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Photochromic Properties of Perfluorosulfonic Membranes Modified by Sodium Molybdate

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Abstract—Transfer of a perfluorosulfonic membrane from the hydrogen form into the sodium form provides accessibility of pore space to sodium molybdate aqueous solution. Charge transfer spectra make it possible to judge the course of polymerization of capsulated molybdate ions and its intensification when the membranes are held in HCl vapor. The UV irradiation of the modified membranes causes a progressing absorption in the visible spectral region. The rate and depth of photoreduction increase as the concentration and degree of polymerization of molybdate ions increase. The scheme of the process was offered, which is based on taking into account a possibility of delocalization of $4d^1$ electrons of molybdenum(V) over the system of metal-metal bonds.

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Photochromic properties of polyoxomolybdates in solutions, films, and in solid state are intensively studied [1–10]. Characteristic dark blue color arising at the irradiation of the specified systems by UV light is connected with the conversion of a part of Mo(VI) atoms, as a rule, in a pentavalent state; the appearance of an electron on metal 4*d* orbitals makes possible *d–d* transitions and defines the absorption in visible region. The fact that photochromism is characteristic of cluster molybdenum oxo species and is not observed in the case of monomeric $[\mathrm{MoO_4}]^{2-}$ allows us to consider it as a “dimensional” property. In this connection it is supposed [3] that the increase in the number of molybdenum atoms in the composition of oxide formations favors stabilization of the forms obtained on the reduction due to an energy gain upon the delocalization of $4d^1$ electrons over the system of a “metal core set” of Mo(V) atoms. The specified viewpoint demands an additional experimental verification, which, in turn, becomes complicated due to known difficulties of the identification of polyoxo forms of molybdenum(VI) in solutions and of their isolation in solid state.

Results of studying photochromic properties of sodium molybdate capsulated in nanosize concavities of a perfluorosulfonic membrane are presented below. The MF-4SK membranes of domestic production used in the work fall into a special type of porous fluorocarbon polymers containing graft sulfonate groups. According to the well-established conception [11, 12], a continuous system of concavities close to spheres with a diameter of ~4 nm connected by narrow canals with the cross-section of ~1 nm is formed in their framework consisting of fluocarbon and ether chains. High transparence and accessibility of the pore space define possibilities of directed modification of the membranes with the purpose of imparting necessary optical properties to them.

In attempting to inject an aqueous solution of sodium molybdate into porous volume of the membrane by simple impregnation, unusual phenomenon was observed: we failed to detect molybdenum in membranes after their arbitrary long-term holding in solutions (in this case the transparence of plates within the whole optical range was completely saved). At the same time it was noted that a rather fast (within 15–30 min) long-wavelength shift of the $2p^{\text{н}}(\mathrm{O}) \rightarrow 4d(\mathrm{Mo})$ charge-transfer band was observed in the absorption spectra of membranes during their contact to solutions, which points to occurring polymerization of molybdate ions. Most likely, it is the circumstance which causes inaccessibility of a membrane pore space: its exterior surface possessing a strong acidity actively provokes the formation of polynuclear molybdenum(VI) oxo-

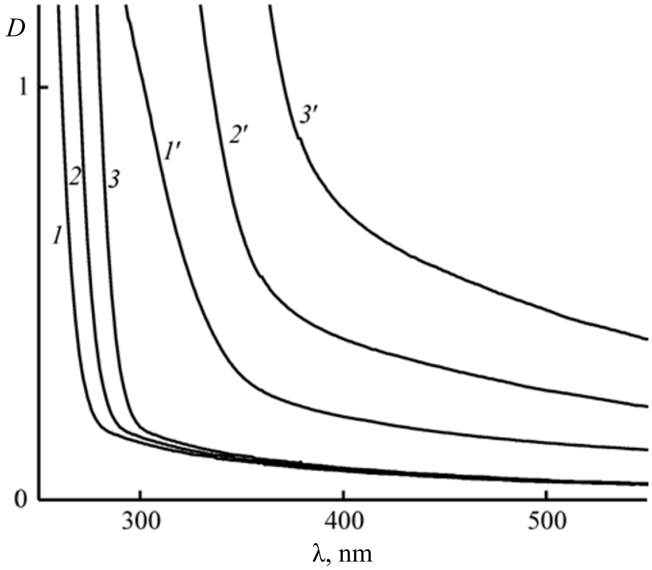

Fig. 1. Absorption spectra of membranes with molybdenum(VI) concentration of (*1*) 0.07; (*2*) 0.13, and (*3*) 0.19 mmol g^{-1} and (*1*', *2*', *3*') their variation as a result of holding in HCl vapor.

anions with sizes exceeding parameters of input channels of the carrying agent. It is significant that arising polymolybdate species are so stable that they are saved when passing into solution.

In view of thus found features we could expect that the effective filling of a membrane with a Na_2MoO_4 solution can be reached by neutralizing its acid centers. Nevertheless, even after transferring membranes into the sodium form the injection of appreciable amounts of sodium molybdate into them was reached only when the concentration of the impregnating solution and temperature were increased (up to 2.5 M and 60°C, respectively). As a result of the increase in the duration of contact under the specified conditions, samples with a concentration of the injected with respect to molybdenum 0.07, 0.13 and 0.19 mmol g^{-1} were obtained.

In spite of the neutralization of acid centers, nevertheless a partial polymerization of molybdate ions occurs in a pore space, as it is seen from the comparison of absorption spectra of modified membranes (Fig. 1): as the concentration the capsulated salt increases, a moderate long-wavelength shift of the charge-transfer band (Fig. 1, curves *1*–*3*) occurs. The further increase in the size of polymolybdate anions can be reached in acid medium. For this purpose we held samples in vapor of wet hydrogen chloride up to reaching a maximal bathochromic shift of spectral bands (Fig. 1, curves *1*–*3*'). The formation of large anionic species in this case is indicated by approaching the edge of the charge-transfer band (λ_{ed} ~400 nm) to its position in the spectrum of polycrystalline MoO_3 (λ_{ed} 420 nm [3, 8]). Recorded charge-transfer spectra are formed on the transfer of electrons from nonbonding (pseudo-atomic) 2*p* orbitals of oxygen on vacant 4*d* levels of molybdenum(VI). As a result of condensation of molybdate anions a proportional increase in the number of system states occurs, which is accompanied by coming closer donor oxygen levels and acceptor 4*d* molybdenum orbitals. The resulting long-wavelength shift of the charge-transfer band is similar to the well-known bathochromic shift of the band of $\pi \rightarrow \pi^*$ transitions in nonsaturated and aromatic hydrocarbons observed on increasing a chain (region) of conjugation, with the difference that in the case of increasing size of molybdate ions the conjugation takes place due to d_π–p_π conjugation along Mo–O–Mo bonds. Prolonging the analogy, it is possible to expect that the shift of the charge-transfer band should occur in a rather narrow size interval so that the charge-transfer spectrum of a large polymolybdate anion can appear close or similar to the spectrum of a massive oxide analog as shows in Fig. 1.

The UV irradiation of the modified membranes is accompanied by the appearance and intensification of dark blue color, the intensity of wide absorption bands in the visible spectral region increasing (Fig. 2). The weak solution of observed bands (formation of the absorption close to "continuous") is the first evidence for the appreciable conjugation of molybdenum(V) $4d^1$ electrons "freed" as a result of a photoreduction. As the concentration of a capsulated salt increases, the degree of delocalization of 4*d* electrons along the system of metal-metal bonds increases, which manifests itself in the rate and attained depth of the photoreduction of the modified plates (Fig. 2).

In addition to it the dependence of the optical density *D* at λ 750 nm on the irradiation time is presented in Fig. 3. The $D(\tau)$ dependence close to linear is observed in all cases, which can be connected with the compensation of a decrease in the concentration of the highest valence form of Mo(VI) by the acceleration of the reaction due to progressing interatomic Mo(V)···Mo(V) interactions. The photoreduction acceleration in the series of samples affects the increase in the slope ratio of straight lines *1*–*3*: 0.09, 0.13, and 0.15.

It is important to note that the found photochromic properties of membranes containing molybdenum(VI)

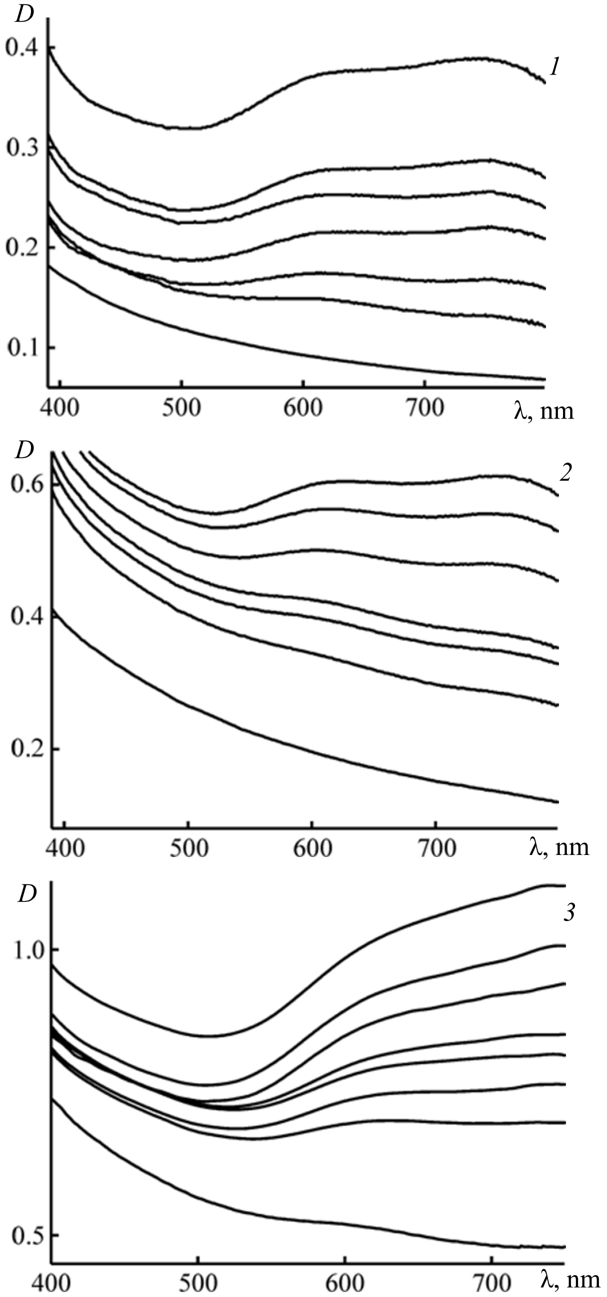

Fig. 2. Increase in optical density in the spectra taken in 5 min intervals and corresponding to the photoreduction of membranes with molybdenum(VI) concentration of (*1*) 0.07; (*2*) 0.13, and (*3*) 0.19 mmol g^{-1} (lower curves correspond to initial states of membranes).

do not depend on the humidity and possible presence of reducing molecules in air. To check qualitatively this viewpoint, we irradiated membranes in quartz tubes evacuated by means of a zeolite trap cooled by liquid nitrogen. In this case we observed a weak, but clearly recorded, acceleration of the photoreduction.

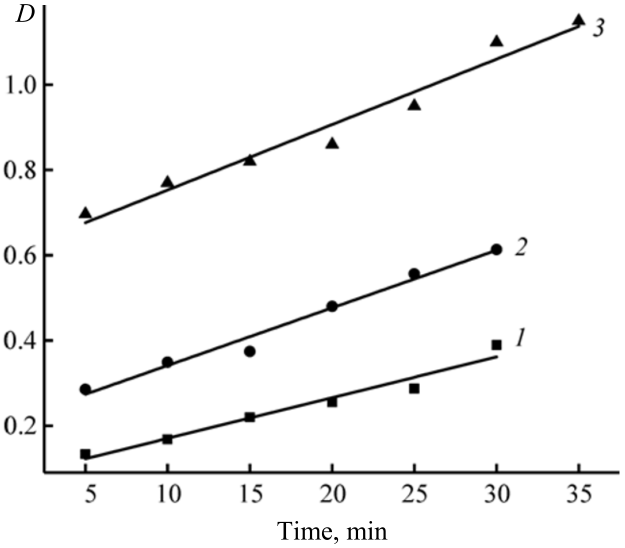

Fig. 3. Kinetic dependences of photoreduction of membranes with molybdenum(VI) concentration of (*1*) 0.07; (*2*) 0.13, and (*3*) 0.19 mmol g^{-1}.

It is known that in ordinary conditions even such strong reducing agents as metal zinc and hydrazine are capable to transform molybdenum(VI) in its compounds only to the state of Mo(V) [13.] Photochromism of the modified membranes, observed in the absence of chemical reducing agents, as well as its clear intensification under evacuation, allow us to suggest that the most probable mechanism of the photoreduction includes the detachment of mobile bridging oxygen as a result of light-initiated transfer of its electron density on atoms of hexavalent molybdenum.

The acceleration and depth of process (1) are defined by the size of polymolybdate ions capable to be stabilized in the reduced state the more successfully, the greater is the energy gain upon the delocalization of $4d^1$ electrons over the system of Mo(V)···Mo(V) bonds.

$$[\mathrm{Mo}^{6+}–\mathrm{O}^{2-}\mathrm{Mo}^{6+}] \xrightarrow{h\nu} [\mathrm{Mo}^{6+}–\mathrm{O}^{-}–\mathrm{Mo}^{5+}]^*$$

$$\xrightarrow{-1/2\mathrm{O}_2} [\mathrm{Mo}^{5+}\cdots\mathrm{Mo}^{5+}]. \qquad (1)$$

It is necessary to note in conclusion that it is the stability of the metal-metal bonds, which can be a reason hampering the process of the reversible oxidation Mo(V)→Mo(VI). The long-term heating of the photoreduced membranes in air at admissible temperature of 90–100°C (dictated by the necessity of the porous structure preservation) is not accompanied by changes in their spectra. Nevertheless, the obtained molybdenum-containing membranes, in spite of the impossibility of their regeneration, are characterized by compactness in combination with a high sensitivity to UV radiation, which allow them to be considered as systems, suitable for ultraviolet dosimetry.

EXPERIMENTAL

Absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer.

Perfluorosulfonic MF-4SK membranes of width 0.25 mm were purified by boiling in concentrated nitric acid within 2.5–3 h with the subsequent careful washing by distilled water up to the absence of acid reaction. The transfer of membranes in the Na form was carried out by heterogeneous pH-metric titration of plates of 0.1–0.15 g in weight placed in 30 ml of water by a 2 M solution of sodium hydroxide (the found amount of accessible sulfo groups of 0.80 mmol g^{-1} is close to the known values [11, 12, 14]). Then the Na-replaced membranes were dried up to a constant weight and impregnated with a 2.5 M solution of sodium molybdate at 60°C within 0.5–1.5 h. Polymerization of molybdate ions was carried out by long-term holding membranes in a desiccator above concentrated hydrochloric acid.

Capsulated salt was extracted by boiling modified membranes in an 1 M solution of nitric acid, molybdenum(VI) was reduced by tin(II) chloride up to Mo(V), which was determined by photometry in the form of a complex with thiocyanate ions [15].

Photoreduction of samples was carried out in air by their irradiation with the total spectrum of an SVD-120A mercury lamp.

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