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Complexation properties of the organic reagent DEDTK Na with $CuSO_4$: a quantum-chemical study using density functional theory (DFT)

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Abstract. Today, the world is increasingly focused on developing effective methods for processing mineral raw materials and polymetallic ores, fully extracting useful minerals from them, increasing the production capacity of rare and rare metals, and creating low-waste and waste-free technologies. Also, the involvement of all types of technogenic waste from the mining and metallurgical industry (waste from the mining industry, enrichment plants, liquid and solid waste from hydrometallurgical and pyrometallurgical processes) in production, and ensuring the extraction of useful components from technogenic waste using low-operational and inexpensive methods with the return of used reagents to the process are urgent issues in this area.

Keywords; DEDTK, $CuSO_4$, HOMO, LUMO, B3LYP, gibrid DFT, GaussView 6.0

Introduction. Many advanced molecular theories have been studied in the literature to study the geometry, electronic states, and chemical reactivity of chemical compounds. The use of density functional theory (DFT) in the study of these properties gives very good results. Taking this into account, the possibilities of DEDTK Na forming complexes with copper metal ions were studied. The calculations were performed using the hybrid DFT method, which takes into account changes in electron density (gradients), as well as improved using the B3LYP functional with additional corrections. Geometry optimization was performed using the 6-31G (d,p) basis set. The results were visualized using the GaussView 6.0 software package. Frontier molecular orbital (FMO) analysis. Frontier molecular orbitals are a very important parameter in quantum chemical calculations, as they are used to determine the stability and reactivity of molecules. A smaller energy difference (Elumo-Ehomo) between the lower unoccupied molecular orbital (LUMO) and the upper occupied molecular orbital (HOMO) indicates that the molecule has a high reactivity. In addition, the HOMO is primarily an electron donor, while the LUMO is mainly an electron acceptor. The HOMO, LUMO energies and their orbital energy gaps (band gap) are calculated using B3LYP/6- 31G (d,p). According to this, the band gap is Eband gap = 0.14 eV. From this, it can be concluded that DEDTK Na has a high reactivity.

When evaluating the complexation of DEDTK Na with copper, it is important to first consider the energies of the HOMO or LUMO orbitals of the metal to be close to those of the orbitals of the organic compound. In addition, it is important to determine which copper compound has the deeper global minima.

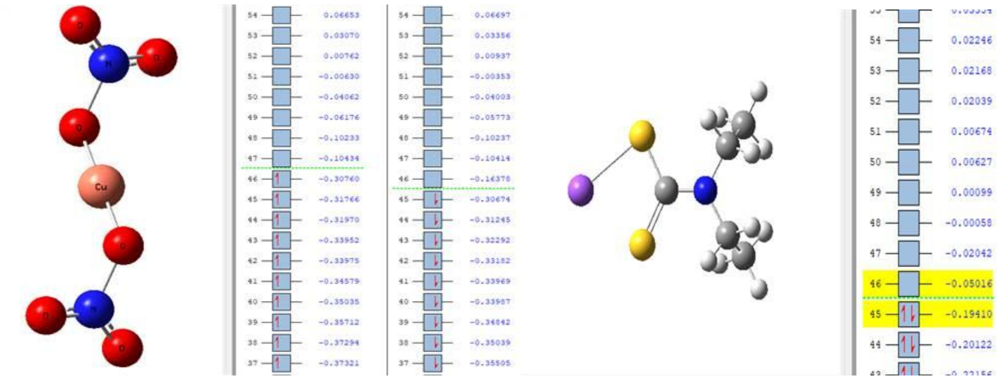

Figure 2. Frontier molecular orbitals of $CuSO_4$ and DEDTK Na

Among the several copper salts, $CuSO_4$ has been found to have a relatively small electron energy (~2.025 10-18 cal.) by quantum chemical calculations. In addition, the difference between the LUMO frontier molecular orbitals of the organic reagent and the HOMO frontier molecular orbitals of the salt is very small ($\Delta \cong 0.11$ eV for electrons in the alpha and beta states), which may lead to the occurrence of cross-bonding between the organic reagent and the metal.

This conclusion can also be confirmed by the electrostatic potential surface of the reagent (Fig. 3).

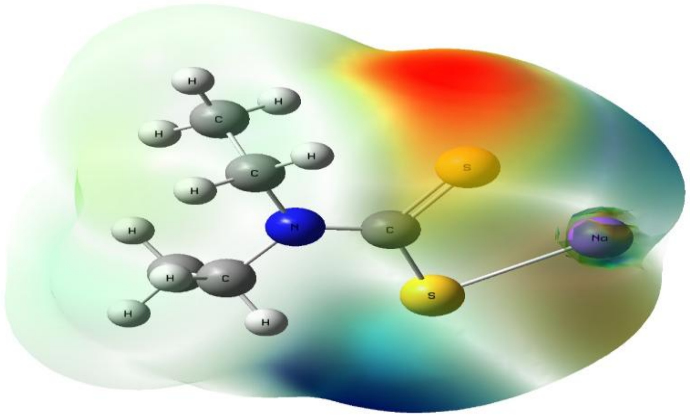

Figure 3. Molecular electrostatic potential surface of DEDTK Na

The charge distribution (electrons and nuclei of a molecule) creates an electrostatic potential (V(r)) in the surrounding space. The electrostatic potential is a real physical property that is very useful for analyzing and predicting the reactivity of molecules. It can be partially known in advance, experimentally determined, or calculated. The electrostatic potential is an important property that indicates in particular which places or regions of the molecule the approaching electrophile or nucleophile will settle. Positive point charges are attracted to areas where V(r) is negative, and the interaction energy is negative (stabilizing). In addition, positive point charges are repelled from areas with a destabilizing positive potential, and the interaction energy is positive.

To determine from which part of the organic reagent the reaction occurs, we can use the Laplacian (∇2ρ) contour map of the electron density.

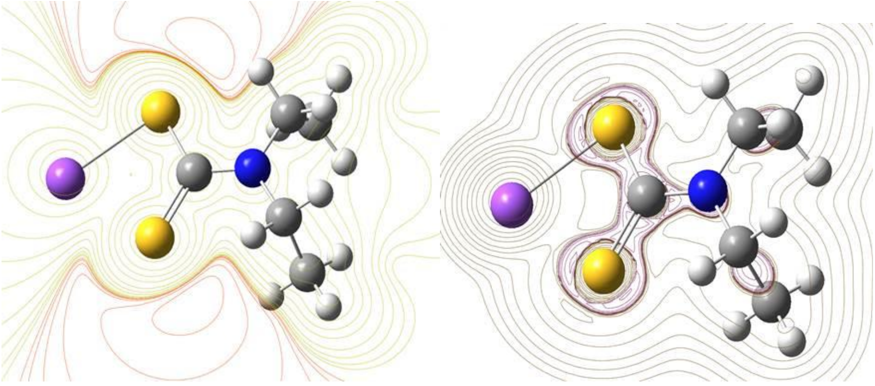

Figure 4. Electrostatic potential contour map of DEDTK Na

From Figure 4.a, we can see that the density of the metal atom is too low for another atom to enter. From Figure 4.b, it is clear that the contours around sodium are too low in density. Based on the above data, the possibility of forming a complex of DEDTK Na with copper metal was studied.

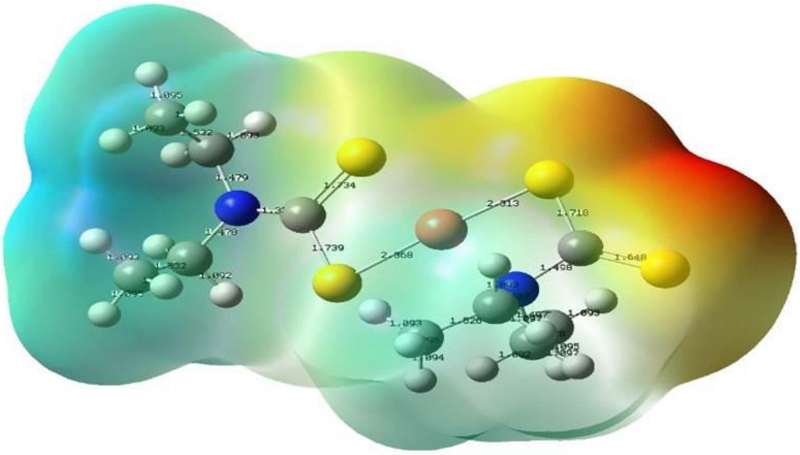

Figure 5. Electronic potential surface of the complex of copper metal with DEDTK Na

Geometry optimization was performed using the 6-31+G (d,p) basis set. The results were visualized using the GaussView 6.0 software package. From Figure 5, it can be concluded that the molecule is strongly polarized (the value of the dipole moment is 8.534D), which indicates its high solubility in water. If we pay attention to the contour map of the complex of copper with DEDTK Na, the electron density around the sulfur atoms is higher than that around the other atoms. This means that particles approaching the complex are primarily affected by these atoms.

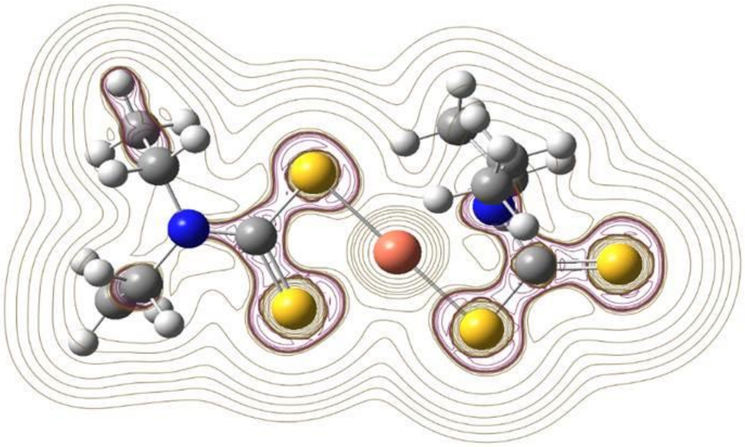

Figure 6. Electrostatic potential contour map of DEDTK Na

In this study, the complexation of the organic reagent DEDTK Na with the $CuSO_4$ salt was studied based on quantum-chemical calculations at the B3LYP/6-31G (d,p) level of density functional theory (DFT). The geometry of the molecule was optimized, the energies of the frontier molecular orbitals (HOMO and LUMO) were determined, and their difference was found to be $\Delta E \approx 0.11$ eV, indicating that this reagent has high reaction activity. It was also found that $CuSO_4$ has a small electron energy (~2.025·10-18 cal.) compared to other copper salts, which indicates that it forms an energetically favorable complex with the DEDTK Na molecule. Based on the electrostatic potential surface and Laplacian ($\nabla^2\rho$) contour maps of the electron density, the reactive centers of the molecule (in particular, the regions around the sulfur atoms) were determined. The electrostatic potential surface of the complex, the high value of the dipole moment (8.534 Debye) and good solubility in water determined its physicochemical stability and potential areas of application. The results obtained scientifically substantiated the high selectivity and binding ability of the DEDTK Na reagent towards Cu (II) ions. This method is one of the most reliable, widespread and influential methods of the current "modern quantum chemistry" and is the most widely used theory in the fields of inorganic, organic, bioorganic, materials science and catalysis.

The ionic flotation method works with high efficiency even at low concentrations of metals in solutions (10-100 mg / l). One of the important factors affecting the effective course of ionic flotation is the pH environment of the solution. The acidity of the medium can affect the solubility of the product being separated in the ionic flotation process, the charge of the ion, change the ion-collector ratio, and affect the stability of the foam. In order to determine the optimal pH environment for conducting the ionic flotation process, experiments were conducted at different pH values. The pH value of the solution under study was adjusted using NaOH solution. Sodium diethyldithiocarbamate

(DEDTK Na) was used as the collecting reagent, and (T-92) as the foaming reagent. The results of the study are presented in Table 1 and Figure 1.

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Results of ionic flotation of metals from solutions with DEDTK Na

The amount of metals in the initial solution, mg/l			Experimental conditions	Solution pH	The amount of metals in the solution after ion flotation, mg/l			Foam product yield, g/l	Foam product extraction rate, %		
Cu	Fe	Ag			Cu	Fe	Ag		Cu	Fe	Ag
860	1200	120	DEDTK Na consumption stoichiometric. height.100%, flotation duration-6 min. T-92 consumption – 3.5 g/m^3	1	86	528	12,5	21	90	56	89,6
				2	27	336	6,4	22	96,8	72	94,7
				3	1,2	120	0,2	24	99,9	90	99,8
				4	1,2	72	0,1	25	99,9	94	99,9
				5	1,2	48	0,1	25	99,9	96	99,9

The efficiency of the process of separating metals from the solution by ionic flotation depends to a certain extent on the pH of the solution, and experiments were conducted in different solution environments. According to the results of the experiment, different separation of metal compounds with DEDTK was observed at all pH values of the solution. The maximum separation of copper and silver metals in the solution was observed at pH values of 3-4. Taking into account economic and technological indicators, it was determined that the optimal pH value for the implementation of the ionic flotation process is in the range of 3-4.

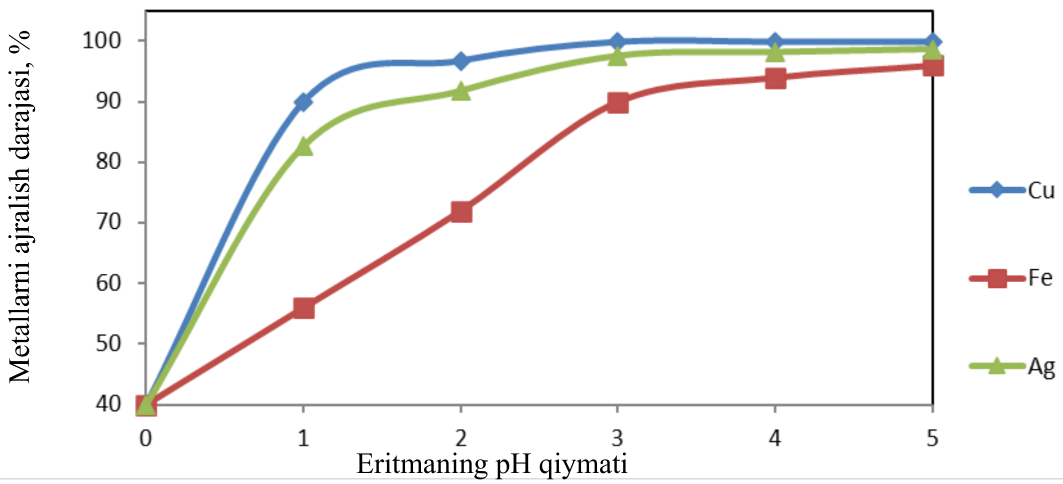
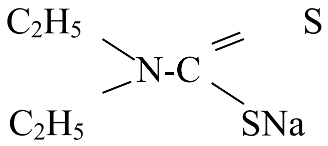


Figure 1. Graph of the degree of metal extraction from solutions versus the pH of the solution

At a pH value that ensures that metals are in the form of hydroxides in solution, complete separation of metals is possible. The decrease in the degree of separation of metals with a decrease in the pH value is associated with the decomposition of the collector in an acidic environment and the transition of metals to the ionic state in solution. The decrease in the degree of separation of metals from solutions at high pH values is explained by the transition of metals to a form that does not interact with other collectors.

The separation of metal cations depends on two main factors: the hydration energy and the stability of the resulting compound. The smaller the cation radius and the greater its charge, the higher the strength of the substrate and the better the flotation process.

The dependence of the efficiency of the separation of metals by ionic flotation on the consumption of the collector reagent was also studied. DEDTKNa is a salt of a monobasic weak diethyldithiocarbamic acid and has the following structural formula.



The theory of the stages of the action of DEDTKNa has now been experimentally confirmed. In the first stage, hydrolysis of the anion occurs according to reaction 3.24.

$$(C_2H_5)_2NC(S)S^- + H^+ = (C_2H_5)_2NC(S)SH \qquad (3.24)$$

In the second, relatively slow, step, the monobasic diethyldithiocarbamide acid decomposes to form the corresponding secondary amine and carbon disulfide.

$$(C_2H_5)_2NC(S)SH^- + H^+ = (C_2H_5)_2NH_2 + CS_2 \qquad (3.25)$$

The ability to separate metal ions in aqueous solutions with high acidity is determined not by the rate of decomposition of the collecting reagent, but by the tendency of a particular metal to form strong compounds with a given reagent.

The solution obtained as a result of selective dissolution of the non-magnetic fraction with sulfuric acid was analyzed mainly for copper, iron and silver metals. In addition to these metals, zinc, molybdenum, nickel and a number of other important metals are also found. Ion flotation has the ability to completely separate all metals present in the solution. The interaction of metals with sodium DEDTC occurs as a result of the following reactions:

$$Cu^{+2} + 2(C_2H_5)_2NC(S)SNa = [(C_2H_5)_2NC(S)S]_2Cu + 2Na^+ \qquad (3.26)$$

$$Fe^{+2} + 2(C_2H_5)_2NC(S)SNa = [(C_2H_5)_2NC(S)S]_2Fe + 2Na^+ \quad (3.27)$$

$$Fe^{+3} + 2(C_2H_5)_2NC(S)SNa = [(C_2H_5)_2NC(S)S]_3Fe + 3Na^+ \quad (3.28)$$

$$Ag^+ + (C_2H_5)_2NC(S)SNa = (C_2H_5)_2NC(S)S]\ Ag + Na^+ \quad (3.29)$$

In order to determine the optimal collector consumption in ionic flotation, experiments were conducted with different amounts of different reagents according to stoichiometry. The results of the experiments are presented in Table 2.

Table 2

High-yield copper extraction rates from solution using various reagents

№	Reagent (Collector)	Type	Optimal pH	Cu separation rate (%)
1	Sodium diethyldithiocarbamate (DEDTKNa)	Complexing anionic	3–4	95–99%
2	Sodium dodecyl sulfate (NaDS, SDS)	Anion active SFM	3–6	82–88%
3	Sodium dodecylbenzenesulfonate (SDBS)	Anionic SFM	4–7	78–85%

As a result of the studies, it was found that increasing the concentration of the collecting reagent leads to a higher degree of metal separation even at low pH values. It turned out that this method is effective in a wide range of pH when the initial concentration of DEDTKNa is 25 g/l.

During the studies, experiments were also conducted to determine the optimal time for the separation of metal precipitates with DEDTKNa. Experiments were conducted to determine the optimal time for ionic flotation for 3, 4, 6, 8, 10 minutes, and the diagram shown in Figure 7 was constructed based on the results of the experiments.

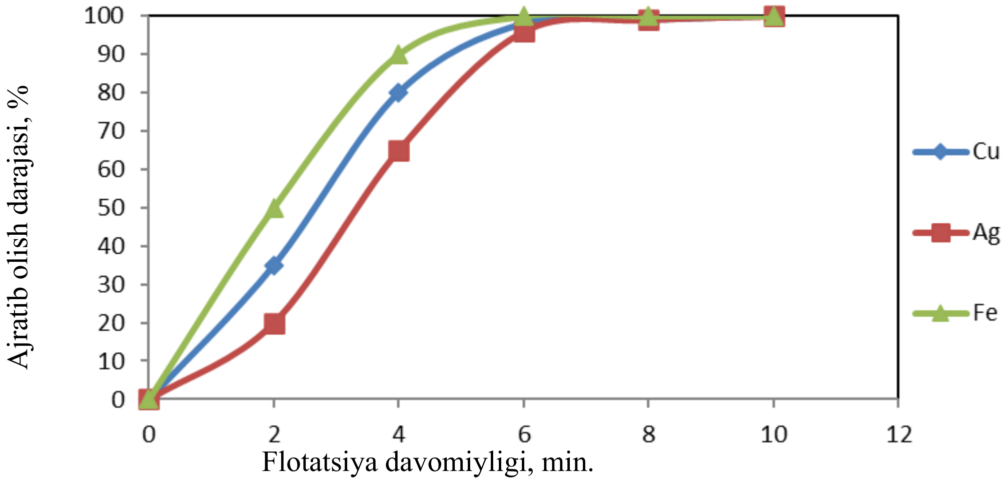


Figure 7. Graph of the degree of separation of metals from solutions into a foam product versus flotation duration

As can be seen from the diagram in Figure 7, flotation for 6-8 minutes is required to completely separate metals from solutions. The flotation kinetics of hydrophobic precipitates is described by an equation similar to the first-order chemical reaction kinetics equation. Here, the equilibrium constant indicates the speed at which the flotation process proceeds, characterizing the flotation properties of the material being separated, the reagent regime of the process, and the design of the implementation machine.

Experimental conditions: pH-3-4, collector reagent consumption-100% of stoichiometry, T-92 consumption-3.5 g/m3. The maximum value of the separation of metals from solutions by ionic flotation was achieved at a temperature of 20-25oC. A further increase in temperature leads to a decrease in the efficiency of the process due to an increase in the solubility of the formed compound (sublate).

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