

LETTERS TO THE EDITOR

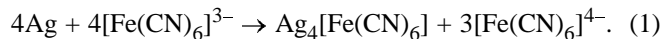
Immobilization of Silver(I) Hexacyanoferrate(II) in Thin Gelatin Layers

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Immobilization of hexacyanoferrates(II) of some p , d , and f elements (M) in thin gelatin layers, based on the electrophilic substitution of Ag(I) by M(II), M(III), and M(IV) on contact of silver(I) hexacyanoferrate(II) (Ag_4FC) immobilized in a gelatin matrix with aqueous solutions of appropriate metal halides MHlg_2 , MHlg_3 , and MHlg_4 ($\text{Hlg} = \text{Cl}, \text{Br}$), was studied in [1]. The initial gelatin-immobilized Ag_4FC matrices were prepared from immobilized systems containing elemental silver (obtained, in turn, from gelatin-immobilized AgHlg matrices by a standard procedure [2]) by treatment with aqueous alkaline solution of potassium hexacyanoferrate(III):



However, the standard electrode potential $E_{\text{Ag}^+/\text{Ag}}^0$ strongly depends on the particle size of silver and varies from -0.10 V for finely dispersed metal to $+0.80$ V for compact metal. With increasing concentration of silver in the matrix the average particle size of immobilized silver and $E_{\text{Ag}^+/\text{Ag}}^0$ increase, and its oxidation with $[\text{Fe}(\text{CN})_6]^{3-}$ becomes more difficult. Our experiments show that reaction (1) in gelatin-immobilized matrix with the above solution is relatively slow, and at concentration of metallic silver in the polymer matrix more than 2.5 mol dm^{-3} the conversion of silver into Ag_4FC does not exceed 40% even upon prolonged contact ($\tau > 2$ h) of the silver-containing matrix with potassium hexacyanoferrate(III) solution. Such conversion degree is insufficient, but our attempts to increase the conversion of silver into Ag_4FC by only changing the concentration of potassium hexacyanoferrate(III) or solution pH failed. We found that at a given process time the $\text{Ag} \rightarrow \text{Ag}_4\text{FC}$ conversion can be significantly increased by addition of potassium hexacyanoferrate(II) $\text{K}_4[\text{Fe}(\text{CN})_6]$ with simultaneous decrease in the concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]$ to 2.5 wt % and almost constant solution

pH. Using Eq. (2) for the potential of the Ag^+/Ag couple, we found that in the absence of $[\text{Fe}(\text{CN})_6]^{4-}$ in the solution this potential is determined by expression (3), and in the presence of this ion, by expression (4).

$$E = E_{\text{Ag}^+/\text{Ag}}^0 - 0.058 \log(a_{\text{Ag}^+}/a_{\text{Ag}}), \quad (2)$$

$$E_1 = E_{\text{Ag}^+/\text{Ag}}^0 - 0.058 \log a_{\text{Ag}} + (1/5) \times 0.058 \log K_s(\text{Ag}_4\text{FC}) + (1/5) \log 4, \quad (3)$$

$$E_2 = E_{\text{Ag}^+/\text{Ag}}^0 - 0.058 \log a_{\text{Ag}} + (1/4) \times 0.058 \log K_s(\text{Ag}_4\text{FC}) - (1/4) \times 0.058 \log a_{\text{FC}}, \quad (4)$$

where a_{Ag} and a_{FC} are the activities of elemental silver and $[\text{Fe}(\text{CN})_6]^{4-}$ anion, respectively, and $K_s(\text{Ag}_4\text{FC})$ is the solubility constant of silver(I) hexacyanoferrate(II). Now, using the above equations, we obtain expression (5).

$$\Delta E = E_1 - E_2 = -0.0029 \log K_s(\text{Ag}_4\text{FC}) + 0.0070 + 0.0145 \log a_{\text{FC}}. \quad (5)$$

At 25°C $K_s(\text{Ag}_4\text{FC}) \approx 1.5 \times 10^{-41}$ [3], which gives Eq. (6):

$$\Delta E = 0.125 + 0.0145 \log a_{\text{FC}}. \quad (6)$$

In particular, at $a_{\text{FC}} 0.1 \text{ M}$ $\Delta E \approx +0.11$ V; the real value is somewhat greater, because the value of $K_s(\text{Ag}_4\text{FC})$ given in [3] is probably underestimated because of the pronounced ability of Ag_4FC to form colloidal solutions [4]. This difference itself is not so large, but taking into account the fact that $E_{\text{Ag}^+/\text{Ag}}^0$ varies from -0.10 to $+0.80$ V and E^0 for the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple ($+0.356$ V) lies in the same range, it can become decisive for the $\text{Ag}(0) \rightarrow \text{Ag}(I)$ redox reaction. In particular, at

given a_{FC} , $25.0 \pm 0.1^\circ\text{C}$, c_{Ag} 2.0, 2.5, 3.0, 3.5, and 4.0 mol dm^{-3} , and τ 1 h, the conversion of metallic silver into Ag_4FC is 93, 90, 87, 85, and 83%, respectively, and at τ 2 h the conversion in all the cases is nearly quantitative and significantly exceeds the results obtained in the absence of excess $[\text{Fe}(\text{CN})_6]^{4-}$ ions.

To determine the chemical composition of the immobilized compound, it was recovered from the matrix using the procedure given elsewhere [5]. The matrix was kept in a 5% aqueous solution of trypsin or proteolytic *Bazillus mesentericus* enzyme for 10–15 min at $25\text{--}30^\circ\text{C}$, then the reaction mixture was treated with hot water, and the residues of immobilized compounds were separated from the mother liquors and dried in air at room temperature. Found, %: C 11.1; Ag 67.2; Fe 8.5; N 13.2. $\text{C}_6\text{Ag}_4\text{FeN}_6$. Calculated, %: C 11.20; Ag 67.06; Fe 8.68; N 13.06.

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