Determination of the Rare Earth–HEDTA Stability Constants by the Mercury Electrode Method[1a]

BY J. E. POWELL AND J. L. MACKEY

The stability constants of the 1:1 complexes formed between the rare earths and the N'-hydroxyethylethylene-diamine-N,N,N'-triacetate (HEDTA) anion have been determined by the mercury electrode method at a temperature of 20° and an ionic strength of 0.10. The mercury(II)–HEDTA formation constant was measured under the same conditions.

Introduction

The stability constants of the complexes formed between the N'-hydroxyethylethylenediamine-N,N,N'-triacetate anion (HEDTA) and the lanthanons at 25° have been reported previously by Spedding, Powell, and Wheelwright[1b] and by Moeller, Thompson, and Ferrús.[2] The methods used by Spedding, *et al.*, were a polarographic method[3,4] and a modified pH method which employed an auxiliary chelating agent, β,β',β''-triaminotriethylamine (tren), and a second metal ion.[1,3,5] The method used by Moeller, *et al.*, was not stated. The pH method, although reasonably accurate in a differential sense, introduced considerable uncertainty in the absolute values of all the constants. The uncertainty was due to possible errors in the auxiliary constants used as a basis for calculating the rare earth–HEDTA stability constants, specifically $K_{\text{H}_3\text{tren}}$, K_{CuV}, and K_{Cutren}. Spedding, *et al.*, estimated that the potentiometric values of log K_{MV} were accurate to ±0.06 in a differential or relative sense, but were subject as a group to a possible error of ±0.2 log unit in absolute magnitude. The polarographically determined log K_{MV} values were estimated to be even less accurate.

The Mercury Electrode Method

Recently a new method for determining formation constants of stable chelates was reported by

Reilley and Schmid.[6] The method involves measuring the potential of a mercury electrode in the presence of mercury ions and has been referred to frequently as the mercury electrode or pHg method.

In the mercury electrode method, rare earth and mercury(II) ions are mixed with an amount of chelating agent equal to about half the sum of the concentrations of the two metal ions. The basic reaction occurring is

$$R^{3+} + HgV^- \rightleftharpoons RV + Hg^{2+} \qquad (I)$$

where R^{3+} represents a rare earth ion and V^{3-} the ligand anion (in this case N'-hydroxyethylethylenediamine-N,N,N'-triacetate). The equilibrium constant for reaction I is then

$$K_I = \frac{[RV][Hg^{2+}]}{[R^{3+}][HgV^-]} = \frac{K_{RV}}{K_{HgV}} \qquad (1)$$

It is possible to write material balance equations which account for all likely species in a solution of the two metals and the chelating agent as

$$[R_t] = [R^{3+}] + 2[R_2V^{3+}] + [RHgV^{2+}] + \sum_{h=0}^{h} [H_hRV^{h+}] \qquad (2)$$

$$[Hg_t] = [Hg^{2+}] + 2[Hg_2^{2+}] + [RHgV^{2+}] + \sum_{p=0}^{p} [H_pHgV^{p-1}] \qquad (3)$$

$$[V_t] = \sum_{h=0}^{h} [H_hRV^{h+}] + \sum_{p=0}^{p} [H_pHgV^{p-1}] + \sum_{n=0}^{n} [H_nV^{n-3}] + [R_2V^{3+}] + [RHgV^{2+}] \qquad (4)$$

$$[H_t] = [H^+] - [OH^-] + \sum_{h=0}^{h} h[H_hRV^{h+}] + \sum_{p=0}^{p} p[H_pHgV^{p-1}] + \sum_{n=0}^{3} n[H_nV^{n-3}] \qquad (5)$$

(1) (a) Contribution No. 1037. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; (b) F. H. Spedding, J. E. Powell, and E. J. Wheelwright, *J. Am. Chem. Soc.*, **78**, 34 (1956).

(2) T. Moeller, L. C. Thompson, and R. Ferrús, "Some Aspects of the Stabilities of Amine Polycarboxylic Acid Chelates of the Tripositive Rare Earth Metal Ions," in "Rare Earth Research," ed. by E. V. Kleber, The Macmillan Co., New York, N. Y., 1961.

(3) E. J. Wheelwright, F. H. Spedding, and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953).

(4) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

(5) H. Ackermann and G. Schwarzenbach, *ibid.*, **32**, 1543 (1949).

(6) C. N. Reilley and R. W. Schmid, *J. Am. Chem. Soc.*, **78**, 5513 (1956).

When measurements are performed in the pH range 4.0–5.0, it is possible to simplify the material balance equations a great deal. Due to the high stability of both the RV and HgV$^-$ species ($K_{MV} > 10^{15}$) and the excess metal ions present, it is not necessary to consider any of the H$_n$V or protonated metal–chelate species. Furthermore, from the fact that K_{HgV} is more than a thousandfold larger than K_{RV} in every case, it can be shown that the concentration of free mercury ions is sufficiently small that it does not contribute appreciably to the material balance. With these assumptions the material balance equations reduce to
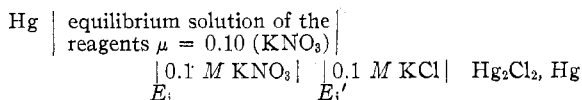
$$[R_t] = [R^{3+}] + [RV] \qquad (2a)$$

$$[Hg_t] = [HgV^-] \qquad (3a)$$

and

$$[V_t] = [HgV^-] + [RV] \qquad (4a)$$

A mercury electrode and a standard calomel electrode with a KNO$_3$ salt bridge, when placed in a solution of mercury(II) ions, rare earth ions, and a chelating agent, can be represented by

Hg | equilibrium solution of the reagents μ = 0.10 (KNO$_3$) | 0.1 M KNO$_3$ | 0.1 M KCl | Hg$_2$Cl$_2$, Hg
E_j | | E_j'

The potential of this cell is given by the Nernst equation

$$E = E^0 + E_j + E_j' + s/2 \log a_{Hg}{}^{2+} \qquad (6)$$

where E^0 is a term that consists of the standard reduction potential of Hg^{2+} to Hg^0 and the potential of a 0.1 M calomel cell and $s = 2.3026RT/F$. E_j is the liquid-junction potential between the experimental solution and the 0.1 M KNO$_3$, and E_j' is the junction potential between 0.1 M KNO$_3$ and 0.1 M KCl. E_j' remains constant throughout a set of experiments, but E_j would be expected to vary at both low and high pH values, due to the large mobilities of H$^+$ and OH$^-$. However, it is reasonable to assume that E_j remains virtually constant between pH 3 and 11. Equation 6 can be rewritten as

$$E = E_0' + s/2 \log [Hg^{2+}] \qquad (6a)$$

where $E_0' = E^0 + E_j + E_j' + s/2 \log \gamma_{Hg}{}^{2+}$ is simply a constant at any fixed ionic strength. E_0' can be considered to be a formal reduction potential at μ = 0.10 (KNO$_3$) and 20° and can be evaluated by making measurements on solutions of known mercury(II) ion concentrations at the given temperature and ionic strength. For a

detailed description of how E_0' is found, the article by Schwarzenbach and Anderegg[7] should be consulted.

Equation 1 can be solved for [Hg^{2+}] to give

$$[Hg^{2+}] = \frac{K_{RV}}{K_{HgV}} \times \frac{[R^{3+}][HgV^-]}{[RV]} \qquad (7)$$

and this can be substituted into equation 6a to give

$$E = E_0' + s/2 \log \frac{[R^{3+}][HgV^-]}{K_{HgV}[RV]} + s/2 \log K_{RV} \qquad (8)$$

It then is possible to solve for $\log K_{RV}$ using the material balance equations 2a, 3a, and 4a so that

$$\log K_{RV} = \frac{E - E_0'}{s/2} +$$
$$\log [Hg_t] \left(\frac{[R_t]}{[V_t] - [Hg_t]} - 1 \right) + \log K_{HgV} \qquad (9)$$

Thus the stability constants of 1:1 metal–HEDTA species can be obtained directly from the potential of the mercury electrode, the total concentrations of metal ions, and the concentration of the chelating agent, provided the mercury–chelate stability constant is known.

The mercury–HEDTA stability constant, upon which other constants measured by the mercury electrode method depend, may be found by measuring the potential of a mercury electrode immersed in a solution of mercuric ion and HEDTA. The stability constant for the mercury(II) chelate is defined as

$$K_{HgV} = \frac{[HgV^-]}{[Hg^{2+}][V^{3-}]} \qquad (10)$$

The complete material balance equations for a solution of mercury(II) and an excess of chelating agent are

$$[Hg_t] = [HHgV] + [HgV^-] + [HgVOH^{2-}] \qquad (11)$$

and

$$[V_t] = [HHgV] + [HgV^-] + [HgVOH^{2-}] + \sum_{n=0}^{3} [H_nV^{n-3}] \qquad (12)$$

Equation 11 then is subtracted from (12) to give

$$[V_t] - [Hg_t] = \sum_{n=0}^{3} [H_nV^{n-3}] \qquad (13)$$

To simplify matters equivalent values in terms of formation constants are substituted for [HHgV] and [HgVOH^{2-}] in (11) and (12), that is

$$[HHgV] = [H^+][HgV^-]K^H{}_{HHgV} \qquad (14)$$

and

$$[HgVOH^{2-}] = [OH^-][HgV^-]K^{OH}{}_{HgVOH} \qquad (15)$$

(7) G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **40**, 1773 (1957).

This gives

$$[Hg_t] = [HgV^-]\alpha \qquad (11a)$$

where

$$\alpha = 1 + [H^+]K^H_{HHgV} + [OH^-]K^{OH}_{HgVOH}$$

Equation 13 may be expressed in terms of the acid association constants of the ligand, $K_n = [H_nV^{n-3}]/[H^+][H_{n-1}V^{n-4}]$, and $[V^{3-}]$. Thus

$$[V_t] - [Hg_t] = [V^{3-}]\{1 + K_1[H^+] + \\ K_1K_2[H^+]^2 + K_1K_2K_3[H^+]^3\} \quad (16)$$

or

$$[V_t] - [Hg_t] = [V^{3-}]\phi \qquad (16a)$$

where

$$\phi = 1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_2K_3[H^+]^3$$

Equations 11a and 16a can be substituted into the expression for the mercury–chelate stability constant to give

$$K_{HgV} = \frac{[Hg_t]\phi}{\alpha[Hg^{2+}]\{[V_t] - [Hg_t]\}} \qquad (17)$$

ϕ can be calculated from the measured pH and the acid association constants of HEDTA, and the concentration of Hg^{2+} can be measured with the mercury electrode.

Experimental

Preparation of Solutions.—The HEDTA was obtained from Geigy Industrial Chemicals and was purified further by a double recrystallization from ethanol. The solution of chelating agent was standardized by potentiometric titration with standard potassium hydroxide and against a standard mercuric nitrate solution using the mercury indicator electrode.[8]

The rare earths were supplied as oxides by the rare earth separation group at the Ames Laboratory of the Atomic Energy Commission and were 99.9% pure or better. Stock solutions of the rare earth nitrates were prepared by dissolving the respective oxides in nitric acid. Aliquots of each solution were titrated potentiometrically to establish the pH of the neutral point, and the stock solutions were adjusted to the proper pH values. Standardization was done gravimetrically by precipitation with oxalic acid, followed by ignition to the oxide.

Carbonate-free potassium hydroxide was prepared by the method of Powell and Hiller[9] and was standardized against potassium acid phthalate. A standard solution of mercuric nitrate was prepared by dissolving reagent grade oxide in nitric acid. The solution was checked against the standard solution of HEDTA using the mercury indicator electrode.

Procedure.—For the determination of the mercury–HEDTA stability constant, two solutions were prepared

(8) C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **25**, 1640 (1953).

(9) J. E. Powell and M. A. Hiller, *J. Chem. Educ.*, **34**, 33 (1957).

having different relative concentrations of mercury(II) and chelating agent. A drop of metallic mercury was added to each of the solutions, which were left in a 20° constant temperature bath for 24 hr. Aliquots of each solution then were transferred to a titration cell and the potential of the mercury electrode and the pH of the system were measured as the solutions were titrated with base.

The acid association constants of HEDTA have been determined at 29.6° by Chaberek and Martell[10] and by Wheelwright[11] at 25°. The values at 20° were found from a plot of log K *vs.* $1/T$ using these values and are shown in Table I.

Ionic strength	Temp., °C.	log K_1	log K_2	log K_3
0.10	29.6	9.73	5.33	2.60
.10	25	9.89	5.41	2.90
.10	20	10.09	5.50	3.23

The value of log K_{HgV}, based on fifteen measurements in the pH range 3.78–5.37, was 20.30 ± 0.06 (95% confidence). The data upon which this value is based may be found in the doctoral dissertation of Mackey.[12] Holloway[13] has determined log K_{HgV} by means of the mercury electrode at 25°. Considering the temperature difference, his value of 20.1 ± 0.1 is in good agreement with our value.

For the determination of the rare earth–HEDTA stability constants, two sets of solutions with different concentrations also were prepared in the case of each rare earth. A drop of mercury was added to each of the solutions, which were left in the 20° constant temperature bath for 24 hr. Each solution was placed in the titration cell, where the pH and the potential of the mercury electrode were measured as the pH was varied from approximately 3.5 to 4.5. The number of measurements with each individual rare earth varied from 10 to 13. The average values of log K_{RV} and the intervals of 95% confidence, including the above-cited uncertainty in the value of log K_{HgV}, are given in Table II. Values reported by other investigators have been included for comparison, although they were determined at 25° instead of 20°.

Discussion

It can be seen that the present K_{RV} values, measured at 20°, are substantially higher than previous values obtained at 25°. The average displacement between our data and the data of Spedding, *et al.*,[1b] is 0.48 log unit, while the average displacement between our data and the 25° data of Moeller, *et al.*,[2] is 0.30 unit. A close examination of the work of Spedding, *et al.*, reveals that these investigators used a value for log K_{CuV}

(10) S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 1477 (1955).

(11) E. J. Wheelwright, doctoral dissertation, Iowa State University, Ames, Iowa, 1955.

(12) J. L. Mackey, doctoral dissertation, Iowa State University, Ames, Iowa, 1960.

(13) J. H. Holloway, *Dissertation Abstr.*, **20**, 2588 (1960).

TABLE II

STABILITY CONSTANTS OF
RARE EARTH–HEDTA CHELATES

Metal	$\log K_{RV}{}^a$ Hg electrode (20°)	$\log K_{RV}{}^b$ modified pH[1] (25°)	$\log K_{RV}$ polaro- graphic[1] (25°)	$\log K_{RV}$ unknown[2] (25°)
La	13.82 ± 0.07	13.22	...	13.46
Ce	14.45 ± 0.08	14.08	...	14.11
Pr	14.96 ± 0.08	14.39	...	14.61
Nd	15.16 ± 0.08	14.71	...	14.86
Sm	15.64 ± 0.08	15.15	15.3	15.28
Eu	15.62 ± 0.08	15.21	...	15.35
Gd	15.44 ± 0.07	15.10	15.4	15.22
Tb	15.55 ± 0.08	15.10	...	15.33
Dy	15.51 ± 0.08	15.08	15.3	15.30
Ho	15.55 ± 0.07	15.08	15.4	15.32
Er	15.61 ± 0.07	15.17	15.4	15.42
Tm	16.00 ± 0.08	15.38	15.5	15.60
Yb	16.17 ± 0.09	15.64	15.8	15.89
Lu	16.25 ± 0.11	15.79	16.0	15.88
Y	15.03 ± 0.07	14.49	14.8	14.65

[a] The limits given represent 95% confidence including the possible deviation in log K_{HgV}. [b] Although these measurements were made at 25°, the value of log K_{CuV}, upon which they depend, was measured at 29.6°. This is tantamount to making the measurements at 29.6°, and accounts for the displacement of approximately 0.2 log unit between the log K_{RV} values listed in columns 2 and 4.

obtained at 29.6° in computing the 25° values of log K_{RV}, under the assumption that the temperature dependence of log K_{CuV} was negligible. It can be seen that log K_1 (Table I), the first acid association constant of the ligand, varied by 0.16 log unit over a temperature range of 4.6 degrees. Furthermore, the value of log K_{HgV} increased 0.2 unit (from 20.1 to 20.3) when the temperature was decreased 5.0 degrees (from 25 to 20°). Employing the 29.6° value of log K_{CuV} to compute log K_{RV} values from the 25° values of K_{ex} = $K_{Cutren}K_{RV}$-/$K_{H_3 tren}K_{CuV}$ is tantamount to making the K_{RV} measurements at 29.6° instead of 25°, if K_{ex} is not temperature dependent. This

assumption is not unreasonable. Note that K_{ex} would be constant if K_{Cutren} and $K_{H_3 tren}$ changed with temperature at the same rate and changes in K_{RV} and K_{CuV} were proportional. If the data of Spedding, *et al.*, actually approximate measurements at 29.6°, the trend observed in the three sets of data can be attributed primarily to temperature dependence of log K_{RV}.

All three sets show a depressed value of log K_{RV} at gadolinium. Due to the depression in the gadolinium–HEDTA chelate stability, it would appear that gadolinium should elute from a cation-exchange column between samarium and neodymium, rather than in the monotonic order observed with citrate and EDTA (Tb–Gd–Eu). The actual order observed with 0.018 M HEDTA at pH 7.5 is Eu–Gd–Sm. Consequently, the depression in stability is real. That the middle lanthanons, terbium through holmium, do not elute ahead of europium and samarium with this eluent can be explained by the small but significant ordering influence of the cation exchanger itself,[14] which must be considered when chelate stabilities are not markedly different. In the case of gadolinium this ordering is sufficient to counteract the decreased stability of gadolinium to some extent and to permit gadolinium to precede samarium, only one position out of monotonic order instead of two.

The ordering influence of the exchange medium likewise accounts for the elution of yttrium between samarium and neodymium, rather than between neodymium and praseodymium as stability data alone would predict.

(14) J. P. Surls and G. R. Choppin, *J. Am. Chem. Soc.*, **79**, 855 (1957).