limited due to the low solubility of the compound. The value for the dipole moment is calculated from an average of the two highest values and, although the selection of these values is not completely justified, the result is probably a close approximation to the true dipole moment.

The high polarity found for $CH_3CN:BF_3$ is consistent with the postulate that the fluorine atoms occupy tetrahedral coördination positions about the boron, with a linear configuration of the carbon, nitrogen and boron atoms. In such a structure there should be large contributions all in the same direction by the $C\equiv N$, N–B and B–F bonds.

Because of the inappreciable solubility of $CH_3CN:BCl_3$ in benzene and other non-polar solvents we were unable to find suitable conditions for measuring its moment. This insolubility in non-polar solvents is strong indication of high polarity for the compound. Ulich and Nespital[12] reported a dipole moment of 7.65 debyes for $CH_3CN:BCl_3$. They gave no data except the final value and did not mention their experimental method so that it is impossible to form an opinion of the accuracy of their figure.

Summary

1. The compounds $CH_3CN:BCl_3$ and $CH_3CN:BF_3$ have been prepared and their properties listed.

2. Saturation vapor pressure measurements have been made. Vapor density measurements lead to the conclusion that the dissociation of these compounds in the vapor phase is virtually complete. From these measurements the heats of dissociation of $CH_3CN:BCl_3(s)$ and $CH_3CN:BF_3(s)$ to the gaseous components are found to be 33.4 and 26.5 kcal., respectively.

3. Heats of formation of $CH_3CN:BCl_3(s)$ and $CH_3CN:BF_3(s)$ from the gaseous components have been determined calorimetrically as 33.8 and 26.5 kcal.

4. Molecular weight determinations made cryoscopically in benzene indicate that the molecule $CH_3CN:BF_3$ exists and is not appreciably dissociated in dilute solutions.

5. Dipole moment measurements on $CH_3CN:BF_3$ indicate that the dipole moment is approximately 5.8 debyes.

ITHACA, NEW YORK RECEIVED JUNE 1, 1944

[12] Ulich and Nespital, *Z. angew. Chem.*, **44**, 752 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Spectrophotometric Studies on Cerium(IV) Sulfate Complex Ions

BY ROBERT LEE MOORE AND ROBBIN C. ANDERSON

There is much evidence for the existence of complex ions in aqueous solutions of cerium(IV) sulfate. This includes observations of transference,[1] electromotive force measurements,[2,3,4] kinetic studies,[5] and the existence of double salts and so-called "cerate" compounds such as $(NH_4)_2Ce(NO_3)_6$,[4] but there is little experimental evidence concerning the actual nature of these complex ions.

In the past several years, the spectrophotometer has been used to study a number of complex ions which show characteristic colors.[6,7,8] Since in general the addition of sulfate to solutions of ceric salts causes readily visible color changes, spectrophotometric studies of cerium(IV) sulfate solutions were undertaken in an attempt to obtain evidence concerning the nature of the complex ions responsible for these color changes.

Experimental

Materials

Cerium(IV) Sulfate Solutions.—These were prepared and standardized by the methods previously described.[5] Ordinary "C. P." cerium(IV) oxide was carefully purified by precipitation of the basic nitrate, and dissolved by digestion with sulfuric acid and dilution with water. The total cerium content was determined by titration with iron (II) ammonium sulfate and the acidity by removing the cerium with oxalate and then titrating with base.

Cerium(IV) Perchlorate Solutions.—These were prepared by a method essentially the same as that described by Smith[9] and Sherrill.[10] Specially purified cerium(IV) oxide was dissolved in sulfuric acid. Cerium(III) oxalate was precipitated and washed free of sulfate. The oxalate was dissolved in nitric acid and the resulting solution digested first with hydrochloric acid and then with perchloric acid to convert to cerium(III) perchlorate. This was oxidized electrolytically, about 97% conversion usually being obtained. The solutions were stored in the dark and standardized just before use by the same methods as used for the cerium(IV) sulfate solutions.

Perchloric Acid.—Solutions were prepared from Baker C. P. 60% perchloric acid and distilled water.

Sodium Sulfate and Sodium Perchlorate.—Solutions of C. P. reagent grade sulfuric acid and perchloric acid were carefully standardized against sodium hydroxide solution. Salt solutions of the desired concentration were then prepared by mixing equivalent quantities of acid and base.

Apparatus and Procedure.—The instrument used was a Beckman Quartz Photoelectric Spectrophotometer[11] covering a range from 200 to 2000 mμ. The wave length scale is accurate to better than 1 mμ and the light transmission measurements are accurate within about 0.2% under the conditions used in this investigation.

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[1] Jones and Soper, *J. Chem. Soc.*, 805 (1935).

[2] Kuntz, THIS JOURNAL, **53**, 98 (1931).

[3] Noyes and Garner, *ibid.*, **58**, 1265 (1936).

[4] Smith and Getz, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 191 (1938).

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

[6] Bent and French, *ibid.*, **63**, 568 (1941).

[7] Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

[8] Rabinowitch and Stockmayer, *ibid.*, **64**, 291 (1942).

[9] Smith, "Cerate Oxidimetry," G. Frederick Smith Chem. Co., Columbus, Ohio, 1942, p. 5.

[10] Sherrill, King and Spooner, THIS JOURNAL, **65**, 170 (1943).

[11] Carey and Beckman, *J. Optical Soc. Am.*, **31**, 682 (1941).

In making optical density measurements, the various proportions of cerium(IV) and sulfate were obtained by mixing cerium(IV) perchlorate and sodium sulfate solutions and diluting to the desired final volume. The acidity of all mixtures was made 2 N by the addition of perchloric acid in order to avoid hydrolysis of the cerium. As varying proportions of cerium(IV) and sulfate were used, sodium perchlorate was added to keep the total ionic strength as nearly constant as possible.

A small amount of auto-reduction accompanies the dilution of the cerium(IV) perchlorate. However, after standing for a short while the rate of change became negligible, and correction could be made by restandardizing the test solutions as soon as possible after the optical density measurements were made.

The spectrophotometer was housed in a constant temperature room held at 25 ± 1.0°. All test solutions were placed in this room several hours in advance so as to attain the temperature of the room.

In making measurements, three cells were used—one containing a blank solution of perchloric acid and the other two containing test solutions. The cells were placed in the instrument and optical density measurements made at two wave lengths. A dozen solutions could be measured in about twenty minutes. Since small temperature variations occur within the instrument, fresh solutions were then used and the series of measurements repeated in reverse order. Comparison of the two series was used to check the extent of experimental error arising from temperature effects, etc.

Calculations.—For a system

$$mA + nB \rightleftharpoons A_mB_n$$

there are two general methods by means of which spectrophotometric methods may be applied to determine m and n.

(a) Limiting Logarithmic Method.—This was the method employed by Bent and French.[6] From the equation for the equilibrium constant for the above system one may obtain the relation

$$\log [A_mB_n] = m \log [A] + n \log [B] - \log K$$

the quantities in brackets denoting activities of the various reagents. From this equation it is evident that if [A] were kept constant and [B] varied, log $[A_mB_n]$ would be a linear function of log [B]. If the logarithm of some quantity—such as the optical density—which is directly proportional to $[A_mB_n]$—be plotted against log [B], a straight line should be obtained, the slope of which would give the value of n.

In systems such as the ceric sulfate solutions, only the total concentration (corresponding to [B]) is available. However, as the solution is diluted and the complex becomes largely dissociated, this concentration approaches the real value. Thus if the logarithm of the optical density were plotted against log [B], a curve would be obtained, but for dilute solutions this curve should approach a straight line of slope n. Similarly, m may be determined.

(b) Method of Continuous Variations.—This method was originally developed by Job and applied to complex ions by Vosburgh and Cooper.[7] If solutions of A and B (each of concentration M moles per liter) are mixed in varying proportions by adding x liters of B to $(1 - x)$ liters of A—thus preparing a series of solutions with a constant total concentration but varying proportions of A and B—the quantity $[A_mB_n]$ reaches a maximum at the point where $n/m = x/(1 - x)$. If A_mB_n has a characteristic color, a graph of the optical density against x should produce a curve showing a maximum point. The location of this maximum will determine a value for n/m.

Preliminary tests showed that the cerium(IV) sulfate solutions show an absorption band beginning at about 540 mμ and absorb very strongly at wave lengths below 480 mμ. The above methods may therefore be applied to solutions containing varying proportions of cerium and sulfate, providing correction is made for any other colored materials present.

Since the cerium(IV) sulfate solutions were prepared by mixing cerium(IV) perchlorate and sodium sulfate, the complex formation would involve some equilibrium such as

$$m\text{Ce(ClO}_4)_4 + n\text{Na}_2\text{SO}_4 \rightleftharpoons \text{Ce}_m(\text{SO}_4)_n(\text{ClO}_4)_{4-2n} + 2n\text{NaClO}_4$$

Sodium sulfate and sodium perchlorate are transparent in the wave lengths used, but it was found that cerium(IV) perchlorate solutions do absorb slightly at wave lengths below 480 mμ. Tests on such solutions also showed that this optical density did not vary with the perchloric acid concentration. There is no evidence for any colored complex involving cerium(IV) and perchlorate ions.

The observed optical densities of the cerium(IV) sulfate mixtures were corrected for the effect of the cerium(IV) perchlorate absorption. For the system above, the optical density would be

$$D_{\text{obs}} = \epsilon_1 c_1 + \epsilon_2 c_2 + \epsilon_3 c_3 + \epsilon_4 c_4$$

where ϵ_1, ϵ_2, etc., and c_1, c_2, etc., denote the extinction coefficients and concentrations of the four reagents as listed. If $\bar{c}_1$ = total original concentration of $\text{Ce(ClO}_4)_4$, and, $\bar{c}_2$ = total original concentration of Na_2SO_4 then

$$c_1 = \bar{c}_1 - mc_3$$
$$c_2 = \bar{c}_2 - nc_3$$
$$c_4 = 2nc_3$$

Substituting in the equation above and solving for c_3 gives

$$c_3 = \frac{D_{\text{obs}} - (\epsilon_1\bar{c}_1 + \epsilon_2\bar{c}_2)}{\epsilon_3 + 2n\epsilon_4 - m\epsilon_1 - n\epsilon_2}$$

ϵ_2 and ϵ_4 are zero in this case, and

$$c_3 \propto D_{\text{obs}} - \epsilon_1\bar{c}_1$$

Thus if the absorption for the total original $\text{Ce(ClO}_4)_4$ is subtracted from the observed optical density, a quantity is obtained which is proportional to the concentration of the cerium(IV) sulfate complex. This is the quantity designated by $\bar{D}$ in the results below.

Results

A typical set of optical density measurements is shown in Table I.

Cerium(IV) Perchlorate.—The results of measurements on cerium(IV) perchlorate solu-

TABLE I

EFFECT OF PERCHLORIC ACID CONCENTRATION ON OPTICAL DENSITY

Solution I: cerium(IV) concentration, 0.0294 *M*; perchloric acid concentration, 1.00 *M*. Solution II: cerium(IV) concentration, 0.0292 *M*; perchloric acid concentration, 3.00 *M*.

λ (mμ)	Optical Densities Soln. I Series 1	Soln. I Series 2	Soln. II Series 1	Soln. II Series 2
420	1.580	1.582	1.555	1.550
430	1.057	1.075	1.023	1.029
440	0.700	0.715	0.680	0.691
450	.460	.477	.452	.460
460	.298	.311	.293	.304
470	.192	.201	.190	.197
480	.123	.130	.124	.132
490	.079	.085	.080	.086
500	.050	.054	.052	.058
510	.032	.036	.032	.038
520	.020	.024	.021	.025

tions of varying concentrations are shown in Fig. 1. The absorption follows Beer's law satisfactorily up to concentrations of about 0.01 *M*. These calibration curves were used to correct the optical density measurements on cerium(IV) sulfate mixtures so as to determine $\bar{D}$ as described above.

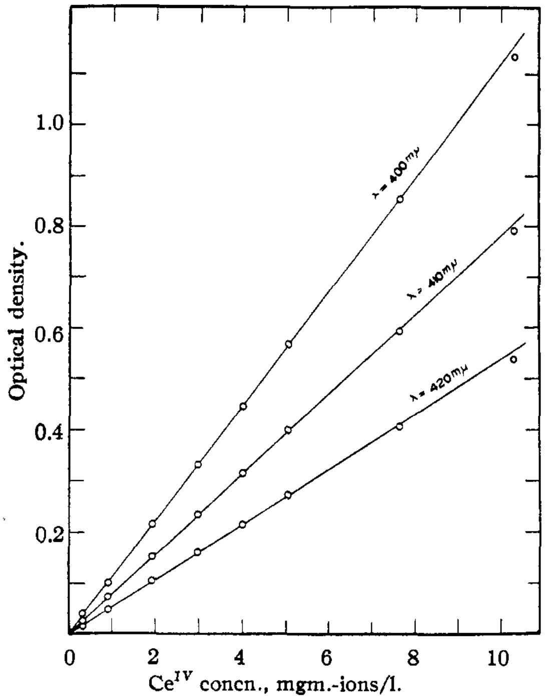

Fig. 1.—Optical density of cerium(IV) perchlorate in 2.00 *M* perchloric acid at 24.5°.

Limiting Logarithmic Method.—In Figs. 2 and 3 are shown typical results for solutions with constant cerium and varying sulfate concentrations and *vice versa*. The dotted lines are calculated assuming values of m and n as indicated.

Such results indicate that in dilute solutions a complex ion containing one cerium(IV) ion and one sulfate is formed.

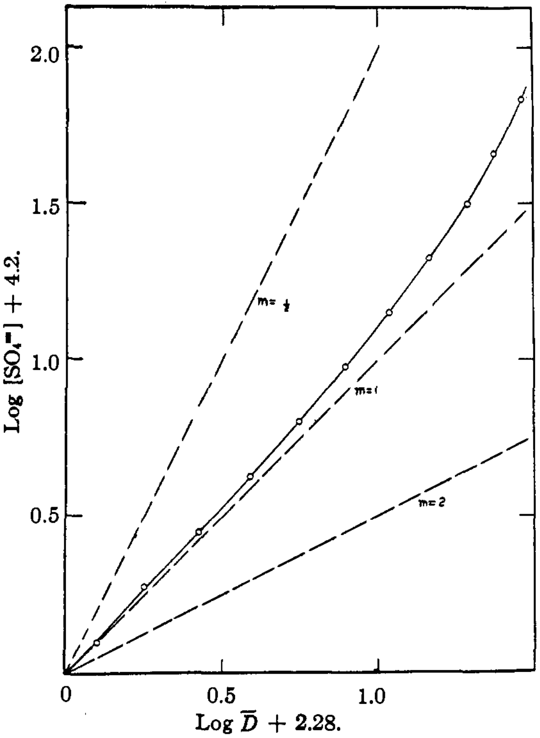

Fig. 2.—Limiting logarithmic method: constant cerium(IV) 0.002 *M*, perchloric acid 2.00 *M*, 24.5°, λ 410 mμ.

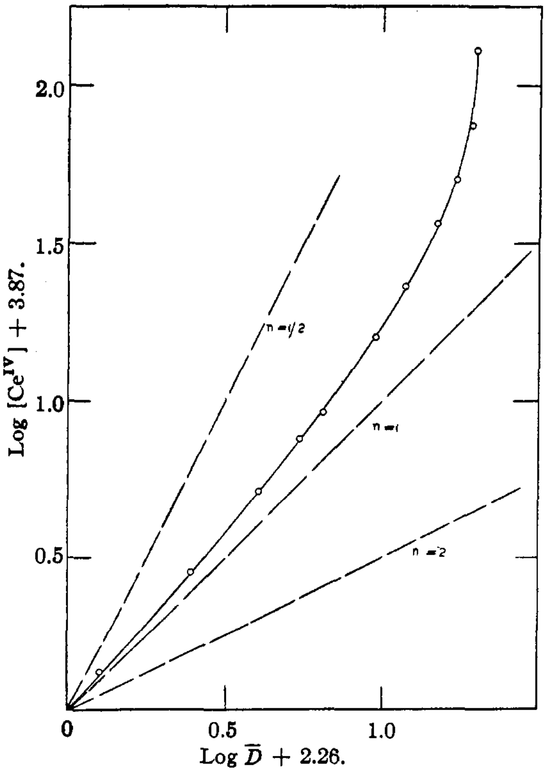

Fig. 3.—Logarithmic method: sulfate 0.00267 *M*, temp. 24°, λ 410 mμ.

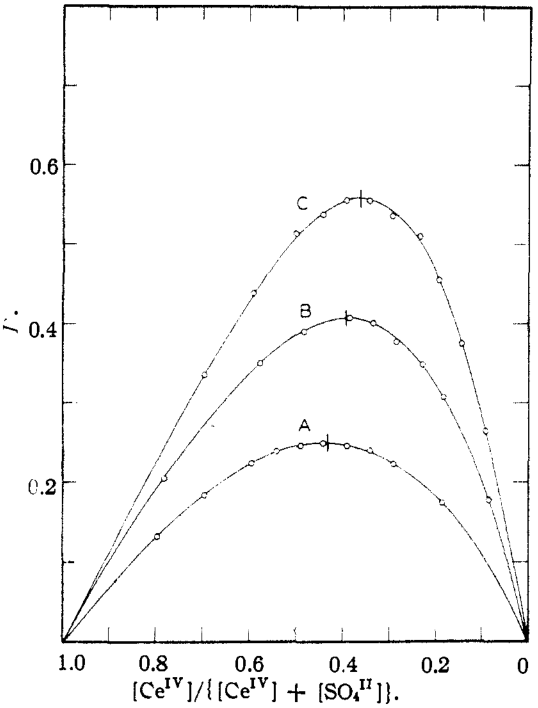

Fig. 4.—Method of continuous variations: A, $[\mathrm{Ce^{IV}}] + [\mathrm{SO_4^{II}}]$ is 0.00493 *M;* B, $[\mathrm{Ce^{IV}}] + [\mathrm{SO_4^{II}}]$ is 0.00988 *M;* C, $[\mathrm{Ce^{IV}}] + [\mathrm{SO_4^{II}}]$ is 0.0198 *M.*

Method of Continuous Variations.—In Fig. 4 are shown some typical results for tests in which three solutions of varying total concentrations were used. The maxima are denoted by a vertical line and were located by drawing a line through the mid-points of chords drawn at various intervals. Tests made with light of different wave lengths showed no variation in the location of the maxima.

The 1:1 ratio of cerium(IV) to sulfate shown by the limiting logarithmic method above would correspond to a maximum at a value of 0.5. The observed maxima deviate very appreciably from this value. However, the limiting logarithmic method essentially determines the ratio of cerium(IV) to sulfate in the complex ions present in the most dilute solutions. It seems unlikely that complex ions containing more than one cerium ion would be formed, but complexes containing more than one sulfate ion (*e. g.*, $\mathrm{Ce(SO_4)_2}$ or $\mathrm{Ce(SO_4)_3^{=}}$) would be feasible in more concentrated solutions. If the various cerium–sulfate linkages cause similar changes in color, the addition of more sulfate ions would tend to shift the optical density maxima toward a higher sulfate–cerium ratio. This would be in accord with the results in Fig. 4.

Further evidence for this explanation is shown in Figs. 5 and 6. In more dilute solutions the 1:1 ratio should be favored and the maxima should fall closer to the value of 0.5. In Fig. 5 it may be seen that if the locations of the maxima are plotted against total concentration, a curve is obtained which may reasonably be extrapolated to 0.5. The results of the method of continuous variations are, therefore, not necessarily in disagreement with those of the limiting logarithmic method.

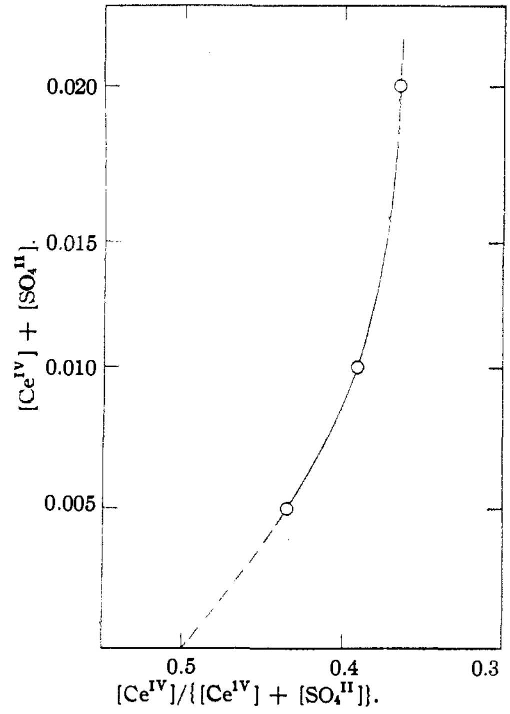

Fig. 5.—Location of maxima.

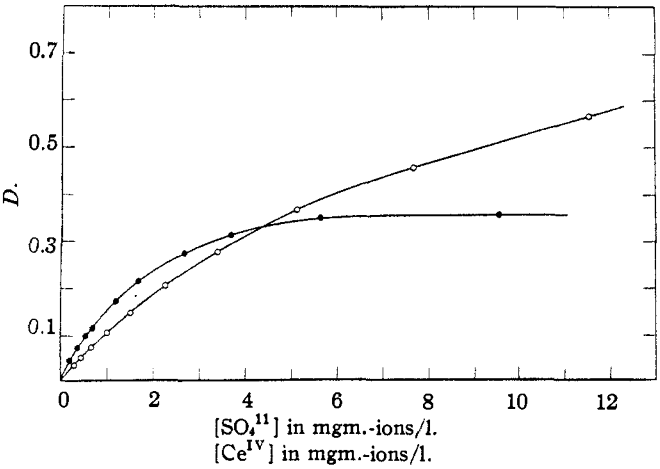

Fig. 6.—●, $[\mathrm{SO_4^{II}}]$ is 0.00267 *M*, $[\mathrm{Ce^{IV}}]$ varying; ○, $[\mathrm{Ce^{IV}}]$ is 0.002 *M*, $[\mathrm{SO_4^{II}}]$ varying.

In Fig. 6 are shown the effects of changing cerium and sulfate concentrations upon $\bar{D}$. It is notable that, if the sulfate concentration is constant, increasing the cerium(IV) concentration increases $\bar{D}$ at first, but later a constant value is reached. This apparently corresponds to a condition in which essentially all sulfate ions are combined in a complex such as $CeSO_4^{++}$. If, however, the cerium(IV) concentration is constant and the sulfate is increased, there is not any such constant value for $\bar{D}$ since additional cerium-sulfate linkages may be formed as other sulfate ions become included in the complex. It may be noted that the experimental curve of $\bar{D}$ *versus* sulfate does not level off at ordinary concentrations.

It may be concluded, therefore, that the complex ion made up of one cerium(IV) and one sulfate ion predominates in solutions less than 0.01 *M* in concentration, with other complex ions being formed at higher concentrations.

Jones and Soper reported a "slight migration of color" toward the anode in transference experiments and concluded a complex anion must exist. This is also in accord with the results above, since these data indicate that in more concentrated solutions complex anions such as $Ce(SO_4)_3^{=}$ may be present.

Instability Constant.—By assuming that the flat portion of the curve in Fig. 6 represented complete combination of sulfate to form complex ions, the extinction coefficient of this complex was calculated from the observed value of $\bar{D}$ and the known concentration of sulfate. With this extinction coefficient and the values of $\bar{D}$ observed for various points on the curves of Fig. 4, equilibrium concentrations of the complex ion, cerium(IV) ion, and sulfate ion were calculated. From these, the instability constant (K) of the ion was calculated. The extent of ionization for the conditions of Fig. 6 was then calculated and corrections made in the extinction coefficient, the equilibrium concentrations and in the values of K. These corrections gave an average value of 4.3×10^{-4} for K in solutions having total cerium(IV) + sulfate concentrations equal to 0.00493 *M*.

The extinction coefficient could also be used to calculate equilibrium concentrations for the points on curves such as those of Fig. 3. From these data, average values of K equal to 4.7×10^{-4} and 5.3×10^{-4} were obtained for solutions 0.0043 *M* and 0.0020 *M*, respectively, in total cerium(IV).

By further approximations in the extinction coefficient, somewhat better agreement in values for K might be obtained, but, because of the lack of temperature control, etc., the results would probably not be significant.

The methods used here did not supply any evidence as to the presence of H^+ or OH^- ions in the complex. With such high acid concentrations, a complex ion containing OH^- is unlikely, but it is quite possible that hydrogen ion may be combined with the cerium(IV) and sulfate.

Experiments are now being carried out in these laboratories to determine whether these results will permit calculations of the influence of sulfate on the rates of reaction of cerium(IV) solutions and to determine the influence of ions such as chloride and nitrate upon the cerium(IV) sulfate complex.

Summary

1. Spectrophotometric studies of cerium(IV) perchlorate solutions showed no evidence of any colored complex ion formation. Cerium(IV) perchlorate solutions obey Beer's law up to concentrations of 0.01 *M*.

2. Spectrophotometric studies on cerium(IV) sulfate solutions indicated that in concentrations up to 0.01 *M*, a complex ion containing one cerium(IV) and one sulfate ion predominates. Complex ions containing more than one sulfate ion may also be formed, but become appreciable only at higher concentrations.

3. An approximate value for the instability constant of the simplest complex ion was determined.

AUSTIN, TEXAS RECEIVED OCTOBER 9, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Preparation and Properties of Inorganic Coördination Compounds. I. The Action of Some Organic Amines upon Dichloro-diethylenediamine Cobaltic Chloride[1]

BY JOHN C. BAILAR, JR., AND LEALLYN B. CLAPP[1]

The chlorine–cobalt bonds in dichloro-diethylenediamine cobaltic ion, $[Co\ en_2Cl_2]^+$, are very weak compared to the nitrogen–cobalt bonds, and the two chlorine atoms can be replaced in a variety of ways. Thus, they are readily displaced from the coördination sphere by carbonate, oxalate, thiocyanate, hydroxide and other anions having strong donor properties. On standing in water, the $[Co\ en_2Cl_2]^+$ ion is aquated with the formation of $[Co\ en_2(H_2O)Cl]^{++}$ and $[Co\ en_2(H_2O)_2]^{+++}$. Upon evaporation, the aquation reactions are reversed.

Anhydrous organic amines behave much as water does, but only one chlorine atom is replaced, and the compounds formed are stable enough that the amine is not readily expelled upon heating. For example, *s*-butylamine reacts with dichloro-diethylenediamine cobaltic chloride to give $[Co\ en_2(C_4H_9NH_2)Cl]Cl_2$. Secondary amines have little tendency to react in this way; tertiary amines (except heterocyclics), almost none.

In aqueous solution, several different types of

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[1] Taken from a portion of the doctorate thesis of Leallyn Burr Clapp, 1941. Present address, Brown University, Providence, R. I.