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Solovyova N. V<sup>1</sup>., Kuznetsova T. Yu<sup>2</sup>., Kurys Yu.O.<sup>2</sup>  
**QUANTUM CHEMICAL MODELING OF ANTI-RADICAL ACTIVITY OF  
GLUTATHIONE INTERACTING WITH FREE RADICALS**

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КВАНТОВОХІМІЧНЕ МОДЕЛЮВАННЯ АНТИРАДИКАЛЬНОЇ  
АКТИВНОСТІ ГЛУТАТІОНУ ПРИ ВЗАЄМОДІЇ З ВІЛЬНИМИ  
РАДИКАЛАМИ.**

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*Abstract. Following the analysis of the results of quantum chemical simulation of interaction between a GSH molecule and oxygen radicals •OH and •OO<sup>•</sup>, it was found that it takes place through the acid-base mechanism, where GSH acts as a base towards •OH, and as an acid towards •OO<sup>•</sup>.*

*Key words: glutathione, hydroxyl radical, free radicals.*

*Анотація. На основі аналізу результатів квантовохімічного моделювання взаємодії молекули GSH з радикалами кисню •OH і •OO<sup>•</sup> встановлено, що вона відбувається за кислотно-основним механізмом, причому GSH по відношенню до •OH виступає як основа, а по відношенню до •OO<sup>•</sup> – як кислота.*

*Ключові слова: глутатіон, гідроксил-радикал, вільні радикали.*

To decrease the negative effect of free oxygen radicals on a living organism practical medicine widely uses endogenous oxidants since they take part in the system of human organism protection from the aggressive action of free radicals, for example [1]. The lack of systematic investigations, especially at the molecular level, of antiradical activity of various antioxidants under their interaction with free radicals in biological systems not only determines availability of contradictory estimates in interpretation of the results of experimental regularities [2,3] but also creates difficulties in development of general ideas concerning the mechanisms of interaction of antioxidants with free radicals and purposeful approach to the control of these processes which are applied to medical practice [4]. The above said actualizes studying the antiradical activity of various antioxidants.

Interaction of antioxidants with free radicals is determined by the influence of the great number of various interrelated kinetic processes which stabilization is rather problematic even in the experiment conditions. Thus, it seem urgent to study efficiency of the influence of endogenous antioxidants by simulating the mechanism of their interaction with free radicals by the methods of quantum chemistry in combination with experimental ones, in particular, with electrochemical method that allows not only obtaining the substantiation of the positive effect of using the antioxidants but also establishing potential significance of these substances as medical remedies.

The work objective was investigation of antiradical properties of endogenous



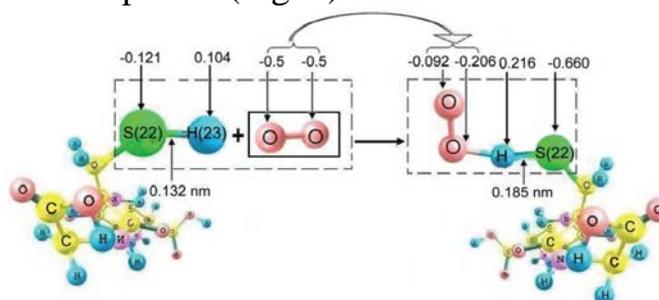
antioxidant glutathione ( $C_{10}H_{17}N_3O_6S$ ) by simulation of the mechanism of its interaction with free radicals (hydroxyl radical ( $\bullet OH$ ) and superoxide-anion-radical ( $\bullet OO^-$ )).

**Materials and methods.** Human organism contains a nonenzymatic antioxidant system of cells protection from the influence of free radicals. The compounds with various properties appear as the system components. One of such compounds is glutathione (GSH) [5] synthesized in each organism cell, but antiradical mechanism of its interaction with active oxygen forms at the microscopic level is not completely understood, except for certain results of macroscopic medical [6] and electrochemical [7] investigations which are unfortunately of phenomenological character and do not give a purposeful approach to such processes control.

One of the key active forms of oxygen is  $\bullet OO^-$ , which is formed when adding one electron to oxygen molecule in the basic state and can be a source of  $\bullet OH$  formation in human organism; it may be the strongest oxidizer among free oxygen radicals, thus  $\bullet OH$  and  $\bullet OO^-$  can exist simultaneously and be used for studying their interaction with glutathione for simulation of its antioxidant activity. The above said has determined the choice of investigation objects.

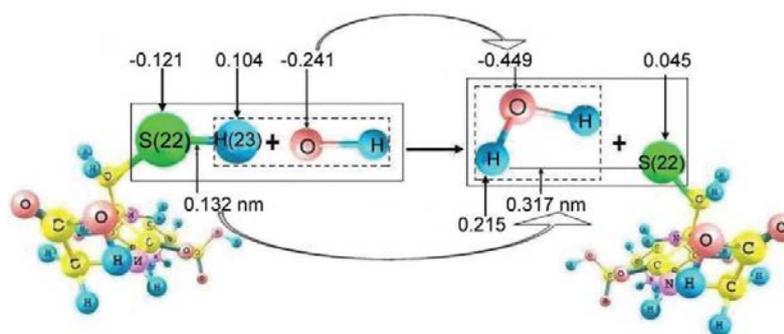
Theoretical study of the mechanism of GSH interaction with  $\bullet OO^-$  and  $\bullet OH$  is performed with the help of the program module GAMESS (version of March 27, 2007) and program module Firefly 8 by the most modern unempirical quantum chemical method in the basis 6-31G\*\* [8].

**Results and Discussion.** When GSH molecules interact with one  $\bullet OO^-$  at the point of global minimum of full interaction energy there occurs redistribution of the charge of  $702e$  with  $\bullet OO^-$  to glutathione molecule through the atom of hydrogen H(23), indicating a possibility of efficient interaction of  $\bullet OO^-$  with GSH, with probable formation of stable complexes (Fig. 1).



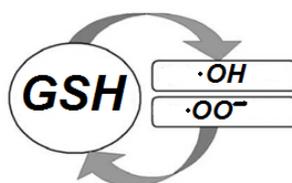
**Fig. 1. Scheme of interaction of GSH molecule with  $\bullet OO^-$  (arrows point to charges on atoms according to Lyovdin)**

Under analogous interaction with one  $\bullet OH$ , on the contrary, there occurs an increase of electron density on oxygen atom of hydroxyl radical by  $0.208e$ , as a result the bond length S(22) - H(23) increases in glutathione molecule from 0.132 to 0.317 nm that points to the possibility of this atom breaking off GSH molecule and its further attachment to  $\bullet OH$  with formation of water molecule (Fig. 2).



**Fig. 2. Scheme of interaction of GSH molecule with  $\bullet\text{OH}$  (arrows point to charges on atoms according to Lyovdin)**

Thus, the interaction of a molecule of studied antioxidant with free oxygen radicals initiates redistribution of electron density in the glutathione molecule in different directions (Fig. 3) [9].



**Fig. 3. Scheme of redistribution of electron density of GSH molecule as a result of interaction with radicals**

To bring the results of quantum-chemical modeling closer to real conditions of interaction of the antioxidant molecule with  $\bullet\text{OH}$  and  $\bullet\text{OO}^-$  in human organism the authors performed simulation of water medium influence on the mechanism of GSH molecule interaction with free oxygen radicals in terms of Firefly 8 program. An analysis of results obtained has shown that the mechanism of electron density redistribution with allowance for water medium influence with dielectric constant  $\epsilon=78.355$  at  $T = 298$  K within the continual model of the solvent PCM for these interactions remains almost unchanged, that is confirmed by comparison of charges distribution ( $q$ ) according to Lyovdin, as well as the values of activation energy ( $E_a$ ) of the reactions of GSH molecule interaction with  $\bullet\text{OH}$  and  $\bullet\text{OO}^-$  (Table 1).

**Table 1**

**Interaction of GSH with free radicals**

Interaction		q, a.u.			$E_a$ , kJ/mol	
		S(22)	H(23)	O*		
GSH	$\bullet\text{OH}$	Without PCM	0.045	0.215	-0.449	101
		PCM	0.036	0.222	-0.465	100
	$\bullet\text{OO}^-$	Without PCM	-0.660	0.216	-0.206	17
		PCM	-0.731	0.211	-0.187	7

\*Indicated atom of radical which directly interacts with atom H(23) of GSH molecule.

Thus, the quantum chemical simulation of glutathione molecule interaction with  $\bullet\text{OH}$  and  $\bullet\text{OO}^-$  has shown that, allowance for the influence of water medium do not practically influence redistribution of electron density of glutathione molecule and permit concluding that the studied reaction proceeds following the acid-base mecha-



nism, under these conditions GSH appears as acid in respect of  $\bullet\text{OH}$  in accordance with the set scheme (Fig. 3).

Thus, the mechanism of glutathione molecule interaction with  $\bullet\text{OH}$  and  $\bullet\text{OO}^\cdot$  has been investigated.

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**АДСОРБЦИЯ ОРГАНИЧЕСКИХ ВЕЩЕСТВ НА НЕПОРИСТЫХ  
УГЛЕРОДНЫХ СОРБЕНТАХ***Национальный университет биоресурсов и природопользования Украины, Киев,  
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*Abstract. The adsorption properties of nonporous carbon sorbents towards organic substances of various types were compared. The studies we performed have revealed that acetylene carbon black is the most effective for removal of dyes such as methylene blue from low concentrated aqueous solutions.*

*Key words: adsorption, surfactant, dye, sorbent.*

*Аннотация. Проведено сравнение адсорбционных свойств непористых углеродных сорбентов по отношению к органическим веществам различных типов. Проведенные исследования показали, что ацетиленовая сажа является наиболее эффективным сорбентом для удаления красителей типа метиленового голубого из низкоконцентрированных водных растворов.*

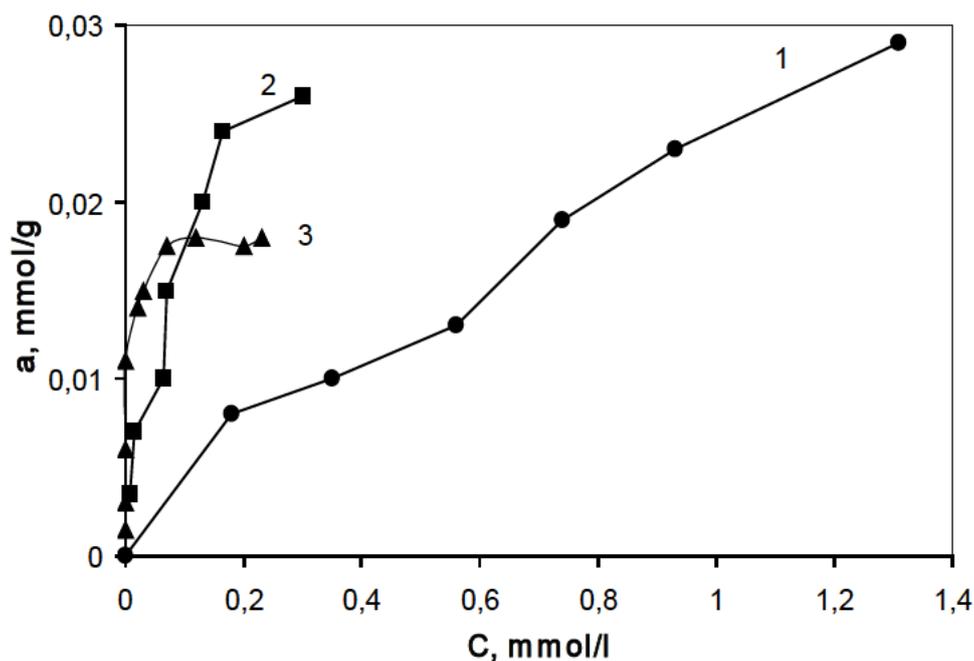
*Ключевые слова: адсорбция, поверхностно-активное вещество, краситель, сорбент.*

The aim of this work was to study the adsorption properties of thermo-expanded graphite (TEG) that was obtained by thermal treatment of graphite crystallite modification. Simple organic compound such p-nitroaniline, surfactant such as polyoxyethylated alkyl phenol (OP-10) and dye such as methylene blue were chosen as adsorbates. Adsorption isotherms were obtained by means of standard protocol. The equilibrium concentrations of adsorbates were determined by spectrophotometric method.

The adsorption isotherms of used adsorbates are shown in Fig.1.

As can be seen in Fig. 1, the adsorption curves differ essentially for all three adsorbates over the studied concentration range. It should be noted that TEG possesses a low adsorption capacity towards p-nitroanilin while a high adsorption capacity towards methylene blue at low equilibrium concentration of solution. Adsorption values of both surfactant and dye are much higher compare to that of p-nitroaniline. The adsorption isotherms for OP-10 and methylene blue tend to saturation at adsorption values of 0,026 mmol/g and 0,018 mol/g respectively, while the adsorption of p-nitroanilin increases almost linearly.

From analytical treatment of initial regions of the curves, it can be concluded that the energy of adsorbate-adsorbent interactions decreases in a row: methylene blue-> OP-10-> p-nitroanilin. Changes in differential free molar energy of adsorption for these adsorbates calculated accordingly to [1] are presented in Table.



**Figure 1. Adsorption isotherms of p-nitroaniline (1), OP-10 (2) and methylene blue (3)**

**Table**

**Change in differential free molar energy of adsorption ( $-\Delta F_a^\circ$ ) organic compounds on thermoexpanded graphite**

Organic compound	$-\Delta F_a^\circ$ , kDg/mol
p-nitroaniline	8,6
OP-10	12,1
methylene blue dye	29,9

Obviously, in this case the adsorption is determined by chemical structure of adsorbate as well as its ability to association. The presence of three benzyl rings in methylene blue molecule as well dye's ability to form associates (dimers) in relatively low concentrated solutions resulting in the most efficient adsorption of this dye on TEG.

Adsorption isotherms of used substances on other carbon sorbents of nonporous structure such as graphite, graphite carbon black and acetylene carbon black were also obtained for comparison.

Adsorption isotherms of methylene blue on graphite, thermoexpanded graphite and acetylene carbon black are presented on Fig. 2.

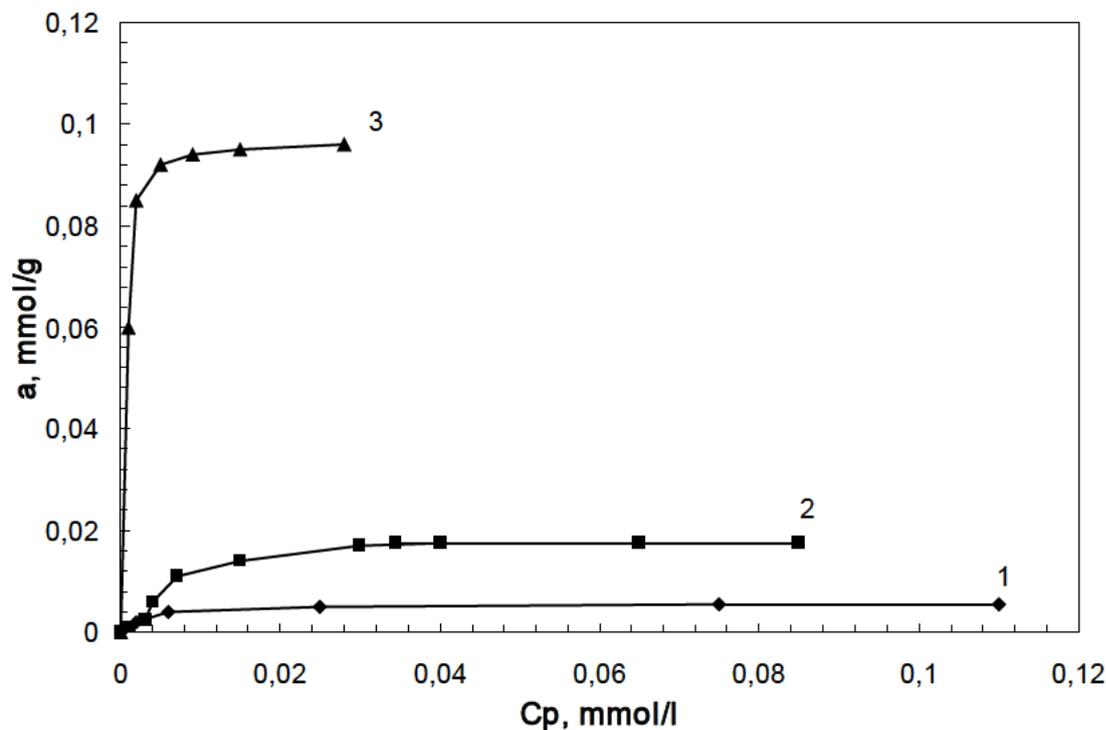
These data have shown the adsorption values are in a direct correlation with the specific surface areas of the sorbents because a degree of surface homogeneity of the sorbents is almost identical.

It was performed a comparison of adsorption properties of TEG with those for other carbon sorbents of porous and nonporous structure. Analysis of available literature data on adsorption of adsorbates under study on carbon sorbents of porous



structure (activated carbons) [2,3] have shown that those adsorption capacities substantially higher comparing with TEG.

To summarize, the studies we performed have revealed that acetylene carbon black is the most effective for removal of dyes such as methylene blue from low concentrated aqueous solutions.



**Figure 2. Adsorption isotherms of methylene blue on graphite(1), thermoexpanded graphite (2) and acetylene carbon black (3).**

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**STATE OF WATER AND THERMODYNAMIC CHARACTERISTICS  
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Кочкодан О.Д., Кармазина Т.В.

**СОСТОЯНИЕ ВОДЫ И ТЕРМОДИНАМИЧЕСКИЕ ХАРАКТЕРИСТИКИ  
ВОДНЫХ РАСТВОРОВ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ***Национальный университет биоресурсов и природопользования Украины,  
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*Abstract. For nonionic and cationic surfactants the quantitative characteristics of thermodynamic process of surfactant's micelle formation were determined and analyzed as a measure of interaction between the molecules of a surfactant and water. It was shown that both the characteristics of molecularly-dynamic state and thermodynamic functions largely depends on concentration conditions.*

*Key words: micelle formation, surfactants, thermodynamic functions, water structure.*

*Аннотация. Определены и проанализированы количественные характеристики термодинамики мицеллообразования на примере неионного и катионного ПАВ как меры взаимодействия между собой молекул воды и ПАВ. Показано, что значения как характеристик молекулярно-динамического состояния, так и термодинамических функций существенно зависят от концентрационных условий.*

*Ключевые слова: мицеллообразование, поверхностно-активные вещества, термодинамические функции, структура воды.*

The goal of this study was to establish the correlation between the alteration of molecularly dynamic parameters of water under the influence of surfactants and thermodynamic characteristics of water–surfactant system. The molecularly–dynamic condition of water was characterized by such parameters as total diffusion coefficient  $D$ ; a coefficient  $D_f$  reflecting the contribution of single particle movement into the total diffusion coefficient and which corresponds to the jumping mechanism of diffusion; a coefficient  $D_l$  describing an input of collective motion to total diffusion coefficient and which corresponds to the mechanism of continuous diffusion;  $\tau_0$  – time life of water molecules at oscillation around the equilibrium center [1]. The qualitative estimation and interpretation of the alteration of molecularly dynamic characteristics under the influence of nonionic and cationic surfactants obtained by means of neutrons quasi-elastic scattering method were presented elsewhere [2,3].

Polyoxyethylated octylphenol Triton X-100 was chosen as nonionic surfactant. Its critical concentration of micelle forming (CCM) is 0,24 mmol/l. Dodecyl and hexadecylpyridine bromides were used as cationic surfactants. These surfactants were repeatedly recrystallized from ethanol to get constant values of CCM of 11,2 and 0,6 mmol/l respectively.



An evaluation of thermodynamic parameters of surfactants micelloforming was done using the temperature dependence of CCM.

It was considered in this work which alterations of molecularly-dynamic condition of water under surfactant presence are associated with enthalpy and entropy changes over the wide concentration range, namely before CCM, at CCM point and above CCM.

Previously it was found that insignificant addition of Triton X-100 as well as dodecyl and hexadecylpyridine bromides to water leads to an decrease in total diffusion coefficient  $\mathbf{D}$  as well as to a decrease in coefficient  $\mathbf{D}_f$  and  $\tau_0$  value [2,3]. It seems that alteration of system's characteristics at micro level should have an effect on macroscopic characteristics of system.

The performed analysis has shown that at low surfactant's concentration in solution the alteration of thermodynamic characteristics correlate with change of total diffusion coefficient  $\mathbf{D}$ . It can be assumed that a decrease of entropy  $\Delta S$  of water molecules as the result of functional interactions and structuration in surfactants solutions will far exceeds an increase in  $\Delta S$  due to disturbing of initial water structure. At micro level this effect is characterized by decreasing of diffusion coefficients  $\mathbf{D}$  and  $\mathbf{D}_f$  in going from pure water to aqueous solutions of surfactants with concentration of 0,005 – 0,15 CCM.

Change of enthalpy  $\Delta H$  in surfactant solution depends on ratio of energy of interaction both hydrophilic and hydrophobic parts of surfactant molecule with solvent. The enthalpy of surfactant dissolving is positive predominatingly. An increase in  $\mathbf{D}_f$  coefficient [2] in going from pure water to solution with concentration 0,05-0,15 CCM corresponds to positive change of the system's enthalpy.

With increasing of surfactant concentration, a decrease in the entropy of the system due to water structuration leads to association of hydrocarbon chains. As result, the initial structuration of water is disturbed while the energy of the system decrease and the entropy grows. When concentration of nonionic surfactant exceeds 0,25 CCM the total diffusion coefficient  $\mathbf{D}$  as well as coefficient  $\mathbf{D}_f$  both also increase. For cationic surfactant an increase in  $\mathbf{D}_f$  occurs at higher concentrations ( $\geq 1$ CCM) whereas the coefficient  $\mathbf{D}$  continuesly decreases over the studied range of concentrations. Such a difference in alteration of diffusive characteristics of molecularly dynamic conditions of water one can be explained by different effects of cationic and nonionic surfactants on water.

The analytical treatment of obtained data permit the assumption that exactly the beginning of association process in solutions leads to alteration of diffusion coefficients of water molecules has an opposite behaviour when the surfactant concentration tends to increase. The regularities of this alteration are different for cationic and anionic surfactants.

To estimate the contribution of enthalpy and entropy changes in micelloforming the enthalpy-entropy compensation of micelloforming and compensatory temperature those characterize the chemical and solvation parts of the micelloforming process were calculated (Table) [4]. As can be seen from Table those values were higher for Triton X-100. This indicate the stronger effect both associative and solvation



interactions in the system with nonionic surfactant [5].

**Table 1**

**Data on enthalpy-entropy correlation at Triton X-100 and dodecylpyridine bromide (DDPB) micelloforming.**

Surfactant	T, K	CCM, mol/l $\times 10^5$	$\Delta H_m$ , kJ/mol	$\Delta S_m$ , kJ/mol	$-\Delta G_m$ , kJ/mol	$-\Delta H_m^*$ , kJ/mol	$T_c$ , K
TX-100	285	26,0	6,4	124,6	29,1	31,0	300
	291	24,0	6,9	124,6	29,9		
	295	23,5	7,3	127,8	30,4		
	310	20,0	8,8	132,5	32,3		
	328	16,0	10,8	139,1	34,8		
DDPB	288	14,7	17,5	130,0	19,8	24,0	270
	298	14,6	12,1	109,5	20,5		
	318	17,5	4,5	81,3	21,3		

The performed studies have shown that dynamic characteristics of aqueous surfactants solutions have been the qualitative images of ordered-reordered processes at water-surfactant interactions. Single particles motion of water molecules at macro level correlates with entropy change. Change of enthalpy correlates with dynamic of cooperative motion. It was found that the alteration both dynamic and thermodynamic characteristics were essentially dependent on concentration conditions.

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**Timofeev A. L., Podkorytov A. L., Shtin S. A., Maltseva V. O.**  
**SOLID-STATE SYNTHESIS AND PROPERTIES OF  $Ni_{4-x}Zn_xNb_2O_9$**   
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*Abstract. This paper reports the solid-state synthesis, characterization, and physicochemical properties of zinc-containing  $Ni_4Nb_2O_9$  based nickel niobates with the general formula  $Ni_{4-x}Zn_xNb_2O_9$  ( $x= 0; 0.1; 0.3; 0.5; 0.75; 1.0$ ). The materials have been identified by X-ray diffraction. We have determined the particle size composition of powder samples, assessed their chemical stability in acid media and measured their electrical conductivity as a function of temperature.*

*Key words: niobates, solid solutions, chemical stability, x-ray diffraction, conductivity, ionometry*

*Аннотация. Работа посвящена твердофазному синтезу, аттестации и исследованию физико-химических свойств цинксодержащих ниобатов никеля на основе  $Ni_4Nb_2O_9$  состава  $Ni_{4-x}Zn_xNb_2O_9$  ( $x= 0; 0.1; 0.3; 0.5; 0.75; 1.0$ ). Полученные образцы аттестованы методом РФА. Определен гранулометрический состав порошкообразных образцов, изучена химическая устойчивость образцов в кислых средах и исследованы температурные зависимости электропроводности.*

*Ключевые слова: ниобаты, твёрдые растворы, химическая устойчивость, рентгенофазовый анализ, электропроводность, ионометрия*

### **Introduction**

Ceramics continue to play a marked role among modern materials. Ceramic products possess a wide range of physicochemical properties, are fabricated from readily available raw materials, offer multifunctionality, and are relatively inexpensive to manufacture [1]. In addition to traditional applications of ceramic materials, recent years have seen the development of a new direction in the use of ceramics: as electrode-active membrane materials for ion-selective electrodes (ISEs) [2–6]. The possibility of doping host compounds with heavy-metal ions allows one to obtain modified materials capable of  $M_{solid}^{z+} \rightleftharpoons M_{aq.sol}^{z+}$  exchange, resulting in a potential jump across the interface [5, 6].

In this paper, we report the synthesis and properties of zinc-doped nickel niobate,  $Ni_4Nb_2O_9$ , with a crystal structure made up of octahedral blocks [7].

### **The main text**

The synthesis technique of  $Ni_{4-x}Zn_xNb_2O_9$  described in [8]. The phase composition of the samples was determined by X-ray diffraction on a Equinox-3000 (Inel, France) powder diffractometer (CuK $\alpha$  radiation).

The chemical stability of the samples was assessed by treating them with a 0.1



M HNO<sub>3</sub> solution for various lengths of time (from 2 h to several weeks).

Since the particle size of powders may influence the quality of the materials produced from them, including ISE membranes, we assessed the particle size composition of powder samples using a Shimadzu SALD-7101 particle size laser analyzer.

The electrical conductivity of the samples was measured as a function of temperature by an RCL meter ( $f = 1$  kHz) in the temperature range 400–1200°C as described previously [6].

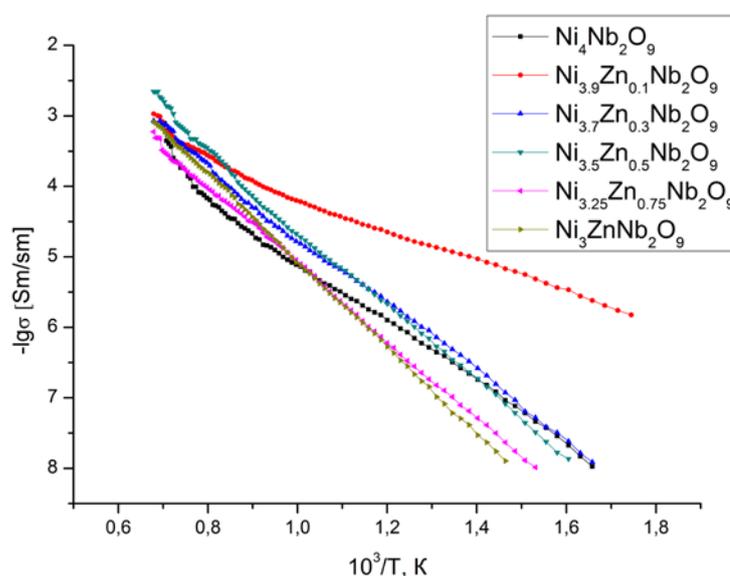
### Results and Discussions

No single-phase samples were obtained by annealing at 1300°C. Additional annealing at 1350°C yielded single-phase samples, isostructural with the host phase Ni<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub> [7]. Parameters of elementary rhombic cell were determined. As expected, parameters of elementary crystal cell changes slightly with increasing concentration of dopant and is:  $a=5.045\pm 0.012$  Å,  $b=8.764\pm 0.023$  Å,  $c=14.288\pm 0.019$  Å.

Chemical analysis showed that, after holding in a HNO<sub>3</sub> solution for 24 h, nickel ions were detected by none of the known qualitative reactions [9]. After holding for a week, the solution contained trace levels of nickel ions.

All of the samples were found to be polydisperse, with the predominant particle size in the range 30 to 90 μm. The particle size distribution had a maximum at 50 μm. The particle size distribution has a nearly Gaussian shape.

That all of the Ni<sub>4-x</sub>Zn<sub>x</sub>Nb<sub>2</sub>O<sub>9</sub> samples are close in particle size will allow one, in subsequent tests of these materials as electrode-active materials, to rule out the influence of the size factor on the electrochemical characteristics of new ISEs.



**Fig. 2 Arrhenius plots of electrical conductivity for Ni<sub>4-x</sub>Zn<sub>x</sub>Nb<sub>2</sub>O<sub>9</sub> samples**

Figure 2 shows the Arrhenius plots of electrical conductivity for the Ni<sub>4-x</sub>Zn<sub>x</sub>Nb<sub>2</sub>O<sub>9</sub> samples. The plots demonstrate semiconducting behavior of conductivity, typical of niobates. Like Ni<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub>, the zinc-containing samples have mixed, ionic–electronic conductivity [5, 6]. From the electrical conductivity data, we evaluated the activation energy for conduction that is 1.04 – 1.24 eV at  $T > 900^\circ\text{C}$  and



0.80 – 1.20 eV at  $T < 900^\circ\text{C}$ . The fact that all of the samples are close in activation energy strongly suggests that the doped niobates have the same conduction mechanism, which is probably similar to that in  $\text{Ni}_4\text{Nb}_2\text{O}_9$  [5].

We have determined the main electrochemical characteristics of ISEs such as: linear region and the slope of the main electrode function (MEF), working range of pH and response time (Table 1).

**Table 1**

**The main electrochemical characteristics of ISEs**

Electrode-active material	Polymer matrix	Linear region of MEF, mole/dm <sup>3</sup>	The slope of the MEF, mV/pNi	Working range pH
$\text{Ni}_4\text{Nb}_2\text{O}_9$	PVC	$10^{-4} - 10^{-1}$	27.5	2.2 – 4.0
	PMMA	$10^{-4} - 10^{-1}$	29.3	2.1 – 4.1
	PS	$10^{-5} - 10^{-1}$	28.1	2.3 – 4.0
$\text{Ni}_{3.9}\text{Zn}_{0.1}\text{Nb}_2\text{O}_9$	PS	$10^{-4} - 10^{-1}$	20.5	3.5 – 4.5
$\text{Ni}_3\text{ZnNb}_2\text{O}_9$	PVC	$10^{-4} - 10^{-1}$	30.4	2.5 – 3.5
	PMMA	$10^{-4} - 10^{-1}$	24.4	3.0 – 4.0

### Summary and Conclusions

We have prepared and characterized new zinc-containing nickel niobates  $\text{Ni}_{4-x}\text{Zn}_x\text{Nb}_2\text{O}_9$ . The materials have been shown to be single-phase by X-ray diffraction. Their stability in acid media has been assessed by a variety of chemical and physico-chemical techniques, and the main parameters of their electrical conductivity have been determined. Showed principal availability of application our ISEs in analytical ionometry.

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