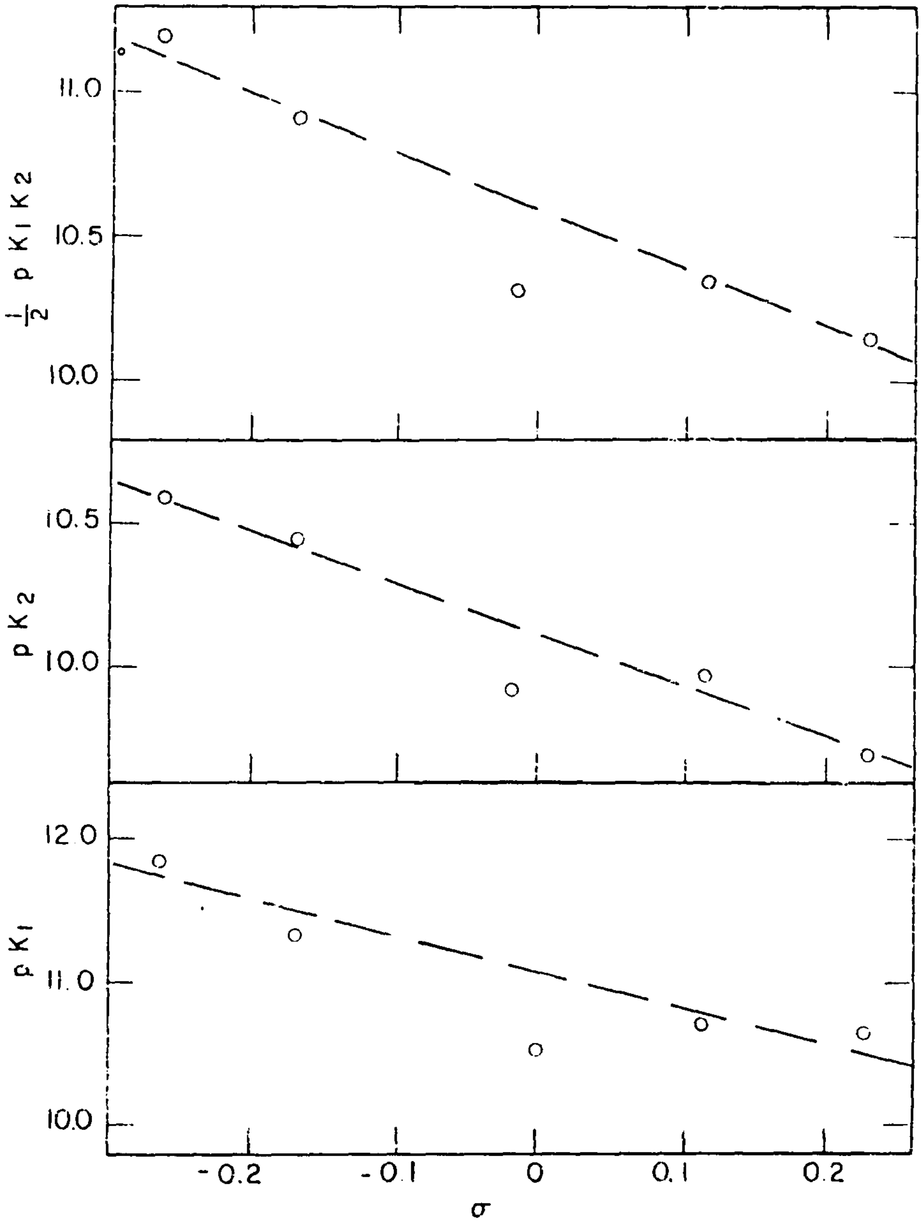

$\frac{1}{2}$ p K$_1$ K$_2$
11.0
10.5
10.0
p K$_2$
10.5
10.0
p K$_1$
12.0
11.0
10.0
- 0.2
- 0.1
0
0.1
0.2
σ

Figure 3. Stability constants of cobalt diaroylmethanes *versus* σ .

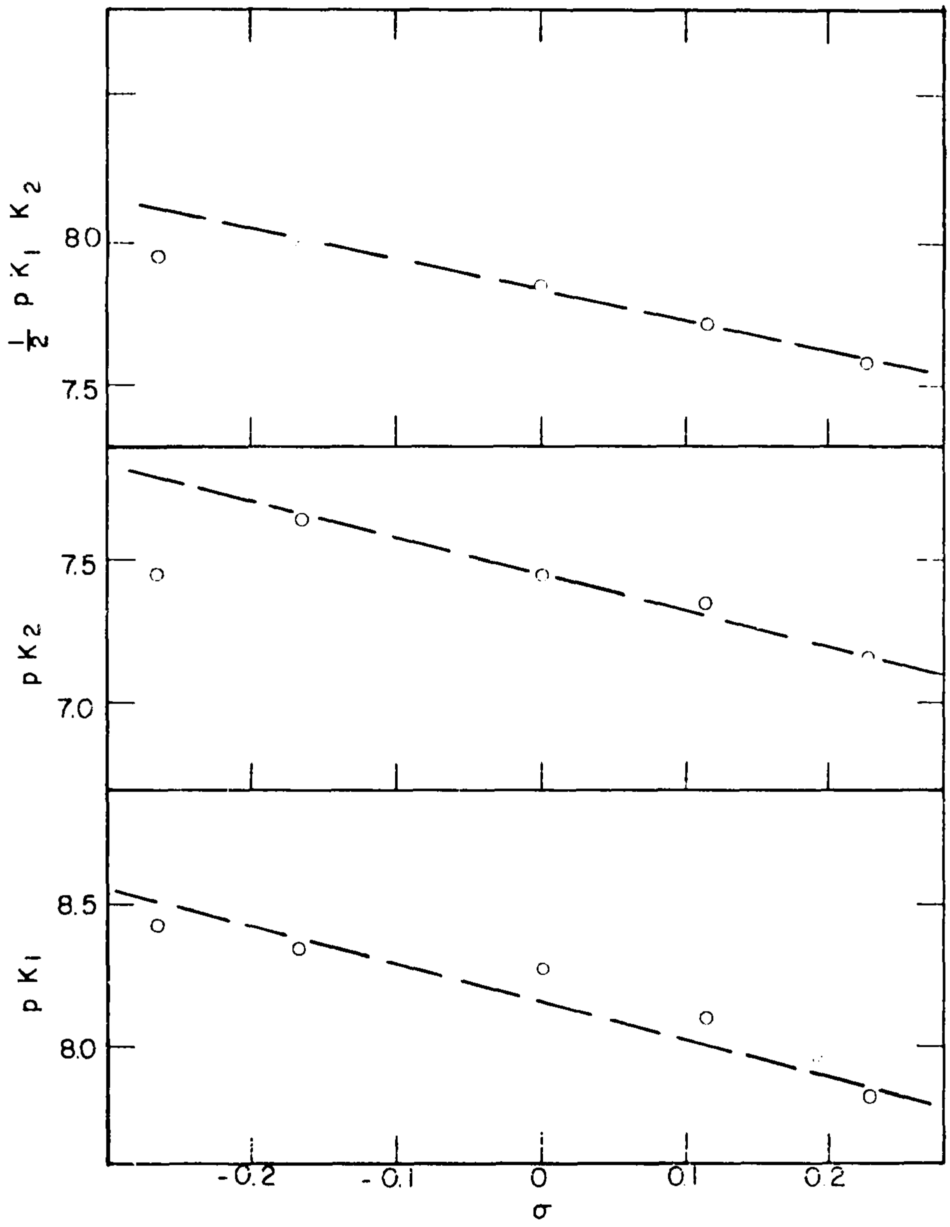

$\frac{1}{2}$ p K$_1$ K$_2$
8.0
7.5
p K$_2$
7.5
7.0
p K$_1$
8.5
8.0
-0.2
-0.1
0
0.1
0.2
σ

Figure 4. Stability constants of copper diaroylmethanes _versus_ σ .

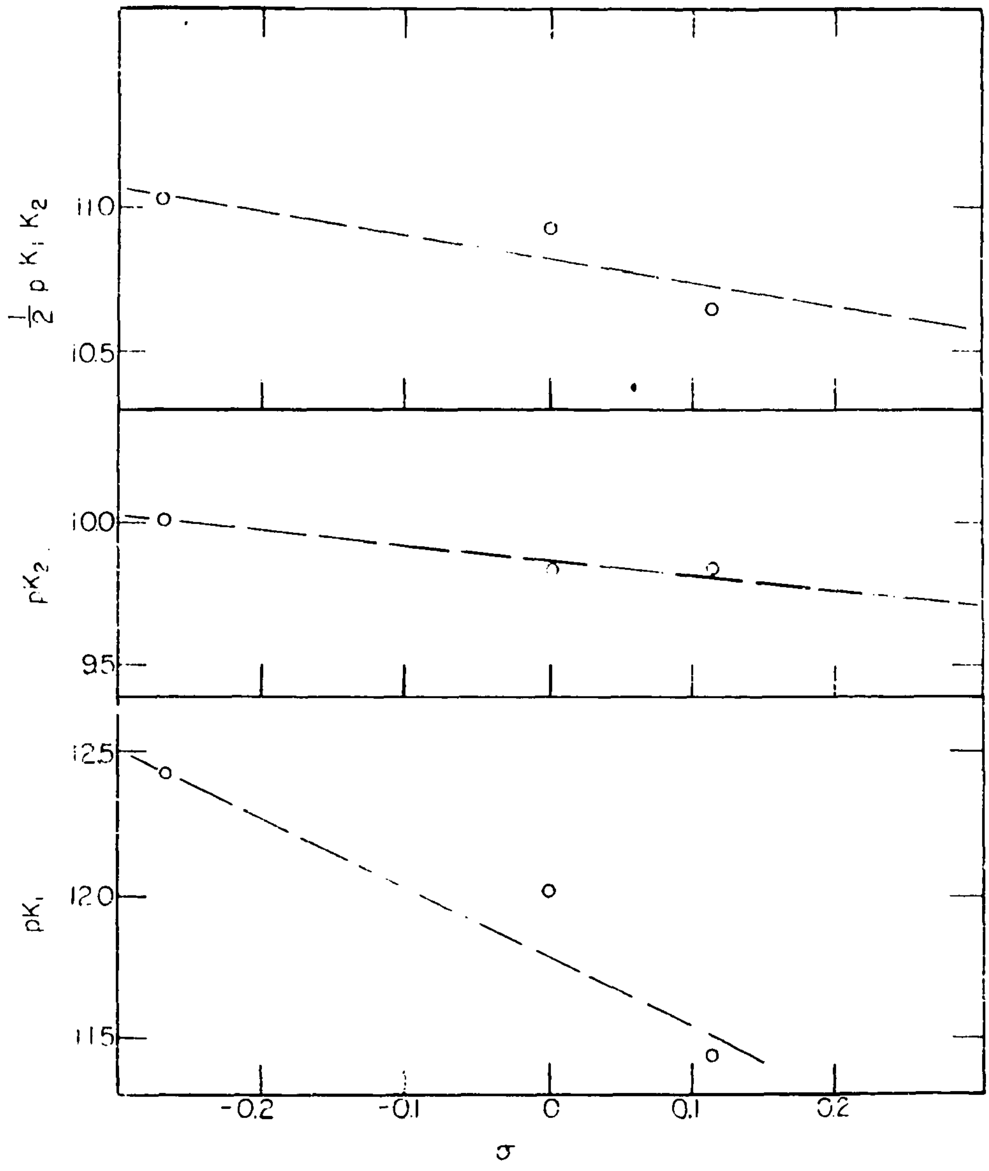

$\frac{1}{2}$ p $K_1 K_2$
11.0
10.5
pK_2
10.0
9.5
pK_1
12.5
12.0
11.5
-0.2
-0.1
0
0.1
0.2
σ

Figure 5. Stability constants of magnesium diaroylmethanes *versus* σ .

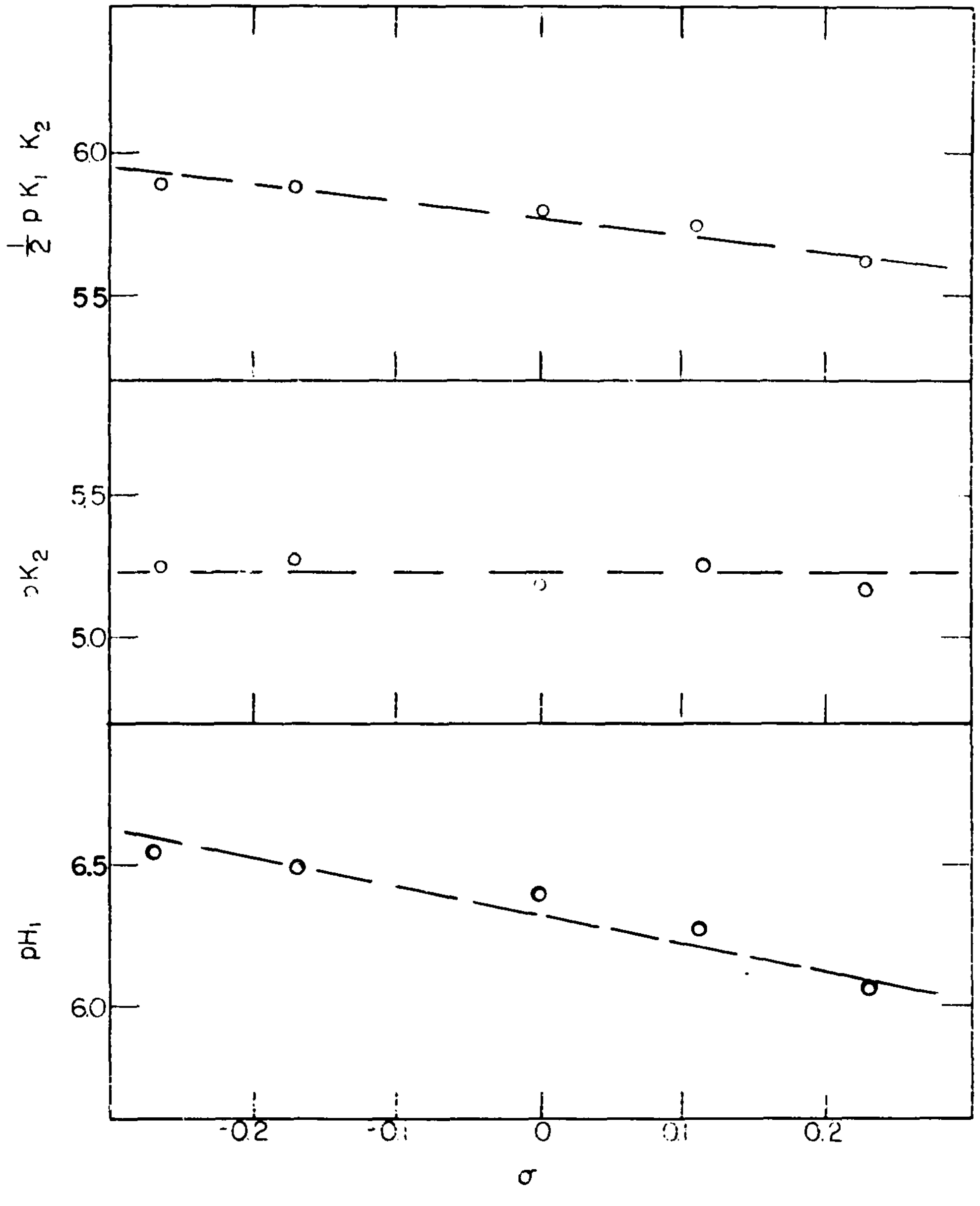

$\frac{1}{2}$ p K$_1$ K$_2$
6.0
5.5
pK$_2$
5.5
5.0
pH$_1$
6.5
6.0
-0.2
-0.1
0
0.1
0.2
σ

Figure 6. Stability constants of nickel diaroylmethanes *versus* σ .

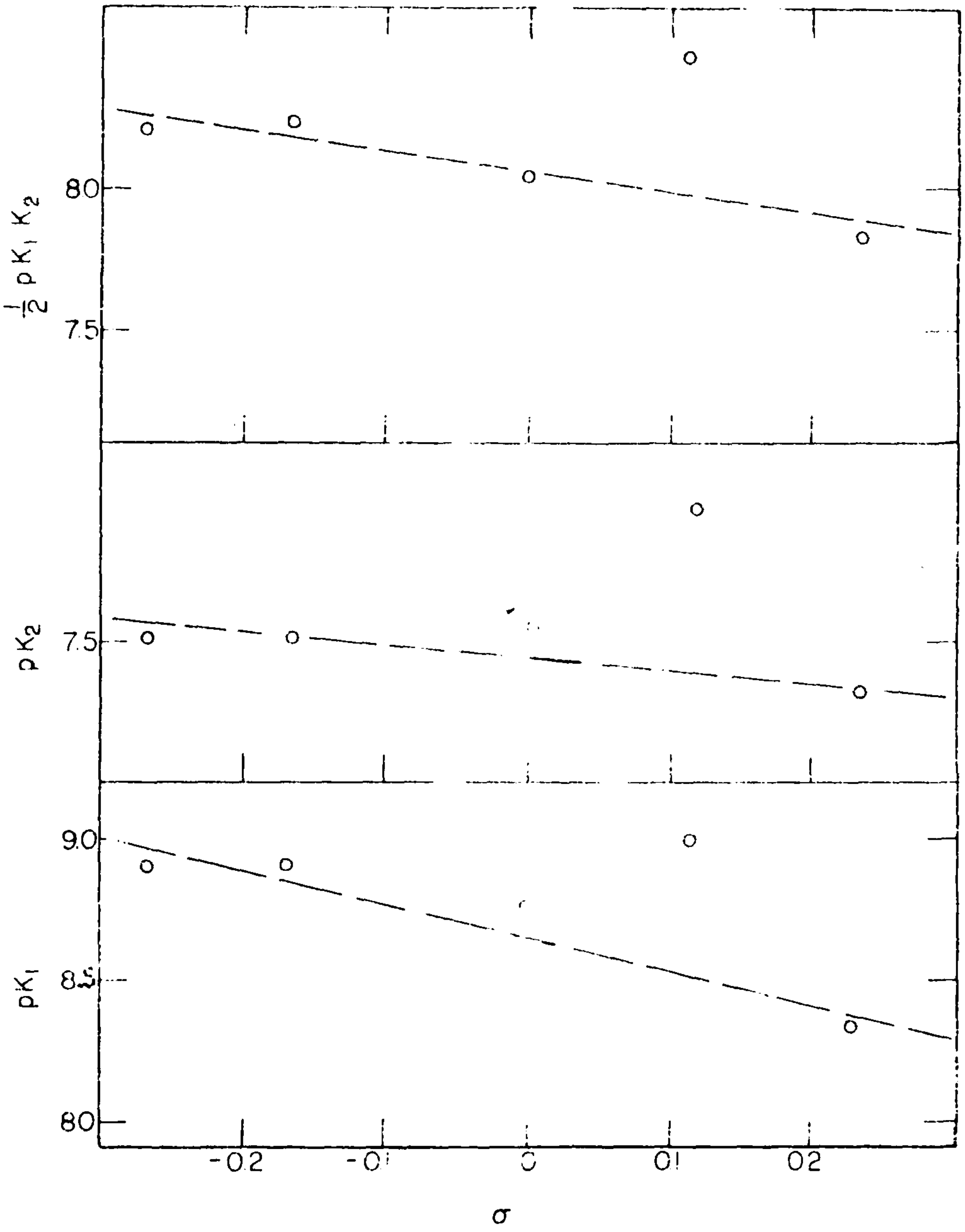
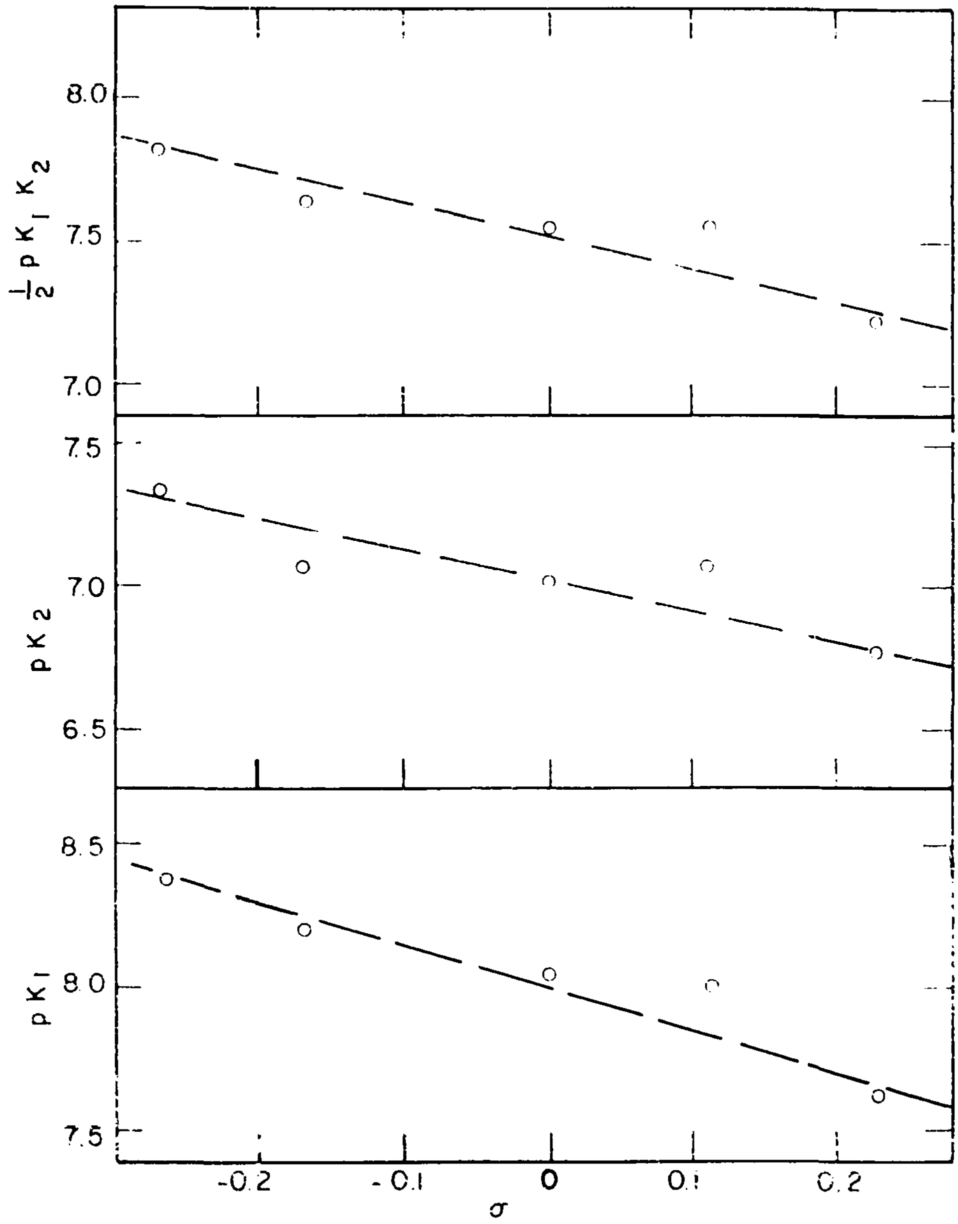

½ pK₁ K₂
8.0
7.5
pK₂
7.5
pK₁
9.0
8.5
8.0
-0.2
-0.1
0
0.1
0.2
σ

Figure 7. Stability constants of zinc diaroylmethanes *versus* σ .


$\frac{1}{2}$ p K_1K_2
8.0
7.5
7.0
p K_2
7.5
7.0
6.5
p K_1
8.5
8.0
7.5
-0.2
-0.1
0
0.1
0.2
σ

are given in Table 3.

It can be seen that the expected correlation of rho value with the ionic-covalent character of the metal-chelate bond is not present. In particular, the value for magnesium is the lowest observed. It would be expected that magnesium should form a very ionic bond; one, therefore, would expect a larger rho value of the order of magnitude of that for the hydrogen chelate. This unexpected behavior can possibly be traced to

Table 3. ρ values for stability of substituted metal dibenzoylmethanes

Metal	pK_1	pK_2	$\frac{1}{2}pK_1K_2$
Be	2.45	2.00	2.08
Ni	1.57	0.48	0.76
Co	1.30	1.28	1.25
Zn	1.25	0.98	1.14
Mg	0.98	0.00	0.45
H	2.63		

one of three things, improper interpretation of the character of the hydrogen chelate, impropriety in comparing rho values of different metals due to lack of cancelling of specific effects such as solvation energies or, finally, systematic breakdown of the Hammett treatment.

Evidence for the highly ionic character of the hydrogen chelate bond is quite convincing (5). Chief among this evidence is the very great similarity between the ultraviolet spectra of the hydrogen chelate and the enolate anion. It does not seem reasonable to attribute lack of the expected correlation to this cause.

In order to examine the second possible reason for the lack of correlation between the values of Hammett rhos and the ionic-covalent character of the metal chelate bond, it will be profitable to separate the free energy terms involved into several parts. The free energy term related to the stability constant of a metal chelate as measured in solution we will label $\Delta F(s)$. This free energy can be stated as the sum of terms involving the free energy of the reaction in the gas phase and the free energies of solvation of the species involved in the reaction. Thus

$$\Delta F(s) = \Delta F(g) + \Delta F_M - \Delta F_K - \Delta F_{MK}$$

where the last three terms represent the free energies of solvation of the metal ion, the chelating agent, and the product chelate, respectively. In the Hammett treatment, what is under observation is the difference between the free energy of formation of a chelate with some standard compound and the free energy of formation of a chelate in which some relatively small modification in structure has been made. Thus

$$\Delta\Delta F(s) = \Delta\Delta F(g) + \Delta\Delta F_{K} + \Delta\Delta F_{MK}$$

The term $\Delta\Delta F(s)$ is representable by the product of two constants if a Hammett treatment is applicable. The term $\Delta\Delta F(g)$ representing the different in free energy changes in the gaseous phase is the term upon which one would rely for a comparison of the Hammett rho values for different metal ions such as was proposed here with the expectation of obtaining information on the bond character of the metal chelate bonds. However, $\Delta\Delta F(s)$ is the term observed experimentally. Therefore, any interpretations of these data involving different metal ions requires that the term $\Delta\Delta F_{MK}$ be known or cancel out for two metals. Sufficient data for the estimation of the free energies of solution of the metal chelates would not be impossible to obtain from solubility measurements. However, in the work presented here, it was assumed that the free energy of solution of different metal chelates were essentially the same for various metals and thus the $\Delta\Delta F_{MK}$ term would be effectively zero. That this is not necessarily the case can be seen by consideration of the first chelation step of a divalent metal in which the product still has a single positive charge. Since we know that the free metal ions vary considerably in their solvation energies, it would not be expected that replacement of a few solvent molecules by a chelating agent reduces this difference to an insignificant amount. Even in the case of the dichelate of a divalent metal which is electrically neutral, there is evidence that the $\Delta\Delta F_{MK}$ term is not the same for different metals. For instance, it is known that the nickel chelates of β-diketones generally form solvates which are isolatable; on the other hand, the copper chelates are only rarely found as solvates. It is quite likely that the overall trends of the sensitivity of metals to substituent effects on the chelating agent molecule are greatly affected by considerations of the $\Delta\Delta F_{MK}$ terms, so much so that it may completely mask the effects relating to the metal chelate bond type.

One effect that should not be masked by the energy of solvation of the metal chelate is the expected deviation of the p-methoxy compounds from a linear Hammett plot in those cases in which a large amount of covalent bonding occurs, since, in this case, a comparison between different metals is not necessary. Examination of the plots of stability constant *versus* Hammett's sigma values that several deviations do indeed occur. One of the unexpected deviations is the behavior of the m-methoxy compound in the cases of nickel and zinc. It is observed that this deviation also occurs to some extent in the plot for the acid dissociation constants of the chelating agents. Further, if the acidity of the dibenzoylmethanes is plotted versus the acidity of substituted benzoic acids as measured in 75 per cent dioxan-water, it is observed that the p-methoxy derivative fits quite well. On this basis the deviation is possibly explainable in terms of a systematic change in the energy of solvation of the m-methoxy group. More difficult to find a possible excuse for is the case of the p-methoxy substituent with cobalt. While deviations were looked for with this group, this deviation is in the opposite direction from that expected in that the formation constants are smaller than predicted by the Hammett relationship. It should be emphasized that these deviations cannot be associated with experimental errors, since in every case the same stock solutions of metal were used with each chelating agent, and the same stock solution of chelating agent was used with each metal. In addition, all the data for the points which deviate most strikingly are internally consistent, indicating that there is little likelihood of any error due to the lack of accuracy in the hydrogen ion concentration measurements or to undetected precipitation of metal chelates.

Finally, it should be mentioned that the only systematic trend in the apparent rho values is a correlation with the order of magnitude of the stability. Smaller stability constants reflect a smaller sensitivity to substituent effects.

This behavior might possibly be taken to indicate that the Hammett plot are not straight lines but are curved. The relatively small effects which cause the scatter of experimental points could readily hide such an effect. Equally possible may be the occurrence of a solvation effect similar to that discussed above which parallels the stability of the chelates.

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PART II. FURTHER RELATIONSHIPS IN THE GRUNWALD TREATMENT OF ACID-BASE EQUILIBRIA IN HYDROXYLIC SOLVENTS

Introduction

The problem under consideration is an attempt to establish a quantitative relationship among the basicities of a series of compounds. Such a problem is trivial in the case in which all of the compounds of interest can be observed in the same medium. However, it frequently occurs that considerations of solubility and leveling effect of a solvent make it difficult or impossible to carry out suitable experiments. In these cases the experimenter's only recourse generally has been to find a more suitable solvent. In this manner one can only hope at best to find qualitative relationships among the basicities of a series of compounds if it be impossible to measure the basicities of all the compounds in the same solvent. In general, one can not even be sure that the order of relative basicities will not be changed on changing solvents. It would be very desirable, therefore, if in some way it were found possible to relate the basicities of compounds to some common reference state, together with the relationships which would make it possible to calculate the basicities in various other solvents. Two attempts at establishing such a relationship for at least a limited series of solvents will be mentioned here; that of Hammett (1) for strong acid solutions and that of Gutebezahl and Grunwald (2) for hydroxylic and mixed hydroxylic solvents.

In 1932 Hammett and Deyrup (3) and Hammett and Paul (4) carried out a spectrometric study of the ratio of concentrations of neutral indicator bases to the concentrations of their conjugate acids when the bases were dissolved in a mixture of water and a strong acid, chiefly sulfuric. On the basis of these studied they concluded that the ratio of activity coefficients of the base and its conjugate acid is independent of the base, and it was tacitly assumed also independent of the solvent components. This extended the range of possibilities of measuring the basicities of compounds too weakly basic to be measured in water because of the leveling effect of that solvent. If it is assumed that the ratio is a constant then it is possible to define for a solvent an acidity function, which they denote by H^o, which is in a sense a measure of the proton donating ability of that solvent with respect to the pH scale in water.

Grunwald and Winstein (5) observed for certain solvents a property of solvents reminiscent of that for which we seek. They found that the rates of solvolysis of a number of compounds could be correlated by the relationship;

$$\log \frac{k}{k_o} = mY$$

wherein k_o is the rate of some standard reaction under some standard conditions of temperature and solvent, m is a constant depending only on the compound undergoing reaction and Y is a constant which is a function of the solvent related to the solvating power of the solvent. This observation suggested a possible similar treatment for equilibrium reactions. Gutebezahl and Grunwald (2) indeed found that acid-base equilibria in a number of pure and mixed hydroxylic solvents could be treated by similar relationship. Grunwald's treatment, together with the Debye-Huckel limiting law, allows one to calculate concentration ionization constants of numerous acids and bases in these media. A quantity denoted by log f_H is also obtained by Grunwald which is a function of the solvent medium and is again in a sense a measure of the solvents' acidic properties. Since log f_H and H^o purport to be measures of the same property, we have attempted to develop the relationship between these two parameters.

Discussion of the Significance of the Grunwald Activity Postulate

Grunwald's treatment of acid-base equilibria in mixed hydroxylic solvents involves the use of an extra-thermodynamic assumption, namely:

$$\log \frac{f_B}{f_{BH}} = m_B Y_S \qquad (1)$$

where f_B and f_{BH} are the degenerate activity coefficients of a base and its conjugate acid, respectively. The f's are called degenerate because they are concentration independent. They are related to the free energy difference between different possible reference states. In this case they represent the difference in molar free energy between the reference state of an infinitely dilute solution in any solvent, S, and infinitely dilute solution of the same solute in water. Thus they are a function of solvent composition. The constant Y_S in Equation 1 is also a function of solvent composition. It is called the solvent power of solvent S. Ideally Y_S should be independent of the choice of base B and depend only on the solvent. However, it is found that Y is also dependent on the charge type of the base. Since we will be interested in only two types of base here, namely, neutral and singly negatively charged bases, no great loss of generality is involved. The constant m_B is as its subscript implies a function of the base B only. That is, it is a measure of the sensitivity of base B to changes in solvent power Y_S.

By utilization of this "activity postulate" Grunwald has derived further functions of the solvent which might be considered a measured part of its relative basicity, namely

$$\log f_H = \Delta pK_B + m_B Y_S \qquad (2)$$

The term ΔpK_B is given by

$$\Delta pK_B = pK_B{}^S - pK_B{}^W \qquad (3)$$

where $pK_B{}^S$ and $pK_B{}^W$ are the thermodynamic pK's for the acid dissociation of BH as measured in solvent S and water, respectively. Thus log f_H can also be written

$$\log f_H = \log a_H - \log a_H{}^* \qquad (4)$$

Where a_H is the proton activity relative to infinite dilution in water and $a_H{}^*$ is the proton activity with respect to solvent S.

Once given log f_H one can define a further function to the solvent, log f_{OH}, which represents the relative acidity of the solvent from the relation

$$pK^S - pK^W = \log f_H - \log f_{OH} \qquad (5)$$

where the pK's now represent the autoprotolysis constants of solvent S and water, respectively. The term log f_{OH} can not be as conveniently expressed as log f_H is in Equation 4. However, the expression

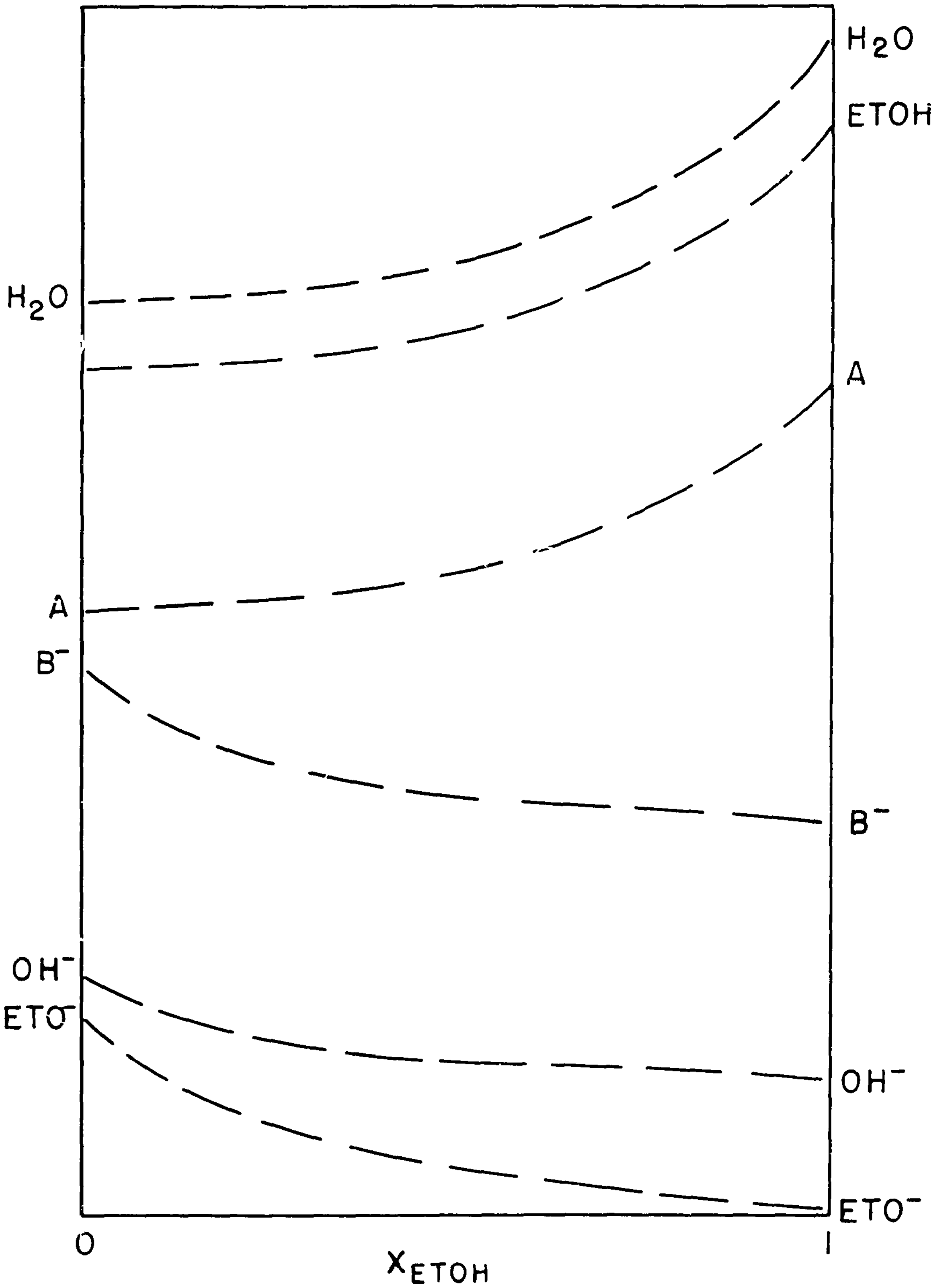
$$\log f_{OH} = \log a_{OH} - \log a_{S^-}{}^* \qquad (6)$$

can be satisfactory if it is remembered that S^- ions may be partly composed of OH^- ions in a mixed solvent. A similar restriction applies to Equation 4 when one recognizes that the proton is not free but attached to some other species, thus Equation 4 becomes

$$\log f_H = \log a_{H_3O^+} - \log a^{*}_{SH^+} \qquad (7)$$

Grunwald has tabulated experimental values of both log f_H and log f_{OH} derived from measured values of the parameters m and Y for a large number of neutral and negatively charged bases in various water-ethanol mixtures. The question arises as to whether or not these data can be represented by m values for water and ethanol together with the already measured Y values. To illustrate the problem further, consider that the ionization constants of bases in some solvent define proton levels for that solvent in terms of free energy. The capacity of a level for protons is of course a function of a concentration of the base. This treatment is quite similar to that of Gurney (6). Solvents, therefore, have associated with them basicity scales which are generally treated as being independent of each other. However, adoption of Grunwald's activity postulate allows one to relate in a definite manner basicity scales of different solvents. Illustrated schematically in Figure 8 are the basicity scales of water and ethanol for different bases A and B^- which are represented by the vertical lines at each side of the diagram. The activity postulate allows one to determine the levels of bases A and B^- in water-ethanol mixtures as a function of composition of the solvent and is illustrated by the dotted lines connecting the two scales. Since the Y values are a monotonic function

Figure 8. Proton levels *versus* mole fraction ethanol.


H_2O
ETOH
A
B^-
OH^-
ETO^-
H_2O
A
B^-
OH^-
ETO^-
0
1
X_{ETOH}

of the composition the mole fraction abscissa can be replaced by one of an appropriate Y scale in which case the dotted curves would become straight lines, the slope of which is equal to appropriate m values. It will be shown that it is possible to obtain m values for the solvent molecules as well as for other bases as is illustrated by the levels indicated for H_2O, OH^-, EtOH, and EtO^-. This will be accomplished by observing what relationship these m values have to Grunwald's log f_H and log f_{OH} functions. In order to do this a somewhat different notation will be introduced. In particular, this notation should be such that it centers attention on the free energy changes involved in the various equilibria under consideration.

Consider a reaction

$$QH + R = Q + RH \qquad (8)$$

for the transfer of proton between bases Q and R of an unspecified charge type. Associated with such a reaction is a standard free energy change given by

$$u_{SH}(Q,R) = 2.3\ RT\ pK = -2.3\ RT\ \log \frac{a_Q a_{RH}}{a_{QH} a_R} \qquad (9)$$

where pK is the negative log of the thermodynamic equilibrium constant for reaction 8 as measured in some solvent S.

The subscript of u, therefore, indicates the solvent with which we are concerned. The order of the terms within the brackets associated with u denote the direction of the reaction, i.e., the transfer of one mole of protons from one mole of QH to one mole of R. It will be convenient to split the left side of Equation 9 into two terms as follows:

$$u_{SH}(Q,R) = u_{SH}(Q) - u_{SH}(R) = -2.3\ RT \left(\log \frac{a_Q}{a_{QH}} - \log \frac{a_R}{a_{RH}} \right) \qquad (10)$$

This corresponds to splitting the expression for the pK of reaction 8 into the two terms

$$pK = -\log \frac{a_Q}{a_{QH}} + \log \frac{a_R}{a_{RH}} \qquad (11)$$

We now define a function $u_S^{*}(Q)$ such that for any base Q

$$u_{SH}^{*}(Q) = u_{SH}(Q) - u_w(Q) \qquad (12)$$

where subscript S again refers to some solvent S and w denotes water as reference solvent. It is seen that $u_S^{*}(Q)$ corresponds, except for the factor 2.3 RT, to the log of the degenerate activity coefficient ratio given in Equation 1. Thus Grunwald's activity postulate becomes,

$$\frac{u_S^{*}(Q)}{2.3\ RT} = m_Q Y_S \qquad (13)$$

We now define a function α_{SH} so that

$$\alpha_{SH} = u_w(H_2O) - u_{SH}(SH) \qquad (14)$$

The last term in this expression is

$$u_{SH}(SH) = -2.3\ RT \log \frac{a_{SH}^{*}}{a_{SH_2^+}^{*}} \qquad (15)$$

where the activities are referred to solvent S. The function α_{SH} is related to Grunwald's $\log f_H$ by

$$\log f_H = \frac{\alpha_{SH}}{2.3\ RT} + \log a_{H_2O} - \log a_{SH}^{*} \qquad (16)$$

in which a_{H_2O} is referred to water and a_{SH}^{*} is referred to solvent S. Similarly, we define a function β_{SH} such that

$$\beta_{SH} = u_w(OH) - u_{SH}(S^-) \qquad (17)$$

where

$$u_{SH}(S^-) = -2.3\ RT \log \frac{a_{S^-}^{*}}{a_{SH}^{*}} \qquad (18)$$

This function is related to Grunwald's $\log f_{OH}$ by the relation

$$\log f_{OH} = \frac{-\beta_{SH}}{2.3\ RT} + \log a_{H_2O} - \log a_{SH}^{*} \qquad (19)$$

The difference in standard free energy changes for the reaction

$$QH + SH = Q + SH_2^+ \qquad (20)$$

as measured in solvent S and water can then be written utilizing Equations 10, 12, 13, and 14

$$\begin{aligned} u_{SH}(Q) &= u_{SH}(Q, SH) - u_w(Q, H_2O) \qquad (21) \\ &= u_{SH}(Q) - u_w(Q) - u_{SH}(SH) + u_w(H_2O) \\ &= u_{SH}^*(Q) + \alpha_{SH} \\ &= -2.3\ RT\ m_Q Y_{SH} + \alpha_{SH} \end{aligned}$$

which is thus related to Equation 2 by a factor of 2.3 RT ($\Delta pK = \log f_H + m_Q Y_{SH}$)

Let us examine more closely the function α_S. Adding the term $-u_w(H_2O, SH)$ to both sides of Equation 14

$$\begin{aligned} \alpha_S - u_w(H_2O, SH) &= u_w(H_2O) - u_{SH}(SH) - u_w(H_2O, SH) \qquad (22) \\ &= u_w(H_2O) - u_{SH}(SH) - u_w(H_2O) + u_w(SH) \\ &= - u_{SH}^*(SH) \end{aligned}$$

If solvent S is a pure compound one obtains

$$\alpha_S = 2.3\ RT\ m_{SH} Y_{SH}^0 + u_w(H_2O, SH) \qquad (23)$$

If solvent S is a mixture, Equation 13 cannot be used since we could not expect to find a suitable constant value for m_{SH}.

In this case $u_{SH}^*(SH)$ is a more complicated function which will be derived farther on. If one adds and then subtracts the term $u_{SH}(H_2O)$ on the right side of Equation 14, which defines α_S, one obtains

$$\begin{aligned}\alpha_S &= u_w(H_2O) - u_{SH}(SH) + u_{SH}(H_2O) - u_{SH}(H_2O) \qquad (24)\\ &= u_{SH}^{*}(H_2O) + u_{SH}(H_2O, SH)\\ &= 2.3\ RT\ m_{H_2O}Y_{SH}^{0} + u_{SH}(H_2O, SH)\end{aligned}$$

It is seen that this relationship is valid regardless of whether or not S is a pure compound or a mixture. Similar relations exist for the function β_{SH}. Thus

$$\beta_{SH} = - u_{SH}^{*}(S^-) + u_w(OH^-, S^-) \qquad (25)$$

and for pure solvent S

$$\beta_{SH} = 2.3\ RT\ m_{S^-}Y_{SH}^{-} + u_w(OH^-, S^-) \qquad (26)$$

Further

$$\begin{aligned}\beta_{SH} &= - u_{SH}^{*}(OH^-) + u_{SH}(OH^-, S^-) \qquad (27)\\ &= 2.3\ RT\ m_{OH^-}Y_{SH}^{-} + u_{SH}(OH^-, S^-)\end{aligned}$$

It should be noticed that the set of Y_{SH}^{0} values in the relation for α is not the same as the set of Y_{SH}^{-} values for the β relation, but differ because the charge type of the base in question is different.

The problem now is to write an expression for standard free energy change of reaction

$$H_2O + S^- = OH^- + SH \qquad (28)$$

and

$$H_3O^+ + SH = H_2O + SH_2^+ \qquad (29)$$

as measured in mixed solvent S such that said expression is a function of the m values of the solvent components, Y, and other readily measured or derivable quantities. These expressions then can be inserted into Equations 24 and 27 to obtain relations for comparison with Grunwald's data. This problem will be attacked by utilizing the fact that the molar free energy of a mixture can be considered as the sum of the contributions of each constituent.

F_Q is the standard molar free energy of substance Q in a reference state of infinite dilute solution in solvent SH. However, if Q is a constituent of the solvent, F_Q is the free energy per mole of Q at its particular concentration; thus it is the partial molar free energy of Q.

The standard free energy changes of reactions 28 and 29 where solvent S is a pure compound, EH, is thus

$$u_{EH}(OH^-, E^-) = F_{OH^-} + F_{EH} - F_{H_2O} - F_{E^-} \qquad (30)$$

and

$$u_{EH}(H_2O, EH) = F_{H_2O} + F_{EH_2^+} - F_{H_3O^+} - F_{EH} \qquad (31)$$

When solvent S is a mixture of water and EH containing X_E mole fraction of EH, the standard molar free energy of solvent S is

$$F_{SH} = X_W F_{H_2O} + X_E F_{EH} \qquad (32)$$

This is true, of course, only when ionization of either of the components does not appreciably alter the composition of undissociated solvent. This would not be true, for instance, if EH was a strong acid because very few solvent molecules would consist of undissociated EH. In other words, the ratio of X_E to X_W must be effectively the same after EH is mixed with water as it was before they were mixed. The case of the standard molar free energy of S^- and SH_2 ion is not quite as simple. In general, we cannot expect that the ratio of E^- to OH^- ions will be the same as the composition of the bulk solvent. In whatever volume is required, one mole of solvent anion (i.e., $E^- + OH^- =$ Avogadro's number) will contain more or less than mole fraction X_W OH^- ions. If we represent the composition of one mole of solvent anion as being made of X_W^* OH^- ions and $X_F{*}E^-$ ions we may write

$$F_{S^-} = X_W^* F_{OH^-} + X_E^* F_{E^-} \qquad (33)$$

A similar expression can be written for the solvent cation

$$F_{SH_2^+} = X_W^0 F_{H_3O^+} + X_E^0 F_{EH_2^+} \qquad (34)$$

where X_W^0 and X_E^0 make up the composition of solvent cation. If p is the difference between $X_W{*}$ and X_W, then

$$X_W^* = X_W + p \qquad (35)$$

and since

$$X_W + X_E = 1$$

$$X_W^* + X_E^* = 1$$

then

$$X_E^* = X_E - p$$

Similarly, if a is the difference between X_W^0 and X_W then

$$X_W^0 = X_W + q \tag{36}$$

$$X_E^0 = X_E - q$$

Thus Equations 33 and 34 become Equations 37 and 38 which define F_{S^-} and $F_{SH_2^+}$

$$F_{S^-} = (X_W + p)\ F_{OH^-} + (X_E - p)F_{E^-} \tag{37}$$

and

$$F_{SH_2^+} = (X_W + q)\ F_{H_3O^+} + (X_E - q)\ F_{EH_2^+} \tag{38}$$

Thus the expression for the standard free energy change of reaction 28 for a mixed solvent becomes

$$u_{SH}(OH^-,\ S^-) = F_{OH^-} + X_W F_{H_2O} + X_E F_{EH} - F_{H_2O} - (X_W - p)F_{OH^-} - (X_E - p)F_{E^-} \tag{39}$$

$$= X_E(F_{OH^-} + F_{EH} - F_{H_2O} - F_{E^-}) - p(F_{OH} - F_{E^-})$$

$$= X_E u_{SH}(OH,\ E^-) - p(F_{OH^-}\ F_{E^-})$$

However, adding and subtracting F_{EH} and F_{H_2O} and using Equation 30

$$u_{SH}(OH^-, S^-) = (X_E - p)\ u_{SH}(OH^-, E^-) + p(F_{EH} - F_{H_2O}) \quad (40)$$

This relationship merely states that the standard free energy for the transfer of proton from OH^- to S^- is proportional to the number of E^- ions in the medium times the difference between the molar free energies of OH^- and E^- plus a term for the difference between the free energies of the solvent constituents.

By a similar treatment, it can be seen that

$$u_{SH}(H_2O, SH) = (X_E - q)\ u_{SH}(H_2O, EH) - q(F_{EH} - F_{H_2O}) \quad (41)$$

Substituting these relations into Equations 24 and 27 one obtains

$$\alpha_S = - u_{SH}^*(H_2O) + (X_E - q)\ u_{SH}(H_2O, EH) - q(F_{EH} - F_{H_2O}) \quad (42)$$

and

$$\beta_S = - u_{SH}^*(OH) + (X_E - p)\ u_{SH}(OH^-, E^-) + p(F_{EH} - F_{H_2O}) \quad (43)$$

Utilizing the relationships,

$$u_{SH}(H_2O, EH) - u_W(H_2O, EH) = u_{SH}(H_2O) - u_W(H_2O) - u_{SH}(EH) + u_W(EH) \quad (44)$$

$$= u_{SH}^*(H_2O) - u_{SH}^*(EH)$$

and,

$$u_{SH}(OH^-, E^-) - u_W(OH, E^-) = u_{SH}(OH) - u_{SH}(E) + u_W (E) \quad (45)$$

$$= u_{SH}^*(OH) - u_{SH}(E^-)$$

Equations 41 and 42 become

$$\alpha_S = -u_{SH}^*(H_2O) + (X_E - q)(u_{SH}^*H_2O) - u_{SH}^*(EH) + \quad (46)$$

$$u_W(H_2O, EH) - q(F_{EH} - F_{H_2O})$$

$$= (X_W + q)\ u_{SH}^*(H_2O) - (X_E - q)\ u_{SH}^*(EH) + (X_E - q)$$

$$u_W(H_2O, EH) - q(F_{EH} - F_{H_2O})$$

and

$$\beta_S = - (X_W + p)\ u_{SH}^*(OH) - (X_E - p)\ u_{SH}^*(E^-) + (X_E - p)$$

$$u_W(OH^-, E^-) + p(F_{EH} - F_{H_2O}) \quad (47)$$

Except for the values of p and q, we now have $_S$ and $_S$ expressed in terms of measures of derivable quantities. The quantities $u_{SH}(H_2O, EH)$ and $u_{SH}(OH^-, E^-)$ are such derivable quantities and also in principle at least are measurable. The quantities q and p are related to these functions. Thus,

$$u_{SH}(H_2O, EH) = 2.3\ RT\ pK_{48}^{S} \quad (48)$$

where pK_{48}^{SH} is related to the reaction,

$$H_3O^+ + EH = H_2O + EH_2^+ \quad (49)$$

as measurable in solvent SH and

$$u_{SH}(OH^-, E^-) = 2.3\ RT\ pK_{50}{}^{S} \tag{50}$$

where $pK_{50}{}^{SH}$ is related to the reaction,

$$H_2O + E^- = OH^- + EH \tag{51}$$

as measured in solvent SH. But, under conditions such that $c_W = a_W$

$$K_{48}{}^{W} = \frac{X_W(X_E - q)}{X_E(X_W + q)} \tag{52}$$

and

$$K_{50}{}^{W} = \frac{X_E(X_W + p)}{X_W(X_E - p)} \tag{53}$$

Thus

$$q = \frac{X_W X_E(1 - K_{48}{}^{W})}{X_E K_{48}{}^{W} + X_W} \tag{54}$$

and

$$p = \frac{X_E X_W(K_{50}{}^{W} - 1)}{X_E + X_W K_{50}{}^{W}}$$

If these relations are valid we should be able to derive suitable m values for water and ethanol, using Grunwald's data for this system. After dividing through by the factor 2.3 RT Equation 45 can be written

$$\frac{\frac{\alpha_S}{2.3\ RT} + \frac{q(F_{EH} - F_{H_2O})}{2.3\ RT} - m_{H_2O}Y_{SH}^{\ 0}}{X_E - q} = (m_{EH} - m_{H_2O})\ Y_{SH}^{\ 0} + pK_{48}^{\ W} \qquad (56)$$

where $pK_{48}^{\ W}$ is associated with reaction 49 as measured in water. Similarly Equation 47 can be written

$$\frac{\frac{-\beta}{2.3\ RT} + \frac{p(F_{EH} - F_{H_2O})}{2.3\ RT} + m_{OH}Y_{SH}^{\ -}}{X_E - p} = (m_{OH} - m_E)Y_{SH}^{\ -} - pK_{50}^{\ W} \qquad (57)$$

where $pK_{50}^{\ W}$ is associated with reaction 51 as measured in water. It can be seen that the right hand side of Equation 56 is equal to $pK_{48}^{\ SH}$ since from Equation 43

$$u_{SH}(H2O,\ EH) = u_{SH}^{\ *}(H_2O) - u_{SH}^{\ *}(EH) + u_W(H_2O,\ EH)$$

$$pK_{48}^{\ S} = (m_{EH} - m_{H_2O})Y_{SH}^{\ 0} + pK_{48}^{\ w} \qquad (58)$$

Similarly, the right side of Equation 57 is equal to $-\ pK_{50}^{\ SH}$ since from Equation 45

$$u_{SH}(OH^-,\ E^-) = u_{SH}^{\ *}(OH) - u_{SH}^{\ *}(E) + u_W(OH^-,\ E^-)$$

$$-pK_{50}^{\ S} = (m_{OH} - m_{E^-})Y_{SH}^{\ -} - pK_{50}^{\ W} \qquad (59)$$

Solution for the Solvent "m" Values

Utilizing Equations 58 and 54, Equation 56 can be written in the form

$$a = (bz + c)\ 10^{-z} \tag{61}$$

where

$$a = \frac{\alpha S}{2.3\ RT} X_W + X_E X_W \frac{(F_{EH} - F_{H_2O})}{2.3\ RT} - X_W m_{H_2O} Y_{SH}^{0}$$

$$b = X_E$$

$$c = \frac{-\alpha S}{2.3\ RT} X_E + X_E X_W \frac{(F_{EH} - F_{H_2O})}{2.3\ RT} + X_E m_{EH} Y_{SH}^{0}$$

$$z = pK_{48}^{S}$$

Utilizing Equations 59 and 55, Equation 57 can be written in the form

$$a' = b'z' + c'10^{z'} \tag{62}$$

where

$$a' = \frac{-\beta S}{2.3\ RT} X_E - X_E X_W \frac{(F_{EH} - F_{H2O})}{2.3\ RT} + X_W m_{OH} Y_{SH}^{-}$$

$$b' = X_E$$

$$c = \frac{\beta S}{2.3\ RT} X_W - X_E X_W \frac{(F_{EH} - F_{H2O})}{2.3\ RT} - X_E m_{OH} Y_{SH}^{-}$$

$$z' = -\ pK_{50}^{S}$$

The functions $\frac{\alpha_S}{2.3\ RT}$ and $\frac{-\beta_S}{2.3\ RT}$ are obtained from Grunwald's data and Equations 16 and 19. This is possible since in each case the applicable activity coefficients are equal to one. Therefore, one need only to calculate molar concentration of solvent form density data and the relation 62

$$c_{SH} = \frac{1000\ d}{18X_W + 46X_E} \tag{62}$$

These data are given in Table 4.

The function $F_{EH}-F_{H_2O}$ is obtained from the standard free energy of formation of pure ethanol and water from their elements, together with activity coefficients obtained from vapor pressure measurements according to the usual relations

$$F_{EH} = F_{EH}^{0} + 2.3\ RT\ \log \tag{63}$$

$$F_{H_2O} = F_{H_2O}^{0} + 2.3\ RT\ \log \tag{64}$$

These data are tabulated in Table 5.

The data in Tables 4 and 5 can be utilized to calculate the parameters m_{H_2O} and m_{EH} from Equation 60 subject to the restriction that

$$z = (m_{EH} - m_{H_2O})Y_S^{0} + \alpha_1 - m_{EH} \tag{65}$$

where α_1 is the value of $\frac{\alpha}{2.3\ RT}$ for pure ethanol. This is so since Grunwald chose $Y_S^{0} = 1$ for pure ethanol. Therefore, in

Table 4. Data for calculation of α and β

Wt. % EtOH	0	20	35	50	65	80	100
X_E	0	0.091	0.177	0.286	0.426	0.615	1.000
$d^{4/25}$[1]	0.9971	0.9664	0.9415	0.9099	0.8753	0.8391	0.7851
C_{SH}	55.4	47.0	41.0	35.0	29.2	23.8	17.1
log C_{SH}	1.744	1.682	1.613	1.544	1.466	1.377	1.232
log C_{H_2O} - log C_{SH}	0	0.062	0.131	0.210	0.278	0.367	0.512
Y^{0}[2]	0	0.057	0.136	0.266	0.379	0.570	1.000
$-Y^{-}$[2]	0	0.349	0.596	0.816	0.924	0.964	1.000
log f_H[2]	0	0.01	0.04	0.25	0.54	1.15	4.71
log f_{OH}[2]	0	0.32	0.53	0.63	0.75	0.76	0.80
α/2.3 RT	0	-0.052	-0.091	0.050	0.262	0.783	4.20
- β/2.3 RT	0	0.258	0.399	0.430	0.472	0.393	0.288

[1] Density data taken from International Critical Tables. McGraw-Hill Book Company, Inc. New York, N. Y. Vol. 3, p. 117. 1933. (9)

[2] B. Gutebezahl and E. Grunwald. J. Am. Chem. Soc. 75: 565. 1953. (2)

Table 5. Data for Equations 60 and 61

Wt. % EtOH	0	20	35	50	65	80	100
$\log \gamma_{EH} - \log \gamma_{W}$[1]	0.576	0.471	0.351	0.295	0.015	-0.171	-0.339
$F^{0}_{EH} - F_{H_2O}/2.3\ RT +$ $\log \gamma_{EH} - \log \gamma_{W}$[2]	8.977	8.872	8.752	9.696	8.416	8.230	8.022
$a + X_W m_{H_2O} Y^0$	0	0.687	1.104	1.811	2.206	2.251	0
$C - X_{EH} m_{H_2O} Y^0$	0	0.739	1.290	1.761	1.943	1.468	---
$a' - X_{EH} m_{OH} Y^-$	0	-0.710	-1.203	-1.652	-1.867	-1.710	---
$c' + X_W m_{OH} Y^-$	0	-0.970	-1.603	-2.082	-2.308	-2.100	0

[1] Activity data taken from R. S. Hansen and F. Miller. J. Phys. Chem. 58: 193. 1954. (10)

[2] International Critical Tables. McGraw-Hill Book Company, Inc. New York, N. Y. 1933. (9)

pure ethanol Equation 23 becomes

$$1 = m_{EH} + pK_{48}^{W} \qquad (66)$$

Substitution of this relation into the right hand side of Equation 56 which is equal to z gives Equation 65. Similarly, Equation 61 can be solved subject to the restriction

$$z' = (m_{OH} - m_E)Y_S^- - \beta_1 - m_E \qquad (67)$$

where β_1 is the value of $\frac{-\beta}{2.3\ RT}$ for pure ethanol, since Y_S^- was chosen equal to minus one by Grunwald for pure ethanol. Thus Equation 26 becomes

$$1 = -m_E + pK_{50}^{W} \qquad (68)$$

Substitution of this relation into the right side of Equation 57 which is equal to z' gives Equation 67.

The actual process used to solve the above expression was to solve Equation 60 for z with various arbitrary choices of m_{H_2O}. This data is tabulated in Table 6 and plotted in Figure 9 at each mole fraction of ethanol. In Figure 10 are plotted values of z <u>versus</u> Y_S for each arbitrary choice of m_{H_2O}. According to the restraint 65, this plot should be a straight line for proper choice of m_{H_2O}. In addition, the intercept at Y = 1 must be equal to $1 - m_{H_2O}$. Except for the point of $X_E = 0.091$, this holds quite well for a value of m_{H_2O} equal to something slightly less than 3.9. Also, the intercept on Y = 0 should be equal to $1 - m_{EH}$. Thus m_{EH} is

Table 6. Values of z for various values of m_{H_2O}

X_E	.091	.177	.266	.426	.615
$m_{H_2O} \neq 0$	z	z	z	z	z
$m_{H_2O} = 0$	.033	.070	-.013	-.061	-.230
$m_{H_2O} = 1$	.073	.127	.058	.027	-.056
$m_{H_2O} = 2$	.116	.190	.143	.116	.089
$m_{H_2O} = 3$	.161	.260	.218	.210	.222
$m_{H_2O} = 4$	.210	.340	.312	.309	.352
$m_{H_2O} = 5$	.266	.432	.419	.418	.484
$m_{H_2O} = 6$	.332	.543	.550	.543	.626
$m_{H_2O} = 7$	.404	.678	.714	.678	.789
$m_{H_2O} = 8$	.484	1.057	1.151	.888	.992

Figure 9. z <u>versus</u> m_{H_2O}.

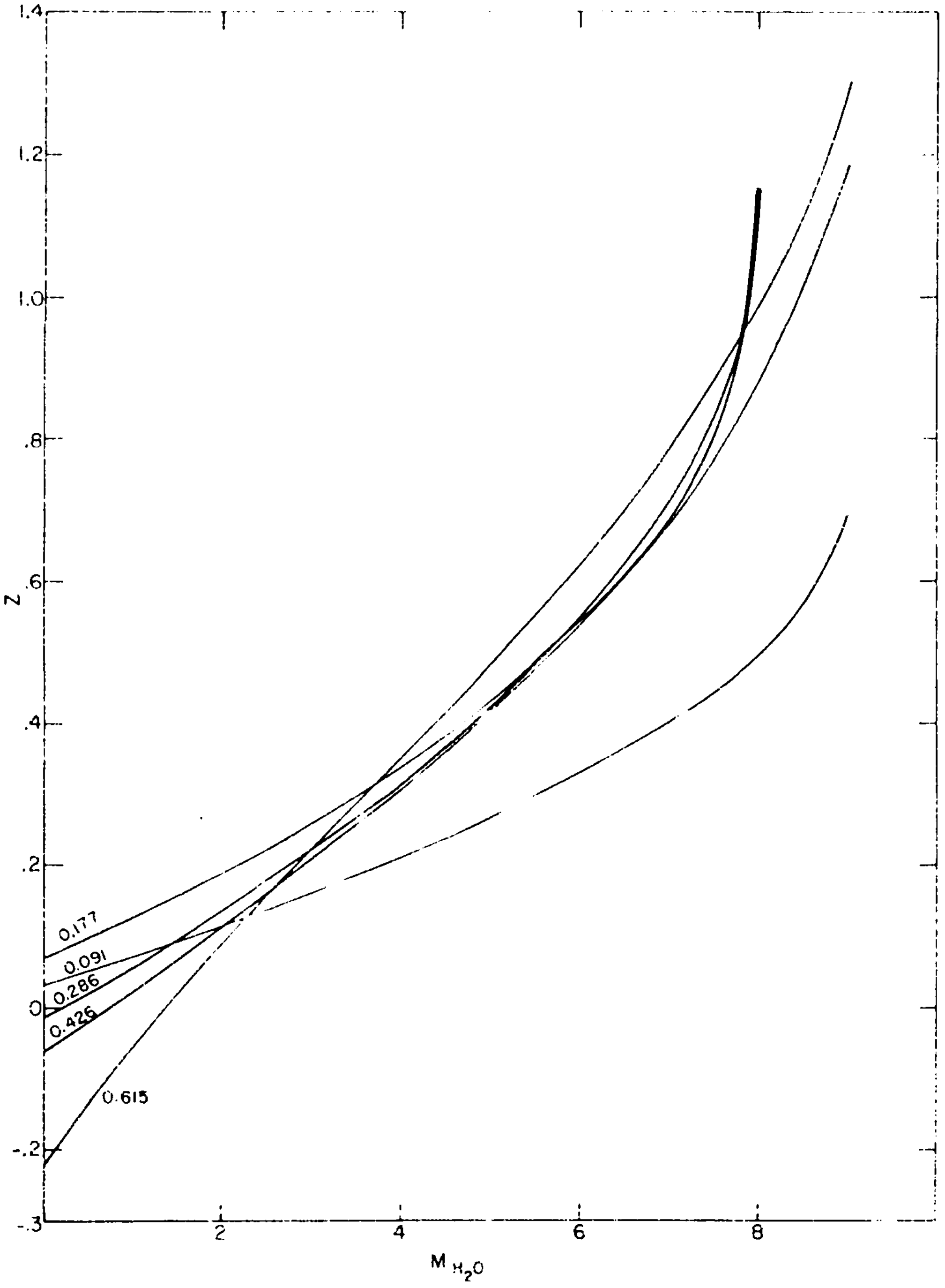
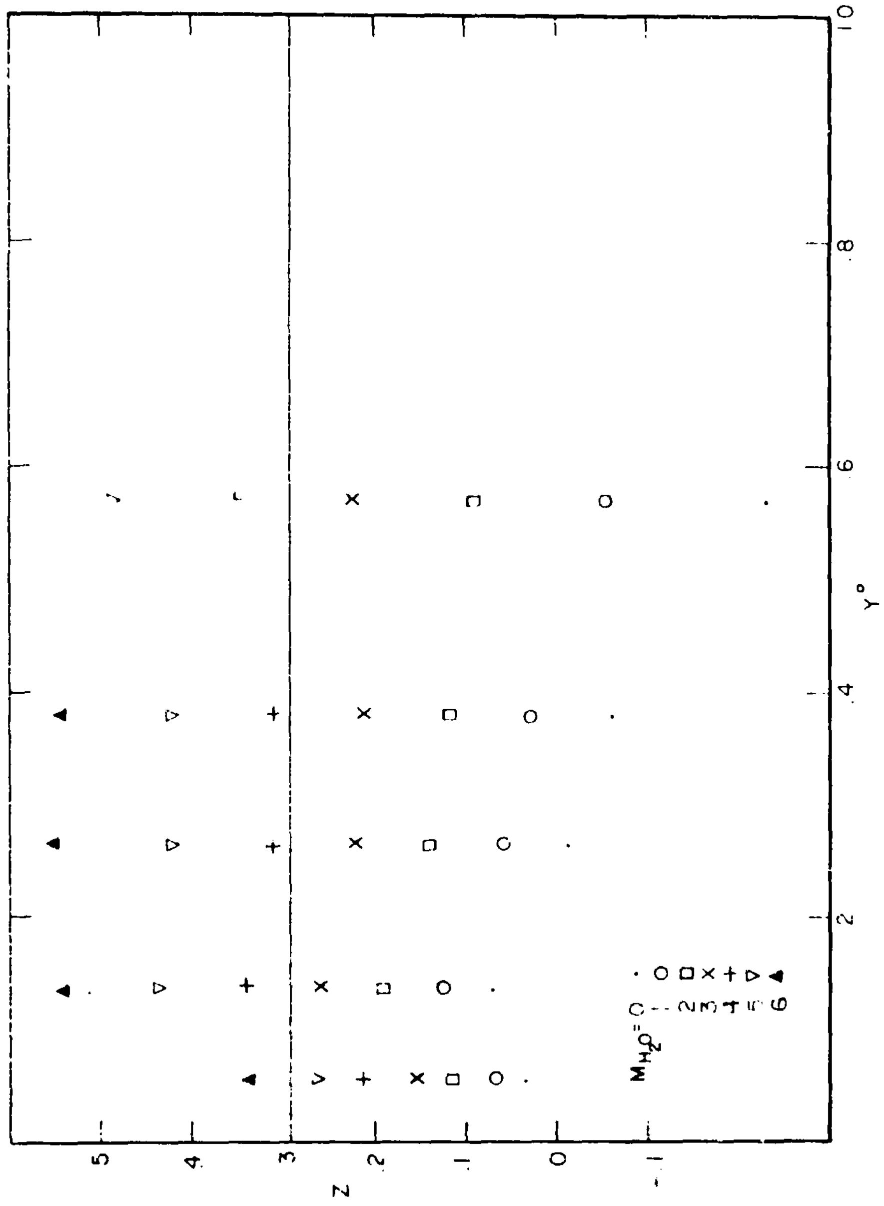

Z
1.4
1.2
1.0
.8
.6
.4
.2
0
-.2
-.3
2
4
6
8
M $_{H_2O}$
0.177
0.091
0.286
0.426
0.615

Figure 10. z *versus* Y^0.


N
.5
.4
.3
.2
.1
0
-.1
Y°
.2
.4
.6
.8
1.0
M_{H_2O} = 0 ·
.1 ○
.2 □
.3 ×
.4 +
.5 ▷
.6 ▲

also about 3.9.

A similar treatment was carried out for Equation 61. The data are given in Table 7 and plotted in Figures 11 and 12. A value of m_{OH} about equal to 0.32 quite adequately fits the requirements and m_E is about equal to 0.43.

A More General Treatment

In general the assumption involved in writing Equation 32 will not be valid. We can define a quantity r in a manner similar to the definitions of p and q, thus

$$F_{SH} = (X_W + r)F_{H_2O} + (X_E - r)F_{EH} \qquad (69)$$

With this relation one can treat mixtures of water and strong or relatively strong acids.

It is also desirable to treat solutions of strong acids in mixed solvents. In order to do this, equations for and must be obtained for at least three components. This is done in the Appendix, where the general case or n components in the solvent is treated together with considerations mentioned above about ionization of the solvent. The treatment follows the same pattern as given previously for binary mixtures. One obtains for α and β the relations

$$\alpha = -u_{SH}^{*}(H_2O) + \sum(X_i + q_i)\left[u_{SH}^{*}(H_2O) - u_{SH}^{*}(Q_iH) + u_W(H_2O, Q_iH)\right] - \sum(r_i - q_i)F_{Q_iH} \qquad (70)$$

Table 7. Values of z'_o for various values of m_{OH}

X_E	.091	.177	.286	.426	.615
m_{OH}	z'	z'	z'	z'	z'
$m_{OH} = 0$	-.143	-.129	-.109	-.102	-.106
$m_{OH} = 0.1$	-.126	-.115	-.089	-.081	-.079
$m_{OH} = 0.2$	-.109	-.096	-.068	-.060	-.052
$m_{OH} = 0.3$	-.090	-.078	-.048	-.038	-.026
$m_{OH} = 0.4$	-.070	-.057	-.027	-.017	-.001
$m_{OH} = 0.5$	-.051	-.036	-.007	+.005	+.024
$m_{OH} = 0.6$	-.031	-.017	+.016	+.026	+.048

Figure 11. z' *versus* m_{OH^-}.

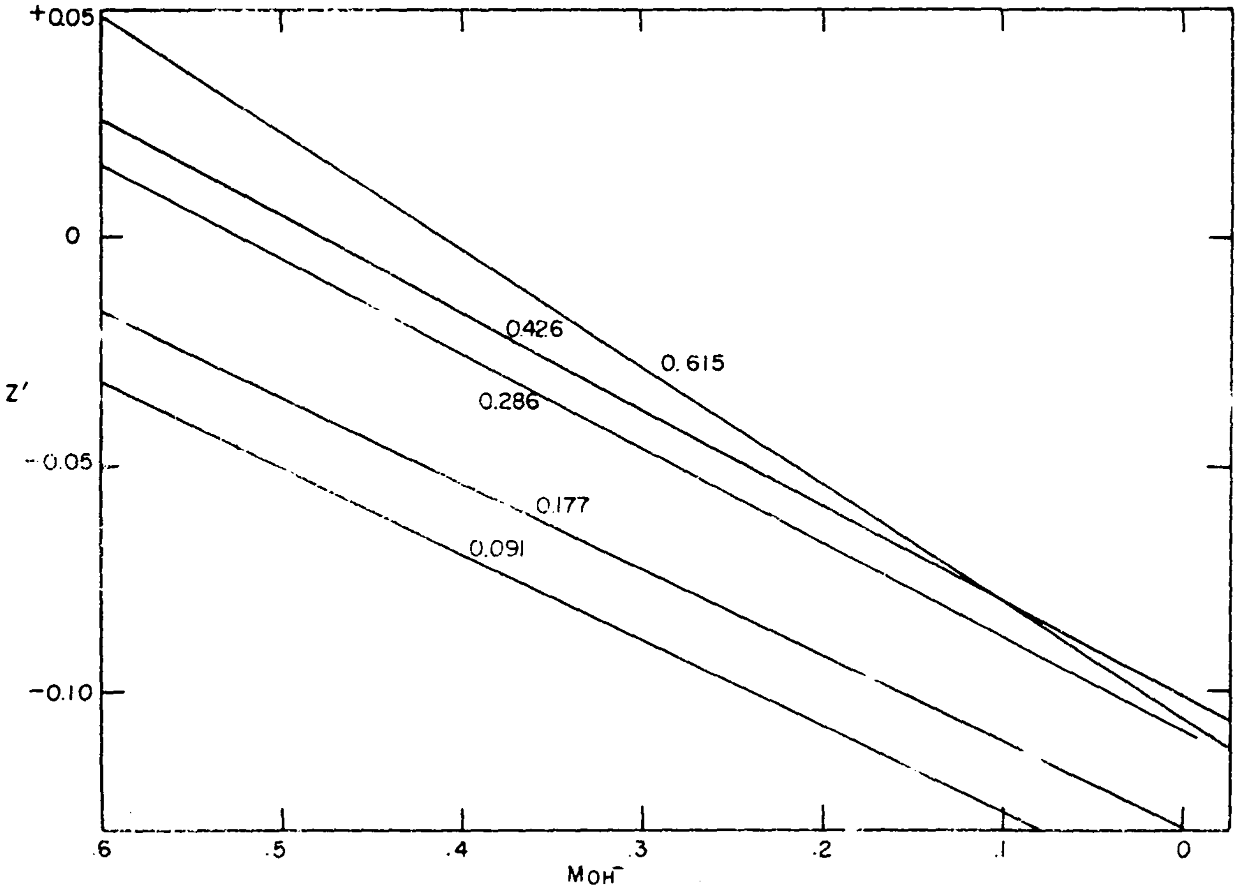
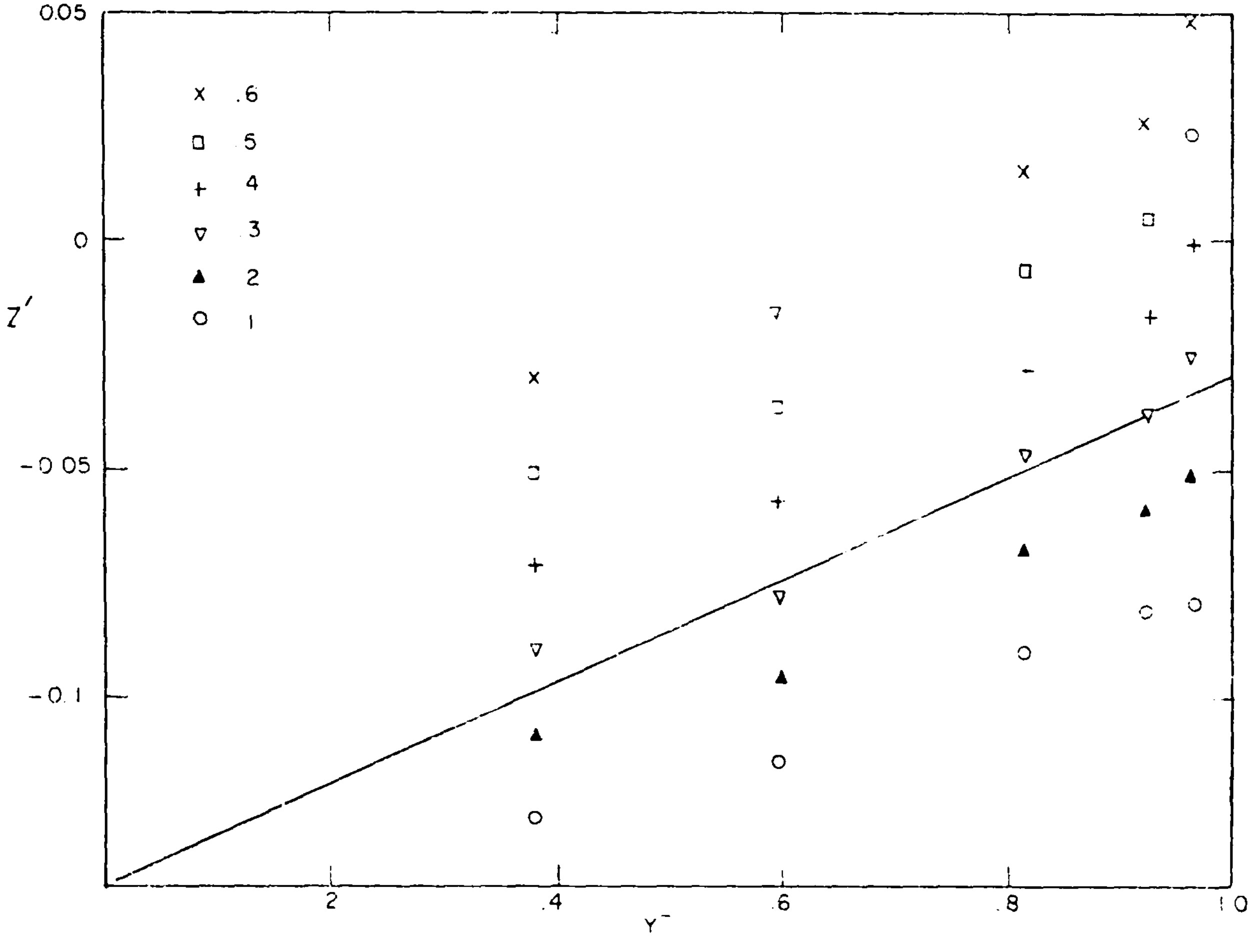

+0.05
0
-0.05
-0.10
Z′
.6
.5
.4
.3
.2
.1
0
M_{OH^-}
0.615
0.426
0.286
0.177
0.091

Figure 12. z' *versus* Y^-.


0.05
0
-0.05
-0.1
Z′
2
.4
.6
.8
1.0
Y⁻
× .6
□ 5
+ 4
▽ 3
▲ 2
○ 1

and

$$\beta = - u_{SH}(OH) + \sum (X_i + p_i) \; \big[u_{SH}^{*}(OH) - u_{SH}^{*}(Q_i^-) + u_W(OH^-, Q_i^-) \sum (r_i - p_i) \; F_{Q_iH} \qquad (71)$$

where the q_i, p_i, and r_i are subject to the restrictions.

Ethanol-Water-Strong Acid Solution

Let us now utilize the above equation to examine the case of a ternary mixture of water, ethanol, and a relatively small concentration of strong acid. The later specification is made so that one will not be too far from the range in which calculation of ionic activity coefficients can be made by the Debye-Huckel laws, as may be necessary in calculating the quantities q_i, p_i, and r_i. The following approximations can be made

$$- (r_E + r_W) = r_A \approx - X_A$$

$$- (q_E + q_W) = q_A = - X_A$$

$$- (p_E + p_W) = p_r \approx X_E + X_W$$

The first states that virtually all of the strong acid AH added to the mixture ionizes. The second states that no species AH_2^+ is formed, and the last states that virtually all of the anions in solution are A^- ions. Equation 70 can then be written

$$\alpha = -\, u_{SH}^{*}(H_2O) + (X_E + q_E)\ u_{SH}^{*}(H_2O) - u_{SH}^{*}(EH) + u_W(H_2O,\ EH) - (r_W - q)F_{H_2O} - (r_E - q_E)F_{EH} \qquad (74)$$

However, from Equation 73

$$(r_E + r_W) = (q_E + q_W) \qquad (75)$$

or

$$(r_E - q_E) = -\ (r_W - q_W)$$

Thus Equation 74 becomes

$$\alpha = -\, u_{SH}^{*}(H_2O) + (X_E + q_E)\ u_{SH}^{*}(H_2O) - u_{SH}^{*}(EH) + u_W(H_2O,\ EH) + (r_W - q_W)(F_{EH} - F_{H_2O}) \qquad (76)$$

It is seen that this expression is essentially the same as Equation 46 except that -q is replaced by + q_E in the second term, and -q is replaced by $(r_W - Q_W)$ in the last term. In general, for relatively dilute solutions of strong acid $(r_W - q_W) \simeq q$ and $q_E \simeq q$ so that Equation 76 is essentially the same as Equation 46. For example, for a 0.1 molar solution of HCl in 65 per cent ethanol water, assuming the density of this solution to be equal to the density in the absence of HCl

$$q = 0.119, \ q_E = - 0.118, \ (r_W - q_W) = - 0.121$$

Examination of the Hammett Acidity Function

In order to find a relationship between the Hammett acidity function and Grunwald's treatment of acid-base reactions in mixed solvents, it will be convenient to examine closely the condition required in order that a Hammett acidity function be defined. This condition is stated as

$$\log \frac{f_B}{f_{BH}} = d \tag{77}$$

where f_B and f_{BH} are degenerate activity coefficients of base B and its conjugate acid, respectively, and d is a constant. This condition must be met for all bases, i.e., d is a constant independent of the base under consideration. There is, however, no restriction on d with regard to the solvent. Equation 1 can be rewritten

$$\log \frac{a_B^*}{a_{BH}^*} - \log \frac{a_B}{a_B} = d \tag{78}$$

where the a^* represents activities in any solvent S and the a represents activities in water. Thus the Hammett acidity function which is written

$$H^0 = - \log \frac{a_H f_B}{f_{BH}} \tag{79}$$

can also be written

$$H^0 = - \log f_H^* - d - \log c_H \qquad (80)$$

For convenience let us define

$$H^* = \log f_H^* - d \qquad (81)$$

which is just the Hammett acidity function without the concentration term. The term by f_H is degenerate activity coefficient of hydrogen ion in solvent S and may be represented by

$$\log f_H^* = \log \frac{f_{SH}^*}{f_{SH}} \qquad (82)$$

or

$$\log f_H^* = \log \frac{a_{SH_2^+}^*}{a_{SH}^*} - \log \frac{a_{H_3O^+}}{a_{H_2O}} \qquad (83)$$

Now, if Equation 78 holds for all bases, there seems to be no good reason to exempt water. Thus,

$$\log \frac{a_{H_2O}^*}{a_{H_3O^+}^*} - \log \frac{a_{H_2O}}{a_{H_3O^+}} = d \qquad (84)$$

Substituting Equations 53 and 84 into Equation 81 one obtains

$$H^* = - \log \frac{a_{SH}^*}{a_{SH_2^+}^*} + \log \frac{a_{H_2O}^*}{a_{H_3O^+}^*} = pK_{85}^{S} \qquad (85)$$

Thus H^* is equal to the pK for the reaction

$$H_3O^+ + SH = H_2O + SH_2^+ \qquad (86)$$

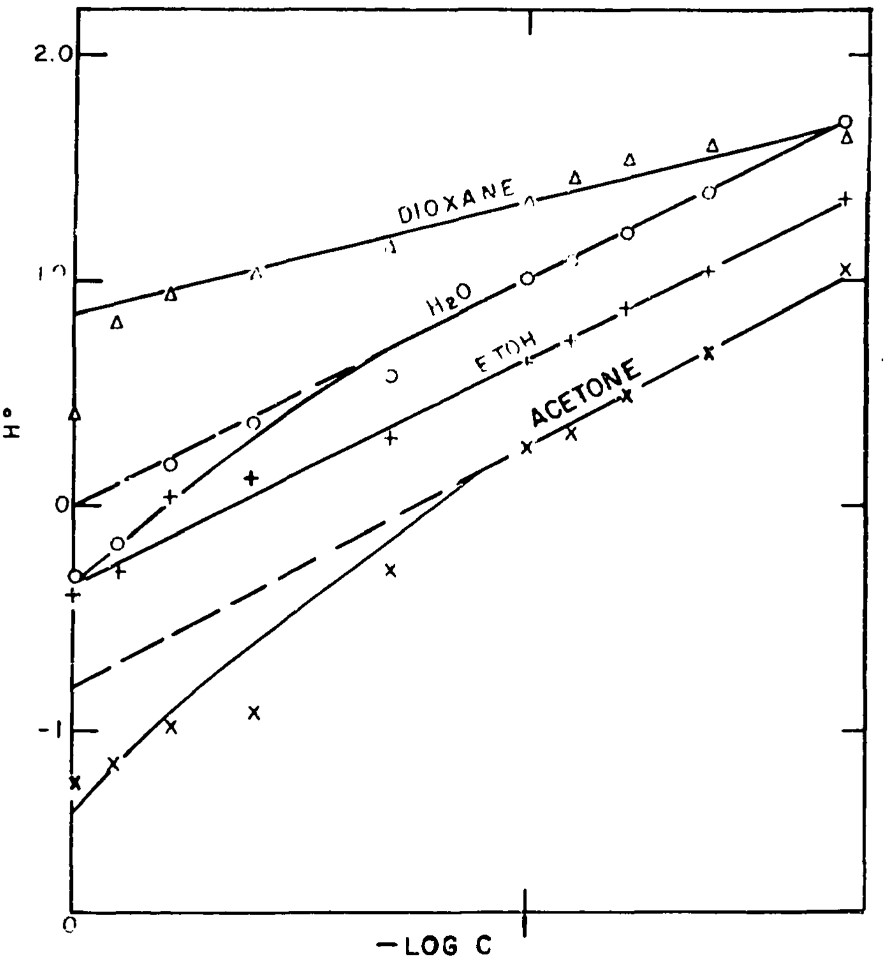
as measured in solvent S. Equation 80 may now be written

$$H^o = pK_{85}^{S} - \log C_H \qquad (87)$$

Thus if H^o is plotted versus log C_H for any solvent a straight line should be obtained with a slope of one. The intercept when $C_H = 1$ must be equal to pK_{85}^{S}. In Figure 13 is shown such a plot for water, ethanol, acetone, and dioxan taken from Braude (7). It is seen that for all solvents the slope is very close to one as predicted, except for dioxan which has a slope of 0.5. It is observed, however, that some of the lines deviate at higher acid concentration. This can be accounted for by pK_{85}^{S} not being independent of the concentration of acid. Indeed, one would not expect this to be so. This point will be taken up again further on, but unfortunately with no completely satisfying explanation.

In the light of the discussion of the Hammett acidity function given in this section, it can be seen that this function is not necessarily a measure of the difference in proton activity between pure water and some other solvent S. Indeed, if the assumptions involved are valid, it is only generally true that the Hammett acidity function is a measure of the difference between the basicity of a water molecule in

Figure 13. Hammett acidity function *versus* logarithm HCl concentrate.


2.0
1.0
0
-1
H°
0
—LOG C
DIOXANE
H₂O
ETOH
ACETONE

the case of mixed solvents.

If the quantity of d in Equation 78 and Equation 84 is essentially constant under all conditions, then the two statements above are equivalent. However, it will be shown in the next section that d is a function of the solvent, so that only the second statement is true.

Relations between Hammett Acidity Function and Grunwald Treatment of Acids and Bases

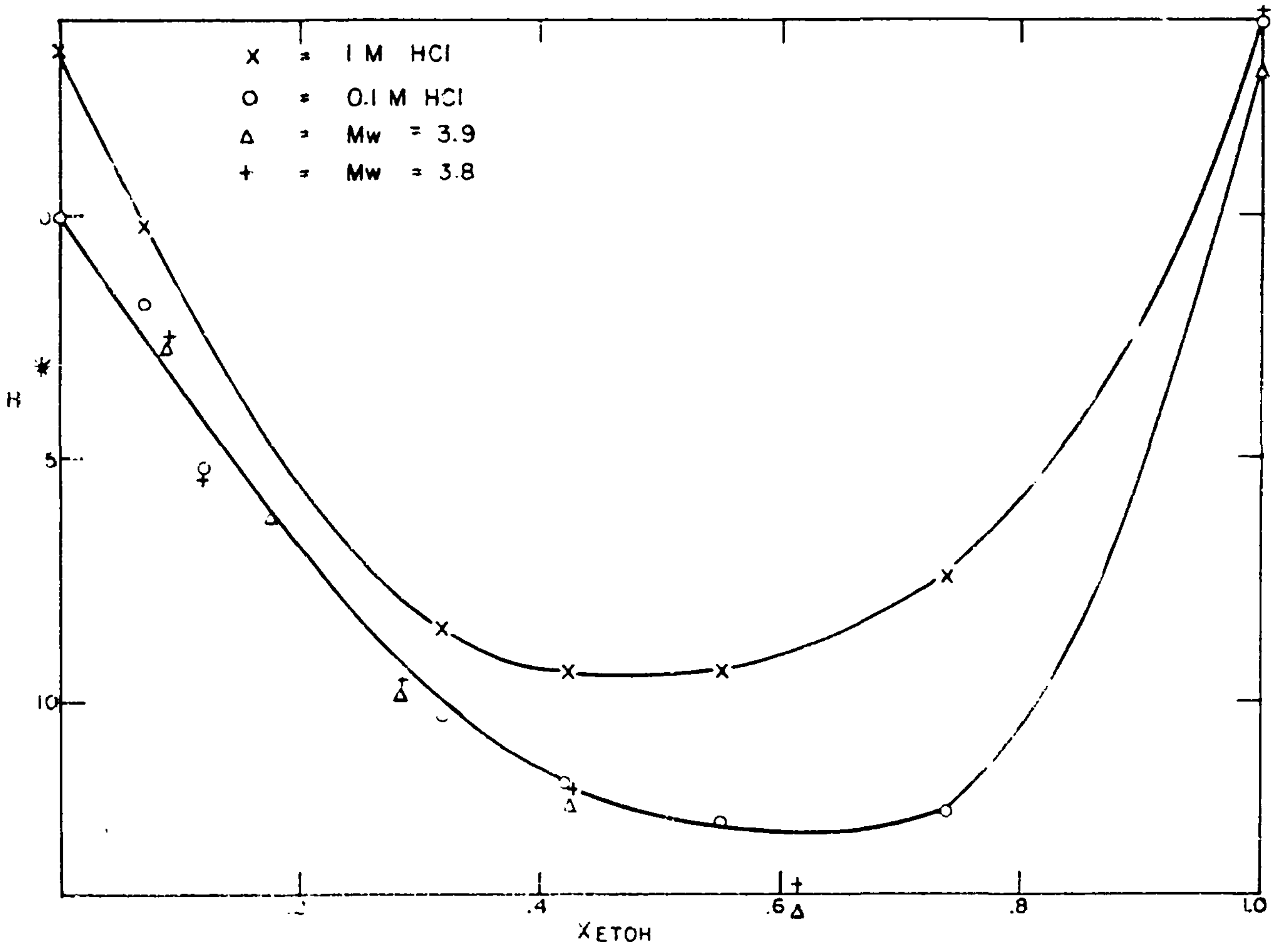
The quantity $pK_{85}{}^{S}$ can be obtained from Equation 24. Thus,

$$pK_{85}{}^{S} = \frac{\alpha_{S}}{2.3\ RT} - m_{W}Y_{SH}{}^{0} = H^{*} \qquad (88)$$

It is seen from the above expression that d is represented by the quantity m_WY from comparison with Equation 81, since the definition of log $f_H{}^{*}$ in Equation 83 is essentially the same as the definition of α in Equations 16 and 7. Thus the d will change with solvent as $Y_{SH}{}^{0}$.

In Figure 14 are plotted values of H^{*} versus mole composition of water ethanol from data by Braude (8) at 0.1 molar and 1 molar HCl, together with values of the function $\alpha - m_WY$ using Grunwald's data and a value of 3.9 for m_W. In a comparison of this data it is assumed that the $Y_{SH}{}^{0}$ values are not generally affected by small concentrations of

Figure 14. Comparison of H^* and the function $\alpha - m_{H_2O}Y^0$ *versus* mole fraction ethanol.


X = I M HCl
O = 0.1 M HCl
Δ = Mw = 3.9
+ = Mw = 3.8
H*
0
5
10
.2
.4
.6
.8
1.0
XETOH

strong acid.

It can be seen that agreement between the data for 0.1M and the calculated values are quite good up to $X_E = 0.5$. The values for 1 molar are all too high. This is probably in greater part correlated with the fact that a large deviation from linearity occurs for water in Figure 13 at this concentration. The lack of agreement of the calculated curve from experimental value for 0.1M HCl is significantly outside of experimental error. It was observed in the discussion of Equation 76 that α is not entirely independent of the concentration of strong acid. The conditions are in the right direction but are much too small to be significant. The most likely explanation of this deviation is that the HCl is incompletely dissociated at higher concentrations of ethanol. If the HCl is not completely dissociated then Equation 76 is not valid, since assumptions in Equation 73 become

$$- (r_W + r_E) = r_A \approx - X_A + (1 - \quad)X_A \qquad (89)$$

$$- (q_W + q_E) = q_r = - X_A$$

where γ is the degree of dissociation of strong acid. Equation 70 then becomes

$$S = - u_{SH}^{*}(H_2O) + (X_E + q_E) \quad u_{SH}^{*}(H_2O) - u_{SH}^{*}(EH) + u_W(H_2O, EH) + (r_W - q_r)(F_{EH} - F_{H_2O}) - (1 - \quad)X_A (F_{EH} - F_{AH}) \qquad (90)$$

Thus Equation 89 differs from Equation 76 only by the addition of the last term. One can estimate the error introduced by neglecting this last term if a suitable value of F_{AH} is assumed. The standard free energy of formation of HCl from its elements is given in the International Critical Tables as about 22.7 kcal/mole. The standard free energy of HCl in infinitely dilute aqueous solutions is about 31.3 kcal/mole.

Assuming that it is in the neighborhood of 23 kcal/mole and using the value 45 kcal/mole for the standard free energy of ethanol let us estimate the degree of association necessary to account for the deviation of the experimental values of Braude at 0.1M HCl in 80 per cent by weight ethanol. If the change in density on adding acid is ignored, the mole fraction of HCl is about 0.04. The deviation of Braude's data from the value calculated using Grunwald's data is about two tenths of a unit. Thus 0.2 =

$$(1 - \alpha)\ 0.04\ \frac{70000}{2.3\ RT} \qquad (1 - \alpha)\ .04 \times 50$$

The value of α is in the neighborhood of 0.9, which does not seem at all unreasonable.

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Appendix

If p_i is the difference between X_i^* and X_i where X_i^* is the mole fraction of anion Q_i^- in one mole of solvent anion and X_i is the amount of Q_iH added to form one mole of the total mixture, one can write,

$$F_5 = \sum_{i=1}^{n} (X_i + p_i)F_{Q_i^-} \tag{1}$$

where the p_i's are subject to the restriction

$$p_j = - \sum_{i=1}^{n} p_i \, \delta_j^j \qquad \delta_j^j = 1 \tag{2}$$

$$\delta_j^j = 0$$

or equivalently

$$\sum_{i=1}^{n} p_i = 0 \tag{3}$$

Analogously for the solvent cation

$$F_{SH_2^+} = - \sum_{i=1}^{n} (X_i + q_i)F_{Q_iH_2^+} \tag{4}$$

in which the q_i are restricted by

$$\sum_{i=1}^{n} q_i = 0 \tag{5}$$

or

$$q_j = \sum_{i=1}^{n} q_i \delta_i^j \qquad (6)$$

and also for the undissociated molecules of the solvent

$$F_{SH} = \sum_{i=1}^{n} (X_i + r_i) F_{Q_iH} \qquad (7)$$

where r_i is restricted by

$$\sum_{i=0}^{n} r_i = 0 \qquad (8)$$

or

$$r_j = - \sum_{i=1}^{n} r_i \delta_i^j \qquad (9)$$

Thus one can write

$$u_{SH}(OH, S^-) = F_{OH^-} + \sum_{i=1}^{n} (X_i + r_i) F_{Q_iH} - F_{H_2O} - \sum (X_i + p_i) F_{Q_i^-} \qquad (10)$$

since

$$- \quad X_i = 1$$

$$= \sum X_i F_{OH^-} + \sum X_i F_{Q_iH} - \sum X_i F_{H_2O} - \sum X_i F_{Q_i^-} + \sum r_i F_{Q_iH} - \sum p_i F_{Q_i^-}$$

$$= \sum X_i (F_{OH^-} + F_{Q_iH} - F_{H_2O} - F_{Q_i^-}) + \sum r_i F_{Q_iH} - \sum p_i F_{Q_i^-}$$

$$u_{SH}(OH, S^-) = \sum X_i \; u_{SH}(OH^-, Q_i^-) + \sum r_i F_{Q_iH} - \sum p_i F_{Q_i^-}$$

The term

$$\sum p_i F_{Q_i^-} = p_{OH} F_{OH} + \sum p_i F_{Q_i} \mathcal{L}_i^{OH} \qquad (11)$$

and since $p_{OH} = - \sum p_i \mathcal{L}_i^{OH}$

$$\sum p_i F_{Q_i^-} = - \sum p_i F_{OH} \mathcal{L}_i^{OH} + \sum p_i F_{Q_i^-} \mathcal{L}_i^{OH} \qquad (12)$$

$$= - \sum p_i (F_{OH^-} - F_{Q_i^-}) \mathcal{L}_i^{OH}$$

However,

$$F_{OH^-} - F_{Q_i} = F_{OH} + F_{Q_iH} - F_{Q_i} - F_{H_2O} - F_{Q_iH} + F_{H_2O}$$

$$= u_{SH}(OH^-, Q_i^-) + (F_{H_2O} - F_{Q_iH}) \qquad (13)$$

Thus 12 becomes

$$\sum p_i F_{Q_i^-} = - \sum p_i u_{SH}(OH, Q_i^-) \mathcal{L}_i^{OH} - \sum p_i (F_{H_2O} -$$

$$F_{Q_iH}) \underset{i}{\overset{OH}{\mathcal{L}}} \tag{14}$$

Since $u_{SH}(OH,\ OH) = 0$ the term

$$+ \sum p_i u_{SH}(OH,\ Q_i^-) \underset{i}{\overset{OH}{\mathcal{L}}} = + \sum p_i u_{SH}(OH^-,\ Q_i^-) \tag{15}$$

the term

$$\begin{aligned} - \sum p_i (F_{H_2O} - F_{Q_iH}) \underset{i}{\overset{OH}{\mathcal{L}}} &= - \sum p_i F_{H_2O} \underset{i}{\overset{OH}{\mathcal{L}}} + \\ &\quad \sum p_i F_{Q_iH} \underset{i}{\overset{OH}{\mathcal{L}}} \\ &= p_{OH} F_{H_2O} + \sum p_i F_{Q_iH} \underset{i}{\overset{OH}{\mathcal{L}}} \\ &= \sum p_i F_{Q_iH} \end{aligned} \tag{16}$$

thus 14 becomes

$$\sum p_i F_{Q_i^-} = - \sum p_i u_{SH}(OH^-,\ Q_i^-) + \sum p_i F_{Q_iH} \tag{17}$$

and 10 becomes

$$u_{SH}(OH,\ S^-) = \sum (X_i + p_i) u_{SH}(OH,\ Q_i^-) + \sum (r_i - p_i) F_{Q_iH} \tag{18}$$

By a similar treatment one also obtains

$$u_{SH}(H_2O,\ SH) = \sum (X_i + q_i) u_{SH}(H_2O,\ Q_iH) - \sum (r_i - q_i) F_{Q_iH} \qquad (19)$$

Introducing these relations into Equations 24 and 27 of the text

$$\alpha = - u_{SH}^{*}(H_2O) + \sum (X_i + q_i) u_{SH}(H_2O,\ Q_iH) - \sum (r_i - q_i) F_{Q_iH} \qquad (20)$$

and

$$\beta = - u_{SH}^{*}(OH) + \sum (X_i + p_i) u_{SH}(OH,\ Q_i^{-}) + \sum (r_i - p_i) F_{Q_iH} \qquad (21)$$

using the relation

$$u_{SH}(H_2O,\ Q_iH) = u_{SH}^{*}(H_2O) - u_{SH}^{*}(Q_iH) + u_w(H_2O,\ Q_iH) \qquad (22)$$

and

$$u_{SH}(OH,\ H_2O) = u_{SH}^{*}(OH) - u_{SH}^{*}(Q_i^{-}) + u_W(CH^{-},\ Q_i^{-}) \qquad (23)$$

Equations 20 and 21 become

$$\alpha = - u_{SH}^{*}(H_2O) + \sum (X_i + q_i) \left[u_{SH}^{*}(H_2O) - u_{SH}^{*}(Q_iH) + u_W(H_2O,\ Q_iH) \right] - \sum (r_i - q_i) F_{Q_iH} \qquad (24)$$

and

$$\beta = - u_{SH}^{*}(OH) + \sum(X_i + p_i)\left[u_{SH}^{*}(OH) - u_{SH}^{*}(Q_i^-) + u_W(OH, Q_i)\right] + \sum(r_i - p_i)F_{Q_iH} \qquad (25)$$

The quantities q_i, p_i, and r_i are not independent of each other. The (n - 1) independent p_i's, the (n - 1) independent q_i's and the (n - 1) independent r_i's are related by equation of the type

$$u_{SH}(OH^-, Q_i^-) = - \log \frac{a_{OH^-}\, a_{Q_iH}}{a_{H_2O}\, a_{Q_i^-}} \qquad (26)$$

of which there are (n - 1)

$$u_{SH}(H_2O, Q_iH) = - \log \frac{a_{H_2O}\, a_{Q_iH_2^+}}{a_{H_3O^+}\, a_{Q_iH}} \qquad (27)$$

of which there are (n - 1), and any (n - 1) equation of the type

$$u_{SH}(Q_i^-, Q_jH) = - \log \frac{a_{Q_i^-}\, a_{Q_jH_2^+}}{a_{Q_iH}\, a_{Q_jH}} \qquad (28)$$

of which only (n - 1) are independent of each other. In particular, one could choose Equation 28 such that $Q_jH = H_2O$. If the concentration of ions is not too large one can write Equation 27 as

$$u_{SH}(OH, Q_i^-) = - \log \frac{(X_{OH} + p_{OH})(X_i + u_i)}{(X_{H_2O} + r_{H_2O})(X_i + p_i)} \qquad (29)$$

Similarly Equation 24 becomes

$$u_{SH}(H_2O, Q_iH) = -\log \frac{(X_{H_2O} + r_{H_2})(X_i + q_i)}{(X_{H_2O} + q_{H_3O^+})(X_i + r_i)} \qquad (30)$$

However, in order to write Equation 28 as a function of the X_i's, r_i's, p_i's, and q_i's one must first find suitable expressions for concentrations. This can be done by solving any 3n of the following equations for n terms X_{Q_iH}, n terms $X_{Q_iH_2^+}$ and n terms $X_{Q_i^-}$ which all added together should total one mole.

$$X_{Q_iH} + X_{Q_iH_2^+} + X_{Q_i^-} = X_i \qquad (31)$$

of which there are n

$$\frac{X_i + p_i}{X_j + p_j} = \frac{X_{Q_i^-}}{X_{Q_j^-}} \qquad (32)$$

of which there are (n - 1) independent

$$\frac{X_i + q_i}{X_j + q_j} = \frac{X_{Q_iH_2^+}}{X_{Q_iH_2^+}} \qquad (33)$$

of which there are (n - 1)

$$\frac{X_i + r_i}{X_j + r_j} = \frac{X_{Q_iH}}{X_{Q_jH}} \qquad (34)$$

of which there are (n - 1), and

$$X_{Q_iH_2^+} = X_{Q_i^-} \tag{35}$$