

**ASSESSMENT OF ELEMENTAL COMPOSITION,  
STRUCTURAL AND QUANTUM-CHEMICAL  
CHARACTERISTICS OF THE REAGENTS  
FOR SUBSTANTIATION OF THEIR  
FLOTATION ACTIVITY**

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### Abstract

Flotation reagents are used in coal flotation to obtain coal concentrates. The aim of this study was to investigate the flotation activity of heteropolar organic compounds, in particular the quantity of extracting combustible mass. The heats of compounds formation and thermodynamic parameters of the compounds were calculated with quantum-chemical modelling. The ratios of the heat of compounds formation (kcal/mol) to its molar consumption (mol/ton of coal) were used to evaluate their flotation activity. Experimental data confirmed an accurate evaluation of flotation activity by means of calculating the energy values of intermolecular hydrogen bonds in the complex between the compounds and active sites of the coal surface. This indicates that the performance of coal flotation is enhanced with the increasing of hydrogen bond energy of intermolecular complexes between 2-methyl-1,3-dioxo-2-silacyclohexane with coal's organic mass compared with the complexes of 2-methyl-1,3-dioxane.

### 1. Introduction

The search for effective flotation reagents used in coal flotation has received much attention in recent years due to continuous deteriorating of the coal quality [1-4]. Flotation reagents are chemical compounds produced by oil treatment. Heteropolar organic compounds have many possible uses in many fields and have also been investigated as potential flotation reagents [4]. However, it has been found that the investigation of mechanism of action of heteropolar organic reagents at coal flotation allows to search high effective and selective flotation reagents. One way to find out the flotation activity of the compounds is to investigate their electronic structures and thermodynamic parameters [5-7]. For example, Solozhenkin et al. [8]; Frantsina et al. [6] showed that quantum-chemical method could be used for selection of flotation reagents and more recently Lavrinenko and Svechnikova [9]; Kubak et al. [10] studied the quantum-chemical characteristics to substantiate the reagent flotation capacity. However, although the increased effectiveness of the coal flotation with quantum-chemical selection of the reagents was demonstrated over two years ago [11-13], little attention has been paid to the selection of silicon-bearing heteropolar analogues. The present paper investigates the quantum-chemical characteristics and the flotation activity of 2 classes

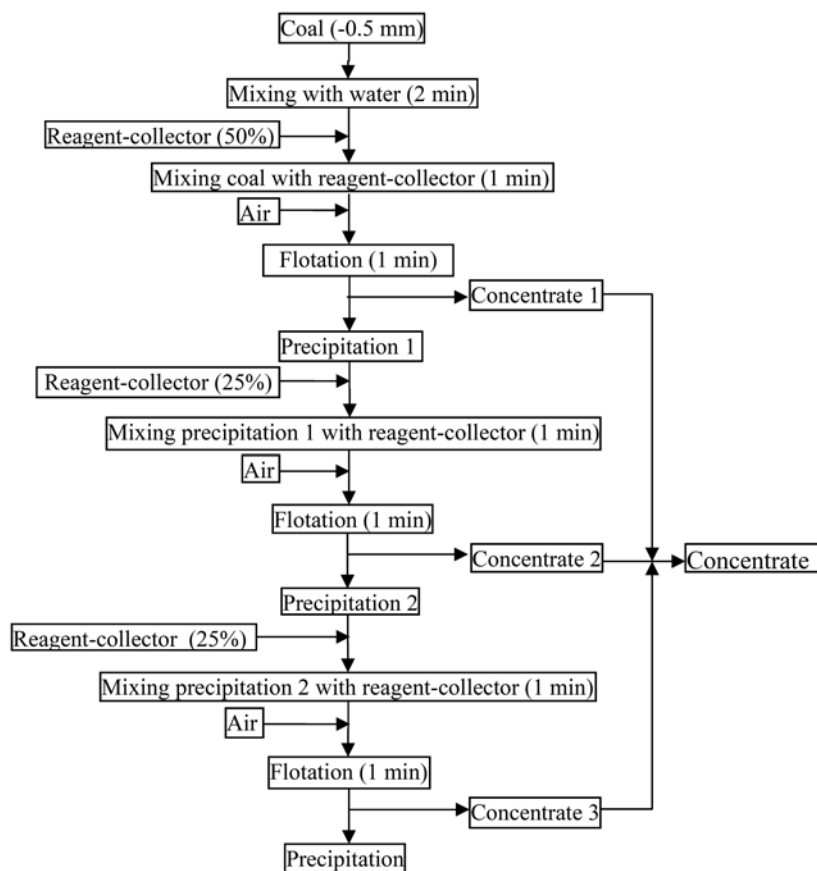
heteropolar organic compounds: 1,3-dioxanes, 1,3-dioxo-2-silacyclohexanes for selecting flotation reagents. On the basis of these characteristics it then describes the flotation activity of the heteropolar compounds. The flotation activity of silicon-bearing heteropolar organic compounds was significantly higher than for oxygen-bearing ones.

## 2. Experimental

The current investigation involved the determination of flotation activity of heteropolar organic compounds relatively to coal samples. The samples were selected from Belovo Coal Factory, the Kuznetsk coal basin, located in Kemerovo region, Russia. The first sample was coal residues left after size reduction using hummer and jaw crush. The second and third samples were gas-coal and bituminous coal. A total of 3 coal samples were collected in 25kg bags separately. The bags with samples were shipped from factory directly to coal laboratory at Nosov State Technical University. Each sample crushed to – 1.0mm grade fraction, thoroughly mixed and then divided into two parts. The first part of the sample was analyzed to define the element and chemical content by means of standard procedures. The second part of the sample was prepared in the laboratory using grinding machine to obtain – 0.5mm grade fraction for the froth flotation tests. The froth flotation test consists of mixing the ground coal sample with each reactant separately in water medium in flotation machine. The resulting products (the concentrate and the precipitation) can be easily dried and stored. The scheme of experiment is presented in Figure 1. The products were subsequently analyzed using standard methods. All coal samples used in the experiment had various grain content. They were ground to – 0.5mm grade fraction to avoid chemical content variability.

The heteropolar organic reactants were synthesized at Ufa State Petroleum Technological University. The purity of the reactants was 99%. In our study was used model system consisted of phenol, benzoic

acid, and benzotiol. The model system was considered as coal organic mass (COM). The intermolecular hydrogen bonds energy between the model system compounds and the reactant were calculated by using software HyperChem Professional 8.0.8. The heat of formation of chemical compounds was taken from the base Chem3D Ultra 8.0 software. The flotation activity of the compounds was evaluated as the ratio of the heat of compound formation (kcal/mol) to their molar flow consumption (mol/ton of coal). The reactant was added partially on the first stage 50% of the whole quantity, on the second and third stages by 25%.



**Figure 1.** The scheme of coal flotation with reagent-collectors.

### 3. Results and Discussion

Data obtained in previous studies using quantum-chemical modelling indicated that electronic structures and thermodynamic parameters of compounds affected the flotation activity. According to [12-14], hydrogen energy bonds in the intermolecular complexes “reagent-COM” could be considered as a criteria for assessment the flotation activity of reagents. In our study, thermodynamic parameters were calculated by using software HyperChem Professional 8.0.8. Modelled results were compared with actual quantites of flotation concentrates. Tables 1 and 2 show the results obtained using modelling and actual extent of extraction. As can be seen, using thiophene and its homologues (2-methylthiophene, 2-ethylthiophene) the effectiveness and selectivity were significantly higher than for thiophene, which is consistent with results obtained in previous studies (Table 1).

**Table 1.** Flotation activity of thiophene and its homologues

Compound	Reagent consumption, kg/ton	Molar weight, g/mol	Reagent consumption, mol/ton	The heat of formation, kcal/mol	Parameter, kcal/ton	Extraction of combustible mass, %
thiophene	5.73	84.14	68.1	115.75	1.7	23.8
2-methylthiophene	5.75	98.17	58.6	83.64	1.4	57.8
2-ethylthiophene	5.78	112.19	51.5	63.00	1.2	89.4

However, the consumption of the reagents were considerably high at the level of 5.73-5.78kg/ton. Although the thermodynamic parameters modelled by HyperChem Professional 8.0.8 were in line with those of Girevaya, a striking difference was noted when 1,3-oxathiolane and its homologues were considered individually (Table 2).

**Table 2.** Flotation activity of oxathiolane and its homologues

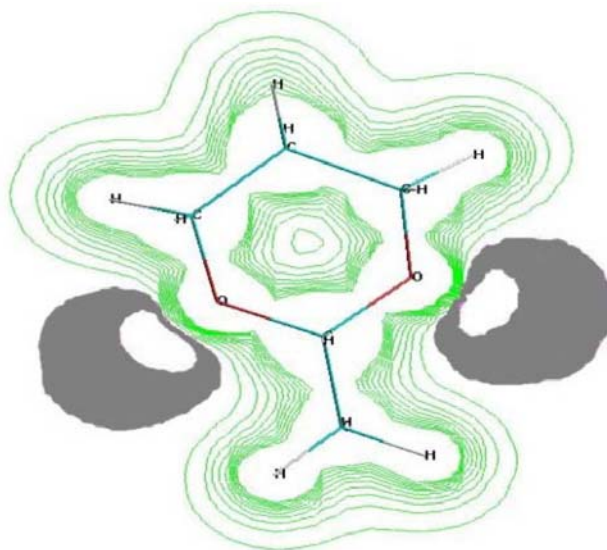
Compound	Reagent consumption, kg/ton	Molar weight, g/mol	Reagent consumption, mol/ton	The heat of formation, kcal/mol	Parameter, kcal/ton	Extraction of combustible mass, %
1,3-oxathiolane	0.98	90.15	10.87	111.17	– 10.2	32.7
2-methyl-1,3-oxathiolane	0.74	104.17	7.1	– 152.15	– 21.4	52.6
2-isoprophyl-1,3-oxathiolane	0.65	132.22	4.9	– 198.71	– 40.4	82.9
2-buthyl-1,3-oxathiolane	0.50	146.25	3.4	– 214.07	– 62.6	96.2
2-hexyl-1,3-oxathiolane	0.55	174.30	3.2	– 225.35	– 71.4	96.6



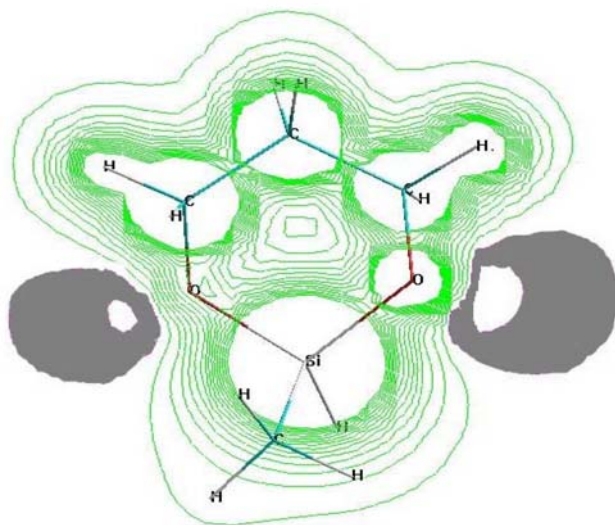
It can be observed that the increasing of hydrocarbon radical length resulted a considerably higher level of combustible mass extraction. Although levels of consumption of oxathiolane homologues were significantly lower than thiophene homologues.

The effectiveness and selectivity of 2-methyl-1,3-dioxa-2-silacyclohexane (2-methyl-1,3-DSC) were significantly higher than for 2-methyl-1,3-dioxane (2-methyl-1,3-D), the quantities of extracted combustible masses were 92% and 87%, respectively. Although levels of consumption of 2-methyl-1,3-DSC and 2-methyl-1,3-D were 0.48kg per ton.

Figure 2 presents projection maps of molecular electrostatic potential for 1,3-dioxane molecule and its silicon-bearing analogue.



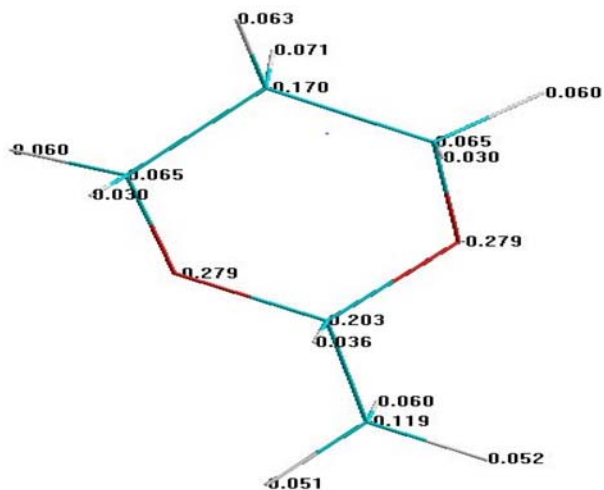
2-methyl-1,3-dioxane



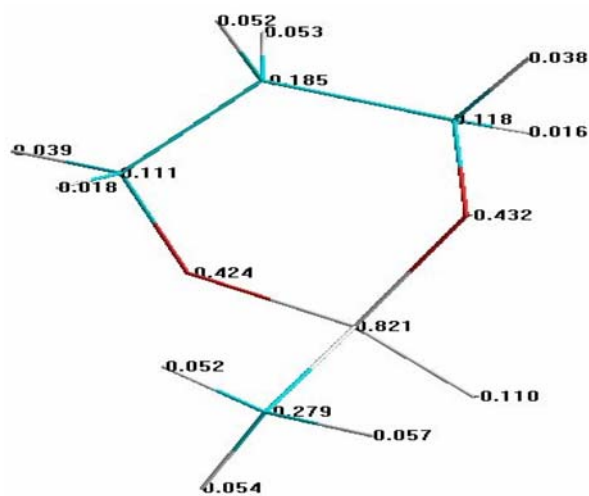
2-methyl-1,3-dioxo-2-silacyclohexane

**Figure 2.** Projection maps of molecular electrostatic potential for 2-methyl-1,3-D molecule and its silicon-bearing analogue.

Figure 3 shows the distribution of electron density in the molecules of the studied compounds. The electron density is 0.821 at the silicon atom in the 2-methyl-1,3-DSC. The electron density is 0.203 at the second carbon atom in the 2-methyl-1,3-D molecule.



2-methyl-1,3-dioxane



2-methyl-1,3-dioxo-2-silacyclohexane

**Figure 3.** The distribution of the electron density in the molecules of 2-methyl-1,3-D and 2-methyl-1,3-DSC.

The presence of silicon atom in the 2-methyl-1,3-DSC molecule causes a change in the electron density on the oxygen atom from  $-0.279$  to  $-0.424$  and  $-0.432$  at the 1st and the 3rd positions, respectively. Changes in the electron density on the oxygen atoms lead to changes in the values of hydrogen bond energy with the COM model compounds.

Silicon atom is more electropositive than the carbon atom that results in a change of 2-methyl-1,3-DSC electronic structure. Reactive centers in the molecules of the investigated compounds are oxygen atoms capable of reacting with the COM active centers to form hydrogen bonds.

Table 3 presents the results of calculating total energy bonds of reagents, water, COM's model compounds and energy of hydrogen bonds of their intermolecular complexes.

**Table 3.** Total energy bonds ( $\sum E_{eb}$ ) of reagents, water, COM's model compounds and energy of hydrogen bonds of intermolecular complexes

Compound/Complex	$\sum E_{eb}$ , kJ/mol	$E_{H-eb}$ , kJ/mol
Water	910.15	–
Reagents		
2-methyl-1,3-D	6649.82	–
2-methyl-1,3-DSC	6646.01	–
COM's model compounds		
Phenol	5947.12	–
Benzoic acid	7099.24	–
Benzotiol	5768.96	–
Complexes «Water – COM»		
«Water – Phenol»	6873.61	16.34
«Water – Benzoic acid»	8018.99	9.60
«Water – Benzotiol»	6684.77	5.66
Complexes «2-methyl-1,3-D – COM»		
«2-methyl-1,3-D – Phenol»	12613.49	16.55
«2-methyl-1,3-D – Benzoic acid»	13758.83	9.76
«2-methyl-1,3-D – Benzotiol»	12430.60	11.82
Complexes «2-methyl-1,3-DSC – COM»		
«2-methyl-1,3-DSC – Phenol»	12871.14	25.94
«2-methyl-1,3-DSC – Benzoic acid»	13763.69	18.44
«2-methyl-1,3-DSC – Benzotiol»	12434.04	19.06

As can be seen, phenol, benzoic acid and benzotiol were considered as COM model compounds. Inspection of Table 3 indicates that the hydrogen bond energy in the intermolecular complexes “Water - COM” and those of “2-methyl-1,3-D-COM” are very similar and vary from 5.66 to 16.34kJ/mol. It can be concluded that 2-methyl-1,3-D had a low competitiveness to COM's hydroxyl and carboxyl groups compared with water. In addition, it should be stressed that the coal surface comprises primarily the hydroxyl and carboxyl groups than the thiol ones [16]. It is worth noting that the hydrogen bond energy is much higher for “2-methyl-1,3-DSC-COM” intermolecular complexes than for the mentioned earlier.

It can be explained that the including of silicon atom into the molecule alters the electronic structure of 2-methyl-1,3-DSC, which leads to increase the electron density on the oxygen atoms, and as a consequence, the hydrogen bond energy in the “reagent - COM” complex.

For example, the difference in hydrogen bond energy varies from 8.84 (carboxyl group) to 13.4kJ/mol (thiol group). This significant difference indicates that the 2-methyl-1,3-DSC should have more competitiveness than 2-methyl-1,3-D, and, hence, the greater the flotation activity (Table 4).

Experimental data have suggested that 2-methyl-1,3-DSC has greater flotation activity. Table 4 presents that the concentrate yield and the extraction of combustible mass are higher for the 2-methyl-1,3-DSC, than those for 2-methyl-1,3-D at almost the same reagent consumption.

**Table 4.** Flotation characteristics of the 1st coal sample using 2-methyl-1,3-D and their silicon-bearing analogue

Reagent	Reagent consumption, kg/ton	Flotation products	Yield, %	Ash, %	Extraction of combustible mass in concentrate, %
2-methyl-1,3-D	0.49	Concentrate	79.4	5.7	86.8
		Wastes	20.6	44.5	
		Initial product	100.0	13.7	
2-methyl-1,3-DSC	0.48	Concentrate	84.1	5.6	92.0
		Wastes	15.9	56.5	
		Initial product	100.0	13.7	

It has been found that the 2,2,4-trimethyl-1,3-DSC reagent increases the yield of the bituminous coal concentrate from 16.3 to 25.1% depending on the reagent consumption in comparison with 2,2,4-trimethyl-1,3-D. The testing of the 3rd coal sample has given the similar results. For 2,2,4-trimethyl-1,3-DSC the yield of concentrate is 29.4-57.0% depending on the reagent consumption compared with 2 2,4-trimethyl-1,3-D (Table 5).

The study of the 2,2,4-trimethyl-1,3-D molecule and its silicon-bearing analogue with respect to the flotation the 2nd and 3rd coal samples allowed to confirm the high flotation activity and the effectiveness of 2,2,4-trimethyl-1,3-DSC due to the presence of two additional methyl groups in the molecule.

**Table 5.** Flotation results for gas and bituminous coals

Reagent	Mine, grade							
	Kirova, gas coal				Shakhtinskaya, bituminous coal			
	Coal characteristics and floatation results							
	$V^{\text{daf}}$ , %	Ash, %	Reagent consumption, kg/ton	Concentrate yield, %	$V^{\text{daf}}$ , %	Ash, %	Reagent consumption, kg/ton	Concentrate yield, %
2,2,4-trimethyl-1,3-D	40.9	14.0	0.14	1.2	29.6	20.6	0.14	13.4
			0.28	4.0			0.28	43.2
			0.42	6.5			0.42	67.8
2,2,4-trimethyl-1,3-DSC			0.13	30.6			0.13	38.5
			0.26	51.6			0.26	81.6
			0.39	63.5			0.39	84.1



The increased adsorption of 2,2,4-trimethyl-1,3-DSC on the coals of different metamorphic stages compared with those of 2,2,4-trimethyl-1,3-D provides enhanced hydrophobization of coal surface and improvement in flotation. Thus, the obtained results show the higher the intermolecular hydrogen bond complex “reagent - COM” energy the stronger the agent is attached to active centers of the coal surface, therefore, the better flotation performance. This provides increased absorption of the 2,2,4-trimethyl-1,3-DSC on the coal surface compared with 2,2,4-trimethyl-1,3-D, especially on gas coal, having an increased number of nucleophilic centers in the COM. The study results allow recommending specifications of petrochemical products containing the chemical composition of silicon compounds as reagents for coal flotation.

A quantitative analysis to evaluate quantum-chemical modelling was applied, based on the thermodynamic characteristics of studied heteropolar organic compounds. Based on this approach, the modelling prediction for this study was confirmed by experiments. Nevertheless, these results suggest that data obtained using quantum-chemical modelling to calculate thermodynamic characteristics may provide more sensitive information for assessing the impact of electronic structures on flotation activity than traditional selection of flotation reagents.

#### 4. Conclusion

Prior work has documented the effectiveness of using flotation reagents in improving coal concentrates quality and reducing the content of mineral part. Girevaya, for example, reports that the increasing of flotation activity of heteropolar organic compounds was connected with electronic density on the heteroatom and stereochemistry of the compounds. However, these studies have either been short-term studies or have not focused on mechanism investigation of silicon-bearing heteropolar organic compounds action. In this study, we investigated the flotation activity of heteropolar organic compounds and calculated their molecular electrostatic field maps. We found that the flotation activity of 2-methyl-1,3-DSC in comparison with 2-methyl-1,3-D was associated

with the silicon atom presence. These findings extend those of Galchenko et al. [17], confirming that quantum-chemical method allows selecting more effective flotation reagents. In addition, the results obtained in our study confirmed that the presence of silicon atom in the acetal molecule changed electronic structure of the compound. This study therefore indicates that the benefits gained from quantum-chemical calculations may simplify the selection of flotation reagents. Most notably, this is the first study to our knowledge to predict the effectiveness of silicon-bearing flotation reagent with quantum-chemical method. Our results provide compelling evidence for using quantum-chemical method and suggest that this approach appears to be effective in searching effective flotation reagents. However, some limitations are worth noting. Although our calculations were supported experimentally, the reagent selected should be assessed. Future work should therefore include follow-up work designed to evaluate whether the flotation activity of silicon-bearing reagent homologues are confirmed with quantum-chemical calculations and also whether the homologues may be used to increase the flotation activity.

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