ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 4, pp. 551–556. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © N.S. Kozhevnikova, A.A. Uritskaya, A.S. Vorokh, A.A. Rempel', 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 4, pp. 568–573.

Ionic Equilibria in Alkaline Aqueous Solutions of Metal Complex Salts

N. S. Kozhevnikova[a,b], A. A. Uritskaya[b], A. S. Vorokh[a], and A. A. Rempel'[a,b]

[a] *Institute of Solid State Chemistry, Ural Division, Russian Academy of Sciences, GSP-145, Ul. Pervomaiskaya 91, Yekaterinburg, 620041 Russia*
e-mail: kozhevnikova@ihim.uran.ru

[b] *Ural State Technical University, Yekaterinburg, Russia*

Received July 24, 2007

Abstract—A thermodynamic analysis of the formation conditions of metal hydroxides was performed. The areas of stable formation of metal hydroxide precipitates in the coordinates pH–metal concentration, including also solutions containing various kinds of complexing agents, were evaluated. With the precipitation of cadmium hydroxide as example, X-ray phase analysis confirmed the formation of metal hydroxide in the chemical composition areas where its formation is predicted by a thermodynamic analysis.

DOI: 10.1134/S1070363208040075

Metal chalcogenides in the form of thin films are used for several decades for optical radiation detection. Recently there has been a trend toward preparing films or dispersions of heavy metal chalcogenides in the nanocrystalline state [1–4], which is stimulated by new important applied properties of nanocrystalline chalcogenides. Usually nanocrystalline chalcogenides have a wider band gap and exhibit a stronger luminescence compared to coarsely crystalline chalcogenides. This property of nanoparticles of such chalcogenides as CdS, PbS, CdSe, ZnSe, CdTe, and PbTe is intended for use in the development of lasers with enhanced emissivity and preset frequency of the generated radiation, as thermoelectrics for efficient direct conversion of heat into electricity and vice versa, in biochemical analysis for medical diagnostics, in monitoring of biological processes in living bodies, and in multicolor coding of the genome structure.

One of the most promising methods for preparing thin semiconductor films based on metal chalcogenides is chemical deposition from aqueous solutions using thiourea [3, 4], which acts as a sulfidizing agent in alkaline solutions [5]. It was found empirically [6, 7] that films of metal sulfides and selenides are formed on nonmetallic surface by chemical deposition from N_2H_4CS solutions only in the range of thermodynamic stability of the corresponding metal hydroxides in solution. Therefore, in this study we performed a thermodynamic analysis of the initial conditions of formation of a metal hydroxide in aqueous solution and determined the area of stable existence of metal complex ions, as influenced by the nature and concentration of a ligand (complexing agent) and by pH at a constant temperature. To check the results of the thermodynamic analysis, we performed a detailed experimental study of the chemical deposition of cadmium hydroxide.

THERMODYNAMIC CALCULATION OF THE AREA OF FORMATION OF METAL HYDROXIDE

It is known that ions of the majority of metals in aqueous solution are subject to hydrolysis, forming hydroxides difficultly soluble in water. In saturated solutions of hydroxides, the state of the equilibrium is described by the solubility product K_{sp}:

$$K_{sp} = [M^{m+}][OH^-]^m, \quad (1)$$

where $[M^{m+}]$ and $[OH^-]$ are the equilibrium concentrations of the free metal ions and hydroxide ions, respectively.

Along with the hydroxide formation, metal ions participate in complexation processes to form mono- and polynuclear hydroxo complexes. In this case, the

hydroxide ions act as substituting ligands. Polynuclear complexes contain several metal atoms, and the equations describing the equilibria are nonlinear in the analytical concentration of metal ions, which complicates the mathematical description of the systems. Therefore, in this study we considered calculation of the initial conditions for the formation of metal hydroxide in aqueous solution according to [8] for metal ions that form mononuclear hydroxo complexes only. These metals are Cu^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+}.

When describing the equilibria in solutions of mononuclear complex ions, we used the stability constants β_i from [9]. For hydroxo complexes $M(OH)_n^{m-n}$ (n is the number of OH^- groups and m is the metal ion charge), the constant β_i has the form

$$\beta_{1,2\ldots n} = [M(OH)_n^{m-n}]/[M^{m+}][OH^-]^n. \quad (2)$$

The condition for the formation of a solid metal hydroxide phase can be determined from Eq. (3):

$$[M^{m+}]_0[OH^-]_0^m > K_{sp}, \quad (3)$$

where $[M^{m+}]_0$ and $[OH^-]_0$ are arbitrary (e.g., initial) concentrations of the free metal ions and hydroxide ions. The concentration of free metal ions $[M^{m+}]_0$ can be determined from the total (analytical) concentration $C_{M,\Sigma}$ of metal in solution: $[M^{m+}]_0 = \alpha_{M^{m+}}C_{M,\Sigma}$, where $\alpha_{M^{m+}}$ is the relative concentration (fraction) of free metal ions, not involved in the complexation. The concentration $C_{M,\Sigma}$ is the total concentration of all the soluble metal species, i.e., of free metal ions and its hydroxo complexes:

$$C_{M,\Sigma} = [M^{m+}] + [MOH^{m-1}] + \ldots + [M(OH)_n^{m-n}]. \quad (4)$$

Taking into account (2) and (4), the fraction of free M^{m+} ions in solution can be calculated from Eq. (5):

$$\alpha_{M^{m+}} = \frac{[M^{m+}]}{C_{M,\Sigma}} = \frac{1}{1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \ldots + \beta_n[OH^-]^n}$$

$$= \frac{1}{1 + \Sigma\beta_i[OH^-]^{\nu_i}}. \quad (5)$$

By expressing the concentration of OH^- ions through the ionic product of water K_w, Eq. (1) in the logarithmic form can be transformed as follows:

$$pC_{M,\Sigma} = pK_{sp} - p\alpha_{M^{m+}} - mpK_w + m\text{pH}, \quad (6)$$

where p denotes the negative decimal logarithm of the corresponding quantity. This equation can be used for calculating the total concentration of soluble metal species and of pH values at which the hydroxide precipitates from a solution containing metal complex ions.

When one more complexing agent is introduced into an alkaline solution, the mutual ligand substitution becomes possible. Let us consider the complexation in an alkaline solution in which the OH^- ion competes with such ligands stable in alkaline solution as ammonia of ethylenediamine-*N*,*N*,*N*',*N*'-tetraacetic acid (EDTA, H_4Y).

In an aqueous solution containing ammonia, the fraction of free metal ions is calculated by Eq. (7):

$$\alpha_{M^{m+}} = \frac{[M^{m+}]}{C_{M,\Sigma}} = \frac{1}{1 + \Sigma\beta_i[OH^-]^{\nu_i} + \Sigma\beta_i'[NH_3]^{\nu_i}}, \quad (7)$$

where $[M(NH_3)_{\nu_i}^{m+}]/\{[M^{m+}][NH_4]^{\nu_i}\}$ are the stability constants of ammine complexes, and $[NH_4]$ is the equilibrium concentration of the molecular form of ammonia, not involved in the complexation, in solution.

To calculate $\alpha_{M^{m+}}$ by Eq. (7), it is necessary to know the concentration of the molecular form of ammonia, because in aqueous solution there is an equilibrium $NH_4 + H_2O \rightleftarrows NH_4^+ + OH^-$, characterized by the equilibrium constant K_{NH_4} at 298 K [9]:

$$K_{NH_4} = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.76\times10^{-5}. \quad (8)$$

The total analytical concentration of ammonia in solution is given by Eq. (9):

$$C_{NH_4} = [NH_3] + [NH_4^+]. \quad (9)$$

Knowing the ionic equlibrium of water at 298 K, $K_w = [H^+][OH^-] = 10^{-14}$, and taking into account expression (8) for the equilibrium constant, we transform Eq. (9) into (10):

$$C_{NH_4} = [NH_3]\{1 + \frac{[NH_4^+]}{[NH_3]}\}$$

$$= [NH_3]\{1 + \frac{K_{NH_4}}{[OH^-]}\} = NH_3\{1 + \frac{K_{NH_4}[H^+]}{Kw}\}. \quad (10)$$

The relative concentration (fraction) of the molecular form of ammonia is given by

$$\alpha_{NH_4} = \frac{[NH_3]}{C_{NH_4}} = \frac{[NH_3]}{[NH_3]\{1 + \frac{K_{NH_4}[H^+]}{K_w}\}} = \frac{K_w}{K_w + K_{NH_4}[H^+]}. \quad (11)$$

Calculation by Eq. (11) shows that, at pH > 10, ammonia introduced into the reaction mixture is virtually entirely present in the molecular form and can participate in formation of ammine complexes.

On introducing EDTA instead of ammonia, complexes MHY^{m-3} and MY^{m-4} are formed in alkaline solution, and, when calculating $\alpha_{M^{m+}}$, the fractions $\alpha_{HY^{3-}}$ and $\alpha_{Y^{4-}}$ of $HY^{3-}$and Y^{4-} ions, determined by relationships (12) and (13) should be taken into account.

$$\alpha_{HY^{3-}} = \frac{[H^+]K_1K_2K_3}{[H^+]^4 + [H^+]^3K_1 + [H^+]^2K_1K_2 + [H^+]K_1K_2K_3 + K_1K_2K_3K_4}, \quad (12)$$

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4}{[H^+]^4 + [H^+]^3K_1 + [H^+]^2K_1K_2 + [H^+]K_1K_2K_3 + K_1K_2K_3K_4}. \quad (13)$$

Here K_1, K_2, K_4, and K_4 are the constants of the first, second, third, and fourth steps of EDTA ionization, respectively. Calculation by Eqs. (12) and (13) showed that, at 8 < pH < 12, the major EDTA species is HY^{3-}, and at pH > 12 EDTA mainly exists in the form of Y^{4-} ions.

For a solution in which the OH– ion competes with HY^{3-} and Y^{4-} ions, the fraction of free metal ions is calculated by formula (14):

$$\alpha_{M^{m+}} = \frac{[M^{m+}]}{C_{M,\Sigma}} = \frac{1}{1 + \sum_{i=1}^{n} \beta_i[OH^-]^{\nu_i} + \beta_1''\alpha_{HY^{3-}}[H_4Y] + \beta_2''\alpha_{Y^{4-}}[H_4Y]}, \quad (14)$$

where β_1'' and β_2'' are the formation constants of the complex ions MHY^{m-3} and MY^{m-4}, and $[H_4Y]$ is the equilibrium concentration of EDTA participating in the complexation.

Cadmium hydroxide plays an important role in chemical deposition of semiconducting nanocrystalline cadmium sulfide of cadmium selenide films on a solid surface. On the other hand, cadmium ions can form mononuclear hydroxo complexes and stable ammine or chelate complexes.

The fraction $\alpha_{Cd^{2+}}$ of free cadmium ions, not involved in the complexation, is calculated by the equaions given below. For a solution containing only one ligand, OH^- ion, this is done by Eq. (15) as a particular case of Eq. (5):

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{C_{Cd,\Sigma}} = \frac{1}{1 + \beta_1[OH] + \beta_2[OH]^2 + \beta_3[OH]^3 + \beta_4[OH]^4} = \frac{1}{1 + \sum_{i=1}^{4} \beta_i[OH^-]^{\nu_i}}. \quad (15)$$

For a solution in which OH^- ions compete with ammonia, this is done by Eq. (16) using Eq. (6):

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{C_{Cd,\Sigma}} = \frac{1}{1 + \sum_{i=1}^{4} \beta_i[OH^-]^{\nu_i} + \sum_{i=1}^{6} \beta_i'[NH_3]^{\nu_i}}. \quad (16)$$

In alkaline solutions of H_4Y, $\alpha_{Cd^{2+}}$ is calculated by Eq. (17):

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{C_{Cd,\Sigma}} = \frac{1}{1 + \sum_{i=1}^{4} \beta_i[OH^-]^{\nu_i} + \beta_1''\alpha_{HY^{3-}}[NY^{3-}] + \beta_2''\alpha_{Y^{4-}}[Y^{4-}]}. \quad (17)$$

In these equations, $C_{Cd,\Sigma}$ is the analytical concentration of cadmium in solution; $[Cd^{2+}]$ is the concentration of free cadmium ions, not involved in the complexation; β_1, β_2, β_4, and β_4 are the stability constants of the complex species $CdOH^+$, $Cd(OH)_2$, $Cd(OH)_4^-$, and $Cd(OH)_4^{2-}$; β_1', β_2', β_3', β_4', β_5', and β_6' are the stability constants of the complex ions $Cd(NH_4)^{2+}$, $Cd(NH_4)_2^{2+}$, $Cd(NH_4)_4^{2+}$, $Cd(NH_4)_4^{2+}$, $Cd(NH_4)_5^{2+}$, and $Cd(NH_4)_6^{2+}$, respectively; β_1'' and β_2'' are the stability constants of the complex ions $CdHY^-$and CdY^{2-}.

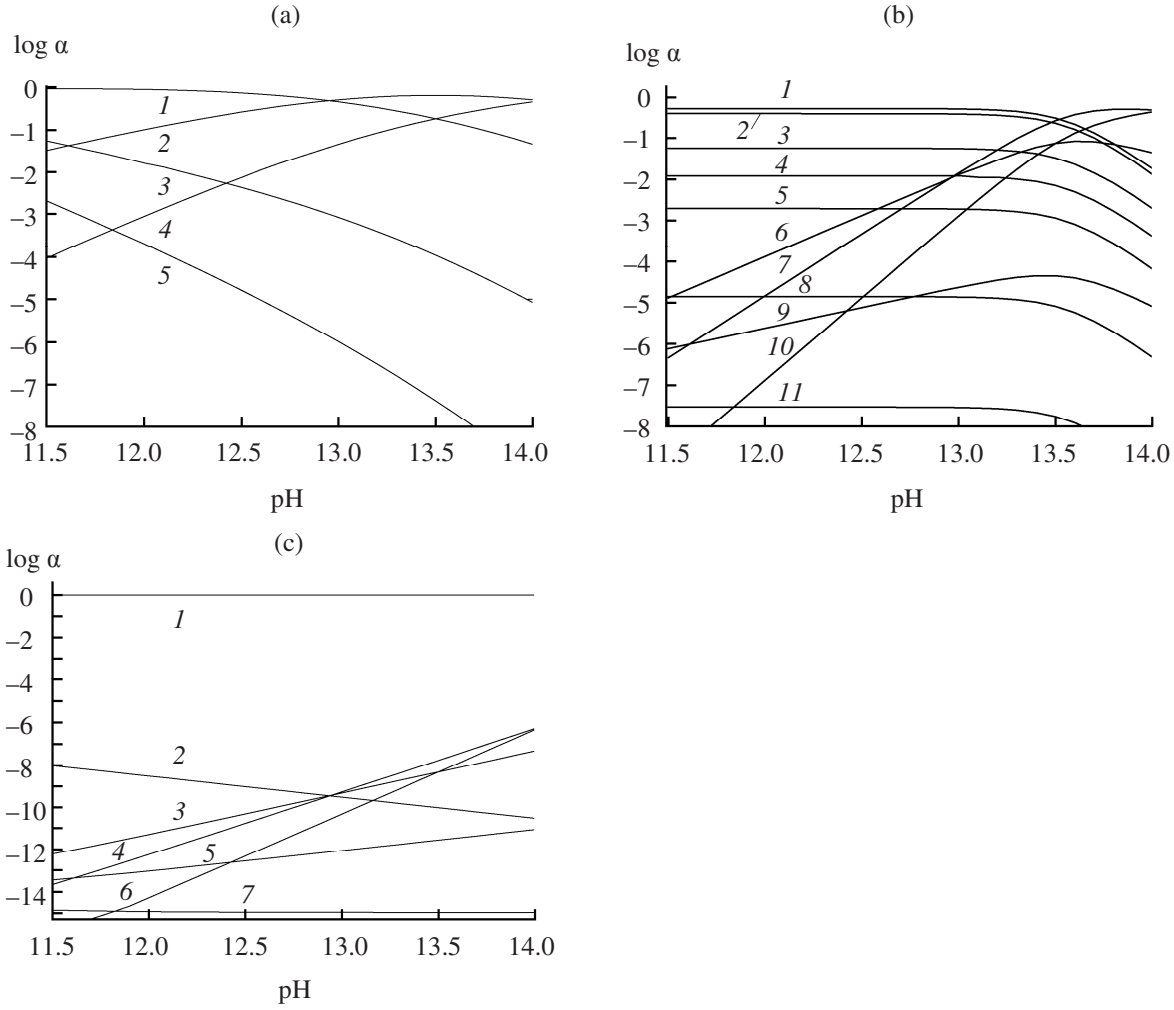

Fig. 1. Distribution diagram of cadmium complex species in aqueous solutions. System: (a) soluble cadmium salt–alkali–water; (b) soluble cadmium salt–ammonia–alkali–water; (c) soluble cadmium salt–EDTA–alkali–water. (a) (*1*) $Cd(OH)_2$, (*2*) $Cd(OH)_4^-$, (*3*) $CdOH^+$, (*4*) $Cd(OH)_4^{2-}$, and (*5*) Cd^{2+}; (b) (*1*) $Cd(NH_4)_4^{2+}$, (*2*) $Cd(NH_4)_5^{2+}$, (*3*) $Cd(NH_4)_4^{2+}$, (*4*) $Cd(NH_4)_6^{2+}$, (*5*) $Cd(NH_4)_2^{2+}$, (*6*) $Cd(OH)_2$, (*7*) $Cd(OH)_4^-$, (*8*) $Cd(NH_4)^{2+}$, (*9*) $CdOH^+$, (*10*) $Cd(OH)_4^{2-}$, and (*11*) Cd^{2+}; (c) (*1*) CdY^{2-}, (*2*) $CdHY^-$, (*3*) $Cd(OH)_2$, (*4*) $Cd(OH)_4^-$, (*5*) $CdOH^+$, (*6*) $Cd(OH)_4^{2-}$, and (*7*) Cd^{2+}.

Similarly to formulas (15)–(17), we can calculate the fraction of any complex ion which will be equal to the ratio of the concentration of the given species to the analytical concentration of cadmium in solution. Figure 1 shows the distribution diagrams for cadmium complexes in the systems soluble cadmium salt–alkali–water (Fig. 1a), soluble cadmium salt–ammonia–alkali–water (Fig. 1b), and soluble cadmium salt–EDTA–alkali–water (Fig. 1c).

Calculation of the fractions of all cadmium species in soluitons in relation to pH of the reaction mixture shows that, in the system soluble cadmium salt–alkali–water (Fig. 1a), at pH < 12.5, the complex $Cd(OH)_2$ prevails in the solution. At pH > 12.5, the fractions of the $Cd(OH)_4^-$ and $Cd(OH)_4^{2-}$ anions increase, and at pH 14 cadmium is present in solution mainly in the form of $Cd(OH)_4^-$ and $Cd(OH)_4^{2-}$.

Analysis of the ionic composition of solution in the system soluble cadmium salt–ammonia–alkali–water (Fig. 1b) shows that the prevalent species at pH < 13 are the complexes $Cd(NH_4)_4^{2+}$ and $Cd(NH_4)_5^{2+}$, whose mole fraction does not noticeably changhe with increasing pH. However, at pH 13–14 the concentration of these complexes decreases, and the hydroxo complexes $Cd(OH)_4^-$ and $Cd(OH)_4^{2-}$ start to prevail.

With EDTA as ligand, free cadmium ions are absent in the solution, and at pH > 7 cadmium occurs in solution virtually exclusively in the form of CdY^{2-} ions (Fig. 1c).

Using Eqs. (15)–(17), we calculated the ranges of existence of cadmium hydroxide for each of the above systems, i.e., we plotted the pH dependence (6) of the equilibrium total concentration of the free and complex cadmium ions in solution:

$$pC_{Cd,\Sigma} = pK_{sp} - p\alpha_{Cd^{2+}} - 2pK_w + 2pH. \qquad (18)$$

The ligand concentrations may vary independently; therefore, presentation of such equilibria requires 3D plotting. For the planar presentation, the concentration of one of the two ligands was set constant (Fig. 2).

According to the calculations for T 298 K, in a solution in which only cadmium hydroxo complexes can be formed, the solubility of cadmium hydroxide $Cd(OH)_2$ drastically decreases with increasing pH.

In the pH range 10.5–12.5, the $Cd(OH)_2$ solubility becomes minimal and virtually equal to its intrinsic solubility, 10^{-6} M. At pH > 12.5, anionic hydroxo complexes start to form, and the solubility of cadmium hydroxide increases to 2×10^{-5} M at pH 14 (Fig. 2, curve *1*).

Introduction of other complexing agents, along with hydroxide ions, into the solution noticeably increases the equilibrium concentration of cadmium in solution and increases the $Cd(OH)_2$ solubility. As seen from Fig. 2 (curve *2*), introduction of ammonia into an aqueous solution of cadmium salt increases the solubility of cadmium hydroxide in the pH range 7–12 owing to formation of stable [9] ammine complexes $Cd(NH_4)_n^{2+}$, n = 1–6. With an increase in pH, the equilibrium concentration of cadmium ions decreases, and at pH > 13.5 ammonia does not participate in the complexation, with only the cadmium hydroxo complexes $Cd(OH)_n^{m-n}$ existing in the solution.

The use of EDTA conisderably extends the area of existence of soluble cadmium species, fully preventing formation of cadmium hydroxide at cadmium concentrations of up to 10^2 M (Fig. 2, area over curve *3*). With EDTA, the so-called chelate effect is observed: enhancement of the stability of an inner complex compound relative to the related complexes with simple ligands [10], e.g., with NH_4 and OH^- .

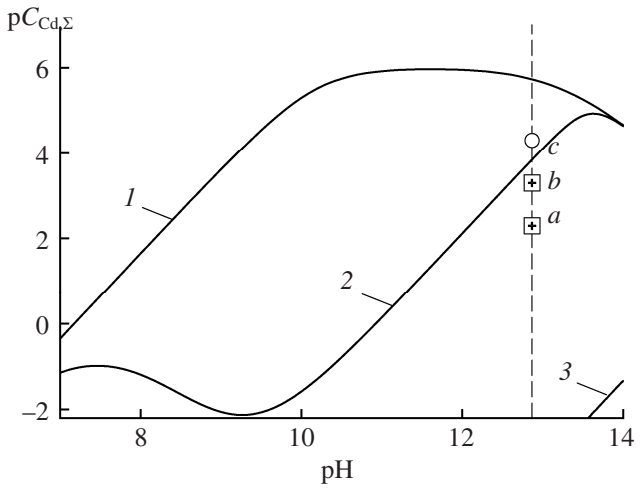

Fig. 2. Total equilibrium concentration of free and complex cadmium ions in solution as a function of pH. System: (*1*) Cd^{2+}–OH^-–H_2O; (*2*) Cd^{2+}–NH_4–OH^-–H_2O, [NH_4] 1.5 M; and (*3*) Cd^{2+}–EDTA–OH^-–H_2O, [EDTA] 0.025 M. In areas over curves *1*, *2*, and *3*, cadmium hydroxide in the corresponding system is not formed. Points *a, b*, and *c* correspond to the compositions of reaction mixtures that were used for experimental check of the thermodynamic calculations. From mixtures *a* and *b*, $Cd(OH)_2$ was obtained, whereas in mixture c no $Cd(OH)_2$ precipitate was found.

EXPERIMENT ON PRECIPITATION OF CADMIUM HYDROXIDE

To check the thermodynamic approach described above, we performed experiments on the precipitation of cadmium hydroxide in various systems. In the experiment on the precipitation of cadmium hydroxide, into an alkaline solution with pH 12.87 we added a cadmium salt in a concentration of 5×10^{-3} M. After the equilibrium was attained, the cadmium concentration in the solution was about 10^{-6} M, being equal to the intrinsic solubility of $Cd(OH)_2$ (Fig. 2, point *a*).

The cadmium concentration in solution was determined by direct complexometric titration with visual detection of the equivalence point using Eriochrome Black T indicator [10]. The structural certification of the cadmium hydroxide obtained was performed by X-ray phase analysis. It is known that cadmium hydroxide has several crystal structures, but in this study we observed only the phase with space group $P\bar{3}m_1$ (no. 164) (PDF-031-0228), with the following unit cell parameters: a 349.47, c 471.06 pm. The theoretical density of the hydroxide phase we detected is 4.81 g cm^{-3}.

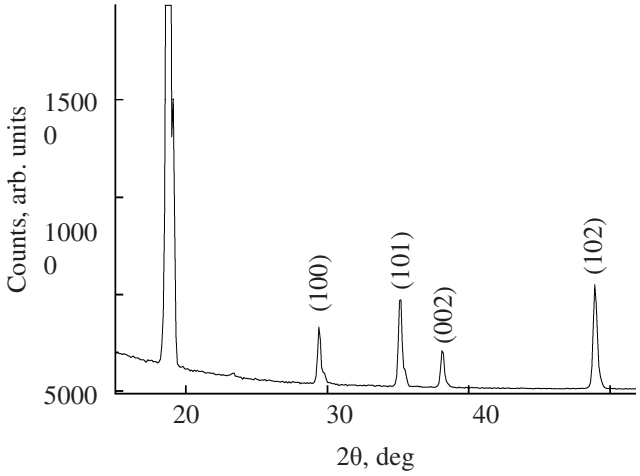

Fig. 3. X-ray diffraction pattern of cadmium hydroxide prepared from a reaction mixture of the initial composition (M) $C_{Cd,\Sigma}$ 0.05, $[NH_4]$ 1.5, and [NaOH] 0.074.

The reflections are observed at 2θ 18.9°, 29.5°, 32.3°, 38.2°, 49.0°, 52.4°, 56.1°, 58.8°, etc. (Fig. 3).

In a solution that had a similar composition but also contained ammonia in a constant concentration of 1.5 M, the equilibrium concentration of the dissolved cadmium species over the $Cd(OH)_2$ precipitate was about 5×10^{-4} M. That is, 10% of cadmium ions were present in the dissolved state, and 90%, in the solid hydroxide precipitate. Thus, the increase in the hydroxide solubility in this system is confirmed experimentally (Fig. 2, point *b*). With EDTA (0.025 M) as complexing agent, no hydroxide precipitated (Fig. 2, point *c*).

Thus, the area of formation of cadmium hydroxide in the metal concentration–ligand concentration–pH diagram, predicted by the calculations, was confirmed experimentally. The calculation formulas given above can be used for choosing quantitative compositions of reaction baths for chemical deposition of metal chalcogenide films, so as to ensure the initial formation of the metal hydroxide in the mixture. Similar calculations can be applied to systems containing metal ions that form mononuclear hydroxo complexes and stable ammine or chelate complexes, such as Cd^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 08-03-00 111a) and by program no. 4-2R of the Division of Chemistry and Materials Science, Russian Academy of Sciences.

REFERENCES

1. Rempel', A.A., *Usp. Khim.,* 2007, vol. 76, no. 5, p. 474.
2. Uritskaya, A.A., Bol'shchikova, T.P., and Kozhevnikova, N.S., *Zh. Obshch. Khim.*, 2007, vol. 77, no. 5, p. 717.
3. Kozhevnikova, N.S., Rempel', A.A., Hergert, F., and Magerl, F., *Zh. Fiz. Khim*., 2007, vol. 81, no. 5, p. 768.
4. Rempel, A.A., Kozhevnikova, N.S., Van den Berghe, S., Van Renterghem, W., and Leenaers, A.J.G., *Phys. Status Solidi*, 2005, vol. 242, no. 7, p. R61.
5. Kitaev, G.A., Bol'shchikova, T.P., Fofanov, G.M., Yatlova, L.E., and Goryukhina, N.M., in *Kinetika i mekhanizm obrazovaniya tverdoi fazy* (Kinetics and Mechanism of Solid Phase Formation), Sverdlovsk: Ural'sk. Politekh. Inst., 1968, p. 113.
6. Kitaev, G.A., Mokrushin, S.G., and Uritskaya, A.A., *Kolloidn. Zh*., 1965, vol. 27, no. 1, p. 51.
7. O'Brien, P. and Saeed, T., *J. Crystal Growth*, 1996, vol. 158, no. 4, p. 497.
8. Butler, J.N., *Ionic Equilibrium* (A Mathematical Approach), Reading, Massachusetts: Addison–Wesley, 1964.
9. Lur'e, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Handbook of Analytical Chemistry), Leningrad: Khimiya, 1989.
10. Schwarzenbach, G. and Přibil, R., *Komplexometrie*, Prague: Chemapol, 1955. Translated under the title *Kompleksonometriya*, Moscow: Goskhimizdat, 1958, p. 5.