Effect of the composition of binary polar solvent mixtures on dye adsorptivity in the polymer matrix

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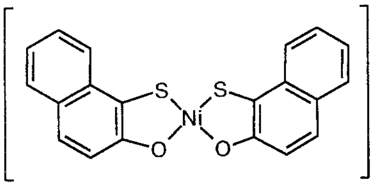
Sorption and diffusion processes of 1-mercapto-2-naphthol nickel complex in a polymer matrix upon surface dyeing of polymethyl methacrylate are studied by near-IR spectroscopy as a function of dye solution composition and technological parameters of the process. The optimum solution composition and technological regime are selected. The diffusion coefficient is evaluated.

Key words: 1-mercapto-2-naphthol nickel complex, polymethyl methacrylate, surface dyeing, IR spectroscopy.

For development of a polymer light filter with high absorption within the range of neodymium laser radiation (λ = 1060 nm) and high transmission within the visible spectral range used for eyes protection from laser radiation, we selected polymethyl methacrylate (PMMA), which has high optical, mechanical, and operational characteristics, and the light filtering additive was 1-mercapto-2-naphthol nickel complex (**1**), known as an efficient IR absorber[1]:



K^+ (**1**),

where K^+ is tetra-*n*-butylammonium cation.

The traditional methods for production of a polymeric material such as volume dyeing upon processing or polymerization appeared to be unacceptable due to the low thermal stability of **1** and its insolubility in the monomer (methyl methacrylate). Therefore, we resticted our selection to surface dyeing of PMMA from a solution of nickel complex **1** to obtain a light filter with the required optical characteristics. Meanwhile, the solvent should dissolve **1**, but should not cause significant swelling of PMMA. The solution of this problem was reduced to obtaining a solid solution of **1** in PMMA and study of sorption and diffusion processes of **1** within the polymer in relation to various factors of the technological regime.

Experimental

The specimens were obtained by means of surface dyeing of AO-120 PMMA sheets with dimensions of 2×2 cm from solution of **1** in acetonitrile-water binary mixture. The concentration of **1** in the solution was varied within the range (4÷12) 10^{-3} mol L^{-1}; the acetonitrile concentration in the binary mixture was 30 to 95 vol.%. The temperature of the process ranged from 40 to 70 °C, the dyeing time was 1 to 9 min.

After dyeing, the specimens were washed with distilled water at ambient temperature and then subjected to heat treatment at the temperature of 60 °C during 1 h to remove the residues of solvent from the surface layer. The optical density of the dyed specimens was measured using a Hitachi-330 spectrophotometer at the wavelength λ = 1100 nm.

Results and Discussion

The optimization of technological parameters in the production of a light filter assumes the study of sorption and diffusion processes of complex **1** within the polymer upon surface dyeing of PMMA as a function of the composition of the dyeing solution, temperature, and time of dyeing. We considered the surface dyeing of PMMA as a process of mass transfer of complex **1** from the surroundings into the polymer. The interphase transfer of **1** was therewith considered as a complex process involving diffusion of the complex within the surroundings to the polymer surface, diffusion into the polymer, and sorption followed by fixation at the inner surface of the polymer. By analogy with the mechanism of dyeing of synthetic fibers with disperse dyes[2], we supposed that the process of surface dyeing of PMMA with complex **1**

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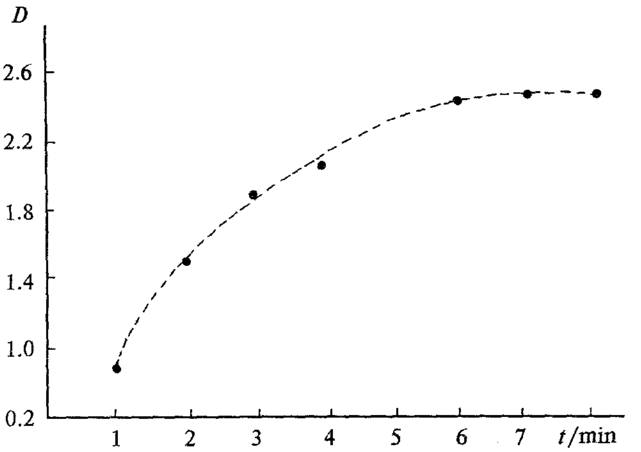

Fig. 1. Dependence of the optical density (*D*) of dyed PMMA specimens on the time of dyeing. Concentration of complex **1** in the dyeing solution (*C*) is $5.8 \cdot 10^{-2}$ mol L^{-1}.

is realized as follows: the complex is adsorbed at the specific centers of the polymer—solvent interface in the form of a monolayer. It is assumed that the polymer contains a certain number of active centers, and the adsorption is accounted for by Van der Waals forces and donor—acceptor interaction. The peculiarities of the structure of **1** and the PMMA macromolecule predetermine the formation of monolayer of complex **1** upon adsorption. The sorption saturation of the polymer with the complex is determined not so much by the number of its potential active centers as by the inner surface of PMMA accessible to sorption[3]. Figure 1 shows the dependence of the optical density of dyed PMMA specimens on the time of dyeing. At a time of dyeing greater than 6 min, the optical density (*D*) of the specimens achieves the maximum value and flattens out. The D_{sat} value is equivalent to the sorption saturation C_{sat} of the polymer, which indicates the maximum amount of complex that can be sorbed by PMMA. The relationship obtained between the optical densities of the dyed PMMA specimens and the dyeing solution with the same temperature and time of dyeing is linear. Therefore, the relationship between the concentration of **1** in PMMA (C^{pol}) and in the solution (C^{solv}) obeys the Henry—Nernst law:[4]

$$C_{\infty}^{pol}/C_{\infty}^{solv} = \text{const.}$$

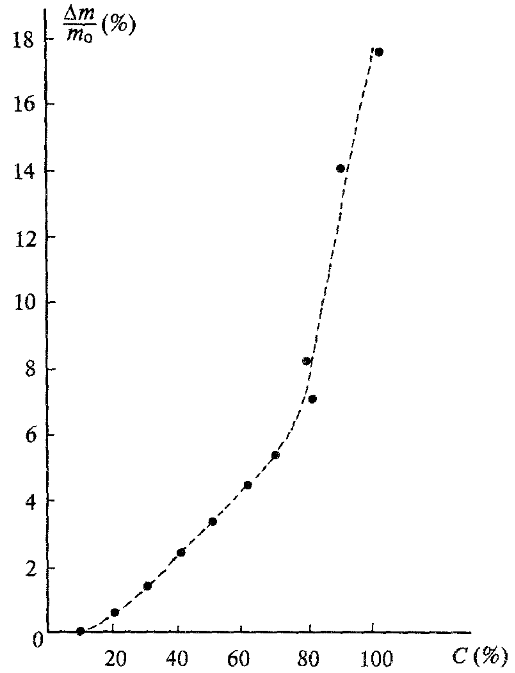

Fig. 2. Variation of the swelling degree ($\Delta m/m_0$) of the PMMA specimens with the MeCN concentration (*C*) in the binary mixture at 60 °C and a dyeing time of 3 min.

Upon dyeing, the molecules of **1** can penetrate and be sorbed within PMMA only in its amorphous zones and at the interfaces between amorphous and crystalline areas, while the dimensions of molecules of **1** cannot exceed the dimensions of micropores at the surface of PMMA. The mechanism of the intensifying effect of acetonitrile involves the influence on complex **1** (dissolution and dispersion) and on PMMA (plasticization). Upon sorption at the outer surface of PMMA, acetonitrile diffuses into the inner structure of the polymer significantly faster than the molecules of **1**, penetrates inside its structural elements, and affects the mobility of chains and sections of macromolecules. Acetonitrile acts as a molecular lubricant promoting the diffusion within the polymer and reducing the activation energy, which is necessary for the molecule of low-molecular component to pass through the tangled polymeric chains. The increase in the acetonitrile concentration in the mixture enhances the probability of destruction of supramolecular formations, which depends upon the dissolving ability of a solvent. If a solvent breaks down the supramolecular formations, all other factors being equal, it has higher mobility and greater diffusion coefficient as compared to the solvent, which cannot disturb the local ordering of the polymeric chains. Among two componets used in the acetonitrile-water mixture for the surface dyeing of PMMA, acetonitrile with its higher affinity to PMMA has the higher penetrability. Figure 2 represents the change of the swelling degree of the polymeric specimen determined by the change of mass m/m_0 with increase in the volume concentration of acetonitrile in the binary mixture. The linear dependence is observed within the range of acetonitrile concentrations 10 to 80 vol.%; further increase in its concentration results in unlimited swelling of PMMA, *i.e.*, its dissolution. Thus, the process of surface dyeing of PMMA should be carried out at the acetonitrile concentration below 80 %. Considering the process of surface dyeing of PMMA, we assume that at the first moment the surface of adsorbent is occupied by the molecules of solvent (acetonitrile and water). The molecules of complex can be adsorbed at the PMMA surface only due to the displacement of the molecules of

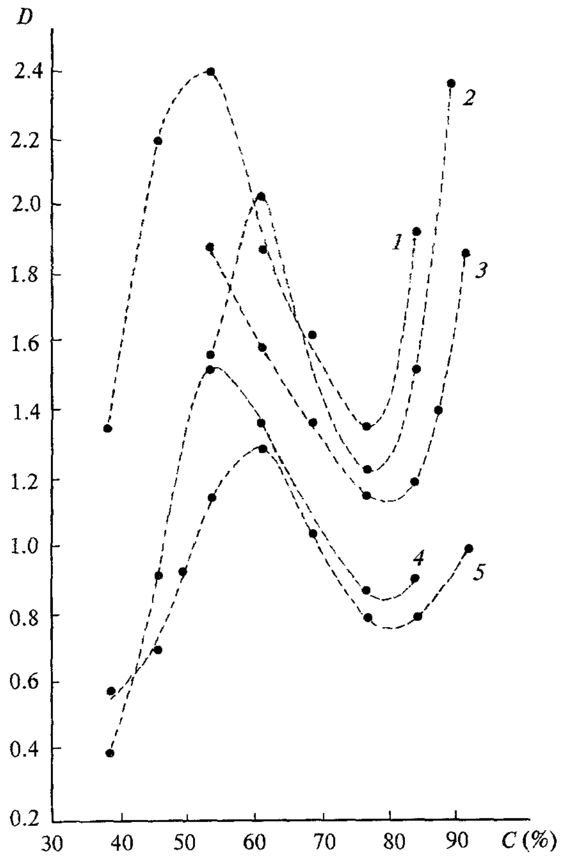

Fig. 3. Dependence of optical density (*D*) of the dyed PMMA specimens on the MeCN concentration (*C*) in the dyeing solution at the following dyeing temperatures, °C: 70 (*1*); 60 (*2*); 50 (*3*); 48 (*4*); and 40 (*5*).

solvent (exchange molecular adsorption). The water molecules will be displaced primarily by the molecules of **1** due to the different surface affinity. We proved experimentally that the increase in the acetonitrile concentration in the dyeing solution enhances the solubility of the complex and reduces its adsorption of the PMMA surface. Figure 3 represents the relationships between the change of optical density of PMMA specimens and the acetonitrile concentration in the dyeing solution at various temperatures of dyeing. The analysis of these curves shows that the change of optical density of the dyed PMMA specimens as a function of the volume concentration of acetonitrile in the binary mixture of solvents has the extremum nature. The maximum optical density corresponds to the specimens dyed from the solutions with the volume acetonitrile concentration from 54 to 61 %, because the system involving complex **1** and binary mixture of solvents exists in the thermodynamic equilibrium under these conditions. The increase in the acetonitrile concentration in the binary mixture of solvents results in the enhancement of solubility of the complex, and, hence, in the reduction of the optical density of the dyed specimens. The decrease in the acetonitrile concentration in the binary mixture of solvents leads to the crystallization of complex **1** followed by the aggregation of particles. Simultaneously, the optical density of the dyed specimens decreases, because only the particles of complex with molecular dimensions having the higher potential energy can be sorbed at the surface of the polymer and diffuse into it. The monomolecular fraction of **1** is specifically filtered out through the polymer acting as a sieve. Thus, the increase in the solubility of the complex in the environment reduces its coefficient of distribution between the polymer and the environment, on the one hand, and between the acetonitrile-water binary mixture, on the other hand. The high solubility of **1** in the environment is caused by the low thermodynamic potential, high affinity of the complex to the environment, and the absence of thermodynamic reasons for the transition from the environment into the polymer.

Since only the particles of complex with molecular dimensions can be adsorbed at the PMMA surface, the maximum optical density shall correspond to the PMMA specimens dyed from the freshly prepared dyeing solution obtained by water dilution of the concentrated solution of **1** in acetonitrile (crystallization of **1** from the solution begins under these conditions). As time passes, the particles of complex aggregate in such solution, their adsorptivity decreases, and the optical density of the dyed specimens reduces. Figure 4 represents the curve for decrease in the optical density of the PMMA specimens dyed in series from the same solution as a function of the number of experiment. In our opinion, the sharp drop in the optical density of specimens upon dyeing in series is not connected with the decrease in the solution

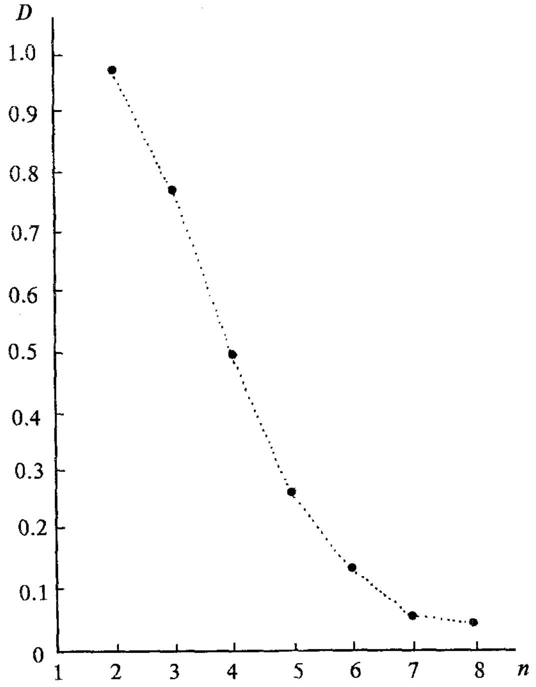

Fig. 4. Variation of the optical density (*D*) of PMMA specimens dyed in series from the same solution.

concentration since the optical density of the dyeing solution and, hence, its concentration did not virtually change. Apparently, this fact results from the aggregation of particles of the complex in the dyeing solution. Thus, the maximum adsorption of complex **1** at the PMMA surface takes place upon the slow shift of the phase equilibrium in the system involving the crystal state and the solution toward the crystallization of the complex from the solution in the acetonitrile—water binary mixture. This fact is confirmed by the microscopic study of the PMMA specimens dyed from the solutions of complex **1** with various volume concentration of acetonitrile. It is known[5] that a specific optical effect takes place upon the solvent diffusion within the optically transparent polymers: one can clearly see a sharp boundary moving toward the diffusate penetration. This boundary is localized within the concentration range 2 to 4 vol. %, and its appearance is connected with the sharp change of the refractive index gradient within a very narrow zone. Upon the microscopic study of the dyed PMMA specimens, we measured the depth of diffusate penetration within the polymeric material. It was found that at the acetonitrile concentration in the dyeing solution between 38.5 and 53.8 % virtually pure solvent diffuses into the polymer, while complex **1** is adsorbed at the PMMA surface in the form of dark layer. This phenomenon is explained by the fact that within this concentration range the swelling degree of the polymer and, hence, the dimensions of micropores at the polymeric surface are insufficient for diffusion of the larger molecules of complex **1** into the polymer. The increase of the volume concentration of acetonitrile in the dyeing solution above 61.5 % enhances the swelling degree of the polymer so that the dimensions of micropores at its surface become comparable with the moleculer dimensions of complex **1**. Adsorbing at the PMMA surface, the molecules of complex **1** also begin to diffuse into the polymer, and the color characteristic for complex **1** appears at the depth of diffusate penetration into the PMMA specimen. The color intensity enhances with increase of the acetonitrile concentration in the dyeing solution; meanwhile, the optical density of specimens reduces due to the decrease in the adsorption of complex **1** at the PMMA surface.

The experimental results obtained are within the scope of concepts concerning the effect of solubility of the sorbing substance on its adsorptivity and enabled us to select the optimum acetonitrile concentration between 58 and 61.5 % in the dyeing solution.

Since the surface dyeing process is determined by the dye diffusion into the polymer and sorption at the outer and inner surface of micropores, and the diffusion occurs in the presence of concentration gradient, the diffusion coefficient $\overline{D}$ is the measure of diffusion rate of the dye into the polymer and falls within the range of $\overline{D}$ from 10^{-7} to 10^{-12} cm^2 s^{-1}.[6] We suppose that the process of diffusion of complex **1** into PMMA is identical to the process of dye diffusion into the polymer. It is known[6] that the rate of dye diffusion within the polymer is determined by the equilibrium sorption value corresponding to the steady dynamic equilibrium between the dye concentrations in the environment and the polymer. For calculation of the diffusion coefficient of complex **1** in PMMA, we used the C_{sat} value detrmined graphically from the kinetic curve (see Fig. 1). Figure 5 represents the relationship between the change of optical density of dyed specimens, which is equivalent to the amount of sorbed substance (complex **1**) *vs.* $t^{1/2}$, where t is the dyeing time of specimens. This relationship corresponds to so called pseudo-Fickian diffusion, which is characterized by fast sorption of the first portion of diffusate.[6] Since the pseudo-Fickian diffusion is close in its mechanism to the diffusion obeying the Fick's law, we used the following relationship for calculation of $\overline{D}$[5]:

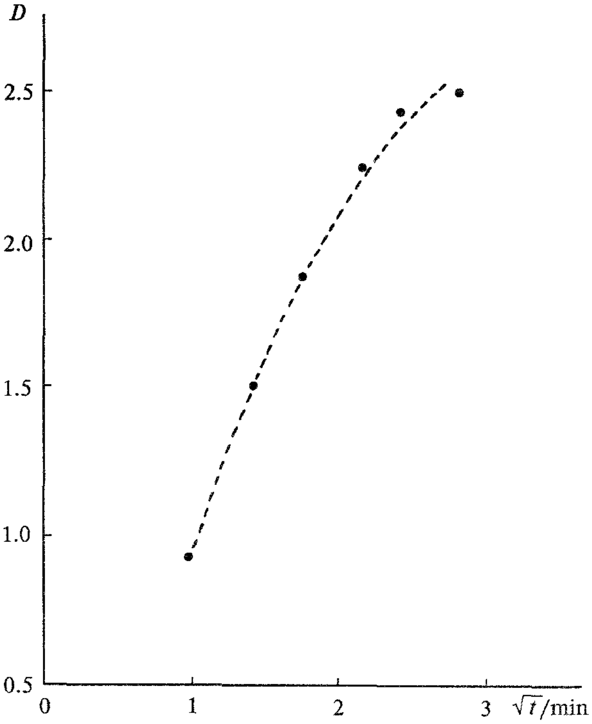

Fig. 5. Relationship between the optical density (D) of the dyed PMMA specimens and $t^{1/2}$, where t is the dyeing time (min).

$$\ln(1-\gamma) = \ln\frac{8}{\pi^2} - \frac{\pi^2 \overline{D} t}{l^2} ,$$

where $\gamma = M_t/M_\infty$; M_t is the amount of substance sorbed by the specimen by the time t; M_∞ is the limiting amount of substance sorbed at $t \to \infty$ at the corresponding concentration C_0; t is the time of dyeing; and l is the depth of diffusate penetration into the polymeric specimen.

Since the optical density of specimens at the wavelength of absorption maximum of complex **1** is proportional to its amount sorbed by PMMA, the M_t/M ratio can be replaced by the D_t/D_∞ ratio, where D_t is the optical density of the specimen at the current time and D_∞ is the optical density of the specimen at the sorption saturation. The D_t and D_∞ values are determined graphically (see Fig. 1). The diffusion coefficient $\bar{D}$ was calculated by the equation[5]:

$$\bar{D} = \frac{l^2}{\pi^2} \mathrm{tg}\alpha \ ,$$

where tgα is the slope of $\ln(1 - \gamma) - t$ curve, which equals 0.511. The D value equals 0.828 10^{-6} cm^2 s^{-1}.

Thus, the diffusion rate of **1** in PMMA upon its surface dyeing is significantly smaller than the diffusion rate of dyes in the liquid media (10^{-5} to 10^{-6} cm^2 s^{-1}).[6] This fact has two causes: the denser polymeric structure, resulting in the steric retardation of the molecules of **1**, whose dimensions are comparable with those of cavities of canals and pores in PMMA, and the sorption interaction of **1** with the active centers of PMMA, which permanently extract the specific fraction of **1** from the diffusion flow in proportion of the affinity to PMMA.

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