Mathematical modeling of the process of interaction of sulfur dioxide with pyrolyzed polyacrylonitrile

O A Kakorina¹, I V Zaporotskova¹, I A Kakorin¹

¹Volgograd State University, Universitetskii prospekt, 100, Volgograd, Russia, 400062

Abstract. The paper presents a study of the interaction of sulfur dioxide with a polymer—pyrolyzed polyacrylonitrile (PPAN). The possibility of using PPAN as an element of an electronic sensor device for recording the presence and identification of sulfur dioxide in the atmosphere is shown. The results of the established geometric and electron-energy characteristics of the polymer interacting with gas are described. Theoretical calculations were performed using the molecular cluster model and the quantum-chemical MNDO method.

1. Introduction

New materials, including nanomaterials [1-3] are used actively in the modern world. The development of science, the increase in production and consumption require the creation of devices based on new principles and the latest technologies with quantum effects. These factors are caused scientists to seek new materials, that have the necessary characteristics and which demonstrate new effects that will become the basis of modern devices, actively [4-6].

The environmental pollution is one of the most important problems. You need to take care of the air that you and your child breathe! Exceeding maximum concentrations of harmful impurities in the atmosphere is fraught with fatal consequences. Recently, sulfuric emissions are observed in developed industrial centers [7-10]. Therefore, it is necessary to develop new devices that can protect people from harmful emissions into the environment [11]. One of the elements of such a device can be pyrolyzed polyacrylonitrile. Polyacrylonitrile is a widely distributed polymer that is the most interesting for possible areas of use [12-16]. To change the physicochemical properties of polyacrylonitrile and to get nano-formations on its basis, the self-organization mechanism of the structure is used when the IR radiation is exposed on the polymer. The result is a new polymer — pyrolyzed polyacrylonitrile (PPAN), which is a graphite-like layer structure, each layer consists of flat hexagonal structures, and the nitrogen content in the system depends on the pyrolysis conditions [17-18].

PPAN has a developed adsorption surface and unique characteristics and can be used in air purification devices. Therefore, a quantum-chemical study of the interaction of sulfur dioxide with a polymer is extremely relevant and the results can be used in the manufacture of devices or sensors to protect the atmosphere from sulfur dioxide.
2. Sulfur gas adsorption on the surface of PPAN

Sulfur gas adsorption was calculated using the semi-empirical MNDO method [19, 20]. As the object of study was selected a PPAN monolayer, containing, aside from carbon, 20% of surface nitrogen atoms (of the total number of atoms). The distance between atoms in the layer is 1.4 Å. The adsorption process of the SO\textsubscript{2} molecule on the PPAN monolayer was considered. Two orientations of a sulphurous gas molecule above the surface of the PPAN were investigated: 1) the molecule was approaching by a sulfur atom; 2) the molecule was approaching the layer by oxygen atoms (Figure 1).

![Figure 1. The orientation of the sulfur dioxide molecule above the surface of the PPAN: a) the molecule is approaching by a sulfur atom; b) the molecule is approaching the layer by oxygen atoms.](image)

In the first case, a sulfur dioxide molecule was attached to the surface atom of the PPAN monolayer, located approximately in the middle of the polymer cluster, this allowed us to exclude the influence of edge effects. The distance between the monolayer and the sulfur atom of the sulfur dioxide molecule was 3 Å. The adsorption process was modeled by stepwise approximation of the molecule to the atom of the layer surface along the perpendicular, drawn through the sulfur atom of the sulfur dioxide molecule and the selected polymer atom, to the surface. The performed calculations made it possible to construct a surface profile of the potential energy of the adsorption process. Analysis of the energy curve found that the sulfur dioxide molecule is not adsorbed on the surface of the PPAN, this is confirmed by the absence of a minimum on the energy curve (Figure 2).

![Figure 2. Surface profiles of potential energy of adsorption processes of a sulfur dioxide molecule at different orientations.](image)

The processes were simulated in a similar way for the second orientation of the sulfur dioxide molecule, initially the molecule was located at a distance of 3.7 Å, while the distance from the layer to the sulfur atom of the molecule was 4.4 Å. There is no minimum on the energy curve of the interaction of the sulfur dioxide molecule and the surface of pyrolyzed polyacrylonitrile, this indicates the impossibility of adsorption on the monolayer of the polymer (Figure 2).

An analysis of the geometry optimization results made it possible to establish the geometric features of the «PPAN-SO\textsubscript{2}» structure (Figure 3). So, in the case of approaching a sulfur dioxide molecule to the polymer layer by oxygen atoms, the molecule is destroyed, the oxygen atom breaks the bond with the sulfur atom and is adsorbed on the carbon atom of the PPAN.
3. The absorption of sulfur dioxide on the surface of the polymer with a defect

Then the adsorption process of a sulfur dioxide molecule on a defective pyrolyzed polyacrylonitrile surface was studied. Namely, the polymer layer contained a vacancy (the so-called V-defect) [21]. The sulfur dioxide molecule was approached by the sulfur atom to the center of the vacancy with a step of 0.1 Å; energy calculations at each step made it possible to construct a surface profile of potential energy (Figure 4).

![Figure 4. The profile of the adsorption process of a sulfur dioxide molecule on PPAN with a vacancy.](image)

It should be noted that a defective structure has a more efficient adsorption ability, and a sulfur dioxide molecule is adsorbed on a monolayer. The carbon atom forming the vacancy leaves the surface of the monolayer at a distance of 0.5 Å, while pulling adjacent atoms along with it, which leads to a distortion of the flat layer. The carbon atom, that forms the vacancy, leaves the surface of the monolayer at a distance of 0.5 Å, while pulling adjacent atoms along with it, this leads to a deformation of the flat layer. This atom interacts with the sulfur atom of the sulfur dioxide molecule. Physical adsorption, what energy is 2.15 eV, is observed at the distance of 1.8 Å (Figure 5).

![Figure 5. The interaction of a PAN with a surface defect with a sulfur dioxide molecule: a) the molecule is approaching by a sulfur atom; b) the molecule is approaching the layer by oxygen atoms.](image)
This fact proves the possibility of using PPAN in sensors for determining the content of sulfur dioxide in the atmosphere, at that the presence of physical adsorption determines the possibility of multiple use of such a sensor.

Then the process of approaching a sulfur dioxide molecule to a vacancy on the surface of a PPAN by oxygen atoms was considering. Quantum-chemical calculations of this process made it possible to construct a surface profile of potential energies. There is no energy minimum on this curve, it means that the adsorption of a sulfur dioxide molecule does not occur. An analysis of the geometry of the structure of the simulated process showed that the approach of a molecule to a layer leads to its destruction into individual atoms, while oxygen atoms are adsorbed on the surface of the PPAN.

The performed calculations made it possible to calculate the bandgap of the PPAN + SO₂ complex. The meaning of bandgap increases with the interaction of a sulfur dioxide molecule with the PPAN surface. Thus, a change in the conductivity of the resulting complex will be a signal of the presence of the sulfur dioxide in the atmosphere.

4. Conclusion
The performed quantum-chemical calculations of the attachment of a sulfur dioxide gas molecule to the surface of a PPAN made us possible to establish, that only physical adsorption of this molecule on the surface of a PPAN is possible, this determines the possibility of multiple use of a sensor, based on this polymer. It is shown that the interaction of sulfur dioxide with PPAN leads to its destruction, this property can be used as protection against the harmful effects of sulfur dioxide. The sensory response can be detected by the modification the potential in the system when the PPAN interaction occurs even with a single molecule, this proves the extreme sensitivity of such a sensor system based on the PPAN. This response is due to a modification in the conductivity of the obtained complex, this is illustrated by a change in the bandgap compared in pure PPAN.

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6. References
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