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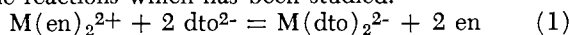
The Ionization Constants for Ethylenediamine

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DESKIN, WILLIAM A., and GARY LORD (Department of Chemistry, Cornell College, Mount Vernon, Iowa 52314). The Ionization Constants for Ethylenediamine. *Proc. Iowa Acad. Sci.* 82(2): 100-101, 1975.

The ionization constants for ethylenediamine have been determined at 25° and at a constant ionic strength of 0.2 M (sodium perchlorate). The following values are reported: $\log Q_1 = 10.22 \pm 0.02$ and $\log Q_{12} = 7.36 \pm 0.04$.

A continuing study in our laboratory has been the determination of formation constants for metal complexes. One of the methods (1) which we have used makes use of a competitive reaction of two ligands for coordination sites on the particular metal ion. The following equilibrium illustrates one of the reactions which has been studied.



In this reaction the metal ion, M^{2+} , is complexed with ethylenediamine, en. An aqueous solution of this complex is mixed with the dipotassium salt of dithiooxalic acid, dto^{2-} . The concentrations of species in the above reaction are adjusted so that the equilibrium proceeds only part way. The ionic strength is adjusted to a prechosen value with an inert electrolyte, usually sodium perchlorate, and the pH of the final solution is either monitored or adjusted to a desired value.

The formation constant, β_2 , for the metal-dithiooxalate complex may be calculated from spectral data. Spectra suggest that mixed ethylenediamine-dithiooxalate complexes are not formed. The solutions were assumed to contain the species $M(en)_2^{2+}$, Men^{2+} , en, $M(\text{dto})_2^{2-}$, and dto^{2-} . The extinction coefficients of these species are known and the formation constants of $M(en)_n^{2+}$ are available (2). This information together with knowledge of the total concentration of metal, ethylenediamine, and dithiooxalate allows one to solve for the value of β_2 for the dithiooxalate complex.

If one chooses a pH value which is neutral or acidic the basicity of the ethylenediamine must also be considered. In our experiments we chose to work at an ionic strength of 0.2 M. In this medium literature values for the ionization constants for ethylenediamine were not available.

EXPERIMENTAL

The chemicals used in this study were reagent grade. The sodium hydroxide solutions were prepared carbonate-free by standard procedures and standardized using primary standard potassium hydrogen phthalate with phenolphthalein as the indicator. The hydrochloric acid solutions were standardized with primary standard sodium carbonate using modified methyl-orange as the indicator. The ionic strength of all solutions was adjusted to 0.2 M by addition of the appropriate amount of sodium perchlorate. Ethylenediamine was purified by refluxing with zinc dust and distilled.

The pH measurements were made with a Brinkman model 102 pH meter, accurate to ± 0.002 pH units, which was standardized with precision buffers prepared by a recom-

mended formula of the National Bureau of Standards. All titrations were made at a constant temperature of 25° under a nitrogen atmosphere to prevent the absorption of carbon dioxide by the ethylenediamine. The activity coefficients of the hydrogen ion and hydroxide ion at an ionic strength of 0.2 M were 0.797 and 0.706, respectively (3).

RESULTS AND DISCUSSION

The quotients for the protonation of ethylenediamine are defined:

$$H^+ + en = enH^+ \quad Q_1 = \frac{[enH^+]}{[H^+][en]} \quad (2)$$

$$H^+ + enH^+ = enH_2^{2+} \quad Q_{12} = \frac{[enH_2^{2+}]}{[H^+][enH^+]} \quad (3)$$

Since concentrations were used in the equilibrium constant expressions instead of activities, these expressions are concentration quotients (at a constant ionic strength). An aqueous solution containing ethylenediamine completely protonated by a strong acid was titrated with a strong base. A proton balance equation and a material balance equation, respectively, for ethylenediamine for this system are:

$$T_A - T_B + [OH^-] = [H^+] + [enH^+] + 2[enH_2^{2+}] \quad (4)$$

$$T_{en} = [en] + [enH^+] + [enH_2^{2+}] \quad (5)$$

$T_A - T_B$ (total acid - total base) represents the amount of hydrogen ions from the acid less the hydrogen ions neutralized by the base. The hydrogen ions from the dissociation of water are represented by $[OH^-]$.

When one assumes that the quotients differ by more than a factor of 100, then $[en] = 0$ in the buffer region of the first half of the titration and $[enH_2^{2+}] = 0$ in the buffer region of the second half of the titration. From these assumptions we may derive an expression for Q_1 and Q_{12} .

$$Q_1 = \frac{T_A - T_B + [OH^-] - [H^+]}{[H^+] \{T_{en} - T_A + T_B - [OH^-] + [H^+]\}} \quad (6)$$

$$Q_{12} = \frac{T_A - T_B - T_{en} + [OH^-] - [H^+]}{[H^+] \{2T_{en} - T_A + T_B - [OH^-] + [H^+]\}} \quad (7)$$

The hydrogen and hydroxide ion concentrations were determined from the pH values and the activity coefficients of both ions. The other terms in equations 6 and 7 were known

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from the volumes and concentrations of the respective solutions added. A program for the IBM 1130 computer, written in Fortran IV, was used for calculating the quotients.

The results of these titrations reported as $\log Q_1$ and $\log Q_{12}$ for ethylenediamine produced the values 10.22 ± 0.02 and 7.36 ± 0.04 , respectively. These results are compared to literature values found at both lower and higher ionic strengths; see Table I.

ACKNOWLEDGMENT

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LITERATURE CITED

TABLE I. PROTONATION QUOTIENTS FOR ETHYLENEDIAMINE AT 25°

Ionic Strength	$\log Q_1$	$\log Q_{12}$	Reference
0	9.87	6.80	(4)
0 ^a	9.81	6.79	(5)
0.1 ^b	10.03	7.22	(6)
0.2	10.22	7.36	this work
0.5	10.18	7.47	(7)
1.3	10.17	7.44	(8)

^a At 30°.

^b At 20°.

Within experimental error, the values determined in this work agree with the pattern of earlier work at lower and higher ionic strength.

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