Stability Constants of Metal Chelates in Anhydrous Ethyl Alcohol

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IN RECENT years there has been an increasing industrial emphasis on chelate formation. It is often possible to correlate various properties of these species with their relative stabilities, and as a consequence a method of determination is required.

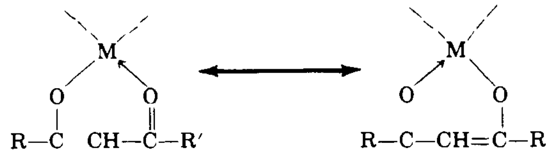
Many chelates are insoluble in an aqueous medium, and this necessitates the use of nonaqueous solvents. Very frequently, a mixed solvent system such as dioxane-water is used. However, there are numerous instances when a purely nonaqueous medium is desirable. Under these conditions a method of study is not always convenient or even available.

Probably the most accurate method for determining chelate stability constants is that of Bjerrum (*1*) as modified by Calvin and Wilson (*2, 6*). This method involves potentiometric techniques, and these are very seriously limited when applied in a purely nonaqueous medium. Because of the potentials of many positive ions, a metal electrode system is usually not applicable. This difficulty can be avoided in a mixed nonaqueous-water system by using a glass electrode. Because a normal glass electrode will not function in the complete absence of water, it would seem that this method could not, in general, be used in a system where water must be completely excluded.

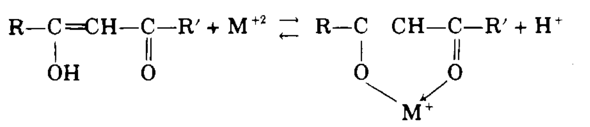
In an effort to overcome such a limitation, this work was undertaken. The technique is not as fundamentally sound as would be desirable. Yet, reproducible results can be obtained from which it is possible to determine relative stability constants. It also is not applicable to all nonaqueous solvent systems. However, it would probably be possible to find a solvent system that could be used.

THEORY

In the particular study, a β-diketone was used as the chelating agent. The very high stability of these chelates can be attributed to the resonant structures



The formation of such a chelate can be thought of as arising from the enol form of the β-diketone. If the enol form reacts with a metal ion M^{+2}, the first molecule enters as follows:



The displaced H^+ can then be followed by potentiometric means.

In general, if HKe is considered to be the chelating agent and M^{+2} the metal ion, the equilibrium can be expressed as

$$HKe \rightleftharpoons H^+ + Ke^-$$

$$M^{+2} + Ke^- \rightleftharpoons MKe^+$$

for the addition of the first molecule of the chelating agent. The first stability constant, k_1, is then given by

$$k_1 = \frac{[MKe^+]}{[M^{+2}][Ke^-]} \tag{1}$$

and the second stability constant, for the equilibrium

$$MKe^+ + Ke^- \rightleftharpoons MKe_2$$

is given by

$$k_2 = \frac{[MKe_2]}{[MKe^+][Ke^-]} \tag{2}$$

Assuming a coordination number of four, the over-all stability constant, k, can be expressed as

$$k = k_1k_2 = \frac{[MKe_2]}{[M^{+2}][Ke^-]^2} \tag{3}$$

To evaluate the stability constants, it is necessary to determine the average number of donor molecules bound to a metal ion in any form—that is, the average number of ligands, $\bar{n}$. This is defined as

$$\bar{n} = \frac{(T_{Ke})_b}{T_{M^{+2}}} \tag{4}$$

where $(T_{Ke})_b$ represents the total amount of chelate bound to a metal ion, and $T_{M^{+2}}$ represents the total amount of metal ion present in any form.

Experimentally, $\bar{n}$ can be determined by evaluating $(T_{Ke})_b$, assuming $T_{M^{+2}}$ is known. This can be done by using the following relations

$$T_{M^{+2}} = M^{+2} + MKe^+ + MKe_2 \tag{5}$$

$$T_{Ke} = HKe + Ke^- + MKe^+ + 2MKe_2 \tag{6}$$

$$MKe^+ + 2M^{+2} + Na^+ + H^+ = X^- + OH^- + Ke^- \tag{7}$$

$$K_d = \frac{[H^+][Ke^-]}{[HKe]} \tag{8}$$

$$X^- = A + 2T_{M^{+2}} \tag{9}$$

where A represents acid that may be added initially, and

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X^- represents the negative ion that is added with the initial acid and as the metal salt. Recognizing that

$$(T_{\text{Ke}})_b = \text{MKe}^+ + 2\text{MKe}_2$$

Equations 5 to 9 may be used to obtain the relation

$$(T_{\text{Ke}})_b = \text{Na}^+ - \text{A} + \text{H}^+ - \frac{10^{-16}}{\text{H}^+} - \frac{K_D}{\text{H}^+}\left[T_{\text{Ke}} + \text{A} - \text{Na}^+ - \text{H}^+ + \frac{10^{-16}}{\text{H}^+}\right] \qquad (10)$$

Although some of the terms in Equation 10 may be only approximate in a nonaqueous medium, it is a reasonable approximation to say that

$$(T_{\text{Ke}})_b = \text{Na}^+ - \text{A} + \text{H}^+ \qquad (11)$$

which provides a means for determining $\bar{n}$.

It is also possible to evaluate $\bar{n}$ in an alternative manner that will lead to the evaluation of the stability constants. Since $\bar{n}$ represents the average number of ligands

$$\bar{n} = \frac{[\text{MKe}^+] + 2[\text{MKe}_2]}{[\text{M}^{+2}] + [\text{MKe}^+] + [\text{MKe}_2]} \qquad (12)$$

If the appropriate substitutions from Equations 1 and 2 are made

$$\bar{n} = \frac{k_1[\text{Ke}^-] + 2k_1k_2[\text{Ke}^-]^2}{1 + k_1[\text{Ke}^-] + 2k_1k_2[\text{Ke}^-]^2} \qquad (13)$$

If Equation 13 is solved for k_1 and k_2,

$$k_1 = \frac{1}{[\text{Ke}^-]}\,\frac{\bar{n}}{(1 - n) + (2 - n)[\text{Ke}^-]k_2} \qquad (14a)$$

$$k_2 = \frac{1}{[\text{Ke}^-]}\,\frac{(\bar{n} - 1) + \left(\frac{\bar{n}}{k_1[\text{Ke}^-]}\right)}{(2 - \bar{n})} \qquad (14b)$$

Taking advantage of the dependence of k_1 and k_2 on $\bar{n}$, a good first-order approximation of the stepwise stability constants can be made. If it is assumed that each coordinating step is completed before the next one begins, then the concentration of MKe_2 can be assumed to be zero as long as M^{+2} and MKe^+ are in equilibrium. Rearranging the equilibrium expression for k_1 to the form

$$k_1 = \frac{1}{[\text{Ke}^-]}\,\frac{[\text{MKe}^+]}{[\text{M}^{+2}]} \qquad (15)$$

$k_1 = 1/[\text{Ke}^-]$ when the ratio $[\text{MKe}^+]/[\text{M}^{+2}]$ is equal to unity. This situation arises when $\bar{n} = 0.5$—that is, when $[\text{MKe}_2] = 0$,

$$\bar{n} = \frac{[\text{MKe}^+]}{[\text{M}^{+2}] + [\text{MKe}^+]} \qquad (16)$$

and when $[\text{M}^{+2}] = [\text{MKe}^+]$, $\bar{n}$ is equal to 0.5. This same argument can be applied to k_2, and, in general,

$$k_n = \left(\frac{1}{[\text{Ke}^-]}\right)_{\bar{n} = n - 0.5} \qquad (17)$$

The over-all stability constant, as defined in Equation 3, can be determined according to the relation

$$k = (k_1k_2) = \left(\frac{1}{[\text{Ke}^-]}\right)_{\bar{n} = 1} \qquad (18)$$

As a result of these simple relations, first-order approximations of k_1 and k_2 can be made graphically if $\bar{n}$ is plotted against pKe^-. Various methods have been proposed to determine the actual stability constants by successive approximations (*1, 3*), and all are probably acceptable.

Finally, the pKe^- can be evaluated from Equation 8 along with the experimental determination of K_D and the hydrogen ion concentration. The pH of the system is followed as base is added, and the first flat portion on the titration curve should be due to the titration of the chelating agent HKe. From this, the value of K_D can be evaluated, and the individual stability constants can then be determined.

EXPERIMENTAL

Solutions and Reagents. Because of the very hygroscopic nature of ethyl alcohol, all solutions were prepared and stored in a nitrogen dry box with phosphorus pentoxide used as a desiccant. The anhydrous ethyl alcohol was prepared from commercial alcohol (U.S. Industrial Chemical Co.) using the method described by Voegel (*8*). The alcoholic hydrogen bromide solutions were obtained by passing hydrogen bromide gas into anhydrous ethyl alcohol, and the sodium ethoxide solutions were prepared by adding metallic sodium to anhydrous ethyl alcohol. The metal ions were obtained from the following anhydrous salts: ZnBr_2, CuBr_2, NiBr_2, CdI_2, and MnCl_2. Anhydrous sodium perchlorate at a concentration of 0.025*M* was used as an inert salt to maintain an approximately constant ionic strength.

Apparatus. The titrations were carried out in a four-necked, round-bottomed flask with an inlet for dry nitrogen gas. The sodium ethoxide was introduced through the center neck with a 5-ml. microburet. The two electrodes and a stirrer were introduced through the remaining three necks. The system was kept at 30° C. The electrode system consisted of an ordinary Beckman calomel electrode and a Beckman blue-tip glass electrode (Type E-2) with a Beckman pH meter Model H-2.

Procedure. The glass electrode would not function properly in the purely anhydrous medium. Apparently, some quantity of water is necessary for the normal operation of the common glass electrode (*4*). This problem was overcome for the anhydrous medium by soaking the electrode in water for approximately 2 minutes before each reading. The electrode was then dried well with an absorbent paper before returning to the ethyl alcohol solution. The electrode system was never completely stable. However, reproducible results could be obtained.

The chelation curves were obtained from the titration with 0.0476*N* alcoholic sodium ethoxide of a solution containing a 10 to 1 ratio of 2,4-pentanedione (acetylacetone) to metal ion in which the metal ion concentration was $2 \times 10^{-3}M$.

Calibration. To determine the stability constant of a chelate by Bjerrum's method, it is necessary to know the hydrogen ion concentration as a function of the milliliters of base added. The reading shown by a pH meter using a glass electrode in anhydrous ethyl alcohol obviously does not give a direct measure of the pH. However, if other conditions such as temperature and ionic strength remain constant, the meter reading appears to be consistent for a given hydrogen ion concentration. A particular meter reading can be converted into $[\text{H}^+]$ from a calibration curve.

Along with a consistent reading by the electrode system, the construction of a calibration curve depends on several assumptions. To obtain the acid half of the curve, the extent of ionization of hydrogen bromide in anhydrous ethyl alcohol must be known. This approaches 100% in dilute solution (*9*), and for this work any error introduced here would be trivial. Thus, by titrating a hydrogen bromide solution of known concentration against the pH meter reading, the acid end of the calibration curve can be obtained.

Since the dissociation constant is known to be $K_D = 2.89 \times 10^{-16}$ for the autoionization of ethyl alcohol (5) into H^+ and $C_2H_5O^-$, the basic half of the calibration curve can be obtained by titrating sodium ethoxide solution of known concentration against the pH meter reading. These lead to the calibration curve shown in Figure 1. Although the unusual shape of the calibration curve is not understood, it does not affect the method because it is strictly empirical in character.

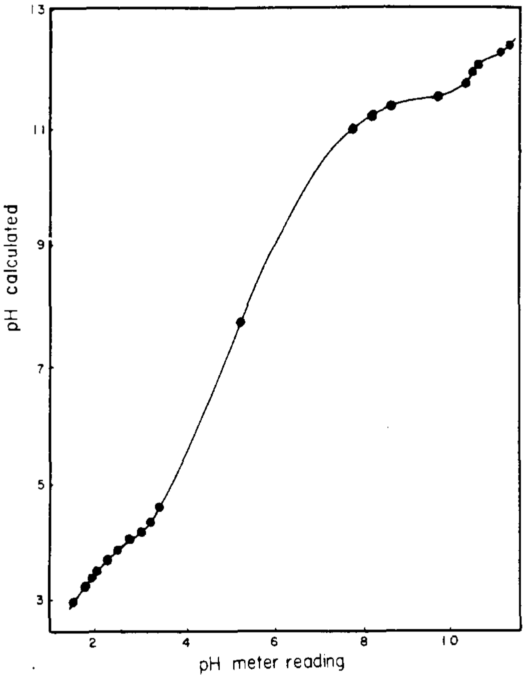

Figure 1. Calibration curve to convert observed pH meter reading to calculated pH

RESULTS AND DISCUSSION

First-order approximations of the stability constants were determined for the chelates of Cd^{+2}, Mn^{+2}, Zn^{+2}, and Ni^{+2} with -4-pentanedione. These are given in Table I. K_D for 2,4-pentanedione was obtained from the last flat portion of the titration curve. Mn^{+2} failed to form a chelate, and only the first stability constant could be determined for Cd^{+2}.

Table I. Approximate Formation Constants

2,4-Pentanedione $pK_D = 11.5$

Metal Ion	Log k_1	Log k_2
Ni^{+2}	8.0	5.1
Zn^{+2}	5.7	4.8
Cd^{+2}	2.7	. . .
Mn^{+2}	. . .	. . .

The titration curves for the various ions are shown in Figure 2. The curve for Cu^{+2} shows that the chelation of the first two groups was complete before the titration was started. Thus, k_1, and k_2 cannot be determined, and the observed flat portion appears to be due to the formation of the hexa-coordinated species.

In Figure 3, the plot of pKe *vs.* $\bar{n}$ is shown for Ni^{+2}. For this particular determination, the portion of the curve of interest is seen to be a straight line. This, however, is not always the case.

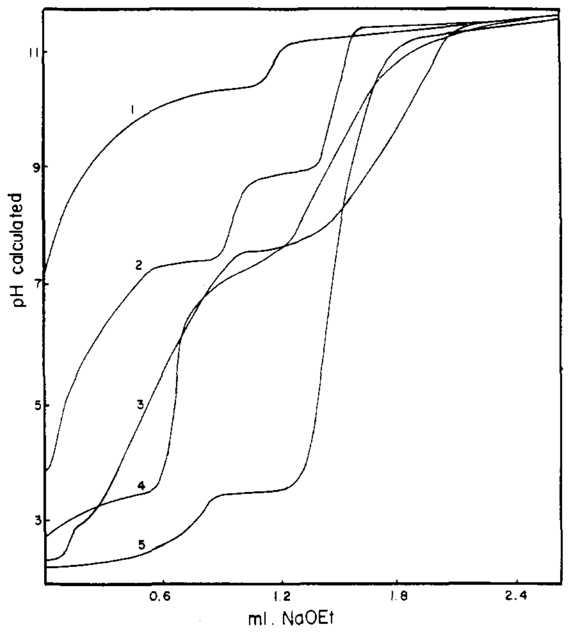

Figure 2. Titration curves showing formation of chelates
1 Cd^{+2}, 2Zn^{+2}, 3Fe^{+2}, 4Ni^{+2}, 5Cu^{+2}

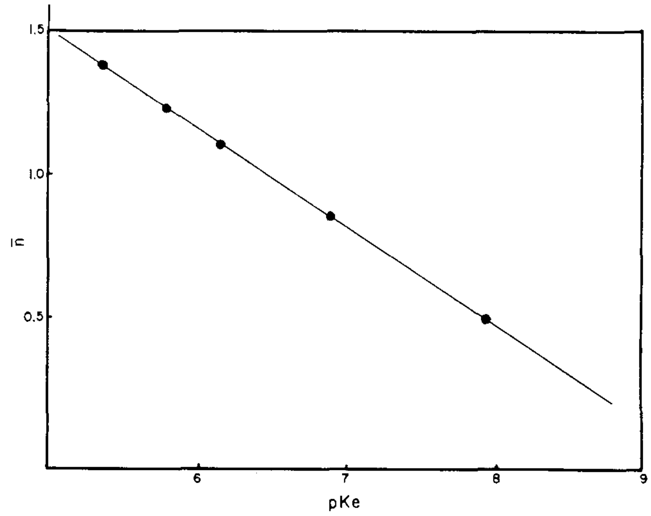

Figure 3. Formation curve for Ni^{+2} with 2,4-pentanedione

Using this particular method of calibration, the stability constants cannot be compared in magnitude with those determined in other solvents, or those determined by Van Uitert, Fernelius, and Douglas (7) for Ni^{+2} in ethyl alcohol. Neverless, their relative values can be determined and this is of primary importance.

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