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USE OF COPPER PHTALOCYANINE ADSORPTION LAYER FOR SUBSTRACTION OF SPIRITS IN GASOCHROMATOGRAPHIC ANALYSIS

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The chromatographic properties of silica gel with copper phtalocyanine surface layer are investigated. Parameters of hydrocarbons and oxygen-containing organic substances retention are different for the layers obtained by sorption method and chemical synthesis that is connected with structure of complex on the carrier surface. Sorbents are used to analyse mixtures of oxygen-containing compounds and to subtract spirits at group analysis of oxygen-containing organic substances.

Usage of metal complexes as chromatographic material modifiers permits to change the sorbent properties systematically with a view to improve the quality of analytical division or sorption concentration according to concrete problem of a researcher [1–3]. The first works in this field are connected with using silver salts [4], carbonyl and β-diketonate complexes of metals [5, 6]. Development of chemical analysis tasks results in complication of complex structures, and most of modern researches are devoted to application of chirasils, calyxorens, nematic liquid crystals, and fullirens with internal metal ion [7–10] as absorption layer and binary phase components in gas chromatography. A large number of already known inner-complex compounds provides variation of sorbent and combined immovable phase in the wide range due to change of nature of ligands, metals and carrier surface properties [11–16].

Usage of complex compounds in composition of sorption materials in gas chromatography has a number of limitations connected with their solubility in immovable phases, thermal stability and strength of fixation with sorbent surface [17, 18]. Phthalocyanine complexes are efficiently distinguished by significant thermal stability and extremely low solubility, which permits to use their adsorptive layers both in catalysis and in chromatography to separate and sample preparation of wide range of substances [19–21].

In the present work the difference in gas-chromatographic properties of copper phthalocyanine layer (CuPhC) obtained by technique of adsorption application of prepared complex and chemical synthesis directly onto Silipor 075 silica gel surface is shown.

Experiment

Surface-grafted CuPhC layer is formed by the method of molecular stratifying [22]. At the first stage copper chloride (II) of ethanol solution to the extent of 10 of mas. % is applied on Silipor 075 at 20 °C. After evaporation of solvent the sorbent is heated at 160 °C during 4 h to fasten ions on the surface. To remove non-immobilized copper ions washing is done sequentially 3–4 times by portions of 25 ml ethanol. Completeness of removing copper ion is controlled by quality reaction with 5 % solution of KOH. CuPhC formation reaction is performed by technique [23] using the obtained sorbent with surface-grafted layer of copper chloride instead of copper salt. The part of fastened complex defined by the method of polarography at ПУ-1 polarograph amounts 3,4 mas. %. Formation on CuPhC carrier surface is verified by comparison of infrared spectrum of synthesized complex and standard CuPhC at Specol-21 spectrophotometer, fig. 1.
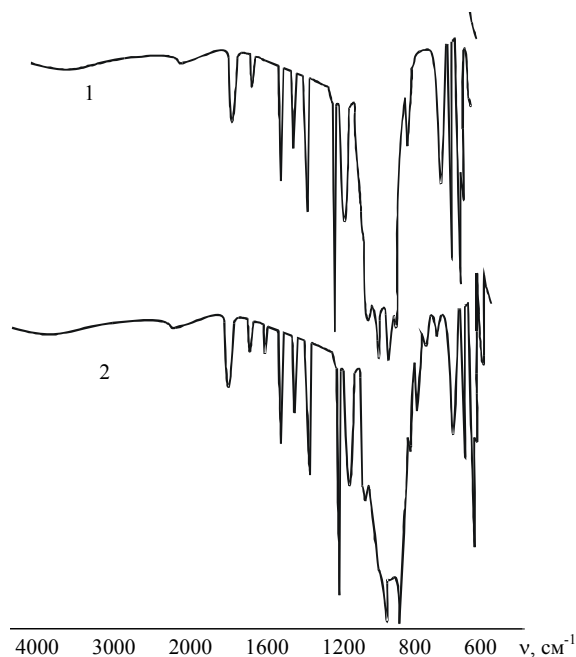

Fig. 1. *Infra-red spectra of copper phthalocyanine on Silipor 075 surface: 1) synthesized and 2) adsorptive*

Sorbent infra-red spectra allow to characterise the surface of chemically modified Silipor as one covered by uniform grafted layer, which is evident from the absence of stripes in the range 3700...3000 sm^{-1}, corresponding to stretching vibrations of -O-H bonds in silanol group. Infra-red spectra of CuPhC absorption CuPhC are reproducible for both techniques of sorbent preparation.

For adsorption application on surface Silipor 075 and CuPhC to the extent of 3,4 % of carrier mass is placed into a glass reactor presenting a tube limited at the top and at the bottom by glass filters to leak helium flow with velocity 3 sm^3/min and prevent from substance burst. The reactor is placed in thermostat at 160 °C. Under such conditions there appear intermolecular inte-

ractions between hydroxyl groups on sorbent surface and complex, they result in CuPhC fastening [22].

Thermal stability of sorbents is investigated by derivatogrph Q-15 («Paulik, Paulik and Erdey», Germany) at temperature 20...800 °C with aluminium oxide as a check standard. Samples have been preliminary dried in desiccator during 72 h to remove sorbed water and solvent leavings.

Chromatographic analysis is carried out by «Chrom-5» gas chromatograph with flame-ionization detector, glass columns of 1,2 м×3 мм. Velocity of gas-carrier (helium) amounts 20 sm³/min. Before the experiment the columns have been conditioned at 200 °C during 4 h in helium flow. The experiment is carried out in the temperature range 10...170 °C.

In the work the reagents of «х.ч.» and «ч.д.а.» qualification are used.

Results and discussion

CuPhC surface layer possesses high stability as complex destruction takes place at the temperature higher than 350 °C and corresponds to calculated loss of CuPhC mass, which is supported by formation of just this complex. In the temperature range up to 300 °C elimination of adsorbed water is observed, fig. 2.
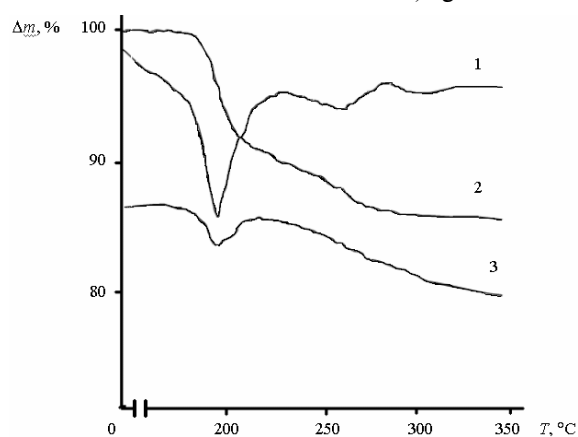

Рис. 2 *CuPhC thermogram, synthesised on the surface of Silipor 075 silica gel: 1) DTG − velocity of sample mass change; 2) TG − sample mass change; 3) DTA − sample energy change*

On DTA function endothermal effect is observed with maximum at 230 °C, which coincides with heat effect on DTA, and corresponds to elimination of physically adsorbed water. Endothermal effects specific for CuPhC decomposition, at temperature up to 350 °C are not observed.

To estimate the polarity of sorbents obtained the chromatographic properties is compared and isothermal numbers of sample compound retention, table 1:

$$I_a^s = 100N + 100n\frac{(\lg t_{R,a}^{/} - \lg t_{R,N}^{/})}{(\lg t_{N-n}^{/} - \lg t_{R,N}^{/})},$$

where N − the number of carbon atoms in n-alkane with a shorter chain; n − difference in the number of carbon atoms between two alkanes used as standards; I_a^s − index

of a substance retention on s phase; $t^{/}$ − corrected time of test substance and n-alkane retention.

Table 1. *Indexes of Rorschneider test compounds retention on modified Silipor 075 at 160 °C*

Way of modification	Benzol	Ethanol	Buta-none-2	Nitro-propane	He-xene-1	Pyridine
−	775	1157	875	876	602	1370
Adsorption	578	786	867	864	617	1338
Chemical	780	−	996	817	635	1210

Investigation of sorbent chromatographic properties is carried out using Rorschneider test compounds and it sows that retention of organic substances on modified surface sufficiently depends on technique of surface layer formation. In comparison with initial Silipor 075 time of organic substance eluting decreases which is connected with lowering porosity and decrease of carrier surface.

Chemical CuPhC draft to silip phthalocyanine results in lowering polarity to all test compounds. In this case sorption occurs mainly on a dense layer of phthalocyanine molecules. Owing to great Van der Waals forces among plane-oriented molecules the concentration of force centres on the surface is less than for thermally modified carriers and the time of sorbent retention for them is less too (table 2). Durability of test compound eluting depends on specific surface and availability of metal ion for contruction of donor-acceptor bonds with electron-donor fragments of sorbate molecules.

Table 2. *Retention factor (f_r) and sorption heat ($\Delta H°$, kJ/mole) of organic substances on Silipor 075: 1) initial; 2) modified by absorption method and 3) chemical synthesis at 140 °C*

Sorbate	1		2		3	
	f_r	$\Delta H°$	f_r	$\Delta H°$	f_r	$\Delta H°$
Methanol	11,39	10,2	12,41	7,3	−	−
Ethanol	13,60	12,0	14,11	8,5	−	−
н-Propanol	16,15	13,4	18,02	9,6	−	−
н-Butanol	18,53	14,4	21,08	11,7	−	−
н-Pentanol	26,86	11,1	30,77	8,5	−	−
Hexene-1	16,66	17,7	18,53	14,9	18,53	14,0
Heptene-1	28,05	12,1	32,13	9,5	32,81	11,4
Octene-1	29,92	14,0	34,34	10,8	34,68	13,2
Benzol	12,58	11,8	14,11	9,2	13,77	10,7
Methyl benzol	14,45	13,4	15,81	11,1	15,64	12,0
1,2-Xylene	15,81	15,4	16,32	13,2	16,66	13,1
1,3,5-Trimethyl benzol	16,66	15,8	18,87	13,8	19,55	13,8
Propanon-2	7,14	8,9	7,48	8,1	11,90	7,8
Bytanon-2	10,88	12,3	9,86	9,4	18,87	10,1
Pentanon-2	14,28	17,7	12,07	11,4	24,99	12,5
Ethanal	7,99	9,2	13,26	11,1	10,54	12,2
Propanal	10,03	10,7	15,3	13,3	13,60	15,3
Butanal	12,41	13,9	20,74	17,3	15,47	18,5
Nitropropane	32,47	16,1	36,55	12,4	37,23	15,1
Pyridine	34,19	16,6	37,91	13,9	39,14	16,1

Adsorption application of CuPhC to Silipor 075 increases polarity to aromatics, spirits, and ketones, which is perhaps connected with plane orientation of complex molecules that is possible due to significant specific surface. Besides, adsorption fastening of CuPhC lowers time of test compound eluting in less degree than at synthesis

of complex on the surface. Owing to plane geometry of complex copper ion keeps availability for intermolecular interactions. For CuPhC synthesized on the surface decrease of surface is accompanied by formation of one-ligand complex. In this case plane structure is destructed and availability of copper ion depends on ligand position.

When using CuPhC as a modifier of initial Silipor 075 with increase of temperature the polarity to electron acceptors rises due to delocalization of unseparated electron couples of ligands. In spite of availability of electron-deficient metal ion in plane complex of CuPhC, sorption heat increases mainly for π-complex-forming compounds. One can suggest that primary interaction of complex with active surface centres manifests itself due to dative interaction of unoccupied d-orbitals with OH groups and heterogeneity of different type in carrier structure.

The sorbents obtained are used to analyse the mixture of oxygen-containing compounds containing aldehydes, ethers, spirits, and ketones. The results show the possibility to apply CuPhC for analysis of widely-used admixture spirit components. On synthesized CuPhC it is possible to subtract and, hence, identification of lower aliphatic alcohols in complex mixtures, fig. 2. Subtraction of alcohols on synthesized CuPhC can be connected with destruction of bond between metal ion and oxygen of silanol group, in this case further retention of CuPhC on the surface is due to coordination of metal and oxygen on the surface.
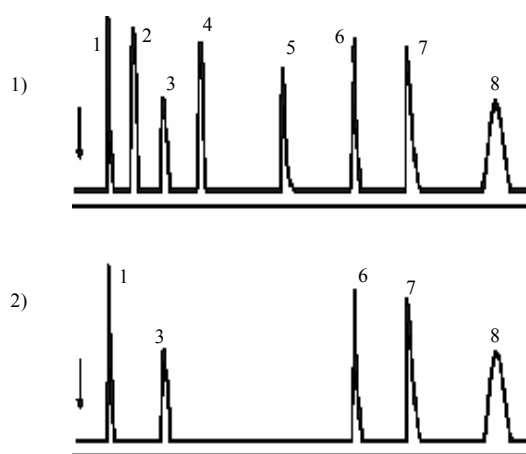

Fig. 2. *Chromatograms of model mixture before (1) and after (2) its leaking through Silipor 075, chemically modified by copper phthalocyanine: 1) propenal; 2) ethanol; 3)butanal; 4) propanol; 5) butanol; 6) ethylisobutirate; 7) isobutyl acetate; 8) butyl acetate*

Thus, new sorbents for gas-adsorption chromatography are synthesised on the bases of Silipor 075 with grafted by different methods copper phthalocyanine. The material obtained possess significant thermal stability, their use is possible up to 350 °C without complex destruction. Their ability to separate selectively mixture of hydrocarbons and oxygen-containing organic compounds in the range of 110...180 °C is shown.

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ESTIMATION OF INTERACTION ENERGY OF SOME FUNCTIONAL GROUPS OF MEDICAL SUBSTANCES WITH PROTEIN MOLECULES IN WATER CONDITION

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The basic energetic effects when forming organic substance complexes with protein molecules which determine thermodynamics of this process are examines using nonempirical quantum-chemical DFT method. Complex formation is considered as a replacement of water in solvated protein and organic compound molecules. Determinative role of strong hydrogen bonds and hydrophobic effect in strength of the complexes is shown.

The estimation of pharmacological and biological substance activity is of great practical importance. The purpose of our work is to describe quantitavely energetic effects of medical substance complex formation with protein molecules in the conditions of interaction in aquatic environment.

Thermodynamic description permits to consider formation of such complexes as a dynamic equilibrium of different energetic states. Calculation of energies in such states is possible using modern methods of quantum chemistry.

Materials and methods

Nonempirical quantum-chemical calculations of DFT was performed by means of standard GAMESS program package by B3LYP/6-311G* method with exchange Bekke B3 functional and LYP correlation functional [1]. Geometries of calculated molecules were fully optimized, the absence of imaginary vibration frequencies proved their stationary character.

Results and discussion

Complex strength constant of medical substance with protein molecules in aquatic environment can be estimated by thermodynamic equation:

$$K_p = e^{\frac{-\Delta G}{RT}} = e^{\frac{-\Delta H}{RT}} \cdot e^{\frac{\Delta S}{R}}. \quad (1)$$

Entropic constituent has the value $T \cdot \Delta S < 4$ kJ/mol [2].

The process of complex formation we consider as a dynamic equilibrium of two energetic states in the conditions of organism (*in vivo*) at 310 K (37 °C). Initial state – hydrated molecules of medical substance (MS) and protein. Second state – complex of MS molecule and protein formed and interaction of liberated water molecules among each other.

Enthalpy constituent of equation (1) can be calculated by the formula:

$$\Delta H = (\Delta H_{ЛВ\text{-}БС} + \Delta H_{В\text{-}В}) - (\Delta H_{ЛВ\text{-}В} + \Delta H_{БС\text{-}В}), \quad (2)$$

where $\Delta H_{ЛВ\text{-}БС}$ – active group interaction energy of medical substance with protein molecule groups; $\Delta H_{В\text{-}В}$ – interaction energy of water molecules with each other; $\Delta H_{ЛВ\text{-}В}$ – hydration energy of active group of medical substance; $\Delta H_{БС\text{-}В}$ – hydration energy of protein active group.

Intermolecular interaction is described by many constituents. Weak Van der Waal's forces of interaction have energy of less than 0,4 kJ/mol, taking into account that in initial state molecules are solvated, i. e. they interact with other molecules, the difference of these energies have an order of magnitude less and is close to zero.

Special role in intermolecular interactions plays hydrogen bond which can have energy in the range of 1...200 kJ/mol comparable with energies of covalent chemical bonds. One distinguishes hydrogen bond with energy up to 20 kJ/mol, average – 20...60 kJ/mol, producing at interaction of neutral molecules and strong hydrogen bond from 60 to 200 kJ/mol which is observed at molecule interaction with charged ions [3].

The calculation of 40 different organic and inorganic molecules including 20 amino acids occurring in organism was made. Also, we performed the calculation of amino acid dimers and trimers that showed that at polymerization effective charges in active centres of aminoacid residuals do not practically change at chain accretion. It permits to model interaction with protein replacing it by interaction with aminoacid residuals. For all molecules involved the energy of interaction of strongly charged centres with water molecules is calculated.

Then energy of replacement for the process of complex formation by equation (2) was calculated. In the