Russian Journal of Applied Chemistry, Vol. 75, No. 7, 2002, pp. 1055–1060. Translated from Zhurnal Prikladnoi Khimii, Vol. 75, No. 7, 2002, pp. 1072–1077. Original Russian Text Copyright © 2002 by Burkov, Sidorov, Sal'nikov, Kryuchkova.

> INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Competition of Hydrolysis and Complex Formation in the Cu(NO₃)₂, (H⁺)-NH₃ · H₂O-H₂O System

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Received November 15, 2001

Abstract—The concentration regions of prevalence of various chemical interactions in the $Cu(NO_3)_2$, $(H^+)-NH_3 \cdot H_2O-H_2O$ system were determined by dilatometry, pH-metry, and electronic spectroscopy of solutions and by X-ray phase and gravimetric analyses of precipitates. The adequacy of the model proposed was confirmed by CPESSP calculations.

Occurrence of equilibria (1) in aqueous ammonia solutions suggests that either ammine complexes or mono- and polynuclear hydroxo complexes, and probably mixed hydroxo ammine complexes can be formed in systems metal ion–ammonia–water:

$$NH_3 + H_2O = NH_3 \cdot H_2O = NH_4^+ + OH^-.$$
 (1)

The hydrolysis and complex formation can compete. Such reactions, which often take place in heterogeneous systems, result in the precipitation of poorly soluble compounds and, in certain cases, in their subsequent dissolution.

It is often difficult to gain insight into the chemical interactions and state of the components in such complicated systems consisting of both solutions and solids. The subject of this work was the Cu(NO₃)₂, (H⁺)–NH₃·H₂O–H₂O system. The experimental data were obtained dilatometrically. This method allows highly accurate monitoring of changes in the solution volume due to chemical interactions. Also, we used potentiometric titration and electronic absorption spectroscopy of solutions (after thorough filtration to remove precipitates, which, in turn, were studied by chemical and X-ray phase analyses). The data of the dilatometric titration were treated with a simulating CPESSP program.

Hydrolysis and complex formation of copper(II) with ammonia were extensively studied as separate processes. The hydrolysis of copper(II) ions was studied previously in [1] by potentiometric titration with an alkali (NaOH) at a constant ionic strength, and also in [2], with 3.0 M NaClO₄ as supporting

electrolyte. It was shown that, along with the dominating binuclear complex $Cu_2(OH)_2^{2+}$, the $CuOH^+$ and $Cu_2(OH)^{3+}$ species are formed in solution. Their hydrolysis constants $\log K_h$, equal to -10.93 ± 0.02 , -7.4 ± 0.1 , and -6.02 ± 0.02 , respectively, were determined, and the stability constants $\log\beta$ were calculated in view of $pK_w = 14.09$ found in [3]: 6.69 for $CuOH^+$, 17.25 for $Cu_2(OH)_2^{2+}$, and 8.07 for $Cu_2(OH)^{3+}$. Several authors also detected the trinuclear species $Cu_3(OH)_4^{2+}$. The most probable hydroxo compounds in the solid state are copper hydroxide $Cu(OH)_2$ and also the binuclear complex $Cu_2(OH)_3NO_3$ characteristic of nitrate systems [4].

In solutions of copper ammines, there are only mononuclear complexes $[Cu(NH_3)_n]^{2+}$, n = 1-4 (however, there are also scarce data on the complexes with n 5 and 6). Their step stability constants were determined by many authors [1]. For example, the following values are given in [5]: $\log k_1 = 4.31$, $\log k_2 = 3.67$, $\log k_3 = 3.04$, and $\log k_4 = 2.30$ (thus, $\log \beta_4 = 13.32$ at 18° C in a 2 N solution of ammonium nitrate).

Attempts were made to gain insight into processes occurring under the action of aqueous ammonia solution on the suspension of copper oxide CuO. Gubeli *et al.* [6], when fitting the CuO solubility curve, suggested the presence of a number of species in the system: Cu^{2+} , $\text{Cu}(\text{OH})_n^{2-n}$ (n = 2-4), $\text{Cu}(\text{NH}_3)_n^{2+}$ (n = 2-4), and also $\text{Cu}(\text{NH}_3)(\text{OH})^+$, $\text{Cu}(\text{NH}_3)_3(\text{OH})^+$, and $\text{Cu}(\text{NH}_3)_2(\text{OH})_2$. At the same time, this conclusion seems doubtful, because the well-known existence of binuclear hydroxo complexes was not included in the model.

Comparison of the published data shows that vari-

Fig. 1. Curves of (*I*) dilatometric and (*II*) potentiometric titration for the system Cu(NO₃)₂, (H⁺)–NH₃·H₂O–H₂O. Concentrations, M: copper(II) nitrate 0.091 and ammonia 0.312; ionic strength of solutions 1 M (NaNO₃). ($\Delta V_{\rm m}$) Change in molar volume and (*N*) the number of NH₃·H₂O moles per mole of Cu(II); the same for Figs. 3 and 5.



Fig. 2. Dilatometric titration curve for the system $Cu(NO_3)_2$, (H^+) –NaOH–H₂O. Concentrations, M: Cu^{2+} ions 0.228, NaOH 0.330; ionic strength of solutions 1 M (NaNO₃). (ΔV_m) Change in the molar volume; $N = [NaOH]/[Cu^{2+}]$.

ous chemical reactions can compete in the system $Cu(NO_3)_2$, $(H^+)-NH_3 \cdot H_2O-H_2O$.

The results of dilatometric and potentiometric titration of copper nitrate solution (with addition of HNO₃ to prevent spontaneous hydrolysis) by an ammonia solution are shown in Fig. 1. The dilatometric curve corresponding to the titration in the system Cu(NO₃)₂, (H⁺)–NaOH–H₂O, i.e., to the hydrolysis of copper(II) ions without complex formation, is shown in Fig. 2. The dilatometric curves were constructed as the plots of changes in the molar volume $\Delta V_{\rm m}$ (cm³ mol⁻¹) vs. the number of added moles of a base N per mole of copper ions, $N = [NH_3 \cdot H_2O]/[Cu^{2+}]$ for Fig. 1 and $N = [NaOH]/[Cu^{2+}]$ for Fig. 2.

For more convenient comparison and interpretation, we accepted the starting point of the hydrolysis of Cu^{2+} ions (i.e., point *B*) as the point of zero value of *N*. Thus, the values N < 0 in the beginning of the curve (straight line *AB*) corresponded to the titration region in which the main component [copper(II) ions] yet do not enter into the reaction, and the possible scatter of the starting points *A* in various titration experiments may be due to different amounts of the acid added.

The dilatometric titration curves for such complicated systems as the system under study consist of a number of linear portions, each of which corresponds to various chemical reactions. We have shown earlier [7–9] that the singular points (according to Mendeleev's definition [10]) in the composition– property diagrams correspond to the boundaries of the regions with prevalence of particular types of reactions, depending on *N*. Thus, the change in the solution molar volume $\Delta V_{\rm m}$ for each particular reaction is determined as the slope of the $\Delta V_{\rm m} = f(N)$ dependence in the dilatometric curve portion under consideration.

A detailed study of the dilatometric titration data for the system $Cu(NO_3)_2$, $(H^+)-NH_3 \cdot H_2O-H_2O$ (Fig. 1) in comparison with the data on bulk properties of the system $Cu(NO_3)_2$, $(H^+)-NaOH-H_2O$ (Fig. 2), and also with the data of other methods, allowed us to reveal and interpret the regions of prevalence of the following chemical reactions.

(1) The neutralization of excess nitric acid, which is usually added to the initial solution to prevent the spontaneous hydrolysis of copper(II). The region of the neutralization corresponds to the linear portion ABin the dilatometric curves shown in Figs. 1 and 2. A set of facts indicate that specifically neutralization takes place in both systems within boundaries of the AB portion. First, point B coincides with the calculated equivalence point with respect to the acid. Second, the first equivalence point in the pH-metric curve corresponds to point B. Furthermore, after this point, hydroxo compounds start to precipitate.

There is principle difference between the courses of volume changes in neutralization with sodium hydroxide and ammonia aqueous solutions. Reaction (2) involving a strong base and a strong acid (Fig. 2, portion AB) is accompanied by an increase in volume



 $(\Delta V_{AB} = 21.06 \text{ cm}^3 \text{ mol}^{-1}):$

$$NaOH + HNO_3 = H_2O + NaNO_3.$$
(2)

The observed positive volume effect agrees well with the published data [9]. The main component of ΔV_{AB} is the partial molar volume of the forming water $(V_{\rm W} = 18.07 \text{ cm}^3 \text{ mol}^{-1} \text{ at } 25^{\circ}\text{C})$. An additional contribution to the volume effect is due to the dehydration of H⁺ and OH⁻ ions and, correspondingly, to their deelectrostriction [11]. Reaction (2) can be written in the ionic form as follows:

$$OH_{aq}^{-} + H_{aq}^{+} = H_2O + aq + \Delta V_{AB},$$
 (3)

where aq is water in the hydration spheres of ions.

With aqueous ammonia solution (Fig. 1), the pattern of volume changes in the *AB* section is opposite, i.e., the volume of the system decreases. The ΔV_{AB} value for reaction (4) [or (5) in the ionic form] is $-4.85 \text{ cm}^3 \text{ mol}^{-1}$:

$$NH_3 \cdot H_2O + HNO_3 = H_2O + NH_4NO_3,$$
 (4)

$$NH_{3(aq)} + H_{(aq)}^+ = NH_{4(aq)}^+.$$
 (5)

At first glance, such a difference in the volume effects (as compared to the neutralization with alkali) seems strange, as in both cases water molecules are formed, and dehydration of the acid protons also makes a certain positive contribution. The observed effect is due to specific features of the neutralization with aqueous ammonia (namely, the partial molar volume of the initial ammonia in solution is larger than the partial molar volume of an aquated ammonium ion formed in the reaction [12, 13]).

To confirm additionally the fact that acid is neutralized in the initial stage of the titration (portion *AB*), we titrated a non-acidified solution of copper(II) nitrate with an ammonia solution [the system $Cu(NO_3)_2-NH_3 \cdot H_2O-H_2O$]. As expected, the resulting titration curve was similar to the curve under consideration, except for the *AB* portion.

(2) After passing point B, a blue precipitate is formed in both systems under consideration, which is accompanied by an increase in volume, suggesting occurrence of a new chemical reaction (Figs. 1 and 2, straight line BC) responsible for a sharp change in the molar volume. Point B is the starting point for measuring the amount N (mol) of a titrant [sodium hydroxide (Fig. 2) or ammonia (Fig. 1)] reacting directly with copper(II). The length of the BC section in



Fig. 3. Plot of the precipitate yield η vs. N. N: (1) 0.5, (2) 1.0, (3) 1.5, (4) 2.3, (5) 3.1, and (6) 4.0; the same for Fig. 4.

both cases corresponded to N = 1.5 mol. The volume changes describing the BC section are $(\text{cm}^3 \text{ mol}^{-1})$ ΔV_{BC} (NaOH) = 31.44 and ΔV_{BC} (NH₃·H₂O) = 6.04. As found previously for induced hydrolysis of iron(III) ions [8], the hydrolytic polymerization under the action of a strong base is accompanied by an additional positive volume effect, as compared to the first section corresponding to the neutralization of an acid. For the systems under consideration, these additional contributions are as follows (cm³ mol⁻¹): ΔV_{BC} (NaOH) – ΔV_{AB} (NaOH) = 31.44 – 21.06 = 10.38 for NaOH titrant and $\Delta V_{BC}(NH_3 \cdot H_2O) - \Delta V_{AB}(NH_3 \cdot H_2O) =$ 6.04 - (-4.85) = 10.89 for NH₃ · H₂O titrant. This fact allows an important conclusion that, in spite of different nature of the bases in the two titration experiments, the volume effect resulting from the hydrolysis and hydrolytic polymerization remains the same.

According to X-ray phase analysis, the solid phase is the same in both cases: the known binuclear copper trihydroxonitrate $Cu_2(OH)_3NO_3$. No ammine and mixed hydroxo ammine complexes were detected in the solid phase.

The *B*'*C*' portion of the plot of the precipitate weight (% of total copper content) vs. *N* in Fig. 3 (in the *B*'*C*' portion, precipitates were isolated at *N* 0.5, 1.0, and 1.5) is a straight line ascending in parallel to the *BC* portion of the dilatometric curve (Fig. 1). The amount of the precipitate linearly increased, reaching a maximum at N = 1.5, i.e., in point *C*'. The electronic absorption spectra (Fig. 4) show that the solutions corresponding to the straight-line portion *BC* of the dilatometric curve contain no Cu(II) ammine complexes (the solutions were prepared by thorough filtration at the same *N* values as the precipitates). The absorption band in the region 600-625 nm, characteristic for copper ammines [14], was absent from the

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Fig. 4. Electronic absorption spectra of solutions obtained in the system $Cu(NO_3)_2-NH_3 \cdot H_2O-H_2O$ at various *N* values. (*D*) Optical density and (λ) wavelength.

spectra of solutions corresponding to N 0.5, 1.0, and 1.5 (curves 1, 2, and 3, respectively). At the same time, a decrease in the intensity of the absorption band in the region of 800 nm, characteristic for copper(II) aqua complexes [15], was indicative of gradual decrease in the copper amount in the solution. At N =1.5 (singular point *C*), Cu²⁺ ions were almost absent from the solution. Thus, in the range of *N* from 0 up to 1.5 in the system Cu(NO₃)₂, (H⁺)–NH₃·H₂O–H₂O, the hydrolysis (i.e., interactions also characteristic of the induced hydrolysis under the action of a strong base) prevailed over the formation of ammine complexes.

The following reactions are presumably responsible for the volume changes in the *BC* portions of the dilatometric curves for both systems under consideration:

$$2Cu^{2+} + NO_3^- + 3OH^- = Cu_2(OH)_3NO_3,$$
 (6)

 $2Cu^{2+} + NO_3^- + 3NH_3 \cdot H_2O = Cu_2(OH)_3NO_3 + 3NH_4^+.$ (7)

Apparently, the hydrolytic transformations described by Eqs. (6) and (7) involve the stages of the formation of copper mono- and polynuclear hydroxo complexes $CuOH^+$, Cu_2OH^{3+} , and $Cu_2(OH)_2^{2+}$, which are precursors of the forming solid phase.

It was shown in [8] that the positive volume effect is due to liberation of water molecules from the hydration shells of the interacting ions upon the hydrolytic polymerization (the molar volume of water in the free state is 18.07 cm³ mol⁻¹, and in hydration shells of double-charged cations of 3*d* metals it is about 15 [16]). Note that a neutral hydroxo complex was formed from six differently charged species in reaction (6) with liberation of water molecules from the hydration shells of the ions.

The potentiometric titration of the system $Cu(NO_3)_2$,

 (H^+) -NH₃·H₂O-H₂O (Fig. 1, curve *II*) in the region corresponding to the *BC* portion reveales a slight increase in pH at *N* from 0 to 1.5. The sharp pH increase in the second equivalence point at N = 1.5coincided with singular point *C* in the dilatometric curve. At N > 1.5, the pH changed only slightly. Hence, the formation of hydroxo species, with binding of hydroxide ions without noticeable pH change, was complete.

(3) Analysis of the ΔV_{CD} (NaOH) and ΔV_{CD} (NH₃. H_2O) values in the *CD* portion (Figs. 1, 2) revealed principal differences in the nature of volume changes and, hence, in chemical reactions in the two systems under consideration (i.e., when sodium hydroxide or aqueous ammonia solution was added). When titrating with sodium hydroxide (Fig. 2), the volume continued to grow up to N = 2, with only the value of the volume effect changed [ΔV_{CD} (NaOH) = 13.56 cm³ mol⁻¹]. The transformations in the system were associated with further hydrolytic reactions whose final solid product was a mixture of copper hydroxide and oxide formed by partial decomposition of Cu(OH)₂ (which was also confirmed by X-ray phase analysis). The CD portion is located between N 1.5 and 2, which apparently corresponds to reaction (8) and parallel partial decomposition (9) of copper hydroxide into copper oxide and water (in the course of the experiment, the precipitate gradually darkens owing to the formation of black copper oxide):

$$Cu_2(OH)_3NO_3 + OH^- = 2Cu(OH)_2 + NO_3^-,$$
 (8)

$$Cu(OH)_2 = CuO + H_2O.$$
(9)

The volume changes are virtually complete in singular point D (N = 2) owing to the completion of main chemical reactions in the system: after N = 2, the titration curve (Fig. 2) flattens out.

At the same time, in titration with aqueous ammonia (Fig. 1), the volume decreased $[\Delta V_{CD}(NH_3 \cdot H_2O) = -2.93 \text{ cm}^3 \text{ mol}^{-1}]$, which continued up to N = 4.

In the Cu(NO₃)₂, (H⁺)–NH₃·H₂O–H₂O system, the *CD* section gives one more evidence of competition between the chemical reactions. In contrast to the previous example (titration with alkali), the further titration with ammonia results in the dissolution of the copper hydroxo complex and in its conversion to copper(II) ammines:

$$Cu_{2}(OH)_{3}NO_{3} + 2nNH_{3} \cdot H_{2}O = 2Cu(NH_{3})_{n}^{2+} + 3OH^{-}$$
$$+ NO_{3}^{-} + 2nH_{2}O.$$
(10)

To examine further changes in m_{Cu} (%), we should note that, according to the plot of the precipitate weight (the precipitates were taken at N 2.3, 3.1, and 4.0) vs. N in the range of N from 1.5 to 4.0 in Fig. 3 (straight line C'D'), the precipitate amount decreases, and in poing D' it dissolves almost completely (the course of the dilatometric curve is almost repeated). According to the X-ray phase analysis, the composition of the precipitate Cu₂(OH)₃NO₃ remains unchanged in the process. No mixed hydroxo ammine complexes were detected. In the electronic spectra (Fig. 4), instead of the completely disappeaing band at 800 nm, an absorption band appears in the range 600-625 nm (spectra of solutions 4-6), which can be assigned, as mentioned above, to copper ammine complexes.

Thus, the nature of the final solid product of hydrolytic transformations of Cu^{2+} ions in $Cu(NO_3)_2$ solutions depends on the titrating base. In the case of NaOH, it is $Cu(OH)_2$, which is converted to CuO with time and in excess of the base, and, in the case of aqueous ammonia, it is $Cu_2(OH)_3NO_3$, which dissolves in excess ammonia to form copper ammines.

Examining Eq. (10), we can characterize the reaction described by the portion CD of the dilatometric curve as reverse of the reaction corresponding to the portion BC, i.e., as $Cu_2(OH)_3NO_3$ depolymerization and dissolution. On addition of uncharged molecules of hydrated NH₃ to one molecule of the neutral hydroxo complex, six ions are formed at once, which causes a reduction in the volume at the expense of their hydration.

The fact that, in the course of further titration after passing singular point D, the molar volume does not change noticeably (straight line DE) is due to the completion of the main chemical reactions in the system.

Dark blue $Cu(NH_3)_2(NO_3)_2$ crystals (identified by X-ray phase analysis) were obtained from the solution at N > 4.

The interactions revealed in the system Cu(NO₃)₂, (H⁺)–NH₃·H₂O–H₂O were confirmed by CPESSP model calculations. The initial model included the dissolved complexes Cu(OH)⁺, Cu₂(OH)₂²⁺, and Cu(NH₃)_n²⁺ (n = 1-4) with the pK values considered above, and also Cu₂(OH)₃NO₃ and Cu(OH)₂ precipitates. The resulting distribution of hydroxide and ammine complexes is given in Fig. 5. It follows from the calculations that ammine complexes appear in the solution at N = 1.5. Under the experimental conditions, the hydroxo complex species Cu(OH)⁺, Cu₂(OH)³⁺, Cu₂(OH)₂²⁺, and also the complex



Fig. 5. Distribution of hydroxide and ammine complexes α in the heterogeneous system Cu(NO₃)₂, (H⁺)–NH₃·H₂O–H₂O as a function of *N*: (*1*) Cu²⁺, (*2*) Cu₂(OH)₃NO₃(s), (*3*) Cu(NH₃)₄²⁺, (*4*) Cu(NH₃)₃²⁺, and (*5*) Cu(NH₃)₂²⁺.

Cu(NH₃)²⁺ are present in the system in minor amounts. Our calculations showed that the volume changes in the system are determined first by neutralization of the acid, then by hydrolytic reactions of copper ions with Cu₂(OH)₃NO₃ precipitation, and finally by its dissolution in excess ammonia with the formation of ammine complexes. The calculated ΔV values (Fig. 1, solid line) nicely agree with the experiment.

EXPERIMENTAL

The dilatometric titration was carried out on a precision installation; its scheme and operation principle were described earlier [17]. The volume changes were detected by the shift of the meniscus of a liquid in a calibrated measuring capillary tube 0.4007 mm in diameter. To ensure the stability of the volume changes, a constant temperature of the system $(25.00\pm0.01^{\circ}C)$ was maintained with two UT-2/77 ultrathermostats and an air thermostat, connected in series.

For each point of the dilatometric curves, $\Delta V_{\rm m}$ was calculated from the experimental data by the following procedure. We determined the absolute changes in the volume (cm³) from the shifts *s* (cm) of the meniscus of a liquid in a calibrated measuring capillary tube by the formula $\Delta V_{\rm abs} = V_{1 \rm cm} s$ ($V_{1 \rm cm}$ is the volume corresponding to 1 cm length of the capillary tube, determined by calibration; for the capillary tube in use, $V_{1 \rm cm} M$ is $1.261 \times 10^{-3} {\rm cm}^3$). For each point, this quantity were converted to $\Delta V_{\rm m}$, equal to the ratio of $\Delta V_{\rm abs}$ to the number of moles of the component being titrated, namely, Cu²⁺ ions.

The pH-metric titration in the system $Cu(NO_3)_2$ -

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 $NH_3 \cdot H_2O$ was carried out on an EV-74 pH meter with a glass electrode. The electronic absorption spectra of solutions were recorded on a Specord UV-VIS spectrophotometer in the range 400–900 nm.

To obtain quantitative characteristics of changes in the volume corresponding to step complex formation, we performed a mathematical simulation using the CPESSP program [18, 19]. The model for processing dilatometric data is based on an additive scheme, which is given in [20], as applied to volume properties.

The basis included the simple species Cu^{2+} , H^+ , OH^- , NH_3 , and NO_3^- , and the complex species NH_4^+ , $Cu(OH)^+$, Cu_2OH^{3+} , $Cu_2(OH)_2^{2+}$, $Cu(NH_3)_n^{2+}$ (n = 1-4), $Cu_2(OH)_3NO_3$, and $Cu(OH)_2$. The distribution of the complexes as a function of N is given in Fig. 5, and the comparison with the experimental data, in Fig. 1.

CONCLUSION

By comprehensive analysis of the data obtained for the system $Cu(NO_3)_2$, $(H^+)-NH_3 \cdot H_2O-H_2O$ by several physicochemical methods, we have determined the ranges of N corresponding to prevalence of various chemical reactions. At N < 0, excess acid is neutralized. The volume effects of the neutralization with an alkali and with an ammonia solution differ significantly, which is due to specific chemical features of ammonia. At N from 0 to 1.5, the hydrolytic polymerization occurs, yielding the poorly soluble complex $Cu_2(OH)_3NO_3$ with both bases. At N > 1.5, the chemical transformations with the two bases are different: in titration with NaOH, solid binuclear copper trihydroxonitrate is converted to copper hydroxide and oxide, and in titration with $NH_3 \cdot H_2O$, it is converted into soluble copper ammines $Cu(NH_3)_n^{2+}$.

ACKNOWLEDGMENTS

The authors are sincerely grateful to I.I. Kozhina for performing the X-ray phase analyses.

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