Complexation in Binary Pb(II)–Dithiooxamide System in Pb$_2$[Fe(CN)$_6$] Gelatin-Immobilized Matrices

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Abstract—Complexation processes that occur when hexacyanoferrate(II) immobilized in gelatin is brought into contact with aqueous solutions of dithiooxamide at pH 12 are studied. Unlike the binary metal ion–dithiooxamide systems studied so far, the final product in this case was Pb(II) sulfide, rather than the Pb(II) complex with the indicated ligand. Concentration of Pb(II) sulfide was shown to depend on dithiooxamide concentration in a solution in contact with the matrix. A scheme for the complexation process is proposed.

Complexation processes in metal hexacyanoferrate(II) gelatin-immobilized matrices (GIM), containing the binary d-metal ion–dithiooxamide ligand (H$_2$L) were previously discussed in [1–6]. However, data on complexation in the binary systems, such as the metal ion–H$_2$L with a p element as the complexing agent, are unavailable. Nevertheless, it is known [7] that the reaction of lead hexacyanoferrate(II) (Pb$_2$[Fe(CN)$_6$]) with dithiooxamide in an alkaline medium can be used for the formation of non-silver photographic images on silver halide photographic materials and is accompanied by a significant increase in their photographic sensitivity. In connection with this, it was of interest to study the processes occurring in the binary Pb(II)–H$_2$L system under the specific conditions produced upon complexation in Pb$_2$[Fe(CN)$_6$]-GIM.

EXPERIMENTAL

Synthesis of the target Pb$_2$[Fe(CN)$_6$]-GIM has not been reported so far and we synthesized it using a specific procedure from the silver-containing GIMs that were obtained from AgHal-GIM [8, 9]. The obtained Ag matrices were treated with a solution containing Pb(NO$_3$)$_2$ (17.0 g/l), K$_3$Fe(CN)$_6$ (10.0 g/l), and nitric acid (1.5 g/l, 68%) for 30 min at 25°C. This process is described by the following reaction:

$$4Ag + 4[Fe(CN)_6]^{3–} + 2Pb^{2+} \rightarrow 2Ag_2Pb[Fe(CN)_6] + 2[Fe(CN)_6]^{4–}.$$  (1)

The matrix was then washed with running water for 5 min at 15–20°C and treated with a 25% aqueous Na$_2$S$_2$O$_3$ solution for 5 min at 20°C. Ag(I) in the matrix was bound into [Ag(S$_2$O$_3$)$_2$]$_{3–}$ and removed from the polymer bulk, while the compound remaining in the matrix was the target Pb$_2$[Fe(CN)$_6$]:

$$2Ag_2Pb[Fe(CN)_6] + 8S_2O_3^{2–} \rightarrow Pb_2[Fe(CN)_6] + 4[Ag(S_2O_3)_2]^{3–} + [Fe(CN)_6]^{4–}.$$  (2)

The obtained matrix was again washed with running water for 15 min and dried for 2–3 h at room temperature.

The analytical or reagent grade Pb(NO$_3$)$_2$, K$_3$[Fe(CN)$_6$], and Na$_2$S$_2$O$_3$·5H$_2$O were used for preparation of such GIMs. Pb$_2$[Fe(CN)$_6$]-GIM thus prepared were then treated with H$_2$L solutions with concentrations varying in the range of $1.0 \times 10^{-3}$–$5.0 \times 10^{-2}$ mol/l and at constant pH $12.0 \pm 0.1$. Solutions of H$_2$L were prepared from commercial product of analytical grade qualification. The temperatures of the ligand solutions and of gelatin materials in contact with them were maintained within the limits of (20.0 ± 0.5)°C. The duration of contact between GIM and the ligand solution was varied from 1 to 10 min. After termination of the complexation process (i.e., the contact of the matrix with the solution), the gelatin bulk with the obtained Pb(II) compounds was thoroughly washed with running water for 15 min at 18–20°C and dried for 2–3 h at room temperature. The complexation processes were described by the plots of $D = f(c_{Fe}, c_{H_2L}, \tau)$, where $D$ is the optical density of the metal chelate matrix corresponding to the initial concentration of Pb$_2$[Fe(CN)$_6$] in GIM ($c_{Fe}$, mol/dm$^3$), H$_2$L concentration in the solution in contact with the matrix ($c_{H_2L}$, mol/l), and to the duration of complexation ($\tau$, min). The plots were further processed as described in [10] using the coordinate sections $c_{Fe} = \text{const}$, varied $c_{H_2L}$, variable $\tau$ and $c_{H_2L} = \text{const}$, varied $\tau$, variable $c_{Fe}$. The compounds immobilized in the respective gelatin matrices were isolated by the known procedure [11]. As a result, pale yellow compound with composition Pb$_2$[Fe(CN)$_6$], as con-
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An analysis of kinetic curves \( D = f(c_{\text{Fe}}, c_{\text{H}_2\text{L}}, \tau) \) for the indicated range of \( c_{\text{Fe}}, c_{\text{H}_2\text{L}} \), and \( \tau > 2 \) min shows that the addition of \( \text{H}_2\text{L} \) molecules does not occur under these conditions. According to [12, 13], at \( \text{pH} 11–13 \), in the Pb(II)–OH system, the Pb(II) hydroxoo complex of the [Pb(OH)]\(^{3–}\) composition is accumulated. Since this complex is readily soluble in water, it is easily removed from the polymer bulk. The following overall reaction is supposed to occur in this case:

\[
Pb_2[\text{Fe(CN)}_6]^{-} + 6\text{OH}^- \rightarrow 2[Pb(\text{OH})_3]^{-} + [\text{Fe(CN)}_6]^{4–}.
\]

When \( \text{Pb}_2[\text{Fe(CN)}_6]\)-GIM (with any \( \text{Pb}_2[\text{Fe(CN)}_6] \) concentration in the matrix in the range of 0.1–1.5 mol/dm\(^3\)) is treated with alkaline \( \text{H}_2\text{L} \) solution with \( \text{pH} > 12 \) and \( c_{\text{H}_2\text{L}} > 2.5 \times 10^{-2} \) mol/l, already at \( \tau = 2 \) min and more (20°C), the initial pale yellow color changes to brown-black color. The typical curves of \( D = f(c_{\text{Fe}}, c_{\text{H}_2\text{L}}, \tau) \) are shown in Fig. 1. Many of these curves have sufficiently involved shapes with the maxima and minima (see in Figs. 1a, 1b). In general, as \( c_{\text{Fe}}, c_{\text{H}_2\text{L}} \), or \( \tau \) increases, the values of \( D \) approach some limits. At the same time, at \( c_{\text{H}_2\text{L}} > 2.5 \times 10^{-2} \) mol/l (see in Fig. 1d), \( D \) gradually increases with \( c_{\text{Fe}} \) and \( \tau \). This fact indicates that in the given interval of the ligand concentrations, only one chemical compound is formed in the binary system under study. The destruction of the matrix materials thus produced gives black compounds that are all identified by the chemical analysis as lead sulfide.

For PbS

\[
\text{Found (\%): Pb, 86.6; \ S, 13.4.}
\]

The electronic absorption spectrum of any GIM incorporating this compound coincides with that for PbS-GIM given in [14], which agrees with the chemical analysis data and confirms that the substance contained and isolated from GIM is one and the same chemical compound. Such compounds have not been reported so far in the studies of complexation in the binary M(II)–H\(_2\text{L} \) systems (M is a metal) [1–6, 15]. Therefore, peculiarity observed in the Pb(II)–H\(_2\text{L} \) system requires interpretation.

One of the possible explanation of this phenomenon suggests that PbS is obtained as a result of the reaction of \( \text{Pb}_2[\text{Fe(CN)}_6] \) or [Pb(OH)]\(_{n}\) with \( \text{H}_2\text{S}, \text{HS}^–, \) or \( \text{S}^2– \) formed as a result of the alkaline hydrolysis of dithiooxamide. Indeed, the latter compound can undergo this decomposition to give \( \text{H}_2\text{C}_2\text{O}_4, \text{NH}_3, \) and \( \text{H}_2\text{S} \) [16], but the time for this process to become essential considerably exceeds the duration of the implant/solution contact (less than 10 min in our case). However, when \( \text{Pb}_2(\text{PO}_4)_2 \)-GIM, produced by reacting \( \text{Pb}_2[\text{Fe(CN)}_6] \)-GIM with sodium, potassium, or ammonium phosphate [17], is treated with an alkaline H\(_2\text{L} \) solution, the pale yellow color typical of the immobilized \( \text{Pb}_2(\text{PO}_4)_2 \)-GIM remains unchanged. If the same treatment with H\(_2\text{L} \) solution is used for \( \text{PbCrO}_4 \)-GIM, produced in the reaction of \( \text{Pb}_2[\text{Fe(CN)}_6] \)-GIM with sodium or potassium chromate, the gelatin bulk becomes brown-black as in the case of \( \text{Pb}_2[\text{Fe(CN)}_6] \). If the ligand under study is changed for thiourea (\( \text{H}_2\text{N} \))C–S or thiosemicarbazide \( \text{H}_2\text{N}–\text{HN}–\text{C}=(\equiv)\text{S})\text{NH}_2 \), then neither \( \text{PbCrO}_4 \), \( \text{Pb}_2(\text{PO}_4)_2 \), nor even \( \text{Pb}_2[\text{Fe(CN)}_6] \)-GIM change their color after contact with the organic compound solution.

Therefore, one can conclude that PbS is produced in the investigated binary system Pb(II)–H\(_2\text{L} \) as a result of the Pb(II) complexation with the indicated ligand, rather than in the reaction of Pb(II) with \( \text{H}_2\text{S} \) or \( \text{S}^2– \), which are formed during an alkaline destruction of H\(_2\text{L} \). The above conclusion is not unexpected, since many publications report that the formation of some metal sulfides (in particular, as a result of Pb(II) interaction with thiourea or thiosemicarbazide) is accompa-