estimate the proportion of chloroform-*d* molecules which are bonded in an equimolar mixture of chloroform-*d* and diethyl ether at room temperature. The value obtained is 60%. This is somewhat higher than the figure of 45% calculated from vapor pressure data reported in the literature.[11]

The intensities of all the bands of symmetry species A_1 of chloroform and those of chloroform-*d* are related[12] to their frequencies in the following way

$$\sum \left(\frac{\gamma_i}{\nu_i^2}\right)_H = \sum \left(\frac{\gamma_i}{\nu_i^2}\right)_D \qquad (13)$$

Of the three vibrations belonging to species A_1 in chloroform, only ν_1, *i.e.*, the C–H stretching mode, is expected to be largely changed on deuteration. Therefore to a certain approximation, one can write

$$\frac{(\gamma_1)_H}{(\gamma_1)_D} \cong \frac{(\nu_1^2)_H}{(\nu_1^2)_D} \qquad (14)$$

The right-hand ratio in equation 14 is calculated as 1.80 from the frequency values. The ratio $(\gamma_1)_H/(\gamma_1)_D$ calculated from the observed values of $(\nu_1)_H$ and $(\nu_1)_D$ is 2.94. The difference shows that eq. 14 is not valid, *i.e.*, that vibration ν_1 is interacting to a considerable extent with ν_2 and ν_3 of the A_1 species in either chloroform-*d* or chloroform or both.

Acknowledgment.—The authors wish to thank Drs. C. M. Higgins and G. C. Pimentel, University of California, for an advance copy of their paper "Infrared Intensity of the C–D Stretch of Chloroform-*d* in Various Solvents." The only solvent studied both by these authors and by us is acetone. The absolute values of the apparent integrated absorption intensity *B* for acetone in their paper is not comparable with ours because of considerable differences in effective slit widths and temperature (32.5° *vs.* 22°). The ratio corresponding to γ_C/γ_D is calculated from their results to be 8.7, whereas we find 12.5. Part of this difference may be ascribed to temperature. Also the influence of carbon dioxide absorption on their readings may be significant. The authors would like to thank Professor George Scatchard for helpful discussion and suggestions.

CAMBRIDGE, MASS.

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[11] A. A. Noyes and M. S. Sherrill, "A Course of Study in Chemical Principles," 2nd edition, The Macmillan Co., New York, N. Y., 1938, p. 260.

[12] B. L. Crawford, Jr., *J. Chem. Phys.*, **20**, 977 (1952).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Rotatory Dispersion of Some Metal–Amine Complexes

BY T. D. O'BRIEN AND R. C. TOOLE

RECEIVED AUGUST 16, 1954

The rotatory dispersion curves of several diamines were compared and found to have a common intercept corresponding to an optically active absorption band at 1380 Å. Active propylenediamine complexes with zinc, cadmium, silver and platinum show a constant dispersion ratio when the ratio of base to metal ion is less than 2. A different but constant ratio is obtained when the ratio is greater than 2. Other amines show similar behavior. This indicates the dispersive power is independent of the nature of the central metal atom and independent of the nature of the active diamines, but is dependent on the formation function *n*. The dispersion ratio for a complex, optically active because of an active ligand, is quite different from the dispersion ratio of a resolved active metal complex, indicating that the source of optical activity differs in the two.

When an optically active base coördinates with a metal ion, the optical rotation of the resulting complex is sometimes opposite in sign to that of the active base and always different from the rotation due to the base alone. These changes in rotation have been explained by some as a partial induced asymmetry in the complex ion itself, and by others as a change in the contribution of the optically active ligand by the coördination .

It has been shown previously[1] that the optical rotation due to *levo*-propylenediamine[2] in a complex is dependent on the formation function $\bar{n}$. This present work was undertaken to see whether dispersive power, as distinct from the sign and magnitude of rotation, changes with complex formation, and is also dependent on the formation function $\bar{n}$. The quantity $\bar{n}$, first defined by Bjerrum,[3] is the average number of ligands bound per metal ion. The value of $\bar{n}$ may be readily determined by $\bar{n} = (C_c - C_l)/C_m$ where C_m = total concentration of all metal species, C_c = total concentration of ligand species present, and C_l = concentration of free or uncomplexed ligand.

The variation of rotatory power with wave length is most simply expressed by the Drude relation $\alpha = k/\lambda^2 - \lambda_0^2$ where α is the observed rotation at wave length λ, k is a constant, and λ_0 is the wave length corresponding to a characteristic frequency of vibration coupled to an optically active center. In general, however, the total rotation of a molecule is the sum of several partial terms of this type, so

$$[M] = \Sigma\, k_i/(\lambda^2 - \lambda_i^2)$$

In order to exhibit optical activity, the absorption bands at λ_1, λ_2, etc., must be optically active. For most colorless compounds these bands lie in the far ultraviolet, and the rotation in the visible increases gradually with decreasing wave length. While a change in solvent or temperature may often cause a change in the magnitude or even the sign of rotation, the dispersion ratio is usually unaffected. As used here the term dispersion ratio means simply the ratio of the optical rotations of a substance at two different wave lengths or $\alpha\lambda_1/\alpha\lambda_2$.

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[1] T. D. O'Brien and R. C. Toole, THIS JOURNAL, **76**, 6009 (1954).

[2] The following abbreviations are used, en = ethylenediamine, *l* = levo, *d* = dextro, *m* = *meso*, pn = propylenediamine, ptn = 2,4-diamino-*n*-pentane, tapn = 1,2,3-triaminopropane, chxn = 1,2-diaminocyclohexane, cptdin = 1,2-diaminocyclopentane, phenen = phenylethylenediamine, stien = stilbenediamine and buten = isobutylenediamine.

[3] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

When the experimental data can be accurately expressed by a one-term Drude equation it is generally designated "simple dispersion" as opposed to "complex dispersion" when more than one term is required. A test frequently employed to distinguish between the simple and the complex dispersion is a graph of $1/\alpha$ against λ^2. The straight line obtained in the case of substances obeying a one-term Drude equation may be extrapolated to obtain λ_0. In such cases this λ_0 acquires a physical meaning only when the equation expresses the entire experimental curve close to the optically active absorption band.

When a two-term Drude equation best describes the dispersion curve of a compound containing only one asymmetric atom, it is believed to be due to "induced asymmetry." This results from a chromophoric group in the molecule acting as a source of optical activity by the coupling effect with the asymmetric atom.

Experimental

Compounds.—The preparation of the optically active propylenediamine and its acid, zinc, cadmium and silver salts were described in a previous paper.[1] [Pt (l-pn)$_3$]Cl$_4$ was prepared by the method of Werner.[4] The corresponding bromide [Pt(l-pn)$_3$]Br$_4$ was prepared by adding 34% HBr to a concentrated solution of the chloride. The white crystalline bromide which precipitated was filtered, washed with alcohol and ether and recrystallized from dilute HBr. [Pt(l-pn)(NH$_3$)$_2$]Cl$_2$ was prepared by adding aqueous ammonia dropwise to 0.2 g. of [Pt l-pnCl$_2$] suspended in 10 ml. of boiling water until clear. The extremely soluble diamine salt was obtained by evaporating the solution to near dryness.

Rotatory Dispersion Measurements.—A carbon arc was used as a source of white light. A monochromatic beam was obtained by interference filters each of which had two narrow transmission bands well separated in the visible region. One of the bands could be eliminated by an appropriate Wratten colored glass filter. All filters, checked on a Beckman spectrophotometer, showed maximum transmission of less than 40%, and half-width of the bands within 10 mμ. A further check was obtained by the excellent comparison of the rotatory dispersion curve obtained for a standard sucrose solution, with the accurately known values.

Results

Propylenediamine and Acid Salts.—The rotations of three solutions of different concentrations of *levo*-propylenediamine were measured at six selected wave lengths and the results are shown in Fig. 1. An arbitrary value K/α is plotted instead of $1/\alpha$ so all solutions may be represented on the same graph. For all solutions the ratio of the rotations at any two wave lengths is the same ($\alpha_{4705}/\alpha_{5880} = 1.615$). Algebraic analysis of the curve leads to a value of the common intercept of 0.01902, corresponding to an optically active absorption band (λ_0) at 1380 Å. It is apparent that the dispersive power of propylenediamine is not influenced by concentration as the specific rotation is. This might indicate that the active chemical species is the same at all concentrations.

Baldwin[5] interpreted his dispersion curve of propylenediamine in terms of two active absorption bands at 1673 and 1900 Å. Figure 1 shows that a one term Drude equation also may be used to express the rotation throughout the entire range 6700–3000 Å. Hunter[6] has shown that in many cases the existence of a second term may cause only a slight deviation from linearity when such a graphical method is applied. Thus, the choice of an empirical relation to satisfy the experimental data remains somewhat arbitrary. However, the single term equation for propylenediamine provides an excellent correlation with a number of other diamines discussed later.

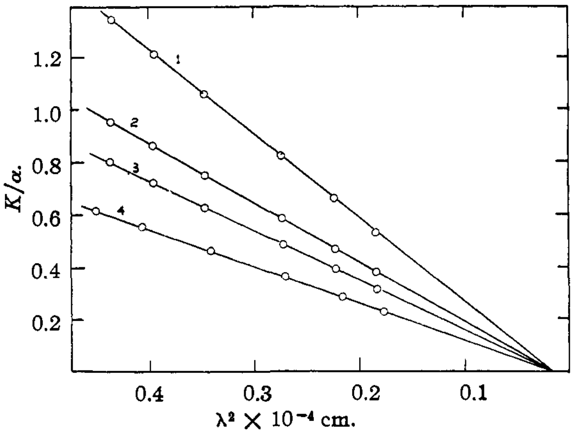

Fig. 1.—Propylenediamine: (1), 6.0 g./100 ml.; (2), 3.0 g./100 ml.; 3, 60.0 g./100 ml.; 4, 80.0 g./100 ml.

For *levo*-propylenediamine (concentration < 20% by wt.) the molecular rotation may be expressed $[M] = -2.68/(\lambda^2 - 0.01902)$. The dispersion ratio, however, is independent of concentration.

Figure 2 shows graphically the results obtained for the acid salts of *levo*-propylenediamine. All give constant dispersion ratios of 1.68 ($\alpha_{4705}/\alpha_{5880}$) and a common intercept of 0.0349 corresponding to a value of λ_0 of 1870 Å.

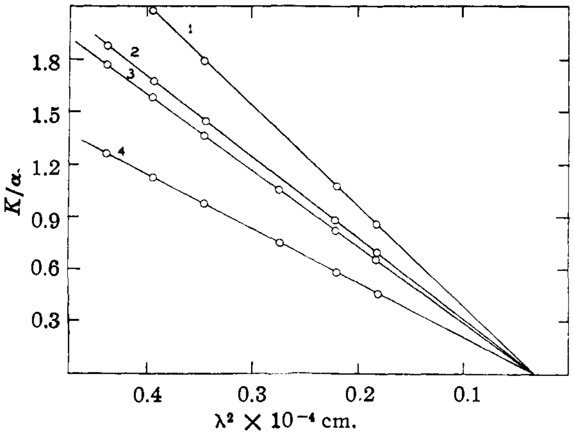

Fig. 2.—1, l-pn·2HCl; 2, l-pn·2HNO$_3$; 3, l-pn·HCl; 4, l-pn·HNO$_3$.

The molecular rotation of the acid salts of propylenediamine can be expressed $[M] = k/(\lambda^2 - 0.0349)$ where k has the values: −2.88 for l-pn·HCl, −3.22 for l-pn·HNO$_3$, + 1.86 for l-pn·2HCl, and +1.65 for l-pn·2HNO$_3$.

In Fig. 3 are plotted all available data on rotatory dispersion for optically active diamines. All have a constant dispersion ratio of 1.615 and a common intercept at 0.019, corresponding to λ_0 of 1380 Å. This common source of optical activity is particularly striking in view of the variation in chemical

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[4] A. Werner, *Z. anorg. Chem.*, **21**, 201 (1899).

[5] W. C. G. Baldwin, *Proc. Roy. Soc.* (*London*), **A167**, 539 (1938).

[6] H. Hunter, *J. Chem. Soc.*, **125**, 1198 (1924).

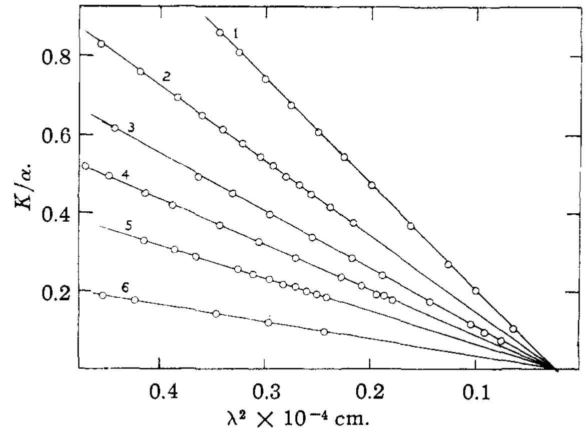

Fig. 3.—1—diaminocyclohexane[7a]; 2—1,2-diaminocyclopentane[7b]; 3—spiroheptanediamine[8]; 4—phenylethylenediamine[9]; 5—1,2,2-trimethyl-1,3-diaminocyclopentane[10]; 6—propylenediamine (this work).

structure of the compounds, which include an open chain molecule, as well as molecules containing four-, five- and six-membered rings. The same dispersive power is shown regardless of whether the amino groups are attached to adjacent carbon atoms or to separated ones.

In all cases where the ultraviolet absorption of amines has been studied, a strong absorption band has been found in the region around 2300 Å. This would indicate that such absorption bands in these diamines are optically inactive. However, when these amines are strongly coördinated to a metal ion they all give a λ_0 value (see Fig. 4) of about 2370 Å. This seems to indicate that the characteristic amine absorption band becomes optically active through complex formation.

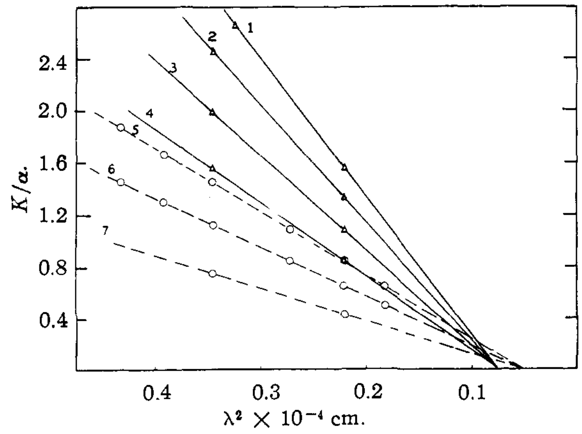

Fig. 4.—1, $[\mathrm{Ag}(l\text{-pn})_{1.56}]^{+}$; 2, $[\mathrm{Pt}(l\text{-pn})(\mathrm{NH_3})_2]^{+2}$; 3, $[\mathrm{Cd}(l\text{-pn})_{1.57}]^{+2}$; 4, $[\mathrm{Zn}(l\text{-pn})_{1.95}]^{+2}$; 5, $[\mathrm{Cd}(l\text{-pn})_{2.18}]^{+2}$; 6, $[\mathrm{Zn}(l\text{-pn})_{2.39}]^{+2}$; 7, $[\mathrm{Pt}(l\text{-pn})_3]^{+4}$.

Propylenediamine–Metal Complexes.—In Fig. 4 are plotted the observed rotations of some *levo*-propylenediamine–metal complexes as a function of wave length. These observed rotations are corrected for the dissociation of the complex as described in a previous paper.[1]

The compounds here fall into two distinct classes: one with a constant dispersion ratio of 1.74 corresponding to λ_0 of 2300 Å., and the other with a constant dispersion ratio of 1.85 and λ_0 of 2740 Å. Thus the dispersion seems independent of the nature of the central metal atom but appears to depend on the coördination geometry of the complex, or on the formation function $\bar{n}$.

When $\bar{n} < 2$ the dispersion ratio is 1.85 and λ_0 is 2740 Å. and when $\bar{n} > 2$ the dispersion ratio is 1.74 and λ_0 is 2300 Å.

In view of the labile nature of the amine complexes of zinc and cadmium it must be assumed that their optical activity does not arise from the fixed asymmetry of the ligands about the central metal atom, but to the presence of optical activity in the ligands themselves. It becomes of interest then to compare these dispersion measurements with those made on the inert or stable complexes where the central metal ion itself may act as a center of asymmetry.

In Fig. 5 are plotted these data. Again the ordinate is an arbitrary K/α in order to get all curves conveniently on the same graph. It is seen that curves 1–4 give constant dispersion ratios of 1.74–1.75 and a λ_0 value of 2370 Å.

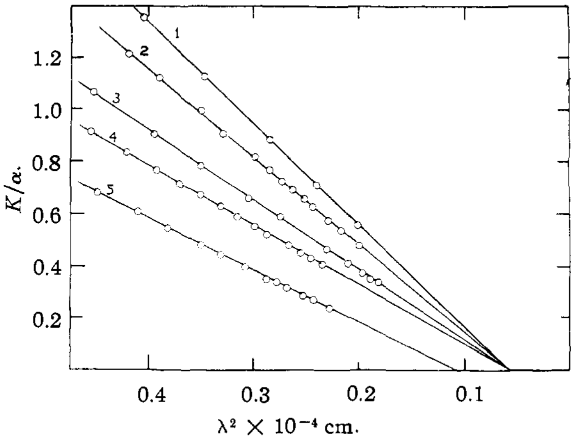

Fig. 5.—1, $[\mathrm{Pt}(d\text{-pn})_2]\mathrm{Cl_2}$(11); 2, $[\mathrm{Rh}(l\text{-chxn})_3]\mathrm{Cl_3}$(6); 3, $[\mathrm{Rh}(d\text{-cptdin})_3]\mathrm{Cl_3}$(7); 4, $\mathrm{Rh}(d\text{-ptn})_3]\mathrm{I_3}$(12); 5, $[\mathrm{Rh}(m\text{-ptn})^3]\mathrm{I_3}$.(12)

It is known that rhodium can act as a center of asymmetry in its 6-coördinate complexes. Indeed, Jaeger[7,12] has shown that the configurational preference of Rh(III) permits a partial resolution of the racemic bases cptdin and ptn. The consistency of the values for this dispersion ratio thus proves particularly striking in that it appears to be independent of the active amine used, and independent of the nature of the metal ion, even when the metal ion itself may act as a center of asymmetry.

The difference in curves 4 and 5 is interesting, and indicates that the optical activity arises from different sources when active and inactive amines

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(7) (a) F. M. Jaeger and L. Bijkerk, *Z. anorg. Chem.*, **233**, 97 (1937); (b) F. M. Jaeger and H. B. Blumendahl, *ibid.*, **175**, 161 (1928).

(8) T. M. Lowry and W. C. G. Baldwin, *Proc. Roy. Soc.* (*London*), **A162**, 204 (1937).

(9) H. Reihlen, E. Weinbrenner and G. v. Hessling, *Ann.*, **494**, 143 (1932).

(10) P. Pfeiffer, *et al.*, *J. prakt. Chem.*, **150**, 261 (1938).

(11) L. Tschugaeff and V. Sokoloff, *Ber.*, **42**, 55 (1909).

(12) C. J. Dippel and F. M. Jaeger, *Rec. trav. chim.*, **50**, 547 (1931).

are used. The inactive meso form has a dispersion ratio of 2.06 and λ_0 of approximately 3200 Å.

In Table I the available data are summarized. Previously published data were used in calculating the dispersion ratio at 4705 and 5880 Å. for some of the compounds.

TABLE I

DISPERSION RATIO OF METAL–DIAMINE COMPLEXES

Complex	$\alpha_{4705}/\alpha_{5880}$	Reference
(1) Complexes containing more than two molecules of an optically active diamine		
[Rh(l-chxn)$_3$]Cl$_3$	1.75	(6)
[Rh(*l*-cptdin)$_3$]Cl$_3$	1.74	(7)
[Rh(*d*-ptn)$_3$]I$_3$	1.75	(12)
[Pt(*l*-pn)$_3$]Br$_4$	1.74	This work
[Pt-(*d*-pn)$_2$]Cl$_2$	1.74	(11)
[Zn(*l*-pn)$_{2-3}$]Cl$_2$	1.74	This work (av. of 3 results)
[Cd(*l*-pn)$_{2-3}$](NO$_3$)$_2$	1.75	This work (av. of 3 results)
(2) Complexes containing less than two molecules of an optically active diamine		
[Pt(*l*-phenen)(en)]I$_2$	1.80	(13)
[Pt(Htapn)Cl$_4$]Cl	1.88	(14)
[Pt(*l*-pn)(NH$_3$)$_2$]Cl$_2$	1.83	This work
[Cd(*l*-pn)$_{1.57}$](NO$_3$)$_2$	1.86	This work
[Zn(*l*-pn)$_{1.95}$]Cl$_2$	1.85	This work
[Ag(*l*-pn)$_{1.56}$](NO$_3$)	1.85	This work
(3) Complexes with inactive diamines		
[Rh(en)$_3$]I$_3$	1.44	(15)
[Ir(en)$_3$]Br$_3$	1.56	(15)
[Pt(en)$_3$]Cl$_4$	1.68	(16)
[Rh(*m*-ptn)$_3$]I$_3$	2.08	(12)
[Pt(*m*-stien)(buten)]Cl$_2$	1.66	(17)

Conclusions

From the results reported here the following conclusions seem justified:

1. The source of optical activity in metal complexes with optically active diamines is different than for the resolved metal complexes with inactive diamines.

2. For the complexes with optically active diamines: A. The dispersive power seems independent of the nature of the metal atom even when the metal atom itself may become a center of asymmetry. B. The dispersive power seems independent of the nature of the optically active diamine. C. The dispersive power appears dependent on the formation function $\bar{n}$. The ratio $\alpha_{4705}/\alpha_{5880}$ is 1.74–1.75 when $\bar{n} > 2$ and 1.85 when $\bar{n} < 2$.

Finally because of the constant dispersion ratio for the optically active amines and for the metal complexes with these amines, it seems fair to presume that the optical activity of the complex arises only from the ligands, and not from any induced asymmetry around the central atom.

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(13) H. Reihlen, G. Seipil and E. Weinbrenner, *Ann.*, **520**, 256 (1935).

(14) F. G. Mann, *J. Chem. Soc.*, 1224 (1927); 890 (1928).

(15) F. M. Jaeger, *Rec. trav. chim.*, **38**, 11 (1919).

(16) J. P. Mathieu, *Bull. soc. chim.*, **6**, 1258 (1939).

(17) W. H. Mills and T. H. Quibell, *J. Chem. Soc.*, 839 (1935).

MINNEAPOLIS, MINNESOTA

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

Complex Ions of Zinc and Hydroxylamine

BY C. J. NYMAN

RECEIVED JUNE 7, 1954

The complex ions formed between zinc ion and hydroxylamine have been investigated by the polarographic method, and two species, $[Zn(NH_2OH)]^{++}$ and $[Zn(NH_2OH)_2]^{++}$, were found to exist in aqueous solution. In solutions of ionic strength 1.0, the formation constants of the ions were found to be 2.5 ± 1 and 10.2 ± 2, respectively. No evidence was found to indicate the presence of any higher species of complex ions up to 1 *M* hydroxylamine concentration.

Introduction

Early reports in the literature by Crismer[2] and by Antonoff[3] indicated the preparation of the solid coördination compound $ZnCl_2 \cdot 2NH_2OH$. Goldschmidt and Syngros[4] reported the preparation of $ZnCO_3 \cdot 2NH_2OH$. These authors also reported the presence of the ion $[Zn(NH_2OH)_2]^{++}$ in aqueous solutions of zinc salts and hydroxylamine, but made no attempt to determine stability constants.

Experimental

The procedures and equipment employed in this investigation were the same as those employed in another study.[5]

All chemicals were of reagent grade and were used without further purification with the exception of hydroxylamine hydrochloride. This salt was purified by recrystallization from 95% ethanol. Stock solutions of 1.920 *M* hydroxylamine hydrochloride, 4.02×10^{-2} *M* zinc chloride, 1.9 *M* potassium hydroxide and 4.0 *M* potassium chloride were prepared. All solutions used in the polarographic runs had a zinc ion concentration of 4×10^{-4} mole per liter, and 1.0 *M* potassium chloride in addition to varying amounts of hydroxylamine. The solutions were prepared from the stock solutions by converting hydroxylamine hydrochloride to free hydroxylamine just prior to use by the addition of potassium hydroxide in such quantity that there was still a small amount of hydroxylammonium ion present. Sufficient potassium chloride was added so that on the final dilution to volume, the ionic strength of the solution was 1.0. The *p*H of the diluted solution was measured with a Beckman Model G *p*H meter, and the free hydroxylamine was calculated by consideration of the equilibrium

$$NH_2OH \cdot H^+ \rightleftharpoons NH_2OH + H^+$$

with equilibrium constant 1.04×10^{-6}.[6] It was assumed

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[1] This project was carried out under support of the Office of Ordnance Research, U. S. Army, Project No. DA-04-200-ORD-65, and the State College of Washington Committee on Research.

(2) L. Crismer, *Bull. soc. chim.*, **3**, 114 (1890).

(3) G. Antonoff, *J. Russ. Phys. Chem. Soc.*, **37**, 476 (1905).

(4) H. Goldschmidt and K. L. Syngros, *Z. anorg. Chem.*, **5**, 129 (1894).

(5) C. J. Nyman, THIS JOURNAL, **75**, 3575 (1953).

(6) H. Hagisawa, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **20**, 251 (1941).