

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. III. A Study of Some Complex Ions in Solution by Means of the Spectrophotometer¹

BY ROBERT K. GOULD AND W. C. VOSBURGH

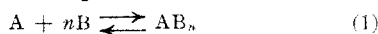
A modification of Job's method² of continuous variations for the identification of compounds formed in solution has been described by Vosburgh and Cooper.³ The modification made it possible to apply the method to cases in which more than one compound is formed from the same components. It was thought desirable to test the method further on a wider variety of systems, and to investigate some more systems to determine how many different complex ions are formed from the same components.

The modified method consists of making a number of mixtures of equimolar solutions of the two reactants and measuring the optical densities of the mixtures at certain pre-selected wave lengths. From the density of each mixture is subtracted the density calculated by the law of mixtures assuming no reaction. The difference, Y , is a maximum or minimum for the mixture in which the two reactants have been brought together in the proportions in which they react.

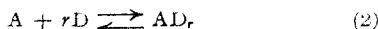
When more than one compound is formed, particular wave lengths can be selected as the most favorable for obtaining evidence of the various compounds. Different wave lengths lead to different composition values for a maximum or minimum in Y when more than one compound is formed. If Y is a maximum or minimum at the same composition for all wave lengths, the probability is that only one compound is formed. The shapes of the curves obtained when the results are plotted help in deciding whether or not more than one compound is formed.

Theoretical

In the course of this work the question arose as to the effect of a second equilibrium in the system being investigated. For example, suppose that substance A in addition to reacting with B in accordance with the equation



reacts also with the substance D



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(2) Job, *Ann. chim.*, (10) 9, 113 (1928).

(3) Vosburgh and Cooper, *THIS JOURNAL*, 63, 437 (1941).

Let us suppose that D is present in the equimolar solutions of A and B so that when these are mixed in varying proportions all mixtures contain the same concentration of D, and further that this concentration is large enough to remain practically constant in spite of Reaction 2. Then the concentration of AD_r is proportional to the concentration of A and can be set equal to Lc_1 . The following equations can be set up, in which c_1 , c_2 and c_3 are the concentrations of A, B and AB_n , respectively, and x is the volume of solution B added to the volume $1 - x$ of solution A to give unit volume of the mixture.

$$c_1 = M(1 - x) - c_3 - Lc_1$$

$$c_2 = Mx - nc_3$$

$$c_1c_2^n = Kc_3$$

On differentiation of each of these equations, setting dc_3/dx equal to zero, and solving the six equations simultaneously, the result is that when c_3 is a maximum, $n = x/(1 - x)$. This is the same as when there is no second equilibrium corresponding to Reaction 2.

If the compound AD_r is colored, but D is colorless, the difference Y between the actual optical density of the solution and the density calculated for no reaction is given by

$$Y = l(\epsilon_1 + \epsilon_4L)c_1 + \epsilon_2c_2 + \epsilon_3c_3 - \epsilon_1M(1 - x)/(1 + L) - \epsilon_2Mx - \epsilon_4LM(1 - x)/(1 + L)$$

in which ϵ_1 , ϵ_2 , ϵ_3 and ϵ_4 stand for the extinction coefficients of the substances A, B, AB_n , and AD_r , respectively, and l is the length of the path of light through the solution. Differentiating and equating dc_3/dx to zero shows that Y is either a maximum or minimum when c_3 is a maximum. Consequently, when a second substance is present that enters into reaction with Reactant A, the method of continuous variations may be used without the necessity of correcting for the second reaction. It should be noted that this is true only when the concentration of the second reactant is practically constant throughout the series of mixtures. Another restriction not mentioned is that the activity coefficients, if not cancelling from the equilibrium equations, must be held constant by constant ionic strength.

Ferric and Thiocyanate Ions.—Bent and French⁴ and also Edmonds and Birnbaum⁵ have shown that in dilute solutions the only compound formed from ferric and thiocyanate ions is the ion FeCNS^{++} . It was of interest to see whether or not the method of continuous variations would lead to the same conclusion.

Solutions containing iron(III) and thiocyanate ions, both at a concentration of 0.02 *M*, and other solutes as shown below, were prepared

Iron(III) ion solution, <i>M</i>	Thiocyanate solution, <i>M</i>
0.02 $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$	0.02 NH_4CNS
.06 H_2SO_4	.16 $(\text{NH}_4)_2\text{SO}_4$
.06 $(\text{NH}_4)_2\text{SO}_4$	

First, mixtures of the two solutions were made in the proportions of 1:1, 1:2 and 1:3 and their absorption spectra were measured by means of a Coleman Double Monochromator spectrophotometer. The slit width was 30 $\text{m}\mu$, and by means of plungers in the sample tubes the length of the path of light through the solution was reduced to 2 mm. The spectra are shown in Fig. 1, in which the density values for the 1:1 mixture have been multiplied by 0.5 and those for the 1:2 mixture by 0.75. The curves are of the same shape and

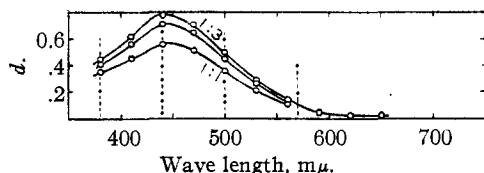


Fig. 1.—Absorption spectra of solutions containing iron(III) and thiocyanate ions in the ratios 1:1, 1:2 and 1:3. Dotted lines represent arbitrarily selected wave lengths.

are in agreement with the conclusion of Bent and French that only a single compound of low stability is formed. No particular wave lengths can be selected in accordance with the rules of Vosburgh and Cooper in this case, since the curves do not cross. A series of mixtures was therefore measured at four arbitrarily selected wave lengths. The values of *Y* as defined above were plotted against *x*, the volume of 0.02 *M* thiocyanate added to the volume (1 - *x*) of 0.02 *M* iron(III) ion solution. The resulting curves are shown in Fig. 2. The curves all have a broad maximum in the vicinity of *x* = 0.5, indicating a compound FeCNS^{++} which is considerably dissociated in solution, in agreement with Bent and

French. There is no indication of the existence of any other compound under these conditions.

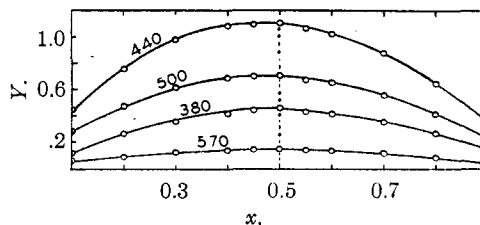


Fig. 2.—Iron(III) and thiocyanate ions; volume (1 - *x*) of 0.02 *M* iron(III) ion solution plus *x* of 0.02 *M* thiocyanate ion solution.

It is shown in the theoretical part that the existence of a complex ion of iron and sulfate ions⁶ would not affect this conclusion provided the sulfate ion concentration is held constant.

Iron(II) Ion and *o*-Phenanthroline.—Ferrari⁷ has presented evidence that iron(II) ion forms only one complex ion with α, α' -dipyridyl in solution. Jaeger and van Dijk,⁸ prepared solid complex sulfates with iron(II) ion and α, α' -dipyridyl in the proportions 1:1, 1:2 and 1:3. However, when it was attempted to convert these into chlorides by treatment with barium chloride, only the tridipyridyl iron(II) chloride was obtained. Vosburgh and Cooper³ found evidence of three complex ions formed from nickel ion and *o*-phenanthroline in solution. Because of the similarity of α, α' -dipyridyl and *o*-phenanthroline, it was of interest to investigate compound formation between iron(II) ion and *o*-phenanthroline by the method of continuous variations.

A 0.004 *M* solution of ferrous ammonium sulfate was prepared by weighing the required amount of reagent grade material. A small amount of sodium bisulfite was included to prevent oxidation. A 0.004 *M* phenanthroline solution was prepared similarly from *o*-phenanthroline obtained from the G. Frederick Smith Chemical Co.

The two solutions were mixed in varying proportions, and the optical densities of the resulting solutions were measured at wave lengths 400, 500, 540 and 570 $\text{m}\mu$ with a length of path of 2 mm. The wave lengths were selected arbitrarily to cover the region of the spectrum absorbed by the iron $\text{Fe}(\text{phen})_3^{++}$. The results are shown in Fig. 3, in which density is plotted against compo-

(6) Kiss, Abraham and Hegedus, *Z. anorg. allgem. Chem.*, **244**, 98 (1940).

(7) Ferrari, *Gazz. chim. ital.*, **67**, 604 (1937).

(8) Jaeger and von Dijk, *Z. anorg. allgem. Chem.*, **227**, 273 (1936).

(4) Bent and French, *THIS JOURNAL*, **63**, 568 (1941).

(5) Edmonds and Birnbaum, *ibid.*, **63**, 1471 (1941).

sition. Since the two original solutions were practically colorless, the density is equal to the difference Y . At all four wave lengths the maximum comes at composition 0.75, and each of the curves consists practically of two intersecting straight lines, indicating only one compound, $\text{Fe}(\text{phen})_3^{+++}$, which is very stable.

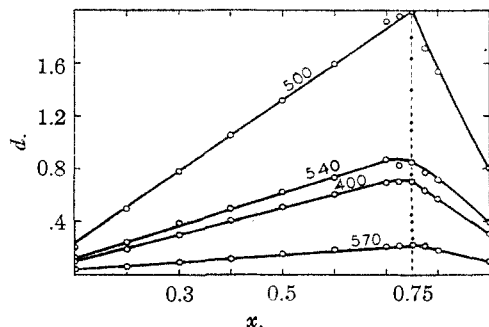


Fig. 3.—Iron(II) ion and *o*-phenanthroline; volume $(1 - x)$ of 0.004 *M* iron(II) sulfate solution plus x of 0.004 *M* *o*-phenanthroline solution.

The difference between the reaction of ferrous ion with phenanthroline and that of nickel ion is striking. There is another important difference between the ferrous phenanthroline and the three nickel phenanthroline ions: the ferrous phenanthroline ion is diamagnetic⁹ while all three of the nickel phenanthroline ions are paramagnetic.¹⁰

The formation of a series of two or more complex ions from the same components is rather common. Bjerrum¹¹ has pointed out that this is to be expected theoretically, though the theory provides that in extreme cases a compound AB_n might be considerably more stable than the possible intermediate compounds. Bjerrum has investigated several series of amines and ethylenediamine complex ions, finding in each case a series AB , AB_2 , . . . , AB_n in which the stability decreases as n increases.

The ferrous phenanthroline complex ion seems to be exceptional in this respect, and the ion $\text{Ni}(\text{CN})_4^{=}$ which is also diamagnetic seems to be another exception. Cambi, Cagnasso and Tremolada¹² have presented evidence from magnetic measurements that hydrated nickel cyanide, $\text{Ni}(\text{CN})_2 \cdot n\text{H}_2\text{O}$ is in reality composed of the paramagnetic cation $\text{Ni}(\text{H}_2\text{O})_n^{++7}$ and the diamag-

netic anion $\text{Ni}(\text{CN})_4^{=}$. Whether these two diamagnetic compounds are special cases or examples of a general rule can be determined by the examination of other ferrous and nickel complex ions.

Nickel and Dithio-oxalate Ions.—A highly colored complex salt formed from potassium dithio-oxalate and a nickel salt was shown by Jones and Tasker¹³ to have the composition $\text{K}_2\text{Ni}(\text{C}_2\text{O}_2\text{S}_2)_2$. Cox, Wardlaw and Webster¹⁴ showed that all atoms in the complex ion $\text{Ni}(\text{C}_2\text{O}_2\text{S}_2)_2^{=}$ are co-planar. According to Pauling, co-planar nickel compounds should be diamagnetic, and potassium nickel dithio-oxalate has been shown to conform.¹⁵ Therefore, it was of interest to see if more than one complex ion formed from nickel and dithio-oxalate ions could be identified.

A 0.004 *M* solution of nickel sulfate was prepared by dilution of a stock solution made from reagent grade material and standardized gravimetrically. A 0.004 *M* solution of potassium dithio-oxalate was prepared by weight. The dithio-oxalate was obviously somewhat impure, and the concentration of the solution was somewhat lower than 0.004 *M*. However, it was felt that purification or standardization was unnecessary, since the main object was to see whether or not evidence could be found for more than one compound, and there was little doubt as to the formula of the known compound.

The two solutions were first mixed in the proportions of one part by volume of nickel sulfate solution to one, two, and three parts of dithio-oxalate solution. The optical densities were measured as described for the iron(III) and thiocyanate ions, and corrected to a nickel ion concentration of 0.001 *M*. The resulting absorption spectra are shown in Fig. 4. Since the curves do

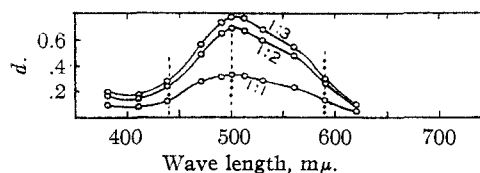


Fig. 4.—Absorption spectra of solutions containing nickel and dithio-oxalate ions in the ratios 1:1, 1:2 and 1:3. Dotted lines represent arbitrarily selected wave lengths.

not cross in the visible region, wave lengths 440, 500 and 590 $\text{m}\mu$ were arbitrarily selected for the

(9) Cambi and Cagnasso, *Gazz. chim. ital.*, **63**, 767 (1933).

(10) Russell, Ph.D. Thesis, Duke University, 1941.

(11) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941, p. 130; *Chem. Abs.* **35**, 6527 (1941).

(12) Cambi, Cagnasso and Tremolada, *Gazz. chim. ital.*, **64**, 758 (1934).

(13) Jones and Tasker, *J. Chem. Soc.*, **95**, 1904 (1909).

(14) Cox, Wardlaw and Webster, *ibid.*, 1475 (1935).

(15) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 111.

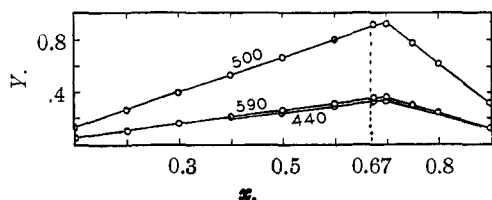


Fig. 5.—Nickel and dithio-oxalate ions; volume $(1 - x)$ of 0.004 M nickel sulfate solution plus x of 0.004 M potassium dithio-oxalate solution.

measurement of the usual series of mixtures. The results of these measurements are shown in Fig. 5. The straight lines, with the points of intersection all coming at about the same composition, indicate the formation of only one compound, which is quite stable. The difference between the 1:2 and 1:3 curves of Fig. 4 might appear to indicate some dissociation of the ion $\text{Ni}(\text{C}_2\text{O}_2\text{S}_2)_2^{2-}$, but the error in concentration of the dithio-oxalate solution is responsible for at least part of the difference.

Copper and Aminoacetate Ions.—Copper aminoacetate, $\text{Cu}(\text{OOCCH}_2\text{NH}_2)_2$, was found by Ley¹⁶ to be little dissociated in solution and was early recognized as a chelate compound.¹⁷ Borsook and Thimann¹⁸ found evidence for four different compounds of copper ion and aminoacetic acid or aminoacetate ion, two in the more acid solutions, one in neutral solution and a fourth in alkaline solutions. These were formed from either 1.5 or 2 moles of aminoacetic acid per gram atom of copper. Ley¹⁹ has recognized the possibility of the stepwise dissociation of copper aminoacetate to give the ion $\text{Cu}(\text{OOCCH}_2\text{NH}_2)^+$. Application of the method of continuous variations to the study of compound formation from copper sulfate and sodium aminoacetate showed that two compounds were formed, with ratios of copper ion to aminoacetate ion of 1:1 and 1:2, respectively.

A 0.02 M copper sulfate solution was prepared from recrystallized material and standardized by iodometric determination of the copper. A 0.02 M sodium aminoacetate solution was prepared by weighing the twice recrystallized acid and adding the equivalent quantity of standard sodium hydroxide solution.

Absorption spectra were measured of a solution 0.01 M with respect to both copper sulfate and

sodium aminoacetate, and of a solution 0.004 M with respect to copper sulfate and 0.08 M with respect to sodium aminoacetate. Circular sample tubes of 16 mm. diameter were used in the spectrophotometer. The optical densities of the second solution were corrected by multiplication by 2.5, and the data for the two solutions and for 0.01 M copper sulfate solution were plotted to give Fig. 6.

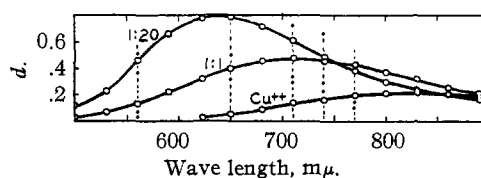


Fig. 6.—Absorption spectra of 0.01 M copper sulfate solution and solutions containing copper and aminoacetate ions in ratios of 1:1 and 1:20, with 0.01 M total copper.

The wave lengths indicated by the dotted lines in Fig. 6 were selected for use in the further investigation of the system. Measurement of a series of mixtures of the 0.02 M solutions described above at these wave lengths gave the data shown in Fig. 7. The Y -values for all of these curves were determined by the subtraction of the calculated densities for no reaction. This is wrong theoretically³ for the curves with the maximum at $x = 0.67$. However, experience has shown that the position of the maximum is usually changed only a little when the correct subtraction is made instead of the one made in this case.

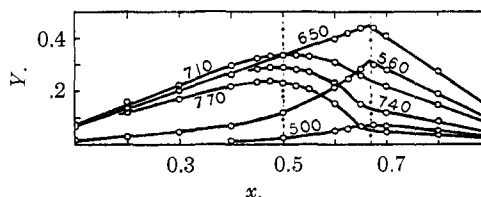


Fig. 7.—Copper and aminoacetate ions; volume $(1 - x)$ of 0.02 M copper sulfate solution plus x of 0.02 M sodium aminoacetate solution.

Figure 7 gives evidence of two compounds, the ion $\text{Cu}(\text{OOCCH}_2\text{NH}_2)^+$ postulated by Ley¹⁹ and the neutral compound $\text{Cu}(\text{OOCCH}_2\text{NH}_2)_2$. It is interesting that the curve for wave length 650 $m\mu$ consists of two intersecting straight lines. Straight lines are generally found when only a single compound of high stability is formed. The straight line on the left for 650 $m\mu$ is the result of a coincidence, since it happens that at 650 $m\mu$ the molar extinction coefficient of the first compound is very nearly half that of the second.

(16) Ley, *Z. Elektrochem.*, **10**, 954 (1904).

(17) (a) Tschugaeff, *J. prakt. Chem.*, [2] **75**, 162 (1907); (b) Ley, *Ber.*, **42**, 354 (1909).

(18) Borsook and Thimann, *J. Biol. Chem.*, **98**, 671 (1932).

(19) Ley, *Z. anorg. allgem. Chem.*, **164**, 387 (1927).

At other wave lengths this is not true, and the curves for 500 and 560 $m\mu$ indicate the existence of a second compound, as do also the right-hand parts of the curves for 740 and 770 $m\mu$. The wave length 740 $m\mu$ is the most favorable one for showing the existence of the first compound, and for this wave length the maximum in the Y -curve comes nearest to $x = 0.5$.

Nickel and Aminoacetate Ions.—Ley¹⁹ has prepared a nickel aminoacetate and has found it to have the composition $Ni(OOCCH_2NH_2)_2 \cdot 2H_2O$. The method of continuous variations shows that in addition a compound is formed from three aminoacetate ions to one nickel ion. The new compound is presumably an anion in which the nickel has a coordination number of six.

A 0.2 M nickel sulfate solution was standardized gravimetrically. A 0.2 M sodium aminoacetate solution was prepared as described above in connection with the copper aminoacetate system. The two solutions were mixed in the ratios 1:1, 1:2 and 1:3, and the absorption spectra of the resulting mixtures measured in the circular sample tubes. The spectra corrected to a concentration of 0.1 M total nickel with the assumption of Beer's law are shown in Fig. 8. An outstanding feature

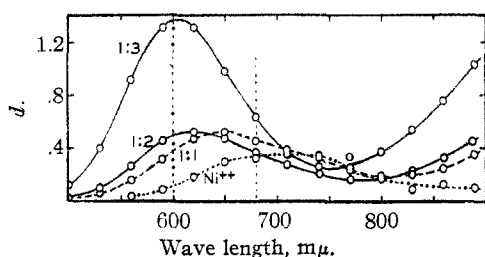


Fig. 8.—Absorption spectra of 0.1 M nickel sulfate solution and solutions containing nickel and aminoacetate ions in ratios of 1:1, 1:2 and 1:3, with 0.1 M total nickel.

of these curves is the large difference between the curve for the 1:3 ratio and the others. This curve lies above the others over so large a portion of the spectrum that it is difficult to select wave lengths that can be used to investigate the existence of other than the compound highest in aminoacetate content. In the region where the 1:1 curve is higher than the 1:3 curve, the curve for

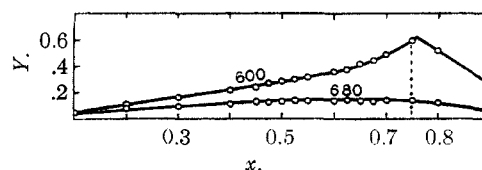


Fig. 9.—Nickel and aminoacetate ions; volume $(1-x)$ of 0.2 M nickel sulfate solution plus x of 0.2 M sodium aminoacetate solution.

nickel ion almost coincides with the 1:1 curve, making this region useless. This system is one in which none but the compound highest in aminoacetate content can be determined with assurance. Wave length 600 $m\mu$ is favorable for showing the highest compound, and the only other that seemed worth while trying was 680 $m\mu$. The usual series of mixtures was examined spectrophotometrically at these wave lengths and the results in Fig. 9 were obtained. At wave length 600 $m\mu$ the maximum comes slightly beyond the composition $x = 0.75$, indicating a compound of the composition $Ni(OOCCH_2NH_2)_3^-$. The curvature of the left-hand line suggests at least one other compound, and the Y -curve for 680 $m\mu$ has a maximum somewhere between $x = 0.5$ and $x = 0.75$, which also indicates another compound. These data give little indication of what the compound might be. Thus, it can be seen that the method of continuous variations does not always give full information about compound formation, and can be relied on for such only when conditions are favorable.

Summary

A number of systems have been examined by the method of continuous variations. In the three systems iron(III) and thiocyanate ions, iron(II) and *o*-phenanthroline, and nickel and dithio-oxalate ions, evidence was obtained for only one compound each, the compounds being already known. From copper and aminoacetate ions evidence of two compounds was obtained, with the components in ratios of 1:1 and 1:2, respectively. From nickel and aminoacetate ions evidence was obtained for a 1:3 compound and one other which could not be definitely identified.

DURHAM, N. C.

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