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QUANTUM-CHEMICAL AND EXPERIMENTAL STUDY OF NITRAZINE YELLOW ON SILICA SURFACE

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The article presents the results of a study on the spectral characteristics (UV-Vis region) of the indicator dye Nitrazine Yellow on the surface of organosilica materials. Experimental data are compared with the results of theoretical (quantum chemical) calculations. Several model scenarios were considered, in which the organosilica surface is represented by characteristic structural features, including isolated Si(OH) groups, vicinal Si(OH)–O–Si(OH) pairs, and geminal $Si(OH)_2$ groups.

Quantum-chemical calculations were carried out using *ab initio* Time-Dependent Density Functional Theory (TD-DFT), CAM-B3LYP functional and LANL2DZ basis set.

The results obtained indicate a satisfactory description of the influence of environmental effects on the absorption spectra of the three forms of nitrazine yellow over the silica surface.

Keywords: nitrazine yellow, silica surfaces, TD-DFT, UV/Vis absorption.

Introduction

The first reference in the literature to the indicator - 2,4-dinitrobenzene-azo-1-naphthol-3,6-disulfonic acid (Nitrazine Yellow, NY) dates back to 1934. Henry Wenker [1] described the synthesis and properties of the azo dye, which, according to the author, is a promising chemical indicator. Indeed, NY is used for the manufacture of indicator paper [1,2], in the analysis of food, fuels and lubricants [3-5]. Due to the fact that the color transition zone of the indicator is located at pH 7 (6.2-7.2), it is widely used in biochemical and medical research. [6]

Modern developments using NY are focused on the creation of reliable sensor materials. Using NY, a portable 3D analytical device based on microfluidic paper was developed for the determination of total ammonia in freshwater. [7]

When creating pH sensor materials, the indicator is introduced into the matrix by sorption, application as a sol-gel coating, or by adding a dye during fiber formation.

Most such materials show a clear visible color change when the acidity of the medium changes. The response of the sensors depends on the density of the tissue, the method of fixation, and the effect of the matrix on the molecule of the embedded indicator.

To produce functionalized nonwovens, the electrospinning method is used, when the formation and functionalization of nanofibers occurs in one step. The polymer solution (which already contains the dye) is exposed to an electric current, which promotes the formation of fibers with a diameter of about several hundred nanometers. The resulting nanofibers made of polycaprolactone (PCL) and polycaprolactone with chitosan showed a reverse color transition, but a significant difference was found between them. For the structure without chitosan, a slow reaction was observed, and for the nanofiber samples containing chitosan, a rapid color transition was observed. In addition, the color transition occurred in the pH range from 4 to 6 for nanofibers with chitosan, and for the polycaprolactone material - in a much wider pH range. [8]

According to the authors, this difference is due to the availability of the dye azo group. In the case of PCL fiber, interaction between the ether group of PCL and the azo group of NY is possible, and for fiber containing chitosan, interaction between the sulfate groups of the dye and the amino groups of chitosan is possible. The speed of the color transition reaction is affected by the presence of chitosan, which increases the hydrophilic nature of the nanofiber, so water molecules easily penetrate the material matrix and reach the dye molecules. In other words, the azo group is not directly involved in the interaction between polycaprolactone and chitosan fibers and remains available to water molecules, and the dye molecule is capable of deprotonation in an alkaline environment and, accordingly, can exhibit halochromic behavior. Theoretical calculations confirmed the experimental observations on the different nature of the interaction of the dye with the polymer chains of polycaprolactone and chitosan. [9]

The possibility of fixing indicator dyes on an ion-exchange membrane with subsequent use as a fiber-optic pH sensor was investigated by the authors in [10]. For the sensor with the embedded NY, they observed a change in the dye dissociation constant and shifts in the absorption spectra. It was found that the characteristics of the resulting sensor are affected by the concentration of the immobilized dye, temperature, and ionic strength of the solution. The pH range of the color transition was 4.8-6.6.

Another interesting chemical approach for the stable immobilization of indicator molecules on textiles is grafting by polymerization [11], which involves the use of reactive monomers that under certain conditions go into the state of free radicals and activate the surface of textiles. In this work, we investigated the photo-grafting of the NY molecule onto the surface of cotton fabric. At the first stage, the NY dye is modified with glycidyl methacrylate (GMA) to obtain a photoreactive dye (GMA-NY), and then potassium persulfate thermally initiates the radical grafting of the functionalized NY onto cellulose. The treated cotton clearly changed color at different pH values. Dye modification and photoinitiation did not change its spectral characteristics. The color transition interval was 6-7. [11]

Guido et al. developed and investigated sol-gel halochromic pH sensors. [12] Using the sol-gel method, a hybrid structure based on 3-glycidoxypropyltrimethoxysilane (GPTMS) in the presence of acid (BF_3OEt_2 at different concentrations) and the dye NY was obtained, which was introduced into a textile matrix (Fig. 1).

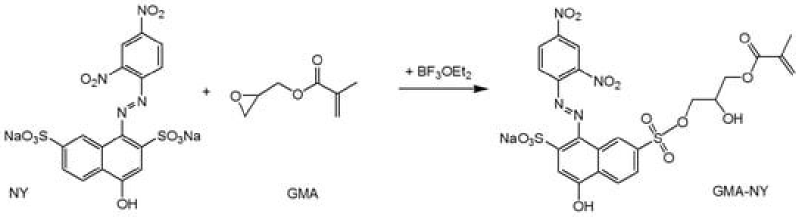

Figure 1. Scheme of preparation of a hybrid structure with the content of NY [12]

The experimental results have shown that the pH-sensitive properties of nitrazine yellow are preserved after covalent immobilization on a silanol matrix due to its sulfo group. The concentration of the catalyst (BF_3OEt_2) significantly affects the opening of the epoxy ring, the formation of the ≡Si-O-Si≡ bond, and the degree of density of the silica matrix. The more cross-linked the inorganic structure is, the more efficiently the hybrid halochromic matrix is fixed to the cotton.

Depending on the form of the dye, the presence of interactions with other molecules, and the nature of fixation in the matrix, the color transition interval and reaction rate can vary significantly. Therefore, the aim of this work was to model the corresponding complexes in the presence of aqueous medium and calculate the absorption spectra.

Experimental part

The initial NY solution was prepared by dissolving an exact weight of the indicator in distilled water. The indicator method was used to study the properties of the medium in the surface layer of sorbents (Table 1).

Table 1. The investigated sorbents

№	Sorbent	Modifier
1	Silica gel (SiO_2)	-
2	Silica gel with grafted n-propylamine groups	~ $(CH_2)_3NH_2$
3	Silica gel with grafted diethyl ester groups of β-(propylamino)-α-dimethylphosphonic acid	~$(CH_2)_3NHC(CH_3)_2PO(OC_2H_5)_2$
4	Silica gel with grafted β-(propylamino)-α-dimethylphosphonic acid groups	~$(CH_2)_3NHC(CH_3)_2PO(OH)_2$

To a sample of each material (0.1 g), 5 ml of indicator solution with a concentration of 0.45 mmol L^{-1} was added. The solvent was removed by evaporation in a drying oven at a temperature of 80-100 0C to a dry suspended state. The absorbance spectrum of NY adsorbed on the surface of the studied materials was measured on a Shimadzu UV-2600 spectrophotometer with an integrating sphere in the range of 300 – 700 nm with a step of 1 nm (slit width 2 nm).

Modelling of complexes

Preliminary NY calculations were carried out by us in [13] in order to highlight quantum-chemical approaches capable of giving adequate estimates of the spectral properties of the system in a reasonable time. According to the obtained data, a convenient method of calculation is DFT with the CAM-B3LYP functional. As a basis we used the double split pseudopotential basis LANL2DZ. The CAM-B3LYP functional gives a slightly underestimated absorption wavelength, but it proved to be significantly better than the B3LYP functional since the latter overestimates the wavelength enormously. This circumstance is due to the apparent intramolecular charge transfer in the molecule. Such situations lead to the necessity of using long-range-corrected exchange functionals and one of them is CAM-B3LYP. We also used a polarization-continuum approach to describe the effects of the water environment. All the calculations were performed using the Gaussian 09 quantum chemistry package [14].

In our calculations we have considered several variants of silicate clusters modeling surface silanol groups. The corresponding structures are presented in Fig. 2. In these clusters, the free valences of silicon were terminated by hydrogen atoms.

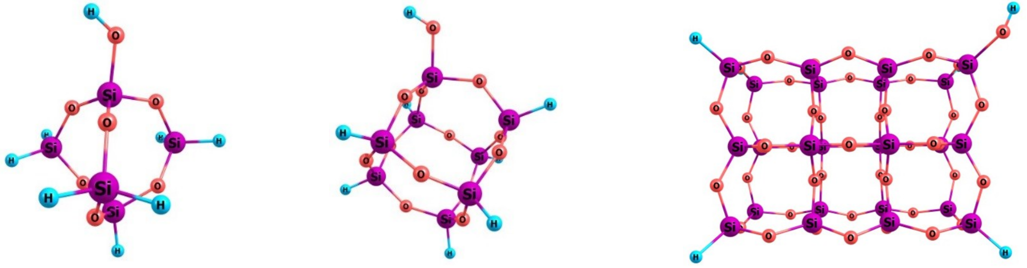

Figure 2. Samples of silanol clusters

We also considered a small cluster that included several silanol groups that realize typical structural situations. This cluster includes so-called vicinal and geminal groups Fig. 3

Figure 3. Schematic representation of the silanole fragment (left) and corresponding 3D structure after the geometry optimization (right).

The ability of NY to change color in solution is due to the presence of azo-hydrazone tautomerism (Fig. 4, A-B). In a neutral aqueous environment, the hydrazone tautomer (Fig. 4, B) is more stable, and in an alkaline environment (pH > 7), the dye molecule appears in a deprotonated form (Fig. 4, C), which leads to a long wave shift of the absorption band. The corresponding forms will be referred to as NY-A, NY-B, and NY-C.

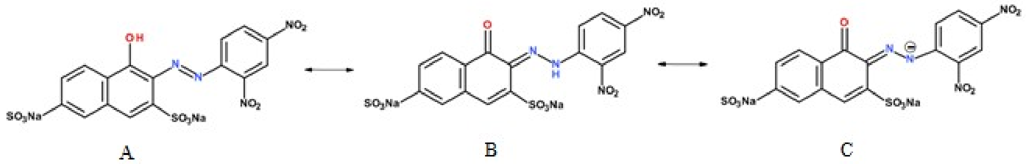

Figure 4. Light-absorbing forms of NY

Optimization of NY geometry together with clusters of Fig. 2 and Fig. 3 in four different positions relative to -SO_3 and -NO_2 groups gave an opportunity to form the structure of possible complexes. Some typical ones are shown in Fig. 5.

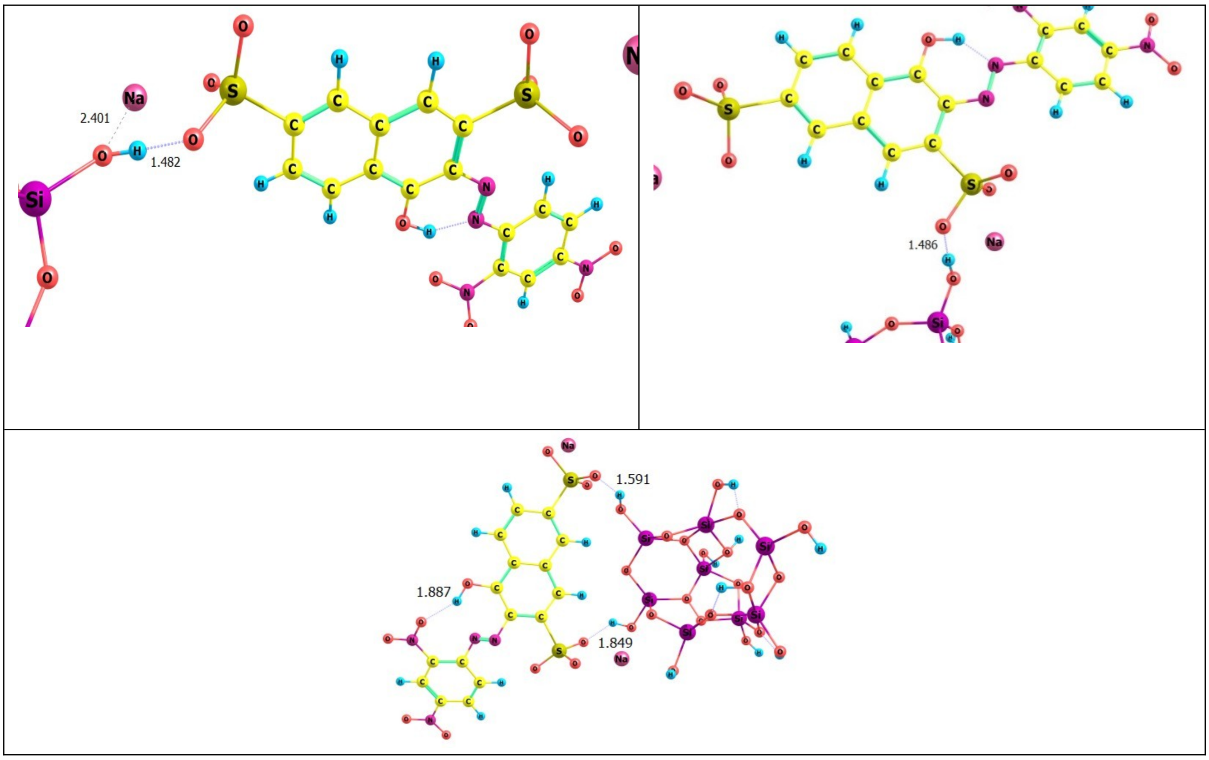

Figure 5. Typical complexes of NY with silanol surface.

Calculations of the NY absorption spectra over the surface of modified organosilica with the description of the medium effects at the level of polarization-continuum model were carried out for different models of complexes (Fig. 5). The calculations showed a relatively small influence of the structures of complexes with silanol groups on the spectrum. For example, while NY-A absorbs at 445 nm in aqueous medium, it absorbs at 432 nm on the surface according to CAM-B3LYP calculations. The first long-wavelength transition of the NY-C form in aqueous medium absorbs at 629 nm, while at the surface – 613 nm. The correspondence between the experimental and calculated data can be seen in Fig. 6. Here the calculated data for the forms NY-A and NY-B are shown in yellow color, whereas the absorption of the deprotonated form is shown in blue.

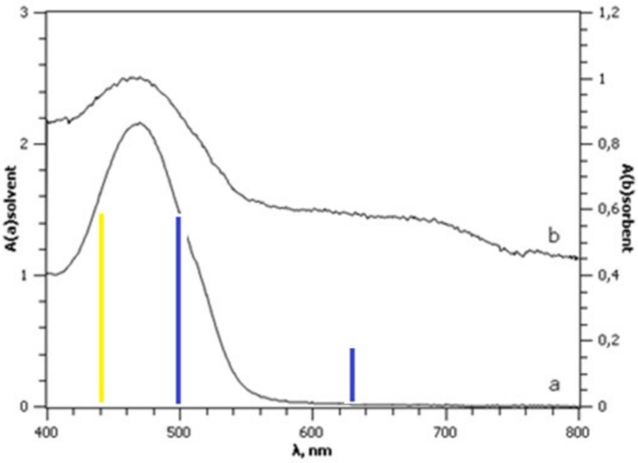

Figure 6. Absorption of the indicator in solution over the sorbent (a) and on the surface of silica gel modified with dimethoxysilane SiO_2~O- $Si(OCH_3)(CH_3)_2$ (b)

In general, it can be seen that the calculated data are in satisfactory agreement with the experimental data.

Conclusion

It is known that silanol groups on the surface of unmodified silica differ in terms of pKa. [15, 16] Chemical modification of the silica surface results in a greater diversity of surface sites differing in their acidity. Analysis of the absorption spectra of NY adsorbed on the surface of various organosilica materials, in combination with theoretical calculations, enables a more accurate evaluation of the influence of different local environments on the spectral characteristics of the indicator.

The presented work describes the application of a quantum-chemical method for calculating the spectral properties of the NY indicator on a silicon surface. It is shown that a satisfactory description of the spectrum can be achieved using a relatively cost-effective method in a sufficiently simple double-split basis.

Acknowledgement

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І. В. Христенко, В. В. Іванов. Квантово-хімічне та експериментальне дослідження нітразинового жовтого на поверхні кремнезему.

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У статті представлено результати дослідження спектральних характеристик (УФ-область) індикаторного барвника нітразинового жовтого (NY), адсорбованого на поверхні кремнійорганічних матеріалів. Експериментальні дані порівнюються з результатами теоретичних (квантово-хімічних) розрахунків.

В спектрах поглинання спостерігається значне розширення смуг поглинання NY, що обумовлено різноманіттям утворених комплексів барвника з поверхневими групами. Враховуючи, що поверхня кремнезему має складну будову, розглянуто кілька модельних сценаріїв, в яких поверхня кремнійорганічних матеріалів представлена характерними структурними особливостями, зокрема ізольованими групами Si(OH), віцинальними парами Si(OH)-O-Si(OH) та гемінальними групами $Si(OH)_2$.

Квантово-хімічні розрахунки були проведені з використанням ab initio теорії функціоналу густини, залежного від часу (TD-DFT), функціоналу CAM-B3LYP та базисного набору LANL2DZ.

Одержані результати свідчать про задовільний опис впливу навколишнього середовища на спектри поглинання трьох форм нітразинового жовтого на поверхні кремнезему.

Ключові слова: *нітразиновий жовтий, поверхня кремнезему, TD-DFT, УФ/Видиме поглинання.*

Конфлікт інтересів: автори повідомляють про відсутність конфлікту інтересів.

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