



Quantum-Chemical Calculations on the Determination of Chromium (VI) Ion with Two Sodium Salts of 1,8-Dioxynaphthalene 3,6-Disulpho Acid

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ABSTRACT

Quantum chemical methods of Gaussian and ORCA software packages were used to calculate the atomic energy of the disodium salt of 1,8-dioxynaphthalene-3,6-disulfoacid, which is used as an analytical reagent for chromium (VI) ions. This reagent contains functionally active and analytically active groups. The geometries of the studied compounds are optimized, the electron density of the molecular orbitals and the total energy of the molecule are calculated.

Keywords:

Chromium (VI) ions, disodium salt of 1,8-dioxynaphthalene-3,6-disulfoacid, quantum chemical methods, B3LYP/def2-TZVP method, ORCA program, Gaussian .

Introduction If the amount of chromium in the soil increases, it has been found that this element has a negative effect on the productivity of plants, as well as its excessive accumulation is dangerous for humans and animals [1].

Chromium is widely distributed in soil and plants, and elemental imbalances are observed in animals and humans, often due to insufficient intake of chromium from the outside. [2].

Chromium is mainly in acid rocks (granites, liparites) about 25 mg/kg, in sedimentary rocks (clays, shales) up to 160 mg/kg [3]. Its average amount in soils is $1.9 \times 10^{-2}\%$. The amount of chromium in the surface layer of the air is 1×10^{-3} ng/m [4]. The concentration of dissolved chromium in unpolluted rivers and lakes is 1-2 $\mu\text{g/l}$, in oceans 0.05-0.5 $\mu\text{g/l}$, and in coastal waters of seas in the range of 5-50 $\mu\text{g/l}$ [5]. Trivalent chromium is found in water in the form of complex compounds, and hexavalent

chromium is found in solutions as anions [6]. Soil is the main source of chromium in plants. The amount of chromium in the soil is determined by its concentration in the parent rock [4]. Acid igneous rocks contain low amounts of chromium (4-25 mg/kg). Sedimentary rocks contain up to 160 mg/kg of this element. In soils, chromium can exist in four states: trivalent form Cr^{2+} and hexavalent form CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ [1]. The mobility of chromium increases with the formation of complex compounds. It forms very strong complexes with humic acids from organic substances. This complex remains dissolved in the soil at pH values higher than 5.5, while free Cr ions are quickly adsorbed and precipitated [7]. In terms of geochemical properties, chromium is very close to Fe^{3+} and Al^{3+} . Trivalent forms predominate in acidic soils. Hexavalent chromium compounds predominate in alkaline environments with high redox potential [1]. Hexavalent chromium is the most favorable for plants, it easily

converts to trivalent chromium and vice versa depending on soil conditions. The state of chromium in the soil largely depends on its valence state, determined by acid-alkaline and oxidation-reduction conditions, soil microbiological activity, sorption capacity, and cationic composition of the complex. For example, with an increase in acidity, the adsorption of Cr^{3+} of the clay fraction increases, while Cr^{6+} decreases. Soil organic matter enhances the reduction of chromium (VI) to chromium (III) [8, 9]. Recently, organic reagents immobilized in various carriers are also used to improve metrological properties [10]. Their use allows to reduce the work in performing the analysis, for example, pre-concentration of sorption with separation, separation of mixtures, direct Elements can be determined spectrophotometrically on the surface of an organic reagent immobilized [11].

Fiber materials based on polyacrylonitrile have recently been widely used as matrices for immobilizing organic reagents [12]. Unlike other sorbents, polymer fibers have a highly developed specific surface area, regeneration ability and improved kinetic properties [13]. In this work, we use theoretical calculations to immobilize the disodium salt of 1,8-dioxynaphthalene-3,6-disulfoacid (DNDK) on a solid support to increase the sensitivity and selectivity of the detection.

Experimental part.

Reagents and equipment. Standard solution of analytical reagents. Disodium salt of 1,8-dioxynaphthalene 3,6-disulfo acid was purchased from Khimreaktivsnab (Russia) OOO "Sintreyd-Kazan" AG (TU 6-09-05-13-71-88). To prepare the DNDK solution, 0.04 g of the reagent was withdrawn and placed in a 100 ml flask and distilled water was added to the mark.

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distilled water was added to the mark. This solution was used as an analytical reagent [14,15].

Devices. The acidity and basicity of the solutions were set with universal buffer solutions ($\text{H}_3\text{PO}_4+\text{H}_3\text{BO}_3+\text{CH}_3\text{COOH}$). This buffer solution was used in the processes of immobilization and complex formation to maintain the acidity and alkalinity of the solution [13].

The medium of the solution was measured using "Mettler-Toledo AG" and "I-130" potentiometer-ionometer. Absorption spectra were measured in EMC-30PC-UV Spectrophotometer and UV-5100 UV VIS Spectrophotometer. Infrared spectra of reagents, carriers and immobilized compounds were obtained by IR-Fur'e-spectrometer "Bruker Invenio S-2021". These devices were used to select the optimal conditions for the formation of the complex, to determine the optical density and the area of light absorption.

To determine the chromium (VI) ion, it is necessary to select an organic reagent specific to it. It is known from literature [16] that chromium (VI) ion forms a complex with heteroatoms such as nitrogen hydroxide. In order to select the correct reagent, the possibilities of selecting organic reagents with pre-calculated functional and analytical groups using quantum chemical calculation methods are considered [17]. Currently, one of the various processes used to increase the selectivity and sensitivity of organic reagents is the immobilization of organic reagents on carrier fibers [18]. The use of quantum-chemical calculations makes it possible to fully describe the electronic structure of organic reagents, including the specificity of their structure, the nature of reaction, distinguishing which group is functional and which is analytically active group, etc. However, the difficulty of the calculation process and the presence of redundant information in the multi-electron wave functions determine the need to develop a system of concepts for applying quantum theory to chemical problems in order to obtain information that has a chemical or physical meaning. In this view, the development of the quantum theory of the

electronic structure of molecules is not only a matter of purely applied mathematics, but this issue also requires chemical approaches [19].

Results of quantum chemical calculations:

Quantum-chemical methods (B3LYP/def2-TZVP method of ORCA program) were used to calculate maximum values of electron density of reagents. Using these methods, as a result of protonation of reagents in solution with an acidic environment, a coordination bond is formed due to the electrostatic attraction of an unpaired pair of electrons. The reagents selected for immobilization contain several potential centers and were found to be concentrated on oxygen atoms with high electrostatic attraction to ions.

On the basis of quantum chemical calculations, the effective charges of donor atoms with the most active reactivity and the character of distribution of electron densities of donor centers in molecules of reagents are found.

We know that the electrostatic potential surface is an important factor in determining the reaction centers of molecules, especially for non-covalent interactions, and indicates the nucleophilic and electrophilic centers of a molecule. In Figure 1, the red dots are the negative region of the Electron Cloud Density (EBZ) surface, where electrons are the most abundant region. The purple centers are the

positive region of the (EBZ) surface, indicating areas with fewer electrons. The disodium salt of 1,8-dioxynaphthalene 3,6-disulfo acid has 2 -OH groups, and the positive values of the level (EBZ) are important in finding the mobile (electron-deficient) hydrogen atom in them. (EBZ) level analysis shows that the distribution of electron density in 2 hydroxyl groups is 2 different. The most active hydrogen, the nucleophilic center, is the hydrogen atom in the hydroxyl group with a maximum value of 60.53 kcal/mol, followed by the hydrogen atom in the sulfo group. Oxygen atoms in the sulfo group of the disodium salt of 1,8-dioxynaphthalene 3,6-disulfo acid can be shown as centers that can participate as electron donors in intermolecular interactions. The ESP analysis showed that the binding of this compound to polymer compounds (glue) can go through the sulfo group, which holds the most mobile hydrogen atom. The electrostatic potential surface is an important factor in determining the reaction centers of molecules, especially for non-covalent interactions, and indicates the nucleophilic and electrophilic centers of a molecule. In Figure 1, the red dots are the negative region of the electron cloud density (EBZ) surface, where the electrons are the majority region. The purple centers are the positive region of the (EBZ) surface, indicating areas with fewer electrons

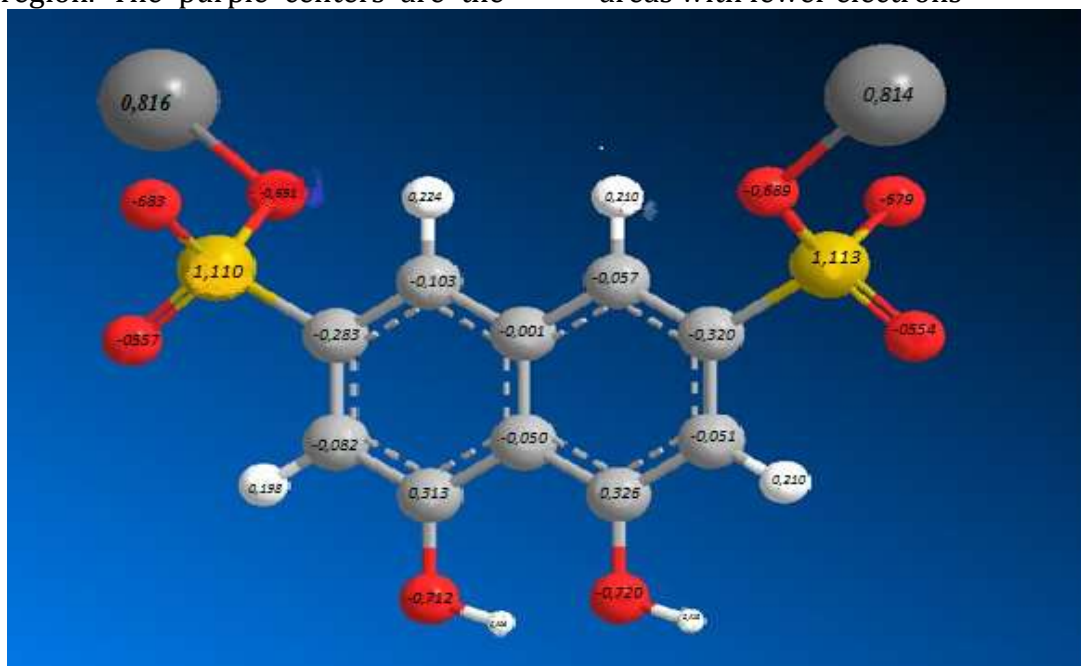


Figure 1. The sulfo group binds to the fiber, forming a complex with metal ions due to hydroxyl.

The results calculated by the Gaussian program are presented in the figure.

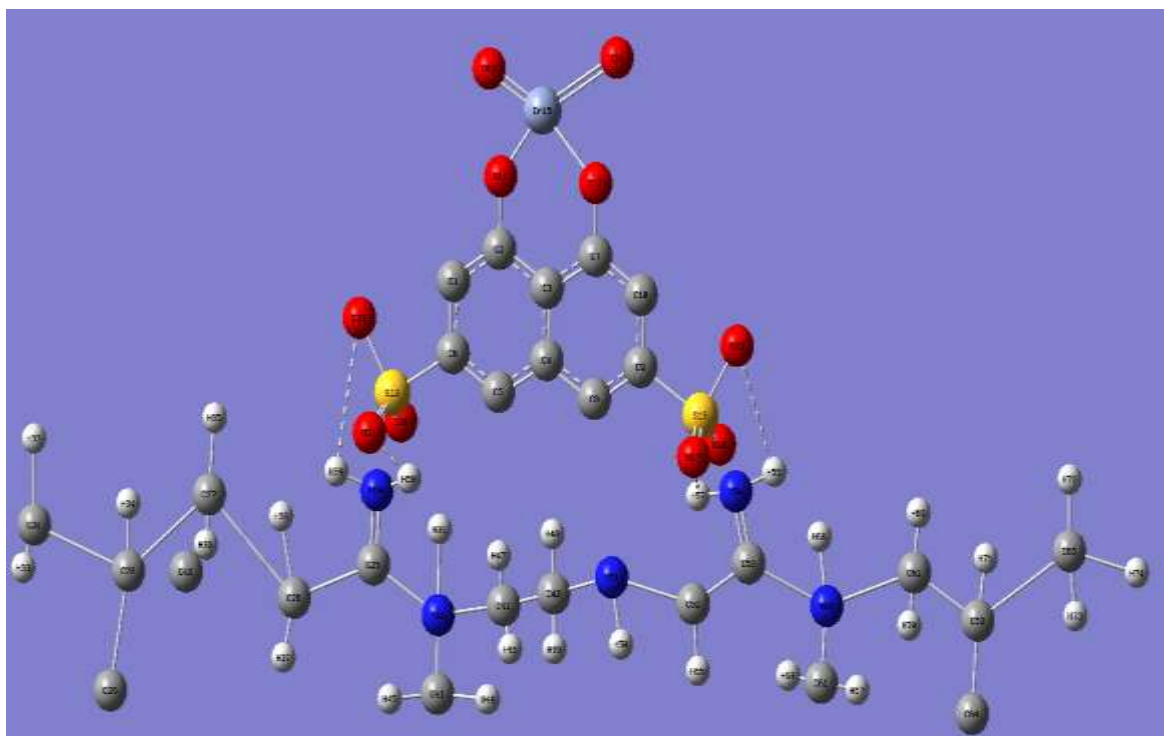
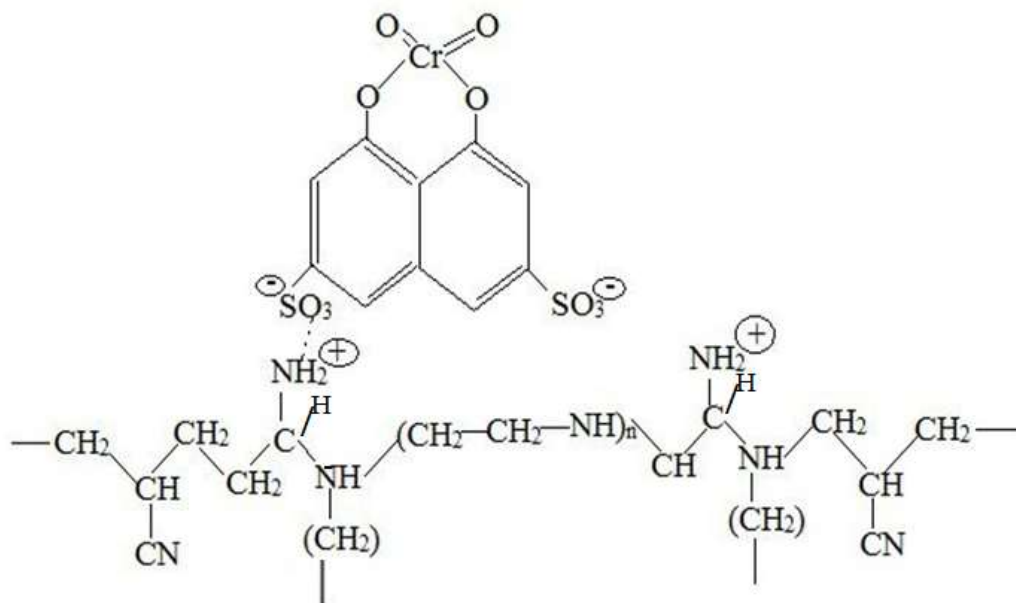


Figure 2. Results of calculations using the Gaussian program

Scheme 1. Approximate structural formula of the complex formed with chromium (VI) ions.

Summary

1. Optimum conditions of chromium (VI) ion immobilization on fibrous sorbents were found. It was found that the sorption of DNDK to the sorbent is 80-92%.

2. It was found that deprotonation occurs when DNDKs are immobilized in polymer fibers, which enables complex-forming

properties of reagents immobilized in an acidic environment.

3. Complex formation reactions of Cr (VI) ions with DNDKs immobilized on polymer matrices were studied. It was found that the polymer matrix has a great effect on the complexing properties of the reagents, just like SFM in solution: the light absorption maxima of

the complexes are formed under acidic conditions.

4. Based on the results of quantum chemical calculations and electronic spectroscopy, it was determined that the immobilization of reagents occurs through sulfo groups, and the ratio of reagent and metal in the formation of a complex is 1:1.

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