neutral and in alkaline solution, but gave none at 310 or 380 mμ.

When a solution of potassium hydroxopentacyanocobaltate(III) was heated just below boiling with excess potassium cyanide, it was found that the absorption maximum at 380 mμ characteristic of these solutions disappeared, and that the resulting curve corresponded simply to that of a mixture of potassium cyanide and $K_3Co(CN)_6$, with the peak at 310 mμ plainly evident.

A pronounced characteristic of solutions of the cyanocobaltate(III) complexes studied was the change in intensity of absorption with time which they showed, as indicated in Fig. 1, for example. Similar studies were made on acidified solutions of the original complex, and both of the characteristic peaks shown in Fig. 2 were found to diminish rather rapidly, especially at first. Solutions of potassium hexacyanocobaltate(III) either in neutral or in acid solutions were likewise found to exhibit a progressive decrease in absorption in the 310 mμ region with age. The reaction responsible for the observed change in absorption in this case may well be retarded or prevented in the presence of excess cyanide, inasmuch as Adamson, Welker and Volpe[11] have shown that hexacyanocobaltate(III) in the presence of equimolar concentrations of radiocyanide shows no exchange of cyanide even after 190 hours. In the present experiment, however, no free cyanide was present in the solution at the beginning. Although the evidence discussed above indicates that reaction (1) occurs probably very soon after the hydroxopentacyano complex is dissolved, it must be borne in mind that other reactions undoubtedly ensue, and that the system is not a particularly simple one.

Miscellaneous Observations.—In the course of some experiments on the reduction of aqueous potassium hexacyanocobaltate(III) with potassium amalgam (3%), no visible change was observed for the first 10 or 15 minutes after which time the solution became reddish-brown in color and then changed to olive-green upon further reaction with the amalgam. The reddish-brown color could be restored by shaking the olive-green solution with air, but the green color returned when the solution was again allowed to stand over the amalgam. These changes could be carried out repeatedly. Both the red-brown solution and the green one gave tests for free cyanide with ammoniacal copper(II) sulfate. Upon decanting the olive-green solution and adding cold 95% ethanol to it, violet crystals of potassium pentacyanocobaltate(II) were obtained. These observations strongly indicate that, in the treatment of aqueous hexacyanocobaltate(III) with potassium amalgam, the replacement of a cyanide group in the complex precedes its reduction to pentacyanocobaltate(II). It is of interest to note in this connection that Hume and Kolthoff[12] found potassium hexacyanocobaltate(III) in the presence of excess potassium cyanide as supporting electrolyte not to be reducible at the dropping mercury electrode.

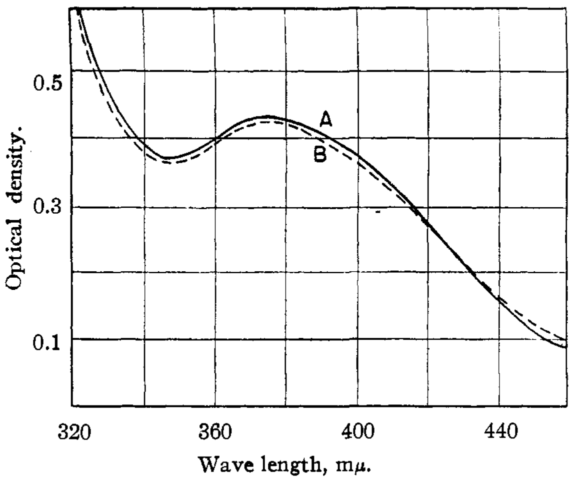

Fig. 3.—Absorption spectra of $K[Co(CN)_4(H_2O)_2]$ in: A, basic solution; B, acidic solution; 7.0×10^{-6} g. cobalt per ml.; cell length, 1.00 cm.; 20°; optical density = log (100/% transmission).

It seems worthwhile to point out also that the reddish-brown solution which appears in the course of the preparation of potassium hexacyanocobaltate(III) from cobalt(II) salts should very probably not be ascribed to the presence of $K_4Co(CN)_6$ as has been assumed,[13] but instead contains at least one cobalt(III) complex having fewer than six cyanide groups coördinated to the cobalt atom.

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(11) A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

(12) D. N. Hume and I. M. Kolthoff, *ibid.*, **71**, 867 (1949).

(13) J. H. Bigelow, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 225.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Studies on Coördination Compounds. I. A Method for Determining Thermodynamic Equilibrium Constants in Mixed Solvents[1,2]

BY LEGRAND G. VAN UITERT AND CHARLES G. HAAS

RECEIVED MAY 2, 1952

In the past "*p*H" titrations in partially non-aqueous solvents have been made in order to determine the stability of coordination compounds. The interpretation of such data has been reconsidered with the object of obtaining thermodynamic stability constants. It is assumed that the activity coefficient of electrolytic solutes in these solvents is determined solely by the solvent composition and the ionic concentration. Experimental substantiation of the assumption is given and the method of calculating thermodynamic stability constants is discussed.

Several years ago Bjerrum introduced[3] the technique of determining the stability of metal ammines by a potentiometric titration in which a glass electrode was used to determine the hydrogen ion concentration during the formation reaction. The ease with which individual equilibrium constants for the *n* successive, reversible, step-reactions of the formation of a complex MA_n[4] could be determined led to the application of the method to other agents.

The stability of complexes with polydentate

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(1) A portion of a thesis presented by L. G. Van Uitert in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

(2) For tables of data from which Figs. 1–4 were plotted order Document 3663 from American Documentation Institute, % Library of Congress, Washington 25, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(3) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

(4) M designates a metal ion; A, a complexing ligand.

amines has been studied,[5-7] and the method has been adapted for use with chelating agents which are weak acids, for example, β-diketones and salicylaldehyde derivatives.[8,9]

In all of the above cases the formation constants so determined have been concentration constants, valid only for a given set of conditions. Since the same conditions were not adopted by all investigators and because of other facts to be presented later, attention has been turned to the determination of activity constants.

In the present case the object is to determine thermodynamic constants for reactions of the type[10]

$$M^{++} + Ch^- \rightleftharpoons MCh^+ \quad K_{f_1} \qquad (1)$$

$$MCh^+ + Ch^- \rightleftharpoons MCh_2 \quad K_{f_2} \qquad (2)$$

The treatment of the experimental data further requires that the acid dissociation constant, K_D, for the chelating agent be known. The problem thus resolves itself into one of determining these three thermodynamic constants.

Preliminary Considerations.—The situation is complicated by the fact that the species MCh_2 is frequently insoluble in water. The application of the Bjerrum method requires that the system be always in a single phase, in order that concentrations at equilibrium be calculatable from the initial composition. Consequently, the use of mixed water–dioxane solvents was introduced by Calvin and Wilson.[8]

The use of such solvents raises the question of the interpretation of the potential obtained in a partially non-aqueous solvent from a cell containing a glass electrode and possessing a liquid junction error. If the glass electrode can be calibrated in terms of hydrogen ion concentration, one can proceed to determine the necessary thermodynamic constants for chelation by the introduction of certain approximations.

The basic assumption which is to be made is that the activity coefficients in water–dioxane mixtures of electrolytes which are strong in water will be determined solely by the solvent composition and the ional concentration. By "strong electrolyte" is meant "strong in water." This qualification is necessary since in solvents of greater than approximately 50% dioxane content all electrolytes are "weak" because of extensive ionic association.

The assumption is essentially one of postulating the application of the principles of the interionic attraction theory, neglecting the difference in ion size (or the Debye–Hückel distance of closest approach). The assumption cannot be completely valid, but the important point is the magnitude of the errors which it introduces. In organic solvents of low dielectric constant, the predictions of the interionic attraction theory will differ more from the observed behavior than in water by reason of the greater effect of the electrostatic interactions and the resulting ion association.

For the present determinations one is concerned not with conformance to the Debye–Hückel behavior but with similarity of behavior exhibited by electrolytes of the same charge type. It is assumed as a first approximation that the variations among the actual coefficients for similar electrolytes are zero. One should recognize that the accuracy necessary in the study of the stability of chelate compounds is less than that which would be desirable for an exact thermodynamic treatment. Much useful information can be obtained from stability constants which have an error of even a few tenths of a log unit.

In the results given below no effort is made to interrelate the thermodynamic constants for different solvents. The standard reference state for the activity coefficients always is the infinitely dilute solution in the solvent in question.

Experimental

The techniques employed are those of Calvin and Wilson.[8] A Beckman model G *p*H meter, a saturated calomel (Beckman No. 1170) electrode and a Beckman type E (No. 8990-75) glass electrode were used. This latter electrode, designed primarily for high *p*H use, functions well in acid solution, though probably with a shortened life. The hydrogen and Ag–AgCl electrodes used were prepared by the usual procedures and checked for reversibility against aqueous hydrogen chloride solutions.

All measurements were made at 30.0 ± 0.1°. The *p*H meter was standardized against aqueous buffers prepared from NBS standard samples. The materials, with the exception of dioxane, were reagent grade used without further treatment. The dioxane was a commercial grade, purified by the method of Weissberger[11] and stored over activated alumina.

Results

In order to avoid confusion in the use of the term "*p*H" this will be reserved for reference to aqueous solutions in which a *p*H scale has been standardized. The indication on the *p*H scale of the Beckman instrument obtained for non-aqueous solutions will be designated by the symbol *B*.

Correlation of Glass and Hydrogen Electrode Measurements.—First it was necessary to verify the response of the glass electrode to hydrogen ions in water–dioxane solutions. Measurements were made on 75 volume % dioxane solutions over the *B* range of 2 to 11. Simultaneous measurements on the same solutions were made with a cell consisting of a hydrogen electrode and a silver–silver chloride electrode. The B values for the glass electrode cell and the corresponding e.m.f. of the hydrogen electrode cell are represented graphically in Fig. 1. The solid line is the Nernst slope for 30°.

These data were obtained by the neutralization of an acetic acid solution containing NaCl at a concentration of 0.03 *F* with a dioxane solution of NaOH, followed by reacidification with HCl to obtain low *B* values. Because of the way in which the experiment was performed, there was a decrease in chloride ion concentration as base was added and then an increase as the acid was added. Corrections for the varying chloride ion concentration have been applied, assuming that the activity of the chloride ion is proportional to the concentration. The correction was negligible for all except the point at each extreme end and here amounted to a maximum of 5 millivolts, or about twice the experimental error.

The results show that the glass-calomel cell measures hydrogen ion activity as defined by a hydrogen electrode; that is, an empirical calibration obtained at a given salt concentration and for a given solvent mixture is valid over a wide range

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[5] H. B. Jonassen, *et al.*, This Journal, **72**, 4968 (1950).

[6] G. A. Carlson, J. D. McReynolds and F. H. Verhoek, *ibid.*, **67**, 1334 (1945).

[7] G. Schwarzenbach, *et al.*, *Helv. Chim. Acta*, **33**, 947 (1950).

[8] M. Calvin and K. W. Wilson, This Journal, **67**, 2003 (1945).

[9] L. E. Maley and D. P. Mellor, *Australian J. Sci. Research*, **2A**, 92 (1949).

[10] Here Ch^- is used to designate the anion of a chelating agent which is a weak acid (HCh).

[11] A. Weissberger and E. S. Proskauer, "Organic Solvents," Oxford University Press, London, 1935, p. 139.

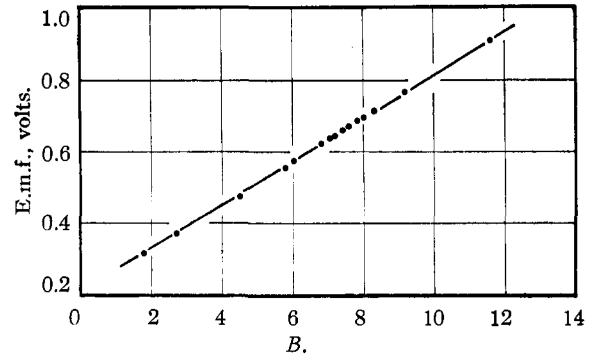

Fig. 1.—The relation between the *p*H-meter readings, *B*, and the e.m.f. of the cell $H_2|H^+, Cl^-|AgCl-Ag$ in 75% dioxane solution. The solid line has slope 0.0601.

of hydrogen ion concentrations. Other more extensive data not presented here in the *B* range of 1.6 to 3.3 confirm constancy of the calibration. These results are in agreement also with the findings of Calvin and Wilson for a 50% dioxane solution.[8]

Calibration of the Glass Electrode in Water-Dioxane Solutions.—An empirical calibration by means of which the *p*H meter reading *B* could be converted to hydrogen ion concentration was made as follows. Readings were made on a series of solutions containing HCl and NaCl in various solvents ranging from pure water to 75 volume % dioxane. From the known stoichiometric hydrogen ion concentration $[H^+]$ a quantity U_H defined as

$$U_H = \text{antilog}\,(-B)/[H^+] \qquad (3)$$

was calculated. U_H then is a conversion factor for obtaining the hydrogen ion concentration from the meter reading *B*

$$-\log\,[H^+] = B + \log U_H \qquad (4)$$

and in general will be a function of solvent composition and ionic concentration.[12]

The values of log U_H obtained for solutions of varying solvent composition and of different salt and acid concentrations are represented by curves A, B and C of Fig. 2. It is seen that U_H is concentration dependent, as one would expect. If this dependence is primarily the result of change in the activity coefficient of hydrogen ion with total ionic concentration, one should be able to correct for the effect by using known activity coefficients and thus obtain a correction factor U_H° which is independent of ionic concentration; *i.e.*, U_H° will correspond to the correction at zero ionic strength in the solvent under consideration.

For this purpose define

$$U_H^\circ \equiv U_H \times 1/\gamma \qquad (5)$$

where γ is the activity coefficient (mean) for the solvent composition and ionic concentration for which U_H was determined. If the assumption of equivalence of ions of the same charge type is valid, then one may use for γ any experimental activity coefficient, provided the coefficient for the appropriate solvent composition and total ionic concentration is selected.

The result of the application of the activity coefficient correction as defined by equation (5) is indicated by curve 0 of Fig. 2. The activity coefficients used were obtained by interpolation from the data of Harned, *et al.*[13] The fact that one obtains the same function U_H° for different salt and acid concentrations furnishes the first substantiation of the basic assumption of equivalence of ions. With the exception of some of the data for curve C the average scattering of points is less than 0.02 log unit.

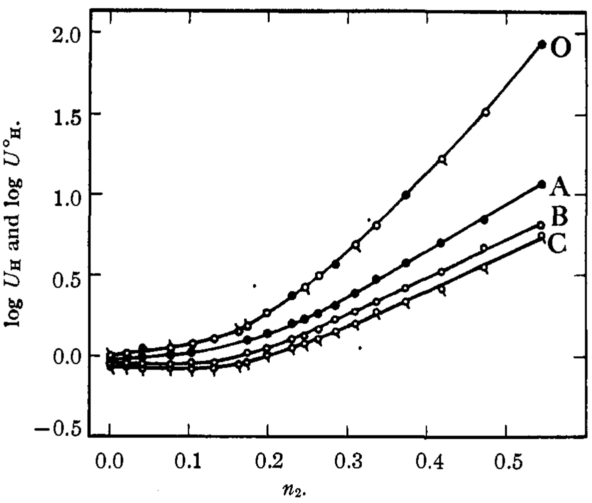

Fig. 2.—Log U_H, for different salt concentrations, and log $U°_H$ as functions of n_2, the mole fraction of dioxane. Total 1–1 electrolyte concentration: O′ and O⸝, 0.0312 *F*; ○, 0.0172 *F*; ●, 0.00586 *F*.

The fact that the e.m.f. of the cell

Glass electrode | HCl in organic solution |
Satd. KCl | Hg_2Cl_2-Hg (I)

varies with solvent composition (as reflected by the value of log U_H°) is attributable to two effects: (1) the partial molar free energy of the hydrogen ion (at infinite dilution) varies with solvent composition, the primary medium effect[14]; and (2) the junction error at the solution—saturated KCl interface varies with solvent composition.

One might expect an effect also from the variation of water activity. Dole[15] has given evidence that the potential of a glass electrode is determined by the transfer of water as well as of protons across the membrane. However, if one calculates the magnitude of this effect by use of the data of Hovorka, *et al.*,[16] he finds that the activity of water at 25° in a 75% dioxane solution differs by only 10% from that of pure water. This corresponds to a potential of about 2.5 millivolts, or about the experimental error. Such an effect would not be observable in the present work. This conclusion is supported by the results discussed below and given in Fig. 3.

Evaluation of the Primary Medium Effect.—It should be possible to separate the two effects by measuring the e.m.f. of the cell

Glass electrode | HCl in organic solution | AgCl-Ag (II)

In this case there is no liquid junction error and the correction term log U_H° becomes equal to log γ_0, the primary medium effect, where γ_0 is the activity coefficient at zero electrolyte concentration in the organic solvent referred to unity in pure water.

Data from such measurements may be treated as follows. Designate the e.m.f. of cell II as *E*. Then

$$E = E^\circ - RT/F \ln C_{H^+} C_{Cl^-} - RT/F \ln \gamma_\pm^2 \qquad (6)$$

For a given solute concentration, at 30°

$$\frac{E^\circ - \text{const.}}{0.0601} = \frac{E}{0.0601} + \log \gamma_\pm^2 \qquad (7)$$

Let X refer to some water–dioxane solvent and 1 refer to water. Then

$$\frac{E_1^\circ - E_X^\circ}{0.0601} = \frac{E_1 - E_X}{0.0601} + \log \frac{\gamma_1^2}{\gamma_X^2} = \log \gamma_0^2 \qquad (8)$$

where log γ_0 is the primary medium effect.

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(12) It should be noted that the hydrogen ion concentration calculated from equation (4) in the case of the calibration experiments is the stoichiometric concentration; the actual free hydrogen ion concentration will be less than this because of ion association. When the U_H determined as above is applied to a solution in dioxane of a weak acid (*e.g.*, acetic acid or a β-diketone) the hydrogen ion concentration calculated will not be the total stoichiometric concentration but will correspond to the concentration which would exist for the same solute in water as a solvent.

(13) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Pub. Corp., New York, N. Y., 1950, p. 548.

(14) Reference 13, p. 516.

(15) M. Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 276–279.

(16) F. Hovorka, R. A. Schaefer and D. Dreisbach, THIS JOURNAL, **58**, 2264 (1936).

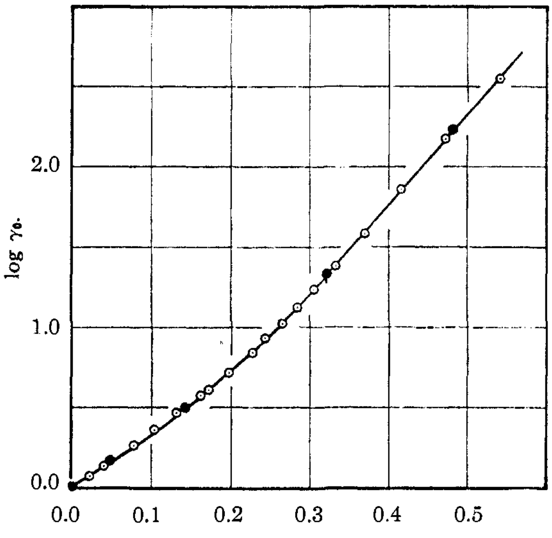

Fig. 3.—The primary medium effect, log γ_0, as a function of mole fraction of dioxane: ●, data of Harned obtained from the cell $H_2|H^+, Cl^-|AgCl\text{-}Ag$; ○, present data calculated from the cell glass electrode$|H^+, Cl^-|AgCl\text{-}Ag$.

The log γ_0 values so calculated for HCl in water–dioxane mixtures are plotted as a function of mole fraction of dioxane in Fig. 3. Values of the same quantity obtained by Harned[17] from thermodynamic cell measurements are also plotted. The agreement again indicates support of the basic assumption, since the activity coefficients used in the calculations were for HCl, whereas they are being applied to a mixed HCl-NaCl solute.

Application to the Dissociation of a Weak Acid.—As an example of the use of the method one may determine the thermodynamic dissociation constant of a weak acid. One can measure B for a series of solutions in various solvents, each solution containing a weak acid HA at concentration C_1, the salt of that acid NaA also at C_1, and inert electrolyte, *e.g.*, NaCl, at concentration C_2. From these measurements one can calculate the thermodynamic acid dissociation constant

$$K_D = \frac{[H^+]\,[A^-]}{[HA]} \times \frac{\gamma_{H^+}\,\gamma_{A^-}}{\gamma_{HA}} \qquad (9)$$

The stoichiometric concentrations are known experimentally and K_D may be calculated by the use of the following approximations: (1) Set γ_{HA} equal to unity. This is an approximation neglecting salt effects on the neutral molecule. (2) For $\gamma_{H^+}\,\gamma_{A^-}$ use $\gamma^2_{\pm}$ obtained for HCl in the same medium and at the same total ionic concentration.[12]

The values of the activity constant so calculated will vary with solvent and in general will decrease as the dielectric constant of the solvent decreases.

Measurements were made for acetic acid by this method. The dissociation constants calculated are represented in Fig. 4, together with values for the same constant determined by Harned and co-workers[18] from measurements made on galvanic cells without liquid junctions. The two measurements of Harned which are used (those to obtain $\gamma\pm$ and those of K_D for comparison) are independent, so that the agreement exhibited by Fig. 4 between the thermodynamic cell data and the *p*H data now determined is a reliable confirmation of the accuracy of the approximations made. It should be noted also that for the solvents of higher dioxane content the correction term for activity coefficients amounts to 1.5 log units; the slight scattering of points is no more than experimental error.

A second similar experiment to determine the dissociation constant of propionic acid was made, this time using $NaClO_4$ instead of NaCl. Again a comparison with data of Harned and co-workers (Fig. 4) illustrates the accuracy of the basic assumption, at least with respect to the ions involved in these two experiments.

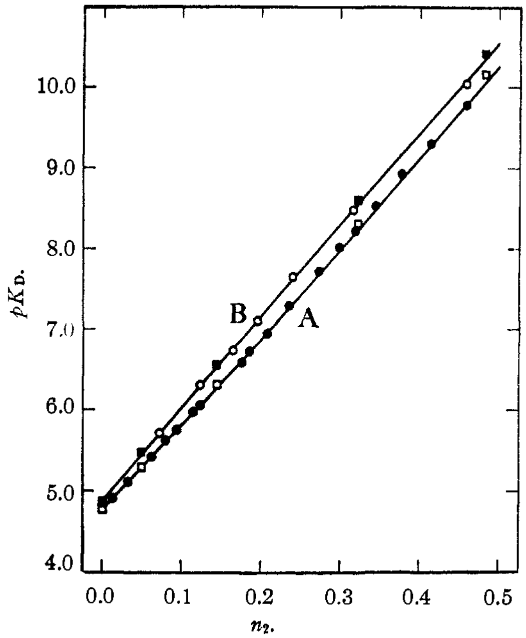

Fig. 4.—pK_D of acetic acid A, and of propionic acid B, as a function of the mole fraction of dioxane: ■ and □, data of Harned obtained using hydrogen and AgCl-Ag electrodes; ○ and ●, values calculated from glass electrode measurements.

Discussion

It now remains to be shown how the determination of K_D, K_{f_1} and K_{f_2} will be made. The acid dissociation constant of a chelating agent HCh will be determined in the same manner as that of acetic acid above. The second chelation constant, for the reaction (2), can be treated as

$$K_{f_2} = \frac{[MCh_2]}{[MCh^+][Ch^-]} \times \frac{\gamma_{MCh_2}}{\gamma_{MCh^+}\,\gamma_{Ch^-}} \qquad (10)$$

Multiplying by K_D one obtains

$$K_{f_2} \times K_D = \frac{[MCh_2]}{[MCh^+[} \times \frac{[H^+]}{[HCh]} \times \frac{\gamma_{MCh_2}}{\gamma_{HCh}} \times \frac{\gamma_{H^+}}{\gamma_{MCh^+}} \qquad (11)$$

The point at which $[MCh_2] = [MCh^+]$ can be determined experimentally; in Bjerrum's notation,[2] here $\bar{n} = 3/2$. Making the assumption that $\gamma_{H^+} = \gamma_{MCh^+}$, one has at $\bar{n} = 3/2$

$$\log K_{f_2} = pK_D + \log\left([H^+]_{\bar{n}=3/2}/[HCh]_{\bar{n}=3/2}\right) \qquad (12)$$

For convenience one may designate the log of the concentration ratio in (12) by C_2. The value of C_2 can be determined experimentally, the hydrogen ion concentration being obtained from a *p*H-meter reading and the concentration of un-ionized chelating agent being calculated from the amount of unbound chelating agent and the acid dissociation constant. From the measured value of pK_D, log K_{f_2} is then calculated.

In the above expression any specific interaction between MCh^+ and inorganic anions other than coulombic attraction has been implicitly assumed absent. That is, it is assumed that the activity coefficients of MCh^+ and H^+ are equal, or that MCh^+ behaves as the cation of a strong electrolyte. This also implies that solvent–ion interactions are the same as for the ion of a strong electrolyte of the same charge type.

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[17] Reference 13, p. 519.

[18] Reference 13, p. 581.

In experimental work to be communicated later, it will be shown that for certain metals and certain chelating agents, C_2 is nearly independent of the inorganic anion present and of the solvent in which the determination is made, whereas for certain other systems large variations are observed for both of the changes. The cases in which such variations are observed will be interpreted as examples of specific interactions of the two types mentioned.

The same type of treatment can be extended to the first chelation step (equation 1) by defining K_{f_1} in a manner analogous to K_{f_2}. As before, multiplying by K_D and setting γ_{HCh} equal unity one obtains

$$\log k_{f_1} = pK_D + \log \frac{[MCh^+]}{[M^{++}]} + \log \frac{[H^+]}{[HCh]} + \log \frac{\gamma^2_{\pm 1-1}}{\gamma_{\pm 2-1}} \qquad (13)$$

where the subscripts on the activity coefficients signify 1–1 and 2–1 electrolytes. The activity coefficient term here causes uncertainty, since it can be approximated only in a rough manner. In the limiting case in which the Debye–Hückel limiting law applies, $\log \gamma_{\pm 2-1} = 2 \log \gamma_{\pm 1-1}$. Hence $\log \gamma^2_{\pm 1-1}/\gamma_{\pm 2-1} = 0$. This result is for ideal behavior and will not be completely valid at finite concentrations.

Again at the point at which $[MCh^+] = [M^{++}]$ (where Bjerrum's $\bar{n} = 1/2$) one obtains

$$\log K_{f_1} = pK_D + \log ([H^+]_{\bar{n}=1/2}/[HCh]_{\bar{n}=1/2}) = pK_D + C_1$$

the log of the concentration ratio being represented by C_1. C_1 has a significance analogous to that of C_2.

Acknowledgment.—The authors gratefully acknowledge financial support furnished for this work by the United States Atomic Energy Commission through Contract AT(30-1)-907.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Studies on Coördination Compounds. II. The Dissociation Constants of β-Diketones in Water–Dioxane Solutions[1]

BY LEGRAND G. VAN UITERT WITH CHARLES G. HAAS, W. CONARD FERNELIUS AND BODIE E. DOUGLAS

RECEIVED MAY 2, 1952

The variation of the pK_D values for several β-diketones with changes in composition of water–dioxane solutions has been found to follow the general pattern for simple acids above a mole fraction of dioxane (n_2) of 0.10. Shifts in the keto–enol equilibrium cause deviations from linearity below n_2 = 0.10 for some compounds studied. A comparison has been made of the effect of various end-groups on the acid strength of the β-diketones and their tendency to coördinate with the sodium ion.

A previous publication[2] reported data to verify the thermodynamic significance of results obtained with a pH meter in water–dioxane solutions. The present paper contains the results of the determination of dissociation constants for a series of β-diketones in water–dioxane solutions. It is of interest to know the values for the dissociation constants of β-diketones with some accuracy in order to make better comparisons of the formation constants of chelate compounds formed between metal ions and the β-diketones. The measurements were made at a mean molarity of strong electrolyte which was the same as that in the previous paper, so the corrections established in that paper were applied to the readings of the pH meter to obtain the final data. The calculation of the negative logarithm of the dissociation constant, pK_D, at each mole fraction of dioxane, n_2, for solutions containing equal concentrations of ionized and un-ionized β-diketones is carried out as

$$pK_D = B + \log U_H + \log 1/\gamma^2$$

where

B = the reading of the pH-meter scale

$\log U_H$ = $-B - \log [H^+]$, this is a constant correction factor for the scale reading in a particular solvent mixture at a mean molality of 0.0172[2]

$\log 1/\gamma^2$ = the negative log of the square of the mean stoichiometric activity coefficient for HCl at the same mean molality (interpolated from the data of Harned and Owen)[3]

Experimental

The tetramethylammonium hydroxide, dibenzoylmethane, benzoylacetone and acetylacetone were obtained from the Eastman Kodak Company; the dimedone (1,1-dimethyl-3,5-cyclohexanedione)[4] and tetra-n-butylammonium iodide were student preparations from this Laboratory. Dr. Robert Levine of the University of Pittsburgh kindly supplied the remainder of the diketones.

The measurements were made using solutions containing equal concentrations of ionized and un-ionized diketone employing a Beckman model G pH meter equipped with a calomel electrode and a "type E" glass electrode in accordance with the procedure previously described.[2]

Solutions used for the measurements contained 0.00172 mole of diketone, 0.72 ml. of 1.20 N tetramethylammonium hydroxide, 40 ml. of dioxane and 10 ml. of distilled water. For the first eleven compounds listed in Table I, these solutions were progressively diluted with a 0.0172 M aqueous solution of tetra-n-butylammonium iodide. For the remaining water-soluble diketones the initial solutions were progressively diluted with an aqueous solution containing the same concentration of ionized and un-ionized β-diketone. By these means a series of water–dioxane solutions of the same mean strong electrolyte molality was obtained. The tetrabutylammonium iodide could not be used as a neutral electrolyte in pure water solutions because the pH meter was found to behave erratically under these conditions.

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[1] A portion of a thesis presented by L. G. Van Uitert in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

[2] L. G. Van Uitert and C. G. Haas, THIS JOURNAL, **75**, 451 (1953).

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 547.

[4] R. L. Shriner and H. R. Todd, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 200.