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SOLVATOCHROMIC EFFECT IN SOLUTIONS OF POLY-ORTHO-TOLUIDINE

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The influence of organic solvents (dimethylformamide, tetrahydrofuran, chloroform, nitrobenzene and toluene) on the spectral characteristics of solutions in doped and non-alloyed forms of poly-ortho-toluidine (PoTi) was studied. The absorption spectra of poly-ortho-toluidine, measured in solvents of different polarity, reveal a change not only the position, but also the intensity and shape of the absorption band, depending on the polarity of the solvent. It was noticed, that different forms of PoTi cause the difference in the coloration of their solutions. Based on the study of optical spectra, temperature dependence of conductivity and the structure of PoTi, it has been founded that this conjugated polymer can be a perspective basis for sensory environments for the molecular recognition of organic solvents.

Keywords: poly-ortho-toluidine, solvatochromic effect, organic solvents, absorption spectra.

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The term “solvatochromism” is used to describe changes in the UV-visible absorption area due to changes in the polarity of the environment. When the absorption spectra were measured in solvents of different polarity, it was discovered that not only the position, but also the intensity and shape of the absorption band may vary, depending on the nature of the solvent [1–3].

The phenomenon of solvatochromism is inherent in a rather broad class of substances, in particular, some dyes, which became the basis for the use of indicator dyes (for example pyridine N-phenoxide betaine) as a spectroscopic sample of solvent polarity [2]. This dye, by virtue of its exceptionally large negative solvatochromy (i.e. the blue shift of the UV-visible absorption band with increasing polarity of the solvent), overcomes some practical limitations of other solvatochromic indicator dyes.

The solvatochromic behavior of macromolecular compounds, in particular, with the system of conjugated π -electron bonds, still not enough researched. Due to the ability of such substances easily change their electron properties, in particular the width of the bandgap and, consequently, optical absorption in the near UV and visible region [4, 5], they can be used for studying and applying for molecular identification of solvents [3].

One of the most interesting polymers with a conjugate system of π -electron bonds in terms of use in optical sensors is poly-ortho-toluidine (PoTi). In contrast to the unsubstituted polyaminoarene polyaniline, insoluble in the conductive form in any solvent [4], the presence of the electron donating methyl substituent in the PoTi molecule (Figure 1) cause the possibility of dissolving this polymer not only in the form of the base, but also in the alloyed conductive state.

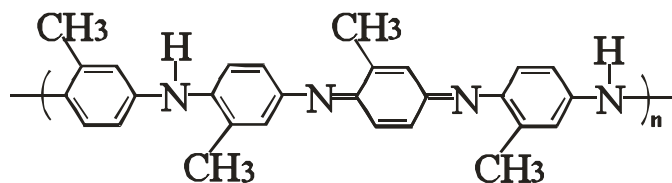


Fig. 1. Chemical structure of elementary PoTi chain

It is known that thin PoTi films show an electrochemical effect – they can change their color under the action of the applied potential. In the case of thin PoTi layers on SnO₂, the transition from colorless to yellow-green-blue-violet color is observed in the potential range $E = -0.3 \dots 1.2$ V, whereas for PAN films, similar color changes are observed in the region $E = -0.2 \dots 0.8$ V [6]. The potentials of the inclusion of the observed electrochemical transitions correspond to the potentials of the redox-maxima on the CVA curves, i.e. the oxidative-reducing reactions in the conjugated polymer chains.

According to well-known literature data, poly-ortho-toluidine can be used for constructing resistive gas sensors [7] and diode structures [8]. Instead, the possibilities of using this polymer as an optical element of the chemicals sensor, including organic solvents, are still not fully discovered.

The purpose of the work was to study the influence of organic solvents on the physical, chemical and optical properties of solutions and films of poly-ortho-toluidine, both non-alloyed and doped with proton acids.

For the synthesis of conductive polymer poly-ortho-toluidine as initial materials were used: o-toluidine – mark “cp” (chemically pure); ammonium persulfate (APS) – mark “pfa” (pure for analysis), toluenesulfonic acid (TSA) – mark “cp”. All solutions for synthesis were prepared in distilled water.

As organic solvents were used dimethylformamide (DMFA), tetrahydrofuran (THF), chloroform, nitrobenzene and toluene. Basic physical and chemical characteristics of the studied solvents are presented in Table 1 [9, 10].

Table 1

Physical-chemical parameters of organic solvents

Name	n_D^{20}	ϵ	μ	η^{25} , MPa·s	Donor number	Acceptor number
DMFA	1,4304	36,7	3,82	0,796	26,6	16,0
THF	1,4050	7,6	1,63	0,48	20,0	8,0
Chloroform	1,4455	4,806	1,15	0,542	–	23,1
Nitrobenzene	1,5562	34,82	4,0	1,838	8,1	14,8
Toluene	1,4969	2,379	4,22	0,5516	0,1	–

For synthesis, were used 0.1 M o-toluidine and APS in 0.1 M solution of TSA. The process was performed by stirring continuously the reaction mixture on a magnetic stirrer for 8 hours and left for 24 hours to complete the process. The resulted precipitate was filtered and washed on a filter with distilled water to obtain a clear filtrate. The product was dried under a dynamic vacuum at 60°C for 6 hours. It was received a self-doped form of PoTi-TSA in the form of emeraldinium salt, what was evidenced by a bright-green color.

Film samples of PoTi were obtained by chemical precipitation of a polymer on a surface of an optically-transparent glass plate (size 1x3 cm) from the same reaction mixture.

To obtain non-alloyed polymer form, the PoTi-TSA powder was washed with 5 % ammonia solution till neutral reaction. As a result was obtained non-alloyed non-conductive form of PoTi in the form of an emeraldine base.

The optical absorption spectra of solutions were received using a spectrophotometer SF-46 (working range 280–1100 nm) and a photoelectrocolorimeter KFK-3 in quartz cell (working range of wavelengths – from 400 to 900 nm).

Optical absorption of polyaminoarenes is observed in a rather wide spectral range: from UV to near-infrared [4–6]. It is known, that the main absorption bands of polyaminoarenes are caused by: electron transitions in the conjugated aromatic system (the so-called π - π^* transition), n - π^* transitions in the aminoquinoid system and the absorption of free charge carriers (polarons and bipolarons).

It was established that the absorption spectra of the doped and non-alloyed forms of PoTi have significant difference (Figure 2, *a*, *b*): for the conductive form there are wide bands in the range from 550 to 650 nm with a maximum at $\lambda=600$ nm and in the near infrared region with a maximum at 850 nm (polaron band), as for non-alloyed form, there absorption in the $\lambda>750$ nm range is practically absent (except PoTi in DMFA, because of physical-chemical parameters of DMFA and physical-chemical interaction between substances), which indicates a low concentration of charge carriers (polarons) in non-alloyed polymer. Similar changes are also observed for PoTi solutions in THF and partly for solutions in chloroform.

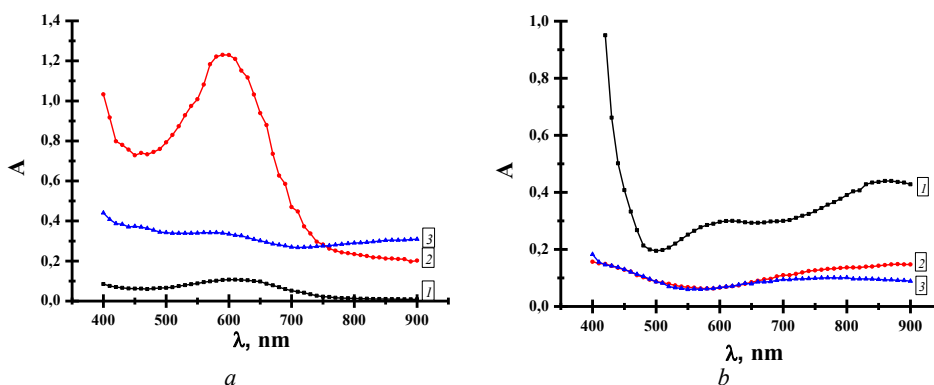


Fig. 2. Spectral dependency of optical absorption of PoTi non-alloyed solutions (*a*) and PoTi solutions doped with TSA (*b*) in DMFA (1), chloroform (2), THF (3)

It was noticed that different forms of PoTi show the difference in the coloration of their solutions: in dimethylformamide, the alloyed form has an intense blue color, and non-alloyed – violet. When PoTi is dissolved in chloroform and THF, there is an apparent solvatochromic effect: the solution in chloroform has an emerald color, and in THF it is green-brown.

Thus, the study of poly-ortho-toluidine optical spectra in solutions of organic solvents showed a significant effect of solvent nature on the optical characteristics of PoTi. This may be due to solvatochromic interaction, in which solvent polarity plays an important role. This parameter probably determines the character of the solvent influence on the optical absorption spectra and the solvation behavior of the substances [1–3], which, in turn, depends on the action of the intermolecular forces of the interaction between solvent and the dissolved substance.

The obtained results predict the possibility of using PoTi as a sensory substance for the detection of solvents in both liquid and gas phases (vapors of organic solvents).

It was investigated the effect of five organic solvents of different nature, namely DMFA, THF, chloroform, toluene and nitrobenzene on optical absorption of PoTi films, doped with TSA (Figure 3, *a-c*), in order to select sensitive elements of optical sensors, that could be used to detect and recognize gaseous substances.

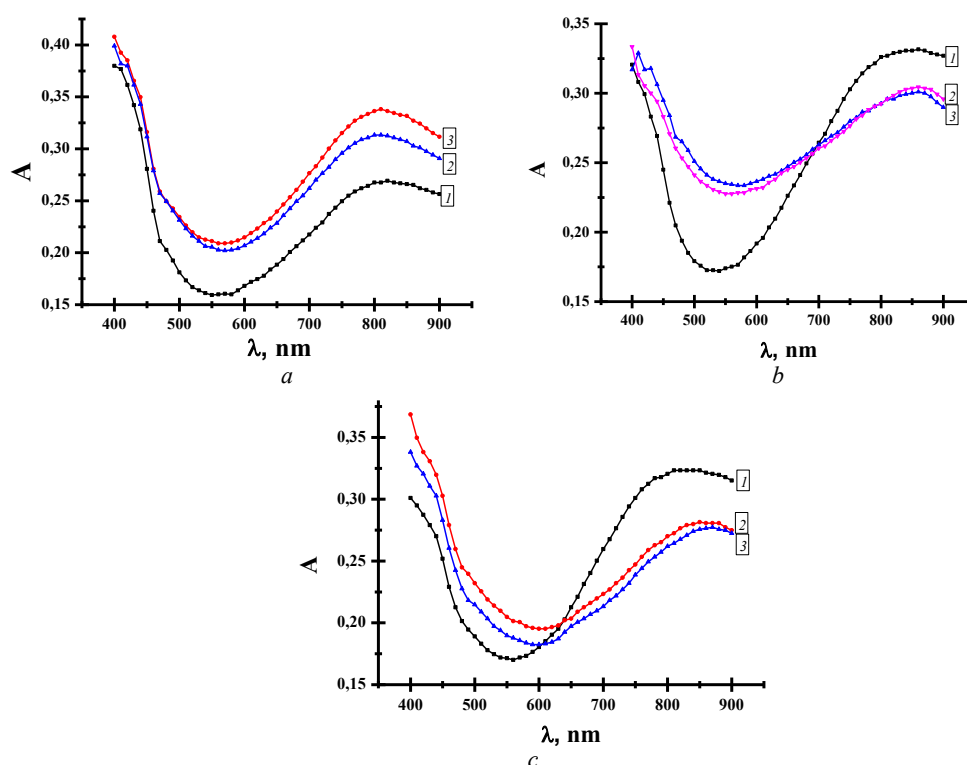


Fig. 3. Spectral curves of absorption of initial PoTi films (1) and in vapours of chloroform (*a*), DMFA (*b*), toluene (*c*) after 30 seconds (3) and 60 seconds (2) of solvent vapour action

Analyzing the graphs given above, we can see that the general form of the spectral curves of a pure film and films after chloroform action are the same along the contour. A similar tendency is observed in the spectral curves of pure film and films that were in vapours of THF. As for DMFA, it can be seen that the nature of the film curves without gas action, and those that interact with the organic solvent, are significantly different, which is probably due to the physical and chemical parameters of the solvent. Solvents related to PoTi, such as nitrobenzene and toluene, show very close similarity in character of their spectral curves.

From graphic spectral dependences, we can obtain a table of films spectral sensitivity to the action of solvents vapors (Table 2). We can see the proximity of the sensitivity values of the film to the action of nitrobenzene and toluene at the three indicated wavelengths, and in both cases the maximum sensitivity is present at 400 nm. The proximity of values can be explained by the related nature of the solvents to the nature of PoTi, which means the insignificant interaction between the solvent and the substance.

Table 2

Sensory sensitivity of PoTi films to organic solvents

Solvent	λ , nm	A_0 , r.u	A_{max} , r.u	$\Delta A/A$, %	μ , D
Chloroform	400	0.3799	0.4078	7.36	1.15
	550	0.1593	0.2111	32.56	
	800	0.2676	0.3363	25.67	
DMFA	400	0.3206	0.3170	1.12	3.82
	550	0.1739	0.2351	35.19	
	800	0.3261	0.2924	10.33	
THF	400	0.3958	0.3575	9.67	1.63
	550	0.1421	0.2197	54.18	
	800	0.3354	0.3665	9.27	
Nitrobenzene	400	0.3010	0.3686	22.45	4.0
	550	0.1713	0.2048	19.55	
	800	0.3206	0.2700	15.78	
Toluene	400	0.2388	0.2899	21.39	4.22
	550	0.1278	0.1427	11.65	
	800	0.2418	0.1931	20.14	

For further analysis of the table, we may notice that the other three solvents show far apart values, but there is also a certain dependence: at 400 nm, the film sensitivity in all three solvents is the smallest of the three selected wavelengths; at 550 nm, there is a maximum of spectral sensitivity (minimum absorption), and at 800 nm, the film sensitivity value for chloroform, DMFA and THF vapors is intermediate between values at 400 nm and 550 nm.

Consequently, on the basis of the study of organic solvents influence on the optical characteristics of the poly-ortho-toluidine solutions and films, it was found that this polymer shows a clear solvatochromic effect, the nature of which is determined by the nature of the solvent. Changing the parameters of the PoTi optical spectra under the influence of organic solvent vapors made it possible to establish that the maximum sensory sensitivity of PoTi to the vapors of organic solvents at 550 nm increases in a row chloroform, DMFA, and THF. The maximum optical response to the adsorption of related solvents, such as toluene and nitrobenzene, is observed at a lower wavelength, namely at 400 nm. Consequently, poly-ortho-toluidine can be a promising basis for sensory environments for the molecular recognition of organic solvents.

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СОЛЬВАТОХРОМНИЙ ЕФЕКТ У РОЗЧИНАХ ПОЛІОРТОТОЛУЇДИНУ

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Термін “сольватохромізм” використовується для опису змін в УФ-видимій області поглинання внаслідок зміни полярності середовища. Коли спектри поглинання виміряні в розчинниках різної полярності, виявлено, що не тільки положення, але й інтенсивність і форма смуги поглинання може змінюватися в залежності від характеру розчинника.

Малодослідженою залишається на сьогодні сольватохромна поведінка макромолекулярних сполук, зокрема, із системою спряжених π -електронних зв'язків. Одним з найбільш цікавих полімерів зі спряженою системою π -електронних зв'язків з точки зору використання в оптичних сенсорах, є полі-орто-толуїдин (ПоТі). На відміну від незаміщеного поліаміноарену поліаніліну, нерозчинного у провідній формі у жодному розчиннику, наявність електрондонорного метильного замісника в молекулі ПоТі зумовлює можливість розчинення цього полімеру не лише у формі основи, а й у легованому провідному стані.

Вивчено вплив органічних розчинників (диметилформаміду, тетрагідрофурану, хлороформу, нітробензену та толуену) на спектральні характеристики розчинів легованої і нелегованої форм поліортотолуїдину (ПоТі). З'ясовано, що спектри поглинання легованої і нелегованої форм ПоТі суттєво відрізняються: для провідної форми простежуються широкі смуги в області від 550 до 650 нм з максимумом при $\lambda=600$ нм та в ближній ІЧ області з максимумом при 850 нм (поляронна смуга), а щодо нелегованої форми, то поглинання в діапазоні $\lambda>750$ нм є слабким, що свідчить про низьку концентрацію носіїв заряду (поляронів) у нелегованому полімері. Спектри поглинання поліортотолуїдину виявляють зміну не тільки

положення, а й інтенсивності і форми смуги поглинання залежно від полярності розчинника. Сенсорна чутливість ПоТі до парів органічних розчинників при 550 нм зростає в ряді хлороформ, ДМФА, ТГФ. Максимальний оптичний відклик на адсорбцію толуену та нітробензену простежується при 400 нм.

Помічено, що різні форми ПоТі зумовлюють відмінність у забарвленні їх розчинів. На основі вивчення оптичних спектрів, температурної залежності провідності та структури ПоТі з'ясовано, що спряжений полімер може бути перспективною основою сенсорних середовищ для молекулярного розпізнавання органічних розчинників.

Ключові слова: поліортотолуїдин, сольваохромний ефект, органічний розчинник, зміна забарвлення, спектри поглинання.

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