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# SPECTROPHOTOMETRIC DETERMINATION OF DISPLACEMENT SERIES OF METAL COMPLEXES OF THE SODIUM SALTS OF ETHYLENEDIAMINETETRAACETIC ACID<sup>1</sup>

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Ethylenediaminetetraacetic acid is a white crystalline amino acid with four replaceable protons. The di-, tri-, and tetrasodium salts of this acid react with metal ions such as lead, zinc, cadmium, chromium, cobalt, nickel, copper, and the alkaline earth metals to form stable complexes which resist the action of most of the agents which precipitate these metals. Discussion of this complexforming action has appeared in various papers (1, 2). The order of stability of these various metal complexes in buffered solutions is the subject of this paper. Of the alkaline earth metals, only calcium has been included in this displacement series, since calcium, barium, strontium, and magnesium have already been thoroughly investigated by Schwarzenbach (2).

#### EXPERIMENTAL

*Purification of ethylenediaminetetraacetic acid:* The pure acid was obtained by acidifying the tetrasodium salt to a pH of 1.2, collecting the precipitate, washing it with hot water, and recrystallizing it from hot water.

Standard solutions of the sodium salt were prepared from weighed quantities of the acid dissolved in carbonate-free sodium hydroxide solution.

Preparation of 0.1000 M metal salt solutions: Solutions of calcium, cadmium,

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zinc, cobalt, nickel, and cupric chlorides were prepared and were standardized with silver nitrate, using fluorescein as indicator. In standardization, sufficient sodium bicarbonate solution was added to the sample to precipitate the metal as carbonate and to regulate the acidity. The chromic chloride solution was standardized by converting the chromic ion to chromate in alkaline solution and precipitating the chromate with lead acetate; then the chloride ion was titrated. After standardization, the concentration of each metal solution was adjusted to 0.1000 M. In the case of lead, lead carbonate was used as a standard and dissolved in hydrochloric acid to produce a 0.0333 M solution.

Preparation of buffer solutions: The buffers used are shown in table 1. Each buffer system was prepared by adding carbonate-free sodium hydroxide to the more acidic component of the system. These buffer solutions permitted measurements to about 222 m $\mu$  in the ultraviolet.

Preparation of complexes and blanks: The concentration used for all complexes was  $0.01 \ M$ . However, more dilute solutions were measured in order to

TABLE	1
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Buffers used

pH	System			
$     \begin{array}{r}       11.00 \\       8.65 \\       6.50 \\       4.00 \\     \end{array} $	0.200 $M$ Na <sub>2</sub> HPO <sub>4</sub> -Na <sub>3</sub> PO <sub>4</sub> 0.200 $M$ NaHCO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> 0.200 $M$ NaH <sub>2</sub> PO <sub>4</sub> -Na <sub>2</sub> HPO <sub>4</sub> 0.200 $M$ CH <sub>3</sub> COOH-CH <sub>3</sub> COONa			

check conformance to Beer's law. In the concentration range of  $0.001 \ M$  to  $0.01 \ M$ , Beer's law was found to hold fairly closely.

The pure metal complexes were prepared by combining equal volumes of equivalent concentrations of a metal chloride solution and a salt of ethylenediaminetetraacetic acid in a volumetric flask. The solution was diluted to the proper volume with the buffer.

Colored mixed metal complexes were prepared in the same manner, except that one volume of each of two metals was used. Noncolored mixed metal complexes at pH 8.65 were prepared just as the colored mixed metal complexes, except that an amount by weight of sodium carbonate equivalent to that precipitated as the normal metal carbonate was added to correct the carbonate content.

The blank solution for measurements in the ultraviolet consisted of a volume of distilled water, equivalent to the total volume of metal and complex-forming agent used, made up to the proper volume with buffer. Distilled water was used as a blank in the visible region.

Attainment of equilibrium: With the exception of the chromic complex, all solutions which did not have a solid phase reached color equilibrium within a few hours. The chromic complex required 1 week to develop its full color. The mixed complex systems which involved a solid phase required about 2 weeks of shaking to reach equilibrium.

*Measurement of solutions:* Measurements were made on a Beckman Model D.U. quartz spectrophotometer. Each solution was filtered through a sinteredglass funnel just before introduction into the absorption cell.



FIG. 1. Absorption spectra of the sodium salt of ethylenediaminetetraacetic acid ( $\blacktriangle$ ) and of the complexes formed by this acid with zinc (O), magnesium ( $\blacksquare$ ), cadmium ( $\square$ ), and calcium ( $\bigcirc$ ).

### RESULTS

## Indication of complex formation

The absorption spectrum (molar extinction coefficient vs. wave length) of the sodium salt of ethylenediaminetetraacetic acid is shown in figure 1, together with that of the calcium, magnesium, cadmium, and zinc complexes. Although the absorption maximum could not be reached, there seems to be a shift towards the ultraviolet. The absorption spectra at pH 4.00 of cobalt, nickel, and cupric chlorides and of the complexes formed from these ions and ethylenediaminetetraacetic acid are shown in figure 2.

At pH values of 6.5 and higher, when no complex-forming agent was present, the cobalt, nickel, and cupric ions precipitated as phosphates, carbonates, or hydroxides, depending upon the buffer solution and the metal, so that no spectra for the metals alone were apparent. However, the complexes are soluble and have characteristic absorption spectra.

The presence of absorption bands not due to the metals alone and the displacement of absorption towards the ultraviolet may be interpreted as an indication of complex formation. These interpretations, when applied to the spectra obtained, lead to the results tabulated in table 2.



FIG. 2. Absorption spectra at pH 4.00 of the chlorides (---) of cobalt, nickel, and copper and of the complexes (-) formed from these ions and ethylenediaminetetraacetic acid: O, cobalt;  $\Box$ , nickel;  $\oplus$  copper.

Complex formation at algerent pill battles								
pH	Ca	Mg	Cd	Zn	Co	Ni	Cu	Cr
4.00	0	0	0	0	x	x	x	x
8.65	x	x	x	x	x	x	x	x
11.00	x	x	x	x	x	x	х	x

TABLE 2 Complex formation at different pH values\*

\* x indicates complex formation; o indicates little, if any, tendency for complex formation.

# Displacement series

Figure 3, a graph of the absorption spectra for the nickel-cobalt mixed complex system, is typical of the curves for mixed complexes showing bands characteristic of each. The amount of each present at equilibrium was calculated by means of the following equation and data at two wave lengths:

$$(E_{n\alpha} - E_{n\gamma})C_{\alpha} + (E_{n\beta} - E_{n\phi})C_{\beta} = d_{n} - (E_{n\gamma} + E_{n\phi})G$$

where d is the observed optical density of the mixed complex system,

- G is the molarity of either metal or of the complex-forming agent,  $\alpha$  is metal 1 which is in a complex,
- a is metal 1 which is in a complex,
- $\beta$  is metal 2 which is in a complex,
- $\gamma$  is metal 1 which is not in a complex,
- $\phi$  is metal 2 which is not in a complex,
- E is the extinction coefficient of each component of the system,
- ${\boldsymbol{C}}$  is the concentration of each component of the system, and
- n is the wave length at which measurements are made.



FIG 3. Absorption spectra at pH 6.50 of complexes formed from ethylenediaminetetraacetic acid:  $\bigcirc$ , cobalt-nickel mixed complexes;  $\Box$ , cobalt complex;  $\blacksquare$ , nickel complex.

 TABLE 3

 Wave lengths used in calculating the amount of each complex present

COMPLEX	λ
Cobalt Nickel	<i>mμ</i> 460 380, 1000 750 560

The above equation is easily derived from the following relationships:

$$d = E_{\alpha}C_{\alpha} + E_{\beta}C_{\beta} + E_{\gamma}C_{\gamma} + E_{\phi}C_{\phi}$$
(1)

$$C_a + C_\gamma = G \tag{2}$$

 $C_{\beta} + C_{\phi} = G \tag{3}$ 

Relationship 1 is Beer's law for a four-component system. Relationships 2 and 3 merely state that all of the metal is either combined in a complex or it is not.

The wave lengths shown in table 3 were found to be satisfactory for the calculation of the amount of each complex present.

The results of calculations by this equation were checked by the relationship  $C_{\alpha} + C_{\beta} = G$ . The mean deviation for this check was 1.5 per cent.

In cases where a mixed complex system of one colored and one noncolored complex was investigated, only one wave length was used in the calculations,



FIG. 4. Absorption spectra at pH 8.65 of complexes formed from ethylenediaminetetraacetic acid: □, cadmium complex; ○, zinc complex; ●, calcium complex; ■, zinc-calcium mixed complexes; ▽, zinc-cadmium mixed complexes; ▼, calcium-cadmium mixed complexes.

since absorption by the colored complex completely masked absorption by the noncolored complex.

At the high pH values, there was an insignificant amount of cobalt, nickel, and cupric ions in equilibrium with the complexes, so that they did not contribute to the density and thus simplified the equation to Beer's law for a twoor three-component system.

At pH 8.65 noncolored mixed complexes of cadmium-calcium, zinc-calcium, and cadmium-zinc were investigated. The results are shown in figure 4. No calculations were made on this data, but examination of the curves shows that the calcium-zinc curve approximates the curve for the pure zinc complex, the calcium-cadmium curve approximates the curve for the pure cadmium complex, and the zinc-cadmium curve approximates the curve for the pure zinc complex. Thus, we may conclude that at pH 8.65 Zn > Cd > Ca, where the inequality signs indicate a power of 10 or more.

The relative strengths of complex formation under the given experimental conditions are best expressed by means of the ratio of the concentration of one metal complex to the concentration in equilibrium with it of an arbitrarily standard metal complex. Thus, the strength S is defined as follows:

$$S = 100 \times \frac{\text{amount of metal 1 combined in a complex}}{\text{amount of metal 2 combined in a complex}}$$

The standard here is taken as the copper complex.

The results of the above methods of calculation as applied to each system at each pH are given in table 4.

The relative formation constants for the reaction of the disodium salt of ethylenediaminetetraacetic acid (pH 4.0) with the divalent metals copper,

METAL	p <b>H 4.00</b>	pH 6.50	pH 8.65	pH 11.00	
Chromium	302			<cd< td=""></cd<>	
Copper	100	100	100	100	
Nickel	39.0	109	419	170	
Lead	27.2				
Cobalt	8.9	83.3	101	213	
Zinc		1	28.2	<cd< td=""></cd<>	
Cadmium		1	<Zn	80	
Calcium		<cd, td="" zn<=""><td><cd< td=""><td></td></cd<></td></cd,>	<cd< td=""><td></td></cd<>		

 TABLE 4

 Relative strengths of complex formation

nickel, lead, and cobalt have been calculated. The ratio of the formation constant of the nickel complex to that of the copper complex is 0.152, of the lead complex to the copper complex is 0.0740, and of the cobalt complex to the copper complex is 0.00792.

This order of stability of the complexes of the heavy metals is the same as that which has been observed by other investigators for other complex-forming agents (3, 4, 5).

The results shown in table 4 for the high pH values are a measure of the tendency for complex formation in the given buffer solutions. There are other equilibria competing with the complex formation for the metal ions at the high pH values. These equilibria involve the precipitated hydroxides, phosphates, and carbonates and, in the cases of zinc and chromium, the soluble zincates and chromites.

#### SUMMARY

The ultraviolet and visible absorption spectra of the sodium salts of ethylenediaminetetraacetic acid and of some of its metal complexes have been determined at pH values of 4.0, 6.5, 8.65, and 11.0. The pH was controlled by preparing the complexes in buffer solutions. The absorption spectra of similarly buffered solutions containing one equivalent each of two metals and one equivalent of the complex-forming agent have been determined. The results of these two sets of data have been combined to evaluate the displacement series of the metal complexes in the given buffer solutions.

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# THE VISCOSITY OF SULFUR VAPOR

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# INTRODUCTION

A search of the literature has indicated that the viscosity of sulfur vapor has never been measured. This information is needed especially for calculations of engineering design. The data are also of physicochemical interest, particularly because sulfur should deviate from the general rule that the viscosities of most gases increase slowly with increasing temperature. In addition, the viscosity should vary with pressure, which also is unusual. These anomalies are, of course, attributable to the fact that sulfur vapor dissociates strongly at a relatively low temperature, the degree of dissociation being sensitive to both temperature and pressure.

The experimental determination of the viscosity of sulfur is somewhat awkward, because the boiling point of sulfur is only slightly below the softening point of Pyrex glass and also because its vapor is so corrosive to most metals. On the other hand, a number of methods are available for estimating the viscosity of gases. Licht and Stechert (2) have reviewed these procedures and have shown that the Sutherland equation (4) yields results which are usually within 1 per cent of experimental values in those cases in which the comparison has been made.

In the investigation recorded in this paper, the viscosity of sulfur vapor has