

COLLOID CHEMISTRY
AND ELECTROCHEMISTRY

Diagrams of the Formation of In_2S_3 and In_2Se_3 Films on Vitroceramic upon Precipitation, According to Potentiometric Titration

S. S. Tulenin^a, S. A. Bakhteev^b, R. A. Yusupov^b, L. N. Maskaeva^{a,c}, and V. F. Markov^{a,c}

^aYeltsin Ural Federal University, Yekaterinburg, 620002 Russia

^bKazan National Research Technological University, Kazan, 420005 Russia

^cUral Institute of GPS MChS of Russia, Yekaterinburg, 620022 Russia

e-mail: mln@ural.ru

Received December 14, 2012

Abstract—Boundary conditions and ranges of the formation of indium(III) sulfide and selenide upon precipitation by thiocarbamide and selenocarbamide are determined. Potentiometric titration of indium chloride (InCl_3) in the concentration range of 0.0001 to 0.100 mol/L by a solution of sodium hydroxide is performed. It is found that the following pH ranges are optimal for In_2S_3 and In_2Se_3 film precipitation: from 3.0 to 4.5 and from 9.0 to 14.0. Indium selenide layers 100 to 300 nm thick are prepared on vitroceramic by hydrochemical precipitation.

Keywords: indium sulfide, indium selenide, ionic equilibria, boundary conditions of formation, complexation, solubility on intermediate, potentiometric titration, thin films.

DOI: 10.1134/S003602441310018X

INTRODUCTION

In recent years, indium selenide and sulfide have found wide use in micro- and optoelectronics as nuclear emission detectors, red and green semiconductor diodes, and microwave shielding due to their unique electrophysical properties [1–5]. Thin films of three-component compounds based on CuInSe_2 and CuInS_2 indium chalcogenides are in high demand as materials for converters of solar radiation. Hydrochemical precipitation is of particular interest as a simple and profitable method for their synthesis and allows us to obtain layers on substrates of various materials, including those of complex configuration, and is intrinsic to the low-temperature regime of precipitation. The nanostructured character of the metal chalcogenide films obtained according to this method shifts the range of photosensitivity to the shorter wavelengths of the spectrum. At the same time, there are virtually no data on physicochemical studies of the hydrochemical film precipitation of individual indium chalcogenides or solid solution solutions based on them in the literature. One reason for this is the stability of the hydroxocomplexes formed by indium.

Choosing the composition of the reaction mixture and determining the conditions of the colloidal chemical precipitation of indium sulfide In_2S_3 and selenide In_2Se_3 is considerably simplified after calculating the ionic equilibria for the boundary conditions of the precipitation of these compounds from aqueous solutions. Earlier, we proposed a procedure for calculating the conditions of the formation of metal sulfides and

selenides in the presence of complexing agents that considered the behavior of the chalcogenizer [6]. This procedure also enabled us to calculate the boundary conditions of the formation of metal hydroxide phase, ensuring the nucleation and formation of chalcogenide films according to the so-called hydroxide scheme. Potentiometric titration of a solution notably corrects the conditions for the formation of solid phases. In [7], an original procedure for treating the results from such titration was proposed that ensured a marked increase in the precision of predictions. Building a mathematical model of the system lays a foundation that includes not only the stability constants of the main components in a solution, but also the constants of complex compounds in negligibly small concentrations that nevertheless affect its precipitation [8]. Ignoring the effect of these complex forms introduces model error as systematic error. The precision of predictions for determining the conditions of the precipitation of thin films is of particular interest.

The aim of this work was to determine the boundary conditions for the chemical precipitation of indium(III) sulfide and selenide based on a complex approach involving the calculation of ionic equilibria in the reaction system and using the results from potentiometric titration.

EXPERIMENTAL

In order to reveal the boundary conditions of hydrochemical precipitation of In_2S_3 and In_2Se_3 , the

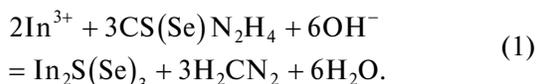
range of metal salt concentration depending on the pH of reaction mixture was determined from calculations using the procedure in [6]. We analyzed the ionic equilibria in two multicomponent systems, indium chloride–sodium hydroxide–thiocarbamide and indium chloride–sodium hydroxide–selenocarbamide.

Potentiometric titration was performed according to the generally accepted procedure using 0.100 to 0.0001 M solutions of indium salt InCl_3 and alkali solutions NaOH (both of pure for analysis grade) and a pH-121 pH-meter. The results from titration were processed with the EQ-5 program designed and proposed in [7].

Indium selenide films were precipitated onto preliminarily degreased ST-50-1 vitroceraamic substrates from a reaction mixture containing indium chloride InCl_3 , sodium hydroxide NaOH, and selenocarbamide CSeN_2H_4 in the temperature range of 333 to 353 K in sealed glass reactors. Reactors were placed in a TS-TB-10 thermostat that maintained the temperature with a precision of ± 0.1 K. The time of film precipitation was 120 min. Film thickness was determined using an MII-4M microinterferometer.

RESULTS AND DISCUSSION

The formation of indium sulfide (selenide) using thio(seleno)carbamide as chalcogenizer can be described as



The correspondence of the solubility product of metal selenide to ionic product, i.e., the product of the concentrations of free (noncomplexed) metal ions and chalcogenide ions was considered a condition of its solid phase formation. The reversible character of the hydrolytic decomposition of indium sulfide and selenide was the basis for our analysis of ionic equilibria upon their precipitation from solutions containing thio(seleno)carbamide [9].

In order to determine the minimum concentrations of indium salt in the reaction mixture that were needed for formation of the solid phase of chalcogenides depending on the pH of the medium when using thiocarbamide and selenocarbamide, we used equations derived from the general equation given in [6] for calculating the boundary conditions for the chemical precipitation of metal chalcogenides,

$$pC_{\text{in}} = \frac{1}{2} p\text{SP}_{\text{In}_2\text{S}_3} - p\alpha_{\text{In}^{3+}} \quad (2)$$

$$- \frac{3}{2} \left(pk_{\text{H}_2\text{S}} - 2p\text{H}_{\text{H}} + \frac{1}{2} pK_{\text{C}} + \frac{1}{2} p[\text{CSN}_2\text{H}_4]_{\text{in}} + \frac{1}{2} p \frac{\beta_{\text{c}}}{\beta_{\text{S}}} \right),$$

$$pC_{\text{in}} = \frac{1}{2} p\text{SP}_{\text{In}_2\text{Se}_3} - p\alpha_{\text{In}^{3+}} \quad (3)$$

$$- \frac{3}{2} \left(pk_{\text{H}_2\text{Se}} - 2p\text{H}_{\text{H}} \right.$$

$$\left. + \frac{1}{2} pK_{\text{C}} + \frac{1}{2} p[\text{CSeN}_2\text{H}_4]_{\text{in}} + \frac{1}{2} p \frac{\beta_{\text{c}}}{\beta_{\text{Se}}} \right),$$

where pC_{H} is the exponent of the concentration of indium salt in the reaction mixture; $p\text{SP}_{\text{In}_2\text{S}_3}$ and $p\text{SP}_{\text{In}_2\text{Se}_3}$ are exponents of the solubility product of indium sulfide and selenide, respectively; $p\alpha_{\text{In}^{3+}}$ is the exponent of the fractional concentration of In^{3+} ions in solution calculated with allowance for the stability constants of In(III) complex compounds [6, 9]; $pk_{\text{H}_2\text{S}}$ and $pk_{\text{H}_2\text{Se}}$ are exponents of full constants of the ionization of hydrogen sulfide and hydrogen selenide; $pk_{\text{CSN}_2\text{H}_4}$ and $pk_{\text{CSeN}_2\text{H}_4}$ are exponents of the constants of hydrolytic decomposition of thiocarbamide and selenocarbamide, respectively; and $p[\text{CSN}_2\text{H}_4]_{\text{in}}$ and $p[\text{CSeN}_2\text{H}_4]_{\text{in}}$ are exponents of the initial concentrations of thiocarbamide and selenocarbamide, respectively. The β_{S} , β_{Se} , and β_{c} values characterizing the decomposition of hydrogen sulfide(selenide) and cyanamide depending on pH are

$$\beta_{\text{S}} = [\text{H}_3\text{O}^+]^2 + k_{\text{HS}^-}[\text{H}_3\text{O}^+] + k_{\text{H}_2\text{S}}, \quad (4)$$

$$\beta_{\text{Se}} = [\text{H}_3\text{O}^+]^2 + k_{\text{HSe}^-}[\text{H}_3\text{O}^+] + k_{\text{H}_2\text{Se}}, \quad (5)$$

$$\beta_{\text{c}} = [\text{H}_3\text{O}^+]^2 + k_{\text{HCN}_2^-}[\text{H}_3\text{O}^+] + k_{\text{H}_2\text{CN}_2}, \quad (6)$$

where pk_{HS^-} , pk_{HSe^-} , and $pk_{\text{HCN}_2^-}$ are exponents of the dissociation constants of hydrogen sulfide (selenide) and cyanamide by the first step, respectively; and $pk_{\text{H}_2\text{CN}_2}$ is the exponent of the full dissociation constant of cyanamide.

Equations (2) and (3) satisfactorily describe the boundary conditions for the formation of indium sulfide and selenide upon the reaction between its salt and the corresponding chalcogenizer. As follows from our equations, the required (initial) concentration of metal salt is determined by a series of thermodynamic constants and depends on the given pH value of reaction mixture; the fraction of free metal ions $\alpha_{\text{In}^{3+}}$ resulting from the concentration of ligands and the stability of complex forms of metal in which they participate; and the content of chalcogenizer in solution.

Along with indium sulfide or selenide in solution, the precipitation of its hydroxide $\text{In}(\text{OH})_3$ is also possible in a broad range of pH. Considering the high stability of this compound, which is capable of influencing reaction (1), it is important to estimate the boundary conditions of its formation. The minimum initial concentration of metal salt pC_{in} ensuring the formation of indium hydroxide phase depending on pH was determined according to the equation [6]

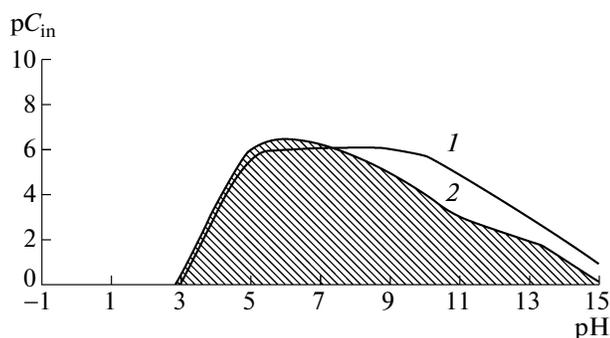


Fig. 1. Boundary conditions of the formation of indium sulfide and hydroxide upon precipitation by thiocarbamide: (1) In_2S_3 and (2) $\text{In}(\text{OH})_3$ (the range of formation is denoted by the dashed line). Calculations were performed at $T = 298 \text{ K}$ and a 0.05 mol/L concentration of thiocarbamide CSN_2H_4 .

$$pC_{\text{in}} = p\text{SP}_{\text{In}(\text{OH})_3} - p\alpha_{\text{In}^{3+}} - 3pK_w + 3pH_{\text{H}}, \quad (7)$$

where $p\text{SP}_{\text{Me}(\text{OH})_n}$ is the exponent of the solubility product of indium hydroxide and pK_w is the exponent of the ionic product of water. It should be noted that the precipitation of indium hydroxide is also determined by the fraction of free indium ions $\alpha_{\text{In}^{3+}}$ in the reaction bath [6, 9].

In the above $\text{InCl}_3\text{--NaOH--CS}(\text{Se})\text{N}_2\text{H}_4\text{--H}_2\text{O}$ systems, indium is represented by several hydroxocomplexes with the following exponents of their instability constants: $\text{In}(\text{OH})^{2+}$ ($pK_{\text{in}} = 9.9$ [10]), $\text{In}(\text{OH})_2^+$ ($pK_{\text{in}} = 19.8$ [10]), $\text{In}(\text{OH})_3$ ($pK_{\text{in}} = 29.6$ [11]), and $\text{In}(\text{OH})_4^-$ ($pK_{\text{in}} = 28.7$ [10]).

Calculations to determine the boundary conditions for the formation of indium sulfide, selenide, and hydroxide were performed at the following values of thermodynamic constants ($T = 298 \text{ K}$): $p\text{SP}_{\text{In}_2\text{S}_3} = 76.6$ [11], $p\text{SP}_{\text{In}_2\text{Se}_3} = 93.0$ [11], $p\text{SP}_{\text{In}(\text{OH})_3} = 36.92$ [12], $pK_{\text{H}_2\text{S}} = 19.88$ [10], $pK_{\text{H}_2\text{Se}} = 14.89$ [10], $pK_{\text{HS}^-} = 6.99$ [9], $pK_{\text{HSe}^-} = 3.89$ [9], $pK_{\text{HCN}_2^-} = 10.33$ [6], $pK_{\text{H}_3\text{CN}_2} = 21.52$ [6], $pK_{\text{CSN}_2\text{H}_4} = 22.48$ [12], $pK_{\text{CSeN}_2\text{H}_4} = 28.05$ [12], and $pK_w = 14$ [10]. The initial concentration of thiocarbamide and selenocarbamide was set at 0.05 mol/L .

Results from our calculations according to Eq. (2) in $pC_{\text{in}} = f(\text{pH})$ coordinates are given in Fig. 1, which shows the boundary conditions for the formation of solid phases In_2S_3 and $\text{In}(\text{OH})_3$ upon precipitation by thiocarbamide.

As follows from the plotted dependences, the precipitation of indium sulfide is accompanied by the formation of its hydroxide $\text{In}(\text{OH})_3$ in an even broader pH range. The synthesis of In_2S_3 is possible in the pH range of 3.0 to 14.0 , presumably as a result of the sulfidization of the formed hydroxide.

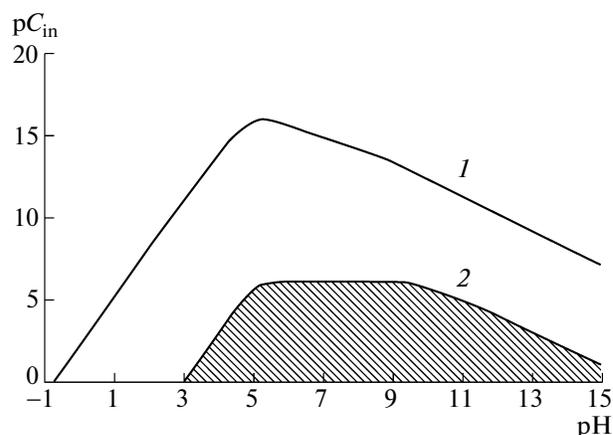


Fig. 2. Ranges of the formation of solid phase In_2Se_3 from the hydroxide system upon precipitation with selenocarbamide: (1) $\text{In}(\text{OH})_3$ (the range of formation is denoted by the dashed line) and (2) In_2Se_3 . Calculations were performed at $T = 298 \text{ K}$ and a 0.05 mol/L concentration of selenocarbamide CSeN_2H_4 .

The results from our calculations using Eq. (3) are given in Fig. 2. As in previous case, we can see that the precipitation of In_2Se_3 chalcogenide is accompanied by the formation of $\text{In}(\text{OH})_3$ in a broad range of pH. The precipitation of In_2Se_3 is possible in the pH range of 2.0 to 14.0 .

As follows from our results, the formation of both sulfides and selenides of indium in the investigated systems proceeds under conditions of coprecipitation with the phase of its hydroxide. It is known that the presence of hydroxide phase at the initial step of process generally has a positive effect on the adhesion of metal sulfide films on a substrate upon hydrochemical precipitation [9] and the optimum pH values of process are usually the values near the boundary of the formation of the metal hydroxide phase. However, the high stability of indium hydroxocomplexes and the broad pH range of the precipitation of $\text{In}(\text{OH})_3$ complicates the selection of precipitation conditions of In_2S_3 and In_2Se_3 . This dictates the need to optimize the pH range of their formation by performing the potentiometric titration of indium salt solutions.

As was shown in [7], a quite reliable model of a metal ion–water–complexing agent system can be plotted using the data from potentiometric titration. This enables us to determine rather quickly the presence of various complex forms of metal in solution and find the optimum pH value for the precipitation of required phase. Having this mathematical model of equilibrium processes in metal ion–water–complexing agents system considerably simplifies the problem of optimizing the synthesis of metal chalcogenides [8]. Thermodynamic descriptions of the reactions and products of hydrolysis allows us to determine the direction and character of various chemical transformations. In studying the hydrolysis of metal salts in

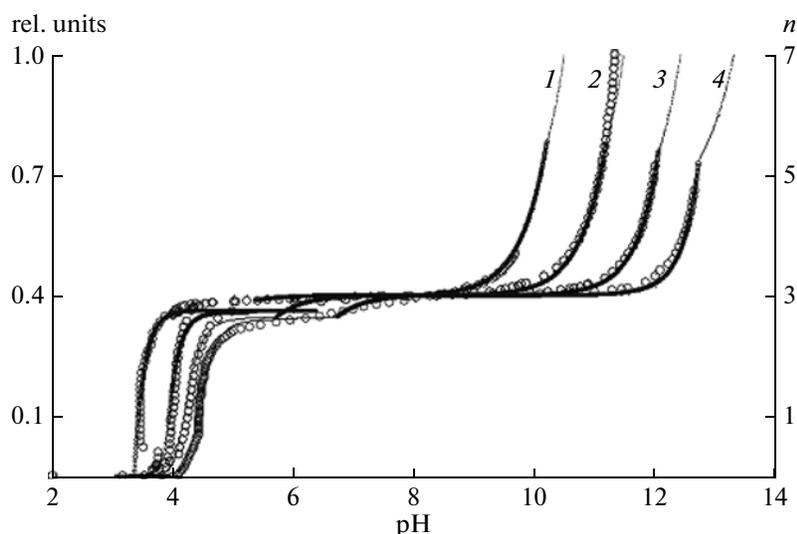


Fig. 3. Function of the formation on hydroxide ions (n) vs. the pH of solution, according to the results from treating experimental (circles) and theoretical (bold lines) potentiometric titration curves at various initial concentrations of indium chloride and alkali, mol/L: (1) $C_{\text{In(III)}} = 0.0001$, $C_{\text{NaOH}} = 0.001$; (2) $C_{\text{In(III)}} = 0.001$, $C_{\text{NaOH}} = 0.010$; (3) $C_{\text{In(III)}} = 0.010$, $C_{\text{NaOH}} = 0.100$; and (4) $C_{\text{In(III)}} = 0.100$, $C_{\text{NaOH}} = 1.00$. The equilibrium constant values given in the table were used to calculate the theoretical titration curves.

highly concentrated solutions (0.01 to 0.5 mol/L), the formation of polynuclear forms intrinsic to most metal hydroxocomplexes was detected in [13]. Mechanisms of the hydrolysis of metal ions in diluted solutions (10^{-4} to 10^{-6} g-ion/L) are mainly characterized by the formation of monomer hydroxocomplexes [14]. For reliable simulations of the formation of metal chalcogenide, we must use the equation for intermediate solubility and consider the hydroxocomplexes formed in the system in appreciable molar fractions, along with the compounds found in molar fractions of less than 0.01 but still determining the conditions for saturation of the solution in a particular solid phase.

Figure 3 shows the experimental curves from the potentiometric titration of indium chloride solutions using sodium hydroxide in $n_{\text{OH}^-} = f(\text{pH})$, where n_{OH^-} is the function of formation or the hydroxide ion ligand number:

$$n_{\text{OH}^-} = C_{\text{titr}}V_i / (C_{\text{Me}}V_{\text{Me}}), \quad (8)$$

where C_{Me} and V_{Me} are the initial concentration of metal ions and the initial volume of the reaction solution of a metal salt prior to adding the titrant, and C_{titr} and V_i are the initial concentration of the titrant and the amount added in titration.

The function of formation per metal ion determines the number of atoms of the complexing agent (metal ions) on one molecule of compound and is estimated from the slope of the initial part of the titration curve. The concept of the function of formation (ligand number) n was proposed for the first time by Bjerrum in [15].

The stoichiometric composition of the evolved solid phase can be estimated by projecting the curve's plateau onto the ordinate axis [7]. As follows from Fig. 3, the length of the plateau grows as the concentration of metal ions in the system rises. At the initial sections of potentiometric titration curve, its slope is constant regardless of the concentration of metal ions. Only at high concentrations of metal ions does this slope become greater, indicating the formation of multinuclear compounds in the solution.

Treating the experimental curves of potentiometric titration with the EQ-5 program for simulating equilibria in aqueous solutions of metal salts enabled us to produce basic equations for the main equilibrium processes notably influencing the changes in system parameters during titration:

$$[\text{In}(\text{OH})^{2+}] = [\text{In}^{3+}] \cdot [\text{OH}^-] \cdot \beta_1, \quad (9)$$

$$[\text{In}(\text{OH})_2^+] = [\text{In}(\text{OH})^{2+}] \cdot [\text{OH}^-] \cdot \beta_2, \quad (10)$$

$$[\text{In}(\text{OH})_3] = [\text{In}(\text{OH})_2^+] \cdot [\text{OH}^-] \cdot \beta_3, \quad (11)$$

$$[\text{In}(\text{OH})_4^-] = [\text{In}(\text{OH})_3] \cdot [\text{OH}^-] \cdot \beta_4, \quad (12)$$

$$[\text{In}(\text{OH})_5^{2-}] = [\text{In}(\text{OH})_4^-] \cdot [\text{OH}^-] \cdot \beta_5, \quad (13)$$

$$[\text{In}(\text{OH})_6^{3-}] = [\text{In}(\text{OH})_5^{2-}] \cdot [\text{OH}^-] \cdot \beta_6, \quad (14)$$

$$[\text{In}_2(\text{OH})_5^+] = [\text{In}(\text{OH})_2^+] \cdot [\text{In}(\text{OH})_3] \cdot \beta_{\text{In}_2\text{X}_5}, \quad (15)$$

$$[\text{In}_3(\text{OH})_8^+] = [\text{In}_2(\text{OH})_5^+] \cdot [\text{In}(\text{OH})_3] \cdot \beta_{\text{In}_3\text{X}_8}, \quad (16)$$

$$[\text{In}_4(\text{OH})_{11}^+] = [\text{In}_3(\text{OH})_8^+] \cdot [\text{In}(\text{OH})_3] \cdot \beta_{\text{In}_4\text{X}_{11}}, \quad (17)$$

where $\beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6, \beta_{\text{In}_2\text{X}_5}, \beta_{\text{In}_3\text{X}_8}$, and $\beta_{\text{In}_4\text{X}_{11}}$ are equilibrium constants of the corresponding processes characterizing the stability of complexes.

Conditions for the formation of In(OH)_{3S} and In₄(OH)₁₁Cl₅ precipitates in a system without chalcogenizer are

$$\text{In(OH)}_{3S} : [\text{In(OH)}_3] > \beta_{3S} \quad (18)$$

(law of molecular solubility),

$$\text{In}_4(\text{OH})_{11}\text{Cl}_5 : [\text{In}_4(\text{OH})_{11}^+] \cdot [\text{Cl}^-] > \beta_{\text{In}_4\text{X}_{11}\text{S}} \quad (19)$$

(law of solubility product).

Here, β_{3S} and $\beta_{\text{In}_4\text{X}_{11}\text{S}}$ are equilibrium constants for the formation of corresponding precipitates.

Our calculated and reference values for the decimal logarithms of the equilibrium constants of (9)–(19) are given in the table.

As follows from the table, there is satisfactory agreement between the calculated and reference values of the decimal logarithms of the equilibrium constants. Equilibrium constant β_1 determines the onset of potentiometric titration at low concentrations of metal ions. The values of constants β_1 , β_2 , and β_3 are close. The value of the β_{3S} constant (the constant of molecular solubility) is determined by the range of existence of In(OH)₃ precipitate at various initial concentrations of metal ions. The β_4 , β_5 , and β_6 values are determined by the right part of the potentiometric titration curve (at high pH values of solution) and at various initial concentrations of metal ions.

The $\beta_{\text{In}_2\text{X}_5}$, $\beta_{\text{In}_3\text{X}_8}$, and $\beta_{\text{In}_4\text{X}_{11}}$ values were calculated from the divergence of the initial sections of the titration curves at various initial concentrations of the metal salts. The composition of the indium compound was determined from the slope of the initial section of the potentiometric titration curve. The composition of the hydroxide ion complex was determined from the value of the function of its formation n , using the plateau of the potentiometric titration curve.

The reliability of $\beta_{\text{In}_4\text{X}_{11}\text{S}}$ and $\beta_{\text{In}_4\text{X}_{11}}$ is determined by the relationship of the processes they described. For example, when the activity factor of ions is less than $\beta_{\text{In}_4\text{X}_{11}\text{S}}$, the solid phase is prone to dissolution until the values of equilibrium activity are achieved. When the activity product of ions is higher than $\beta_{\text{In}_4\text{X}_{11}\text{S}}$ (the oversaturated solution state), solid phase is formed until the equilibrium state of the system is attained.

Figure 4 shows the theoretical curves of potentiometric titration along with the calculated curves for the rate of transformation of indium salt at initial concentrations of 0.0001, 0.001, 0.010, and 0.100 mol/L. As follows from Fig. 4, there is good agreement between the experimental and theoretical dependences.

Because films of most metal chalcogenides are precipitated at pH \approx 9–13, calculations of the ionic equilibria tell us we can ignore the protonated forms of thio(seleno)carbamide, since their concentrations at pH > 4.5 are already very low. Note that at pH > 12, the

Decimal logarithms of the equilibrium constants of complexation, calculated according to potentiometric titration

| Constants of process | Calculated value |
|--|--------------------------|
| $\log \beta_1$ (9) | $8.2 \pm 0.1, 10.0$ [10] |
| $\log \beta_2$ (10) | $8.1 \pm 0.2, 10.2$ [10] |
| $\log \beta_3$ (11) | $8.0 \pm 0.2, 9.4$ [10] |
| $\log \beta_4$ (12) | $7.4 \pm 0.3, 4.3$ [10] |
| $\log \beta_5$ (13) | 1.6 ± 0.2 |
| $\log \beta_6$ (14) | 0.1 |
| $\log \beta_{3S}$ (18) | -7.6 ± 0.2 |
| $\log \beta_{\text{In}_2\text{X}_5}$ (15) | 11.0 ± 0.4 |
| $\log \beta_{\text{In}_3\text{X}_8}$ (16) | 7.8 ± 0.3 |
| $\log \beta_{\text{In}_4\text{X}_{11}}$ (17) | 7.2 ± 0.3 |
| $\log \beta_{\text{In}_4\text{X}_{11}\text{S}}$ (19) | -7.6 ± 0.3 |

cyanamide formed at the first stage is almost completely transformed into urea [9, 16].

Figure 4 presents the combined data from potentiometric titration. It can be seen that several solid phases were formed in the investigated system. The transitions from one phase to another is observed as kinks on the curve of residual concentration and as a step on the potentiometric titration curve. With an increase in the concentration of In(III), the beginning of the potentiometric titration curve shifts to the lower pH range due to hydrolysis. We can also see that the projection of the plateau onto the ordinate axis corresponds to $n_{\text{OH}^-} = 3.0$, confirming that the In(OH)₃ compound precipitated from the solution in the range of existence of plateau.

With the increase in the concentration of In(III), final part of plateau at $n_{\text{OH}^-} = 3.0$ shifts to the range of higher pH values of solution characterizing the increase in the range of formation of In(OH)₃ precipitate. On the whole, the range of formation for the solid phase of In(OH)₃ lies in the pH range of 7 to 9, but with the increase in the concentration of indium salt it gradually shifts to pH 12. At pH \approx 4, the range of the formation of $n_{\text{OH}^-} \approx 2.75$ compounds starts for 0.01 and 0.1 mol/L concentrations of indium salts and continues up to pH \approx 6.5. This testifies to the evolution of a compound with an assumed composition of In_x(OH)_{2.75x}Cl_{0.25x}. At lower indium concentrations of 0.0001 and 0.001 mol/L in the pH range of 4.5 to 6.5, there is an area with $n_{\text{OH}^-} \approx 2.55$ corresponding to a compound of In_x(OH)_{2.55x}Cl_{0.45x} composition.

We may conclude that the range of solid phase formation expands with an increase in the concentration of indium salts. The start of the range of formation of indium hydroxide shifts to the range of higher pH values of the solution. As a rule, the range of the

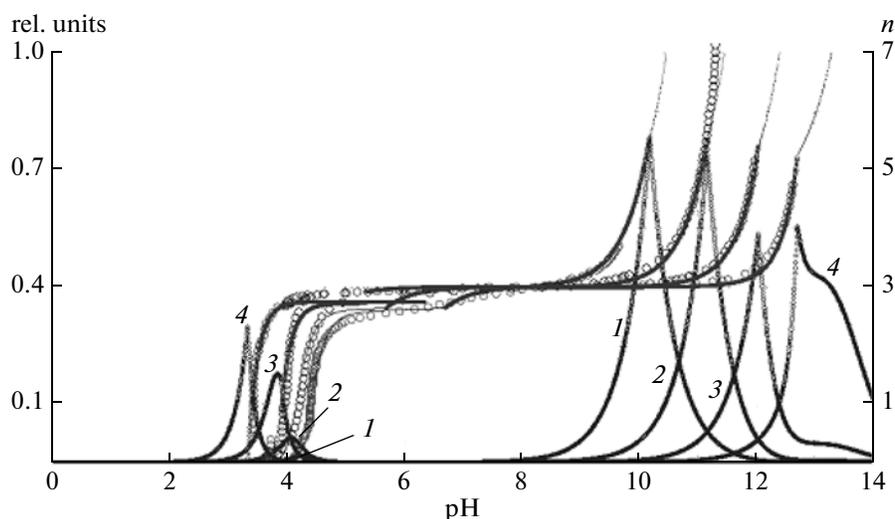


Fig. 4. (1–4) Calculated rates of the transformation of indium salt vs. pH at various initial concentrations of metal in solution. Shown are the experimental and theoretical dependences of function of formation (n) vs. pH of solution at: (1) $C_{\text{In(III)}} = 0.0001 \text{ mol/L}$, $C_{\text{NaOH}} = 0.001 \text{ mol/L}$, $t = 16.5^\circ\text{C}$; (2) $C_{\text{In(III)}} = 0.001 \text{ mol/L}$, $C_{\text{NaOH}} = 0.010 \text{ mol/L}$, $t = 18.0^\circ\text{C}$; (3) $C_{\text{In(III)}} = 0.010 \text{ mol/L}$, $C_{\text{NaOH}} = 0.100 \text{ mol/L}$, $t = 18.0^\circ\text{C}$; and (4) $C_{\text{In(III)}} = 0.100 \text{ mol/L}$, $C_{\text{NaOH}} = 1.00 \text{ mol/L}$, $t = 17.5^\circ\text{C}$.

formation of neutral indium hydroxocomplex ends at $\text{pH} \approx 13$.

As follows from the dependences plotted in Figs. 1 and 2, the precipitation of indium chalcogenides without allowance for the formation of precipitates of complex In(III) compounds virtually corresponds to the range of formation of indium hydroxide in a broad range of pH. In turn, we can see from the plotted dependences in Figs. 3 and 4 that the precipitation of indium chalcogenides with allowance for the formation of precipitates of complex In(III) compounds corresponds to the boundaries of the ranges of formation of indium hydroxide in a broad range of pH with allowance for the initial concentration of metal salts. The pH ranges of 3.0 to 4.5 and 9.0 to 14.0 must be considered optimal for the synthesis of indium selenides and sulfides.

Our results can be used for the formation of the reaction mixture upon the precipitation of indium selenide. On vitroceraic substrates, In_2Se_3 layers 100 to 300 nm thick, formed from aggregates with sizes of 30 to 70 nm, were obtained at $\text{pH} 11.0$. We suggest that the nucleation of selenide film is of a homogeneous character and requires such additional conditions as an increase in the initial concentrations of reagents in the reaction mixture or increasing the adhesion of metal chalcogenide particles to the substrate. In other words, in order to attain stable synthesis, we must ensure the redistribution of the solid phase of indium selenide from bulk solution to the surface of substrate.

CONCLUSIONS

The boundary conditions and ranges of the formation of indium sulfides and selenides were determined by calculating ionic equilibria with allowance for the behavior of chalcogenizers in indium chloride–sodium hydroxide–thiocarbamide and indium chloride–sodium hydroxide–selenocarbamide systems. It was found that the formation of chalcogenide solid phase is possible in a broad range of pH from 3.0 to 14.0, which virtually coincides with the range of formation of indium hydroxide. Potentiometric titration of indium chloride solutions (InCl_3) in the concentration range of 0.0001 to 0.100 mol/L was conducted with sodium hydroxide; treatment of the results with the EQ-5 software package revealed two optimum pH ranges for the precipitation of indium chalcogenides: 3.0 to 4.5 and from 9.0 to 14.0, which are promising for realizing the hydroxide model of the nucleation of films. Nanostructured layers of indium selenide 100 to 300 nm thick were obtained using the results from potentiometric titration by hydrochemical precipitation on a vitroceraic substrate.

REFERENCES

1. A. V. Goetzberger and V. U. Hoffmann, *Photovoltaic Solar Energy Generation* (Springer, Berlin, 2005).
2. P. P. Hankare, M. R. Asabe, P. A. Chate, and K. C. Rathod, *J. Mater. Sci.: Mater. Electron.*, No. 19, 1252 (2008).
3. S. V. Kurdakov and A. G. Makarov, *Vestn. OGU*, No. 5, 61 (2006).

4. K. Chopra and S. Das, *Thin Film Solar Cells* (Plenum, New York, 1983).
5. S. A. Zolotovskaya, N. N. Posnov, P. V. Prokoshin, et al., *Semiconductors* **38**, 812 (2004).
6. V. F. Markov and L. N. Maskaeva, *Russ. J. Phys. Chem. A* **86**, 1288 (2010).
7. R. A. Yusupov and S. A. Bakhteev, *Russ. J. Phys. Chem. A* **83**, 2188 (2009).
8. R. A. Yusupov, S. A. Bakhteev, and S. G. Smerdova, *Russ. J. Phys. Chem. A* **84**, 1263 (2010).
9. V. F. Markov, L. N. Maskaeva, and P. N. Ivanov, *Hydrochemical Deposition of Metal Sulfide Films: Simulation and Experiment* (Ural. Otd. RAN, Yekaterinburg, 2006) [in Russian].
10. Yu. Yu. Lur'e, *Handbook of Analytical Chemistry* (Khimiya, Moscow, 1989).
11. V. N. Kumok, O. M. Kuleshova, and L. A. Karabin, *Solubility Products* (Nauka, Novosibirsk, 1983).
12. V. F. Markov, L. N. Maskaeva, G. G. Divinskaya, et al., *Vestn. UGTU-UPI, Ser. Khim.* **23** (3), 120 (2003).
13. S. A. Bakhteev and R. A. Yusupov, *Vestn. KGTU*, No. 6, 62 (2009).
14. V. A. Nazarenko, V. P. Antonovich, and E. M. Nevskaya, *Hydrolysis of Metal Ions in Diluted Solutions* (Atomizdat, Moscow, 1979) [in Russian].
15. J. Bjerrum, *Metal Ammine Formation in Aqueous Solution: Theory of the Reversible Step Reactions* (Haase, Copenhagen, 1957; Khimiya, Moscow, 1961).
16. L. G. Berg, K. K. Meshchenko, and Yu. I. Bogomolov, *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.* **6**, 1337 (1970).

Translated by A. Muravev