given at higher concentrations (it appears that a negative term in m^2 would have to be added to equation 1 to keep $\Delta\phi$ small at the higher concentrations).

We notice that $\mathring{a}$ for the platinum compound (11.5) is somewhat greater than the 8–10 Å. we might expect, if we consider the crystal radii[5] of $Pt(en)_3^{+4}$ and ClO_4^-, but perhaps it is not unreasonably large. Thus, this compound may represent a strong 4–1 electrolyte.

If equation 1 is used in treating the data for $K_4Mo(CN)_8$ instead of the simple form previously employed,[2] $\mathring{a}$ can be increased only from 4.33 to about 4.85 and the activity coefficients are changed by less than 1%. It appears, then, that the much larger $\mathring{a}$ for the platinum salt is not wholly a result of using a different extrapolation than was used for $K_4Mo(CN)_8$.

It is certain that $Co(en)_3Cl_3$ is not strong and perhaps should not even be considered a 3–1 electrolyte. The osmotic coefficients do not resemble those of other 3–1 chlorides at similar concentrations.[3] It is not surprising that this is not a strong electrolyte for conductance measurements[9] also suggest incomplete dissociation.

In view of the manner of calculating the osmotic coefficients and of the smallness of $\Delta\phi$, the activity coefficients of $Pt(en)_3(ClO_4)_4$ and of $Co(en)_3Cl_3$ (up to $m = 0.25$) were calculated by the method Smith[10] employed for sodium chloride solutions at the boiling points.

$$\ln \gamma\pm = -\frac{2.303 S_m(\mathrm{f})\sqrt{m}}{1 + A'_m\sqrt{m}} - Bm + \int_0^m \frac{\Delta\phi}{m}\,\mathrm{d}m + \Delta\phi \qquad (2)$$

Since $\Delta\phi$ becomes large for $Co(en)_3Cl_3$ at concentrations above 0.25 m, the values of $\ln \gamma\pm$ from $m = 0.25$ to $m = 1.110$ were determined by graphical integration of

$$\ln \gamma\pm = -(1 - \phi) - 2\int_{0.25}^{m} \frac{(1 - \phi)}{\sqrt{m}}\,\mathrm{d}\sqrt{m} - 1.4862 \qquad (3)$$

where 1.4862 is twice the calculated (from 2) value of the integral from $m = 0$ to $m = 0.25$.

In Table II are given the smoothed values of the osmotic and activity coefficients for solutions of $Pt(en)_3(ClO_4)_4$ and $Co(en)_3Cl_3$. Those for $Pt(en)_3(ClO_4)_4$ differ considerably from those for $K_4Fe(CN)_6$[3] and $K_4Mo(CN)_8$,[2] but that may be due to its being a stronger electrolyte. Not only is $\mathring{a}$ large, but isopiestic molalities of KCl and $Pt(en)_3(ClO_4)_4$ are nearly in a ratio of 5:2 (*i.e.*, at equilibrium, $\nu_1 m_1 \cong \nu_2 m_2$). This is not true in the case of $K_4Mo(CN)_8$.

TABLE II

SMOOTHED ACTIVITY AND OSMOTIC COEFFICIENTS FOR $Co(en)_3Cl_3$ AND $Pt(en)_3(ClO_4)_4$ AT 25°

	$Co(en)_3Cl_3$		$Pt(en)_3(ClO_4)$	
m	$\gamma\pm$	ϕ	$\gamma\pm$	ϕ
0.01	0.508	0.7993	0.502	0.8463
.025	.384	.7326	.426	.8301
.050	.295	.6802	.372	.8147
.075	.264	.6513	.339	.7960
.10	.221	.6266	.308	.7770
.15	.188	.5975	.270	.7395
.2229	.156	.5660	.227[a]	.6785
.2500	.148	.5580		
.50	.101	.5003		
.75	.0805	.4774		
1.00	.0691	.4687		
1.110	.0659[a]	.4833		

[a] Saturated solutions.

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[9] R. Lorenz and I. Posen, *Z. anorg. allgem. Chem.*, **96**, 81 (1916)

[10] R. P. Smith, THIS JOURNAL, **61**, 500 (1939).

[CONTRIBUTION OF THE RICHARDSON CHEMISTRY LABORATORIES OF TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. XIV. The Stability of the Complexes Formed between the Nickel(II) Ion and Tetraethylenepentamine

BY HANS B. JONASSEN AND LOWELL WESTERMAN

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The basicity constants of tetraethylenepentamine and the formation constants of the complex ions formed between nickel (II) and tetraethylenepentamine were measured by the method of Schwarzenbach. The formation constant of the complex was also measured by the method of Bjerrum. The complex ions $NiHtetren^{+3}$ and $Nitetren^{+2}$ were found to be present in aqueous solution having log K values of 12.6 ± 0.1 and 17.6 ± 0.1, respectively, at 25°.

Introduction

The stability of complexes of various metal ions of the transition series with members of the polyethyleneamine series has been the subject of considerable investigation. Bjerrum[1] developed a method for determining the stability constants for the formation of metal amine complexes in aqueous solution which is based upon the stepwise formation of the complex ion. Jonassen, *et al.*,[2–4] extending the equations derived by Bjerrum measured the dissociation constants of diethylenetriamine and triethylenetetramine and also the formation constants of the complexes formed between these ligands and the nickel(II) ion.

Schwarzenbach[5] has pointed out that "hydrogen complexes" (complexes formed by adding one or more protons to the polyamine(s) coördinated to the metal ion) also must be considered in addition to the simple MZ_x type, where Z is the polyamine and x equals 1,2,3,. . .n. Schwarzenbach developed a method for determining these complexes from a study of neutralization curves, and studied the complexes of nickel(II) with all of the members of

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

[2] H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm and R. M. Rogan, THIS JOURNAL, **72**, 2430 (1950).

[3] H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, *ibid.*, **72**, 4968 (1950).

[4] H. B. Jonassen and A. W. Meibohm, *J. Phys. Chem.*, **55**, 726 (1951).

[5] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 947 (1950).

the polyethyleneamine series below tetraethylenepentamine and measured their stabilities.[6–8]

Previous work in these laboratories[9] has indicated the presence of complexes of nickel(II) with tetraethylenepentamine other than the simple MZ_x type. The purpose of this investigation was to utilize the methods of Schwarzenbach and Bjerrum to identify and measure the stabilities of the complexes formed in aqueous solution.

Experimental

A. Reagents and Instruments.—Carbide and Carbon Chemicals Corporation technical grade tetraethylenepentamine (abbreviated tetren) was purified as the pentahydrochloride salt by methods developed in these laboratories.[10]

Freshly boiled distilled water was used in the preparation of all solutions. Solutions 0.00200 M in respect to tetren·5HCl and 0.15 M in respect to $KClO_4$ were prepared from the purified tetren·5HCl and Baker C.P. $KClO_4$.

G. Frederick Smith and Company reagent grade $Ni(ClO_4)_2$ and Baker C.P. potassium hydroxide were used in the preparation of the nickel perchlorate and carbonate-free base solutions. The KOH solutions were standardized by titration against primary standard potassium acid phthalate using phenolphthalein as an indicator. Nickel perchlorate solutions were standardized by quantitatively precipitating nickel as nickel dimethylglyoxime. The tetren·5HCl solutions were standardized potentiometrically by titration with standard KOH solution.

All *p*H determinations were made with a Beckman, model G *p*H meter using a glass electrode with a saturated calomel electrode as the reference electrode. The instrument was standardized against Beckman standard buffer solutions *p*H 4, 7 and 10.

B. "Metal-free" Curve.—The "metal-free" curve was obtained as follows. Fifty milliliters of 0.00200 M tetren·5HCl in 0.15 M $KClO_4$ was measured into a four-necked flask immersed in a constant temperature bath regulated to ±0.1°. This was diluted with 50 ml. of distilled water resulting in a solution which was 0.00100 M with respect to tetren·5HCl and 0.075 M with respect to $KClO_4$. The four-necked flask was equipped with a stirrer, glass and calomel electrodes, and nitrogen bubbler. Nitrogen was passed through the solution for at least 15 min. prior to the titration. The titration was carried out by the addition of 0.100 N KOH solution from a 5-ml. buret.

C. "Excess-metal Ion" Curve.—The "excess-metal ion" curve was obtained in the same fashion as the "metal free" curve by titrating a solution 0.00100 M in respect to tetren·5HCl, 0.075 M in $KClO_4$, and 0.0100 M in respect to nickel(II) perchlorate with 0.100 N KOH.

D. "Equivalent" Curve.—The "equivalent" curve was obtained by measuring 25 ml. of 0.00200 M tetren·5HCl in 0.15 M $KClO_4$ and 25 ml. of 0.00200 M $Ni(ClO_4)_2$ solution into 60-ml. glass-stoppered bottles. To each bottle was added various volumes of 0.0500 N KOH solution, after nitrogen had been passed through the solution for at least 15 min. The bottles were suspended in a constant temperature bath for a period of one week, after which *p*H measurements were made on each solution.

All the above measurements were made at 15, 25 and 35 ± 0.1°, numerous curves being taken of each type and the best curves picked for calculations. The neutralization curves obtained at 25° are shown in Fig. 1.

E. Bjerrum's Method.—For determination of the stability constant of the nickel(II)-tetren complex by the method of Bjerrum, a titration of a solution 0.000500 M in tetren·5HCl and 0.000500 M in $Ni(ClO_4)_2$ with 0.0125 N KOH was conducted in the same fashion as described above for the "equivalent" curve. This titration was only conducted at 25 ± 0.1°.

Method of Calculation and Results

A. Basicity Constants for Tetraethylenepentamine by the Method of Schwarzenbach.

—Using the general method derived by Schwarzenbach[5] the basicity constants for tetren may be calculated from the neutralization curve obtained from the titration of tetren·5HCl with KOH ("metal-free" curve). The following equilibria and equations apply to the case of tetren (abbreviated T in the following equations)

$$T + H^+ \rightleftarrows TH^+;\ K^H_{TH} = [TH^+]/[H^+][T]$$

$$TH^+ + H^+ \rightleftarrows TH_2^{2+};\ K^H_{TH_2} = [TH_2^{2+}]/[H^+][TH^+]$$

$$TH_2^{2+} + H^+ \rightleftarrows TH_3^{3+};\ K^H_{TH_3} = [TH_3^{3+}]/[H^+][TH_2^{2+}]$$

$$TH_3^{3+} + H^+ \rightleftarrows TH_4^{4+};\ K^H_{TH_4} = [TH_4^{4+}]/[H^+][TH_3^{3+}]$$

$$TH_4^{4+} + H^+ \rightleftarrows TH_5^{5+};\ K^H_{TH_5} = [TH_5^{5+}]/[H^+][TH_4^{4+}]$$

total concn. of tetren present in soln. =

$$[T]_t = [T] + [TH^+] + [TH_2^{2+}] + [TH_3^{3+}] + [TH_4^{4+}] + [TH_5^{5+}] \quad (1)$$

If a = apparent degree of neutn. of cation acid, TH_5^{5+} = (ml. base added) (N base)/(concn. of tetren)(ml. soln.) and g = number of protons which appear on the average to be bound to tetren· = true degree of neutn., then

$$[H^+]_t = [T]_t(5 - a) = [H^+] - [OH^-] + [TH^+] + 2[TH_2^{2+}] + 3[TH_3^{3+}] + 4[TH_4^{4+}] + 5[TH_5^{5+}]$$

and

$$[T]_t \times g = [TH^+] + 2[TH_2^{2+}] + 3[TH_3^{3+}] + 4[TH_4^{4+}] + 5[TH_5^{5+}] \quad (2)$$

but

$$g = m - a + ([OH^-] - [H^+])/[T]_t \quad (3)$$

where m = maximum number of protons which may be associated with tetren = 5.

Combining equations 1, 2 and 3 the following equation is obtained

$$g + (g - 1)[H^+]K^H_{TH} + (g - 2)[H^+]^2\bar{K}^H_{TH_2} + (g - 3)[H^+]^3\bar{K}^H_{TH_3} + (g - 4)[H^+]^4\bar{K}^H_{TH_4} + (g - 5)[H^+]^5\bar{K}^H_{TH_5} = 0 \quad (4)$$

where $\bar{K}^H_{TH_n}$ = product of the constants from K^H_{TH} to $K^H_{TH_n}$. The first two constants may be considered in the first approximation, allowing equation 4 to be reduced to

$$g + (g - 1)[H^+]K^H_{TH} + (g - 2)[H^+]^2\bar{K}^H_{TH_2} = 0 \quad (5)$$

Dividing equation 5 through by $\bar{K}^H_T$ the following equation results

$$g(1/K^H_{TH}) + (g - 1)[H^+] + (g - 2)[H^+]^2K^H_{TH} = 0 \quad (6)$$

if we let $x = 1/K^H_{TH}$, and $y = K^H_{TH_2}$ then

$$gx + (g - 1)[H^+] + (g - 2)[H^+]^2y = 0 \quad (7)$$

solving for y

$$y = -\{gx/(g - 2)[H^+]^2\} - \{(g - 1)[H^+]/(g - 2)[H^+]^2\}$$

If $A = -g/(g - 2)[H^+]^2$, and $B = -(g - 1)[H^+]/(g - 2)[H^+]^2$ then equation 7 becomes

$$y = Ax + B \quad (8)$$

which is the slope intercept form of the linear equation.

A and B may be found for a number of points on the curve where the first two constants are important (a = 3–5) and equation 8 may be solved graphically or algebraically for x and y thus yielding approximate values for K^H_{TH} and $K^H_{TH_2}$.

Using these approximate values it is now possible

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(6) G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 963 (1950).

(7) G. Schwarzenbach, *ibid.*, **33**, 974 (1950).

(8) G. Schwarzenbach and J. E. Prue, *ibid.*, **33**, 985 (1950).

(9) H. B. Jonassen and L. Westerman, *J. Phys. Chem.*, **61**, 1006 (1957).

(10) R. I. Stearns, a thesis, Tulane University, 1955.

to solve for $K^{H}_{TH_3}$ by using equation 4 omitting the last two terms. $K^{H}_{TH_3}$ is thus obtained in the first approximation from

$$K^{H}_{TH_3} = \frac{-g - (g-1)[H^+]K^{H}_{TH} - (g-2)[H^+]^2\bar{K}^{H}_{TH2}}{(g-3)[H^+]^3\bar{K}^{H}_{TH2}} \quad (9)$$

Having found $K^{H}_{TH_3}$ to the first approximation the fourth term of equation 4 may be used to redetermine K^{H}_{TH} and $K^{H}_{TH_2}$ in the same manner as described above. By recourse to equation 9, a better value for $K^{H}_{TH_3}$ may be obtained. This process of successive approximations is repeated as many times as necessary to get consistent values for K^{H}_{TH}, $K^{H}_{TH_2}$ and $K^{H}_{TH_3}$.

The best values for these first three constants may then be used to calculate $K^{H}_{TH_4}$ and $K^{H}_{TH_5}$ using equation 4, and solving sets of simultaneous equations in two unknowns from the points on the curve between $a = 0$ and 2.

The results of these calculations are given in Table I.

TABLE I

BASICITY CONSTANTS FOR TETREN

	Temp., °C. 15	25	35
log K^{H}_{TH}	9.90	9.78	9.60
log $K^{H}_{TH_2}$	9.51	9.38	9.23
log $K^{H}_{TH_3}$	8.22	8.14	8.09
log $K^{H}_{TH_4}$	4.94	4.83	4.73
log $K^{H}_{TH_5}$	3.17	3.15	3.12

B. Apparent Basicity Constants for Tetren in the Presence of Excess Nickel(II) Ion and Formation Constants for the Nickel–Tetren Complexes by the Method of Schwarzenbach.—The apparent basicity constants of tetren in the presence of excess nickel(II) ion may be calculated from the neutralization curve obtained by titrating tetren·5HCl in the presence of a tenfold excess of the nickel(II) ion, with KOH. Since only a small fraction of the nickel(II) ion is removed from the solution due to complex formation the concentration $[Ni^{2+}]$ may be considered to be practically constant.

This "excess-metal ion" curve then follows equation 10 where $'K^{H}$ refers to the apparent basicity constants. This equation has the same form as equation 4.

$$g + (g-1)[H^+]\,'K^{H}_{TH} + (g-2)[H^+]^2\,'\bar{K}^{H}_{TH_2} + (g-3)[H^+]^3\,'\bar{K}^{H}_{TH_3} + (g-4)[H^+]^4\,'\bar{K}^{H}_{TH_4} + (g-5)[H^+]^5\,'\bar{K}^{H}_{TH_5} = 0 \quad (10)$$

From this equation may be calculated the apparent basicity constants in a manner similar to that described above for the basicity constants. In the case of the nickel(II) ion with tetren, however, a buffer zone ($a = 1$ to $a = 4$) characteristic of a "three-proton in one step" process is indicated as shown in Fig. 1, so that the terms $(g-2)[H^+]^2\,'\bar{K}^{H}_{TH_2}$ and $(g-3)[H^+]^3\,'\bar{K}^{H}_{TH_3}$ are smaller in comparison to the preceding and following terms in equation 10. Equation 10 may then be reduced to

$$g + (g-1)[H^+]\,'K^{H}_{TH} + (g-4)[H^+]^4\,'\bar{K}^{H}_{TH_4} + (g-5)[H^+]^5\,'\bar{K}^{H}_{TH_5} = 0 \quad (11)$$

The constants $'K^{H}_{TH}$, $'\bar{K}^{H}_{TH_4}$ and $'\bar{K}^{H}_{TH_5}$ may be obtained by solving sets of simultaneous equations in three unknowns using successive points on the "excess-metal ion" curve. By appropriate division, $'K^{H}_{TH}$, $'K^{H}_{TH_2}$, $'K^{H}_{TH_3}$, $'K^{H}_{TH_4}$ and $'K^{H}_{TH_5}$ may be obtained. The results of these calculations are given in Table II.

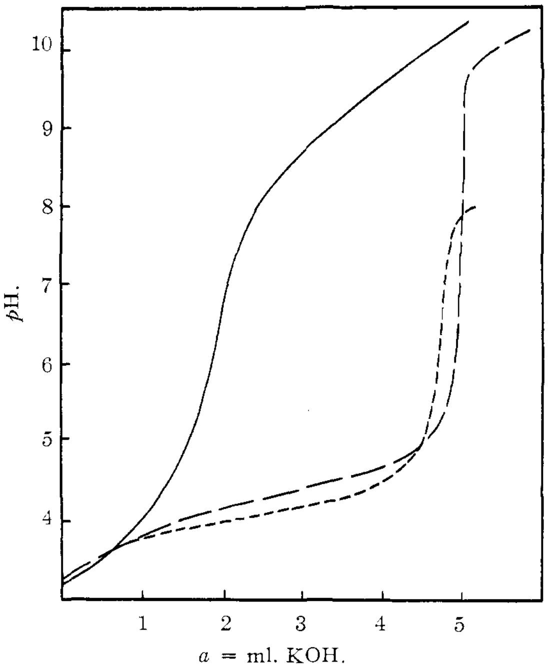

Fig. 1.—Neutralization curves at 25°: ———, "metal free" curve; — — —, "equivalent" curve; - - - - -, "excess metal ion" curve.

TABLE II

APPARENT BASICITY CONSTANTS OF TETREN IN PRESENCE OF TENFOLD EXCESS OF NICKEL(II) ION

	Temp., °C. 15	25	35
log $'K^{H}_{TH}$	5.08	5.11	5.09
log $'K^{H}_{TH_2}\,'K^{H}_{TH_3}\,'K^{H}_{TH_4}$	12.87	12.46	12.13
log $'K^{H}_{TH_5}$	3.18	3.15	3.13

From consideration of the equilibria of the nickel(II) ion with tetren the following equations may be derived to determine the formation constants $K^{Ni}_{NiHT^{+3}}$ and $K^{Ni}_{NiT^{-2}}$

$$K^{Ni}_{NiHT^{3-}} = \frac{1}{[Ni^{2+}]}\left[\frac{\bar{K}^{H}_{TH_2}K^{H}_{TH_3}K^{H}_{TH_4}K^{H}_{TH_5}}{'K^{H}_{TH_2}\,'K^{H}_{TH_3}\,'K^{H}_{TH_4}\,'K^{H}_{TH_5}} - 1\right] \quad (12)$$

$$K^{Ni}_{NiT^{2+}} = \frac{1}{[Ni^{2+}]}\left[\frac{\bar{K}^{H}_{TH_5}}{'\bar{K}^{H}_{TH_5}} - 1\right] \quad (13)$$

These equations are derived on the assumption that no polynuclear complexes are formed. The proof of the absence of polynuclear complexes is obtained if the value of $K^{Ni}_{NiT^{2+}}$ obtained from the "excess-metal ion" curve agrees with that calculated, as follows, from the "equivalent" curve.

The "equivalent" curve is obtained through the neutralization of tetren·5HCl in the presence of an equal molar quantity of the nickel(II) ion. Since the concentration $[Ni^{2+}]$ of the free nickel(II) ion is not constant, equation 10 is not applicable. If the assumption is made that no complexes with more than one T per complex species is formed then the equations may be written

$$[\mathrm{Ni}^2]_t = C = [\mathrm{Ni}^{2+}] + [\mathrm{NiT}^{2-}] + [\mathrm{NiHT}^{3+}] + [\mathrm{NiH_2T}^{4+}] + [\mathrm{NiH_3T}^{5+}] + [\mathrm{NiH_4T}^{6+}] \quad (14)$$

$$[\mathrm{T}]_t = C = [\mathrm{T}] + [\mathrm{HT}^{+}] + [\mathrm{H_2T}^{2+}] + [\mathrm{H_3T}^{3+}] + [\mathrm{H_4T}^{4+}] + [\mathrm{H_5T}^{5+}] + [\mathrm{NiT}^{2+}] + [\mathrm{NiHT}^{3+}] + [\mathrm{NiH_2T}^{4-}] + [\mathrm{NiH_3T}^{5+}] + [\mathrm{NiH_4T}^{6+}] \quad (15)$$

$$[\mathrm{H}]_t = Cg = [\mathrm{HT}^{+}] + 2[\mathrm{H_2T}^{2-}] + 3[\mathrm{H_3T}^{3+}] + 4[\mathrm{H_4T}^{4+}] + 5[\mathrm{H_5T}^{5+}] + [\mathrm{NiHT}^{3+}] + 2[\mathrm{NiH_2T}^{4-}] + 3[\mathrm{NiH_3T}^{5-}] + 4[\mathrm{NiH_4T}^{6+}] \quad (16)$$

Using the values $K^{\mathrm{Ni}}_{\mathrm{NiHT^{3+}}}$ and $K^{\mathrm{Ni}}_{\mathrm{NiT^{2+}}}$ obtained from the "excess metal ion" curve the basicity constants of the complex may be calculated from the equation

$$K^{\mathrm{H}}_{\mathrm{NiHT^{3+}}} = \frac{[\mathrm{NiHT}^{3+}]}{[\mathrm{H}^+][\mathrm{NiT}^{2+}]} = \frac{K^{\mathrm{Ni}}_{\mathrm{NiT^{3+}}}}{K^{\mathrm{Ni}}_{\mathrm{NiT^{2-}}}} K^{\mathrm{H}}_{\mathrm{TH}} \quad (17)$$

By appropriate substitutions equations 14, 15 and 16 may be reduced to

$$C = [\mathrm{Ni}^{2+}] + \gamma[\mathrm{NiHT}^{3+}] \quad (18)$$

$$C = \alpha[\mathrm{TH_4}^{4+}] + \gamma[\mathrm{NiHT}^{3-}] \quad (19)$$

$$gC = \beta[\mathrm{TH}_4^{4+}] + \delta[\mathrm{NiHT}^{3+}] \quad (20)$$

where

$$\gamma = \frac{[\mathrm{H}^+]^{-1}}{K^{\mathrm{N}}_{\mathrm{HiHT^{3+}}}} + 1$$

$$\alpha = \frac{[\mathrm{H}^+]^{-4} + [\mathrm{H}^+]^{-3}\bar{K}^{\mathrm{H}}_{\mathrm{TH}} + [\mathrm{H}^-]^{-2}\bar{K}^{\mathrm{H}}_{\mathrm{TH_2}} + [\mathrm{H}^+]^{-1}\bar{K}^{\mathrm{H}}_{\mathrm{TH_3}} + \bar{K}^{\mathrm{H}}_{\mathrm{TH_4}}}{\bar{K}^{\mathrm{H}}_{\mathrm{TH_4}}}$$

$$\beta = \frac{[\mathrm{H}^+]^{-3}\bar{K}^{\mathrm{H}}_{\mathrm{TH}} + 2[\mathrm{H}^+]^{-2}\bar{K}^{\mathrm{H}}_{\mathrm{TH_2}} + 3[\mathrm{H}^+]^{-1}\bar{K}^{\mathrm{H}}_{\mathrm{TH_3}} + 4\bar{K}^{\mathrm{H}}_{\mathrm{TH_4}}}{\bar{K}^{\mathrm{H}}_{\mathrm{TH_4}}}$$

$$\delta = \frac{K^{\mathrm{H}}_{\mathrm{NiHT^{3+}}}\,[\mathrm{H}^+]}{K^{\mathrm{H}}_{\mathrm{NiHT^{3+}}}\,[\mathrm{H}^+]} = 1$$

For the reaction

$$\mathrm{Ni}^2 + \mathrm{TH}_4^{4-} \rightleftarrows \mathrm{NiHT}^{3+} + 3\mathrm{H}^+;\quad K_\mathrm{I} = \frac{[\mathrm{NiHT}^{3+}][\mathrm{H}^-]^3}{[\mathrm{Ni}^{2+}][\mathrm{TH}_4^{4+}]} \quad (\mathrm{I})$$

The concentrations $[\mathrm{NiHT}^{3+}]$, $[\mathrm{H}^+]$, $[\mathrm{Ni}^{2+}]$ and $[\mathrm{TH}_4^{4+}]$ thus can be obtained easily and K_I may be calculated.

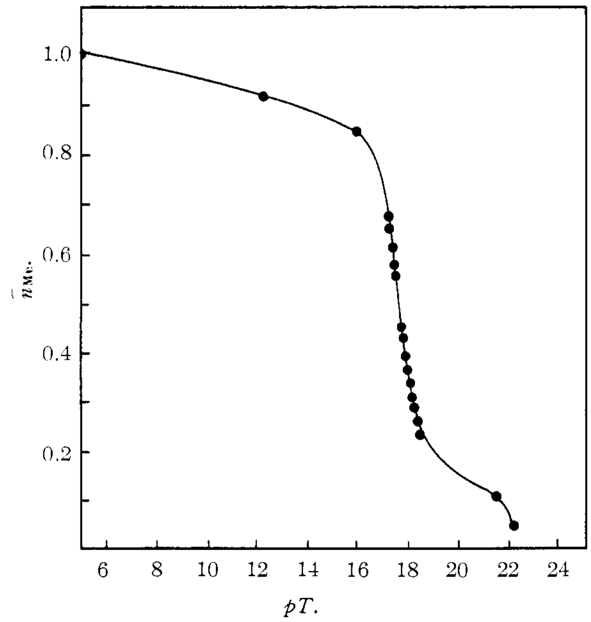

Fig. 2.—Formation curve for the complex species formed between $\mathrm{Ni(ClO_4)_2}$ and tetren at 25°.

Having found K_I the formation constants of any of the metal complexes are easily obtained, thus for $K^{\mathrm{Ni}}_{\mathrm{NiT^{2-}}}$ and $K^{\mathrm{Ni}}_{\mathrm{NiHT^{3+}}}$ the following equations are used to calculate the constants.

$$K^{\mathrm{Ni}}_{\mathrm{NiT^{2+}}} = \frac{K_\mathrm{I}\bar{K}^{\mathrm{H}}_{\mathrm{TH_4}}}{K^{\mathrm{H}}_{\mathrm{NiHT}}} \quad (21)$$

$$K^{\mathrm{Ni}}_{\mathrm{NiHT^{3+}}} = \frac{K^{\mathrm{H}}_{\mathrm{TH_5^{5+}}}}{K_\mathrm{I}} \quad (22)$$

The results of the calculations for these constants are given in Table III.

TABLE III

FORMATION CONSTANTS FOR NICKEL(II)–TETREN COMPLEXES

	Temp., °C. 15	25	35
	"Excess-metal Ion" curve		
log $K^{\mathrm{Ni}}_{\mathrm{NiT^{2+}}}$	18.00	17.78	17.74
	"Equivalent" curve		
log $K^{\mathrm{Ni}}_{\mathrm{NiHT^{3+}}}$	13.04	12.66	12.20
log $K^{\mathrm{Ni}}_{\mathrm{NiT^{2-}}}$	17.63	17.51	17.39

C. Formation Constants by the Method of Bjerrum.—The calculation of the formation constants for metal ions with amines has been described by Bjerrum[1] and the extension of his equations has been given by Jonassen, *et al.*,[2,3] for the formation constants of metal ions with polyamines. The acid constants used in the calculations were those measured by Jonassen, Frey and Schaafsma.[11] The formation curve obtained is shown in Fig. 2, and the results of the calculations are given in Table IV, where

C_{Me} = total concn. of metal ion
C_{HCl} = total concn. of HCl
C_T = total tetren concn. in the soln.
C_A = concn. of hydrogen ions bound to uncomplexed tetren
$\bar{n}_\mathrm{T}$ = av. no. of hydrogen ions bound to tetren = $C'_\mathrm{A}/C'_\mathrm{T}$
C'_T = total concn. of tetren not bound to the metal ion

$$\bar{n}_{\mathrm{Me}} = \frac{(C_\mathrm{T} - C_\mathrm{A})/\bar{n}_\mathrm{T}}{C_{\mathrm{Me}}}$$

$$\log K = pT + \log \bar{n}_{\mathrm{Me}}/(1 - \bar{n}_{\mathrm{Me}})$$

Discussion

The basicity constants of tetren given in Table I are slightly higher than those reported by Jonassen, Frey and Schaafsma.[11] This is as would be expected due to the higher ionic strength at which they were determined.

Comparison of the apparent basicity constant $'K^{\mathrm{H}}_{\mathrm{TH_5}}$ with the basicity constant $K^{\mathrm{H}}_{\mathrm{TH_5}}$ shows equality of the two constants. This indicates that no complex formation takes place in the region $a = 0$ to $a = 1$, which is in agreement with conclusions drawn previously.[9] Only the product of the apparent basicity constants, $'K^{\mathrm{H}}_{\mathrm{TH_2}}$ $'K^{\mathrm{H}}_{\mathrm{TH_3}}$ $'K^{\mathrm{H}}_{\mathrm{TH_4}}$ could be calculated in the buffered region of the "Excess-metal ion" curve, $a = 1$ to $a = 4$, indicating a "three-proton in one step" neutralization and complex formation process is taking place. This

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[11] H. B. Jonassen, F. W. Frey and A. Schaafsma, *J. Phys. Chem.*, **61**, 504 (1957).

TABLE IV

FORMATION CONSTANT CALCULATED BY METHOD OF BJERRUM FOR THE EQUILIBRIUM BETWEEN NICKEL(II) PERCHLORATE AND TETREN AT 25°

pH	$C_{Me} \times 10^4$	$C_{HCl} \times 10^3$	C_T	C_A	$\bar{n}_T$	pT	$C_T - C'_T$	$\bar{n}_{Me}$	log K
4.26	4.505	1.014	4.505	0.9590	3.547	17.91	1.801	0.40	17.73
4.29	4.484	0.9524	4.484	.9011	3.527	17.83	1.929	.43	17.70
4.33	4.464	.8929	4.464	.8461	3.502	17.71	2.048	.46	17.69
4.39	4.405	.7154	4.405	.6747	3.464	17.59	2.457	.56	17.69
4.44	4.386	.6579	4.386	.6216	3.433	17.45	2.570	.59	17.60
								Av. log K	17.68

may be illustrated by the equation

$$\text{Ni}^{2+} + \text{tetrenH}_4^{4+} \rightleftharpoons [\text{Ni Htetren}]^{3+} + 3\text{H}^+$$

The formation constant for the "hydrogen" complex formed in this process was calculated, the results being given in Table III.

The agreement of the formation constants calculated from the "Excess-metal ion" curve and the "Equivalent" curve indicates that no polynuclear complexes are formed. Thus for the over-all neutralization process and complex formation the following equations are descriptive.

$$\text{tetrenH}_5^{5+} \xrightarrow[-\text{H}^+]{} \text{tetrenH}_4^{4+} \xrightarrow[-3\text{H}^+]{\text{Ni}^{2+}} \text{NiHtetren}^{3+} \xrightarrow[-\text{H}^+]{} \text{Nitetren}^{2+}$$

The formation constant for Nitetren^{2+} obtained by the method of Bjerrum is in excellent agreement with that obtained by the method of Schwarzenbach; however, the former method does not yield formation constants for the "hydrogen complex." Attempts also were made to measure the formation constants polarographically, but due to irreversibility of the system this method was unsuccessful.

Thermodynamic data calculated from the variation of log K with temperature are no more accurate than the reliability limits of the constants and hence are not reported.

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[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY AT TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. XVI. A Study of the Complex Ions Formed by the Copper(II) Ion with Triethylenetetramine, Tetraethylenepentamine and Pentaethylenehexamine[1]

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The complexes of the copper(II) ion with triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine have been studied polarographically. It has been shown that the copper(II) ion exhibits an amine coördination number of five with these compounds and that hydrogen complexes are formed.

Introduction

The polarographic study of complex ions is a well established method[2] provided that the complex ion to be investigated is reduced reversibly at the dropping mercury electrode. If a plot of $E_{d.e.}$ *versus* the corresponding values of log $(i_d - i)/i$ from equation I is a straight line with slope 2.303 (RT/nF) the reduction process is reversible.

$$E_{d.e.} = E_{1/2} + 2.303\ RT/nF \log (i_d - i)/i \qquad \text{(I)}$$

Where

$E_{d.e.}$ = voltage at the dropping mercury electrode
$E_{1/2}$ = half-wave potential of the complex
i_d = diffusion current
i = current at any $E_{d.e.}$
n = number of electrons transferred

The composition of the complex can be determined from the equation

$$(E_{1/2})_c - (E_{1/2})_s = 2.303\ RT/nF \log K_c - 2.303\ RT/nFp \log C_x \qquad \text{(II)}$$

Where

$(E_{1/2})_c$ = half-wave potential of the complex
$(E_{1/2})_s$ = half wave potential of the simple aquo metal ion
K_c = dissociation constant of the complex
p = no. of moles of ligand per mole of metal ion in the complex
C_x = concn. of ligand in moles/l. (C_x must be in considerable excess over the concn. of the metal ion in order that the concn. of the simple aquo metal ion will be negligible.)

A plot of $(E_{1/2})_c$'s of several solutions of varying C_x *versus* log C_x will yield a straight line of slope 2.303 RT/nFp from which p can be calculated.

Using the value of p established in equation II pK_c can be calculated.

The polyamines which become protonated to varying degrees depending upon the pH of the solution become a special case. Their dissociation occurs as shown in the reaction

$$\text{H}_z(\text{H}_q\text{X})_p^{+(z+q)} \rightleftharpoons z\text{H}^+ + p\text{H}q\text{X}^{+q}$$

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[1] Abstracted in part from the Master's Theses submitted to Tulane University, New Orleans, Louisana, by J. Aaron Bertrand, 1956, Frank R. Groves, Jr., 1951, and Robert I. Stearns, 1955.

[2] I. M. Kolthoff, "Polarography," Interscience Publishers, New York, N. Y., 1952.