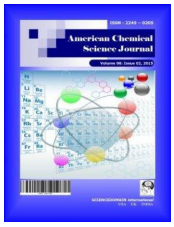

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Synthesis of Sulfomethylated Urea, Thiourea, Aniline Derivatives and Their Application

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Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

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ABSTRACT

A prospective study on the synthesis of sulfomethylated urea, thiourea and aniline is presented. Experiments were performed under atmospheric pressure. The obtained products and compositions based thereon can be used as inhibitors of mineral scales. Products were prepared at four different composition of components and named DASS-1 to DASS-4. Optimal conditions for the production of desired products are defined. All synthesized products have inhibitory properties, but their individual application for waters with high hardness do not provide the desired result and approximately 50-80 % lower than the standard reference industrial scale inhibitors. However, high effective inhibitors were developed through preparing a composition in equimolecular proportions of the synthesized products with IOMS-1 and OEDP. The inhibition efficiency of the product of DASS-1+OEDP with a concentration of 3.0+2.0 reaches 96.5% at a water hardness of 4-5 mEq/L (about 30% efficiency) and 92.0% at 13-14 mEq/L (10% efficiency). It is proved that the inhibitory properties of complexons (chelating agents) were clearly affected by the denticity of complexing ligands.

Keywords: Scale inhibitor; complexon; urea; aniline; OEDP; IOMS-1.

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ABBREVIATIONS

OEDP : Oxyethylidenediphosphonic Acid;
IOMS-1 : Inhibitor of Mineral Salts Deposits.

1. INTRODUCTION

The sulfur-containing organic compounds is dominated more and more practical applications in almost all areas of life [1]. Particular attention is given to obtain sulfur-containing plastics, synthetic rubbers, artificial and synthetic fibers, as well as other polymeric materials, surfactants, synthetic odoriferous substances, physiologically active substances and synthetic medicinal products, sulfur-containing organic compounds for agricultural purposes, solvents and technical fluids, corrosion inhibitors, flotation agents, emulsifiers, etc.

The sulfur-containing organic compounds are also can be implemented to the chemistry of chelates and chelators. Thiols (mercaptans) have been applied as ligands in the chemistry of coordination compounds.

Many rigorous researches have been conducted in the synthesis and application of a dithiol – Dithiolpropanesulfonatesodium or unithiol (universal thiol) [2-4]. The attractiveness of the research of unithiol interaction with metal salts is primarily caused by uniqueness of organic ligand. Unithiol ($CH_2S – CHS – CH_2SO_3Na$) is a bidentate ligand and forms strong complex compounds with many metals, due to the complexing abilities of two sulfhydryl groups and oxygen atoms of sulfo groups.

These synthesized products and compositions can be applied as raw materials for the production of anti-scaling and corrosion inhibitors. In recent years, water as thermal fluid in different purposes, such as steam boilers, distillation system is widely used in industrial and heating processes [5-7]. The main scale forming particles and minerals for water used in these systems are $CaCO_3$, $Mg(OH)_2$ and non-alkaline scales (e.g., $CaSO_4$) [8-10]. There are many classes of components used as scale inhibitors to prevent scale formation.

The aim of the present work is to study the feasibility of the different proportions of components for developed scale inhibitors based on sulfur containing organic compounds and their blending with standard inhibitors (e.g., OEDP, IOMS-1).

2. EXPERIMENTAL DETAILS

To produce sulfur-containing complex organic compounds, sulfomethylation of urea (thiourea) with formaldehyde and sodium bisulfite is proposed. Sulfomethylation of amides - urea and thiourea with formaldehyde and sodium bisulfite is conducted under conditions of carboxymethylation. Liu et al. proposed research on the at first, during interaction of urea (thiourea) with formaldehyde, in the result of nucleophilic connection, mono-, di-, tri- and tetramethylol derivatives are formed according to the following scheme (Fig. 1).

Due to steric hindrance, the product yield of III and IV (in particular) is low. Products of I (a, b) - IV (a, b) are not stable, in storage they are oligomerized, thereby lose the ability of solubility in water. In order to obtain a stable, water-soluble product, the mixture of compounds I (a, b) - IV (a, b) is treated with sodium pyrosulfite. At first, the sodium pyrosulfite reacts with water, existing in the reaction medium with formation of a sodium bisulfite.

$$Na_2S_2O_5 + H_2O \rightarrow 2NaHSO_3 \quad (1)$$

In turn, the products I (a, b) - IV (a, b) with sodium bisulfite reacted with the formation of the mixture of methylenesulfonate urea (thiourea) derivatives, as depicted in Fig. 2.

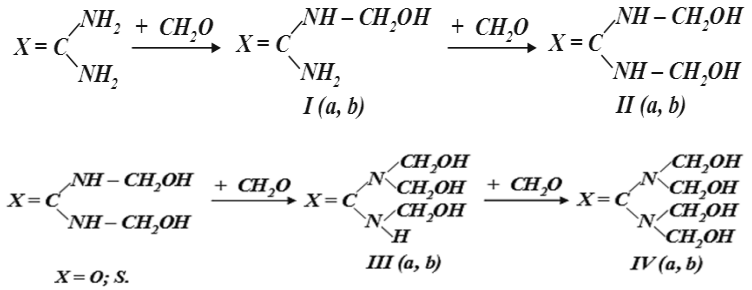


Fig. 1. Mechanism of the formation of mono-, di-, tri- and tetramethylol derivatives

The reaction is conducted at the temperature range of 60°C to 80°C and a molar ratio of the starting products of urea: formaldehyde: sodium bisulfite is 1:2:1.1 and 1:4:4 mol in the presence of a catalytic amount of sodium hydroxide. The average reaction time is about 150–180 minutes. Herewith produces a mixture of aqueous solution of methylenesulfite urea derivatives, containing the basic products of 45 – 50 mol %.

The product yield depending on the ratio of the starting materials and temperature is shown in Fig. 3.

As shown in Fig. 3, by increasing the temperature from 30 to 70°C the reaction yield is increased smoothly and reaches a maximum (24.6%) at the initial reagents ratio is 1:1:1 (curve 1); in this case the optimal ratio is 1:2:2 (curve 2), in which the yield is 76.8%. Further increasing of temperature leads to decrease the yield of the target product, thus creating favorable conditions for the occurrence of side reactions with increasing their yield.

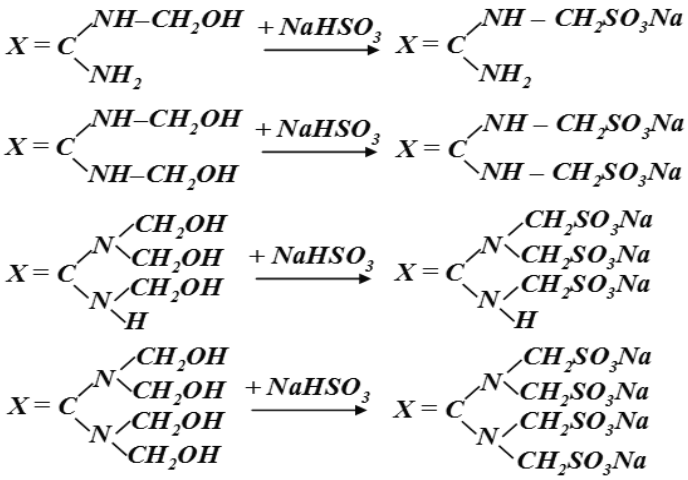


Fig. 2. Mechanism of the formation of the mixture of methylenesulfonate urea (thiourea) derivatives

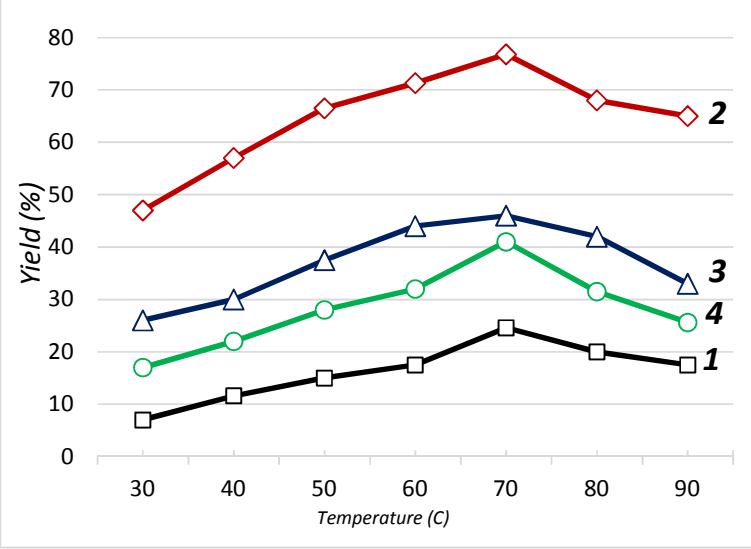


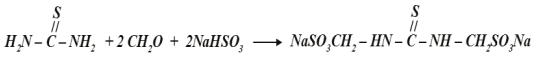
Fig. 3. Yield of the mixture of methylenesulfite urea derivatives depending on temperature. The molar ratios of urea: formaldehyde: sodium bisulfite are following: *1* – 1:2:1; *2* – 1:2:2; *3* – 2:2:1; *4* – 1:4:4

The progress of consecutive reactions shown by infrared spectroscopy, gas chromatography and confirmed by elemental analysis.

In the IR spectrum of products shows strong absorption bands in the regions of 1500 - 1450 cm^{-1} stretching vibrations of the C–N bonds; 1735 - 1750 and 1770 cm^{-1} stretching vibration of C=O bonds; 1400 cm^{-1} stretching vibration of C=S bonds (Fig. 4).

The mixture of obtained methylenesulfite urea derivatives, tentatively called DASS-1, is highly soluble in water.

Under similar conditions, the condensation reaction of thiourea with formaldehyde in the presence of sodium bisulfite is studied (eq. 2):



(2)

The reaction is conducted in a weakly alkaline medium at different temperatures, time and different ratios of the starting components (Fig. 5).

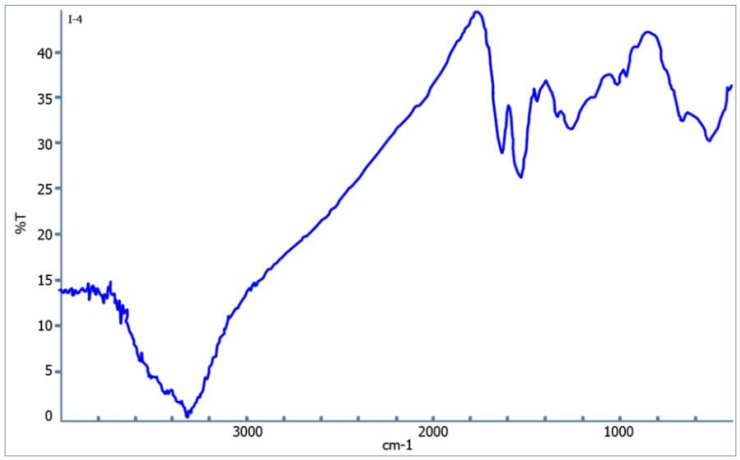


Fig. 4. IR-spectrum of the product of sulfomethylation of urea

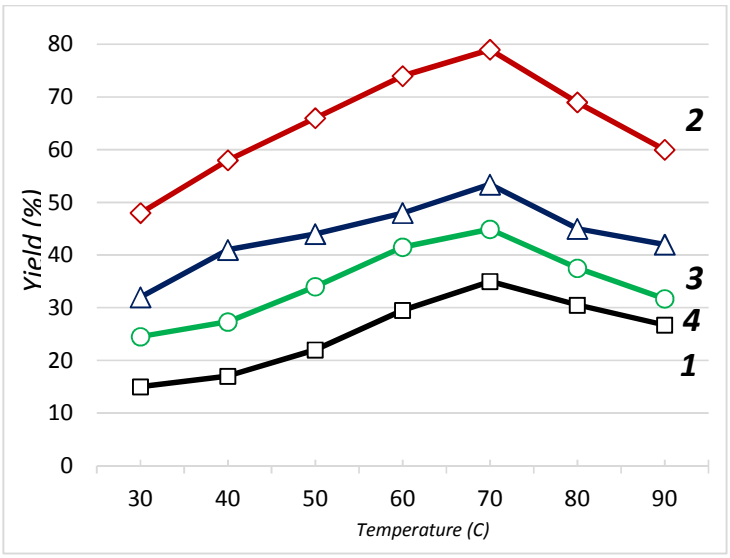


Fig. 5. The yield of the mixture of methylenesulfite thiourea derivatives depending on temperature. Molar ratios of thiourea: formaldehyde: sodium bisulfite are following: *1* – 1:2:1; *2* – 1:2:2; *3* – 2:2:1; 4 – 1:4:4

In this research, the reaction took approximately 180 minutes. The molar ratios of initial products are 1:1:1, 1:2:2, 2:2:1 and 1:4:4 and the temperature range is between 30 and 90°C.

As a result, we have determined that the highest yield of the desired product (79%) is achieved when the reaction time is 180 minutes, the optimal temperature is 70°C and the molar ratio of thiourea: formaldehyde: sodium bisulfite is 1:2:2 (curve 2). Increasing amounts of formaldehyde and sodium bisulfite relation to thiourea leads to reducing the yield of the final product, to 53.4 and 44.9%, respectively (curves 3 and 4). Composition and structure of intermediate products of the reaction and construction, structure and elemental composition of the obtained product are analyzed. The construction of the synthesized compounds determined by IR - spectroscopy and the composition determined by elemental analysis.

The IR spectra, showed N–H stretching peak at 3425-3445 cm^{-1}, O=S=O stretching peak at 1045-1070 cm^{-1} and C–S stretching peak at 740-760 cm^{-1}. CH_2 and C=N bonds show stretching bands at 1450-1470 cm^{-1} and near 1200 cm^{-1}, respectively (Fig. 6).

The mixture obtained methylenesulfite thiourea derivatives are also moderately soluble in water and conventionally called as DASS-2.

In order to expand the range of sulfomethylated products, condensation reaction of aniline and sulfanilic acid with formaldehyde in the presence of sodium bisulfite in weakly acidic medium is studied. The reaction can be represented as shown in Fig. 7.

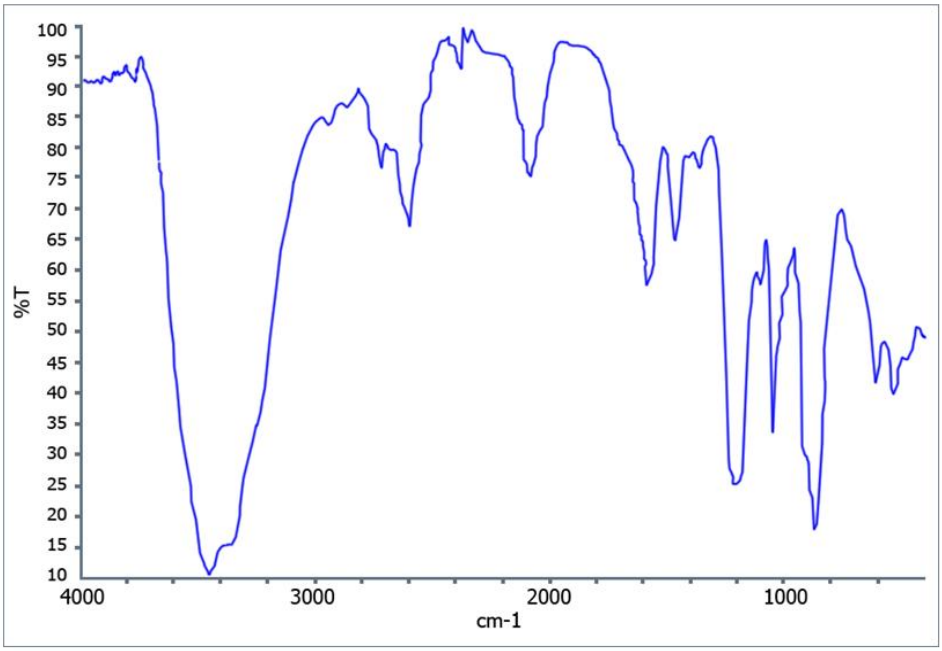


Fig. 6. IR-spectroscopy results for the product of sulfomethylation of thiourea

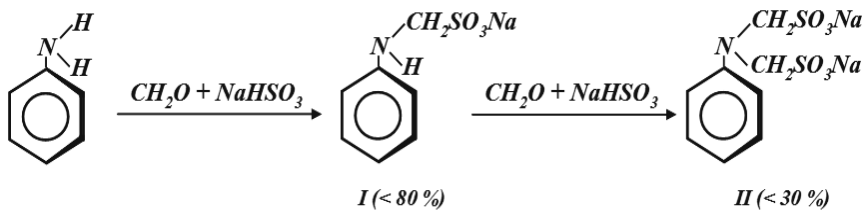


Fig. 7. Condensation reaction mechanism of aniline and sulfanilic acid with formaldehyde in the presence of sodium bisulfite

The condensation of aniline and sulfanilic acid with formaldehyde and sodium bisulfite were carried out at 60 - 70°C for 180 minutes. A 35% of formaldehyde solution is used. Sodium bisulfite was prepared by decomposition of sodium persulfite ($Na_2S_2O_5$) with water (50% solution). Sodium hydroxide was used as a catalyst at the concentration of 3% by weight of the reactants. Unreacted formaldehyde linked with sodium bisulfite.

As shown from condensation reaction scheme that at interaction of starting materials aniline: formaldehyde: sodium bisulfite in the ratio 1:1:1 and 1:2:2 is formed N-methylaniline sodium sulfonate (product I - DASS-3) and N,N-dimethylaniline sodium sulfonate (product II - DASS-4).

Experimental results indicated that the product II is not formed in 1:1:1 molar ratio of starting materials and at a minimum temperature. At 50°C its traces can be found, whereas the maximum amount of the mixture of product I reached to 80%. By increasing the ratio of starting products to 1:2:2 at a temperature of 70°C, the yield of product mixture increases and product I and II reach to 57% and 29% respectively (Fig. 8). Small amount of product II is compatible with the theoretical laws and explained by steric factors.

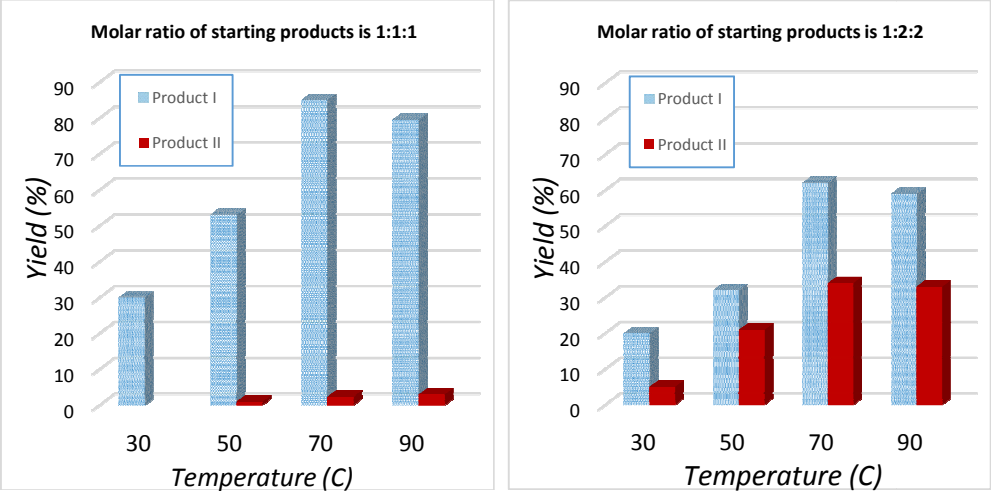


Fig. 8. The dependence of the yield of products I and II on temperature (Reaction time: 180 minutes)

Finished products are regulated by the following indicators:

N-methylaniline sodium sulfonate is white powder, poorly soluble in water.

Empirical formula: $C_7H_8O_3NNaS$
Molecular weight: *209.36*
Elemental composition:

	Found, %	Calculated, %
C : H : N : O : S : Na	40.2 : 3.8 : 6.6 : 23 : 15.4 : 11	40.1 : 3.9 : 6.7 : 22.9 : 15.3 : 11.1

Dimethylaniline sodium sulfonate is white powder, poorly soluble in water.

Empirical formula: $C_8H_9O_6NNa_2S_2$
Molecular weight: *325.86*
Elemental composition:

	Found, %	Calculated, %
C : H : N : O : S : Na	29.7 : 2.9 : 4.4 : 29 : 19.7 : 14.3	29.6 : 2.8 : 4.3 : 29.5 : 19.7 : 14.1

The structure of the synthesized compounds was proved by IR and NMR spectroscopy. The IR spectra of product-I, showed C–N stretching peak at 1190-1205 cm^{-1}, O=S=O stretching peak at 1048-1075 cm^{-1}, N–H stretching peak at 3422-3448 cm^{-1} and CH_2 stretching peak at 1454 - 1472 cm^{-1}. The absorption compounds containing C=S bond and C–C bond of aromatic ring show stretching bands at 734-758 cm^{-1} and 1663 cm^{-1}, respectively.

3. RESULTS AND DISCUSSION

The molecular models and the electron density distribution in the molecules of DASS-1, DASS-2 and DASS-3 are shown in the Figs. 9, 10 and 11, respectively.

In order to find a practical application of the obtained products, effectiveness of these products in inhibiting of mineral salts in waters with different hardness from 4 to 14 mEq/L is examined and compared with the standard scaling inhibitors (Table 1).

As seen from the table, the results of studied products are lower than the reference inhibitors – IOMS-1 and OEDP, but the existing data gives confidence on perspectives of application of these components as components of scale inhibitors.

Different compositions based on DASS-1, DASS-2 and OEDP were therefore prepared and tested (Table 2).

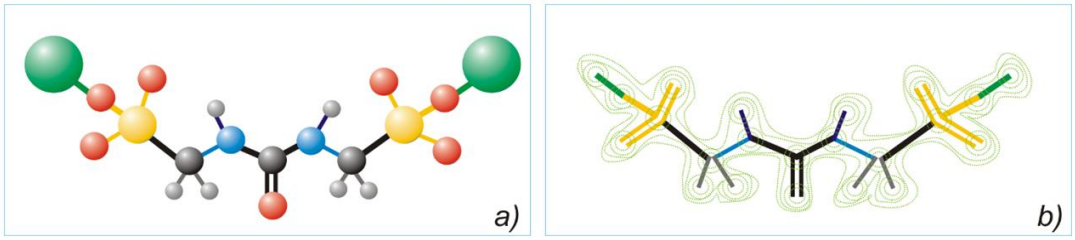


Fig. 9. The molecular model (a) and the electron density distribution in the molecules (b) of DASS-1

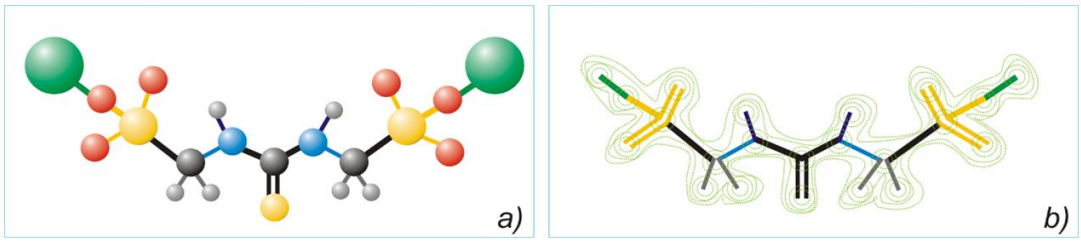


Fig. 10. The molecular model (a) and the electron density distribution in the molecules (b) of DASS-2

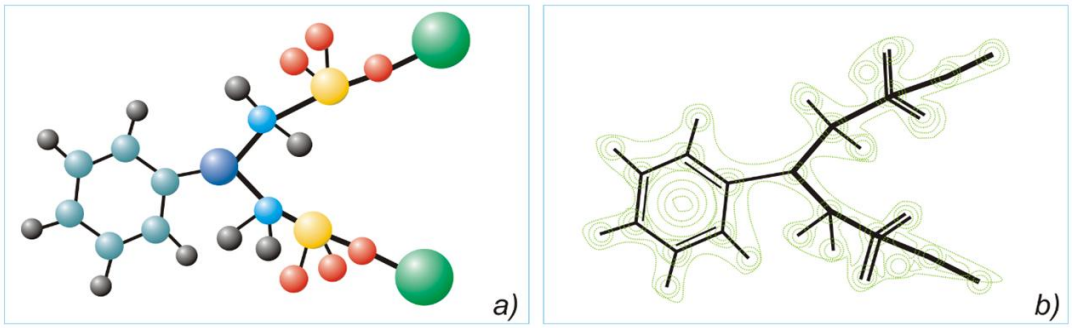


Fig. 11. The molecular model (a) and the electron density distribution in the molecules (b) of DASS-3

Table 1. Dependence of the inhibitory activity of *DASS-1* on concentration at a temperature of 90°C

Inhibitor concentration, mg/L	Efficiency of inhibition, %			
	Water hardness, mEq/L			
	4 – 5	6 – 7	8 – 11	13 – 14
	Product-I DASS-1			
1.0	67.0	62.0	59.0	61.0
2.0	73.5	69.0	62.0	63.5
3.0	79.0	77.0	75.0	76.0
4.0	80.0	79.0	75.5	76.5
5.0	81.0	80.0	78.0	79.0
6.0	82.0	81.0	79.0	81.0
7.0	82.0	81.5	79.5	81.0
	Product-I DASS-2			
1.0	71.0	65.0	62.0	65.0
2.0	76.0	70.5	66.0	66.5
3.0	81.0	80.5	76.5	71.0
4.0	82.5	81.0	78.0	77.0
5.0	83.0	82.0	80.0	79.0
6.0	83.0	84.0	81.0	82.0
IOMS-1 – 4.0	90.0	88.0	87.0	86.0
OEDP – 4.0	93.0	92.0	91.0	90.0

Table 2. Dependence of the inhibitory activity of *DASS-1* on concentration at a temperature of 90°C

Inhibitor concentration, mg/L	Efficiency of inhibition, %			
	Water hardness, mEq/L			
	4 – 5	6 – 7	8 – 11	13 – 14
	DASS-1 + OEDP			
1.0 + 1.0	76.0	72.0	69.0	71.0
1.0 + 2.0	82.5	79.0	72.0	73.5
1.0 + 3.0	88.0	77.0	85.0	86.0
2.0 + 1.0	80.0	79.0	85.5	86.5
2.0 + 2.0	91.0	90.0	88.0	89.0
2.0 + 3.0	92.0	91.0	89.0	91.0
3.0 + 1.0	95.0	93.5	91.5	91.0
3.0 + 2.0	96.0	95.5	92.0	92.0
3.0 + 3.0	98.5	96.0	92.5	92.0
	DASS-2 + OEDP			
1.0 + 1.0	81.0	75.0	73.0	70.0
1.0 + 2.0	86.0	80.5	76.0	76.5
1.0 + 3.0	91.0	89.5	86.5	81.0
2.0 + 1.0	82.5	81.0	78.0	77.0
2.0 + 2.0	93.0	82.0	90.0	89.0
2.0 + 3.0	93.0	94.0	91.0	90.0
3.0 + 1.0	84.0	88.0	87.0	86.0
3.0 + 2.0	94.0	92.0	91.0	90.0
3.0 + 3.0	95.0	93.0	91.0	90.0
IOMS-1 – 4.0	90.0	88.0	87.0	86.0
OEDP – 4.0	93.0	92.0	91.0	90.0

The results show that the scale prevention is much higher for the compositions of DASS-1+OEDP than DASS-1+OEDP and efficiency increases with increasing concentration from 2.0 to 9.0 mg /L, reaching a peak with 90.0 – 98.5% depending on water hardness.

Table 3. Inhibitory efficiency of product (I+II): IOMS-1 at a ratio of 1:1

Inhibitor concentration, mg/L	Efficiency of inhibition, %			
	Water hardness, mEq/L			
	4-5	6-7	8-11	13-14
1.0	81.0	78.0	69.0	67.0
2.0	87.0	81.0	73.0	71.0
3.0	91.0	91.0	85.0	82.0
4.0	95.0	94.0	91.0	90.0
IOMS-1 – 4.0	93.0	92.0	91.0	90.0

In addition, inhibitory activity of DASS-3 with water hardness of 4–14 mg/L is also studied. The analyzed data shows that the maximum efficiency of the inhibition of DASS-3 is achieved the highest point at a concentration of 4.0 mg/L of water, and reaches 78.0%, which does not compatible with modern requirements for inhibitors.

In order to obtain high effective scale inhibitor a composition of product I, II and IOMS-1 is prepared at a ratio of 1:1 (Table 3).

Table 3 represents that the prepared compositions at a concentration of 4.0 mg/L have an efficiency of 90.0 - 95.0%, and achieve average 1.0 - 4.0% compared to the standard IOMS-1.

4. CONCLUSION

As it follows from this study, all synthesized and tested products have inhibitory properties, but their individual application for waters with high hardness do not provide the desired result and approximately 1.2–1.8 times lower than the standard reference industrial scale inhibitors.

It is proved that through preparing a composition in equimolecular proportions of the synthesized products, IOMS-1 and OEDP, can be obtained high effective inhibitors. The inhibition efficiency of the product of DASS-1+OEDP with a concentration of 3.0+2.0 reaches 96.5% at a water hardness of 4-5 mEq/L (about 30% efficiency) and 92.0% at 13-14 mEq/L (10% efficiency).

Studying the properties of the scaling effectiveness of synthesized products and compositions on their basis enable us to determine the following series on their effectiveness:

DASS-3 < DASS-2 < DASS-1 < IOMS-1 < OEDP

DASS-3 + IOMS-1 < DASS-2 + OEDP < DASS-1 + OEDP

This proves that the inhibitory properties of complexons depend mainly on the denticity of the complexing ligand. The more denticity of ligands, the more and stronger connection formed with metal ions and higher inhibition efficiency of complexions.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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