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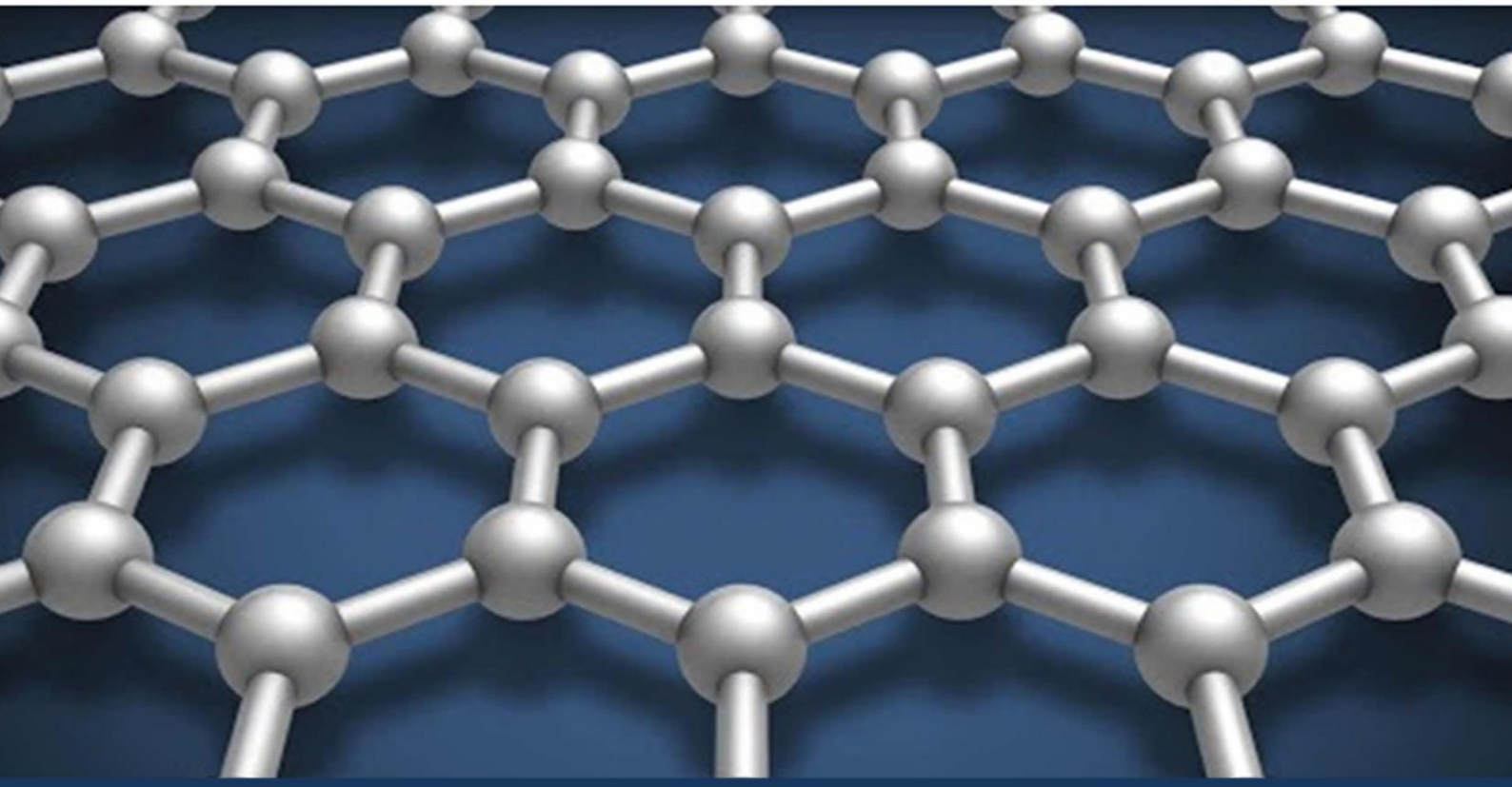

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Композиционные материалы

STUDY OF PROTOLYTIC PROPERTIES OF ORGANIC REAGENTS USED IN THE DETERMINATION OF ALUMINUM AND GALLIUM IONS IN THE LUMINESCENT METHOD

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Abstract. In this work, the protolytic properties of organic reagents used in the determination of aluminum and gallium ions by the luminescent method were studied. The effect of immobilization on the protolytic properties of organic luminophore reagents was studied. Protolytic indicators of reagents in solution and immobilized state were compared.

Key words: luminescence, immobilization, aluminum, gallium, luminophore, protolytic property, morin, quercetin.

Introduction. In connection with the increase in requirements for the metrological and analytical properties of the developed methods for the determination of heavy and toxic metals, it is important to create new high-sensitivity, selective and effective methods for monitoring the content of ecotoxicants in environmental objects [1-3]. The fluorescent method of analysis is promising due to its high sensitivity and relatively cheap equipment [4-5].

Despite the rapid development of new developments in the field of fluorescent analysis based on the use of modern instruments, their basis is the interaction of organic reagents with metal ions. Therefore, improving the chemical-analytical properties of organic reagents, their theoretical and practical substantiation, as well as expanding the scope of use of fluorescent reagents are urgent and attract the attention of chemists [5, 6]. To improve the analytical properties of fluorescent reagents, it should be noted the immobilization of organic reagents on solid carriers [7-9]. This direction is very promising, combining the main advantages of immobilization of the reagent with the determination of the concentration directly from the surface of the immobilized reagent, that is, it makes it possible to simplify the analysis and increase the expressivity of the method [10-12]. Therefore, studying the effect of immobilization on the analytical properties of an organic reagent is important in the development of this direction.

Methods. An organic reagent-carrier system was proposed for the determination of aluminum and gallium ions by fluorescent method. The electronic absorption spectra of the investigated solutions and their complex compounds formed with these metals were measured in an SF-46 spectrometer with a deuterium lamp and a heated lamp with a cuvette thickness of l=1 cm. Excitation and fluorescence spectra were obtained using an Agilent Cary Eclipse UF spectrofluorimeter and an SDL-2 spectrometer with an MS 0507 computer.

Results and discussion. Among the organic fluorescent reagents used in the determination of aluminum and gallium ions, oxyazobirims and polyoxyflavones are distinguished by their good metrological properties [12-16]. The available data and the results of the analysis showed that eriochrome red B is a good reagent for the determination of aluminum and gallium ions by fluorescent method. The structure of the reagents shows that the complex formed by it with aluminum ion can be luminescent. The dissociation constant pK decreases when the organic reagent molecule is transferred to an excited state, which requires transfer in a more acidic environment. Therefore, there is increasing interest in studying the use of eriochrome red B as a luminescent reagent.

For this purpose, by forming a complex of aluminum and gallium with eriochrome red B, that is, the development of a fluorescent method of their detection was studied.

Preliminary data on the fluorescence reactions of eriochrome red B with aluminum were obtained by carrying out qualitative reactions in different media. Complex formation fluorescent reactions were carried out in the medium of organic solvents (acetone, ethanol, DMFA) that activate the radiation intensity of their complexes.

It can be seen from the results that the complexes formed by aluminum and gallium ions with the studied organic reagents are intensely luminescent. The radiation intensity of the complexes formed by the ions of the studied metals with the reagents was higher.

The properties of organic analytical reagents are determined by the distribution of electron density to donor atoms of functional-analytical groups. Immobilization of an organic reagent molecule on one side in a photo-excited state on the other side causes a protolytic equilibrium and redistribution of electron density in the molecule, resulting in the formation of a complex.

The deprotonation constants of functional-analytical groups are the most important physico-chemical properties of the reagent, they determine the optimal conditions of interaction, selectivity, its complexation with metal ions and the stability of the resulting complex, etc. Therefore, it is necessary to assess the applicability of highly efficient organic

reagents that form a highly luminescent complex with metal ions under acidic conditions, i.e., the change in acid-base properties.

Establishment of protolytic properties of organic fluorescent reagents in solution and in immobilized state allows to demonstrate the benefits of immobilization. In the study of the acid-base properties of the examined organic reagents, the pH value was carried out in the range from 0 to 12.

Protolytic properties of the studied reagent were studied based on the balance of excited and immobilized excited states of absorption and luminescence spectra in solution and immobilized state. Studying the protolytic property of the organic reagent in comparison with the immobilized state allows to study the extent of the effect of immobilization on luminescence.

To study the protolytic equilibrium of the reagents, absorption and luminescence spectra of their ground, excited and excited-immobilized states in solution and in the immobilized state were obtained.

Methodology of sample preparation for determination of protolytic balance (acid-base property): 2 ml of a solution of the studied organic reagent (C_R=1.10^{-4} M), dissolved in ethanol (A_1-A_2) or water (B_1-B_2) (or 0,4 g of the immobilized reagent with the optimal "load") is poured into a 15 ml volumetric flask. Different buffer mixtures with pH values from 1 to 12 are prepared at intervals of 0,5. After pouring the prepared solutions (immobilized systems) of the components, the solutions were photometered and fluorimetered in the optimal excitation field in suitable cuvettes

Spectral analysis shows that polyoxyflavones (A_1-A_2) and oxyazobirims (B_1) are in equilibrium in three different forms: molecular, ionized, doubly ionized (for A_1 and A_2) and protonated (for B_1) in the studied acidic interval. With the change of acidity in the basic state, little changed in the excited state and virtually unchanged in the excited immobilized state (Table 1).

Table 1

Spectral-luminescence properties for various forms of polyoxyflavones and oxyazocompounds

Reagent	pH			Reagent form	λ *exc*, нм	λ fluorenci, нм	
	Excited state	Excited immobilized state	Basic case			Excited form	Excited immobilized form
Morin (A_1)	4,0 3,0	3,0 2,0	5,0 1,0	RO$^-$(RO)* R (R)*	370 360	500 490	510 490
Kverceti n (A_2)	4,0 1,0	3,0 1,0	5,0 1,0	RO$^-$(RO)* R (R)*	365 365	475 475	490 475
Kalcon (B_1)	5,5 5,0	4,3 2,0	8,5 5,0	RO$^-$(RO)* R (R)*	544 503	592 545	592 545

Similar studies for eriochrome red B (B_2) were not performed due to the lack of luminescence of the reagent.

The main attention was paid to the study of the protolytic equilibrium of the first and second ionized form of polyoxyflavones, and the ionization constants of C_3 and C_5 hydroxyls and the ionized form of the B_1 form were carried out, because according to the analysis of the literature, these are the ones involved in the formation of the complex.

Comparing the obtained results and literature data shows that the B_1 electron-donating property of polyoxyflavones (A_1 and A_2) and oxyazocompounds increases by 1-3 units when excited compared to the basic state, and increases by 0,6-1,5 units compared to excited in the excited-immobilized state. The obtained results show that the effect of immobilization on luminescence is significant (Table 2)

Table 2

Change of the donor-acceptor properties of reagents in the primary-ionized state in different states

Reagent	**Excited immobilized state**	**Excited form**	**Basic case**	**Change in properties**	
				Excited - Excited immobilized	**Main -excited-immobilized**
	pK$_1$ + 0,2	**pK$_1$ + 0,2**	**pK$_1$ + 0,2**	**Δ pK + 0,2**	**Δ pK + 0,2**
Morin (A_1)	2,3	3,8	5,3	1,5	3,0
Kvercetin (A_2)	2,8	3,4	4,8	0,6	2,0
Kalcon (B_1)	4,6	5,7	8,7	1,1	4,1

Ionization constants for A_1, A_2, and B_1 ionized states were determined and calculated using the Komar method, Fersted method, and graphical methods. The obtained results are presented in Table 3.

Table 3

Comparison of pK results determined by different methods in basic excited, excited-immobilized states

Reagent	Calculation method			Graphically determined		
	pK**	pK*	pK imm	pK**	pK*	pK imm
Morin (A_1)*	2,32 7,20	3,00 7,20	5,32 8,65	2,00 7,30	3,50 7,40	5,70 9,00
Kvercetin (A_2)*	2,82 6,15	3,41 6,41	4,82 7,40	2,50 6,00	3,00 6,00	4,90 7,50
Kalcon (B_1)**	2,50 4,60	2,50 5,70	-0,90 8,70	2,30 4,20	2,40 6,00	-1,20 8,50

* - Determined by the Komar method

** - Determined by the Fersted method

This proves that when the organic reagent is immobilized and in the photoexcited state, the electron density in the luminophore molecule is redistributed. This is confirmed by the formation of a chemical bond (hydrogen, etc.) between the polar groups of the reagent and the carrier.

The obtained results will be useful in comparing the mechanism of organic reagent immobilization and metrological properties of complex formation compared to solution.

Conclusion. Examination of the analytical reactivity of metal ions by the fluorescent method is determined by the photoinduced change of the donor-acceptor properties of the functional and analytically active groups involved in the formation of a complex in the organic reagent molecule.

In the case of photoinduced excitation of existing groups, the redistribution of the electron density in the reagent molecule reflects the change in the charge of atoms forming chemical bonds with metal ions. It can be seen that the greater the value of the photoinduced changes, the greater the difference in the strength of the metal-chelate bonds formed in the complexes in the excited state.

Taking these into account, it can be concluded that the effect of photoinduced excitation leads to a significant improvement of the chemical-analytical parameters of the excited-state oxyazobirim and polyoxyflavones in the solid carrier. That is, when an organic reagent is immobilized on a solid carrier, the stiffness of the luminophore reagent molecule increases, which in turn causes an increase in the luminescence intensity.

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