

PHYSICO-CHEMICAL ANALYSIS OF AQUEOUS SOLUTIONS OF NICKEL AND COPPER-AMMONIA COMPLEXES

by K. B. JATSIMIRSKY, Z. M. GRAFOVA and E. E. NATAN, *Ivanovo Institute of Chemistry and Technology, U.S.S.R.*

(Communicated by D. S. Kothari, F.N.I.)

(Received April 1; read December 6, 1957)

ABSTRACT

1. With the help of the Ostromislensky-Job method the formation of many complex compounds has been found in the investigated systems. In the case of the $\text{NiSO}_4\text{-NH}_3\text{-H}_2\text{O}$ system a number of irrational maxima are observed, which change their position with the change in wavelength. In the $\text{Cu}(\text{NH}_3)_2\text{-NH}_3\text{-H}_2\text{O}$ system two maxima are observed, one of which is clearly expressed.

2. While investigating the same systems, the constant initial concentration of ammonia being preserved, curves passing through one or two extrema have been obtained. From the analysis of the curves obtained conclusions have been drawn concerning the composition and stability of ammonia complexes.

Aqueous solutions of nickel and copper-ammonia complexes are widely used in industry and in chemical analysis. A great number of investigations applying various methods are devoted to the study of these solutions. The nickel and copper-ammonia complexes are coloured and therefore optical methods may also be used here.

Job (1928), Bjerrum (1933), Vosburg and Cooper (1941) and other investigators (Dey, 1946, 1947; Kubota, 1943) have investigated copper-ammonia complexes in comparatively concentrated solutions in the presence of a great excess of ammonia salts. Nickel-ammonia complexes have not yet been investigated with the help of optical methods, though Geczy (1952) suggested applying them for colorimetric analysis.

This paper deals with the possibility of determining the composition and stability of ammonia complexes of copper and nickel, formed in solutions, on the basis of data characterizing the composition and optical density of solutions. As the solutions in question have been investigated earlier with the help of different methods, it is possible to establish a number of peculiarities in the application of optical methods of physico-chemical analysis by comparing the obtained data with already established facts.

In order to determine the composition of compounds that are formed in solutions, the Ostromislensky-Job method is widely used, which is one of the particular applications of N. S. Kurnakov's method of physico-chemical analysis. The Ostromislensky-Job method has certain limitations. With the help of this method it is possible to determine the composition of a compound in case only one compound is formed in the solution. If several compounds are formed, the maximum position may not correspond to the composition of any of the compounds (irrational maximum). Foley and Anderson (1948) have observed such cases in solutions of sulfosalicylate complexes of iron.

Vosburg and Cooper (1941) proved that in some particular cases it is possible to find several compounds in the solution, by observing the maximum position on the curves of optic density-composition, with light of different wavelengths. The same device was applied by Babko and Drako (1949) when investigating rhodanide complexes of cobalt. We do not believe, however, that this device could be

universally used. The best possible result in this case would be the establishing of limits for the composition of the compounds that are formed.

It is hardly possible to suppose that together with an uninterrupted change in the wavelength of the absorbed light the position of maxima should change suddenly.

In Fig. 1 we see composition-growth of molar coefficients of extinction curves for system $\text{NiSO}_4\text{--NH}_3\text{--H}_2\text{O}$, taken at different wavelengths. All the measurements were made with the help of a photometer *PhM*. In all the cases the sum of molarities NiSO_4 and NH_3 was constant and amounted to 0.1 m. Mean molar coefficients of extinction (\bar{E}) were found according to the formula

$$\bar{E} = \frac{D}{Cl} \quad (\text{A})$$

where D is optical density, C the concentration of NiSO_4 , and l the thickness of the absorbing layer. The growth of the molar coefficient of extinction ($\Delta\bar{E}$) is the difference between \bar{E} and the molar coefficient of extinction, that has been calculated on the assumption of the absence of complex formation.

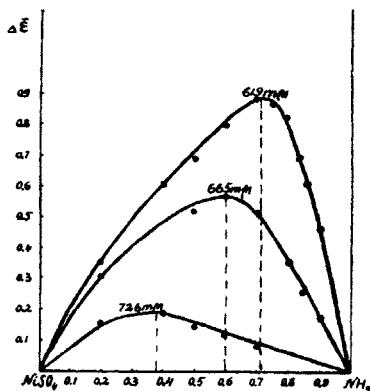


FIG. 1

All the curves on the composition- $\Delta\bar{E}$ diagrams pass through the maximum. As a rule, the position of the maximum does not correspond to rational relations and changes together with the change of the wavelength. In this case the composition of the complex compounds that are formed cannot be determined with the help of the Ostromislensky-Job method. It may be supposed, however, that the limits, within which the position of the maximum changes together with the change of the wavelength (from 1:1 to 1:4), correspond to the limit relations of nickel and ammonia in the compounds in question at chosen concentrations.

When the total concentration of reacting substances increases from 0.1 to 0.5 H the position of the maximum at $\lambda = 547 \text{ m}\mu$ changes; the maximum moves in the direction of the compounds that are richer in ammonia ($\approx 1:5$). A change in the position of the maximum following a change in concentration is also observed at other wavelengths.

The change in the position of the maximum that follows a change in the wavelength of the absorbed light and a change in the concentration of reacting substances is accounted for by the presence of a number of compounds in the system. The diagrams in this case refer to the type of diagrams with an irrational maximum; this type for other properties was known long ago.

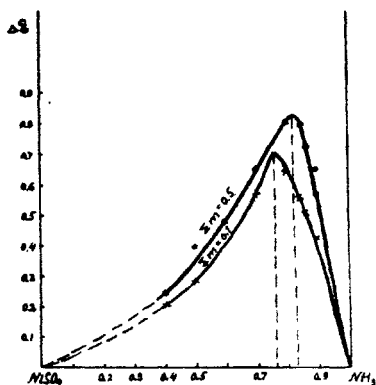


FIG. 2

The Ostromislensky-Job method was also applied for the investigation of the composition of copper-ammonia complexes that are formed in solutions. Our research differs from the above-mentioned investigations in one respect; we investigated solutions which did not contain ammonia salts. We used solutions with a low general concentration of copper and ammonia nitrate (the summary molarity was $4 \cdot 10^{-3} M$), because in case of higher general concentrations a formation of the sediment of basic salts was possible.

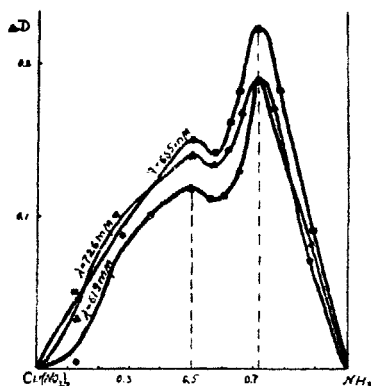


FIG. 3

Diagrams obtained in this case differ considerably from the ones we have dealt with above. The form of the curve changes little when the wavelength of the absorbed light changes. On all the curves there is one well expressed maximum, with a relation of the mole number $Cu : NH_3$ that equals 1: 2, 3 and corresponds, evidently, to the formation $Cu(NH_3)_2^{2+}$. The formation of the same compound was also found with the help of the Ostromislensky-Job method by Vosburg and Cooper at higher general concentrations.

All the curves are obviously asymmetric and have a second, less definite maximum corresponding to the formation $Cu(NH_3)^{2+}$. The compound has been found on such diagrams for the first time.

When several compounds are formed, the shape of the curve is determined on the Ostromislensky-Job diagrams by the composition of these compounds, their

stability and optical properties (relations between the molar coefficients of extinction of separate compounds). Owing to this, the shape of the curves may vary, and curves with irrational maxima must be observed rather often.

It is possible to judge about the composition of the compounds, which are formed, by the change of the position of the maximum connected with the change in the wavelength and in the concentration, as well as by the shape of the curve (the presence of a breaking and of hardly expressed maxima).

All the conclusions, arrived at in this way, must be regarded with a certain amount of caution and verified by applying other methods.

A number of investigators, and in the first place Babko (1948), widely used the method of investigating the optical properties of complexes in solutions with a constant initial concentration of one of the components and a changing concentration of the other component. In such solutions when one of the compounds is formed, the optic density changes monotonically, and with the growth of concentration of the second component in most cases it asymptotically approaches a definite limit.

Let us consider this case in its most general form. If there is equilibrium in the system, then



between the molar coefficients of extinction we find the following relations:

$$\bar{\epsilon}C_0 = E_1C_1 + E_2(C_0 - C_1); \quad \dots \quad (2)$$

$$\bar{\epsilon}C_0 = E_1(C_0 - C_2) + E_2C_2; \quad \dots \quad (2a)$$

where E and E_2 are molar coefficients of extinction for AB_n and AB_{n+m} respectively. C_1 and C_2 are concentrations of these compounds and C_0 is the summary (initial) concentration of component A ($C_0 = C_1 + C_2$).

After the transformation of equations (2) and (2a) we have the following relations

$$\frac{\Delta \bar{E}_2}{\Delta E_{12}} = \frac{C_1}{C_0} \quad \dots \quad (3)$$

$$\frac{\Delta \bar{E}_1}{\Delta E_{21}} = \frac{C_2}{C_0} \quad \dots \quad (3a)$$

where $\Delta \bar{E}_2 = \bar{E} - E_2$; $\Delta \bar{E}_1 = \bar{E} - E_1$; $\Delta E_{21} = E_1 - E_2$

From the relation

$$\frac{C_1 C_B^m}{C_2} = K \quad \dots \quad (4)$$

and from the equations (3) and (3a) we obtain

$$\Delta \bar{E}_2 = \frac{K \Delta E_{12}}{C_B^m + K}; \quad \dots \quad (5)$$

$$\Delta \bar{E}_1 = \frac{\Delta E_{12} C_B^m}{C_B^m + K} \quad \dots \quad (5a)$$

By differentiating equations (5) and (5a) we obtain:

$$\frac{d\bar{E}}{dc} = - \frac{n \Delta E_{12} K C_B^{m-1}}{(K + C_B^m)^2} \quad \dots \quad (6)$$

With increasing concentration of NH_3 the derivative $d\bar{E}/dc$ approaches zero. The smaller the value K , the lower the concentration at which the minimum value of the derivative is obtained.

If several compounds of the type $AB_n, AB_{n+1}, AB_{n+2}, \dots, AB_{n+m}$ are formed in the solution, and the molar coefficient of extinction of one of the intermediate member of this row is larger (or smaller) than the molar coefficients of both of the neighbouring members of the same row, then the mean molar coefficient of extinction passes through the extremum when concentration B increases.

It is easy to prove that the extremum position, as a rule, does not coincide with the maximum accumulation of the given compound in the solution.

The maximum \bar{E} and the maximum accumulation of the given compound come close together only in case of a greater stability of the intermediate compound as compared with the following compound of the given row (for instance, AB_n and AB_{n+1}), or in case of equality of the molar coefficients of extinction, AB_n and AB_{n+1} .

The results of measuring the optical density in systems of that kind are given in Fig. 4 and Fig. 5. In order to make the construction of the diagram easier, the logarithm of concentration NH_3 was indicated on the axis of the abscissae.

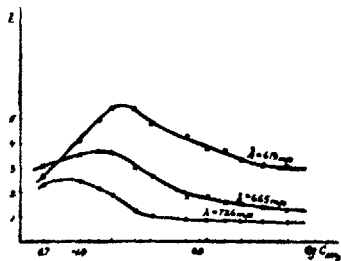


FIG. 4

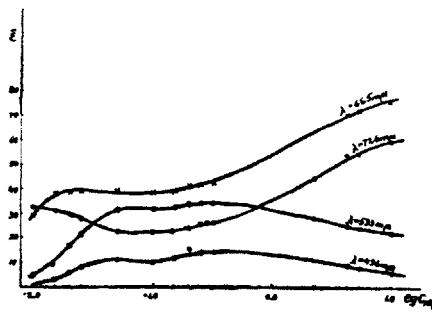


FIG. 5

All the experiments with nickel-ammonia complexes were made at a constant summary concentration of NiSO_4 (0.049 m.). The summary concentration of ammonia changed from 0.049 to 5.07 m. In order to prevent the dropping out of the sediment of basic salts a high constant concentration of NH_4Cl (0.5 m.) was preserved in the solution.

The curves of light absorption with wavelength 726 μ , 665 μ and 619 μ pass through the maximum. When we have high concentrations of ammonia all the curves become more flat. The positions of the maxima are different at different wavelengths. The curves indicate the presence of many complex compounds in the solution. The flatness of the curves in cases of high concentrations of ammonia show that in these conditions only one compound is formed, namely $\text{Ni}(\text{NH}_3)_6^{2+}$.

All the experiments with copper-ammonia complexes were made at a constant general concentration of CuCl_2 (0.005 m.); the summary concentration of ammonia changed from 0.0047 to 10 m. The concentration of NH_4Cl was 0.4 m. in all the experiments.

The curves of light absorption at 533 μ and 496 μ wavelength pass through the maximum, and the light absorption curve at 726 μ wavelength passes through the minimum. On the curve taken at 665 μ we find the maximum and the minimum are both very flat.

Four extrema lie on the curves approximately in one and the same region of summary concentrations of ammonia (from 0.1 to 0.2 m.). In this region evidently

there exists in the main one complex ion $\text{Cu}(\text{NH}_3)_4^{2+}$. The fact that on the rest of the curves in this region of concentrations there is a clearly seen platform (flatness) also speaks in favour of this supposition. According to the data of Bjerrum (1841) concerning the constants of instability of copper-ammonia complexes, more than 95 per cent of copper is actually found in the form of $\text{Cu}(\text{NH}_3)_4^{2+}$.

If the concentration of ammonia is above 0.2 m., an obvious change of mean molar coefficients of extinction begins on all the light filters with the exception of one (574 m μ).

Here the formation of complex compounds takes place with the co-ordination figure above four.

By means of the simplest transformations of equations (5) and (5a) we may obtain:

$$\frac{1}{\Delta \bar{E}_2} = \frac{1}{\Delta E_{12}} + \frac{K}{\Delta E_{12}} C_B^m, \quad \dots \dots \dots (7)$$

and

$$\frac{1}{\Delta \bar{E}_1} = \frac{1}{\Delta E_{21}} + \frac{K}{\Delta E_{21}} \frac{1}{C_B^m} \quad \dots \dots \dots (7a)$$

If we indicate C^m or $\frac{1}{C^m}$ along the abscissae and $\frac{1}{\Delta \bar{E}_2}$ or $\frac{1}{\Delta \bar{E}_1}$, along the ordinates then—in case the M value has been correctly chosen—a linear dependence between these two values must take place. In this way it is possible to determine the stoichiometric coefficient in equation (A), to calculate the molar coefficient of extinction AB_n and AB_{n+m} and evaluate the equilibrium constant of reaction (1). This method of analysis of experimental data was first applied by Kosjakov and Sikman (1946).

To solve equations (7) and (7a) it is necessary to know the molar coefficient of extinction of one of the complexes (AB_n or AB_{n+m}). In the case of nickel-ammonia complexes the molar coefficients of extinction $\text{Ni}(\text{NH}_3)_6^{2+}$ were calculated on the basis of data concerning the optical density of solutions of NiSO_4 in concentrated ammonia ($> 5^{\text{mol}}$). Later equation (7) was used with $m = 2$, because the linear dependence between $1/\Delta \bar{E}_2$ and C^m was observed only in this case (see Fig. 6).

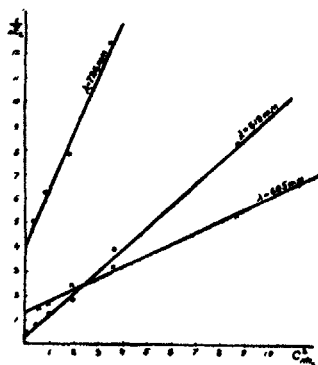


FIG. 6

Consequently, at comparatively high concentrations of ammonia (> 0.1 m.) only one reaction actually takes place in the solution



We arrived at the same conclusion earlier through the analysis of thermochemical data and of data concerning the solubility of complex salts in ammonia (Jatsimirsky and Grafova, 1952). The equilibrium constant of their reaction may be approximately evaluated according to equation (7) and appears to be equal to 1.0 ± 0.4 , differing little from the value that was calculated earlier.

In order to determine the composition of copper-ammonia complexes at high concentrations of ammonia, equation (7a) was used: the molar coefficients of extinction of $\text{Cu}(\text{NH}_2)_4^{2+}$ were found from the optic density of solutions of CuCl_2 with a concentration of ammonia 0.1 m. At this concentration of NH_3 , as has been mentioned above, only one complex ion $\text{Cu}(\text{NH}_3)_4^{2+}$ practically exists in the solution.

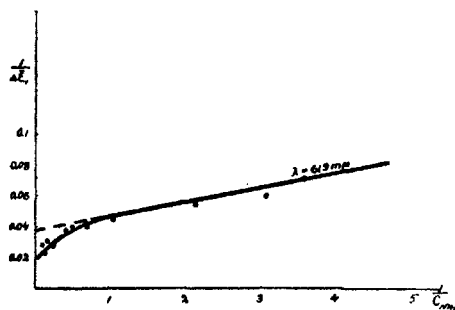


FIG. 7

The dependence $\frac{1}{E - E_0}$ on $\frac{1}{C}$ is shown in Fig. 7.

At small concentrations of ammonia a linear dependence is preserved: only $\text{Cu}(\text{NH}_3)_6^{2+}$ is formed in the solution. At higher concentrations of NH_3 obvious deviations from the linear dependence are observed, which indicate the formation of new complexes, evidently $\text{Cu}(\text{NH}_3)_6^{2+}$.

Solutions with a considerable excess of ammonia sulfate and ammonia nitrate (in the absence of chloride in the solution) have been investigated. In these cases the same form of the curve is observed, but the deviation from linearity occurs at lower concentrations of ammonia.

REFERENCES

- Babko, A. K. (1948). *J. O. Ch.*, **18**, 816.
 Babko, A. K., and Drako, O. F. (1949). *J. O. Ch.*, 1809.
 Bjerrum, J. (1841). *Metal Ammine Formation in Aqueous Solutions*. Copenhagen.
 ——— (1933). *C. A.*, **27**, 36.
 Dey, A. K. (1946). *C. A.*, **40**, 6360.
 ——— (1947). *C. A.*, **41**, 5046.
 Foley, R. T., and Anderson, R. C. (1948). *J. Am. Chem. Soc.*, **70**, 1195.
 Geczy, G. (1952). *C. A.*, **46**, 376.
 Jatsimirsky, K. B., and Grafova, Z. M. (1952). *J. O. Ch.*, **22**, 1726.
 Job, P. (1928). *Ann. Chim.*, **10**, 9, 113.
 Kosjakov, S., and Sikman, D. V. (1946). *J. Am. Chem. Soc.*, **68**, 442.
 Kubota, Masao (1943). *C. A.*, **37**, 4010.
 Vosburg, V. C., and Cooper, S. R. (1941). *J. Am. Chem. Soc.*, **63**, 437.