Investigation of interaction of molecules of inorganic gases with surface of copper-containing polyacrylonitrile

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Abstract. The possibility of adsorption of inorganic gases onto the surface of copper-containing polyacrylonitrile (PAN) films was studied by molecular modeling and quantum chemical calculations. For this, the model of a copper-containing PAN cluster was obtained by these methods, which interacted with the adsorbed gas molecule. Based on the results of the simulation, it was established that when adsorbing gas molecules, intermolecular bonds arise between them and the surface of a cluster of copper-containing PAN. A high probability of adsorption on the surface of copper-containing PAN is manifested in chlorine, hydrogen sulfide, and carbon dioxide molecules. Low probability of adsorption - for molecules of ozone and nitrogen dioxide

1. Introduction
Thermally stabilized polyacrylonitrile (PAN) is an electrically conductive material that exhibits sensitivity to various gases at room temperature [1-3]. Based on this material, high-sensitivity gas sensors (nitrogen dioxide, hydrogen sulfide and chlorine) have been constructed [1]. Actual is the possibility to add PAN with various modifying additives, as a rule, with metal compounds [4].

The object of our study is the copper-containing PAN. The structure of the copper-containing PAN is a PAN with incorporated molecules of copper oxide, copper chloride and metallic copper [1]. Copper compounds that are part of this material have a positive effect on the growth of the film surface and lead to a decrease in the resistivity of the films [5]. Therefore, copper-containing PAN is a promising material for use in gas sensors.

In the available scientific works there is no explanation of the sensitivity of copper-containing PAN to various gases. In [6-8], we explained the gas sensitivity of PAN and cobalt-containing PAN films by mathematical modeling. The purpose of this study is to study the possibility of adsorption of inorganic gaseous pollutants to the surface of copper-containing PAN by quantum chemical calculations and molecular modeling.

2. Experimental
It was found in [5] that the structure of the copper-containing PAN consists of a PAN with molecules of copper oxide, copper chloride and metallic copper embedded in it. Therefore, for a theoretical study of the copper-containing PAN, a cluster was modeled which was formed at an IR annealing temperature of 350-500 °C. The cluster consists of two parallel arranged conjugate macromolecules of
PAN pentamers with the molecules of copper oxide, copper chloride and a copper atom atom built in between them. Initially, spatial configurations of the PAN pentamer macromolecules were obtained in the Hyper Chem program. To estimate the thermodynamic parameters of the obtained structures, the software package GAUSSIAN07 was used using the 6-31 G * basic set in the framework of density functional theory (DFT) [9-11]. Semiempirical calculations of the spatial configurations of macromolecules were carried out using the B3LYP exchange-correlation functional [9, 10]. Then, a simulation of the cluster of copper-containing PAN was carried out using the meteoric calculation of the steric energy of the system in the Chemoffice 2010 software package (Chem3D subroutine). The Chem3D subroutine uses one of the methods of molecular modeling - the method of minimizing the potential energy of the system in a modified version of the force field (MM2), developed by Allinger [12-16].

In the next stage, Chemoffice subroutines Chem3, Chem, the molecules of copper and copper compounds in different versions were built between the layers of the PAN cluster. As a result of the simulation it was established that the energy minimum is characteristic for a cluster of copper-containing PAN, in which the molecules of copper compounds are located between PAN macromolecules in the sequence: a molecule of copper chloride - a molecule of copper oxide - a copper atom. The distance between the particles of the dopants and the layers of the PAN is 3.6-4.2 Å (Fig. 1).

Then the possibility of adsorption of molecules of inorganic gases (nitrogen dioxide, methane, ammonia, sulfur oxide (II), hydrogen sulfide, ozone, carbon monoxide, carbon monoxide (II), chlorine) to the surface of a cluster of copper-containing PAN was analyzed in the Chem3D program [12, 13]. For this purpose, different positions of the gas molecules relative to the cluster were set: (1) - (12) - see Fig. Position 1 assumed that the molecules of inorganic gases were built into the structure of PAN, and positions 2 - 12 showed the location of the water molecule above the surface of the cluster.

Figure 1. The configuration of a copper-containing PAN cluster.

Figure 2. The arrangement of the gas molecule upon interaction with the surface of a copper-containing PAN cluster.

Further, the steric energy was calculated and the more favorable location of the molecules in question relative to the PAN cluster was found. In addition, the calculation of the energy of formation
of the bond between the cluster and the gas molecule $\Delta E$ was carried out, as the difference in the energies of the system with the distance between the molecule and the cluster at the maximum distance and at the point of the energy minimum. At the same point, the distance ($l_{\text{min}}$) between the gas molecule and the cluster surface was estimated.

Figure 3. Dependence of the steric energy of the system "molecule of inorganic gas - cluster of copper-containing PAN" at the point of energy minimum.

Figure 4. Dependence of the value of the steric energy of the system of a molecule of inorganic gas - a cluster of copper-containing PAN "on the distance between the molecule of inorganic gas and the surface of the cluster.

Table 1. Thermodynamic parameters of the system "copper-containing PAN cluster - gas molecule"

| №  | Gas molecule | $E_{\text{min}}$ (kJ/mol) | $\Delta E$ (kJ/mol) | $l_{\text{min}}$, Å |
|----|--------------|-----------------|----------------|-----------------|
| 1. | NO$_2$       | 6182,76         | 107,68          | 3,7             |
| 2. | Cl$_2$       | 2615,40         | 5,49            | 3,2             |
| 3. | NH$_3$       | 5120,93         | 7,37            | 2,5             |
| 4. | SO$_2$       | 3501,16         | 3,85            | 3,5             |
| 5. | H$_2$S       | 2931,58         | 2,68            | 3,5             |
3. Result and Discussion

Based on the results of the simulation, it was established that the cluster of copper-containing PAN is a structure of PAN macromolecules, between which the molecules of copper and copper compounds are located in the sequence: a molecule of copper chloride - a molecule of copper oxide - a copper atom. Based on the results of molecular modeling, it is determined that chemical interactions between PAN macromolecules and dopants do not occur.

Table 1 presents the thermodynamic parameters of the system "molecule of inorganic gas - cluster copper-containing PAN" results of calculations of the steric energy of the given system (E). Figure 4 shows the energy values of the system "gas molecule - a cluster of copper-containing PAN" from the distance of the gas molecule and the surface of the cluster.

According to the results presented in Table 1 and Fig. 4 that the smallest value of steric energy in the "copper-containing PAN cluster-the gas molecule" system is characteristic for the adsorption of the chlorine molecule (Emin = 2615.40 kJ/mol). Also, low values of steric energy are inherent in hydrogen sulfide molecules (Emin = 2931.58 kJ/mol) and carbon dioxide (Emin = 3251.94 kJ/mol). High values of the steric binding energy are characteristic for ozone molecules (Emin = 7610.59 kJ/mol) and nitrogen dioxide (Emin = 6182.76 kJ/mol).

Based on the results of molecular modeling, it was established that the energetically favorable arrangement of gas molecules is above the cluster surface with a distance from the cluster lmin of 2.5-3.7 Å in the region where the lowest values of the steric energy of the system for the gases under study are observed. As the gas molecule approached the cluster for a shorter distance, the steric energy of the system grew. At the same time, the adsorption energy does not exceed 108 kJ/mol (Table 1). This means that in the system "molecule of inorganic gas-cluster copper-containing PAN" intermolecular bonds arise. Moreover, the strongest connection with the cluster is observed in molecules of ozone and nitrogen dioxide. The remaining gases, on the other hand, have weak intermolecular bonds with a cluster of copper-containing PAN.

4. Conclusion

A theoretical study of the gas sensitivity of copper-containing PAN films by quantum-chemical calculations and molecular modeling was carried out. As a result of modeling, a copper-containing PAN cluster was obtained and the possibility of adsorption of molecules of various inorganic gases to this cluster was estimated numerically.

Based on the results of the simulation, it was established that when adsorbing gas molecules, intermolecular bonds arise between them and the surface of a cluster of copper-containing PAN. A high probability of adsorption on the surface of copper-containing PAN is manifested in chlorine, hydrogen sulfide, and carbon dioxide molecules. Low probability of adsorption - for molecules of ozone and nitrogen dioxide.

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