

additional carboxylate ion in either a five- or six-membered bidentate. It is reasonable to assume that the succinic acid analogs form tridentate chelates since it is known that chelates become more stable as the number of chelate rings in the molecule increases.<sup>37</sup> The chelate stability constants for the series of metals with a given ligand

is linearly related to the ionic radii of the metal in the series.

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## Acetate Complexes of the Rare Earth and Several Transition Metal Ions<sup>1</sup>

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The first two complex-formation constants of acetate anion with trivalent rare earth and divalent copper, zinc, cadmium, and lead ions have been determined. The temperature was controlled at 20° and an ionic strength of 0.1 was used. Hydrogen ion concentrations were measured using a glass electrode.

### Introduction

It is a well known fact that trivalent lanthanon ions exhibit extensive hydrolysis when placed in an aqueous medium. Thus, when neutral rare earth salts are dissolved in water, a distinct lowering of the *p*H is noted. The extent of the lowering depends on the concentration of the rare earth salt and the particular rare earth. Since the ionic radius decreases from lanthanum to lutetium, the heavier the rare earth the greater is the tendency to hydrolyze.

Measurements made on rare earth solutions often must be corrected for hydrolysis. The necessity for correction frequently can be eliminated by making the measurements in solutions in which hydrolysis has been suppressed by the addition of excess hydrogen ions. This is conveniently achieved by introducing an acid buffer into the solution. It has been found that acetic acid-sodium acetate buffer systems provide the *p*H necessary to prevent hydrolysis of dilute rare earth solutions. This buffer has been used in the determination of stability constants of rare earth chelates with ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) and N'-hydroxyethylethylenediamine-N,N,N'-triacetic acid (HEDTA).<sup>2</sup> Since

the measurement of stability constants involves either direct or indirect determination of free metal ion concentrations, it is imperative to consider the possibility of complex formation between the various metal ions and the buffer ligand.

Sonesson has shown that complexes between the lanthanons and acetate do form.<sup>3-5</sup> He determined the stepwise formation constants of rare earth-acetate species at an ionic strength of 2.0, but data for lower ionic strengths are not available. The present investigation, therefore, considers the magnitude of these formation constants at an ionic strength of 0.1.

In many systems used to determine chelate stability constants, competing metal ions are involved.<sup>2</sup> For this reason the stepwise formation constants of the acetate complexes of divalent copper, zinc, cadmium, and lead ions also have been included in the present investigation.

The determination of the acetate formation constants has an additional purpose. The variation in stability of the complexes formed with members of the rare earth sequence thus far has been studied extensively only for the case of polydentate ligands, and the observed trends have not yet been explained satisfactorily. The distinct drop in stability at gadolinium is presently

(1) Contribution No. 1050. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) (a) E. J. Wheelwright, F. H. Spedding, and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953); (b) F. H. Spedding, J. E. Powell, and E. I. Wheelwright, *ibid.*, **78**, 34 (1956).

(3) A. Sonesson, *Acta Chem. Scand.*, **12**, 165 (1958).

(4) A. Sonesson, *ibid.*, **12**, 1937 (1958).

(5) A. Sonesson, *ibid.*, **14**, 1495 (1960).

a subject of much discussion. A study involving monodentate ligands such as acetate may lead to a better understanding of such phenomena.

**Methods Used for the Calculation of Acetate Formation Constants.**—In a solution containing metal ions and acetate ions, the hydrogen ion concentration affords a means of measuring the degree of complexation of the metal ion. From the initial concentrations of metal ion and acetate buffer (sodium acetate–acetic acid) and the dissociation constant of acetic acid, the amount of ligand bound to the central metal ion can be determined by potentiometric measurement of the hydrogen ion concentration. The theoretical treatment of this problem was formulated by Leden<sup>6</sup> and Fronaeus<sup>7</sup> and a good review has been given by Sonesson.<sup>8</sup> The calculations are quite lengthy and need not be restated here. Symbols used in this manuscript will be the same as those of Sonesson.

### Experimental

Standard solutions were prepared from rare earth oxides supplied by the rare earth separation group of the Ames Laboratory of the U. S. Atomic Energy Commission. All of the oxides were of 99.9% or greater purity as determined by emission spectroscopy. Each rare earth oxide was dissolved in perchloric acid and the excess acid was removed by evaporation to incipient dryness. The resulting basic perchlorate then was dissolved in water and a portion titrated with perchloric acid to determine the equivalence point. This titrated portion then was mixed with the remaining solution and the entire solution was brought to the desired pH. In the case of cerium, it was found that the cerium(III) reverted to the original cerium(IV) oxide before all of the excess acid could be removed. Excess cerium(IV) oxide was mixed with perchloric acid and the mixture heated and stirred for several hours with hydrogen peroxide being added continually. The resulting slurry was filtered and the unused acid was determined by titration with standard base. This excess acid then was taken into account in subsequent calculations. Each solution was standardized by precipitation of the rare earth content as the oxalate and ignition to the oxide.

Standard solutions of copper, zinc, cadmium, and lead were prepared by dissolving the corresponding nitrates in water. The copper solution was standardized by electro-deposition of the copper on platinum and weighing. The zinc, cadmium, and lead solutions were analyzed by titration with a standard solution of EDTA using Eriochrome Black T as an indicator. The chelate solution was standardized by using pure metallic zinc. All chemicals used to prepare the solutions were of reagent grade quality.

A buffer solution of acetic acid and sodium acetate was made up by adding a measured amount of standard

sodium hydroxide solution to a known amount of standard acetic acid solution. An aliquot of the resulting buffer solution then was titrated with base as a check. Varying amounts of the buffer were added to a series of 50-ml. volumetric flasks and a known amount of metal ion was added. The ionic strength was adjusted to 0.1 using a sodium perchlorate solution and the samples were placed in a 20° bath for 12 hr. Since the ionic strength changes as the metal ion associates with acetate, the formation constants first were determined roughly and new solutions were prepared taking into account the change in ionic strength. All pH measurements were made with a Beckman Model GS pH meter using a glass electrode. A pH 4.0 ± 0.01 buffer was used to calibrate the instrument. The same buffer solution was used throughout the experiments so that errors due to pH changes in different buffer samples were eliminated. The observed pH measurements were converted into hydrogen ion concentrations before being used in the calculations.

Although the dissociation constant of acetic acid was not necessary for the calculation of the constants (see ref. 3), the constant was determined at 20° and an ionic strength of 0.1 in sodium perchlorate. The constant was evaluated by titrating a 0.01 M acetic acid solution with standard potassium hydroxide and calculating the constant at various degrees of neutralization. The value  $2.799 \times 10^{-5}$  agreed well with that calculated from the observed pH of the buffer solution used in the experiments.

### Determination of Acetate Constants

The observed pH values of a number of solutions containing metal ion, acetate ion, and acetic acid are tabulated in Table I. Only a few rare earths were chosen for purposes of illustration. It is apparent that significant variations in hydrogen ion concentration occur from one metal ion to another. Bjerrum defines the average ligand number,  $\bar{n}$ , as the average number of ligand molecules bound to the central metal ion.<sup>8</sup> By plotting  $\bar{n}$  vs. [A], where [A] is the free ligand concentration in the solution, one obtains the complex formation curve. The complex formation curves of several of the metals studied are shown in Fig. 1. Constants calculated for all of the metals studied are listed in Table II. The constants are defined as



$$k_n = \frac{[\text{MA}_n]}{[\text{MA}_{n-1}][\text{A}]} \quad (1)$$

$$\beta_n = \frac{[\text{MA}_n]}{[\text{M}][\text{A}]^n} \quad (2)$$

### Discussion of Results

One first must consider the applicability of the glass electrode to the determination of the acetate

(6) I. Leden, "Potentiometrisk undersökning av några kadmium-salters komplexitet," Dissertation, Lund, 1943.

(7) S. Fronaeus, "Komplexsystem hos koppar," Dissertation, Lund, 1948.

(8) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Dissertation, Copenhagen, 1941.

TABLE I  
 OBSERVED pH VALUES OF ACETATE BUFFER SOLUTIONS

Ml. buffer <sup>a</sup> 50 ml. soln.	Metal						
	Cu <sup>+2</sup>	Zn <sup>+2</sup>	Cd <sup>+2</sup>	La <sup>+3</sup>	Eu <sup>+3</sup>	Gd <sup>+3</sup>	Tb <sup>+3</sup>
2.50	4.353	4.519	4.467	4.479	4.400	4.432	4.458
3.75	4.357	4.526	4.471	4.489	4.412	4.438	4.458
5.00	4.364	4.526	4.474	4.500	4.422	4.447	4.453
7.50	4.376	4.524	4.472	4.503	4.438	4.454	4.467
10.00	4.391	4.524	4.475	4.511	4.455	4.467	4.475
15.00	4.409	4.527	4.481	4.525	4.473	4.486	4.484
20.00	4.433	4.530	4.486	4.534	4.492	4.499	4.496
25.00	4.450	4.535	4.491	4.542	4.505	4.509	4.506
30.00	4.464	4.538	4.502	4.550	4.516	4.520	4.515
35.00	4.475	4.543	4.507	4.556	4.525	4.528	4.523
45.00	4.506	4.548	4.526	4.570	4.538	4.542	4.540

<sup>a</sup> Buffer solution, 0.08807 M acetic acid-0.07740 M sodium acetate; Cu<sup>+2</sup>, 0.01132 M; Zn<sup>+2</sup>, 0.01041 M; Cd<sup>+2</sup>, 0.01004 M; rare earth, 0.0040 M.

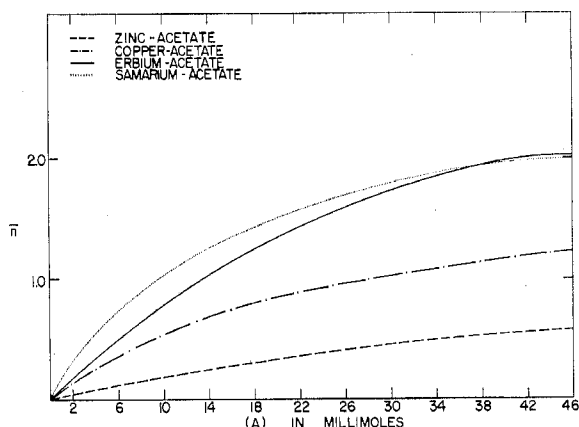


Fig. 1.—Complex formation curves of several acetate systems.

constants. The pH meter will detect variations of  $\pm 0.0025$  pH unit; therefore, the relative values of the individual constants are very good. Using the above variation in the pH reading and errors involved in the calculations, an error of about  $\pm 3\%$  is probable between the constants. The absolute error in the constants is much greater than the relative error. The error in the standard buffer pH used in the experiments, for example, is  $\pm 0.01$  pH unit. The variation in converting the observed activity of the hydrogen ion to concentration of hydrogen ion by various workers in this Laboratory amounts to  $\pm 0.02$  pH unit. Considering these possible deviations, an error of approximately  $\pm 10\%$  is probable in the absolute magnitude of the constants. It also should be mentioned that indeterminate errors due to salt bridge effects and the thermodynamic definition of pH are not considered in the above errors<sup>9,10</sup>; but some of these errors would be accounted for in the  $\pm 0.02$  pH unit variation.

TABLE II

COMPLEX FORMATION CONSTANTS OF THE ACETATE LIGAND

Metal	$k_1 = \beta_1$	$k_2$	$\beta_2$	$k_1/k_2$
La <sup>+3</sup>	105	17.2	1810	6.1
Ce <sup>+3</sup>	124	27.5	3410	4.5
Pr <sup>+3</sup>	150	28.1	4220	5.3
Nd <sup>+3</sup>	166	34.8	5780	4.8
Sm <sup>+3</sup>	201	38.4	7710	5.2
Eu <sup>+3</sup>	202	39.7	8020	5.3
Gd <sup>+3</sup>	146	39.8	5810	3.7
Tb <sup>+3</sup>	118	39.3	4640	3.0
Dy <sup>+3</sup>	108	40.4	4360	2.7
Ho <sup>+3</sup>	101	39.3	3970	2.6
Er <sup>+3</sup>	102	38.8	3960	2.6
Tm <sup>+3</sup>	104	38.9	4050	2.7
Yb <sup>+3</sup>	107	43.3	4630	2.5
Lu <sup>+3</sup>	111	43.6	4840	2.5
Y <sup>+3</sup>	94	42.7	4010	2.2
Cu <sup>+2</sup>	78	15.8	1230	4.9
Zn <sup>+2</sup>	19	6.5	123	2.9
Cd <sup>+2</sup>	41	11.7	482	3.5
Pb <sup>+2</sup>	159	24.6	3910	6.5

Sonesson has shown that at least three, and possibly four, acetate groups will attach themselves to a central rare earth ion.<sup>3</sup> Only the first two constants are reported in this paper, since the amount of acetate ion added to the solutions was limited by the low ionic strength value. The  $k_1$  constants obtained at  $\mu$  equal to 0.1 are approximately two and one-half times as large as those obtained at  $\mu$  equal to 2.0.<sup>4</sup> This factor is about the same for  $k_2$ , the second constant. Using this as a basis, one may predict the values of  $k_3$  and  $k_4$  at  $\mu$  equal to 0.1 from the known values of  $k_3$  and  $k_4$  at  $\mu$  equal to 2.0.  $k_3$  should be of the

(9) R. G. Bates, G. D. Pinching, and E. R. Smith, *J. Research Natl. Bur. Standards*, **45**, 418 (1950).

(10) I. Feldman, *Anal. Chem.*, **28**, 1859 (1956).

order of 8 for the lighter members and 15 for the heavier members of the rare earth sequence. Likewise,  $k_4$  should be of the order of 2 to 3 for all of the rare earths. The ratio  $k_1/k_2$  for the complexes at  $\mu$  equal to 0.1 compare well with those obtained at  $\mu$  equal to 2.0.

Variations in the acetate stability constants of the rare earths, as one proceeds through the series, are very interesting. From lanthanum through samarium there is a definite rise in the first complexation constant which may be explained by the decrease in the ionic radius of the central atom. The europium constant is about the same as samarium. Since the ionic radius of europium is smaller than that of samarium, this constant is lower than expected from the previous trend. If the generally observed trend for rare earth stability constants were followed, one would expect the constant to drop at gadolinium and then rise again at terbium. However, with the acetates the constant for terbium drops below that of gadolinium and the downward trend continues through holmium. The erbium constant is about the same as that of holmium, but a small rising trend is noted throughout the remainder of the series. With the second constant,  $k_2$ , the

anomaly disappears and the trend more or less substantiates the ionic radii concept. Variations are noted, but it is difficult to say whether these are real or simply due to experimental error. The  $k_2$  values of holmium, erbium, and thulium, for example, appear to be slightly depressed. Similar trends have been found at  $\mu$  equal to 2.0, lending credence to the observed variations.

Sodium perchlorate was used as the supporting electrolyte in this work. Quite frequently other highly ionized salts are used. That the constants obtained in this work are applicable to solutions containing other supporting electrolytes is indicated by a comparison of the ionization constants of acetic acid obtained in various media. The constant found using sodium perchlorate was  $2.799 \times 10^{-5}$  at  $\mu$  equal to 0.1, whereas Harned and Owen list values of 2.874, 2.891, and  $2.850 \times 10^{-5}$  at  $\mu$  equal to 0.11 using lithium chloride, sodium chloride, and potassium chloride, respectively.<sup>11</sup> The behavior of acetate complexes in the different solutions should be similar to acetic acid.

(11) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1958.

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## Cerium(IV) Gluconate Complexes

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The cerium(IV) ion forms extremely stable complexes with sodium gluconate in basic solutions. Spectrophotometric, polarimetric, potentiometric, polarographic, and pH measurements have been used to study these complexes. At pH 14 and 0.08 *F* sodium gluconate the molar absorptivity for the complex is 4200 at 288 m $\mu$ , the absorption maximum. Addition of excess cerium(IV) to a basic gluconate solution initially forms soluble polymers containing approximately six ceric ions per gluconate ion. The polymers hydrolyze slowly to give ceric hydroxide plus a stable gluconate complex. A number of independent studies have been used to establish that the most stable complex contains two cerium(IV) ions per three gluconate ions; at pH 7.3 the formula for this complex is  $\text{Ce}_2(\text{GH}_4)_3(\text{OH})_9^{-4}$  and at pH 11 it is  $\text{Ce}_2(\text{GH}_4)_3(\text{OH})_{11}^{-6}$ . Potentiometric measurements plus several assumptions permit a reduction reaction to be proposed for the complex at pH 11;  $\text{Ce}_2(\text{GH}_4)_3(\text{OH})_{11}^{-6} + 2e^- = \text{Ce}_2(\text{GH}_4)(\text{OH})_6^- + 2\text{GH}_4^- + 5\text{OH}^-$ , where the cerium(IV) complex is reduced to the cerium(III) complex. Tentative formation constants have been estimated for both the cerium(IV) and the cerium(III) complexes on the basis of the potentiometric data together with a series of assumptions.

Gluconic acid has been shown to be an effective complexing agent for a number of metal ions. Cannan and Kibrick<sup>1</sup> investigated the complexes

(1) R. K. Cannan and A. Kibrick, *J. Am. Chem. Soc.*, **60**, 2314 (1938).

formed between ions of the Group II elements and gluconic acid, but only observed weak complexes. The gluconate chelates of copper(II), iron(III), lead(II), and cadmium(II) have been studied by Pecsok and co-workers,<sup>2</sup> and the