4. The conductivity of ammonium chloride has been measured in ethanol containing small amounts of water, and values for the equivalent conductance at infinite dilution and for the dissociation constant have been calculated.

5. The equivalent conductance at infinite dilution undergoes a much smaller change than in the case of hydrogen chloride, passing through a shallow minimum at 2.5 M H_2O.

6. Values for the Onsager slopes are larger than the theoretical for all the solvent mixtures investigated; correspondingly, association is large in all the solvent mixtures, for ammonium chloride.

Columbus, Ohio Received April 18, 1945

[Contribution from the Chemical Laboratory of The Ohio State University]

Equilibrium Constants for the Formation of Ammine Complexes with Certain Metallic Ions[1]

By Gordon A. Carlson, James P. McReynolds, and Frank H. Verhoek

The study of the complexes formed between metallic cations and ammonia or amines has usually been directed toward the establishment of complex formation, or at most to a determination of the equilibrium constant for the over-all reaction

$$M + NA \rightleftarrows MA_N \qquad (1)$$

Bjerrum,[2] however, has emphasized the importance of investigating the intermediate steps which enter into the over-all reaction

$$\begin{aligned} &M + A \rightleftarrows MA \\ &MA + A \rightleftarrows MA_2 \\ &\cdots\cdots\cdots\cdots \\ &MA_{n-1} + A \rightleftarrows MA_n \\ &\cdots\cdots\cdots\cdots \\ &MA_{N-1} + A \rightleftarrows MA_N \end{aligned} \qquad (2)$$

In these equations M represents the central ion, A the coördinating ligand and MA_N the coordinatively saturated complex ion. The concentration equilibrium constants for equations (2), written

$$k_n = [MA_n]/[MA_{n-1}][A] \qquad (3)$$

Bjerrum calls formation constants, while that for equation (1)

$$K_N = [MA_N]/[M][A]^N \qquad (4)$$

is called the complexity constant. Bjerrum shows how measurements of the hydrogen-ion concentrations of solutions containing amines and salts of complex-forming metals may be used to determine the successive formation constants and the composition of the coördinatively saturated complex ion.

This paper reports the results of a study of the formation of ethylenediamine and propylenediamine complexes of copper, nickel, cadmium and zinc ions and the complexes of silver ion with ethyl and diethyl-amine.

Calculation of the Constants

Since the maximum value of N for the systems investigated here is three, only the equations needed for those systems will be developed. The development is due to Bjerrum,[2] who has also treated the general case.

Let $\bar{n}$ be the ratio of the concentration of complex-bound ligand—for the moment not a basic substance—to the total concentration of central ion.

$$\bar{n} = \frac{C_A - [A]}{C_M} = \frac{[MA] + 2[MA_2] + 3[MA_3]}{[M] + [MA] + [MA_2] + [MA_3]} \qquad (5)$$

Here C_A is the total concentration of ligand, C_M the total concentration of metal ion, and [A] the concentration of free ligand. If equations of the type (3) are solved for $[MA_n]$ and substituted in (5), one obtains

$$\bar{n} = \frac{k_1[A] + 2k_1k_2[A]^2 + 3k_1k_2k_3[A]^3}{1 + k_1[A] + k_1k_2[A]^2 + k_1k_2k_3[A]^3} \qquad (6)$$

Bjerrum calls $\bar{n}$ the formation function of the system, and the curve obtained by plotting $\bar{n}$ against $-\log [A] = p\,[A]$ is called the formation curve.

If the ligand is basic, allowance also must be made for the fact that ligand is removed by reaction with hydrogen ion as well as with metal ion. For a monamine, for example, the total amine concentration is given by

$$C_A = [A] + [AH^+] + \bar{n}C_M \qquad (7)$$

Defining α as the fraction of the amine not complex bound which exists as free amine and $\bar{n}_A$ as the mean number of hydrogen ions bound to not-complex-bound amine, we have

$$\alpha = \frac{[A]}{[A] + [AH^+]} = \frac{k_{AH}}{k_{AH} + [H^+]} \qquad (8)$$

$$\bar{n}_A = \frac{[AH^+]}{[A] + [AH^+]} = \frac{[H^+]}{k_{AH} + [H^+]} \qquad (9)$$

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(1) From a dissertation submitted by Gordon A. Carlson to the Graduate School of The Ohio State University in June, 1944, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The problem was suggested by Professor James P. McReynolds; the major portion of the work was carried out after his death in June, 1943, under the direction of Professor Frank H. Verhoek.

(2) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941. A complete review is given in *C. A.*, **35**, 6527–6534 (1941).

where k_{AH} is the acid dissociation constant of the amine. Eliminating ([A] + [AH$^+$]) from equations (7) and (9), and (8) and (9), we have

$$\bar{n} = \frac{C_A - \frac{[AH^+]}{\bar{n}_A}}{C_M} = \frac{C_A - \frac{C_H - [H^+]}{\bar{n}_A}}{C_M} \qquad (10)$$

and

$$[A] = \frac{\alpha\,[AH^+]}{\bar{n}_A} = \frac{\alpha}{\bar{n}_A}\,(C_H - [H^+]) \qquad (11)$$

where C_H is the total concentration of added strong acid. Thus $\bar{n}$ and [A] can be determined from the values of the measured total concentrations of metal ion, amine, and acid, a knowledge of the dissociation constant of the ammonium ion, and a measurement of the hydrogen ion concentrations.

If the ligand is a diamine, we have

$$C_A = [A] + [AH^+] + [AH_2^{++}] + \bar{n}C_M \qquad (12)$$

$$k_{AH} = [A][H^+]/[AH^+] \qquad (13)$$

$$k_{AH_2} = [AH^+][H^+]/[AH_2^{++}] \qquad (14)$$

$$\alpha = \frac{k_{AH}k_{AH_2}}{k_{AH}k_{AH_2} + k_{AH_2}[H^+] + [H^+]^2} \qquad (15)$$

$\bar{n}_A$ becomes

$$\bar{n}_A = \frac{[AH^+] + 2[AH_2^{++}]}{[A] + [AH^+] + [AH_2^{++}]}$$

$$\bar{n}_A = \frac{k_{AH_2}[H^+] + 2[H^+]^2}{k_{AH}k_{AH_2} + k_{AH_2}[H^+] + [H^+]^2} \qquad (16)$$

and the third terms of equations (10) and (11) have the same form as for the monoacid base.

Every set of experimental values of $\bar{n}$ and [A] will give an equation corresponding to (6) in the unknown k's. Solving these equations for the individual constants gives

$$k_1 = \frac{1}{[A]}\,\frac{\bar{n}}{(1-\bar{n}) + (2-\bar{n})[A]k_2 + (3-\bar{n})[A]^2k_2k_3}$$

$$k_2 = \frac{1}{[A]}\,\frac{(\bar{n}-1) + \frac{\bar{n}}{[A]k_1}}{(2-\bar{n}) + (3-\bar{n})[A]k_3} \qquad (17)$$

$$k_3 = \frac{1}{[A]}\,\frac{(\bar{n}-2) + \frac{\bar{n}-1}{[A]k_2} + \frac{\bar{n}}{[A]^2k_1k_2}}{(3-\bar{n})}$$

These equations can be turned into approximation formulas by observing that, when [A] has such a value that $\bar{n} = n - 1/2$, there will be about equal amounts of MA_{n-1} and MA_n present, so that as a first approximation

$$k_n = \left(\frac{1}{[A]}\right)_{\bar{n}=n-1/2} \qquad (18)$$

Substituting these values into (17), one gets

$$k_1 = \frac{1}{[A]_{\bar{n}=1/2}} \times \frac{1}{1 + 3k_2[A]_{\bar{n}=1/2} + 5k_2k_3[A]^2_{\bar{n}=1/2}}$$

$$k_2 = \frac{1}{[A]_{\bar{n}=3/2}} \times \frac{1 + \frac{3}{k_1[A]_{\bar{n}=3/2}}}{1 + 3k_3[A]_{\bar{n}=3/2}} \qquad (19)$$

$$k_3 = \frac{1}{[A]_{\bar{n}=5/2}} \times \left(1 + \frac{3}{k_2[A]_{\bar{n}=5/2}} + \frac{5}{k_1k_2[A]_{\bar{n}=5/2}}\right)$$

If the constants are not too close together, these equations converge very rapidly.

When $N = 2$ it is easier to make use of the slope of the formation curve at the midpoint where $\bar{n} = 1$. Express the formation constants in terms of the complexity constant and a parameter x, so that

$$k_1 = 2x\sqrt{K_2} \qquad k_2 = \sqrt{K_2}/2x \qquad (20)$$

and substitute in (6)

$$\bar{n} = \frac{2x\sqrt{K_2}[A] + 2K_2[A]^2}{1 + 2x\sqrt{K_2}[A] + K_2[A]^2} \qquad (21)$$

When $\bar{n} = 1$

$$K_2 = 1/[A]^2_{\bar{n}=1} \qquad (22)$$

which gives the complexity constant for the system. Differentiating (21) logarithmically

$$\frac{d\bar{n}}{d\ln[A]} = \frac{2xK_2^{1/2}[A] + 4K_2[A]^2 + 2xK_2^{3/2}[A]^3}{(1 + 2xK_2^{1/2}[A] + K_2[A]^2)^2} \qquad (23)$$

When $\bar{n} = 1$, since $K_2^{1/2}\,[A]_{\bar{n}=1} = 1$, the slope of the formation curve is

$$\left(\frac{d\bar{n}}{d\ln[A]}\right)_{\bar{n}=1} = -0.4343\left(\frac{d\bar{n}}{dp[A]}\right)_{\bar{n}=1} = \frac{1}{1+x} \qquad (24)$$

so that k_1 and k_2 may be calculated from $[A]_{\bar{n}=1}$ and $(d\bar{n}/dp[A])_{\bar{n}=1}$.

The application of the above calculations demands that (C_A − [A]) in equation (5) be large enough so that $\bar{n}$ is accurately defined. This was true in each of the systems investigated here. Further in these systems complex formation occurs at such a pH value that [H$^+$] is small with regard to C_H and (C_H − [H$^+$]) may be set equal to C_H.

In order to avoid difficulties due to changes in activity coefficient, the measurements were made in the presence of 0.5 m or 1.0 m neutral salt.,

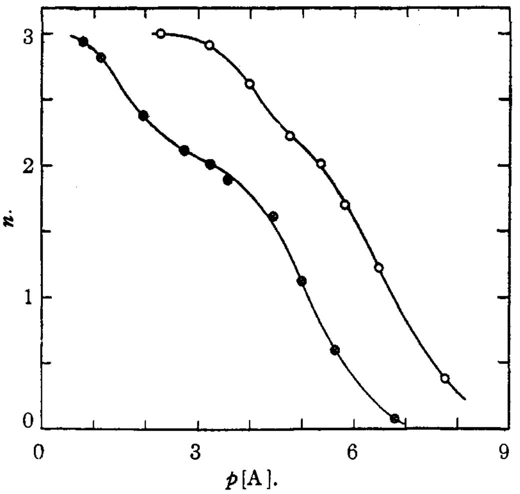

Fig. 1.—Formation curves of ethylenediamine with zinc and nickel ions: ⊗, zinc ion; O, nickel ion.

Experimental

The pH measurements were made with a glass electrode and Coleman Style 200 electrometer. Both the solution being measured and the calomel electrode were maintained at 30° during the measurement, the connection between the two compartments being made through the bore of a stopcock. For the measurements with silver ion, a potassium nitrate salt bridge was interposed between the two solutions. The electrometer was adjusted for asymmetry and temperature differences several times during each measurement by checking against 0.5 *m* potassium acid phthalate solution at 30°. In none of the solutions measured was the *p*H greater than 10.

Each *p*H measurement was made on a separate sample of solution made by adding a known amount of amine solution from a 10 ml. buret to 50 ml. of a standard solution of metal ion, acid, and neutral salt, care being taken to avoid exposure of the amine solution to carbon dioxide of the air. The glass electrode compartment was then rinsed and filled with the solution, and the measurement made after temperature equilibrium had been attained. In some of the experiments more elaborate precautions were taken to avoid exposure to carbon dioxide by adding and mixing amine, and rinsing and filling the cell in an atmosphere of carbon dioxide-free nitrogen; no difference in values was observed.

The ethylenediamine solution used was a 10 molar constant-boiling solution which had been redistilled through a Vigreux column. The propylenediamine (1,2-diaminopropane) solution was 5 molar, prepared from a commercial product after refluxing over barium oxide and distilling from potassium hydroxide. The 7 molar ethylamine solution commercially available was used without further purification. Diethylamine was distilled from potassium hydroxide, and the fraction boiling between 55–56° diluted to make 4 molar solution. The concentrations of all the solutions were determined by titrating against standard acid.

Table I

Acid Dissociation Constants of Amines in Salt Solutions at 30°

Amine	Solution	pK_{AH_2}	pK_{AH}
Ethylamine	0.5 *m* KNO_3		10.61
Diethylamine	0.5 *m* KNO_3		10.96
Propylenediamine	0.5 *m* KNO_3	7.00	9.78
Propylenediamine	0.5 *m* KCl	7.07	9.83
Ethylenediamine	0.5 *m* KNO_3	7.23	9.87
Ethylenediamine	1.0 *m* KCl	7.19	9.92

Table II

Acid Dissociation Constant of Propylenediamine in Salt Solutions at 30°

$Ba(NO_3)_2$, 0.05 *m*; KNO_3, 0.5 *m*; H = HNO_3

C_A m./liter	C_H m./liter	*p*H	pK_{AH_2}	pK_{AH}
0.0663	0.0986	7.02	6.99	
.0663	.0986	7.03	7.01	
.0750	.0984	7.35	6.99	
.0754	.0984	7.36	7.00	
.0850	.0982	7.72	7.00	
.1500	.0968	9.51		9.79
.1486	.0969	9.51		9.78
.1560	.0967	9.56		9.77
.1578	.0967	9.58		9.78
$BaCl_2$, 0.05 *m*; KCl, 0.5 *m*; H = HCl				
0.05698	0.0998	6.60	7.08	
.06260	.0997	6.90	7.06	
.06633	.0996	7.07	7.07	
.07195	.0994	7.28	7.07	
.07380	.0994	7.32	7.08	
.1490	.0979	9.56		9.83
.1508	.0978	9.56		9.82
.1574	.0975	9.62		9.83

Data and Results

Dissociation Constants of the Amines.—The amine dissociation constants were determined in the same manner as the formation constants, substituting non-complex-forming ions (potassium ion for the monamines and barium ion for the diamines) for the complex forming metal ion. In calculating the values for the diamines, advantage was taken of the fact that the constants are different enough to be considered independent in the appropriate *p*H ranges. The results are given in Table I; the data are in agreement with those of previous workers. Table II gives the complete data for propylenediamine, which has not been studied previously.

Metal Ammine Formation.—A portion of the experimental data for the determination of the formation constants of nickel ion with propylenediamine are given in Table III as an example of the type of measurement made. The first column gives the volume of 4.822 *m* propylenediamine solution added to 50.19-ml. portions of a solution 0.500 *m* in potassium chloride, 0.1009 *m* in hydrochloric acid, and 0.04725 *m* in nickel chloride. The second, third, and fourth columns give the resulting concentrations of acid, nickel ion, and amine, volumes being assumed additive. The fifth column gives the measured *p*H, and the last four columns are calculated from equations (15), (16), (10), and (11). Each horizontal row represents a new filling of the glass electrode cell; the procedure was not to add additional portions of

Table III

Hydrogen Ion Concentrations of Nickel Ion Solutions Containing Propylenediamine

V_A, ml.	C_H, m./liter	C_{Ni}, m./liter	C_A, m./liter	*p*H	$\alpha \times 10^6$	$\bar{n}_A$	$\bar{n}$	*p*[A]
0.598	0.0997	0.04669	0.05677	5.00	0.0132	2.000	0.148	8.18
.705	.0995	.04659	.06679	5.25	.0414	1.984	.356	7.68
.790	.0994	.04652	.07472	5.38	.0733	1.978	.527	7.43
.995	.0990	.04633	.0937	5.61	.213	1.965	.937	6.97
1.200	.0987	.04615	.1136	5.89	.746	1.938	1.337	6.42
1.396	.0982	.04597	.1305	6.16	2.46	1.888	1.708	5.89
1.624	.0978	.04577	.1511	6.56	13.7	1.763	2.091	5.12
1.802	.0974	.04561	.1671	6.89	47.5	1.597	2.326	4.54
2.000	.0971	.04544	.1848	7.14	115	1.458	2.601	4.11
2.207	.0967	.04526	.2031	7.40	259	1.312	2.859	3.72
2.295	.0965	.04518	.2108	7.56	427	1.233	2.933	3.48

amine to the same solution. The data in the last two columns are plotted in Fig. 2 and used in calculating the formation constants recorded in Table V.

The initial concentrations of the solutions to which varying amounts of amine were added are given for the other metal ions and amines in Table IV. Measurement of pH and calculation of $\bar{n}$ and [A] yield the results which are recorded as formation curves in Figs. 1 to 5. From these curves the formation constants given in Tables V and VI, are calculated, applying equations (18) and (19) to the curves of Figs. 1 to 3, and equations (20), (22) and (24) to those of Figs. 4 and 5. Table VI also contains data on the ammonia[2,3] and pyridine[4] complexes with silver ion.

TABLE IV

INITIAL CONCENTRATIONS IN THE MEASURED SOLUTIONS

Metal salt, m		Acid, m		Neutral salt, m		Formation curve
Amine: Ethylenediamine						
$NiCl_2$	0.1	HCl	0.2	KCl	1.0	Fig. 1
$ZnCl_2$	.095	HCl	.2	KCl	1.0	Fig. 1
$Cd(NO_3)_2$	.05	HNO_3	.2	KNO_3	0.5	Fig. 3
$CdCl_2$	.09	HCl	.2	KNO_3	0.5	Fig. 3
$Cu(NO_3)_2$	.057	HNO_3	.2	KNO_3	0.5	Fig. 4
$CuCl_2$	.093	HCl	.2	KCl	1.0	Fig. 4
Amine: Propylenediamine						
$NiCl_2$	0.04725	HCl	0.1009	KCl	0.5	Fig. 2
$ZnCl_2$	.047	HCl	.1	KCl	.5	Fig. 2
$Cd(NO_3)_2$	.049	HNO_3	.098	KNO_3	.5	Fig. 2
$Cu(NO_3)_2$	.057	HNO_3	.1	KNO_3	.5	Fig. 4
Amines: Ethylamine and diethylamine						
$AgNO_3$	0.02	HNO_3	0.1	KNO_3	0.5	Fig. 5

TABLE V

FORMATION AND COMPLEXITY CONSTANTS OF METAL ION-DIAMINE SYSTEMS

	Nickel	Zinc	Cadmium	Copper
Ethylenediamine				
log k_1	7.52[a]	5.71	5.47[b]	10.55
log k_2	6.28	4.66	4.55[b]	9.05
log k_3	4.26	1.72	2.07[b]	...
log K_N	18.06	12.09	12.09[b]	19.60
Propylenediamine				
log k_1	7.41	5.89	5.42	10.58
log k_2	6.30	4.98	4.55	9.08
log k_3	4.29	1.70	2.15	...
log K_N	18.00	12.57	12.12	19.66

[a] Using a hydrogen electrode, the corresponding values for these constants obtained by Bjerrum in solutions of the same composition were: 7.66, 6.40, 4.55, 18.61. [b] Nitrate solution.

TABLE VI

FORMATION AND COMPLEXITY CONSTANTS OF SILVER-AMMINES

Amine	log k_1	log k_2	log K_2	pK_{AH}	k_1/k_2	pK_{AH} − log k_1
Ammonia	3.23	3.83	7.06	9.26	0.25	6.03
Ethylamine	3.30	3.84	7.14	10.61	.29	7.31
Diethylamine	2.98	3.22	6.20	10.96	.57	7.98
Pyridine	2.00	2.11	4.11	5.63	.80	3.63

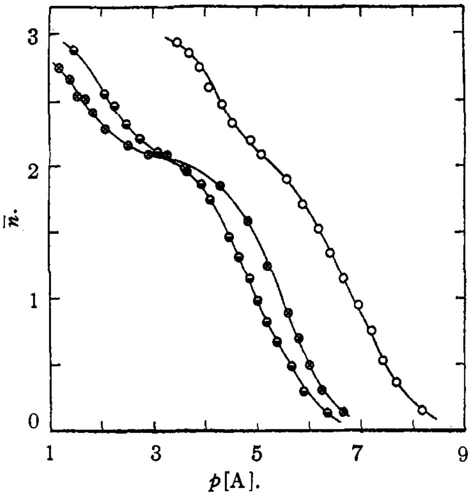

Fig. 2.—Formation curves for propylenediamine with zinc, cadmium and nickel ions: ⊗, zinc ion; ⊖, cadmium ion; ○, nickel ion.

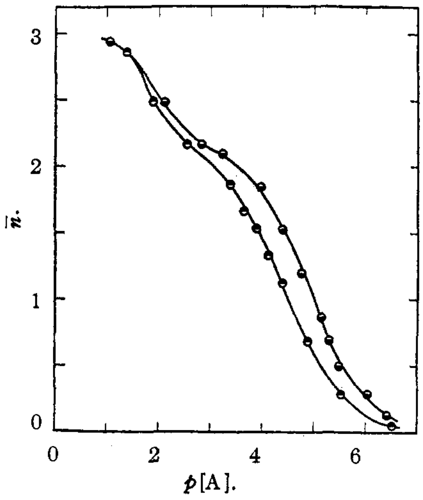

Fig. 3.—Formation curve for ethylenediamine and cadmium ion: ⊖, Cl^- absent; ⊖, Cl^- present.

Discussion

The data for the diamine solutions show that nickel, zinc and cadmium ions form triammine complexes. The case of zinc ion is interesting in that Bjerrum[2] was able to establish only the presence of a tetrammine with zinc ion and ammonia, even in solutions 10 m in ammonia. The triammine formation with ethylenediamine and propylenediamine reflects the greatly increased stability of diamine complexes compared to ammonia complexes. A decreased stability of the triammine zinc ion compared to the triammine cadmium ion is still evident, however, from Fig. 2, where the formation curve for the zinc ion flattens

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(3) Vosburgh and McClure, THIS JOURNAL, **65**, 1060 (1943).

(4) Vosburgh and Cogswell, *ibid.*, **65**, 2412 (1943).

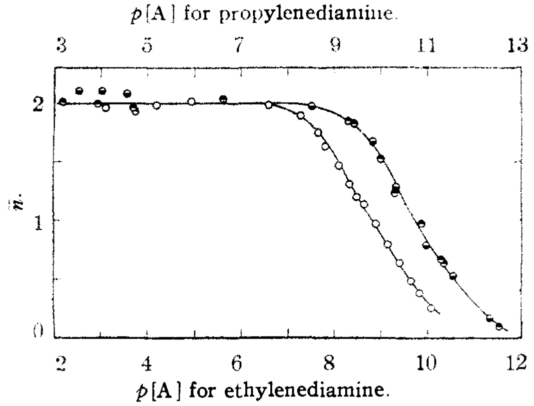

Fig. 4.—Formation curves for the copper ion–ethylenediamine and –propylenediamine systems: ◒, ethylenediamine in nitrate solution; ◓, ethylenediamine in chloride solution; O, propylenediamine (scale at top).

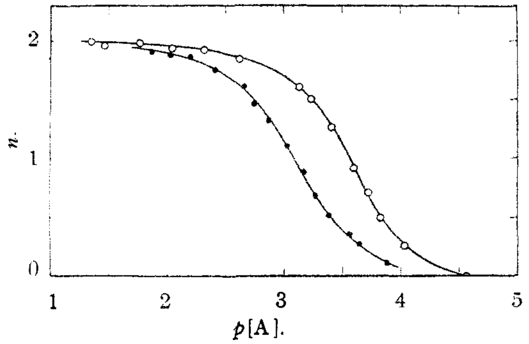

Fig. 5.—Formation curves for amines with silver ion: circles, ethylamine; dots, diethylamine.

out at $\bar{n} = 2$ and rises toward $\bar{n} = 3$ only after a considerable increase in amine concentration. Bjerrum attributed the difference in the behavior of the cadmium and zinc ammonia complexes to the fact that cadmium ion exists in solution as a hexaquo ion (octahedral) while zinc ion is a (tetrahedral) tetraquo ion. Coördination with six nitrogens would then require for zinc ion a change from the tetrahedral structure to an octahedral structure, resulting in a corresponding instability of the hexammine compared to the tetrammine. The data for the diamines are consistent with this point of view.

The formation curve for copper ion and the diamines shows no indication of the formation of a triammine in the concentration range investigated. This is in agreement with the observation of Werner,[5] that salts of the ion Cu en_3^{++} dissociated to Cu en_2^{++} salts when dissolved in water. The extreme stability of the Cu en_2^{++} and Cu pn_2^{++} ions is shown by the fact that complex formation in the solutions investigated began at a concentration of free amine of 10^{-12} *m* and was complete at 10^{-7} *m* when the solution was still acid (*p*H approx. 5.5). In the corresponding ammonia system,[2] complex formation begins at an ammonia concentration of 10^{-5} *m* and reaches the tetrammine stage at 10^{-1} *m*, indicating again the greater stability of the diamine complexes. For all the ions other than copper, the solution was basic when ammine formation approached completion.

Comparison of the values for ammine formation with ethylenediamine and with propylenediamine shows that there is no difference except in the case of zinc. In view of the similarity between the two amines no difference is to be expected. It should be noted in the case of zinc that the measurements with propylenediamine were made in 0.5 *m* potassium chloride while those with ethylenediamine were made in 1.0 *m* potassium chloride. The difference might be due to the formation of a chloro complex with zinc ion, thus lowering the concentration of zinc ion available for ammine formation. Available evidence[6] however, indicates that chloro complex formation is insignificant for zinc ion.

The two curves in Fig. 3 show that chloro complex formation in the case of cadmium ion is appreciable, as is to be expected.[7] That only a single curve is obtained with ethylenediamine and copper ion (Fig. 4), shows the absence of copper chloro complexes at these concentrations, contradicting previous evidence.[8]

For the case of the silver ammines, several workers have attempted to compare the complexity constant for ammine formation with the basic strength of the amine. It has been reported that a parallelism between changes in the two exists[9] and that a parallelism does not exist.[4,10] In making the comparison, however, care should be taken to make a fair one. The comparison should be that between the addition of a hydrogen ion to the amine molecule and the addition of a silver ion to the amine molecule

$$RNH_2 + H^+ \rightleftarrows RNH_3^+ \qquad (25)$$

$$RNH_2 + Ag^+ \rightleftarrows Ag(RNH_2)^+ \qquad (26)$$

It can hardly be expected that a relationship might exist between the equilibrium constant for equation (25) and that for an equation of the type

$$2RNH_2 + Ag^+ \rightleftarrows Ag(RNH_2)_2^+ \qquad (27)$$

because each equation of type (27) involves the step

$$RNH_2 + Ag(RNH_2)^+ \rightleftarrows Ag(RNH_2)_2^+ \qquad (28)$$

For each amine considered, equation (28) involves the comparison of the addition of a cation which is different for each amine, rather than the same cation for each amine as in (25) or (26).

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(5) Werner, *Z. anorg. Chem.*, **21**, 200 (1899).

(6) Doehlemann and Fromherz, *Z. physik. Chem.*, **A171**, 353 (1934).

(7) Riley and Gallafent, *J. Chem. Soc.*, 514 (1932); Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

(8) Riley and Smith, *J. Chem. Soc.*, 1448 (1934). For a criticism of this paper, see Stackelberg and Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

(9) Larsson, *Z. physik. Chem.*, **A169**, 215 (1934).

(10) Britton and Williams, *J. Chem. Soc.*, 796 (1935).

The existing data on monammine formation with silver ion are collected in Table VI. The last column indicates a lack of parallelism between k_1 and pK. Even here, however, the comparison has not been made in the most favorable case; it might be that if a series of primary amines was compared, and a series of secondary amines, etc., a parallelism within each series might still be found.

The sixth column in Table VI gives the ratio of the two successive formation constants for the silver ammines; this measures the relative stability of the mono- and di-ammine. The data would indicate that with increasing size and degree of substitution of the amine the stability of the monammine increases with respect to the diammine. The number of cases is, however, small, and more data may be necessary before drawing a final conclusion.

The junior author (G. A. C.) wishes to thank the Development Fund of The Ohio State University for a Kimberly Fellowship.

Summary

1. The formation curves for the reactions of cadmium, zinc, nickelous and cupric ions with ethylenediamine and propylenediamine, and of silver ion with ethylamine and diethylamine have been determined; from the data the formation constants for the intermediate steps in the formation of the complex ions, and the complexity constants for the over-all reactions, have been calculated.

2. Under the conditions of the experiments, cadmium, zinc and nickel ions form triammine complexes, while copper and silver ions form only diammines.

3. There is no difference in complex formation with ethylenediamine and with propylenediamine for cadmium, nickel and copper ions.

4. Formation of a chloro complex is appreciable with cadmium ion, but is absent with copper ion.

5. The data available indicate that the formation constants for silver monammines do not change in the same order as the dissociation constants of the amines.

6. Values for the dissociation constants of ethylenediamine, propylenediamine, ethyl- and diethyl-amine in salt solutions at 30° have been determined.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Electrolytic Polarization of Solutions of Tributylammonium Picrate in Tricresyl Phosphate at 40°

BY RAYMOND M. FUOSS AND MYRON A. ELLIOTT[1]

Introduction

The literature contains many studies of polarization in aqueous solutions of electrolytes,[2] but little attention has been given to non-aqueous systems. The latter offer a number of advantages: a wide range of viscosity and dielectric constant can be investigated and, most important of all, quite low ionic concentrations can be studied with precision. In this paper, we present the results of a preliminary investigation of solutions of tributylammonium picrate in tricresyl phosphate at 40°.

Experimental

Preparation and purification of salt and solvent are described in an earlier paper.[3] Part of the measurements were made in a cell[4] whose electrodes were concentric platinum cylinders 3 mm. apart, with cell constant 0.004423. Other measurements were made in the guarded cell with gold-plated nickel electrodes[5]; here the electrode spacing was 2.1 mm. with cell constant 0.002720. The volume of electrolyte between the test and high potential electrodes was about 15 cc. The cells were immersed in an oil thermostat held at 40 ± 0.01° for the conductance experiments. Conductances at 60 cycles were measured on the Schering bridge.[5]

The polarization phenomena appeared when the conductance was measured on the d. c. bridge.[6] It was observed that the apparent resistance of a given solution increased with time if the bridge voltage was kept on, until eventually a steady resistance much higher than the a. c. or initial d. c. value was reached. In order to study the changes quantitatively, the pointer type microammeter in the plate circuit of the amplifier was replaced by a recording microammeter. Suitable switches made it possible to short the grid-cathode line[6] of the 6J7 tube through 10^5 ohms and ground the cathode, so that the zero of the meter could be checked without interrupting cell current. Measurements were then made as follows. The variable arm of the bridge, R_4, was set to a value somewhat lower than that calculated to balance for the a. c. resistance. The zero point for bridge balance was set on the center line of the recorder chart, and the recorder started. At time "zero," bridge current was turned on. After the recorder pen showed that the bridge had gone through balance, the zero was checked, R_4 set to another round value in the direction toward which the resistance was heading, and another balance recorded. This procedure was repeated until a steady R_4 was obtained. Then from the recorder chart, the times for balance at the different R_4 values were read off, and the specific conductance of the solution (which is proportional to R_4) was calculated as a function of time. After standing or stirring to restore the initial conductance,

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[2] Jones and Christian, THIS JOURNAL, 57, 272 (1935); Acree, Bennett, Gray and Goldberg, *J. Phys. Chem.*, 42, 871 (1938).

[3] Elliott and Fuoss, THIS JOURNAL, 61, 294 (1939).

[4] Deitz and Fuoss, *ibid.*, 60, 2394 (1938).

[5] Fuoss, *ibid.*, 59, 1703 (1937).

[6] Fuoss, *ibid.*, 60, 451 (1938).