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Considering the Polynuclear Complexes in the Ionic Equilibria of the Pb^{2+}–H_2O System

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Abstract—Analysis of conditions of the lead hydroxide and sulfide formation in the Pb^{2+}–H_2O system was carried out with accounting for the formation of polynuclear hydroxo-complexes. This allows predicting a possibility of the lead hydroxide formation in the solution before the beginning of the synthesis of lead sulfide. The domains of the stable formation of $Pb(OH)_2$ and PbS were calculated for the systems containing lead citrate complexes and hydroxo-complexes. The proposed calculation method can be used for the quantitative determination of the reaction mixture composition and development of the chemical deposition technology of lead chalcogenides in different morphological forms: nanocrystalline powders (hydrophobic sol), quantum dots, heterostructures of the *core@shell type* or films. The proposed calculation method is applicable to other chalcogenide systems containing metal ions forming mononuclear and polynuclear hydroxo-complexes.

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Among the methods for producting semiconductor nano-sized crystalline metal sulfides, a promising one is the chemical precipitation from aqueous solutions [1, 2]. This method being simple and accessible makes it possible to obtain metal sulfides in the form of quantum dots, hetero-nanostructures of the *core@-shell* type, nano-crystalline films, and colloidal solutions. A feature of the method is a possibility to proceed in aqueous solution, in addition to the lead sulfide formation, side reactions generating oxygen-containing metal compounds, in particular, hydroxides. Since in aqueous solution the ions of most metals are subjected to hydrolysis, the probability of the formation of hydroxides poorly soluble in water is rather high.

The role of the metal hydroxide in the chemical deposition was a subject of many studies, for example, [3–7]. It was discovered empirically [8, 9], and then repeatedly confirmed that the formation of metal sulfides in the form of thin films [3–5, 10–13] on metallic surfaces at the chemical deposition from aqueous solutions of thiocarbamide $(NH_2)_2CS$ occurred only in the region of thermodynamic stability of metal hydroxide in the solution (in the hydroxide domain). The medium pH and the presence in the reaction mixture of the metal hydroxide govern the microstructure of the chemically deposited sulfide films [14]. The metal hydroxide plays an important role in the creation of sulfide heteronanostructures of the *core@shell* type, such as $CdS/Cd(OH)_2$ [15, 16]. Therefore the development of the methods for calculating the concentration region of the metal hydroxide formation, which would allow the prediction of the possibility of its formation in solution prior to the synthesis of the metal sulfide, is one of the relevant problems in performing chemical precipitation from aqueous solutions. Such methods exist and are used for a long time. The basis for these calculations is the comparison of the solubility product of the metal hydroxide $K_{sp} = [M^{m+}][OH^-]^m$, where $[M^{m+}]$ and $[OH^-]$ are equilibrium concentration of free metal ions and hydroxide ions, respectively, with the ionic product.

In aqueous solution the metal ions together with an insoluble hydroxide form soluble hydroxo-complexes, the compounds in which hydroxy ions are the substituting ligands. Many metals (e.g., lead, iron, nickel, bismuth, tin, beryllium, etc.) form with the OH^- ions not only mononuclear hydroxo-complexes $M(OH)_n$, but also polynuclear neutral or charged hydroxo-complexes $M_p(OH)_n$ ($n \geq 1$, $p \geq 2$, both are integers). The publications [6, 7, 17, 18] on the determination of conditions for the formation of the hydroxide in the process of chemical deposition of sulfides and selenides take into account the mononuclear hydroxo-complexes of metals, or only some of the polynuclear complexes. In the polynuclear complexes the number of ligands associated with the metal atom depends both on the concentrations of ligand and metal. For this reason, the equations describing the equilibrium conditions are not linear with respect to the analytical concentration of the metal ions M^{m+} that greatly complicates or even makes it impossible to solve the equations analytically. Apparently, this is a reason for taking into account only mononuclear hydroxo-complexes in the calculations of the concentration domains of formation [6, 7, 17], although in recent years the software have appeared for the calculations and simulation of ionic equilibrium in aqueous solutions [19]. Another reason for considering only the mononuclear hydroxo-complexes lies in the fact that in the systems with ligands that form more stable complexes than hydroxo-complexes, the impact of polynuclear hydroxo-complexes on the equilibrium is rather weak. However, the exclusion from the calculation of polynuclear hydroxo-complexes leads, as shown below, to a significant shift of the boundaries of the concentration domains.

There is only limited published information on the formation of lead hydroxide in the system of Pb^{2+}–H_2O which accounts for the existence of polynuclear hydroxo-complexes. The data are controversial due to discrepancy in the numerical values of the constants of formation of polynuclear complexes. Therefore in this paper we propose a method and present the results of the calculation of the distribution diagrams for the complexes in the Pb^{2+}–H_2O system with accounting for the polynuclear hydroxo-complexes, whose formation constants have been critically evaluated and recommended by the IUPAC [20] in 2009. For this system we found the domain of stable existence of complex lead ions depending on the nature and concentration of the ligand (the complexing agent), as well as on the pH at a constant temperature. While accounting for the lead polynuclear hydroxo-complexes, we ascertained the region of the lead sulfide PbS formation in aqueous solutions of thiocarbamide $(NH_2)_2CS$ and gave theoretically evidenced practical recommendations on the preparation of solutions for the deposition of PbS films.

Determining the stability domain of lead hydroxide. The equilibrium state in a saturated solution of lead hydroxide is described by Eq. (1):

$$K_{sp} = [Pb^{2+}]\cdot[OH^-]^2, \qquad (1)$$

where $K_{sp} = (1.0–1.2)\times10^{-15}$ [21–23] is the solubility product of lead hydroxide at the normal conditions. In accordance with Eq. (1) the equilibrium concentration of free ions of lead $[Pb^{2+}]$ is:

$$[Pb^{2+}] = K_{sp}/[OH^-]^2 \equiv K_{sp}[H^+]^2/K_w^2, \qquad (2)$$

where $K_w = [H^+][OH^-] = 10^{-14}$ is the ion product of water at 298 K.

Many studies of hydrolysis suggest that the distribution of lead(II) between its individual hydroxo-complexes depends on three most important variables: the concentration of the lead salts, the medium pH, and the temperature. For example, according to [24–26], in very dilute solutions with a total concentration of Pb(II) 1×10^{-9} M, the hydrolysis is detected at pH > 4, and increase in pH to 9 leads to the formation of $PbOH^+$ only. With further increase in pH the $PbOH^+$ fraction in solution decreases, while the accumulation occurs of di- and tri-hydroxo-complexes $Pb(OH)_2$ and $Pb(OH)_3^-$. At pH up to ~10.5 both complexes are formed in comparable amounts, and in more alkaline environment the fraction of trihydroxo-complex rapidly increases, so at pH > 12 it becomes the only form of the Pb(II) existence [26, 27]. With the increase in the total concentration of lead, in solution the formation occurs of the polynuclear hydroxo-complexes [20, 24, 25]. At the Pb(II) concentration equal to 5×10^{-5} M the solution contains complexes of $Pb_3(OH)_4^{2+}$, and at a higher concentration, of 1×10^{-3} M, the complexes $Pb_4(OH)_4^{4+}$ and $Pb_6(OH)_8{}^{4+}$. When the concentration of Pb(II) is above 0.5 M the hydroxo-complex $Pb_2(OH)^{3+}$ appears [24]. The complexes $Pb_3(OH)_3^{3+}$ [24] and $Pb_3(OH)_5^+$ [25, 28] were detected, but, according to [29], the experimental evidence of their existence is not reliable enough.

Using the general approach to the analysis of ionic equilibria proposed in [30], we calculated the ionic composition of the system Pb^{2+}–Cit^{3-}–OH^-–H_2O, taking into account not only mononuclear, but also the polynuclear Pb(II) hydroxo-complexes in aqueous solution. In describing the equilibria in solutions of complex lead ions we use the equilibrium constant β_{ij} recommended in [20, 31, 32] (see the table). Note that in alkaline solution the OH^- ion competes with such a stable in an alkaline environment ligand as citrate ion

The conditions of equilibrium and equilibrium constants in the systems of Pb^{2+}–OH–H_2O [20, 31] and Pb^{2+}–OH–Cit^{3-}–H_2O [31, 32]

Equilibrium conditions	Equilibrium constant at 298.15 K, 10^5 Pa and ionic strength $I_m = 0$ mol kg^{-1}
$Pb^{2+} + H_2O \leftrightarrow Pb(OH)^+ + H^+$	$\beta_{11} = [Pb(OH)^+]\cdot[H^+]/[Pb^{2+}] = 3.47\times10^{-8}$
$Pb^{2+} + 2H_2O \leftrightarrow Pb(OH)_2 + 2H^+$	$\beta_{12} = [Pb(OH)_2]\cdot[H^+]^2/[Pb^{2+}] = 1.15\times10^{-17}$
$Pb^{2+} + 3H_2O \leftrightarrow Pb(OH)_3^- + 3H^+$	$\beta_{13} = [Pb(OH)_3^-]\cdot[H^+]^3/[Pb^{2+}] = 9.33\times10^{-29}$
$3Pb^{2+} + 4H_2O \leftrightarrow Pb_3(OH)_4^{2+} + 4H^+$	$\beta_{34} = [Pb_3(OH)_4^{2+}]\cdot[H^+]^4/[Pb^{2+}]^3 = 9.77\times10^{-24}$
$4Pb^{2+} + 4H_2O \leftrightarrow Pb_4(OH)_4^{4+} + 4H^+$	$\beta_{44} = [Pb_4(OH)_4^{4+}]\cdot[H^+]^4/[Pb^{2+}]^4 = 2.69\times10^{-21}$
$6Pb^{2+} + 8H_2O \leftrightarrow Pb_6(OH)_8^{4+} + 8H^+$	$\beta_{68} = [Pb_6(OH)_8^{4+}]\cdot[H^+]^8/[Pb^{2+}]^6 = 1.29\times10^{-43}$
$2Pb^{2+} + H_2O \leftrightarrow Pb_2OH^{3+} + H^+$	$\beta_{21} = [Pb_2OH^{3+}]\cdot[H^+]/[Pb^{2+}]^2 = 5.25\times10^{-8}$
$Pb^{2+} + Cit^{3-} \leftrightarrow PbCit^-$	$\beta_1 = [PbCit^-]/[Pb^{2+}]\cdot[Cit^{3-}] = 3.07\times10^6$
$Pb^{2+} + 2Cit^{3-} \leftrightarrow Pb(Cit)_2^{4-}$	$\beta_{12\,\text{cit}} = [Pb(Cit)_2^{4-}]/[Pb^{2+}]\cdot[Cit^{3-}]^2 = 3.03\times10^8$
$Pb^{2+} + OH^- + Cit^{3-} \leftrightarrow Pb(OH)Cit^{2-}$	$\beta_3' = [Pb(OH)Cit^{2-}]/[Pb^{2+}]\cdot[OH^-]\cdot[Cit^{3-}] = 5.25\times10^{13}$

$C_6N_5O_7^{3-}$ (Cit^{3-}) forming stable enough complexes with the lead ions [32].

For the citrate system Pb^{2+}–Cit^{3-}–OH^-–H_2O the condition of material equilibrium in all eleven soluble forms of lead Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2$, $Pb(OH)_3^-$, $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$, $Pb_2(OH)^{3+}$, $PbCit^-$, $Pb(Cit)_2^{4-}$, $Pb(OH)Cit^{2-}$ we write as follows Eq. (3):

$$c_{\text{Pb},\Sigma} = [Pb^{2+}]\ 1 + \frac{[Pb(OH)^+]}{[Pb^{2+}]} + \frac{[Pb(OH)_2]}{[Pb^{2+}]} + \frac{[Pb(OH)_3^-]}{[Pb^{2+}]} + \frac{3[Pb_3(OH)_4^{2+}]}{[Pb^{2+}]} + \frac{4[Pb_4(OH)_4^{4+}]}{[Pb^{2+}]} + \frac{6[Pb_6(OH)_8^{4+}]}{[Pb^{2+}]}$$

$$+ \frac{2[Pb_2OH^{3+}]}{[Pb^{2+}]} + \frac{[PbCit^-]}{[Pb^{2+}]} + \frac{[Pb(Cit)_2^{4-}]}{[Pb^{2+}]} + \frac{[Pb(OH)Cit^{2-}]}{[Pb^{2+}]}. \tag{3}$$

Let us represent the ratio of the concentrations of complexes to the concentration of $[Pb^{2+}]$ in Eq. (3) through the equilibrium constant (see the table) and transform it into a form more convenient for further analysis:

$$c^{\text{cit}}_{\text{Pb},\Sigma} = [Pb^{2+}]\Bigg\{1 + \frac{\beta_{11}}{[H^+]} + \frac{\beta_{12}}{[H^+]^2} + \frac{\beta_{13}}{[H^+]^3} + \frac{3\beta_{34}[Pb^{2+}]^2}{[H^+]^4} + \frac{4\beta_{44}[Pb^{2+}]^3}{[H^+]^4} + \frac{6\beta_{68}[Pb^{2+}]^5}{[H^+]^8} + \frac{2\beta_{21}[Pb^{2+}]}{[H^+]}$$

$$+ \beta_1[Cit^{3-}] + \beta_{1,2}[Cit^{3-}]^2 + \beta_1' \frac{K_w[Cit^{3-}]}{[H^+]}\Bigg\}. \tag{4}$$

If the concentration of citrate ion $[Cit^{3-}] = 0$, then Eq. (4) is converted to a particular form, which describes the condition of the material balance of the lead soluble forms in a citrate-free system Pb^{2+}–OH^-–H_2O:

$$c^{\text{cit}}_{\text{Pb},\Sigma} = [Pb^{2+}]\left\{1 + \frac{\beta_{11}}{[H^+]} + \frac{\beta_{12}}{[H^+]^2} + \frac{\beta_{13}}{[H^+]^3} + \frac{3\beta_{34}[Pb^{2+}]^2}{[H^+]^4} + \frac{4\beta_{44}[Pb^{2+}]^3}{[H^+]^4} + \frac{6\beta_{68}[Pb^{2+}]^5}{[H^+]^8} + \frac{2\beta_{21}[Pb^{2+}]}{[H^+]}\right\}. \tag{5}$$

In accordance with Eq. (5) the fractional concentration of free Pb^{2+} ions in the system $Pb^{2+}–OH^{-}–H_2O$ is:

$$\alpha_{Pb^{2+}} = \frac{[Pb^{2+}]}{c_{Pb,\Sigma}} = \left\{1 + \frac{\beta_{11}}{[H^+]} + \frac{\beta_{12}}{[H^+]^2} + \frac{\beta_{13}}{[H^+]^3} + \frac{3\beta_{34}[Pb^{2+}]^2}{[H^+]^4} + \frac{4\beta_{44}[Pb^{2+}]^3}{[H^+]^4} + \frac{6\beta_{68}[Pb^{2+}]^5}{[H^+]^8} + \frac{2\beta_{21}[Pb^{2+}]}{[H^+]}\right\}^{-1}. \tag{6}$$

Using Eq. (6), the fractional concentrations $\alpha_i = Ci/c_{Pb,\Sigma}$ of all Pb(II) hydroxo-complexes in the system $Pb^{2+}–OH^{-}–H_2O$ can be written as a function of the concentrations of H^+ and Pb^{2+} ions:

$$\alpha[Pb(OH)^+] = \beta_{11}\alpha_{Pb}2+/[H^+],$$
$$\alpha[Pb(OH)^+] = \beta_{12}\alpha_{Pb}2+/[H^+]^2, \tag{7.1}$$

$$\alpha[Pb(OH)_2] = \beta_{13}\alpha_{Pb}2+/[H^+]^3,$$
$$\alpha[Pb_3(OH)_4^{2+}] = 3\beta_{34}\alpha_{Pb}2+[Pb^{2+}]^2/[H^+]^4, \tag{7.2}$$

$$\alpha[Pb_4(OH)_4^{4+}] = 4\beta_{44}\alpha_{Pb}2+[Pb^{2+}]^3/[H^+]^4,$$
$$\alpha[Pb_4(OH)_4^{4+}] = 6\beta_{68}\alpha_{Pb}2+[Pb^{2+}]^5/[H^+]^8, \tag{7.3}$$

$$\alpha[Pb_2OH^{3+}] = 2\beta_{21}\alpha_{Pb}2+[Pb^{2+}]/[H^+]. \tag{7.4}$$

Equations (5) and (6) are of 6-th degree with respect to the concentration of Pb^{2+} ions and do not have analytical solutions of a general form. Still, the problem of hydrolysis of the Pb^{2+} ion described by a set of Eqs. (6), (7) can be solved numerically.

Indeed, at a known total concentration $c_{Pb,\Sigma}$ of the soluble forms of lead the dependence of $[Pb^{2+}]$ on the concentration of protons H^+ (that is, the solution pH) can be found by means of self-consistent numerical solution of Eq. (6) by the successive approximation procedure. In other words, at a given concentrations $c_{Pb,\Sigma}$ we can calculate the dependence of the fraction of uncomplexed lead ions on the pH. For this purpose, using a software package SigmaPlot 2001 for Windows [33] a special program was written. With the numerical relationship $[Pb^{2+}] = f([H^+])$ found from the Eq. (6) it is easy to obtain fractional concentrations α_i of free ions and all the Pb(II) hydroxo-complexes at different pH values.

Figure 1 shows the fractional concentrations of free ions and the Pb(II) hydroxo-complexes in solution for the system $Pb^{2+}–OH^{-}–H_2O$ depending on the pH value, calculated with the Eqs. (6), (7) for three values of $c_{Pb,\Sigma}$ 0.001 M, 0.01 M, and 0.1 M. As seen, the hydrolysis of lead ions begins at pH ≥ 6. The increase in the analytical concentration of lead ion shifts the Pb^{2+} hydrolysis in the region of lower pH values (Fig. 1a). When $c_{Pb,\Sigma} = 0.001$ M, at pH = 8–10 lead exists mainly in the form of complex ions, $Pb_3(OH)_4^{2+}$ and $Pb_6(OH)_8^{4+}$, at pH ≥ 11 sharply increased the fraction of $Pb(OH)_2$ and $Pb(OH)_3^-$ (Figs. 1c, 1d). When $c_{Pb,\Sigma} = 0.1$ M, at pH = 7–12 lead forms in solution the ion $Pb_6(OH)_8{}^{4+}$ (Fig. 1h). Thus, an increase in $c_{Pb,\Sigma}$, expands the pH range of existence of complexes $Pb_3(OH)_4^{2+}$ and $Pb_6(OH)_8^{4+}$, and the fraction of the complex $Pb_6(OH)_8^{4+}$ in solution increases. The only polynuclear complex, the relative content of which is negligible, is Pb_2OH^{3+} (this is consistent with the results of [18]), it exists in a narrow range 3 < pH < 8 (Fig. 1g). At pH ≥ 12 for all concentrations used in the calculations of $c_{Pb,\Sigma}$ the main form of existence of lead in solution is a mononuclear complex $Pb(OH)_3{}^-$ (Fig. 1d). Thus, for the precise analysis of ionic equilibria in aqueous solutions of lead salts the polynuclear hydroxo-complexes should be taken into account, which are the main form of existence of lead in solution in the pH range from 7 to 12.

Note that all dependences (6) and (7) of the fractional concentrations α_i are power functions of $[H^+]$ (or pH), that is, smooth functions with no break point or discontinuity. However, in [20, Fig. 1a] the break points were observed in the calculated dependences of the fractional concentrations of $Pb_3(OH)_4^{2+}$ and $Pb_6(OH)_8^{4+}$ on the pH in the $Pb^{2+}–OH^-$ system with $c_{Pb,\Sigma} = 0.00048$ M at pH ~ 9.25. This is due to the fact that in [20] the fractional concentrations were calculated taking into account the abrupt change in the total concentration of lead in solution due to precipitation of lead oxide at pH > 9.3.

Let us now determine the stability domain of lead hydroxide $Pb(OH)_2$ in the citrate-free system $Pb^{2+}–OH^{-}–H_2O$. The conditions of formation of solid phase $Pb(OH)_2$ in water solution can be found from the relation (8):

$$K_{sp} < [Pb^{2+}][OH^-]^2. \tag{8}$$

Substituting the expression (2) in (5) for the concentration of $[Pb^{2+}]$, we obtain the relation (9), which is the Eq. of the boundary of the $Pb(OH)_2$ solid phase deposition.

$$c_{\mathrm{Pb},\Sigma} = \frac{K_{\mathrm{sp}}[\mathrm{H^+}]^2}{K_{\mathrm{w}}^2}\left\{1 + \frac{\beta_{11}}{[\mathrm{H^+}]} + \frac{\beta_{12}}{[\mathrm{H^+}]^2} + \frac{\beta_{13}}{[\mathrm{H^+}]^3} + \frac{3\beta_{34}K_{\mathrm{sp}}^2}{K_{\mathrm{w}}^4} + \frac{4\beta_{44}K_{\mathrm{sp}}^3[\mathrm{H^+}]^2}{K_{\mathrm{w}}^6} + \frac{6\beta_{68}K_{\mathrm{sp}}^5[\mathrm{H^+}]^2}{K_{\mathrm{w}}^{10}} + \frac{2\beta_{21}K_{\mathrm{sp}}[\mathrm{H^+}]}{K_{\mathrm{w}}^2}\right\}. \quad (9)$$

Figure 2 shows the dependence of the boundary of formation of lead hydroxide $Pb(OH)_2$ in the system Pb^{2+}–OH^-–H_2O at accounting of only mononuclear or both mononuclear and polynuclear lead hydroxo-complexes. The calculation is made according to Eq. (9). As can be seen, the effect of polynuclear complexes on the equilibrium position of the heterogenic equilibrium $Pb(OH)_2$ hydroxide–Pb(II) ions is very strong in the region of $pH < 10.5$. In the alkaline region due to amphoteric nature of lead hydroxide $Pb(OH)_2$ the deposition begins and occurs at $pH \leq 13$, which agrees well with the reference and experimental data [21, 34]. Sulfide formation in the form of thin films on nonmetallic substrates by chemical deposition from aqueous solutions of thiocarbamide occurs only in the region of stability of the metal hydroxide [3–5, 10]. Figure 2 clearly shows that at accounting for all mononuclear and polynuclear hydroxo-complexes the PbS films can be obtained in alkaline solutions with $9 < pH < 13$, which fully agrees with the experimental data, for example, [3–5, 8–13]. If the polynuclear complex is not taken into account, the left boundary of lead hydroxide formation is displaced to the acid region, where the hydroxide $Pb(OH)_2$ is not really formed. Thus, the consideration of polynuclear hydroxo-complexes is important not only theoretically, but also practically, for the synthesis of the films.

We now define the stability domain of lead hydroxide $Pb(OH)_2$ in the solution, where, in addition to hydroxo-complexes the citrate complexes are present. In this case, the condition of the material balance is described by Eq. (4), and the Eq. of the deposition boundary, taking into account Eq. (2) and Eq. (4), has the form (10):

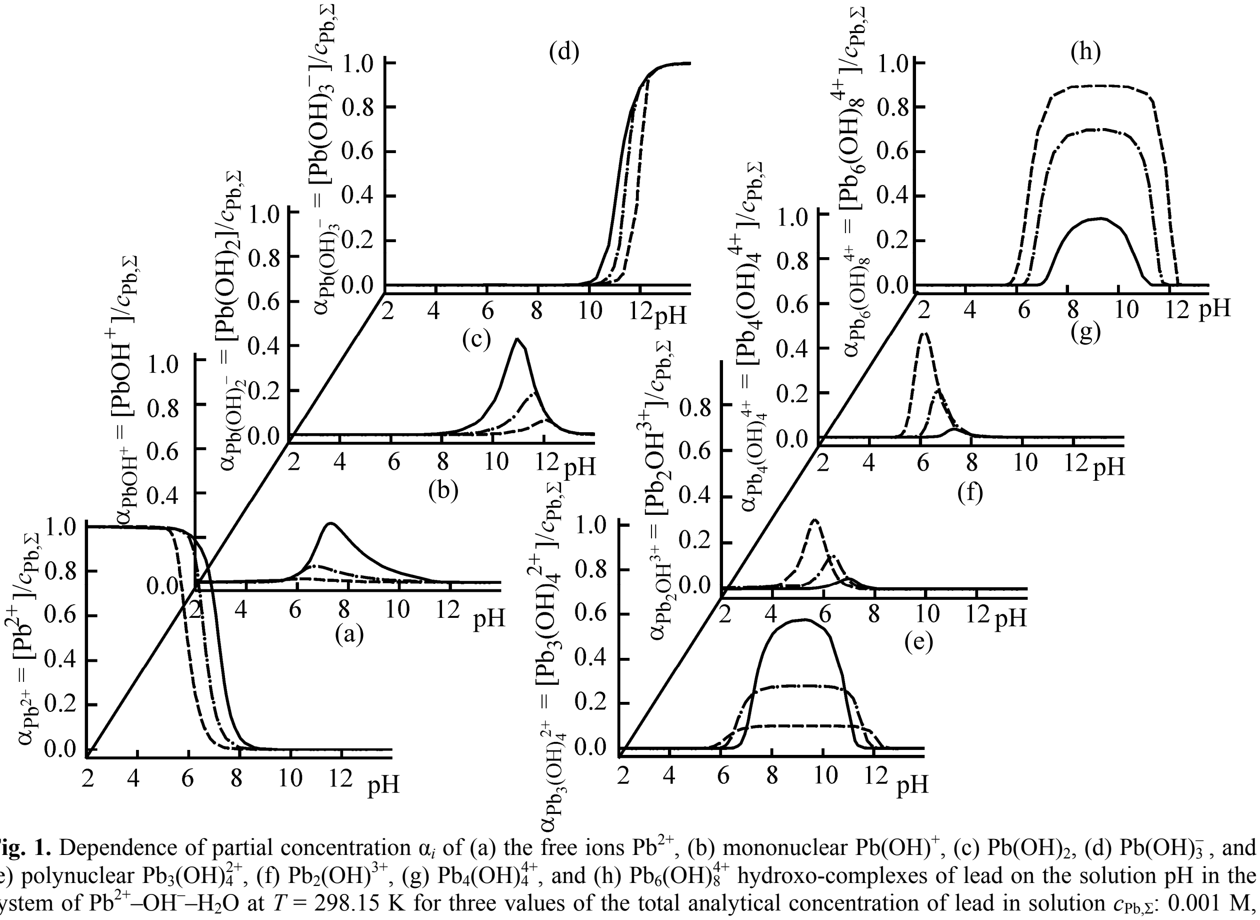

Fig. 1. Dependence of partial concentration α_i of (a) the free ions Pb^{2+}, (b) mononuclear $Pb(OH)^+$, (c) $Pb(OH)_2$, (d) $Pb(OH)_3^-$, and (e) polynuclear $Pb_3(OH)_4^{2+}$, (f) $Pb_2(OH)^{3+}$, (g) $Pb_4(OH)_4^{4+}$, and (h) $Pb_6(OH)_8^{4+}$ hydroxo-complexes of lead on the solution pH in the system of Pb^{2+}–OH^-–H_2O at $T = 298.15$ K for three values of the total analytical concentration of lead in solution $c_{Pb,\Sigma}$: 0.001 M, 0.01 M and 0.1 M.

$$+ c^{\mathrm{cit}}_{\mathrm{Pb},\Sigma} = \frac{K_{\mathrm{sp}}[\mathrm{H}^+]^2}{K_{\mathrm{w}}^2}\left\{1 + \frac{\beta_{11}}{[\mathrm{H}^+]} + \frac{\beta_{12}}{[\mathrm{H}^+]^2} + \frac{\beta_{13}}{[\mathrm{H}^+]^3} + \frac{3\beta_{34}K_{\mathrm{sp}}^2}{K_{\mathrm{w}}^4} + \frac{4\beta_{44}K_{\mathrm{sp}}^3[\mathrm{H}^+]^2}{K_{\mathrm{w}}^6} + \frac{6\beta_{68}K_{\mathrm{sp}}^5[\mathrm{H}^+]^2}{K_{\mathrm{w}}^{10}} + \frac{2\beta_{21}K_{\mathrm{sp}}[\mathrm{H}^+]}{K_{\mathrm{w}}^2} + \beta_1[\mathrm{Cit}^{3-}] + \beta_{12\mathrm{cit}}[\mathrm{Cit}^{3-}]^2 + \beta_1'\frac{K_{\mathrm{w}}[\mathrm{Cit}^{3-}]}{[\mathrm{H}^+]}\right\}. \quad (10)$$

The dependence of the solubility of lead hydroxide on the medium pH in the presence of sodium citrate, as Fig. 3 shows, defines the boundary conditions of existence of homogeneous and heterogeneous systems. Homogeneous region is the region of the lead existence only in the dissolved form, that is, free form and the complex ions. This region is located below the boundary surface of the heterogeneous equilibrium $Pb(OH)_2$ hydroxide–Pb(II) ions. Above this surface is a heterogeneous domain, where lead hydroxide $Pb(OH)_2$ is also formed. As can be seen, the solubility of lead hydroxide decreases with increasing pH, and at

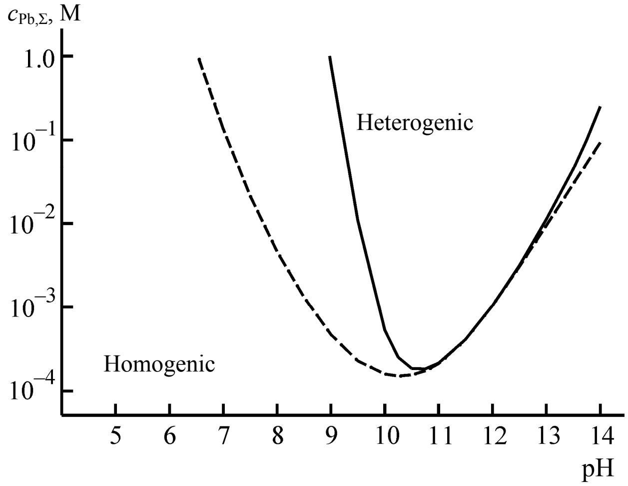

Fig. 2. Effect of accounting for the polynuclear hydroxo-complexes of lead on the position of the boundary of the lead hydroxide $Pb(OH)_2$ formation in the system pf Pb^{2+}–OH^-–H_2O at the different pH values at 298.15 K: (solid line) considering all mono- and polynuclear hydroxo-complexes, (dashed line) considering only the mononuclear hydroxo-complexes. The total concentration of lead $c_{\mathrm{Pb},\Sigma}$ in the solution is shown in a logarithmic scale.

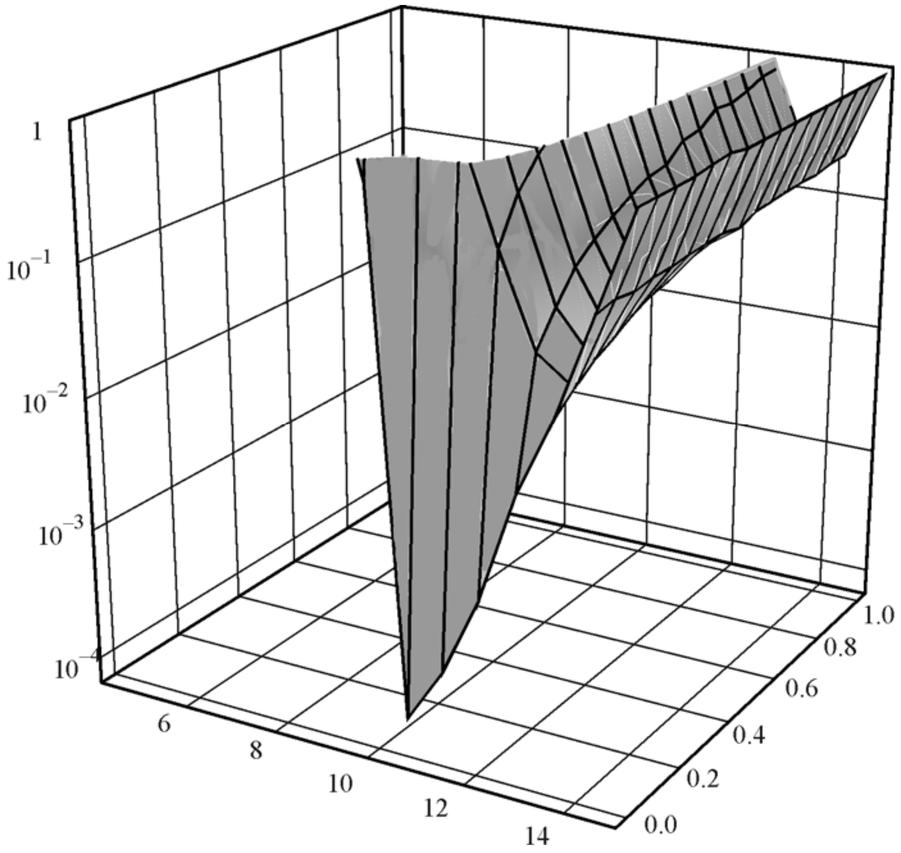

Fig. 3. The dependence of the solubility of lead hydroxide $Pb(OH)_2$ on the medium pH and the citrate ions concentration in the system of Pb^{2+}–Cit^{3-}–OH^-–H_2O calculated according to Eq. (11). The total concentration of lead $c_{\mathrm{Pb},\Sigma}$ in the solution is shown in a logarithmic scale.

$[Na_3Cit] = 0$ (that is, in the system Pb^{2+}–OH^-–H_2O) reaches its minimum value ~2×10^{-4} M at pH ≈ 10.5. In the region of pH > 10.5 lead hydroxo-complexes are formed, so that the total concentration of lead in solution increases.

Increasing concentrations of citrate leads to an increase in the absolute values of the $Pb(OH)_2$ solubility and the solubility minimum is shifted to the region of higher pH values. For example, for the concentration of $[Na_3Cit] = 0.05$ M the lead hydroxide solubility in the system of Pb^{2+}–Cit^{3-}–OH^-–H_2O reaches its minimum value of 3.6×10^{-2} M at pH ≈ 13, for $[Na_3Cit] = 1.0$ M the minimum solubility equal to 0.146 M corresponds to pH ≈ 14 (Fig. 3).

Thus, the calculation with Eqs. (9) and (10) allowed us constructing a dependence of the total equilibrium concentration of lead ions in solution on the pH value and find the stability domain of lead hydroxide for the system of Pb^{2+}–Cit^{3-}–OH^-–H_2O (Fig. 3) and its specific section Pb^{2+}–OH^-–H_2O (Fig. 2). From the calculation it follows that introduction of citrate ion to the solution increases the equilibrium concentration of lead and solubility of $Pb(OH)_2$ due to the formation of citrate and hydroxo-citrate complexes.

In aqueous solution at 298 K a three-stage dissociation of citric acid occurs [30] with the equilibria (11):

$$H_3Cit \leftrightarrow H^+ + H_2Cit^-,$$

$$K_1 = [H^+][H_2Cit^-]/[H_3Cit] = 7.4\times10^{-4}, \qquad (11.1)$$

$$H_2Cit^- \leftrightarrow H^+ + HCit^{2-},$$

$$K_2 = [H^+][HCit^{2-}]/[H_2Cit^-] = 1.8\times10^{-5}, \qquad (11.2)$$

$$HCit^{2-} \leftrightarrow H^+ + Cit^{3-},$$

$$K_3 = [H^+][Cit^{3-}]/[HCit^{2-}] = 4.0\times10^{-7}. \qquad (11.3)$$

In accordance with Eq. (11), the total analytical concentration of citric acid in solution can be calculated with Eq. (12):

$$c(H_3Cit,\Sigma) = [H_3Cit] + [H_2Cit^-] + [HCit^{2-}] + [Cit^{3-}]. \qquad (12)$$

With Eqs. (11) and (12), the fractional concentration of molecular and ionized form of citric acid are estimated as Eq. (13):

$$\alpha(H_3Cit,) = [H_3Cit]/c(H_3Cit,\Sigma) = [H^+]^3/\{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3\}, \qquad (13.1)$$

$$\alpha(H_2Cit^-) = [H_2Cit^-]/c(H_3Cit,\Sigma) = K_1[H^+]^2/\{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3\}, \qquad (13.2)$$

$$\alpha(HCit^{2-}) = [HCit^{2-}]/c(H_3Cit,\Sigma) = K_1K_2[H^+]/\{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3\}, \qquad (13.3)$$

$$\alpha(Cit^{3-}) = [Cit^{3-}]/c(H_3Cit,\Sigma) = K_1K_2K_3/\{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3\}. \qquad (13.4)$$

Calculations based on Eqs. (13) show that at pH < 2 the citric acid exists in solution in molecular form. In the pH range from 2 to 8 in addition to the molecular form the ions H_2Cit^- and $HCit^{2-}$ appear and at pH > 8 the solution contains only Cit^{3-} ions. Hence, it is clear that Cit^{3-} ion is involved in complex formation only at pH > 8.

The domain of the lead sulfide formation. As a final step, we consider the ionic equilibrium in the system Pb^{2+}–$Cit^{3-}OH^-$–$(NH_2)_2CS$–H_2O and taking into account the polynuclear hydroxo-complexes refine the field of formation of lead sulfide in an aqueous solution of the sulfidizer, thiocarbamide $(NH_2)_2CS$. A spontaneous formation of metal sulfide is possible when the ion product of this sulfide IP_{PbS} is higher than the solubility product $K_{sp,MS}$. In the considered case the lead sulfide formation will occur if $IP_{PbS} = [Pb^{2+}]\times[S^{2-}]$ is higher than the lead sulfide solubility product, $K_{sp,PbS} = [Pb^{2+}]_{eq}\cdot[S^{2-}]_{eq}$, that is, $IP_{PbS} > K_{sp,PbS}$, where $[Pb^{2+}]$,$[S^{2-}]$, $[Pb^{2+}]_{eq}$ and $[S^{2-}]_{eq}$ are arbitrary (e.g., primary) and equilibrium concentration of ions Pb^{2+} and S^{2-}, respectively. Thus, to discuss the possible formation of metal sulfide it is necessary to know the initial concentration of the ions Pb^{2+} and S^{2-}. The initial concentration of free lead ions was calculated according to Eqs. (4) or (6).

The basis for the calculation of the sulfide ion concentration is the concept of the reversible decomposition of the thiocarbonic acid diamide in the aqueous alkaline solution by the reaction $(NH_2)_2CS \leftrightarrow H_2S + H_2NCN$, which was first developed in detail and justified in [10]. According to [10], the initial concentration of the S^{2-} ions is equal to

$$[S^{2-}] = \frac{K(H_2S)}{[H^+]^2}\left\{\frac{K_c[(NH)_2CS]\beta_c}{\beta_s}\right\}^{1/2}, \qquad (14)$$

where $K_c = 1.6\times10^{-23}$ is the $(N_2H_2)_2CS$ hydrolysis constant [10]; $\beta_s = [H^+]^2 + K_1[H^+] + K(H_2S)$ [10]; $\beta_c = [H^+]^2 + K_1^{'}[H^+] + K(H_2NCN)$ [10]; $K(H_2S)$ 1.1×10^{-20} [34] and $K(H_2NCN)$ 7.95×10^{-23} [35], K_1 8.9×10^{-8} [36] and $K_1^{'}$ 5.25×10^{-11} [35] are the complete dissociation constants and the first stage dissociation constants of hydrogen sulfide and cyanamide, respectively.

Next, from the found initial concentration of ions Pb^{2+} and S^{2-} we determine the value of the ion product and compare it with the solubility product $K_{sp,PbS} = 2.5\times10^{-27}$ of lead sulfide PbS [36].

Replacing in Eq. (4) the concentration $[Pb^{2+}]$ by its value expressed as a solubility product and concentration of sulfide ions $[Pb^{2+}] = K_{sp,PbS}/[S^{2-}]$, we obtain the expression (15):

$$c^{cit}_{Pb,\Sigma} = \frac{K_{sp,PbS}}{[S^{2-}]}\,1 + \left\{\frac{\beta_{11}}{[H^+]} + \frac{\beta_{12}}{[H^+]^2} + \frac{\beta_{13}}{[H^+]^3} + \frac{3\beta_{34}K^2_{sp,PbS}}{[H^+]^4[S^{2-}]^2} + \frac{4\beta_{44}K^3_{sp,PbS}}{[H^+]^4[S^{2-}]^3} + \frac{6\beta_{68}K^5_{sp,PbS}}{[H^+]^8[S^{2-}]^5} + \frac{2\beta_{21}K_{sp,PbS}}{[H^+][S^{2-}]}\right.$$

$$\left. + \beta_1[Cit^{3-}] + \beta_{1,2}[Cit^{3-}]^2 + \beta_1' \frac{K_w[Cit^{3-}]}{[H^+]}\right\}. \qquad (15)$$

Thus, based on Eqs. (4) and (14) we obtain the necessary data to build the dependence $c_{Pb,\Sigma} = f(pH)$, which characterizes the equilibrium in the system between the precipitate PbS and dissolved thiocarbamide and the lead complex compounds.

Figure 4 shows the boundaries of lead sulfide deposition at different concentrations of $(NH_2)_2CS$ calculated with Eq. (16). From a comparison of the boundaries of the lead hydroxide formation (the line at $[(NH_2)_2CS] = 0$ in Fig. 4) and the boundaries of the lead sulfide formation follows that the lead hydroxide formed at pH ≥ 11.1 should transform inevitably into the sulfide PbS, as the equilibrium concentration of lead above the $Pb(OH)_2$ precipitate is much higher than that of the sulfide. For example, at pH = 12 the lead concentrations above the precipitate of $Pb(OH)_2$ hydroxide is equal to 0.132 M, and above the sulfide PbS precipitate is just 1.3×10^{-7} M (at $[N_2H_4CS] = 0.025$ M) or 6.5×10^{-8} M (at $[N_2H_4CS] = 0.1$ M).

Thus, the calculation method proposed in this paper allows the prediction of the formation of solid phases of lead hydroxide and sulfide from the solution, as well as reliable choice of the compositions of reaction mixtures for the deposition of lead sulfide as a sol (outside of the hydroxide domain) or film (in the hydroxide domain).

Thus, in this paper by the example of $Pb(OH)_2$ the conditions of the metal hydroxide formation in an aqueous solution were first analyzed, taking into account the polynuclear hydroxo-complexes. In the coordinates pH–metal concentration the domains are calculated of the stable formation of the $Pb(OH)_2$ precipitate and the *hydroxide domain* is refined. The formation domains are found for the solutions containing two types of the lead complex compounds: hydroxo-complexes and citrate complexes. The formulas obtained allow the prediction of the possibility of formation of lead hydroxide depending on the composition of the reaction mixture.

We ascertained the concentration range of the lead sulfide formation in aqueous solutions of $(NH_2)_2CS$, taking into account the existence of both mononuclear and polynuclear hydroxo-complexes of lead. The proposed method of calculation permits the prediction of the formation of solid phases of lead hydroxide and sulfide in the solution and the selection of the compositions of reaction mixtures required for the deposition of lead sulfide as a hydrophobic sol, quantum dots, the *core@shell* heterostructures and the films, that is, in different morphological forms .

In particular, our calculations allow us recommending a sequence of operations required for the deposition of PbS films. Thus, for the deposition of films of lead sulfide, in the volumetric flask we poured an appropriate amount of alkali and a complexing agents like sodium citrate, and then slowly added dropwise the desired amount of lead salts under continuous stirring to prevent formation of basic salt or $Pb(OH)_2$ which just precipitated. Then we poured thiocarbamide solution to the homogeneous solution obtained. This sequence is consistent with the experiment, since the addition of alkali to a solution of lead salts creates a local oversaturation by alkali which leads to immidiate

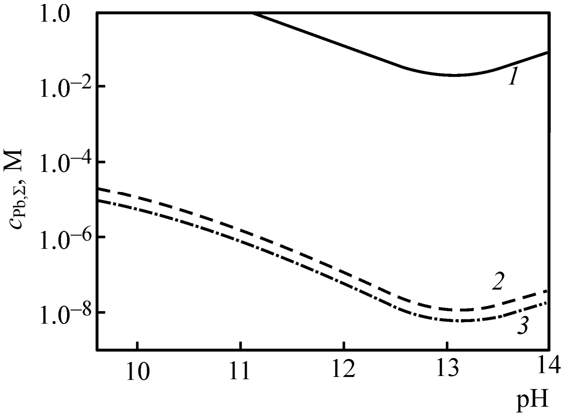

Fig. 4. The domains of lead sulfide PbS formation in the form of sol and film during the precipitation with aqueous thiocarbamide $(NH_2)_2CS$ of different concentrations, [NaCit] = 0.025 M, T = 298.15 K. Total concentration of lead $c_{Pb,\Sigma}$ in the solution is shown in a logarithmic scale.

precipitation of lead hydroxide, which should be avoided because it does not dissolve upon further addition of alkali, and obtaining a homogeneous solution with a desired pH value becomes impossible.

The proposed method of analysis and calculation of conditions for the formation of hydroxides and chalcogenides can be applied to other systems containing metal ions capable of forming mono- and polynuclear hydroxo-complexes.

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