

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]¹

Complex Ions of Zinc and Pyridine

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The formulas and the formation constants of zinc-pyridine complex ions in aqueous solution were evaluated by measuring the shift in the polarographic half-wave reduction potential of zinc ion as a function of pyridine concentration. The ionic species found to exist in solutions of ionic strength 0.1 at 25° were $Zn(py)^{++}$, $Zn(py)_2^{++}$, $Zn(py)_3^{++}$ and $Zn(py)_4^{++}$.²

The preparation of solid coordination compounds of pyridine and zinc salts have been reported, and an investigation has been made of complex species in solution, but the reported measurements of the individual complexity constants of the various complex species present in solution are incomplete. Dubsy and Rabas,³ Reitzenstein,⁴ Euler,⁵ Lang⁶ and Varet⁷ have prepared a number of solid pyridine complexes of zinc salts in which the ratio of pyridine molecules to zinc ion was 6, 4, 3, 2 and 1 to 1.

Hara⁸ has found by high-frequency titration methods, that complexes with one to six molecules of pyridine to one zinc ion exist in aqueous solution.

Bjerrum⁹ has given information from which the mean complexity constant for the zinc pyridine system can be calculated as 1.6. The mean complexity constant k is defined by the equation $k = \sqrt[k_1 k_2 \dots k_j]} = \sqrt[k_j]} K_j$, where k_j represents the formation constant of the j th complex from the $(j - 1)$ complex, and K_j represents the formation constant of the j th complex from the metal ion and ligand. The mean complexity constant is a measure of the tendency to complex formation in a system. Euler⁵ on the basis of some rather brief e.m.f. measurements, reported the formation constant of the complex ion $Zn(py)_2^{++}$ to be 12.

The present investigation of the complexity constants in aqueous solution was carried out by measuring the shift in the polarographic half-wave reduction potential of zinc ion as a function of pyridine concentration, which was varied from 0.02 to 0.5 mole per liter. The formulas for the ions present and the consecutive complexity constants were evaluated by the method of DeFord and Hume.¹⁰

Experimental

All chemicals were of reagent grade and were used without further purification. A solution of 2.01 M pyridine was prepared and standardized by potentiometric titration with standard hydrochloric acid. A solution of zinc chloride, $4.02 \times 10^{-3} M$, was prepared and standardized by precipitation of $ZnNH_4PO_4$ and subsequent ignition to $Zn_2P_2O_7$. A solution of potassium chloride, 2.0 M , was prepared for

a stock solution of supporting electrolyte, and a freshly prepared 1% gelatin solution was used as a maximum suppressor. All solutions used in polarographic measurements had, in addition to pyridine, a zinc ion concentration of $4 \times 10^{-4} M$ per liter, 0.1 M supporting electrolyte, and 0.01% maximum suppressor, and were prepared by dilution of the above stock solutions. The pyridine concentration was varied from 0.02 to an upper limit of 0.5 mole per liter, which was imposed because of the excessive amounts of gelatin required to suppress the maximum in any higher concentration of pyridine. Oxygen was removed from the solution by passing oxygen-free nitrogen through the solution.

The electrolysis cell employed was an "H-type" cell with an agar salt bridge to a "bulb-type" saturated calomel electrode.¹¹ The dropping mercury electrode had a drop time of 5.0 seconds and a rate of flow of mercury of 1.100 mg. per second at a potential of -1.18 v. vs. the S.C.E. A model XXI Sargent Recording Polarograph was employed in obtaining all polarograms. The potentials were measured at various intervals during the course of a polarogram, by means of a Rubicon potentiometer, and the potentials at various points of the wave thence determined by interpolation. Polarographic half-wave potentials were determined by a plot of $E_{d.e.}$ vs. $\log i/(i_d - i)$, the half wave potential then being the potential at which $\log i/(i_d - i)$ is zero. The half-wave potentials were measured to 0.0001 v. and it was found that these potentials were reproducible within ± 1 mv. In all cases, the reciprocal slope of the log plot was found to be between 0.030 and 0.033 v. and thus reversibility of the electrode reaction was established.¹²

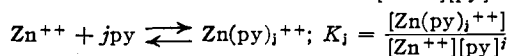
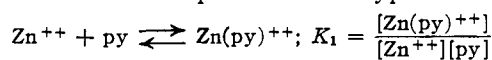
Data and Discussion

In Table I are recorded the data obtained for the shift in half-wave potential of zinc ion with increasing concentration of pyridine in a supporting electrolyte of potassium chloride.

TABLE I
SHIFT IN $E_{1/2}$ WITH INCREASING CONCENTRATION OF PYRIDINE

C(py), mole/l.	$-E_{1/2}$, volts vs. S.C.E.	i_d , microamp.
0.000	1.0012	2.03
.0201	1.0062	1.91
.0402	1.0096	1.91
.0804	1.0147	1.85
.1005	1.0165	1.76
.2010	1.0241	1.70
.3015	1.0308	1.72
.4020	1.0365	1.74
.5025	1.0520	1.73

For a number of equilibria of the type below



which represent formation of a particular complex

(11) I. M. Kolthoff and H. A. Laitinen, "pH and Electrotitrations," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 162.

(12) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Vol. 1, Interscience Publishing Co., New York, N. Y., 1952, p. 194.

(1) This project was carried out in part under support of the Office of Ordnance Research, U. S. Army, Project No. DA-04-200-ORD-65.

(2) The symbol py is used as an abbreviation for the pyridine molecule.

(3) J. Dubsy and A. A. Rabas, *Publ. fac. sci. Univ. Masaryk*, **115**, 1 (1929).

(4) F. Reitzenstein, *Z. anorg. Chem.*, **18**, 253 (1898).

(5) H. Euler, *Ber.*, **37**, 2776 (1904).

(6) W. Lang, *ibid.*, **21**, 1578 (1888).

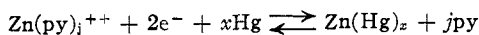
(7) M. R. Varet, *Compt. rend.*, **112**, 622 (1891); **124**, 1156 (1897).

(8) Reinosuke Hara, *J. Pharm. Soc. Japan*, **71**, 1122, 1128 (1951).

(9) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(10) D. D. DeFord and D. N. Hume, *THIS JOURNAL*, **78**, 5321 (1951).

ion from zinc ion and pyridine molecules, a formation constant for each equilibrium may be written. It is well known that the reduction of the metal ion according to the equation



becomes more difficult as the concentration of the complexing agent increases. In more precise terminology, the half-wave potential of zinc ion is shifted to more negative potentials as the concentration of pyridine is increased.

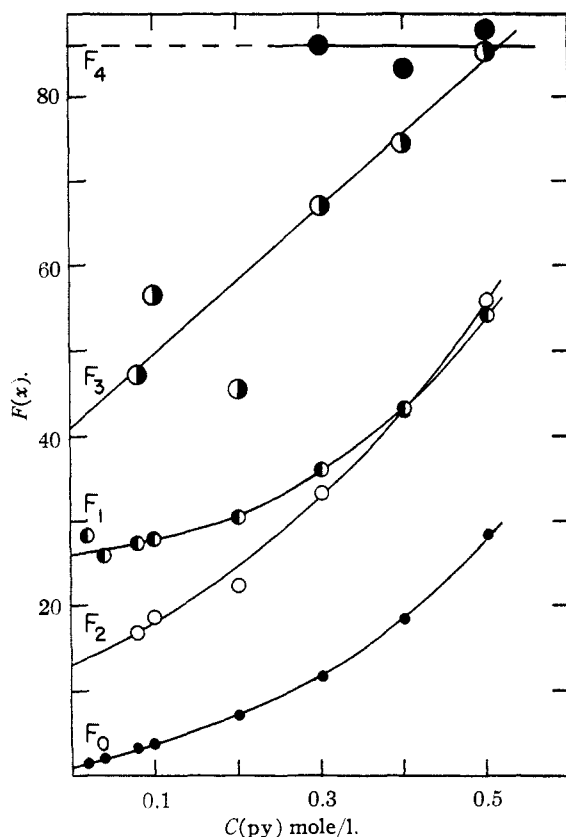


Fig. 1.—Values of $F(x)$ for zinc ion in pyridine solution.

DeFord and Hume⁹ related this shift in half-wave potential to the formation constants of the various complex ions by the following expression

$$\sum_j K_j C_x^j = \text{antilog} \left\{ 0.435 \frac{nF}{RT} [(E^{\circ}_{1/2})_s - (E_{1/2})_c] + \log \frac{I_s}{I_c} \right\} \quad (1)$$

where C_x is the concentration of pyridine in moles per liter, $(E^{\circ}_{1/2})_s$ and $(E_{1/2})_c$ are the half-wave

potentials of the simple and complex ions, respectively; and I_s and I_c are the diffusion current constants of the simple and complex zinc ions, respectively. Activity coefficients have been neglected as it is assumed that they do not change markedly in solutions of constant ionic strength. The result of this assumption is, however, to make the formation constants formal constants and not thermodynamic constants.

The right-hand side of equation 1 is set equal to $F_0(X)$, and DeFord and Hume defined the quantity $F_1(X)$ as equal to $(F_0(X) - K_0)/C_x$ where K_0 is unity and $F_j(X) = (F_{j-1}(X) - K_{j-1})/C_x$.

If $F_1(X)$ is plotted against C_x and extrapolated to $C_x = 0$, the value of $F_1(X)$ at the intercept is equal to K_1 and similarly, if $F_j(X)$ is plotted against C_x and extrapolated to $C_x = 0$, the value of $F_j(X)$ at the intercept is K_j .

Plots of $F(X)$ for potassium chloride supporting electrolyte are shown in Fig. 1. The ionic species identified and the values thus obtained for the formation constants are as follows: Zn(py)^{++} , $K_1 = 26 \pm 2$; Zn(py)_2^{++} , $K_2 = 13 \pm 4$; Zn(py)_3^{++} , $K_3 = 41 \pm 20$; Zn(py)_4^{++} , $K_4 = 86 \pm 40$. While not shown, similar curves were obtained in a preliminary investigation in which sodium perchlorate was used as a supporting electrolyte. It is seen that there is some scattering of points below 0.3 M pyridine in the plot of $F_3(X)$, and these points were disregarded in the plot of $F_4(X)$. The justification for the plot of $F_4(X)$ is the fact that the best plot of $F_3(X)$ is a straight line, and that the slope of this line is about 85. If this is correct, then the plot of $F_4(X)$ should be a straight line with slope of zero, indicating that the complex Zn(py)_4^{++} is the highest specie present in solution under the conditions of this investigation. Because of the uncertainties involved, the values obtained for K_3 and K_4 serve only to indicate their order of magnitude.

The finding that j can have values of 1 to 4 is compatible with the results of Hara, except that no evidence was found to support his claim of complex ions with 5 and 6 molecules of pyridine per zinc ion. The same may also be said with respect to the various solid coordination compounds mentioned earlier.

The value of K_2 of 13 ± 4 determined here is in good agreement with the value of 12 listed by Euler. The mean complexity constant for the zinc pyridine system found here is $\sqrt[4]{86} = 3.1$ as compared with the value 1.6 estimated from information listed by Bjerrum.

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