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Complexing of Cu(II) with *N*,*N*'-Diphenylthiooxamide and *N*,*N*'-Diphenyldithiooxamide in a Gelatin-Immobilized $Cu_2[Fe(CN)_6]$ Matrix

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Abstract—A study was made of complexing in Cu(II)–*N*,*N*'-diphenylthiooxamide and Cu(II)–*N*,*N*'-diphenyldithiooxamide systems in gelatin-immobilized $Cu_2[Fe(CN)_6]$ matrices brought into contact with aqueous alkaline (pH 12.0 ± 0.1) solutions of these ligands. In both cases, complexing is preceded by alkaline breakdown of copper(II) hexacyanoferrate(II) into Cu(II) hydroxide or oxohydroxide which is the species reacting with the ligands. In each system, complexing yields a $Cu(HL)_2$ chelate (HL^- is the single-deprotonated form of *N*,*N*'-diphenylthiooxamide or *N*,*N*'-diphenyldithiooxamide).

In our previous works [1–3] we characterized complexing in Cu(II)–dithiooxamide $[H_2NC(=S)\cdot C(=S)NH_2]$ system in gelatin-immobilized copper(II) hexacyanoferrate(II) matrices. We showed that the coordination compounds formed under these conditions differ from those formed in a solution and in a solid phase. This makes it of interest to elucidate whether this holds also for such analogs of dithiooxamide as *N*,*N*'-diphenyldithiooxamide $[PhHNC(=S)\cdot C(=S)NHPh]$ and *N*,*N*'-diphenylthiooxamide $[PhNHC(=O)C(=S)NHPh]$. Another reason stems from the fact that comparison of the complexing in Ni(II)–dithiooxamide, Ni(II)–*N*,*N*'-diphenylthiooxamide, and Ni(II)–*N*,*N*'-diphenyldithiooxamide systems in solutions or solid phase, on the one hand, and in gelatin-immobilized Ni(II) hexacyanoferrate(II) matrix materials, on the other, reveals a very clear difference for the first two systems and no difference for the third system [4–7]. It should also be noted that, similar to dithiooxamide, *N*,*N*'-diphenylthiooxamide and *N*,*N*'-diphenyldithiooxamide can, in principle, act as one of ligand precursors in template synthesis [8].

At very low ligand concentrations in solution, $c_L^0 < 10^{-5}$ M {whatever the $Cu_2[Fe(CN)_6]$ concentration in the matrix c_F}, in both the Cu(II)–*N*,*N*'-diphenylthiooxamide and Cu(II)–*N*,*N*'-diphenyldithiooxamide systems the optical density D of the matrix permanently decreases with increasing contact time τ with the solution throughout the interval studied (1–10 min). In this process, the gelatin layer of the immobilized matrix changes its color from red-brown to grayish-blue. In our previous works we reported on this phenomenon for a number of systems involving Cu(II) and ligands with donor centers of different nature, in particular, Cu(II)–8-mercaptoquinoline [9], Cu(II)–2,7-dimethyl-8-mercaptoquinoline [10], and Cu(II)–3-benzoyl-1-methyl-1-phenylthiourea [11]. In those works, we ascribed this phenomenon to alkaline breakdown of gelatin-immobilized copper(II) hexacyanoferrate(II) into polymeric copper(II) hydroxide. In this work, we carried out mathematical analysis of the kinetic curves $D = f(c_F, c_L^0, \tau)$ in the coordinate profiles [c_F = const, varied c_L^0, variable τ] and [c_L^0 = const, varied τ, variable c_F] for the (c_F, c_L^0, τ) range within which $(dD/d\tau) < 0$ holds throughout the τ range studied by us, namely, 1–10 min. The analysis showed that, under the actual conditions, none of the ligands is involved in complexing. When the polymeric binder of the gelatin-immobilized matrix systems formed under such conditions is degraded by any proteolytic enzyme, a grayish-blue substance is isolated which, according to chemical analysis, is a polymeric copper(II) hydroxide. For the Cu(II)–*N*,*N*'-diphenyldithiooxamide system, the chemical analysis data are as follows: found, %: H 2.2; Cu 65.0; O 32.8; and for the Cu(II)–*N*,*N*'-diphenylthiooxamide system: found, %: H 2.1; Cu 64.8; O 33.1; H_2CuO_2; calculated, %: H 2.07; Cu 65.13; O 32.80. The abovesaid suggests that complexing in both systems is preceded by breakdown of immobilized $Cu_2[Fe(CN)_6]$ by the hydroxide anions contained in the alkaline solution:

$$nCu_2[Fe(CN)_6] + 4nOH^- \longrightarrow 2\ [Cu(OH)_2]_n + n[Fe(CN)_6]^{4-}. \qquad (1)$$

At higher ligand concentrations in solution, namely,

c_L within 1.0×10^{-3}–1.0×10^{-2} M, both Cu(II)–*N,N'*-diphenyldithiooxamide and Cu(II)–*N,N'*-diphenylthiooxamide systems are characterized by the $D = f(c_F, c_L^0, \tau)$ dependences in the coordinate profile [c_F = const, varied c_L^0, variable τ] passing through minima. With decreasing copper(II) hexacyanoferrate(II) concentration c_F and increasing ligand concentration in the solution contacting the matrix, c_L^0, these minima gradually shift toward smaller τ and disappear at $c_L^0 \geq 1.0 \times 10^{-2}$ M. At $\tau > 4$ min, both systems form in the gelatin body compounds imparting a greenish-brown (*N,N'*-diphenyldithiooxamide) or yellow-brown (*N,N'*-diphenylthiooxamide) color to this body. The typical $D = f(c_F, c_L^0, \tau)$ dependences shown in Figs. 1 and 2 support the above-said. The spectral characteristics of the gelatin bodies formed at $c_L^0 \geq 1.0 \times 10^{-2}$ M correspond in both cases to those reported in [12] for the complexes formed by copper(II) with *N,N'*-diphenyldithiooxamide and *N,N'*-diphenylthiooxamide at the 1:2 ratio of the copper(II) ion to the single-deprotonated ligand. We carried out mathematical analysis of the $D = f(c_F, c_L^0, \tau)$ kinetic curves using both the above-mentioned coordinate profiles for the (c_F, c_L^0, τ) range corresponding to formation of the compound imparting the greenish-brown or yellow-brown color to the gelatin layer. This analysis clearly demonstrated that, during contact of the immobilized matrix with the ligand solution, two ligand molecules add per $Cu(OH)_2$ formula unit. This unambiguously proves complexing of Cu(II) with *N,N'*-diphenyldithiooxamide and *N,N'*-diphenylthiooxamide under the examined conditions. Also, upon degradation of the gelatin bodies containing the complex formed, we isolated, in the case of the Cu(II)–*N,N'*-diphenyldithiooxamide system, a greenish-brown substance of the composition $C_{28}H_{22}CuN_4S_4$ (found, %: C 55.9; H 3.4; Cu 10.7; N 9.4; S 21.0; calculated, %: C 55.45; H 3.63; Cu 10.56; N 9.24; S 21.12). In the case of the Cu(II)–*N,N'*-diphenylthiooxamide system, we isolated a yellow-brown substance of the composition $C_{28}H_{22}CuN_4O_2S_2$ (found, %: C 58.3; H 3.7; Cu 11.5; N 9.9; S 11.0; calculated, %: C 58.59; H 3.83; Cu 11.13; N 9.75; S 11.17). In both cases, the composition of the resulting substances corresponds to the formula $Cu(HL)_2$, where H_2L is the ligand molecule. Both $Cu(HL)_2$ compounds isolated from the gelatin-immobilized matrix systems are paramagnetic (μ_{eff} = 1.95 and 1.91 μ_B, respectively), and their ESR spectra are characterized by g factors typical for planar four-coordinate Cu(II) chelate complexes ($g_\perp = 2.09$, $g_\| = 2.24$ for the chelate with *N,N'*-diphenyldithiooxamide and $g_\perp = 2.11$ and $g_\| = 2.25$, with *N,N'*-diphenylthiooxamide). These data suggest that the chelates formed by Cu(II) and the *N,N'*-substituted (di)thiooxamides are monomers with approximately planar rhombic coordination of the donor centers with respect to the central ion. Identification of particular donor centers involved in the coordination (both ligands studied are ambivalent) requires special consideration.

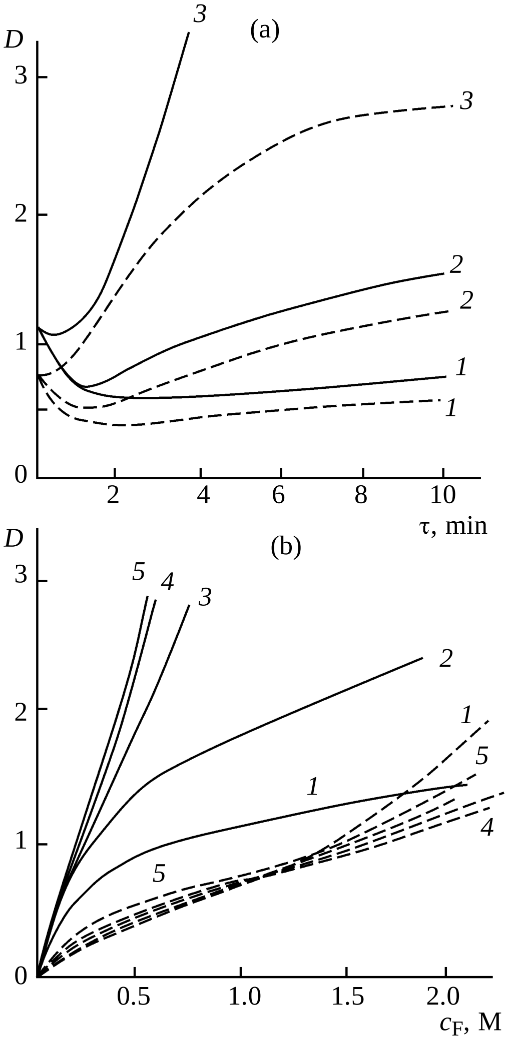
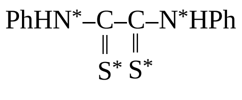
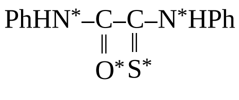


Fig. 1. Optical density of the gelatin-immobilized copper(II) hexacyanoferrate(II) matrices at λ = 450 nm as a function of (a) time of their contact with the *N,N'*-diphenyldithiooxamide solution τ [c_F: (dashed line) 0.55 and (solid line) 1.20 M; c_L^0: (*1*) 10^{-3}, (*2*) 4.0×10^{-3}, and (*3*) 2.0×10^{-2} M] and (b) $Cu_2[Fe(CN)_6]$ concentration in the matrix [c_L^0: (dashed line) 4.0×10^{-3} and (solid line) 2×10^{-2} M; τ: (*1*) 1, (*2*) 2, (*3*) 4, (*4*) 6, and (*5*) 10 min].

Both *N,N'*-diphenyldithiooxamide and *N,N'*-diphenylthiooxamide have four potential donor centers (marked with an asterisk).


$\mathrm{PhHN^*{-}\underset{\underset{S^*}{\|}}{C}{-}\underset{\underset{S^*}{\|}}{C}{-}N^*HPh}$


$\mathrm{PhHN^*{-}\underset{\underset{O^*}{\|}}{C}{-}\underset{\underset{S^*}{\|}}{C}{-}N^*HPh}$

However, three coordination modes (**I**–**III**) are

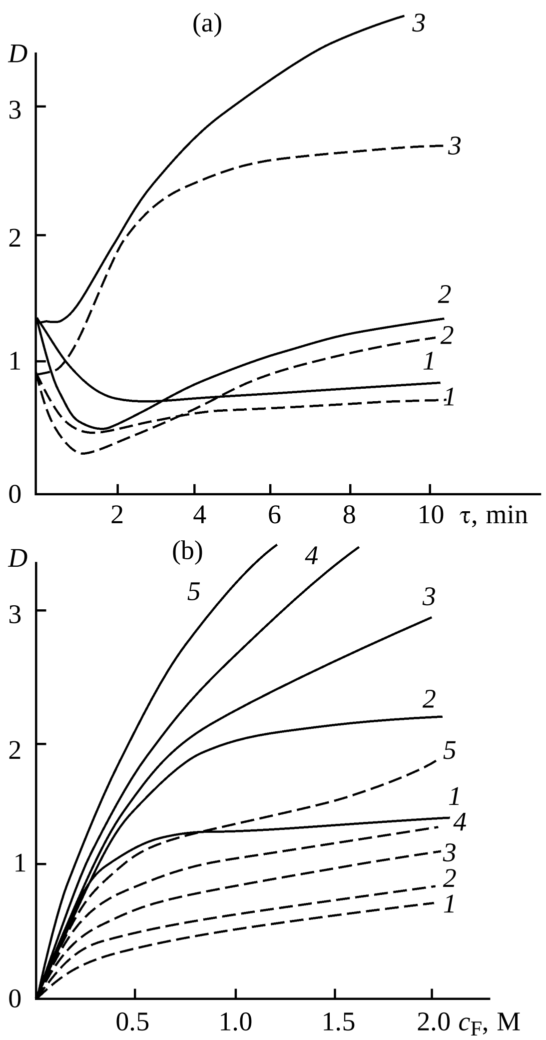
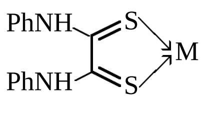
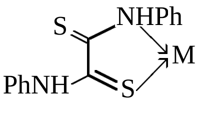


Fig. 2. Optical density of gelatin-immobilized copper(II) hexacyanoferrate(II) matrices at λ = 450 nm as a function of (a) the time of their contact with the *N*,*N*'-diphenylthiooxamide solution τ [c_F: (dashed line) 0.75 and (solid line) 1.20 M; c_L^0: (*1*) 8.0×10^{-4}, (*2*) 3.0×10^{-3}, and (*3*) 1.2×10^{-2} M] and (b) $Cu[Fe(CN)_6]$ concentration in the matrix [c_L^0: (dashed line) 3.0×10^{-3} and (solid line) 1.2×10^{-2} M; τ: (*1*) 1, (*2*) 2, (*3*) 4, (*4*) 6, and (*5*) 10 min].

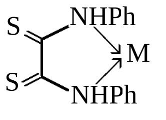
possible for the first ligand, and four modes (**IV**–**VII**), for the second ligand (the schemes are presented below for the neutral H_2L species).



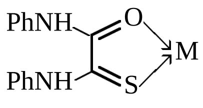
I



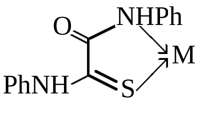
II



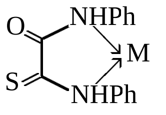
III



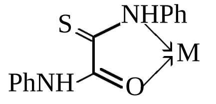
IV



V

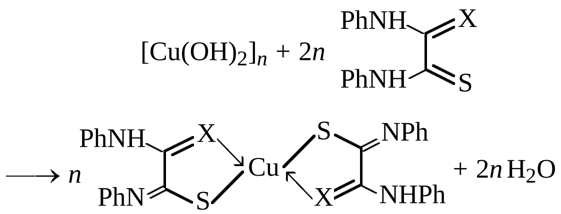


VI



VII

The IR spectra of both copper(II) chelates contain a pronounced ν(N–H) band at 3430 and 3420 cm^{-1}, respectively, which is typical for the spectra of coordination compounds whose nitrogen atoms are not coordinated to the metal ion (in the spectra of *N*,*N*'-diphenyldithiooxamide and *N*,*N*'-diphenylthiooxamide this band is observed at 3440 and 3420 cm^{-1}, respectively). Thus, in both cases the nitrogen atoms bonded to the hydrogen atoms are not chemically bonded to the central ion. This is not surprising, since each nitrogen atom in the molecules of both *N*,*N*'-diphenyldithiooxamide and *N*,*N*'-diphenylthiooxamide is surrounded by bulky phenyl groups which, on the one hand, preclude coordination of these atoms to the metal ions and, on the other, withdraw a part of the electron density from the nitrogen atom, thus decreasing its donor power. This suggests that these nitrogen atoms will not participate in coordination with Cu(II). The spectrum of the chelate formed by Cu(II) and *N*,*N*'-diphenyldithiooxamide contains the following absorption bands: ν(C=N) at 1670 cm^{-1}, ν(S=C–N) at 1500 cm^{-1}, and ν(C–S) at 960 cm^{-1}. Similar bands are observed in the spectrum of the chelate formed by Cu(II) and *N*,*N*'-diphenylthiooxamide at 1660, 1505, and 960 cm^{-1}, respectively. At the same time, the spectra of both ligands lack the ν(C–S) band. These features of the spectra of the ligands and complexes suggest that, in the case of *N*,*N*'-diphenyldithiooxamide and *N*,*N*'-diphenylthiooxamide, some of the C=S bonds become single, with formation of a bond between the sulfur and metal atoms. This suggests that sulfur atoms act as donor centers in the case of *N*,*N*'-diphenyldithiooxamide, and sulfur and oxygen atoms, in the case of *N*,*N*'-diphenylthiooxamide, Then, complexing between Cu(II) and these ligands can be described as Eq. (2).

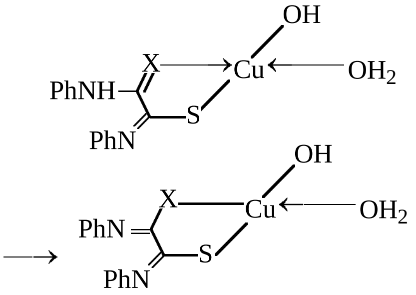


(2)

It should be noted that *N*,*N*'-diphenylthiooxamide is coordinated with Cu(II) by scheme **IV** via a “hard” oxygen atom and a “soft” sulfur atom rather than by scheme **V** via a “softer” nitrogen atom and a “soft” sulfur atom {the latter mode might seem preferential for such a relatively “soft” (according to Pearson) acid as Cu(II) [13]}. As mentioned above, this is probably due to a fairly pronounced π-accepting power of the phenyl radical weakening the donor power of the nitrogen atom.

The above-said suggests that both systems, Cu(II)–*N,N'*-diphenyldithiooxamide and Cu(II)–*N,N'*-diphenylthiooxamide, participate in only one complexing process yielding only one complex species $Cu(HL)_2$. The same processes occur in these systems in solution and solid phase; thus, complexing in the gelatin-immobilized $Cu_2[Fe(CN)_6]$ matrices studied in this work yields the same products as complexing under the “conventional” conditions. This substantially distinguishes both systems studied in this work from Cu(II)–dithiooxamide system which, according to our previous data [1–3], forms in gelatin-immobilized copper(II) hexacyanoferrate(II) matrix at least three complex species of the compositions $[CuL(H_2O)_2]_n$, $[Cu(HL)_2]_n$, and $[Cu(HL)_2(HL)]^-$, and in solution and solid phase, $[Cu(HL)_2]_n$ only (H_2L is ligand) [12].

These distinctions can be explained as follows. Both crystalline and gelatin-immobilized polymeric copper(II) hydroxides $[Cu(OH)_2]_n$ (whose formation, as mentioned above, is preceded by complexing proper in gelatin-immobilized $Cu_2[Fe(CN)_6]$ matrix in the systems studied) always contain certain amount of Cu(II) ions whose OH^- coordination is defective and has one or two vacant positions. The resulting square-pyramidal (C_{4v}) or square-planar (D_{4h}) coordination of OH^- with respect to Cu(II) is, according to the Langford–Gray concept, the most favorable for their substitution by ligand donor centers. Though capable, in principle, of forming two species with different degrees of deprotonation, both organic compounds studied in this work are very weak proton donors ($pK_{a1} > 10$). This means that, at the actual concentrations and acidity of the medium ($pH \approx 12$), only molecular HL_2 and single-deprotonated HL^- forms (with the latter prevailing) occur in appreciable amounts in aqueous solutions. This makes the most probable participation of specifically HL^- species in formation of Cu(II) chelates. Complexing in solution yields a 1 : 2 chelate with the HL^- form of the corresponding ligand (both are bidentate, as follows from the above-said) as the final complexing product. By contrast, in a gelatin-immobilized matrix contacting an alkaline solution of the ligand, the reaction volume of the matrix is characterized by a very high concentration of the hydroxide anions, which allows them to substitute one ligand molecule in the 1 : 2 chelate. By applying the concepts discussed in [14] to this specific case (like in our previous work [15]), we can conclude that, initially, a complex between Cu(II) and one water molecule, OH^- ion, and single-deprotonated ligand species HL^- is formed, and then a proton from the nitrogen atom of the amine group is transferred to form an uncharged chelate of the composition $[CuL(H_2O)_2]$ by the general scheme (3).



(3)

As known [13], in heteroligand complexes with σ-donor and π-acceptor ligands, strengthening of the π-acceptor power of any of these ligands is accompanied by strengthening of the acid power of σ-donor inner-sphere molecules. Two phenyl groups in the *N,N'*-diphenylthiooxamide and *N,N'*-diphenyldithiooxamide molecules make them stronger π-acceptors compared to dithiooxamide. Thus, it can be expected that the complexes of the $CuL(H_2O)(OH)]^-$ type formed by these ligands will be much weaker proton acceptors than the analogous dithiooxamide-containing complex. Furthermore, the Cu(II)–ligand bonds in both ligands studied in this work are characterized, along with an efficient σ-donor interaction, also by a substantial π-dative charge transfer from the metal ion to the ligand. By contrast, in the case of dithiooxamide, the contribution from this charge transfer to formation of the Cu(II)–ligand bond is much smaller. This suggests that polarization of the Cu(II)–donor atom bonds in the chelate complexes of Cu(II) with *N,N'*-diphenylthiooxamide and *N,N'*-diphenyldithiooxamide of the composition $Cu(HL)_2$ is much weaker than in the analogous complex with dithiooxamide. Therefore, substitution of each of these two ligands by the OH^- ion is less probable than in the case of dithiooxamide. Thus, it is not improbable that, in the Cu(II)–ligand systems studied in this work, proton addition to $[CuL(H_2O)(OH)]^-$ complexes will not to form $[CuL(H_2O)_2]$ chelates occur to an appreciable extent. As to complexes with more than two HL^- ions per Cu(II) ion, their formation by the ligands studied must be much less probable than in the case of dithiooxamide because of much greater steric hindrance (as suggested by the Stuart–Briggleb modeling). The equilibrium constant of transformation of the 1 : 2 to the 1 : 3 chelate, similar to that in the Cu(II)–dithiooxamide system, is very small. Therefore, accumulation of such complexes in appreciable amounts in each of the systems studied requires very high concentrations of the ligands in the solution contacting the matrix. This is, however, prevented by their very poor solubility. Thus, it should be expected that, most probably, in the case of the Cu(II)–*N*,*N'*-diphenyldithiooxamide and Cu(II)–*N*,*N'*-diphenylthiooxamide systems, complexing in gelatin-immobilized copper(II) hexacyanoferrate(II) matrix, like that in solution, will not yield the compounds detected in the Cu(II)–dithiooxamide system. This is actually the case.

Special experiments on complexing in the Cu(II)–*N*,*N'*-diphenyldithiooxamide and Cu(II)–*N*,*N'*-diphenylthiooxamide systems immobilized in various kinds of gelatin showed that the nature of the processes occurring in these systems is unaffected by the kind of gelatin. This suggests that, similar to the previously studied Cu(II)–(N,O,S)-donor ligand systems, in the actual case gelatin does not act as ligand in complexing.

EXPERIMENTAL

The gelatin-immobilized copper(II) hexacyanoferrate(II) matrices were synthesized by the procedure from [9]. The inorganic compounds for preparing such immobilized systems {copper(II) sulfate pentahydrate $CuSO_4 \cdot 5H_2O$, potassium hexacyanoferrate(III) $K_3[Fe(CN)_6]$, potassium oxalate $K_2C_2O_4$, potassium carbonate(IV) K_2CO_3, and sodium thiosulfate pentahydrate $Na_2S_2O_3 \cdot 5H_2O$} were of analytically or chemically pure grade. The resulting gelatin-immobilized copper(II) hexacyanoferrate(II) matrices were further treated at 20°C with *N*,*N'*-diphenyldithiooxamide and *N*,*N'*-diphenylthiooxamide solutions with the concentrations of 1.0×10^{-3}–5.0×10^{-2} M and pH 12.0 ± 0.1. The solutions of both organic compounds were prepared from the commercial analytically pure grade chemicals which were additionally tested by measuring the IR spectra and melting points. The contact time of the matrix with the ligand solution τ was varied within 1–10 min. Upon completion of complexing (actually, of the matrix3solution contact), the gelatin layers incorporating the copper(II) complexes formed were washed in running water for 15 min at 18–20°C and dried for 2–3 h at room temperature.

To describe the complexing in the systems studied, we plotted the $D = f(c_F, c_L^0, \tau)$ dependences. Here, D is the optical density of the gelatin-immobilized metal chelate matrix corresponding to the preset copper(II) hexacyanoferrate(II) concentration in the immobilized matrix c_F (M), ligand concentration in the solution contacting the matrix c_L^0 (M), and complexing time τ (min). These curves were further processed by the technique from [12] using the coordinate profiles [c_F = const, varied c_L^0, variable τ] and [c_L^0 = const, varied τ, variable c_F]. Figures 1 and 2 present such curves for the Cu(II)–*N*,*N'*-diphenyldithiooxamide and Cu(II)–*N*,*N'*-diphenylthiooxamide systems.

The immobilized chemical compounds were isolated from the corresponding gelatin matrices by the procedure from [16]. The optical densities of the gelatin-immobilized metal chelate matrices were measured on a Macbeth TD-5J04 photometer in the D = 0.1–5.0 range accurately to within 2% using a blue light filter (transmission maximum at λ = 450 nm). The electronic spectra of the gelatin-immobilized matrices were recorded on a Specord UV-Vis spectrophotometer within 400–800 nm.

ACKNOWLEDGMENTS

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