



Short communication

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Complexation processes in aqueous solutions of lead acetate and thiourea

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Abstract

Purpose: The aim of the article is to study the processes of complexation in aqueous solutions containing lead acetate and thiourea and to establish the optimal concentration regions for the existence of thiocarbamide coordination compounds.

Modeling: The study of ionic equilibria was carried out by means of theoretical calculation taking into account the stability constants of various complex forms. Slices of concentration dependences of fractions of coordination compounds on initial concentrations of lead ions and thiourea, as well as predominance diagrams and distribution diagrams in three-dimensional space were constructed using the COMSOL Multiphysics application package by the Newton-Raphson method.

Conclusions: concentration ranges of existence of coordination compounds formed in aqueous solutions of lead acetate and thiourea at varying concentrations of components have been determined. It was revealed that at low concentrations of lead salt in solution the homogeneously liganded thiourea complexes dominate. With increasing thiocarbamide concentration, the total fraction of homogeneously liganded and dissimilarly liganded thiourea coordination compounds increases.

Keywords: Thiourea coordination compounds, Complexation, Distribution diagrams, Predominance diagram, Lead sulfide films, Aerosol pyrolysis method

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1. Introduction

Thiourea coordination compounds of lead are in demand in practical terms due to the possibility of their application as precursors in the preparation of lead sulfide films. Semiconductor films of narrow-gap PbS with a forbidden bandgap width of $E_g = 0.41$ eV [1] are used in the fabrication of various photovoltaic and optoelectronic devices: photovoltaic converters, photodetectors, various sensors, IR detectors in the infrared region of the spectrum, and other devices [2–6].

Among a large number of methods for deposition of lead sulfide films with controlled crystalline structure and properties, chemical deposition from solutions and aerosol pyrolysis can be distinguished [7–11]. The method of aerosol pyrolysis of solutions of thiourea coordination compounds (TCC) allows the formation of a solid phase of metal sulfide in the process of thermal destruction of complex compounds on a heated substrate [12, 13]. The composition and structure of the initial coordination compound determines the type of crystal structure, optical, photoelectric and electrophysical properties of the deposited sulfide layers.

The processes of formation of coordination compounds in aqueous solutions of various lead and thiourea salts were previously studied and the domination regions of different TCC of lead were determined [10, 12, 14–16]. The spatial structure of the thiourea-acetate complex $\text{Pb}((\text{NH}_2)_2\text{CS})_2(\text{mono-CH}_3\text{COO})_2$ was determined by quantum-chemical modeling in [17].

The aim of this work was to study the processes of complexation in aqueous solutions of lead acetate and thiourea and to establish the optimal concentration regions of thiocarbamide coordination compounds, which are precursors in the preparation of pyrolytic films of lead sulfide.

2. Modeling

When studying the processes of complexation, we considered ionic equilibria in an aqueous solution of lead salt and thiourea (TM), calculated the fractions (α) of all complex forms present in it, constructed three-dimensional distribution diagrams and predominance diagram according to the method described in [10, 14, 16]. Based on the dependence of the molar fractions of complex compounds on the analytical concentration of

lead salt and thiocarbamide, the domination areas of specific complex forms were identified and the points (lines) where the fractions of the predominant coordination compounds in aqueous solution are equal were fixed.

From the presented diagram of the predominance of coordination compounds in the system “ $\text{Pb}(\text{CH}_3\text{COO})_2 - (\text{NH}_2)_2\text{CS}$ ” it can be seen that in low-concentration solutions ($C_{\text{Pb}^{2+}} = 10^{-5} - 2 \cdot 10^{-3}$ mol/L and $C_{\text{TM}} = 10^{-5} - 2 \cdot 10^{-1}$ mol/L) a wide region of existence of aquacomplexes of $\text{Pb}(\text{H}_2\text{O})_n^{2+}$ is observed (Fig.). When increasing the concentration of lead acetate up to 1 mol/L in the same concentration range of thiourea, there is an increase in the proportion of complex ions $\text{Pb}(\text{CH}_3\text{COO})^+$. Thus, the specified range of concentrations of components of the initial solution “ $\text{Pb}(\text{CH}_3\text{COO})_2 - (\text{NH}_2)_2\text{CS}$ ” is not suitable for obtaining PbS films.

In the deposition of metal sulfide films, the formation of coordination compounds whose inner sphere includes thiourea is of greatest interest. Among thiourea coordination compounds in the aqueous solution of “ $\text{Pb}(\text{CH}_3\text{COO})_2 - (\text{NH}_2)_2\text{CS}$ ” the complex ions PbTM_4^{2+} , $\text{PbTM}_5(\text{CH}_3\text{COO})^+$, $\text{PbTM}_2(\text{CH}_3\text{COO})_2$ are dominant. The maximum fractions of these complexes in solution have values of 0.87, 0.34, 0.33, 0.32, respectively. The distribution diagram in three-dimensional space and cross sections of lines of equal fractions for some complexes are given in [16, 18]. The fraction of lead hydroxocomplexes in the considered system does not exceed 0.03 %, their concentration sharply increases with increasing pH.

The studies have shown that of the other existing complex compounds in aqueous solution of lead acetate and thiourea, $\text{PbTM}(\text{CH}_3\text{COO})_3^-$ ($\alpha = 0.2$), PbTM_2^{2+} ($\alpha = 0.14$), $\text{PbTM}(\text{CH}_3\text{COO})^+$ ($\alpha = 0.06$), $\text{PbTM}(\text{CH}_3\text{COO})_2$ ($\alpha = 0.06$) are relatively stable [16]. The maximum fraction of homogeneously liganded TCCs increases in the series $\text{PbTM}_3^{2+} < \text{PbTM}_2^{2+} < \text{PbTM}^{2+} < \text{PbTM}_4^{2+}$, and for the differently liganded complexes: $\text{PbTM}_2(\text{CH}_3\text{COO})^+ < \text{PbTM}(\text{CH}_3\text{COO})_2 \approx \text{PbTM}(\text{CH}_3\text{COO})^+ < \text{PbTM}(\text{CH}_3\text{COO})_3^- < \text{PbTM}_2(\text{CH}_3\text{COO})_2 < \text{PbTM}_3(\text{CH}_3\text{COO})^+$. It should be noted that of all the thiourea complex forms formed in aqueous solution of lead chloride and thiourea, the PbTM_4^{2+} ($\alpha = 1$) is also predominant [14].

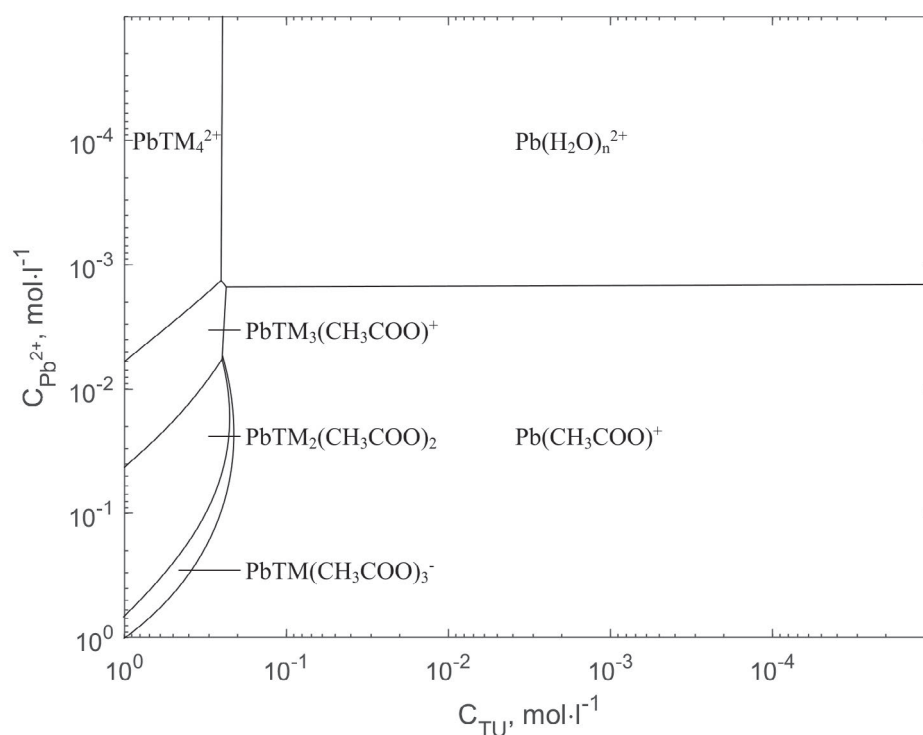


Fig. Diagram of the dominance of complex compounds in an aqueous solution of lead acetate and thiourea

The distribution diagrams were used to obtain data on the quantitative distribution of thiourea coordination compounds contained in the initial solution at a constant concentration of lead acetate and varying concentration of thiocarbamide. Thus, at the lead salt concentration of 0.1 mol/L, thiourea complexes with acetate ion in the inner sphere exist in solution, and their total fraction has values from 0.384 to 0.825 (Table). The total content of acetate TCCs increases with increasing thiourea concentration. At $C_{\text{Pb}^{2+}} = 0.01$ mol/L, the initial solution contains all homogeneously

liganded thiourea complexes $\text{Pb}(\text{TM})_m^{2+}$ as well as heterogeneously liganded $\text{PbTM}_n(\text{CH}_3\text{COO})_m^{2-m}$. With increasing thiourea content in the initial solution, the total fraction of all TCCs increases.

Analyzing the obtained results, it can be noted that the most probable precursors in the process of deposition of PbS films using different concentrations of lead salt can be complex forms of PbTM_4^{2+} , PbTM^{2+} , $\text{PbTM}(\text{CH}_3\text{COO})_3^-$, $\text{PbTM}_2(\text{CH}_3\text{COO})_2$, $\text{PbTM}_3(\text{CH}_3\text{COO})^+$. Varying the concentration of thiourea and lead acetate allows the formation of a complex of the desired

Table. Content of thiocarbamide coordination compounds at different concentrations of thiourea in solution ($C_{\text{Pb}^{2+}} = 0.1$ mol/l)

Proportion of complexes	Concentration of thiourea, mol/l				
	0.2	0.4	0.6	0.8	1
$\text{PbTM}(\text{CH}_3\text{COO})^+$	0.040	0.041	0.034	0.019	0.009
$\text{PbTM}(\text{CH}_3\text{COO})_2$	0.048	0.048	0.047	0.038	0.026
$\text{PbTM}(\text{CH}_3\text{COO})_3^-$	0.145	0.183	0.190	0.198	0.180
$\text{PbTM}_2(\text{CH}_3\text{COO})^+$	0.014	0.018	0.018	0.017	0.015
$\text{PbTM}_3(\text{CH}_3\text{COO})^+$	0.035	0.082	0.198	0.215	0.278
$\text{PbTM}_2(\text{CH}_3\text{COO})_2$	0.102	0.193	0.238	0.310	0.317
Total proportion of thiourea complexes	0.384	0.565	0.725	0.797	0.825

composition in the initial solution for the synthesis of PbS films with controlled properties depending on the practical purpose of the formed layers [19]. Thus, at the stage of coordination compound formation in aqueous solution, “metal-sulfur” bonds are formed, which are fragments of the metal sulfide structure released during thermal decomposition of TCC on a heated substrate.

Thermolysis of homogeneously liganded thiocarbamide complexes PbTM^{2+} , PbTM_2^{2+} , PbTM_3^{2+} , PbTM_4^{2+} leads to the deposition of more stoichiometric in composition PbS films with higher sulfur content. To obtain such samples it is necessary to use low concentrations of lead salt from 10^{-5} to $\sim 5 \cdot 10^{-2}$ mol/L, and thiourea from $4 \cdot 10^{-2}$ to $8 \cdot 10^{-1}$ mol/L.

In the concentration ranges of $C_{\text{Pb}^{2+}} = 10^{-3} - 6.5 \cdot 10^{-1}$ mol/L and $C_{\text{TM}} = 9 \cdot 10^{-2} - 1$, acetate TCCs are formed in which the lead atom is linked by covalent bonds with the sulfur atom of the thiocarbamide molecule and the oxygen atom of the acetate ion. Thus, according to quantum-chemical calculations of the structure of the coordination compound $\text{PbTM}_2(\text{CH}_3\text{COO})_2$, the nearest environment of the metal atom is a strongly distorted tetrahedron of the composition PbS_2O_2 [16]. During the thermal degradation of acetate complexes, oxygen enters the formed sulfide, replacing sulfur in the anionic sublattice (O_s), which can affect its photovoltaic and electrophysical properties.

It was previously found [20] that oxygen impurities and oxide phases affect the mechanism of current transfer and photoconductivity in films of various sulfides. In the presence of oxygen in the samples, the potential barriers controlling the current transfer increase in the intergranular interlayers, and as a result, the electrical conductivity may decrease. The electrical conductivity and photosensitivity of PbS films are enhanced by annealing in air, during which oxygen adsorption on the sample surface, changes in its defect structure, and ordering of the crystalline structure of the sulfide [12, 19]. PbS films synthesized by aerosol pyrolysis of TCC solutions have a cubic structure regardless of the type of the initial thiourea complex [10, 17, 18].

Previous IR spectroscopic studies of TCC formed in a solution of lead acetate (0.1 mol/L)

and thiourea [15] showed that at three-, four-, and fivefold excess of $(\text{NH}_2)_2\text{CS}$, the coordination compound $\text{PbTM}_2(\text{CH}_3\text{COO})_2$ predominates in the solution, while an excess of thiourea molecules remains in an unbound state. Also, with increasing concentration of $(\text{NH}_2)_2\text{CS}$ in solution, the formation of PbS films with more developed surface topography and less dense packing of grains occurs [18]. Thus, to obtain high-quality lead sulfide layers, it is desirable not to exceed a fivefold excess of thiocarbamide in the initial solution.

The concentration of $(\text{NH}_2)_2\text{CS}$ in the stock solution also affects the photoelectric and electrophysical properties of the sulfide films. According to [21], with increasing thiourea concentration in the initial solution, the resistivity and differential TEDS of the deposited PbS layers decrease, while the specific conductivity increases. It was also revealed in [22] that the use of different concentration ratios of lead acetate and thiourea allows to vary not only the resistivity of PbS films, but also their structural and morphological characteristics. According to the authors [23] an increase in the synthesis temperature leads to a decrease in the resistivity of pyrolytic lead sulfide layers.

3. Conclusion

On the basis of predominance diagrams and three-dimensional distribution diagrams, the domination regions of various coordination compounds formed in aqueous solutions of lead acetate and thiourea have been determined. It is established that the concentration range of $C_{\text{Pb}^{2+}} = 10^{-5} - 1$ mol/L and $C_{\text{TM}} = 10^{-5} - 2 \cdot 10^{-1}$ mol/L is not suitable for the preparation of lead sulfide films, since aqua- and acido complexes of $\text{Pb}(\text{H}_2\text{O})_n^{2+}$ and $\text{Pb}(\text{CH}_3\text{COO})^+$ predominate in it. It is shown that of all thiourea coordination compounds existing in solution, the complex forms dominate: PbTM_4^{2+} , PbTM_2^{2+} , $\text{PbTM}_3(\text{CH}_3\text{COO})^+$, $\text{PbTM}_2(\text{CH}_3\text{COO})_2$. The maximum proportion of homogeneously liganded complexes increases in the series $\text{PbTM}_5^{2+} < \text{PbTM}_2^{2+} < \text{PbTM}_3^{2+} < \text{PbTM}_4^{2+}$, and for the dissimilarly liganded TCCs: $\text{PbTM}_2(\text{CH}_3\text{COO})^+ < \text{PbTM}(\text{CH}_3\text{COO})_2 \approx \text{PbTM}(\text{CH}_3\text{COO})^+ < \text{PbTM}(\text{CH}_3\text{COO})_3^- < \text{PbTM}_3(\text{CH}_3\text{COO})^+ < \text{PbTM}_2(\text{CH}_3\text{COO})_2$. When the concentration of thiourea in the stock solution

increases, the total fraction of thiourea complex compounds increases.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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