[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Stability Constants for Some Metal Chelates of Pyridine-2-azo-*p*-dimethylaniline

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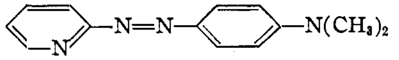
The properties of a metal-dye chelate which might be adaptable as an indicator in measuring other metal-complex stability constants, have been examined. Stability constants for the 1:1 chelate of pyridine-2-azo-*p*-dimethylaniline with metals at 25°, *p*H 6, and ionic strength 0.15 fall in the order Cu > Hg > Ni > Co > Zn > Mn > Ca, Mg. Hydrolytic effects play a dominant role in the equilibria of the copper and of the mercury chelates. Variation in temperature or ionic strength affects the stability constant only slightly.

Introduction

A variety of methods has been developed recently for the evaluation of stability constants of metal complexes.[1] These present difficulties in application to some situations, particularly to metal–protein interactions in which a large fraction of the metal ion is free. An attempt has been made, therefore, to utilize an approach in which the concentration of unbound metal is determined by the effect of the metal on the color of a dye with which it forms a complex of only moderate stability. In essence this method corresponds to the indicator technique of determining acid–base dissociation constants.

Schwarzenbach and his co-workers[2] have already shown that colored metal complexes may be used as end-point indicators in metal titrations, and have determined the stability constants of a number of such complexes. The complex-forming characteristics of a number of metals with other azo dyes have also been described recently.[3] The substance which most nearly fulfilled our requirements, however, is pyridine-2-azo-*p*-dimethylaniline (I).



I

The stability constants of the 1:1 chelate of this molecule and each of several metals have, therefore, been determined.

Experimental

Reagents.—A sample of pure pyridine-2-azo-*p*-dimethylaniline was kindly supplied by Dr. E. V. Brown[4] of Fordham University. All inorganic chemicals were reagent grade. Zinc nitrate solutions were prepared by dilution of a stock solution, obtained in turn by dissolution of a weighed quantity of pure zinc metal in a calculated amount of nitric acid. Mercuric(II) chloride, calcium chloride and $MgSO_4 \cdot 7H_2O$ were used as starting materials for the respective cations. A solution of manganese nitrate was used for manganous(II) ions and its concentration was determined by the bismuthate method.[5] $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ served as sources for the corresponding cations. The purity of these salts was established by electrolytic methods.[6]

Measurements.—Hydrogen-ion concentrations were measured with a Beckman Model G *p*H meter.

Absorption spectra were obtained with a Beckman spectrophotometer, Model DU, using one-centimeter cells. The temperature of the solutions was maintained constant by circulation of water from a constant-temperature bath through the block adjoining the absorption cell chamber. Molecular extinction coefficients, ϵ, were calculated from the equation

$$\log_{10} (I_0/I) = \epsilon cd$$

where I_0 is the intensity of the light emerging from the pure solvent, I the intensity of the light emerging from the solution, c is the molar concentration of absorbing species and d is the thickness of the cell in centimeters.

Calculations.—The first stability constant, K_1, for the formation of the 1:1 metal chelate, MeD^{++}, from the free metal ion, Me^{++}, and azopyridine molecule, D, may be expressed as

$$Me^{++} + D = MeD^{++};\ K_1 = (MeD)/(Me)(D) \quad (1)$$

In all experiments described in this paper, the concentration of metal was high compared to that of the ligand, so that negligible quantities of MeD_2 were present.[7] If c represents in moles/liter the total amount of dye, α the fraction of dye bound to the metal ion, *i.e.*, as MeD, and C the total molar concentration of metal ion, then

$$K_1 = \frac{\alpha c}{(C - \alpha c)[(1 - \alpha)c]} = \frac{\alpha}{(C - \alpha c)(1 - \alpha)} \quad (2)$$

In practice C and c are known from the quantities weighed into the solution; α may be determined spectrophotometrically.

If Beer's law is valid, a reasonable assumption in these dilute solutions, then in any given mixture, the observed optical density, $\log (I_0/I)$, is the sum of the contributions of each species, represented by appropriate subscript, in the equation

$$\log (I_0/I) = \log (I_0/I)_D + \log (I_0/I)_{MeD} + \log (I_0/I)_{Me} \quad (3)$$

If ϵ_1 is the molecular extinction coefficient of D and ϵ_2 the corresponding value, at the same wave length, for MeD, then

$$\log (I_0/I) - \log (I_0/I)_{Me} = \epsilon_1(D)d + \epsilon_2(MeD)d \quad (4)$$

By simple algebraic manipulation equation (4) can be converted into

$$\frac{\log (I_0/I) - \log (I_0/I)_{Me} - \epsilon_1 cd}{(\epsilon_2 - \epsilon_1)cd} = \alpha \quad (5)$$

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[1] (a) For a description of these methods and references to original papers, see A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, Chap. 3; (b) J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **74**, 6091 (1952).

[2] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 678 (1948); G. Schwarzenbach and H. Gysling, *ibid.*, **32**, 1314 (1949).

[3] J. C. Bailar and C. F. Callis, THIS JOURNAL, **74**, 6018 (1952); F. A. Snavely and W. C. Fernelius, *Science*, **117**, 15 (1953).

[4] R. W. Faessinger and E. V. Brown, THIS JOURNAL, **73**, 4606 (1951).

[5] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 709.

[6] Reference 5, p. 420; D. H. Brophy, *Ind. Eng. Chem., Anal. Ed.*, **3**, 363 (1931).

[7] For example, consider the data with zinc, where $(Zn^{++}) \simeq 10^{-3}$, $(D) \simeq 10^{-5}$. Even if $K_2 = (MeD_2)/(MeD)(D)$ were of the order of magnitude of K_1 (about 10^2), then $(MeD_2)/(MeD) = K_2(D) \simeq 10^{-3}$. Clearly the proportion of di-chelate is negligible.

In actual practice, log $(I_0/I)_{Me}$ was negligible in most cases, since the metal ions used were either colorless (*e.g.*, Zn^{++}) or if colored (*e.g.*, Cu^{++}) combined strongly with dye so that the cation concentration was very small and the actual absorption of Me^{++} below the limits of detection. With Co^{++} and Mn^{++}, however, large concentrations of cation were necessary to produce appreciable complex formation. In these cases the fraction of metal in the form MeD was far below 0.1%. The contribution of log $(I_0/I)_{Me}$ to the observed optical density was obtained, therefore, from a separate set of absorption measurements in solutions containing only the free metal ion at the same total concentration as in the chelate-containing solution.

Values for ϵ_1 may be obtained directly from the optical density of a solution containing dye alone at a known concentration. Evaluation of ϵ_2 is not so simple, for in any solution of Me and D not all of the dye is in the form MeD. For a set of solutions containing the same total concentration of dye, the optical density increases (at the MeD absorption maximum) with increase in metal ion concentration as a consequence of the increased amounts of metal chelate. Recourse was had, therefore, to an extrapolation, for which optical density was plotted *versus* the reciprocal of total metal concentration (Fig. 1). As is evident from Fig. 1, the optical density at the intercept on the ordinate axis can be estimated with a precision equal to that of the experimental absorption measurements.

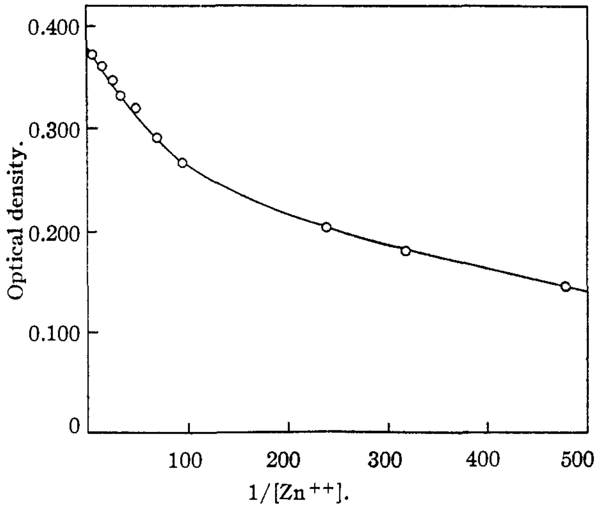
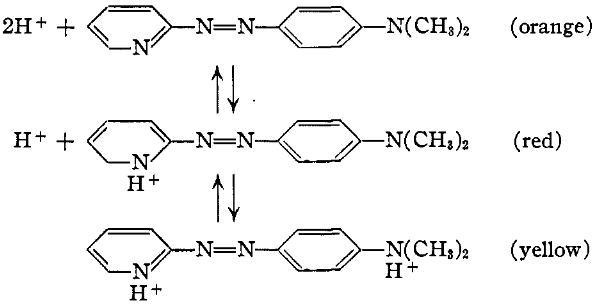


Fig. 1.—Extrapolation of optical densities (at 538 mμ) to obtain ϵ_2 for zinc–dye chelate. Concentration of pyridine-2-azo-*p*-dimethylaniline = 1.11×10^{-5} *M*.

For the purpose of these computations of K_1, optical densities at the wave lengths of the respective maxima of the metal chelates were used.

Results and Discussion

Effect of *p*H on Dye.—It was necessary to establish first the *p*H region in which the chelating molecule (I) is actually uncharged. As would be expected from the structure, the following hydrogen-ion equilibria may be obtained



The spectra of pyridine-2-azo-*p*-dimethylaniline at a series of *p*H's are summarized in Fig. 2. From the observed optical changes one can estimate readily that the doubly-charged dye dissociates with *p*K's of approximately 2 and 4.5. At *p*H's above 6, the dye is almost entirely in form (I).

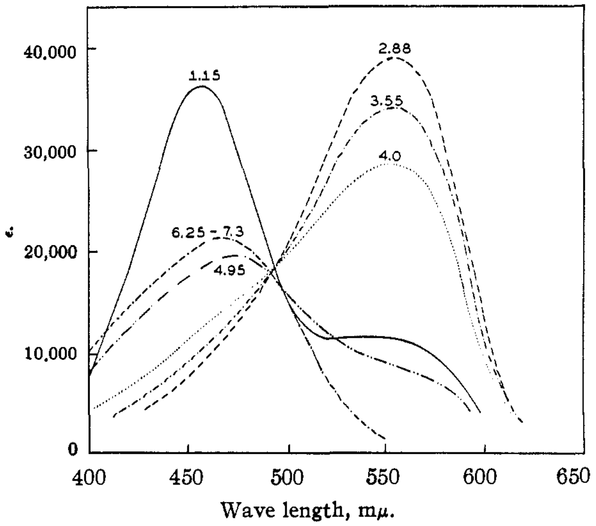


Fig. 2.—Absorption spectra of pyridine-2-azo-*p*-dimethylaniline at various *p*H's.

Spectra of Metal Chelates.—Interaction of the metal ions with dye is evident from the marked changes in the absorption spectra. The molecular extinction coefficients, ϵ_2, used in the computations of K_1 are assembled in Table I. Values of ϵ_2 were obtained by the extrapolation of data at finite concentrations by the procedure described in the experimental section.

TABLE I

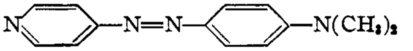
MOLECULAR EXTINCTION COEFFICIENTS OF METAL CHELATES OF PYRIDINE-2-AZO-*p*-DIMETHYLANILINE

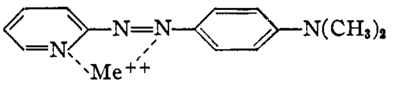
Complexing metal	ϵ_2	Absorption max. (mμ)
None (free dye)	2.12×10^4	470
Cu^{++} (*p*H 6.2)	3.39×10^4	575
Cu^{++} (*p*H 7.0)	3.63×10^4	565
Hg^{++}	3.93×10^4	550
Ni^{++}	3.28×10^4	550
Co^{++}	3.20×10^4	540
Zn^{++}	3.42×10^4	538
Mn^{++}	3.27×10^4	540

No changes in absorption were observed when 0.05 *M* calcium chloride or 0.05 *M* magnesium sulfate were added to the azopyridine compound I.

Evidently the stability constant for chelates of the alkaline earth metals is near zero.

Structure of Metal Complex.—Absorption spectra were also obtained for solutions of pyridine-4-azo-*p*-dimethylaniline (II) in the presence of Zn^{++} and of Cu^{++} ions at *p*H's above 6. In neither case did the metal modify the absorption of the dye. It is apparent, therefore, that the pyridine nitrogen must be ortho to the azo group and hence that the structure of the complex is truly a chelate III. A five-membered chelate ring is drawn in III since it is more likely than the possible four-membered one.


II


III

Stability Constants.—The chelate formation constants, K_1, calculated as described above, are assembled in Table II. All the values listed refer to an aqueous solution containing 0.15 *M* sodium nitrate to maintain a fixed ionic strength.

TABLE II

STABILITY CONSTANTS FOR THE 1:1 CHELATE OF PYRIDINE-2-AZO-*p*-DIMETHYLANILINE AND METAL IONS

$\mu = 0.15;\ t = 25°$

Metal ion	Metal ion concn., moles/l.	*p*H	K_1	Av. dev. of K_1, %
Cu^{++}	1×10^{-3}–5×10^{-6}	6.2	1.3×10^5	±15
Cu^{++}	5×10^{-4}–5×10^{-6}	7.0	2.1×10^5	±17
Hg^{++}	5×10^{-5}–3×10^{-6}	6.0	8.3×10^4	±10
Hg^{++}	5×10^{-5}–6×10^{-6}	5.8	1.72×10^5	± 4
Ni^{++}	5×10^{-3}–4×10^{-5}	6.4–6.6	1.72×10^4	± 6
Co^{++}	1×10^{-2}–4×10^{-4}	6.2–6.5	2.14×10^3	± 3
Zn^{++}	5×10^{-2}–1×10^{-4}	6.1–6.5	2.29×10^2	± 2
Mn^{++}	1–9×10^{-2}	6.0–6.5	5	± 2
Ca^{++}	0.05–0.02	6–7	0	..
Mg^{++}	0.05–0.02	6–7	0	..

Except for Hg^{++}, the order of stability for the metals $Cu^{++} > Ni^{++} > Co^{++} > Zn^{++} > Mn^{++} > Ca^{++}$, Mg^{++} parallels that found in many other systems[8,9] and hence indicates again the involvement of *d* orbitals in chelate bond formation for these metals.[10]

The anomalous position of Hg^{++}, which would be expected to be above Cu^{++} on the basis of experience with other complexes, seems to be a result of hydrolytic equilibria. Likewise the marked differences in the precision of the calculated K_1's depend on hydrolytic effects. These may best be considered in connection with the influence of *p*H described below.

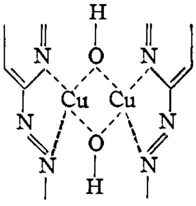
Effect of *p*H on Chelates.—As has been stated above, the protonic equilibria of the dye become significant slightly below *p*H 6. Many of the metal ions examined begin to precipitate from aqueous solutions above *p*H 7. The range of *p*H 6–7 was used, therefore, for all the equilibrium measurements.

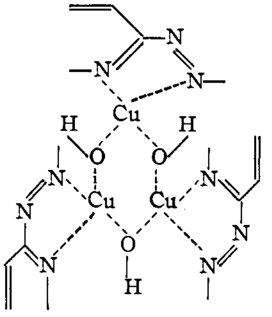
With Zn^{++}, Co^{++} and Ni^{++}, *p*H variations within the range of 6–7 had no effect on the chelate equilibrium. For Hg^{++}, however, K_1 showed a marked decrease when the *p*H was raised from 5.8 to 6.0 (Table II). Since the hydrolysis constant[11–13] for Hg^{++} is relatively large it seems apparent that the equilibrium which actually is being studied in this case is

$$Hg(H_2O)_x(OH^-)_y^{2-y} + D = Hg(H_2O)_{x'}(OH^-)_{y'}(D)^{2-y'} + (x - x')H_2O + (y - y')OH^- \quad (6)$$

i.e., that some hydroxyl ions are displaced by the entering chelating molecule. From equation (6) it is obvious that K_1, as defined by equation (1), would decrease with an increase in *p*H. In contrast, the hydrolysis constants[11,12] for Zn^{++}, Co^{++} and Ni^{++} are relatively small and the formation of the corresponding metal hydroxide complexes would not be appreciable until the *p*H attains values above 7.

The behavior of Cu^{++} in this connection is more puzzling. The hydrolysis constant[11,12] for this cation is sufficiently large so that hydrolytic equilibria are significant even at *p*H 6. For the copper chelate K_1 is indeed *p*H dependent, but it *increases* with a rise in OH^- concentration. Furthermore, in contrast to the other metal chelates (including mercury), the position of the absorption maximum and the value of ϵ_2 for CuD vary with *p*H (Table I). It seems likely, therefore, that an equation analogous to (6) is not an adequate explanation of the behavior of the copper chelate. Since increasing (OH^-) seems to favor formation of the complex, structures such as IV or V may be involved.


IV


V

The relatively poor precision in the K_1 for the copper chelate is a reflection of the sensitivity of the copper chelate spectrum to *p*H. A large average deviation in K_1 is also found at the other end of Table II, *i.e.*, for Mn^{++}. In this case also hydrolytic effects are responsible, although in a different way. The stability constant for the manganous chelate is relatively small. As a result reliable extrapolations of the optical density to $1/(Mn^{++}) = 0$ could not be made until data were accumulated at very high manganous ion concentrations ($\sim$1 *M*). In these concentrated solutions precipitation slowly occurred.

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(8) D. P. Mellor and L. Maley, *Nature*, **159**, 370 (1947); **161**, 436 (1948).

(9) Reference 1a, Chapt. 5.

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(11) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941, p. 75.

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(13) S. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, **6**, 747 (1952).

Effect of Ionic Strength.—K_1 was determined for the zinc chelate in the absence of any salt, as well as in 0.15 M sodium nitrate. The stability constant in the former case is 213 as compared to 229 (Table II). Little sensitivity to ionic strength is to be expected for an isoelectric reaction such as that represented by equation (1).

Effect of Temperature.—The stability constant for the zinc chelate was measured at 35° ($K_1 = 2.08 \times 10^2$) as well as at 25° ($K_1 = 2.29 \times 10^2$). The drop with increasing temperature is small but significant. The enthalpy change in the formation of the complex, calculated from the equation

$$\mathrm{d}\ln K/\mathrm{d}T = \Delta H^\circ/RT^2 \qquad (7)$$

is −1750 cal./mole. Since at 25° the free energy change for the reaction is

$$\Delta F^\circ = -RT\ln K = -3200 \text{ cal./mole} \qquad (8)$$

the entropy change may be computed to be

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} = 4.8 \text{ cal./mole deg.} \qquad (9)$$

The positive sign and the magnitude of ΔS° are consistent with a more detailed picture of reaction (1)

$$\mathrm{Zn(H_2O)_4^{++} + D = Zn(H_2O)_2D + 2H_2O} \qquad (10)$$

in which the chelate is assumed to displace two water molecules and thus produce a net increase of one in the number of molecules present.

Conclusion.—The chelates of pyridine-2-azo-*p*-dimethylaniline thus possess many of the characteristics desirable for measurements of formation constants of metal complexes of moderate stability. (1) The extinction coefficient of the dye is very high so that its concentration can be kept so small as to exert no appreciable influence on the cation equilibrium of interest. (2) The absorption peak is shifted appreciably when the dye forms a complex with the cation. (3) For many cations the stability constant is not dependent on *p*H within a suitably chosen range. (4) The stability constants are relatively insensitive to changes in temperature or ionic strength. (5) The magnitudes of the stability constants are not too high.

Limitations in application may arise, nevertheless, from a number of causes. For complexes of high stability, other colored chelates[2,3] must be used, since the stability constant of the metal–dye combination must be of the order of magnitude of the complex under investigation if maximum precision is to be obtained. Furthermore, the range of *p*H in which this particular azopyridine dye can be conveniently used is fairly restricted, particularly if hydrolytic equilibria of the metal became significant. Finally, the dye chelate, in principle, may complex further with other ligands in solution; the seriousness of this complication must be examined in each individual system.

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EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Manganese(II), -(III), -(IV) Equilibrium in Iodic Acid[1]

BY GLENN R. WATERBURY AND DON S. MARTIN, JR.

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The equilibrium of the disproportionation reaction of manganese(III) has been measured in various aqueous iodate systems by a potentiometric titration method. The dependence of the equilibrium state upon iodate ion, hydrogen ion and iodic acid concentrations and upon the ionic strength and temperature has been studied. The behavior indicates the equilibrium: $\mathrm{Mn^{IV} + Mn^{II} + 4IO_3^- + 3H^+ \rightleftarrows 2Mn^{III}}$, is rapidly established, and equilibrium constants are reported for this reaction. A colorimetric procedure has been developed for the analysis of iodate solutions of manganese(III), -(IV). The possible ionic species contributing to the equilibrium are discussed.

Introduction

In a previous study of the kinetics for the well-known periodate oxidation of manganese(II) to permanganate[2] a mechanism was postulated which assumed a rapid establishment of the equilibrium

$$\mathrm{Mn^{II} + Mn^{IV} \rightleftarrows 2Mn^{III}} \qquad (1)$$

Various investigators have postulated the existence of the equilibrium in systems containing complexing agents such as fluoride, oxalate, phosphate and sulfate ions. Several studies[3–10] of the rapidity of the establishment of the equilibrium have been made, and measurements of the equilibrium constant have been made by Grube and co-workers for systems containing sulfuric acid[11a] and phosphoric acid.[11b] In both these cases the equilibrium constants were calculated from the potential difference between a solution containing equal concentrations of manganese(III) and manganese(II), and a solution containing equal concentrations of manganese(III) and manganese(IV). In the most dilute acid solutions studied they obtained the equilibrium constants for reaction 1:14.3 at 12° in 4.55 M $\mathrm{H_2SO_4}$ and 1.25×10^4 at 17° in 3.33 M $\mathrm{H_3PO_4}$. The equilib-

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(1) Contribution No. 239 from the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa. Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) G. R. Waterbury, A. M. Hayes and D. S. Martin, Jr., THIS JOURNAL, **74**, 15 (1952).

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(11) (a) G. Grube and K. Huberich, *Z. Elektrochem.*, **29**, 8 (1923); (b) G. Grube and M. Staesche, *ibid.*, **31**, 362 (1925).