Complexation reaction on the immobilized matrices: Complexes of iron(III) hexacyanoferrate(II) and some N, O and N, S containing ligands formed on a thin gelatin layer

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Complexation reaction occurring between mixed potassium-iron(III) hexacyanoferrates(II), KFe[Fe(CN)₆]₄, and N, S or N, O-containing ligands such as 8-hydroxyquinoline (1) and its alkyl- and oxyalkyl derivatives, 1-nitroso-2-naphthol (2) and its isomer 2-nitroso-1-naphthol, isonitrosoacetone (3), α-benzoinoxime (4), 8-mercaptoquinoline (5) and some of its substituted derivatives (halide, alkyl, S-methyl), dithiooxamide (6) and its N,N'-diphenylsubstituted derivatives have been studied in thin gelatin layers. With KFe[Fe(CN)₆]-matrix, complexation proceeds according to pseudo-SN₈-mechanism. The complexation occurs after iron(III) hexacyanoferrate(II) dissociates in the alkaline medium which proceeds according to two possible ways; one leads to Fe₃O₄ and [Fe(CN)₆]⁴⁻ anion, the other to Fe(OH)₃ and [Fe(CN)₆]⁴⁻ anion. It is noted that in the case of N, O-containing ligands, Fe(II) chelates are formed and in the case of N, S-containing ligands, Fe(III) chelates are formed. It is shown that in the case of N, S containing ligands, there is a participation of molecular oxygen in the complexation reactions. Examples of kinetic curves for the particular systems “potassium, iron(III)-hexacyanoferrate(II)-ligand” are presented.

One of the important problems of silver halide photography is cutting down of silver consumption and its replacement by less costly and more easily available chemical compounds. The possibility of utilization of Ni(II) and Cu(II) complexes of N, S-containing ligands formed during heterogeneous complexation reaction of Ni(II)/Cu(II) hexacyanoferrate(II) matrices immobilized in thin gelatin layers, as possible carriers of photographic images has previously been pointed out. From the practical point of view, of particular interest are insoluble iron(II) or iron(III) chelates with N, O and N,S-containing ligands, being relatively cheap and easily available. In the present paper, complexation reactions occurring on Fe(III) hexacyanoferrate(II) matrices during the reaction with the solutions of bidentate ligands of types I-V are investigated (here Z is either a closed-ring system or open-ring group of atoms).

Experimental

Matrices containing iron(III)-potassium hexacyanoferrate(II) (KFe[Fe(CN)₆]) were obtained as done in the case of conventionally formed silver images (by the development and fixation of the silver halide photographic material), by means of the two-stage chemical treatment. The first stage includes oxidation of elemental silver into Ag₄[Fe(CN)₆], together with the co-precipitation of KFe[Fe(CN)₆] upon reaction with the iron(III) complexes of citric and tartaric acids.

\[
2Fe₂(HCt)(HTr) + 4Ag + 4[Fe(CN)₆]^{3-} + 3K⁺ → 3KFe[Fe(CN)₆] + ~[Fe(CN)₆]^{3-} + 2HCt^{3-} \]  

(1)

(where H₄Ct is citric acid, H₄Tr is tartaric acid).

The second stage involves dissolution of Ag₄[Fe(CN)₆] upon reaction with an aqueous thiosulfate solution according to Eq. 2 which results in the formation of a water-soluble complex:

\[
Ag₄[Fe(CN)₆] + 8S₂O₃^{2-} → 4[Ag(S₂O₃)₂]^{3-} + [Fe(CN)₆]^{4-} \]  

(2)

Between the two stages as well as upon the completion of the second stage, the material comprising a metal hexacyanoferrate(II) matrix is washed with running water for a few minutes, and then the matrix is processed in alkaline solutions of S-containing ligands such as 8-hydroxyquinoline (1) and its alkyl- and oxyalkyl derivatives, 1-nitroso-2-naphthol (2) and its isomer 2-nitroso-1-naphthol, isonitrosoacetone (3), α-benzoinoxime (4), 8-mercaptoquinoline (5) and some substituted (halide, alkyl, S-methyl) derivatives, dithiooxamide (6) and its N,N'-diphenyl-substituted derivatives.

The ligand concentrations in the solutions varied in the range of 10⁻³-10⁻¹ mol.dm⁻³, the pH value was maintained at 12 ± 0.1, since these parameters provide a high concentration of the deprotonated
forms of ligands, which are directly involved in complexing processes. The matrices were kept in solution for about 1-10 min at 20°C. Optical densities of thin gelatin layers containing chelate complexes of iron(III) and iron(II) with these ligands were measured on a "Macbeth-TD-504" densitometer (Kodak Co., USA) in the region of 0.1-4.0 with an accuracy of ± 2%. The absorption spectra were measured on a "Specord" spectrophotometer in the region 10,000-30,000 cm⁻¹ (350-1000 nm). Using the results of measurements, kinetic curves were plotted with D as function of C_F, C_L and t, D = f(C_F, C_L, t), where D is the density of a thin gelatin layer containing the chelate complex formed upon the chemical processing of the immobilized matrix, C_L is the ligand concentration in solution, C_F is the concentration of KFe[Fe(CN)₆] in the immobilized matrix, t is the time taken in complexation. Examples of such relationships are given in Fig. 1.

Fig. 1 — Kinetic curves for D = f (C_F, C_L, t) for the system containing immobilized KFe[Fe(CN)₆] matrix-8-hydroxyquinoline [Fe(III) hexacyanoferrate(II) concentrations (C_F) 5.0 × 10⁻³ mol·m⁻² (---) and 2.0 × 10⁻² mol·m⁻² (-----) in the gelatin layer; ligand concentrations (C_L) in the solution 3.5 × 10⁻³ mol·dm⁻³ (1.1'), 1.4 × 10⁻² mol·dm⁻³ (2.2') and 5.5 × 10⁻² mol·dm⁻³ (3.3'). Optical densities measured through a blue filter with a transmission maximum at 450 nm].

Results and discussion

In the system containing Fe(III) hexacyanoferrate(II) matrix, complexation process occurs according to pseudo-S_n 1-mechanism where ligand entering into the inner coordination sphere is preceded by the dissociation of KFe[Fe(CN)₆] molecules under the influence of OH⁻ ions. The chemical analyses showed that during complexing process by ligand (C_L < 10⁻⁵ mol·dm⁻³) iron(II) hydroxide and iron(III) oxide were formed in thin gelatin layer, and in solution in contact with immobilized matrix, [Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻ anions are formed. It is clear that KFe[Fe(CN)₆] dissociation can occur by two pathways (Eqs 3,4).

2KFe[Fe(CN)₆] + 6OH⁻ → Fe₃O₄ + 2[Fe(CN)₆]⁴⁻ + 2K⁺ + 3H₂O ... (3)

KFe[Fe(CN)₆] + 2OH⁻ → Fe(OH)₂ + [Fe(CN)₆]³⁻ + K⁺ ... (4)

Hexacyanoferrate(II) and hexacyanoferrate(III) anions, and iron(III) oxide (Fe₂O₃) are quite stable and do not interact with the ligands used in the present study. It is obvious that in complexing process iron(II) hydroxide is taking part.

On a KFe[Fe(CN)₆] matrix, complex formation resulting in insoluble chelates in a thin gelatin layer is observed in the case of N,O containing ligands of types I and II and in the case of N,S containing ligands of type IV. However, the complexation processes in the case of N,O containing ligands and N,S containing ligands are essentially different. In the case of ligands I and II, 1 : 2 chelates (metal : ligand) of Fe(II) are formed (Eqs 5,6).

Fe(OH)₂ + 2[Fe(CN)₆]⁴⁻ → (OH)Fe[Fe(CN)₆]O₂⁻ + 2H₂O ... (5)

Fe(OH)_2 + 2[Fe(CN)_6]^{3-} → (OH)Fe[Fe(CN)_6]O_2^{2-} + 2H_2O ... (6)

Fe + O₂ + 4Z → (O₂)Fe[Fe(CN)₆]O₄⁻ + 2H₂O ... (7)

Fe + O₂ + 4Z → (O₂)Fe[Fe(CN)₆]O_4^{2-} + 2H_2O ... (8)

Fe + O₂ + 4Z → (O₂)Fe[Fe(CN)₆]O_4^{2-} + 2H_2O ... (9)
The complexes formed have quite diverse colours varying from dark-blue (in case of Fe(II) chelate with isonitrosoacetone) to almost black in the case of Fe(II) chelate with 8-hydroxyquinoline. It should be noted, however, that the rates of the complex formation are relatively slow, and at first the transition from the initial KFe[Fe(CN)₆]_₅ immobilized matrix is usually accompanied by a considerable decrease in the absorption intensity, together with the change of the blue colour to brown-yellow, and subsequently, as complexing process is proceeding, the thin gelatin layer acquires a yellow-gray and later black colour (in case of Fe(II) chelate with 8-hydroxyquinoline) or a blue-green and later blue colour (in case of Fe(II) chelate with isonitrosoacetone). At relatively lower concentrations of ligands in the solution in contact with KFe[Fe(CN)₆] immobilized matrix, the above colour transformation takes quite a long period of time (at the concentrations $C_L > 4.0 \times 10^{-2}$ mol.dm$^{-3}$ and $C_L = (1.0-5.0) \times 10^{-2}$ mol.dm$^{-3}$, the disappearance of the blue colour of KFe[Fe(CN)₆] is not observed even after 10 min). With the increase in ligand concentration the time period of colour change tends to gradually decrease (in the case of 8-hydroxyquinoline, for example, for $C_L = 5.0 \times 10^{-2}$ mol.dm$^{-3}$, time required = 1 min).

In case of 8-hydroxyquinoline, with the increase in ligand concentration in the solution to about $C_L = (1.5-2.0) \times 10^{-2}$ mol.dm$^{-3}$ in areas having $C_r < 1.0 \times 10^{-2}$ mol.m$^{-2}$ as well as the increase in time $t$, optical density $D$ first reaches a peak value and then begins to drop. Further increase in ligand concentration in the solution causes $C_r$ region to increase. It implies that under such conditions, the dissociation of Fe(II) complex with 8-hydroxyquinoline starts; as the process becomes more intense greater is the concentration of the ligand in the solution in contact with a KFe[Fe(CN)₆] immobilized matrix indicating the participation of 8-hydroxyquinoline in the process. Besides, Fe(II) and Fe(III) ions are not detected even at high ($> 10^{-1}$ mol.dm$^{-3}$) ligand concentrations in the solution; therefore, their contents in the thin gelatin layer remain unchanged. The cause of a slight decrease in optical density with the increase in time $t$ is Fe(II) → Fe(III) oxidation with the formation of an insoluble 8-hydroxyquinoline-Fe(III) chelate, according to the reaction (7).

The various alkyl derivatives of 8-hydroxyquinoline behave just as 8-hydroxyquinoline, and this is an indication of the weak effect of the substituents in the quinoline ring on the complexation process on the immobilized KFe[Fe(CN)₆] matrix. It is interesting, however, that reaction (7) is not observed for ligands of type(II) (1-nitroso-2-naphthol, its isomer 2-nitroso-1-naphthol, isonitrosoacetone etc.), even at high concentrations ($> 10^{-1}$ mol.dm$^{-3}$) in the aqueous solution.

Unlike the complexation on a KFe[Fe(CN)₆] matrix in the case of nitrogen-oxygen-containing ligands, where 1 : 2 (metal : ligand) Fe(II) chelates are formed, in the case of nitrogen-sulfur-containing ligands 1 : 3 Fe(III) chelates are formed immediately.

Their formation occurs in the presence of molecular oxygen in two stages; initially formed Fe(II) chelates are oxidized into Fe(II) chelates according to Eqs (8-9).

The compounds impart to thin gelatin layers different shades of red brown colour and give absorption in the region $\nu_{max} = 20,500-22,000$ cm$^{-1}$ ($\lambda_{max} = 450-490$ nm). The marked difference for nitrogen-sulfur-containing ligands is quite clear—since nitrogen-oxygen-containing ligands, are much better in stabilizing Fe(III) oxidation state. It is interesting to note that the formation of Fe(II) or Fe(III) chelates with ligands of type(III) for example, with α-benzoinoxime (4) and its analogues on an immobilized KFe[Fe(CN)₆] matrix is not possible to observe although iron chelates of this ligand series can be prepared in the aqueous solution. Some factors which may be the cause of this phenomenon are: (1) Poor diffusion of molecules of type (III) ligands to the gelatin layer owing to small rate of complexing process; (2) low stability of Fe(II) chelates with these ligands under OH$^-$ ions influence; and (3) retardation by these ligands of KFe[Fe(CN)₆] decomposition according to Eq. 4. For the same time $t$ of complexation process, in case solutions of ligands of type (III) in contact with an immobilized KFe[Fe(CN)₆] matrix, smaller concentrations of free [Fe(CN)₆]³⁻ anions are recorded than concentrations of free [Fe(CN)₆]³⁻ in solution of ligands (I), (II) and (IV) contacting a KFe[Fe(CN)₆] matrix. The absence of complexation of a KFe[Fe(CN)₆] immobilized matrix with ligands of type (V) can be explained in terms of Fe(III) being the “hard” Lewis acid, Fe(II) “average” Lewis acid, and ligands of type (V) “soft” Lewis base; hence, the complexes of Fe(II) and Fe(III) with ligand of type (V) must be unstable compounds. Moreover, Fe(III) stabilization is for N,S containing ligands. Therefore, initial Fe(II) complex which is formed by reaction of Fe(OH)$_2$ with dithiooxamide or its analogous ligands, transforms to Fe(III) chelate. It decomposes in an alkaline solution to Fe(III) oxide or Fe(III) hydroxide, and this is in agreement with absence of complexation process.

In summary, it may be noted that complexation processes at KFe[Fe(CN)₆] immobilized matrix

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which have been studied in the present paper, are accompanied by formation of iron chelates that absorb intensely in visible region, and therefore, they can be used in silver halide photography for the amplification of the initial silver image (especially noticeable in the low density value region).

References


