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The Stability of Metal–Tetraethylenepentamine Complexes

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The stability constants for the reaction between a series of divalent and trivalent metal ions with tetraethylenepentamine have been determined by potentiometric measurements. The complexes studied were those of Hg^{++} (27.7), Cu^{++} (22.9), Ni^{++} (17.8), Zn^{++} (15.4), Cd^{++} (14.0), Pb^{++} (10–11), Mn^{++} (7.0), Bi^{+3} (>0), Ca^{++} (—), Mg^{++} (—), Sr^{++} (—), Ba^{++} (—), Al^{+3} (—) and La^{+3} (—). The reported log K values were obtained at 25.00 ± 0.01° and at an ionic strength of 0.10. A new method for determining the acidity constants of tetraethylenepentamine is described.

Introduction

The stability constants for some of the lower members of the polyethyleneamine series with metal ions have been compiled by Bjerrum, Schwarzenbach and Sillen.[1] Some recent work on the polyethyleneamines has been reported by Jonassen[2,3] and Reilley.[4] These ligands, containing only nitrogens as coördinating atoms, are of particular interest since they offer a basis for the selective titration of metal ions such as cobalt, copper, nickel, zinc, cadmium and mercury which form more stable bonds with nitrogen than with oxygen.[5] These metal ions form stable ammine complexes in ammoniacal solution while certain other metal ions (such as alkaline and rare earths, aluminum, bismuth and scandium) either do not react or form hydrous oxide precipitates.

Previous work in this Laboratory had shown that tetraethylenepentamine (*tetren*) formed very stable complexes with certain metal ions. The purpose of this investigation was to measure the chelate stability constants for a series of divalent and trivalent metal ions with tetren. The data obtained have been utilized in the development of procedures for selective metal titrations.[6]

Experimental

A. **Reagents.**—All chemicals except tetren used were AR grade. The metal ion solutions were prepared from the metal nitrate and distilled water, and were standardized against standard EDTA solutions. The tetren pentahydronitrate solution was prepared by dissolving the purified tetraethylenepentamine pentahydronitrate in distilled water. The tetren (pentahydronitrate) solution was standardized against standard mercury(II) and zinc solutions. *All solutions were made 0.10 M in KNO_3 to maintain constant ionic strength.*

B. **Purification of Tetraethylenepentamine.**—The commercial product, obtained from Union Carbon and Carbide Chemicals Co., was purified as the pentahydronitrate. One hundred fifty grams of crude tetren was dissolved in 300 ml. of 95% ethanol and cooled to 0°. Four and one-half moles of HNO_3 is mixed with 300 ml. of water, 300 ml. of 95% ethanol, and also cooled to 0°. The HNO_3–ethanol mixture is added *slowly* to the tetren–ethanol mixture and the temperature maintained *below 10°*. *This procedure is potentially hazardous and extreme care must be taken to keep the temperature low.* A yellow precipitate, which appears near the end of the addition, was filtered by suction and recrystallized five times from aqueous 5% HNO_3 solution. The resulting white precipitate is washed with acetone and absolute alcohol and dried at 50°. (A similar procedure has been employed by Jonassen.[2])

C. **Determination of Potential-*p*H Diagrams.**—The potential-*p*H data were collected at 25.00 ± 0.01° by a procedure previously described.[7] Equilibrium (± 1 mv.) was reached within 1 minute except with the nickel–tetren solution where the time required to reach equilibrium was decidedly longer. Deaeration of the solutions was necessary in order to obtain accurate potentials in the more negative potential regions where the presence of oxygen interferes ("mixed potentials").

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[1] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants of Metal-ion Complexes," Part I, Special Publication No. 6, The Chemical Society, London, 1957.

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

[3] H. B. Jonassen and L. Westerman, THIS JOURNAL, **79**, 4275, 4279 (1957).

[4] C. N. Reilley and R. W. Schmid, *J. Elisha Mitchell Soc.*, **73**, 279 (1957).

[5] N. V. Sidgwick, *J. Chem. Soc.*, 433 (1941).

[6] C. N. Reilley and A. Vavoulis, unpublished results.

[7] R. W. Schmid and C. N. Reilley, THIS JOURNAL, **78**, 5513 (1956).

Calculations

A. Metal–Tetren Stability Constants.—The potentiometric method employed for determining the stability constants of the metal–tetren complexes has been described earlier.[4,7] Essentially, the method consists of measuring the extent to which the exchange reaction

$$\mathrm{HgZ^{++} + Me^{+n} \rightleftharpoons MeZ^{+n} + Hg^{++}}$$

takes place by means of the mercury electrode. Log K values for various metal complexes were calculated at 25° by substitution into equation 1.

$$E_{\mathrm{Hg}} = E_{\mathrm{Hg}}{}^{0} + 0.0296 \log \frac{[\mathrm{Mn}^{+n}][\mathrm{HgZ}^{++}]}{[\mathrm{MeZ}^{+n}]\mathrm{K}_{\mathrm{HgZ}}} + 0.0296 \log K_{\mathrm{MeZ}} \quad (1)$$

The value for the standard potential of the mercury electrode was given by Latimer[8] as 0.612 volt *vs.* the S. C. E. at 25°; the concentrations of the mercury chelate, metal ion and metal chelate were kept constant (0.001 M) throughout each measurement.

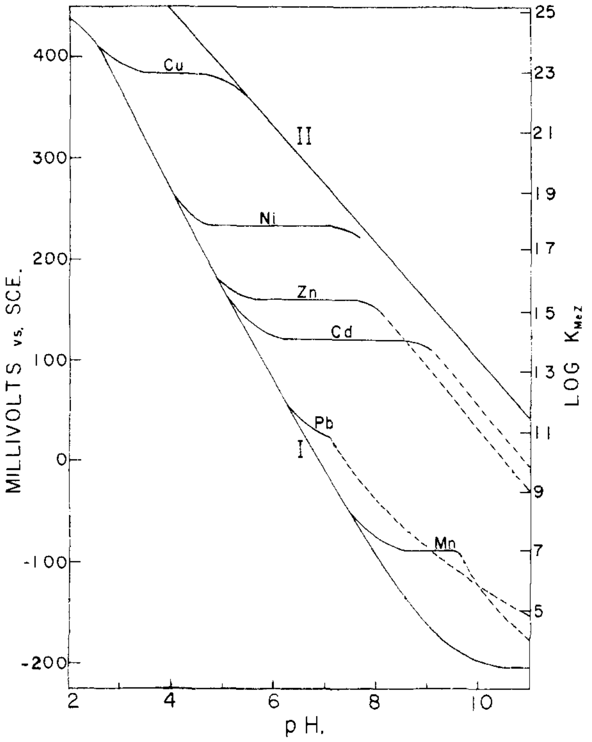

Fig. 1.—Potential-pH diagram for the determination of tetren stability constants (25.00° in 0.10 M $\mathrm{KNO_3}$). Curve I, 0.001 M $\mathrm{HgZ^{++}}$ + 0.001 Z; curve II, calculated (W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 179) potential for $\mathrm{Hg + 2OH^- \rightarrow HgO + H_2O + 2e^-}$; metal–tetren curves, 0.001 M $\mathrm{HgZ^{++}}$ + 0.001 M $\mathrm{MeZ^{+n}}$ + 0.001 M $\mathrm{Me^{+n}}$; curve I was also obtained for $\mathrm{Mg^{++}}$, $\mathrm{Ca^{++}}$, $\mathrm{Sr^{++}}$, $\mathrm{Ba^{++}}$, $\mathrm{La^{+3}}$, $\mathrm{Al^{+3}}$ and $\mathrm{Bi^{+3}}$

The stability constant for the mercury–tetren chelate, K_{HgZ}, was also determined experimentally by potentiometric measurements. At 25°, the potential of the mercury electrode in a solution containing free tetren and mercury–tetren chelate is given by the relationship

$$E_{\mathrm{Hg}} = E_{\mathrm{Hg}}{}^{0} + 0.0296 \log \frac{[\mathrm{HgZ}^{++}]\alpha_{\mathrm{H}}}{[\mathrm{Z}]^{*}\, K_{\mathrm{HgZ}}} \quad (2)$$

where [Z]* represents the stoichiometric concentration of tetren

$$\alpha_{\mathrm{H}} = 1 + K_5[\mathrm{H}^+] + K_5K_4[\mathrm{H}^+]^2 + K_5K_4K_3[\mathrm{H}^+]^3 + K_5K_4K_3K_2[\mathrm{H}^+]^4 + K_5K_4K_3K_2K_1[\mathrm{H}^+]^5 \quad (3)$$

and K_5, K_4, K_3, K_2 and K_1 are the acidity (reciprocal dissociation) constants of tetren. With a knowledge of α_{H}, K_{HgZ} was calculated from potential-pH measurements and the concentrations involved. For a solution containing equal amounts of free tetren and mercuric–tetren chelate, the experimentally determined potential-pH relationship is shown in Fig. 1 (curve I).

Alternatively, K_{HgZ} was determined from the potential of curve I at high pH values (>11) where tetren exists only in the free base form and $\alpha_{\mathrm{H}} = 1$. In this way the stability constant of the mercury chelate can be determined *without knowledge of the tetren acidity constants.*

With a knowledge of K_{HgZ}, a log K scale was calculated from equation 1 and plotted at the right-hand side of Fig. 1. Next, a potential-pH diagram was constructed from experimental data for the various metal ions in such a way that, for definite concentrations of the chemicals involved in equation 1, the log K value for the metal chelate could then be read directly from the measured potential of the mercury electrode, in its pH-independent region (Fig. 1). A difference in log K of one unit corresponds to a difference in potential of 29.6 mv.

Because curve I was also obtained in the presence of $\mathrm{Mg^{++}}$, $\mathrm{Ca^{++}}$, $\mathrm{Sr^{++}}$, $\mathrm{Ba^{++}}$, $\mathrm{La^{+3}}$ and $\mathrm{Al^{+3}}$, no stable tetren complex of these metal ions exist ($\mathrm{Bi^{+3}}$ showed a slight tendency to form a stable tetren complex at pH 8). The dotted lines in Fig. 1 represent the hydrolysis of the metal ions to form hydrous oxide precipitates. This indicates the applicability of the electrode system

$$\mathrm{Hg} \mid \mathrm{Hg\text{-}tetren^{++},\ Me\text{-}tetren^{+n},\ Me^{+n}}$$

for the study of metal ion hydrolysis. As an example, the hydrolysis constant, $K_{\mathrm{H}} = [\mathrm{M(OH)_2}]/[\mathrm{M^{++}}][\mathrm{OH}]^2$, was calculated for zinc ($\sim 1.6 \times 10^{15}$) and cadmium ($\sim 1.0 \times 10^{13}$) from Fig. 1. Likewise, this electrode may be employed for determining the stability constants of the metal complexes (*e.g.*, zinc acetate) provided that the metal ion reacts more strongly with the complexing agent than with tetren.

B. Dissociation Constants of Tetraethylenepentamine.—The acidity constants of tetren were also determined from potential-pH measurements on a solution containing equal amounts of free tetren and mercuric–tetren chelate (curve I). Inspection of equation 2 shows that, other terms being held constant, the potential of the mercury electrode depends linearly on α_{H}, or at 25°

$$E_{\mathrm{Hg}} = E_{\mathrm{Hg}}{}^{0} + 0.0296 \log [1 + K_5(\mathrm{H}^+) + K_5K_4(\mathrm{H}^+)^2 + K_5K_4K_3(\mathrm{H}^+)^3 + K_5K_4K_3K_2(\mathrm{H}^+)^4 + K_5K_4K_3K_2K_1(\mathrm{H}^+)^5] \quad (4)$$

From equation 4 it can be seen that the value of α_{H} at any pH can be calculated from the corresponding potential reading. In this way the value of α_{H} at five different pH values can be obtained and substituted into equation 3. Solution of these

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(8) W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, New York, N. Y., 1952.

simultaneous equations yields the desired acidity constants.

For optimum accuracy in the calculations, the pH values must be properly selected. For each simultaneous equation, the pH chosen should correspond to the point where successive terms on the right side of equation 3 have their maximum contribution.

As an approximation, the five pH values corresponding to the points at which $d(\alpha_H)/d(pH)$ is 1, 2, 3, 4 and 5 were selected. This was accomplished by drawing tangents to curve I corresponding to these preselected slopes.

Because of the highly acidic character exhibited by K_1 and K_2, no attempt was made to evaluate their magnitudes by this procedure. Instead, three simultaneous equations involving three unknowns were set up and solved at the selected pH values for K_5, K_4 and K_3. An approximate value of K_2 was then calculated by substitution into equation 3 using α_H corresponding to a pH (~3) where the K_2 term is significant. The results of these calculations, together with the values reported in the literature,[2] are listed in Table I.

TABLE I

DISSOCIATION CONSTANTS OF TETRAETHYLENEPENTAMINE

	Potentiometric method[a]	Lit.[b]
pK_1	....	2.65
pK_2	4.1 ± 0.1	4.25
pK_3	8.2 ± .1	7.87
pK_4	9.2 ± .1	9.08
pK_5	10.0 ± .1	9.92

[a] 25.00° in 0.10 M KNO_3. [b] 25.0°.

Results and Discussions

The stability constants for the complexes formed between the various metal ions and tetraethylenepentamine are listed in Table II, together with the values reported in the literature.[3]

The interpretation of potential–pH diagrams for the formation of metal chelate complexes has been adequately discussed by previous investigators[4,7,9,10]; only a few of the many interesting results obtainable from Fig. 1 will be discussed. For example, using tetren as the chelating agent, metal ions such as calcium, barium, magnesium, strontium, aluminum, lanthanum (and possibly other rare earths) would not interfere in the titration of bivalent copper, nickel, mercury, zinc or cadmium. Also, at a pH of approximately 4.5, copper may be titrated in the presence of nickel, zinc, manganese, etc.

TABLE II

STABILITY CONSTANTS FOR METAL–TETREN COMPLEXES

Metal ion	Stability constant Potentiometric method[a]	Lit.[b]
Hg^{++}	27.7 ± 0.1	....
Cu^{++}	22.9 ± .1	~24
Ni^{++}	17.8 ± .1	17.6
Zn^{++}	15.4 ± .1	....
Cd^{++}	14.0 ± .1	....
Pb^{++}	10–11[c] ± 1	....
Mn^{++}	7.0 ± 0.1	....
Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Al^{+3}, Bi^{+3}, La^{+3}	Negligible	....

[a] 25.00° in 0.10 M KNO_3. [b] 25.0°. [c] Reproducible results are difficult to obtain due to the formation of hydrous oxide precipitate near the beginning of the constant potential–pH region.

Another interesting observation is that metal–tetren chelates are usually more stable (by a difference of about 3 in the log K) than the corresponding metal–trien complexes. Thus many indicators, forming metal–indicator complexes too stable to be used for metal–trien titrations, are now applicable for the titrations involving tetren. The enhanced stability of the metal–tetren complexes such as copper may be attributed to a tendency toward octahedral structure so that the extra ligand would play an important role in addition to a statistical increase in the probability of chelate formation. Also, the basic character of the nitrogen atoms on the tetren molecule is greater than on the trien molecule. The difference in basicity of the four more basic nitrogens may be designated as, $\sum_{2}^{5} pK_{a\ \mathrm{tetren}} - \sum_{1}^{4} pK_{a\ \mathrm{trien}}$, which equals 2 units.

Similar studies on metal–pentaethylenehexamine complexes are now in progress.

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(9) C. N. Reilley and R. W. Schmid, *Anal. Chem.*, in press.

(10) R. W. Schmid and C. N. Reilley, *ibid.*, **29**, 264 (1957).