was measured at constant ionic strength. Since the activity coefficient of an ion in dilute solution is a function of the total ionic strength of the solution, the activity coefficients of the ionic species, at constant ionic strength, will not vary with changes in the actual concentration of the species. An "equilibrium constant" can then be determined on the basis of concentration rather than activities of the ions involved in the reaction. This constant, however, is not of thermodynamic significance but serves only to characterize the reaction taking place. For these measurements, a weighed amount of $FeCl_2 \cdot 2H_2O$ was added to the cell together with sufficient recrystallized KCl to bring the total ionic strength to a value of 0.50. The data and results, tabulated in Table II, substantiate the conclusions arrived at by the "activity" method.

TABLE 11

Moles $FeCl_2$/1000 g. H_2O	pH	$K_1 \times 10^8$
0.022	4.41	6.9
.036	4.30	6.7
.045	4.26	6.8
.050	4.23	6.9
.071	4.16	6.8

The second basic dissociation constant, K_{b2}, of ferrous hydroxide for the reaction

$$FeOH^+ \leftrightarrows Fe^{++} + OH^-$$

can be calculated from the hydrolysis constant and the ion product of water

$$K_{b2} = \frac{a_{Fe^{++}}\, a_{OH^-}}{a_{FeOH^+}} = \frac{K_w}{K_1}$$

$$K_{b2} = \frac{1 \times 10^{-14}}{1.12 \times 0^{-8}} = 8.3 \times 10^{-7}$$

The standard free energy of the reaction governed by the thermodynamic constant may be calculated from the expression

$$\Delta F^\circ = -RT \ln K$$

This gives, for the free energy of the hydrolysis of ferrous chloride

$$\Delta F^\circ = 11000 \text{ cal./mole}$$

and, for the free energy of the secondary dissociation of ferrous hydroxide

$$\Delta F^\circ = 8300 \text{ cal./mole}$$

The authors wish to acknowledge gratefully the support of the Charles F. Kettering Foundation in sponsoring this work.

DETROIT 1, MICHIGAN

[CONTRIBUTION FROM WESTINGHOUSE RESEARCH LABORATORIES]

The Viscosities of Aqueous Solutions Containing Metal Chelates Derived from Ethylenediaminetetraacetate[1]

BY ROBERT G. CHARLES

RECEIVED MARCH 22, 1956

The viscosities of dilute aqueous solutions containing divalent metal chelates of ethylenediaminetetraacetate have been determined. For comparison the viscosities of solutions containing the simple dihydrogen-, monohydrogen- and ethylenediaminetetraacetate anions also have been studied. The viscosities of all such solutions can be related to concentration by the equation of Jones and Dole. The Jones–Dole viscosity B-coefficients characteristic of the simple anions increase in the order dihydrogen-, monohydrogen-, ethylenediaminetetraacetate. B-coefficients characteristic of the metal chelates were found to be related to quantities involving metal ion electronegativity (or second ionization potential of the metal), and reciprocal metal cation radius. The results obtained suggest that all the chelates studied, with the exception of the lead chelate, have similar structures in solution, involving the same number of ligand groups donated by the ethylenediaminetetraacetate ion to the metal cation.

Ethylenediaminetetraacetic acid has received considerable attention in recent years due to the ability of the ethylenediaminetetraacetate (EDTA) ion to react with a large number of different metal ions in solution to form water soluble metal chelates.[2] Despite the great amount of work done on such reactions, there is comparatively little information available concerning the structures of such complexes in solution, particularly in regard to the number of reactive groups of the EDTA ion actually bonded to the metal atom. It was felt that a study of some of the fundamental physical properties of aqueous solutions containing such chelates might prove profitable in this respect. A study has accordingly been made of the viscosities of dilute solutions containing the chelates resulting from the reaction of EDTA with a number of different divalent metal cations. For comparison, viscosities were also determined for solutions containing the EDTA ion itself and two other anions derived from ethylenediaminetetraacetic acid (H_4 EDTA), through the stepwise loss of protons: dihydrogen ethylenediaminetetraacetate (H_2 EDTA), and monohydrogen ethylenediaminetetraacetate (HEDTA).

Experimental

Reagents.—Bersworth reagent grade disodium dihydrogen ethylenediaminetetraacetate (Na_2H_2EDTA) dihydrate was further purified by the method of Blaedel and Knight.[3] Ethylenediaminetetraacetic acid was prepared by acidifying a solution of the disodium salt, filtering and washing the precipitate, and drying the precipitate at 110°.[4] Approximately one molar metal nitrate solutions were prepared and standardized as described previously.[4] The standard sodium and potassium hydroxide solutions employed were carbonate free. Disodium calcium ethylenediaminetetraacetate ($Na_2CaEDTA$) and the corresponding Mg compound ($Na_2MgEDTA$) were kindly donated by the Alrose Chemical Company. They were purified by dissolving in a small

---

(1) Presented, in part, at the Cincinnati Meeting of the American Chemical Society, April, 1955.

(2) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hill, Inc., New York, N. Y., 1952.

(3) W. J. Blaedel and H. J. Knight, *Anal. Chem.*, **26**, 741 (1954).

(4) R. G. Charles, THIS JOURNAL, **76**, 5854 (1954).

amount of water, filtering, and precipitating with an excess of ethanol (for CaEDTA) or methanol (for MgEDTA). The purified salts were dried at 80°.

Solutions.—Solutions containing the H_2EDTA ion were made up by weight from the purified disodium salt and distilled water.

The most concentrated solution containing the HEDTA ion was prepared by adding the calculated amount of standard sodium hydroxide solution to a weighed quantity of Na_2H_2EDTA and diluting to volume in a volumetric flask, to give a solution of 0.2500 *M* in Na_3HEDTA. More dilute solutions were prepared from this solution by volumetric dilution.

The EDTA ion has been reported[5] to form a complex of significant stability with Na^+. No similar complex appears to exist with K^+. A solution 0.1000 *M* in K_4EDTA was prepared from the calculated amounts of H_4EDTA and standard potassium hydroxide. The other solutions were obtained by dilution.

In order to avoid the necessity of separately preparing and purifying salts of each of the eleven metal chelate anions studied, the procedure was adopted of forming the required ions in solution. The calculated amounts of Na_2H_2EDTA, NaOH solution and metal nitrate solutions were mixed in a volumetric flask and made up to volume with distilled water. The resulting solutions were 0.1007 *M* in Na_2MEDTA (where M represents the divalent metal employed) and 0.2014 *M* in $NaNO_3$. Solutions 0.0504 *M* in Na_2MEDTA and 0.1007 *M* in $NaNO_3$ were prepared by volumetric dilution of the above solutions. As described below, results obtained for solutions containing $NaNO_3$ were corrected for the presence of Na^+ and NO_3^- ions. To establish the validity of the procedure, aqueous solutions containing only $Na_2MgEDTA$ or $Na_2CaEDTA$ (no $NaNO_3$) were also studied. These solutions were prepared by dissolving the purified salts in distilled water. The resulting solutions were analyzed for Mg or Ca by conventional methods, after destroying the organic portion of the complexes by digesting with acid.

Measurements.—Densities of the solutions were determined with a 25-ml. pycnometer of the Weld type.[6] This was recalibrated daily with distilled water. Measurements were made in a constant temperature water-bath maintained at 30 ± 0.01°. Weights were corrected *in vacuo*.

Viscosities were determined with Cannon–Fenske capillary viscometers having efflux times greater than 200 seconds.[7] The viscometers were recalibrated with distilled water before each series of measurements. Efflux times were measured with a stopwatch to the nearest 0.1 second. At least two runs were made for each solution. Efflux times were easily reproducible to 0.2 second. Measurements were made in the same constant temperature bath used for the densities.

Calculations.—Viscosities were calculated from the efflux times and densities of the solutions in the usual manner. No kinetic energy corrections were made.

It was found convenient, for each of the systems studied, to express the variation of viscosity with solute concentration by means of the Jones–Dole equation 1[8-10]

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc \qquad (1)$$

η = viscosity of solution
η_0 = viscosity of water
c = solute molarity
A and B = constants characteristic of the solute

The Jones–Dole equation, as such, has been used largely to describe the viscosity behavior of aqueous solutions of inorganic electrolytes.[10] Examination of viscosity data for aqueous solutions of a variety of organic substances,[11] however, shows that (1) applied reasonably well to these also, both for organic salts and also for solutions containing neutral organic molecules.

For solutions containing Na_2H_2EDTA, Na_3HEDTA, K_4EDTA, $Na_2MgEDTA$ or $Na_2CaEDTA$, the constants A and B were evaluated by a plot of $((\eta/\eta_0) - 1)/\sqrt{c}$ *vs.* $\sqrt{c}$. A straight line was obtained in each case at concentrations below about 0.16 *M*. In each case A was found to be within experimental error of zero. The constants B for the solutions containing $NaNO_3$ were taken to be equal to the quantity $((\eta/\eta_0) - 1)/c$ for the more concentrated of the two solutions in each case. Since the error $(\eta/\eta_0) - 1$ is greater for the more dilute solutions containing $NaNO_3$, the data obtained for the latter solutions were used only to establish the general validity of the above procedure, *i.e.*, that $A \approx 0$. It should be pointed out that a small finite value for A, comparable to the values found for other salts,[9] would not significantly alter the values obtained here for B.

It has been shown to be true, for a wide variety of solutions, that B in equation 1 is composed additively of contributions from each of the solute species present in solution.[8-10] Based on this observation it has been found possible to assign constant B values to a number of individual ions, which values, for sufficiently dilute solutions, are independent of the other kinds of ions which may also be present in solution. By using these published values,[9,10] and the values of B found for the solutions studied in the present work it becomes possible to calculate B values characteristic of each of the individual simple anions, or chelates, derived from H_4EDTA. For example the B value characteristic of the simple anions derived from H_4EDTA are given, respectively, by (2), (3) and (4)

$$B_{\mathrm{H_2EDTA}} = B_{\mathrm{soln}} - 2B_{\mathrm{Na^+}} \qquad (2)$$

$$B_{\mathrm{HEDTA}} = B_{\mathrm{soln}} - 3B_{\mathrm{Na^+}} \qquad (3)$$

$$B_{\mathrm{EDTA}} = B_{\mathrm{soln}} - 4B_{\mathrm{K^+}} \qquad (4)$$

To calculate the B values characteristic of the EDTA metal chelate anions from data obtained for solutions containing Na_2MEDTA and $NaNO_3$, equation 5 was used.

$$B_{\mathrm{MEDTA}} = B_{\mathrm{soln}} - 4B_{\mathrm{Na^+}} - 2B_{\mathrm{NO_3^-}} \qquad (5)$$

It should be pointed out that the values of B for the anions or chelates derived from H_4EDTA are very much larger than B for any of the other ions present in the solutions. The application of equations 2 through 5 therefore consists essentially of subtracting a relatively small correction term from B_{soln}. It was found that B values calculated for MgEDTA and CaEDTA for solutions containing only $Na_2MgEDTA$ or $Na_2MgEDTA$ were, in both cases, about 0.04 unit lower than the corresponding quantities obtained for solutions also containing $NaNO_3$. This difference does not greatly exceed experimental error. The empirical correction factor 0.04 was nevertheless subtracted from all the values calculated from equation 5.

B values and the data used in their calculation are given in Tables I, II and III. Since the data obtained for solutions 0.0504 *M* in MEDTA, and containing $NaNO_3$, were not used in subsequent calculations, they are not included in Table III.

Discussion

From Table I it is noted that the Jones—Dole B values characteristic of the simple anions derived from H_4EDTA increase in the order $B_{\mathrm{H_2EDTA}} < B_{\mathrm{HEDTA}} < B_{\mathrm{EDTA}}$. It was of interest to compare these values with the B values for other organic acids and their conjugate bases. Since few such quantities are recorded in the literature a number of values have been calculated from existing viscosity data[9,11,12] and are listed in Table IV. There are several conclusions to be drawn from Table IV. First, in agreement with the results of the present study, the loss of a proton by an acid invariably leads to a conjugate base characterized by a higher value of B than that of the parent acid. This is true regardless of whether the acid hydrogen

---

(5) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1942).

(6) A. Weissberger, Editor, "Physical Methods of Organic Chemistry," Vol. 1, Second Ed., Interscience Publishing Inc., New York, N. Y., 1949, p. 265.

(7) M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 298 (1938).

(8) G. Jones and M. Dole, THIS JOURNAL, **51**, 2950 (1929).

(9) R. W. Gurney, "Ionic Processes in Solution," McGraw–Hill Book Co., New York, N. Y., 1953.

(10) E. Asmus, *Z. Naturforschung*, **42**, 489 (1949).

(11) "International Critical Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1929.

(12) G. Hedestrand, *Z. anorg. allgem. Chem.*, **124**, 153 (1922).

TABLE I

VISCOSITY AND DENSITY DATA FOR AQUEOUS SOLUTIONS OF SALTS DERIVED FROM ETHYLENEDIAMINETETRAACETIC ACID

Salt	Concn. (moles/l.)	d^{30}_4	η_{30} (cp.)
Na_2H_2EDTA	0.0000	0.9957	0.8007
	.0189	0.9991	.8171
	.0341	1.0016	.8282
	.0784	1.0095	.8636
	.1391	1.0202	.9140
	.3178	1.0509	1.0913
	B_{soln} = 1.00	B_{H_2EDTA} = 0.83	
Na_3HEDTA	0.0117	0.9982	0.8152
	.0313	1.0022	.8367
	.0469	1.0053	.8529
	.0625	1.0084	.8701
	.0938	1.0148	.9044
	.2500	1.0455	1.0996
	B_{soln} = 1.38	B_{HEDTA} = 1.12	
K_4EDTA	0.0100	0.9985	0.8122
	.0200	1.0011	.8231
	.0400	1.0066	.8440
	.0750	1.0160	.8821
	.1000	1.0226	.9089
	B_{soln} = 1.34	B_{EDTA} = 1.37	

TABLE II

VISCOSITY AND DENSITY DATA FOR AQUEOUS SOLUTIONS CONTAINING DISODIUM METAL ETHYLENEDIAMINETETRAACETATES

Salt	Concn. (moles/l.)	d^{30}_4	η_{30} (cp.)
$Na_2CaEDTA$	0.0057	0.9969	0.8067
	.0295	1.0019	.8296
	.0560	1.0074	.8554
	.1011	1.0169	.9018
	.1653	1.0290	.9670
	.2682	1.0494	1.0950
	B_{soln} = 1.24	B_{CaEDTA} = 1.07	
$Na_2MgEDTA$	0.0109	0.9977	0.8113
	.0218	0.9997	.8200
	.0418	1.0033	.8360
	.0589	1.0064	.8503
	.0903	1.0120	.8919
	.2027	1.0333	.9888
	B_{soln} = 1.06	B_{MgEDTA} = 0.89	

TABLE III

VISCOSITIES AND DENSITIES OF AQUEOUS SOLUTIONS CONTAINING DISODIUM METAL ETHYLENEDIAMINETETRAACETATES AND $NaNO_3$[a]

Metal	d^{30}_4	η_{30}	B_{soln}	B_{MEDTA}
Cu	1.0300	0.8904	1.11	0.82
Ni	1.0296	.8937	1.15	.86
Co	1.0296	.8950	1.17	.88
Zn	1.0302	.8953	1.17	.88
Mn	1.0300	.8976	1.20	.91
Cd	1.0350	.9028	1.27	.98
Pb	1.0431	.8907	1.12	.83
Mg	1.0255	.8953	1.17	.88
Ca	1.0283	.9106	1.36	1.07
Sr	1.0322	.9155	1.42	1.13
Ba	1.0345	.9250	1.54	1.17

[a] Solutions are 0.1007 *M* in Na_2MEDTA and 0.2014 *M* in $NaNO_3$ except for Ba. Latter solution is 0.1007 *M* in $Na_2BaEDTA$ and 0.2014 *M* in NaCl.

in bonded to nitrogen or oxygen, and regardless of whether the acid is positively charged, neutral, or a zwitterion (or, on the basis of the present study, negatively charged). The *B* values listed in Table IV are, in all cases, appreciably smaller than B_{H_2EDTA}, B_{HEDTA} or B_{EDTA}. The larger values found for the latter ions are probably associated with the fact that each of these ions has a larger number of groups capable of interacting with the solvent than any of the species listed in Table IV.

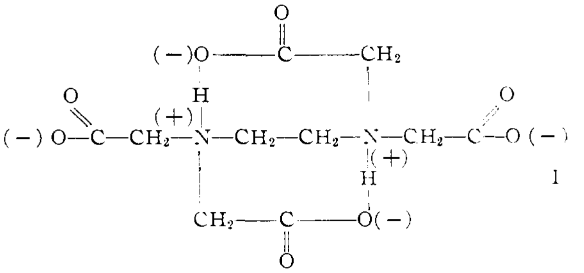
TABLE IV

VISCOSITY *B*-VALUES FOR ACIDS AND THEIR CONJUGATE BASES IN AQUEOUS SOLUTION[a]

	B	Temp., °C.	$B_{CB} - B_{acid}$[d]
CH_3COOH	0.12[b]	25	0.13
CH_3COO^-	.25[b]	25	
CH_3CH_2COOH	.19	25	.15
$CH_3CH_2COO^-$	.34	25	
$CH_3CH_2CH_2COOH$	.25	25	.18
$CH_3CH_2CH_2COO^-$	.43	25	
$(CH_3)_2NH_2^+$	.11	25	.13
$(CH_3)_2NH$	.24	25	
$(CH_3)_3NH^+$	.41	25	.14
$(CH_3)_3N$	.55	25	
$^+NH_3-CH_2-COO^-$	.14[c]	18	.10
$NH_2-CH_2-COO^-$	.24[c]	18	
$^+NH_3-CH_2-COO^-$	.15[c]	40	.12
$NH_2-CH_2-COO^-$	.27[c]	40	
$CH_3-CH(NH_3^+)-COO^-$	.27[c]	18	.11
$CH_3-CH(NH_2)-COO^-$	.25[c] .38[l] .37[c]	40 18 40	.12

[a] Except where noted, values are estimated from viscosity data given in the International Critical Tables.[11] Values of *B* for ions were calculated from *B* for the salt solution by subtracting the values of *B* for the other ions present in solution.[9,10] [b] Reference 9. [c] Calculated from data given in reference 12. [d] CB = conjugate base.

The quantities ($B_{CB} - B_{acid}$) listed in Table IV are of interest. These are roughly constant regardless of the type acid involved, averaging 0.13 ± 0.02. The corresponding quantities ($B_{HEDTA} - B_{H_2EDTA}$) and ($B_{EDTA} - B_{HEDTA}$), from the present work, were found to be 0.29 and 0.25, respectively, very nearly twice the average for the species listed in Table IV. A possible explanation for these larger values involves the presence of some type of internal hydrogen bonding within the two ions H_2EDTA and HEDTA. The release of a hydrogen, bonded in this way to two different atoms, would make available two groups for interaction with the solvent, rather than one as is the case for the acids in Table IV. A plausible structure of this type for the H_2EDTA ion, which does not seem to have been previously suggested, is I.


I

A Fisher–Hirschfelder model of this structure shows it to be essentially strain free and shows it also to have the favored linear O---H—N configuration for both hydrogen bonds.

Too close a comparison of B_{H_2EDTA}, B_{HEDTA} and B_{EDTA} with the B values found for the metal chelate anions of EDTA (Table III) is probably not justified in view of the obvious differences in structure between the two classes of ions. In particular, the ions HEDTA and EDTA have different over-all charges (-3 and -4, respectively) than the metal chelate anions studied here (charge $= -2$). H_2EDTA, however, has the same over-all charge as the metal chelates studied. B_{H_2EDTA} is approximately the same as the B values found for PbEDTA and CuEDTA and is not greatly different from the B values for the Ni, Zn and Co chelates. If this agreement is not fortuitous it may indicate a similarity in shape between H_2-EDTA and the metal chelate anions mentioned. This suggests some sort of chelated structure for H_2EDTA, structure I being one such possibility.

B-values found for the metal chelate anions of EDTA vary from 0.82 to 1.17. Several factors are probably important in determining the value of B for a given chelate. These include (1) the size of the ion, (2) the number of "free" reactive groups derived from EDTA, not bonded to the metal cation, and (3) the polarity of the metal–ligand bonds. A fourth factor, the shape of the ion, is probably determined largely by factor (2). A fifth factor, the over-all charge of the anion, is constant throughout the series studied.

The size of the MEDTA ions should be a function of the metal cation radius, at least for those ions having the same number of groups from EDTA bonded to the metal. Van Uitert and Fernelius[13] have suggested that metal–ligand ionic character (and hence polarity) is, for a given chelating agent, a function of the electronegativity of the bonded metal cation. It was found, in the present work, that the empirical equation 6, which involves metal cation radius[14] (r) and metal ion electronegativity[15] (X_M), represents all the data obtained within experimental error, with the single exception of the data for PbEDTA. A similar equation 7, involving the second ionization potential of the metal, represents the data equally well.[16] The second ionization potential of a metal has been used as a measure of divalent metal ion electronegativity by several authors.[13,17] While probably not as fundamental a measure of electronegativity as the values of Haissinsky, second ionization potentials are known with much greater accuracy than are the Haissinsky electronegativity values.

$$B_{MEDTA} = 1.55 - 0.332/r - 0.136X_M \qquad (6)$$

$$B_{MEDTA} = 1.54 - 0.280/r - 0.0162I_2 \qquad (7)$$

In Fig. 1 the B_{MEDTA} values calculated from equations 6 and 7 are plotted against the corresponding experimental values. The satisfactory agreement of all the points, except that for Pb-EDTA, to the two straight lines indicates that metal ion radius and electronegativity are the only important variables affecting B_{MEDTA} for this series of chelates. A pronounced difference in structure for a given chelate, such as a difference in the number of groups from the EDTA ion bonded to the metal, would be expected to affect measurably the value found for B_{MEDTA}. It therefore seems reasonable to conclude from Fig. 1 that those chelates whose points lie near the two lines all have the same gross structure in solution, involving the same number of groups donated by the EDTA ion to the metal.

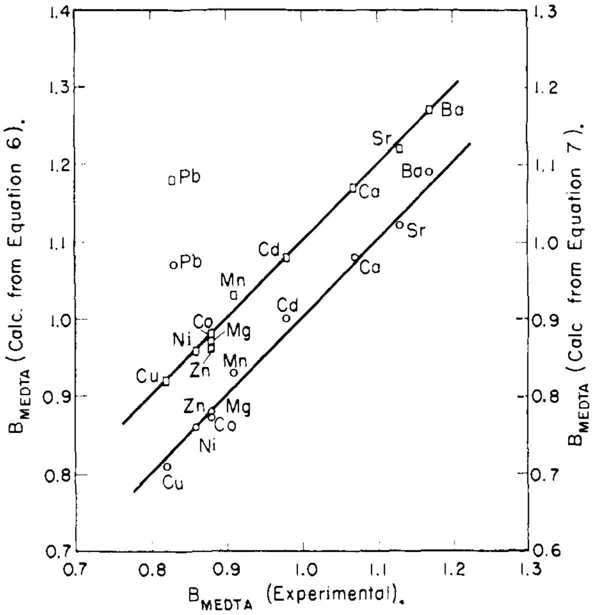


Fig. 1.—Relation between experimental viscosity B-coefficients for ethylenediaminetetraacetate chelates and values calculated from empirical equations 6(○) and 7(□).

The fact that the data for PbEDTA do not fit the observed relationships in Fig. 1 would seem to indicate that PbEDTA differs in structure, in some manner, from the other MEDTA chelates studied. Independent evidence is available supporting such a structure difference. A linear relationship has been shown to exist between the partial molal entropies of aqueous metal cations and $\Delta S°$ for the formation of many of the corresponding EDTA chelates in solution.[4] The data for PbEDTA, however, showed marked disagreement from the observed relationship.[4]

The evidence presented here does not permit a decision to be made between the several structures which have been proposed for MEDTA ions in solution.[18-20] It is of interest that the Cu(II) ion,

---

[13] L. G. Van Uitert and W. C. Fernelius, THIS JOURNAL, **76**, 379 (1954).

[14] R. J. P. Williams, *J. Phys. Chem.*, **58**, 121 (1954).

[15] M. Haissinsky, *J. Phys. Radium*, [8] **7**, 7 (1946).

[16] In the case of the alkaline earth chelates, linear relationships are obtained by plotting B_{MEDTA} separately against *each* of the quantities X_M, I_2 or $1/r$. Straight lines are also obtained for the transition metal chelates by plotting B_{MEDTA} against the same quantities. The lines obtained in the latter case are of different slopes from the corresponding plots for the alkaline earth chelates. These various relationships follow from equations 6 and 7 since, for both the alkaline earth and transition metals, approximately linear relationships exist between X_M and $1/r$ (or between I_2 and $1/r$).

[17] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

[18] S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **74**, 6228 (1952).

[19] R. L. Pecsok, *J. Chem. Ed.*, **29**, 597 (1952).

[20] D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **75**, 4575 (1953).

which is generally considered to be characterized by a coördination number of four, gives rise to an EDTA chelate which apparently has the same gross structure as the other MEDTA chelates studied (with the exception of PbEDTA). This might suggest that all the MEDTA ions, with the possible exception of PbEDTA, have four EDTA groups (presumably the two nitrogens and two carboxyl groups) bonded to the metal. Recent evidence,[21] however, favors a structure for the CuEDTA ion in which all six of the groups from the EDTA, ion are bonded to the metal. This evidence, together with Fig. 1, would seem to favor a hexa-coördinated structure for all the MEDTA ions studied here (again with the possible exception of PbEDTA).

Acknowledgments.—The writer is indebted to Mr. J. F. Reed for a number of the metal analyses and to Dr. H. E. Mahncke, M. Ostrofsky and D. H. Shaffer for very helpful discussion.

PITTSBURGH 35, PA.

[21] S. Kirschner, THIS JOURNAL, **78**, 2372 (1955).

[CONTRIBUTION NO. 1356 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Kinetics of the Iodide-catalyzed Reaction between Cerium(IV) and Arsenic(III)[1]

BY JOHN STANLEY YATES[2] AND HENRY C. THOMAS

RECEIVED JANUARY 19, 1956

The rates at 25° of reactions in sulfuric acid solutions between ceric sulfate and arsenious acid catalyzed by iodide have been measured for a variety of concentrations of reactants and catalyst. A mechanism for the reaction is proposed. Except at low cerium/arsenic ratio, a steady-state equation derived from the mechanism adequately describes the results. Possible limitations of the treatment are discussed.

It is well known that compounds of iodine at quite low concentration are catalysts for the reaction between Ce(IV) and As(III). Micro-determinations of iodine have been based on the effect,[3-5] but the kinetics of the processes involved have not been extensively studied. Stefanovskii[6] and Moore and Anderson[7] have reported studies on the apparently uncatalyzed reaction. The effect of catalysts has been the explicit concern of Anderson, Lasater and Lippman.[8] The present work was undertaken in the hope of finding a reasonable explanation for the somewhat singular behavior of the catalyst in this reaction.

The salient qualitative features of the reaction between ceric sulfate and arsenious acid in sulfuric acid solution are simple and striking. If the solutions are mixed in the absence of added catalysts, the reaction is slow, and reproducible rate determinations are difficult to obtain. In one such experiment of ours, with concentrations about 0.02 N in the reactants and 2 M in sulfuric acid, two hours were required for 50% reaction. If potassium iodide, in amount sufficient to give a concentration of 1.6×10^{-7} M in the reaction mixture, is initially mixed with the *arsenite* solution, the reaction proceeds smoothly and is some 60% complete in ten minutes. If, on the other hand, the iodide is added to the ceric solution 15 minutes or so before this is mixed with the arsenite solution, no catalytic effect is observed—even 20 minutes after mixing no certainly detectable reaction has taken place.

We have measured the kinetic behavior of the catalyzed reaction at 25° and suggest a mechanism which gives an adequate interpretation of all of our experimental results.

Experimental

The experiments were designed so as to permit the independent variation of the initial concentrations of the reactants, the catalyst and of the sulfuric acid. Each of these substances in the form of standardized solutions was introduced volumetrically into the legs of a Λ-shaped reaction vessel. After at least 15 minutes in a water thermostat at 25 ± 0.02°, the solutions were mixed and the reaction allowed to proceed for a measured time interval, when the reaction was quenched by the rapid admixture of a measured excess of standard ferrous sulfate solution. The extent of the reaction was then determined by titrating the excess ferrous ion.

It was shown that ferrous sulfate does not react with any substance in the solution (*e.g.*, arsenate) in such a way as to affect the results of the determinations. To this end the reactions were carried out with a small excess of arsenite and the solutions allowed to stand at elevated temperatures for several hours after the ceric color disappeared. Ferrous sulfate was added and the solution again allowed to stand for periods up to 100 minutes. Titration with ceric sulfate showed that no ferrous ion had been oxidized.

The ceric sulfate used in the rate determinations was prepared *via* hydrous ceric oxide precipitated from reagent grade ammonium hexanitratocerate. A solution of the washed precipitate in a weighed amount of sulfuric acid was standardized against National Bureau of Standards arsenious oxide. The arsenious acid solution used was prepared from Bureau of Standards arsenious oxide and analyzed by titration with ceric sulfate. Solutions of sulfuric acid, prepared by diluting J. T. Baker Analyzed reagent, were standardized through a precipitation of barium sulfate. The catalyst was a very dilute solution of potassium iodide (9.81×10^{-7} M) prepared by successive dilutions of a solution of a weighed amount of reagent grade salt. Ferrous sulfate solution for quenching purposes was kept under hydrogen and standardized each day it was used.

The distribution of the reagents in the legs of the reaction vessels was arranged so as to keep the sulfuric acid concentration nearly the same in both in order to minimize temperature changes on mixing.

The reactions were started by vigorous shaking of the vessels, and times were noted from an electric clock to the

---

(1) The experimental part of this paper has been taken from the dissertation presented in 1944 by John Stanley Yates to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Dr. Yates died in 1945 as the result of a tragic accident in his home. The publication of Dr. Yates' excellent experimental work has been so long delayed because of lack of adequate interpretation.

(3) E. B. Sandell and I. M. Kolthoff, *Microchim. Acta*, **1**, 9 (1937).

(4) H. Yoto and E. Sudo, *J. Chem. Soc. Japan*, **63**, 1324 (1942).

(5) A. Lein and N. Schwartz, *Anal. Chem.*, **23**, 1507 (1951).

(6) V. F. Stefañovskii, *J. Gen. Chem. U. R. S. S.*, **XI**, 970 (1941).

(7) J. W. Moore and R. C. Anderson, THIS JOURNAL, **66**, 1476 (1944).

(8) R. C. Anderson, J. A. Lasater and D. Lippman, *ibid.*, **71**, 2577 (1949).