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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 $MHlg_4$ (Hlg = Cl, 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):

$$4Ag + 4[Fe(CN)_6]^{3-} \rightarrow Ag_4[Fe(CN)_6] + 3[Fe(CN)_6]^{4-}. \quad (1)$$

However, the standard electrode potential $E^0_{Ag^+/Ag}$ 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 $E^0_{Ag^+/Ag}$ increase, and its oxidation with $[Fe(CN)_6]^{3-}$ 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 $Ag \rightarrow Ag_4FC$ conversion can be significantly increased by addition of potassium hexacyanoferrate(II) $K_4[Fe(CN)_6]$ with simultaneous decrease in the concentration of $K_3[Fe(CN)_6]$ 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 $[Fe(CN)_6]^{4-}$ in the solution this potential is determined by expression (3), and in the presence of this ion, by expression (4).

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

$$E_1 = E^0_{Ag^+/Ag} - 0.058\log a_{Ag} + (1/5)\times 0.058\log K_s(Ag_4FC) + (1/5)\log 4, \quad (3)$$

$$E_2 = E^0_{Ag^+/Ag} - 0.058\log a_{Ag} + (1/4)\times 0.058\log K_s(Ag_4FC) - (1/4)\times 0.058\log a_{FC}, \quad (4)$$

where a_{Ag} and a_{FC} are the activities of elemental silver and $[Fe(CN)_6]^{4-}$ anion, respectively, and $K_s(Ag_4FC)$ is the solubility constant of silver(I) hexacyanoferrate(II). Now, using the above equations, we obtain expression (5).

$$\Delta E = E_1 - E_2 = -0.0029\log K_s(Ag_4FC) + 0.0070 + 0.0145\log a_{FC}. \quad (5)$$

At 25°C $K_s(Ag_4FC) \approx 1.5\times 10^{-41}$ [3], which gives Eq. (6):

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

In particular, at a_{FC} 0.1 M $\Delta E \approx +0.11$ V; the real value is somewhat greater, because the value of $K_s(Ag_4FC)$ 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 $E^0_{Ag^+/Ag}$ varies from –0.10 to +0.80 V and E^0 for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple (+0.356 V) lies in the same range, it can become decisive for the $Ag(0) \rightarrow Ag(I)$ redox reaction. In particular, at

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given a_{FC}, 25.0 ± 0.1°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 $[Fe(CN)_6]^{4-}$ 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 trypsine or proteolytic *Bazillus mesentericus* enzyme for 10–15 min at 25–30°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. $C_6Ag_4FeN_6$. Calculated, %: C 11.20; Ag 67.06; Fe 8.68; N 13.06.

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REFERENCES

1. Mikhailov, O.V., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 5, pp. 874–875.
2. Kirillov, N.I., *Osnovy protsessov obrabotki kinofotomaterialov* (Basis of Treatment of Movie and Photographic Materials), Moscow: Iskusstvo, 1978.
3. Pearce, J. N. and Ough, L.D., *J. Am. Chem. Soc.*, 1938, vol. 60, no. 1, pp. 80–84.
4. Tananaev, I.V., Seifer, G.B., Kharitonov, Yu.Ya., and Korol’kov, A.P., *Khimiya ferrotsianidov* (Chemistry of Hexacyanoferrates), Moscow: Nauka, 1971, p. 43.
5. Mikhailov, O.V., *Indian J. Chem., Ser. A*, 1991, vol. 30, no. 3, pp. 252–254.