Photophysical Properties of Acridine in Solutions and SiO₂ Thin Films. Materials for Optical Sensors

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Experimental and quantum-chemical investigation of the spectral and luminescent properties of acridine, and its protonated form was performed. The electronic absorption and fluorescence spectra of the acridine were studied at room temperature in ethanolic solutions at different pH values and in other solvents of different chemical nature and polarity.The energies of the excited states, the deactivation rate constants for the excited states, and the dipole moments are presented, which were obtained by calculations using the INDO/S method. Sensor properties of acridine immobilized into SiO₂ thin films to gaseous ammonia was studied.

Keywords: Luminescence, Acridine, Quantum chemical calculations, SiO₂ thin films, Optical chemical sensor.

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Optical chemical sensors that use luminescence, including changes of the radiation intensity, radiation wavelengths, spectral shape, and luminescence lifetime possess high sensitivity and selectivity toward molecules of different analytes. The targeted search of compounds exhibiting sensor properties and the design of optical sensor materials on their basis is a topical task.

The acridine (Fig. 1) is suitable compound for creation of a material for an optical sensor. The spectral, luminescent properties, dipole moment in base and in excited states, photophysical processes of deactivation of excitation energy for acridine and for its protonated form were investigated experimentally and using quantum chemical simulation [1].
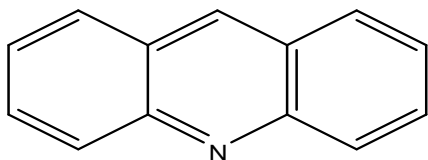

Fig. 1 – Structural formula of acridine

It was shown that in this molecule the nitrogen of acridine cycle is a protonation site. The changes in the acridine absorption spectra in acidified solutions show an extremely specific pattern. In parallel with the emergence of a band in the long-wavelength edge of acridine absorption around 400 nm, there is also an increase in the intensity of the long-wavelength acridine absorption band at ~ 350 nm (Fig. 2a). This is observed very rarely in the ion-neutral equilibrium state of organic compounds in solutions. Similar results were reported in [2, 3]. The cationic form of acridine, unlike the neutral one, exhibits moderate fluorescence. For a hydrochloric acid concentration as low as 10^{-5} M in solution, there is intense fluorescence around 479 nm along with weak fluorescence belonging to the neutral form around 415 nm. The fluorescence spectra of acridine and those of its protonated form are shown in

Fig. 3b. The fluorescence maximum of protonated form considerably shifted in the red region and a fluorescence quantum yield increased up to 0,27 (for neutral form it is equal 0,03).
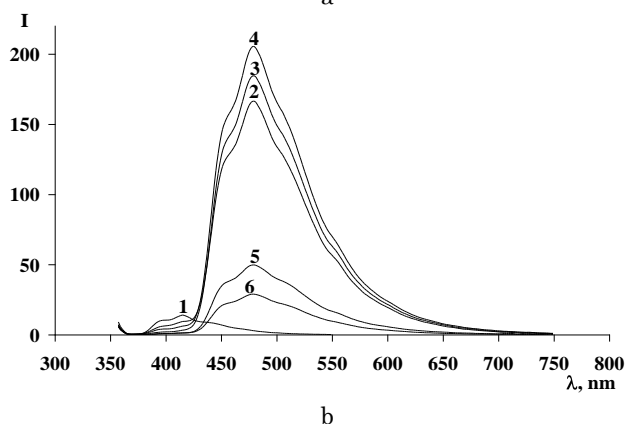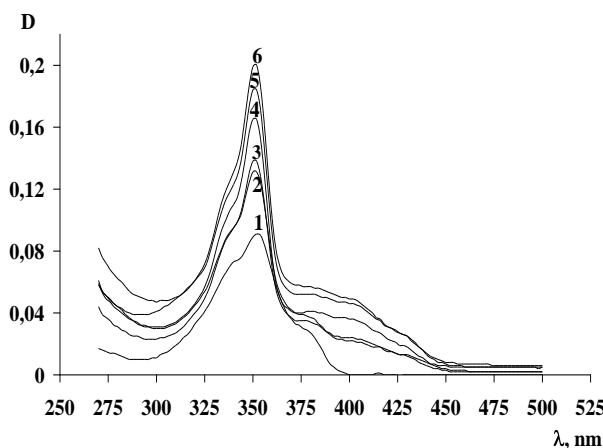

a

b

Fig. 2 – Absorption (a) and fluorescence spectra of acridine in ethanol (b) for $C_{HCl} = 0$ (1), 10^{-5} (2), 10^{-4} (3), 10^{-3} (4), 10^{-2} (5), and 10^{-1} M (6)

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For a deeper understanding of the relevant experimental evidence, we have performed quantum chemical investigations on the examined molecules.

The first three singlet states of acridine have close energy values and lie in the following order: La, nπ*, and Lb. The optical activity of the S_1 state of the ππ*-orbital nature with oscillator strength of 0.24 in the $S_0 \rightarrow S_1$ electronic transition is the highest one among these. The S_1 state neighbors on the close-lying T_3 (nπ*) state. The calculation of the excited state deactivation constants shows that the main decay channel for the S_1 state is the $S_1 \rightarrow T_3$ intersystem crossing ($k_{ST} = 1.5 \cdot 10^{11}$ s^{-1}). Because of this, the calculated fluorescence quantum yield is low ($\varphi \approx 10^{-4}$). As a result, in the absence of specific interactions in low-polarity inert solvents, acridine may not exhibit fluorescence, which is confirmed experimentally.

We have calculated the energy of the excited states and the rate constants of the photophysical processes at work in the molecule with the protonated nitrogen atom in the acridine cycle. For structure such as these, the calculations of the energy of the excited states are in close agreement with the experimental absorption spectra. It follows from the calculations that the protonation is, on the whole, responsible for the decrease in the energy of the S_1 state as compared to the neutral form and for the decay of close-lying states of the nπ* nature. For the acridine cation, the lowest singlet and triplet states are of the ππ*-orbital nature. The rate of the singlet-triplet conversion to the lowest triplet states of the same orbital nature decreases by several orders of magnitude, which gives rise to the activation of fluorescence of the acridine cation.

So considerable change of spectral-luminescent properties enables to use acridine protonated form as the active medium for detection of small amount of substances with the basic properties, for example ammonia (Fig. 3).

Suitable material for a matrix of an optical sensor is the material made from tetraethoxysilane (TEOS) received sol-gel method and doped with organic compound (acridine). Since in synthesis acid hydrolysis was used acridin was in protonated form in the final product. The sensor material was made in form of thin (< 1 μm) films by spin-coating method.

Fig. 3 – Fluorescence response of acridine in SiO_2 film to ammonia content in gas mixture with argon (a) and calibration curve for ammonia (MAC – maximum allowable concentration) (b)

To study the capability of the received material to be a sensor for ammonia the investigation of spectral-luminescent properties of samples doped the acridine at contact with ammonia vapor was carried out. In result of interaction ammonia vapor with film surface the fluorescence intensity of protonated acridine fall down (Fig. 3). It was caused by greater basicity of ammonia in comparison with a molecule acridine, that leads to transition of a proton from acridine nitrogen to a molecule of ammonia at their contact. The dependence of ammonia vapors concentration on fluorescence intensity was investigated.

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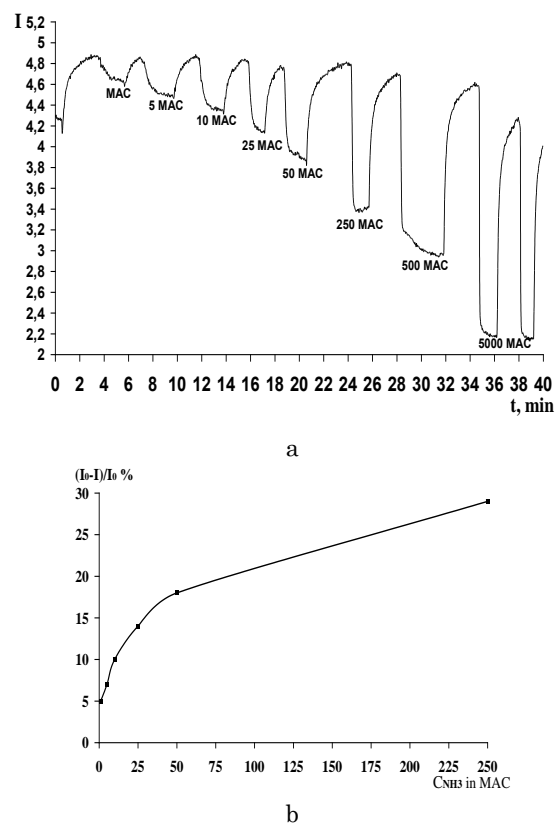2. T. Pedzinski, B. Marciniak, G. L. Hug, *J. Photochem. Photobiol. A: Chem.* **150**, 21 (2007).
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