

POLYMERS FOR ADVANCED TECHNOLOGIES

Processing, Characterization and Applications

Editors

Gennady E. Zaikov, DSc

Liliya I. Bazyljak, PhD

Jimsher N. Aneli, PhD



Apple Academic Press



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Edited by

**Gennady E. Zaikov DSc, Liliya I. Bazylyak, DSc
and Jimsher N. Aneli, DSc**



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List of Abbreviations

APCL	Anionic ring-opening polymerization of ϵ -caprolactam
CNF	Carbon nanofibers
CNT	Carbon nanotubes
Co/C NC	Cobalt/carbon nanocomposite
CHEC	Cold-hardened epoxy composition
Cu/C NC	Copper/carbon nanocomposite
DMF	N,N-dimethylformamid
DSC	Differential scanning calorimetry
DMSO	Dimethylsulfoxide
CL	ϵ -caprolactam
ED	Electron diffraction
EMD	Electron microdiffraction
EDR	Epoxy-diane resin
ER	Epoxy resin
EPS	Expanded polystyrene
FS	Fine suspensions
GHG	Greenhouse gas
HDPE/CaCO ₃	High density polyethylene/calcium carbonate
HSC	High-strength concrete
ILs	Ionic liquids
IROM	Inverse rule of mixture
LLDPE	Linear low density polyethylene
LDPE	Low density polyethylene
LLDPE/MMT	Low density polyethylene/Na ⁺ -montmorillonite
MMT	Montmorillonite
MBT	Mechanical-biological treatment
MSW	Municipal solid waste
NS	Nanostructures
Ni/C NC	Nickel/carbon nanocomposite
OPC	Ordinary Portland cement
PCA	Polycaproamide
PC	Polycarbonate
PDPP	Polydiphenylenephthalide
PE	Polyethylene
PEPA	Polyethylene polyamine
PCM	Polymeric composite materials
PP	Polypropylene
PVDF	Polyvinilidene fluoride
RH	Rice husk ash
ROM	Rule of mixture
SF	Silica fume

SEI	Spatial-energy exchange interactions
SEP	Spatial-energy parameter
TU	Technical condition
TGA	Thermo gravimetric analysis
TEM	Transmission electron microscopy
WTE	Waste-to-energy

Preface

This book is primarily designed for students of bachelor, diploma, and master courses of materials science, materials technology, plastic technology, mechanical engineering, process engineering, and chemical engineering. It can be used by students, teachers at universities, and colleges for supplementary studies in the disciplines of chemistry and industrial engineering. The polymer testing methods are essential to the development and application of biomedical or nanostructured materials.

This book is an outgrowth of an organized compilation of the notes the authors have used to teach advanced courses of polymers for many years.

The authors have long held the view that the lack of knowledge of the fundamental aspects of polymer materials is a serious shortcoming in undergraduate as well as graduate science and engineering education. This is especially important in our present society because the use of polymeric materials pervades our experience both in our daily lives and in our engineering profession. Still, the basic thrust of undergraduate and graduate education to some degree is in the areas of mechanical and civil engineering is toward traditional materials of metal, concrete, etc. Until about twenty-five years ago, undergraduate textbooks on materials had little coverage of polymers. Today, many materials texts have several chapters on polymers, but in general, the thrust of such courses is toward metals. Even the polymer coverage that exists now stresses the analysis of polymers using the same procedures as for metals and other materials and, therefore, often misleads the young engineer on the proper design of engineering plastics.

Thus, it is not surprising that some structural products made from polymers are often poorly designed and do not have the durability and reliability of structures designed with metallic materials.

With the publication of this book, we hope to not only serve the important task of training young scientists in physical and materials oriented disciplines but also to make a contribution to further the education of professional polymer testers, design engineers, and technologists.

— Gennady E. Zaikov, DSc

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1 Updates on Application of Silver Nanoparticles

*N. I. Naumkina, O. V. Mikhailov,
and T. Z. Lygina*

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1.1 INTRODUCTION

Small sized colloid elemental silver particles formed in gelatin layers during the development of silver halide photographic emulsions find a mention about more than 40 years ago [1]. In a number of studies, there are indications of the existence of a separate phase of the elemental silver consisting of nanoparticles and are received as a result of photochemical reduction of Ag(I) salts. It appeared lately in the literature [2-11]. It has been noted that [10, 11], during the development of gelatin layers of silver halide photographic emulsions by alkaline water solutions containing tin(II) dichloride and some inorganic or organic substance forming stable coordination compounds with Ag(I), the formation of elemental silver occurs too. However, the gelatin layer is either tinged brown or red but not black color due to the fact that it takes place at standard development by using hydroquinone developers. It is significant to note that with the increase of optical densities of the gelatin layer with elemental silver, red tone coloring of gelatin layer becomes more and more clearly expressed. The similar phenomenon takes place when instead of silver halide AgHal in gelatin matrix, there is such silver(I) compound as silver(I) hexacyanoferrate(II) $\text{Ag}_4[\text{Fe}(\text{CN})_6]$. Whether this totality of particles is a novel phase of elemental silver? Or is it only a variety of known phases of the given simple substance? These questions remain unanswered till now and deserve special consideration.

1.2 EXPERIMENTAL

As the initial material to obtain silver-containing gelatin-immobilized matrix implants (GIM), X-ray film Structurix D-10 (Agfa-Gevaert, Belges) was chosen. Samples of

the given film (which actually was nothing but AgHal-GIM) having format 20×30 cm² were exposed to X-ray radiation with an irradiation dose at range 0.05-0.50 Röntgen. These exposed samples were further subjected to processing according to the following technology [10, 11]:

- Development in D-19 standard developer as it was indicated in [10, 11], for 6 min at 20-25°C;
- Washing with running water for 2 min at 20-25°C;
- Fixing in 25% water solution of sodium trioxosulphidosulphate(VI) ($\text{Na}_2\text{S}_2\text{O}_3$) for 10 min at 20-25°C;
- Washing with running water for 15 min at 18-25°C.

First three stages of standard processing (development, washing, and fixing) were carried out at non-actinic green-yellow light, and final washing at natural light. The samples of GIM containing elemental silver (Ag-GIM) were processed according to the next following technology:

- (1) Oxidation in water solution containing (gl⁻¹)

Potassium hexacyanoferrate(III)	50.0
Potassium hexacyanoferrate(II)	20.0
Potassium hydroxide	10.0
Sodium trioxocarbonate(IV) (Na_2CO_3)	5.0
Water	up to 1000 ml

 for 6 min at 20-25°C;
- (2) Washing with running water for 2 min at 20-25°C;
- (3) Reduction in water solution containing (gl⁻¹)

Tin(II) chloride	50.0
Sodium N,N-ethylene diaminetetra acetate	35.0
Potassium hydroxide	50.0
Reagent formed water soluble complex with Ag(I)	1.0-100.0
Water	up to 1000 ml

 for 1 min at 20-25°C;
- (4) Washing with running water for 15 min at 18-25°C;
- (5) Drying for 2-3 h at 20-25°C.

As complex forming reagents that form water soluble complexes with Ag(I), ammonia NH_3 , potassium thiocyanate KSCN, sodium trioxosulphidosulphate(VI) $\text{Na}_2\text{S}_2\text{O}_3$, ethanediamine-1,2 $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$, 2-aminoethanol $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$, and 3-(2-hydroxyethyl)-3-azapentanediol-1,5 $\text{N}(\text{CH}_2-\text{CH}_2-\text{OH})_3$ were used. At the first stage of given processing of Ag-GIM obtained, conversion of Ag-GIM into $\text{Ag}_4[\text{Fe}(\text{CN})_6]$ -GIM occurred; in the second stage, reduction of $\text{Ag}_4[\text{Fe}(\text{CN})_6]$ -GIM with Sn(II) from elemental silver took place. And so, peculiar “re-precipitation” of elemental silver into gelatin matrix occurred incidentally.

An isolation substance from Ag-GIM was carried out by means of influence on them of water solutions of some proteolytic enzymes (for example, trypsin or *Bacillus mesentericus*) destroying the polymeric carrier of GIM (gelatin) and the subsequent separation of a solid phase from mother solution according to a technique described in

[16]. The substances isolated thus from GIM were further analyzed by X-ray diffraction method by using spectrometer D8 Advance (Bruker, Germany). A scanning was carried out in interval from 3 to $65^\circ \times 2\theta$, a step was $0.05 \times 2\theta$.

Calculation of intensities of reflexes (I) and inter-plane distances (d) was carried out with application of standard software package EVA. Theoretical XRD spectra (X-ray patterns) were calculated under Powder Cell program described in [17, 18]. Optical density Ag-GIM was measured by means of Macbeth TD504 photometer (Kodak, USA) in range 0.1 - 5.0 units with accuracy of $\pm 2\%$ (rel.).

1.3 RESULTS

Already at visual observation over a course of transformation process of $\text{Ag}_4[\text{Fe}(\text{CN})_6]$ -GIM to Ag-GIM, the following circumstance attracts its attention. The Ag-GIM received as a result of standard processing of exposed AgHal-GIM, at small optical density (D^{Ag}), has gray color, and at big D^{Ag} , black color. The colored Ag-GIM containing the “re-precipitated” elemental silver varies from black-brown to red, depending on the nature and quantity of complex forming reagent present in the solution.

It is significant, however, that absorption spectra of both initial and the “re-precipitated” elemental silver in visible area do not contain any accurately expressed maxima. Besides, as per rule, optical density Ag-GIM with the “re-precipitated” silver (D^{Ag}) at the same volume concentration of elemental silver (C_{Ag}^{v}) in GIM is essentially more than D^{Ag} values and also it depends on the nature and quantity of complex forming reagent in solution contacting with GIM. Examples of $D = f(D^{\text{Ag}})$ и $D = f(C_{\text{Ag}}^{\text{v}})$ dependence for inorganic and organic reagents are presented in Figures 1-6.

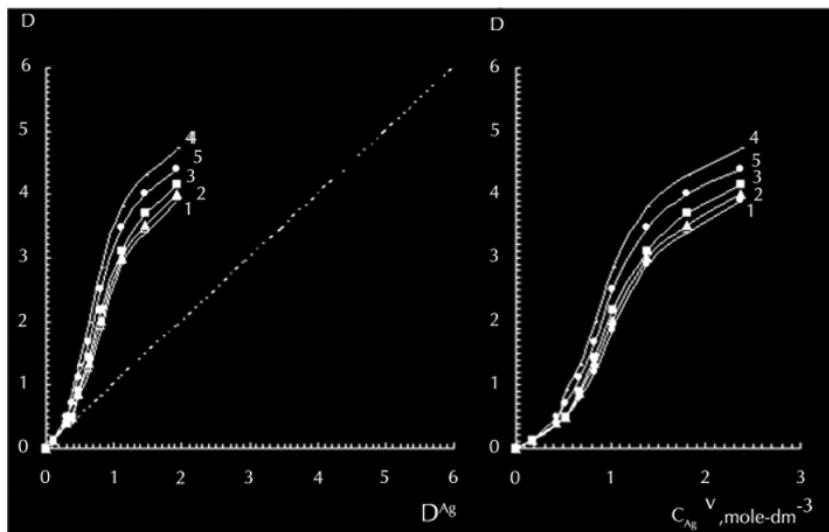


FIGURE 1 Dependence of $D = f(D^{\text{Ag}})$ and $D = f(C_{\text{Ag}}^{\text{v}})$ in reduction process of $\text{Ag}_4[\text{Fe}(\text{CN})_6] \rightarrow \text{Ag}$ using NH_3 at concentration 1.5 g l^{-1} (curve 1), 3.0 g l^{-1} (2), 4.5 g l^{-1} (3), 6.0 g l^{-1} (4), and 7.5 g l^{-1} (5). Optical densities D^{Ag} and D were measured with blue light-filter with a transmission maximum at 450 nm .

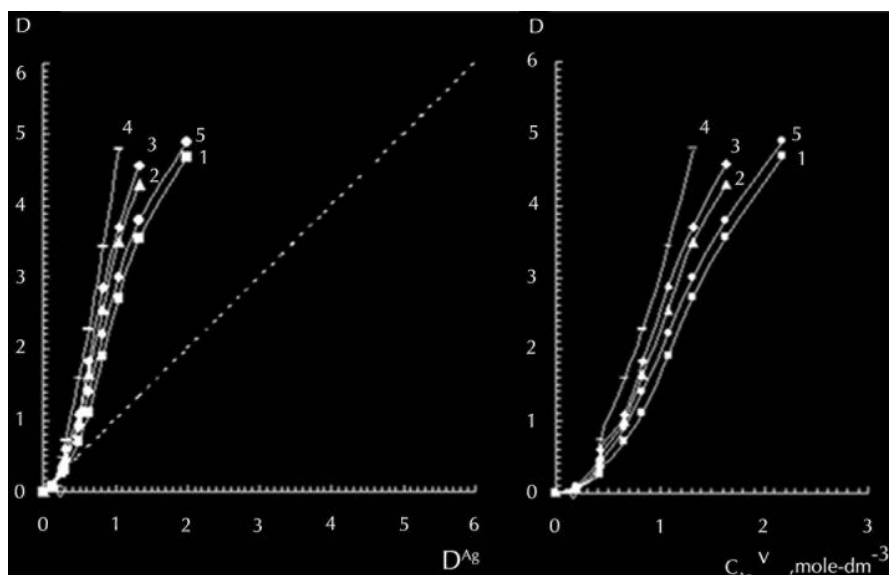


FIGURE 2 Dependence of $D = f(D^{Ag})$ and $D = f(C_{Ag}^v)$ in reduction process of $Ag_4[Fe(CN)_6] \rightarrow Ag$ using $Na_2S_2O_3$ at concentration 2.0 g l^{-1} (curve 1), 4.0 g l^{-1} (2), 8.0 g l^{-1} (3), 24.0 g l^{-1} (4), and 40.0 g l^{-1} (5). Optical densities D^{Ag} and D were measured with blue light-filter with a transmission maximum at 450 nm .

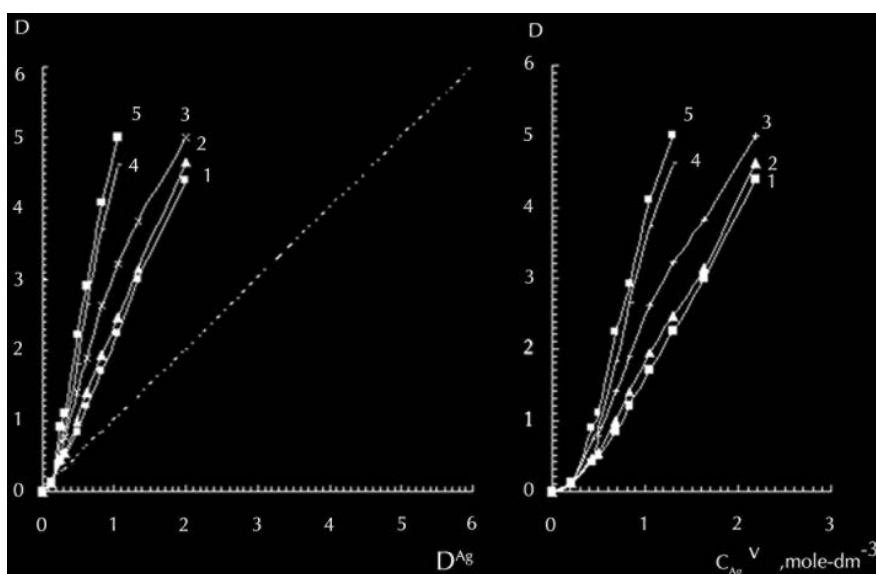


FIGURE 3 Dependence of $D = f(D^{Ag})$ and $D = f(C_{Ag}^v)$ in reduction process $Ag_4[Fe(CN)_6] \rightarrow Ag$ using $KSCN$ at concentration 2.0 g l^{-1} (curve 1), 4.0 g l^{-1} (2), 8.0 g l^{-1} (3), 24.0 g l^{-1} (4), and 60.0 g l^{-1} (5). Optical densities D^{Ag} and D were measured with blue light-filter with a transmission maximum at 450 nm .

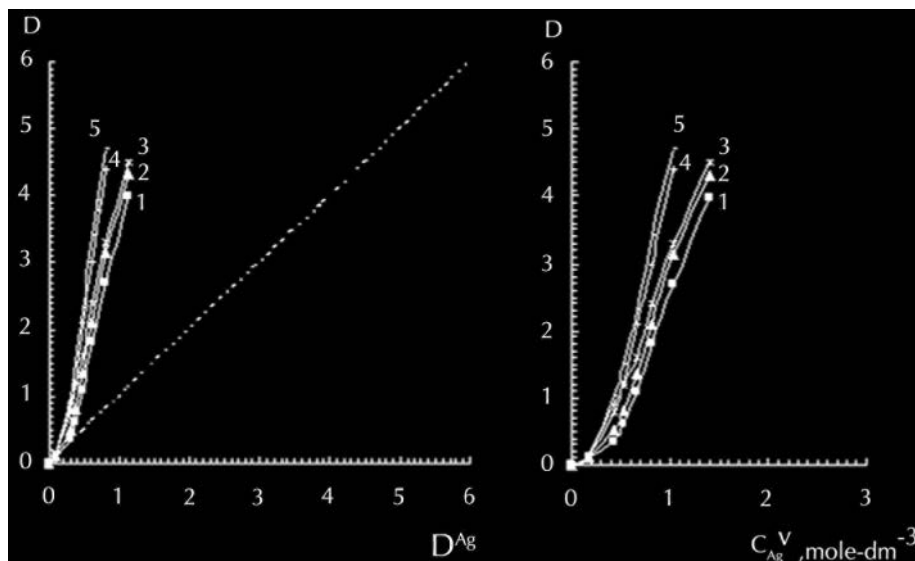


FIGURE 4 Dependence of $D = f(D^{Ag})$ and $D = f(C_{Ag}^v)$ in reduction process of $Ag_4[Fe(CN)_6] \rightarrow Ag$ using 2-aminoethanol $H_2N-(CH_2)_2-OH$ at concentration 7.5 gl^{-1} (curve 1), 15.0 gl^{-1} (2), 55.0 gl^{-1} (3), 110.0 gl^{-1} (4), and 150.0 gl^{-1} (5). Optical densities D^{Ag} and D were measured with blue light-filter with a transmission maximum at 450 nm .

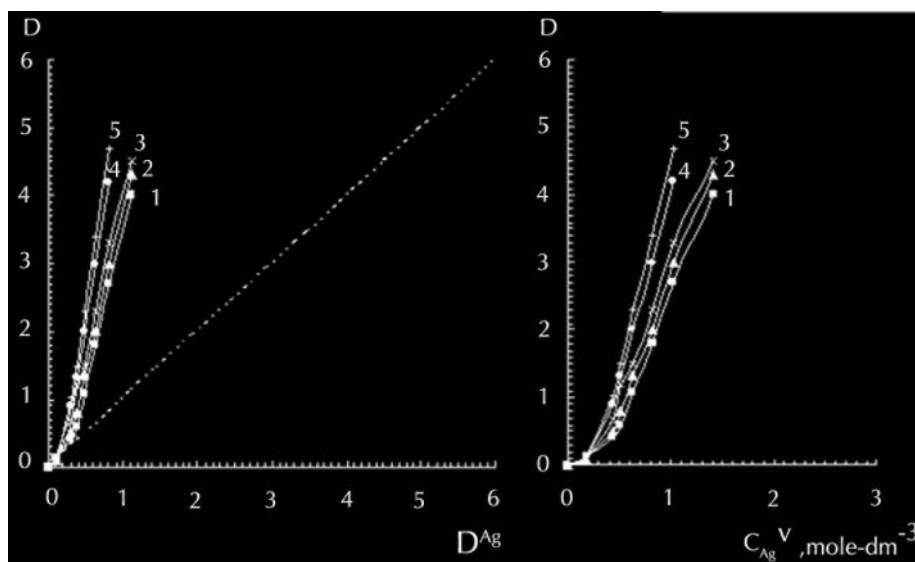


FIGURE 5 Dependence of $D = f(D^{Ag})$ and $D = f(C_{Ag}^v)$ in reduction process $Ag_4[Fe(CN)_6] \rightarrow Ag$ using ethanediamine-1,2 $H_2N-(CH_2)_2-NH_2$ at concentration 5.0 gl^{-1} (curve 1), 10.0 gl^{-1} (2), 20.0 gl^{-1} (3), 40.0 gl^{-1} (4), and 80.0 gl^{-1} (5). The optical densities D^{Ag} and D were measured with blue light-filter with a transmission maximum at 450 nm .

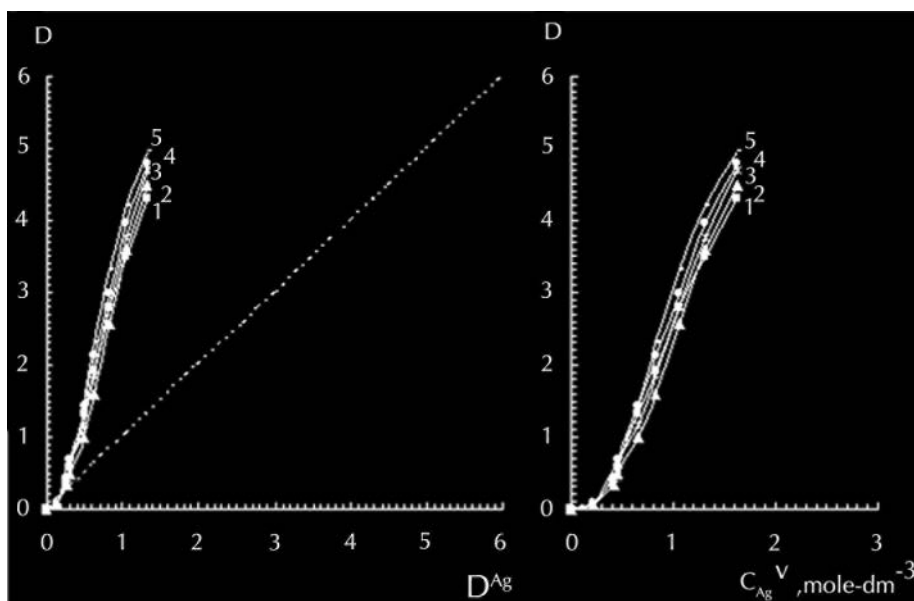


FIGURE 6 Dependence of $D = f(D^{Ag})$ and $D = f(C_{Ag}^V)$ in reduction process of $Ag_4[Fe(CN)_6] \rightarrow Ag$ using 3-(2-hydroxyethyl)-3-azapentanediol-1, 5 $N(CH_2-CH_2-NH_2)_3$ at concentration 10.0 gl^{-1} (curve 1), 20.0 gl^{-1} (2), 35.0 gl^{-1} (3), 50.0 gl^{-1} (4), and 100.0 gl^{-1} (5). The optical densities D^{Ag} and D were measured with blue light-filter with a transmission maximum at 450 nm .

The D/D^{Ag} value, as a rule, greater than 1.0, and in some cases, it reaches very high values (as in the case of potassium thiocyanate--nearly 5.0). Attention is drawn to the fact that the stronger the color of the gelatin layer with the "re-precipitated" elemental silver, different from the gray-black tones of the gelatinous layer and initially Ag-gelatin-immobilized matrix, the greater is the D/D^{Ag} value. The maximal degree of amplification $(D/D^{Ag})_{\max}$ is also very much dependent on the nature of the complex forming reagents (Table 1). The most profound effect on this parameter has etandiamin-1,2 [$(D/D^{Ag})_{\max} = 5.80$], the least severe ammonia, the degree of possibility is also quite high [$(D/D^{Ag})_{\max} = 3.40$]. For ammonia, the growth (D/D^{Ag}) value is typical with increasing concentration of NH_3 in reducing solution to a relatively smaller value ($\sim 0.30 \text{ mol}^{-1}$), after which the optical density D begins to fall (Figure 1). It is noteworthy that red-brown color of gelatin layer attained at the indicated concentration, with further increase in the concentration of ammonia, does not change. Analogous situation occurs in the case of the other two we studied inorganic complex forming reagent--trioxosulfidosulfate(VI) and the thiocyanate anion (Figures 2-3), with the only difference being that in the case of $S_2O_3^{2-}$, maximum degree of amplification is achieved with less high in comparison with NH_3 concentration (0.15 mol^{-1}), in the case of SCN^- --at a higher concentration ($\sim 0.70 \text{ mol}^{-1}$). In this regard, it was quite natural to try the difference marked with different stability of 1:2 complexes formed by Ag(I) with NH_3 , $S_2O_3^{2-}$ and SCN^- ($pK = 7.25, 13.32$, and 8.39 , respectively). However, in the presence of such correlation, the value of concentration indicated

for SCN^- should be lower than for NH_3 , which in fact, is not observed. In reality, for the three organic complex forming reagents studied, molar concentrations at which the maximum value of D/D^{Ag} is reached are significantly greater than those for inorganic complex forming reagents (Table 1). Stability of the complexes of silver(I) with each of these ligands is lower than with NH_3 , and the correlation function between these concentrations and the stability of coordination compounds of Ag(I) with given ligands in varying degrees, is still visible. But any explosion term relationship, the stability of the (D/D^{Ag}) values do not see: How it may be easily noticed while comparing the data of Table 1, the maximum degree of amplification decreases in the direction of ethanediamine-1,2 > 2-aminoethanol > SCN^- > $\text{S}_2\text{O}_3^{2-}$ > NH_3 > 3-(2-hydroxyethyl)-3-azapentane-diol-1,5, while the resistance formed by these ligands complexes with silver(I)--in the direction $\text{S}_2\text{O}_3^{2-}$ > SCN^- > ethanediamine-1,2 > NH_3 > 2-aminoethanol > 3-(2-hydroxyethyl)-3-azapentanediol-1,5. Thus, the complex is though important but not the sole determinant of the degree of influence of complex forming agents on the redox process considered.

At the first stage of the given process, reaction described by general Equation (1), takes place (in the braces {...}, formulas of gelatin-immobilized chemical compounds have been indicated):

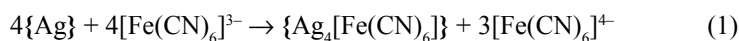


TABLE 1 The maximal (D/D^{Ag}) and $\text{p}K_s$ values of Ag(I) complexes for various complex forming reagents.

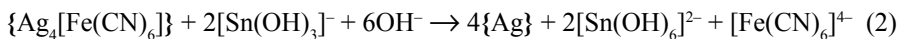
Complex forming reagent	$(D/D^{\text{Ag}})_{\text{max}}$	Concentration of complex forming reagent in solution at which reaches $(D/D^{\text{Ag}})_{\text{max}}$, g l^{-1} (mole l^{-1})	$\text{p}K_s$ of Ag(I) complex having 1:2 composition
NH_3	3.40	4.5 (0.27)	7.25
$\text{Na}_2\text{S}_2\text{O}_3$	4.13	23.7 (0.15)	13.32
KSCN	4.92	69.7 (0.70)	8.39
$\text{HO}-(\text{CH}_2)_2-\text{NH}_2$	5.40	109.8 (1.80)	6.62
$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2$	5.80	77.0 (1.28)	7.84
$\text{N}(\text{CH}_2-\text{CH}_2-\text{OH})_3$	3.93	99.8 (0.67)	3.64

Each of complex forming reagents under examination forms with Ag(I) soluble complex having a metal ion: ligand ratio of 1:2. That is why, formation of silver(I) complex with corresponding CR will occur to some extent when $\text{Ag}_4[\text{Fe}(\text{CN})_6]\text{-GIM}$ is at the contact with the solution containing any of complex forming reagent indicated. Gelatin-immobilized silver(I) hexacyanoferrate(II) as well as any of these soluble complexes can participate in the process of reduction with Sn(II) . In this connection, proceeding two parallel processes $\text{Ag(I)} \rightarrow \text{Ag(0)}$ will take place in contact of $\text{Ag}_4[\text{Fe}(\text{CN})_6]\text{-GIM}$ with solution indicated above, containing Sn(II) and complex forming reagent:

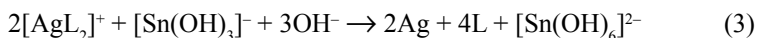
- Gelatin-immobilized silver(I) hexacyanoferrate(II) reduction proceeding in a polymer layer,

- Ag(I) complex with complex forming reagent reduction proceeding on interface of phases GIM/solution.

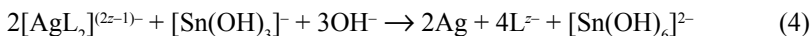
In water solutions at pH = 12-13, Sn(II) is mainly in a form of hydroxo complex $[\text{Sn}(\text{OH})_3]^-$. In this connection, general Equation (2) may be offered for the first of these processes:



For the second of these processes, general Equation (3)



In the case of non-charged ligands and general Equation (4)



In the case of negative charged “acid” ligands may be ascribed (L--symbol of ligand and z--its charge). The particles of elemental silver, formed as a result of Equations (3) and (4), theoretically should have smaller sizes than the particles of elemental silver arising in polymer layer of GIM. To be a part of substance immobilized in GIM, these particles should place freely in intermolecular cavities of gelatin layer. Only in this case, they may diffuse in GIM and may be immobilized in gelatin mass.

Gelatin has an extremely high surface area and an extensive system of micropores. The fragment of its structure has been shown in Figure 7; as may be seen, it contains many intermolecular cavities. It may be valued the average size of intermolecular cavity in the gelatin structure [12-15].

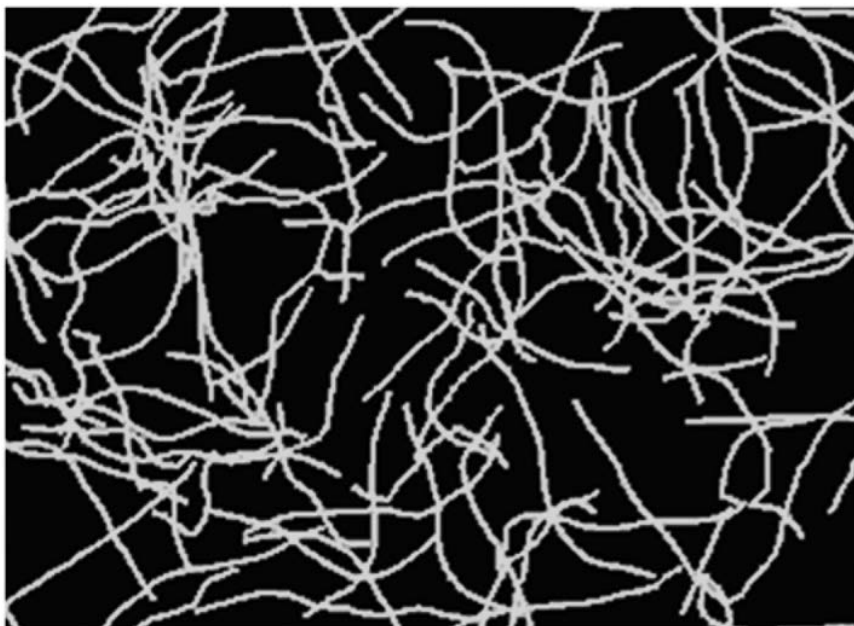


FIGURE 7 The fragment of gelatin structure containing intermolecular cavities.

For example, the volume of polymer layer of GIM (V_{gl}) having area 1 cm^2 and thickness $20 \text{ }\mu\text{m}$ is $(1.0 \times 1.0 \times 20 \times 10^{-4}) \text{ cm}^3 = 2.0 \times 10^{-3} \text{ cm}^3$, so that the mass of gelatin contained in such a layer, at average value of its density 0.5 g cm^{-3} , is $(0.5 \times 2.0 \times 10^{-3}) \text{ g} = 1.0 \times 10^{-3} \text{ g}$. Molecular mass of gelatin (M_{Gel}) is known to be $\sim(2.0\text{--}3.0)10^5 \text{ c.u.}$ [12, 13], the number of its molecules in given mass will be $(1.0 \times 10^{-3}/M_{Gel})(6.02 \times 10^{23}) = (2.0\text{--}3.0)10^{15}$. As it was already mentioned above, gelatin molecule in average has length $\sim 28,5000 \text{ pm}$ and diameter $\sim 1,400 \text{ pm}$, and if it is considered as narrow cylinder, total volume of gelatin molecules V_M will be equal to $(1/4)\pi D^2 h = (1/4) 3.14 (285,000 \times 10^{-10} \text{ cm})(1,400 \times 10^{-10} \text{ cm})^2 = 4.38 \cdot 10^{-19} \text{ cm}^3$. In the case of maximal compact arrangement, these molecules occupy total volume equal to $4.38 \times 10^{-19} \text{ cm}^3 \times (2.0\text{--}3.0)10^{15} = (8.76\text{--}13.15)10^{-4} \text{ cm}^3$. It may be postulated that the volume of cavities indicated, is equal to total volume of polymer massif minus the volume occupied by gelatin molecules, namely $(2.0 \times 10^{-3} - (8.76\text{--}13.15)10^{-4}) \text{ cm}^3$ that will be in the end $(0.69\text{--}1.12)10^{-3} \text{ cm}^3$. Then, the average volume of one intermolecular cavity may be found as a quotient from division of their total volume to number of gelatin molecules and, as it may be easily noted, will be $(3.4\text{--}5.6)10^{-19} \text{ cm}^3 = (3.4\text{--}5.6)10^{11} \text{ pm}^3$. The linear size of such an “average” cavity in the case when it has spherical form, will be equal to $d = (6V/\pi)^{1/3} = [6 \times (3.7\text{--}5.6)10^{11} \text{ pm}^3/3.14]^{1/3} = (89.1\text{--}102.2)10^2 \text{ pm}$; when it has cubic form, equal to $a = V^{1/3} = [(3.7\text{--}5.6)10^{11} \text{ pm}^3]^{1/3} = (71.8\text{--}82.4)10^2 \text{ pm}$. As one can see from these values, these cavities are nanosized. Therefore, only nanoparticles of substance can enter into these cavities. By entering into such cavities, nanoparticles of elemental silver are isolated from each other. In consequence of thereof, their aggregation with each other becomes rather difficult.

With the concentration growth of any of the complex forming reagent mentioned above, the concentration of coordination compounds formed given complex forming reagent with Ag(I) must increase. Correspondingly, the quantity of nanoparticles of the elemental silver formed as a result of reduction of these coordination compounds by $[\text{Sn}(\text{OH})_3]^-$ complex should also increase.. In this connection, it may be expected that when concentration of these complex forming reagent in solution increases, the share of nanoparticles contained in the “re-precipitated” elemental silver, should accrue gradually. Thus, at the same concentration nanoparticles of elemental silver owing to their higher dispersion degree in comparison with microparticles should provide higher degree of absorption of visible light (and, accordingly, higher optical density) in polymeric layer GIM. The experimental data presented in Figures 1-6, are in full conformity with the given prediction.

The particles of elemental silver formed as a result of Equations (3) and (4) are one or two nuclear. While it is not enough of them [it occurs, when concentration of Ag(I) complexes on interface of phases, these particles owing to their remoteness from each other have no time to be aggregated. They diffuse in polymeric layer of GIM, and are immobilized without change of their sizes. With the increase of complex forming reagent concentration [and, accordingly, of concentration of Ag(I) complex with given reagent], the quantity of nanoparticles indicates on interface of phases the GIM/solution accrues. It leads to increase of a number of such particles, diffused into GIM. However, at some rather high concentration complex forming reagent in solution, the

effect of aggregation of nanoparticles of elemental silver starts to affect. One and two nuclear particles of elemental silver formed at reduction of corresponding Ag(I) complex, to some extent begin to unite with each other in larger particles. Polynuclear particles of elemental silver resulting such an association are not so mobile and consequently, will not be diffused into polymeric layer of GIM. They will be precipitated in it near to interface GIM/solution (or even to escape as solid phase in the solution contacting with GIM). As a result, rates of an increment of number of one and two nuclear particles of elemental silver with further growth of concentration complex forming reagent begin to be slowed down. Thus, the moment should come inevitably there when the number of similar particles will reach some limiting value. That is why, since certain “threshold” concentration complex forming reagent in solution is there, growth of D^{Ag} values must stop. Moreover, at excess of this “threshold” concentration, certain decrease in D^{Ag} values should begin. The point is that an alignment between number of the aggregated particles and number one and two nuclears with growth of concentration of Ag(I) complex continuously grows and has no restrictions. These polynuclear particles are precipitated in Frontier zone GIM on small depth and form, as a matter of fact, the microparticles of elemental silver formed as a result of reduction of gelatin-immobilized $Ag_4[Fe(CN)_6]$ according to Equation (2). Since D^{Ag} values with increase of complex forming reagent concentration at first increase, they reach a maximum and then decrease.

It may be assumed that “re-precipitated” gelatin-immobilized silver should contain, as a minimum, two phases of the silver particles, one of which is formed by nanoparticles, and another, by microparticles. In order to corroborate the given conclusion, we carried out the analysis of elemental silver isolated from initial Ag-GIM after the end of “re-precipitation” process by X-ray powder diffraction method. X-ray powder diffraction patterns (XRD-patterns) of samples obtained are presented in Figures 8-10. As may be seen from them, XRD-pattern of initial elemental silver with gray-black color of gelatin layer (Figure 8) and XRD-patterns of “re-precipitated” elemental silver (Figures 9-10), rather essentially differ from each other. So, in XRD-patterns of “re-precipitated” elemental silver obtained at an availability of any of studied CR in solution contacting with GIM, there are accurate reflexes having $d = 333.6, 288.5, 166.7,$ and 129.1 pm that are absent in XRD-pattern of initial elemental silver. At the same time, reflexes with $d = 235.7, 204.1, 144.4, 123.1,$ and 117.9 pm are observed on them. These reflexes are characteristics for the known phase of elemental silver isolated from initial Ag-GIM. In this connection, there are all reasons to believe that the “re-precipitated” elemental silver obtained on using solution containing any of complex forming reagent indicated above, contains at least two structural modifications of elemental silver.

The next curious circumstance attracts its attention: reflexes with $d = 333.6, 288.5, 204.2, 166.7,$ and 129.1 pm are rather close to d values of reflexes of silver(I) bromide AgBr (number of card PDF 06-0438, parameter of an elementary cell $a_0 = 577.45$ pm, face-centered lattice, cubic syngonia, $Fm\bar{3}m$ group of symmetry according to the international classification [14, 15]). In this connection, it may be assumed that the structure of the novel phase contained in “re-precipitated” elemental silver, at least in outline, resembles structure AgBr and its crystal lattice is similar to a lattice of silver(I) bromide where positions of atoms Br occupy atoms of silver.

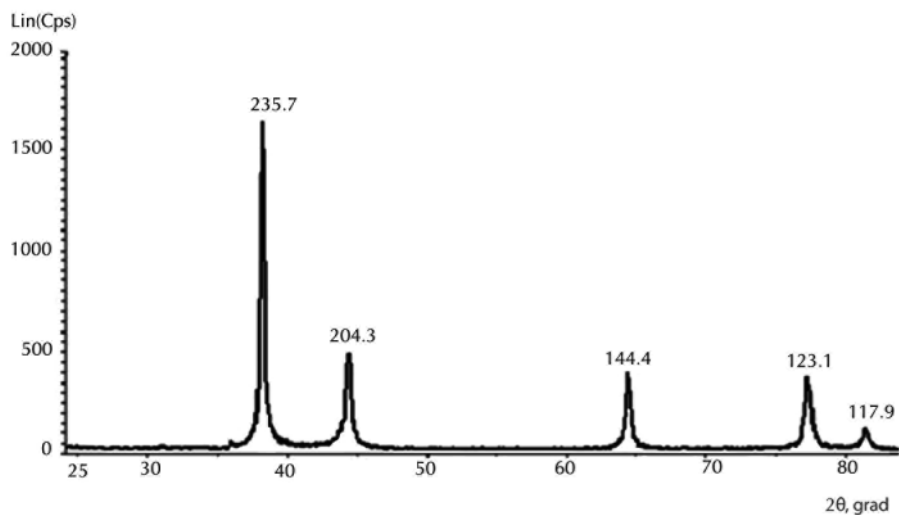


FIGURE 8 The XRD-pattern of elemental silver isolated from initial Ag-GIM.

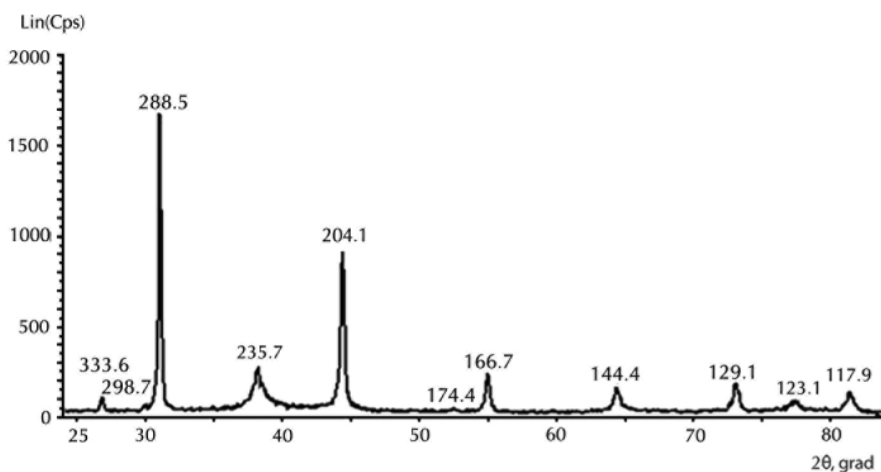


FIGURE 9 The XRD-pattern of substance isolated from Ag-GIM containing “re-precipitated” elemental silver and obtained with using of solution containing $\text{Na}_2\text{S}_2\text{O}_3$ in concentration 20.0 g/l.

To answer the question whether the reflexes indicated can belong to elemental silver with such a space structure in principle, theoretical XRD-patterns of assumed structure of elemental silver with the use of program powder cell described in work [18] have been constructed by us. These XRD-patterns are presented in Figure 11. As may be seen from them, the theoretical d values, calculated by us (333.6, 288.7, 204.2, 174.1, 166.7, 144.4, 132.5, 129.1, and 117.9 pm) for specified above structure with an elementary cell parameter $a = 288.72$ pm and $Pm3m$ symmetry group, practically