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Complexing Processes on the Immobilized Matrices of Hexacyanoferrate(II)-Nickel(II) and Nitrogen-Sulfur Ligands in Thin Gelatin Layer

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Summary. Complexing processes occurring between immobilized matrices obtained from Ni(II) hexacyanoferrates(II) and solutions of various nitrogen-sulfur-containing chelating ligands in thin gelatin layers have been studied. With $Ni_2[Fe(CN)_6]$-matrix, the complexing process is found to proceed according to a S_N^2-mechanism. The schemes of the processes in each of the above matrices are given. Examples of kinetic curves for particular systems "hexacyanoferrate(II) nickel(II)-ligand" are presented.

Keywords. Immobilized matrix; Complexing; Thin gelatin layer.

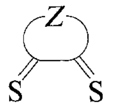
Komplexierungsprozesse auf den immobilisierten Matrices von Hexacyanoferrat(II)-Nickel(II) und Stickstoff-Schwefel-Liganden in dünnen Gelatin-Schichten

Zusammenfassung. Es wurden Komplexierungsprozesse auf immobilisierten Matrices, die von Ni(II)-Hexacyanoferrat(II) und Lösungen verschiedener Stickstoff-Schwefel-Liganden erhalten wurden, in dünnen Gelatin-Schichten untersucht. Mit einer $Ni_2[Fe(CN)_6]$-Matrix wurde festgestellt, daß der Komplexierungsprozeß nach einem S_N^2-Mechanismus verläuft. Es werden die entsprechenden Reaktionsschemata angegeben. Beispiele für den kinetischen Verlauf für bestimmte „Hexacyanoferrat(II)-Ni(II)-Ligand"-Systeme werden präsentiert.

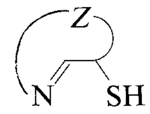
Introduction

One of the ways of overall cutting down the silver consumption in chemical photographic industry is the so-called silver recovery. One of the methods of silver recovery consists in the following: silver, as the "working material" for the formation of a photographic image by means of a number of specific chemical reactions, is substituted with chelate complexes of 3d-elements having various nitrogen-sulfur-containing ligands. From the chemical point of view, the formation of non-silver images with such carriers is nothing but a complexing process on immobilized matrices, and the investigation of the latter is both of academic and practical interest.

In the present paper electron spectroscopy and spectrophotometry were used to investigate the complexing processes on the immobilized matrices occurring in thin gelatin layer. Various silver halide materials uniformly dispersed in the gelatin binding agent were obtained from Ni(II)-hexacyanoferrate(II) upon the reaction with alkaline solutions of chelating ligands of types **I** and **II**



I



II

(where Z is either a closed-ring system or an open-ring group of atoms).

Experimental

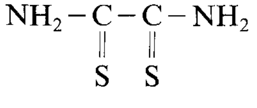
Matrices containing hexacyanoferrate(II) nickel(II) ($Ni_2[Fe(CN)_6]$) were obtained on the basis of conventionally formed silver images (by the development and fixation of the silver halide photographic material) [1], by means of the two-stage chemical treatment. The first stage includes oxidation of elemental silver into its hexacyanoferrate(II) and halide, together with the co-precipitation of $Ni_2[Fe(CN)_6]$ upon reaction with a solution containing potassium hexacyanoferrate(III) and a complex with the corresponding metal ion with citric acid [2, 3]:

$$\begin{aligned}&6[Ni(HCt)_3]^{7-} + 4[Fe(CN)_6]^{3-} + 4\,Ag + 4\,Cl^- \\ &\quad \rightarrow 3\,Ni_2[Fe(CN)_6] + 4\,AgCl + [Fe(CN)_6]^{4-} + 18\,HCt^{3-}\end{aligned} \tag{1}$$

(H_4Ct is citric acid). The second stage involves the transition of AgCl into the solution upon the reaction with an aqueous thiosulfate solution according to (2) at the expense of the formation of a water-soluble complex:

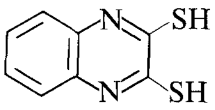
$$AgCl + 2\,S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + Cl^- . \tag{2}$$

Between the stages, as well as upon the completion of the second stage, the material comprising a metal hexacyanoferrate(II) matrix was washed with running water for a few minutes, and then the matrix was processed in alkaline solutions of sulfur-containing ligands such as dithiooxamide (**1**), its N,N'-diphenyl substituted en-thiol derivative, quinoxaline-2,3-dithiol (**2**) 8-mercaptoquinoline (**3**) and its halide, alkyl, and S-methyl derivates. 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 ± 0.1, since these parameters provide a high concentration of the thiol form of ligands, which is 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 were measured on a "MACBETH TD-504" densitometer (Kodak Co., USA) in the region of 0.1–4.0

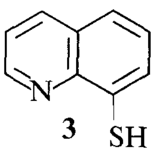


$$NH_2-\underset{\underset{S}{\|}}{C}-\underset{\underset{S}{\|}}{C}-NH_2$$

1



2



3

with an accuracy of ± 2% (relatively). The absorption spectra were measured on a "Specord" spectrophotometer in the region 10 000–30 000 cm^{-1} (350–1 000 nm). Using the results of the measurements, kinetic curves were plotted with D as a 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 $Ni_2[Fe(CN)_6]$ in the immobilized matrix, t is the complexing process time. Examples of such relationships are given in Figs. 1–4. An analysis of the relationships allows to draw certain conclusions which are given in the section below.

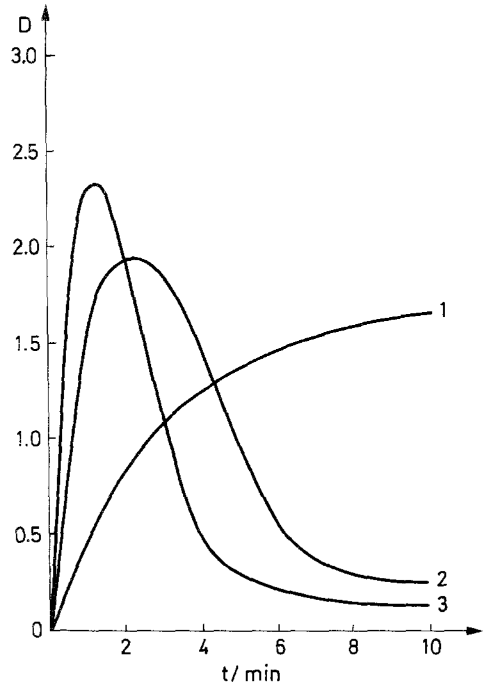


Fig. 1. Kinetic curves $D = f(C_F, C_L, t)$ for the system containing immobilized $Ni_2[Fe(CN)_6]$ matrix-dithiooxamide (for the "acid form"); fixed Ni(II) hexacyanoferrate(II) concentration ($C_F = 2.0 \cdot 10^{-2} mol/m^{-2}$) in the gelatin layer, variable complexing process time *t*, and ligand concentrations C_L in the solution $4.0 \cdot 10^{-3} mol/dm^{-3}$ (*1*), $2.0 \cdot 10^{-2} mol/dm^{-3}$ (*2*), and $3.5 \cdot 10^{-2} mol/dm^{-3}$ (*3*); optical densities measured through a yellow filter

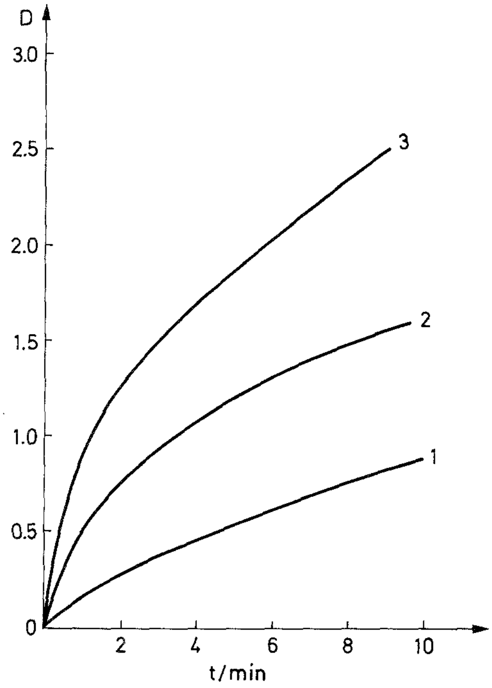


Fig. 2. Kinetic curves $D = f(C_F, C_L, t)$ for the system containing immobilized $Ni_2[Fe(CN)_6]$ matrix – N,N′-diphenyldithiooxamide; fixed Ni(II) hexacyanoferrate(II) concentration ($C_F = 2.0 \cdot 10^{-2} mol/m^{-2}$) in the gelatin layer, variable complexing process time *t*, and ligand concentrations C_L in the solution $3.0 \cdot 10^{-3} mol/dm^{-3}$ (*1*), $1.2 \cdot 10^{-2} mol/dm^{-3}$ (*2*), and $2.7 \cdot 10^{-2} mol/dm^{-3}$ (*3*); optical densities measured through a green filter

Results and Discussion

Two different types of a ligand – $Ni_2[Fe(CN)_6]$-matrix interaction can be distinguished. In the processes of the first type (such as complexing in $Ni_2[Fe(CN)_6]$ – 8-mercaptoquinoline or its substitutes and in $Ni_2[Fe(CN)_6]$ – N,N′-diphenyldithio-

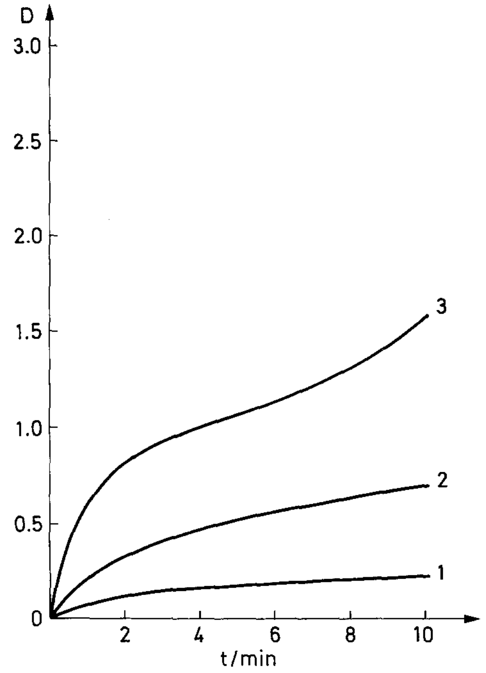


Fig. 3. Kinetic curves $D = f(C_F, C_L, t)$ for the system containing immobilized $Ni_2[Fe(CN)_6]$matrix −quinoxaline-2,3-dithiol (for the "acid" form); fixed Ni(II) hexacyanoferrate(II) concentration ($C_F = 2.0 \cdot 10^{-2}$ mol/m^{-2}) in the gelatin layer, variable complexing process time *t*, and ligand concentrations C_L in the solution $2.0 \cdot 10^{-3}$ mol/dm^{-3} (*1*), $6.0 \cdot 10^{-3}$ (*2*), and $2.0 \cdot 10^{-2}$ mol/dm^{-3} (*3*); optical densities measured through a red filter

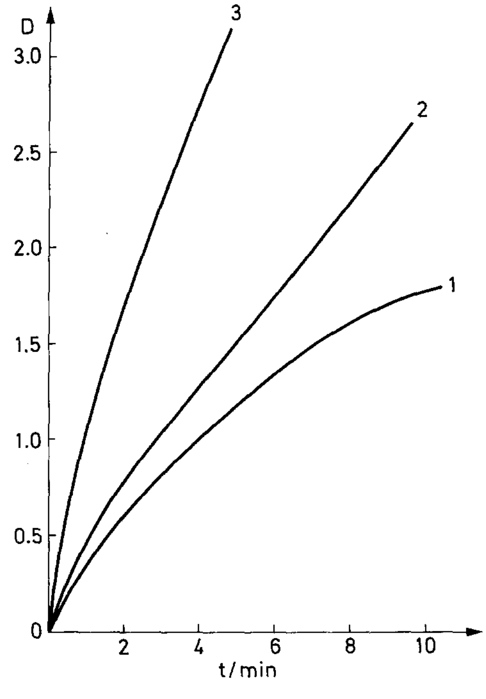
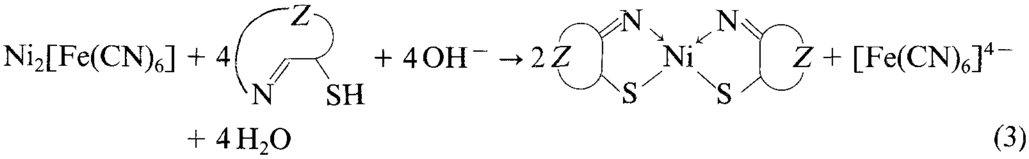
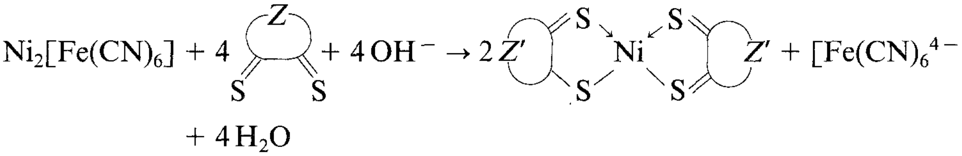


Fig. 4. Kinetic curves $D = f(C_F, C_L, t)$ for the system containing immobilized $Ni_2[Fe(CN)_6]$matrix −8-mercaptoquinoline; fixed Ni(II) hexacyanoferrate(II) concentration ($C_F = 2.0 \cdot 10^{-2}$ mol/m^{-2}) in the gelatin layer, variable complexing process time *t*, and ligand concentrations C_L in the solution $6.0 \cdot 10^{-3}$ mol/m^{-2} in the gelatin layer, variable complexing process time *t*, and ligand concentrations C_L in the solution $6.0 \cdot 10^{-3}$ mol/dm^{-3} (*1*), $1.2 \cdot 10^{-2}$ mol/dm^{-3} (*2*) and $3.0 \cdot 10^{-2}$ mol/dm^{-3} (*3*); optical densities measured through a blue filter

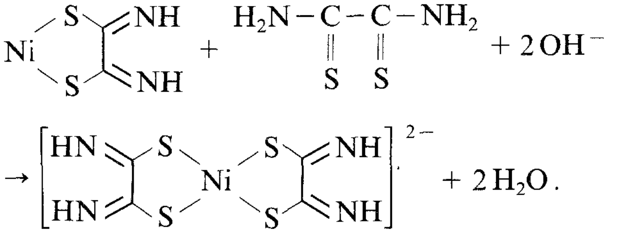
oxamide) insoluble chelates having a metal : ligand ratio of 1 : 2 with a singly deprotonated form of a ligand are formed. Such chelates do not decompose considerably even under the influence of excessive ligand concentrations in a solution directly contacting the thin layer. The colour of such chelates is usually from pink to violet at $\nu_{max.} = 18\,000$–$20\,000\,cm^{-1}$ ($\lambda_{max.} = 500$–550 nm). It should be noted that with *pH* changes these chelates do not change their optical characteristics. The formation process can be described by the general equations (3) and (4),


(3)

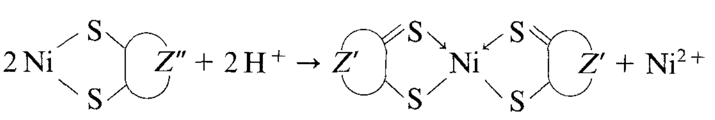

(4)

(Z' is a singly deprotonated group).

In a number of cases when a ligand is capable of forming a double-deprotonated form, another type of complexing is possible which can be found in systems containing $Ni_2[Fe(CN)_6]$-dithiooxamide and $Ni_2[Fe(CN)_6]$-quinoxaline-2,3-dithiol, where two types of insoluble chelates having a partially or completely deprotonated form of the ligand are obtained. For systems of the first type, at a highly excessive ligand concentration, the initially formed insoluble 1 : 1 complex can pass into the soluble one diffusing from the gelatin layer into the solution; the process is accompanied by the decrease in optical densities of the thin layer.


(5)

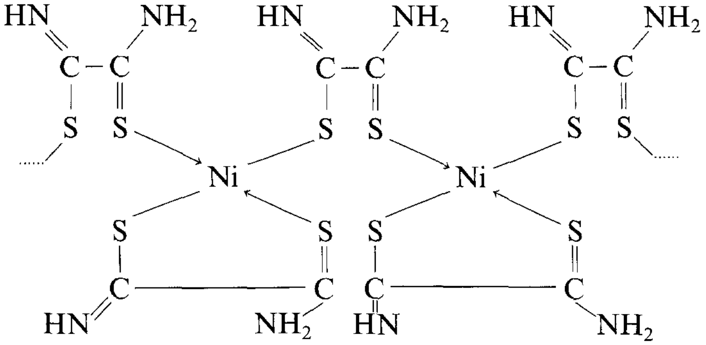
It is interesting to note that in case of such systems the transition from the chelate with a completely deprotonated form to that with a partially deprotonated ligand form is also observed; the above-mentioned transition can be realized simply by a *pH* decrease in the gelatin layer. The complexing process can be described by the general equation (6),


(6)

(Z'' is a double deprotonated group).

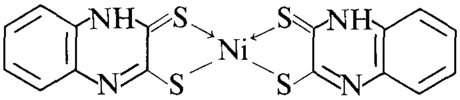
In case of the $Ni_2[Fe(CN)_6]$ – quinoxaline-2,3-dithiol system, the pink colour of the thin chelate-containing layer is changed to green, shifting the absorption maximum from $\nu_{max.} = 19\,200\,cm^{-1}$ ($\lambda_{max.} = 520\,nm$) to $\nu_{max.} = 15\,900\,cm^{-1}$ ($\lambda_{max.} = 635\,nm$) and the emergence of another band $\nu_{max.} = 14\,300\,cm^{-1}$ ($\lambda_{max.} = 700\,nm$) belonging to the 1 : 2 chelate [2]. Processing of the gelatin layer containing a cyan chelate results in the reduction of the pink colour. In the $Ni_2[Fe(CN)_6]$ – dithiooxamide system a similar change of colour is observed (from pink-violet into blue) which is accompanied by the bathochromic shift of the absorption maximum from $\nu_{max.} = 18\,000\,cm^{-1}$ ($\lambda_{max.} = 560\,nm$) to $\nu_{max.} =$

15 600 cm^{-1} ($\lambda_{max.}$ = 640 nm); however, compared to the previously mentioned system, the colour change here is found to be irreversible. The main cause of this difference lies in the structure of the "acid" chelates. In case of dithiooxamide the structure is polymeric (**III**)



III

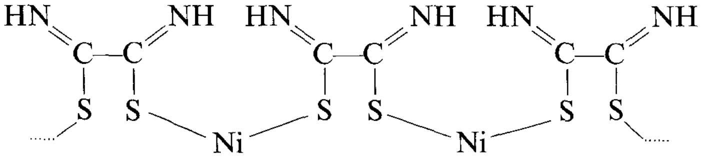
while in quinoxaline-2,3-dithiol it is monomeric (**IV**)



IV

since steric effects prevent polymer formation. Deprotonation in the "stiff" polymer structure **III** seems to be rather difficult and is not observed even at high *pH* values.

In the $Ni_2[Fe(CN)_6]$ – dithiooxamide system, at high hexacyanoferrate(II) and ligand concentrations, an insoluble 1 : 1 chelate complex **V** is also formed having a double deprotonated ligand form which is uncapable of proton addition; this is due to the characteristics of the coordination polymer **V**.



V

Summarizing the above considerations, it should be noted that testing of non-silver images containing metallorganic dyes obtained by complexing described in this paper, showed that alongside with silver removal and good storability of images, an increase in photographic sensitivity can also be obtained, which is of great practical importance. The process described here can also be used for mono- and polychromatic dyeing of silver images and, in particular, for the production of "blue slides" [4, 5].

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