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Theoretical Investigations of the Interaction of Gaseous Pollutants Molecules with the Polyacrylonitrile Surface

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Abstract: This work presents theoretical studies of the interaction of molecules of several gaseous pollutants with polyacrylonitrile (PAN) surface in the presence of a water and/or oxygen molecule. For this purpose, a PAN cluster model has been proposed by the methods of quantum chemical calculations and molecular modeling. The energy-favorable positions, in which the gas molecules are located relative to the surface of the PAN cluster, are determined and the thermodynamic and the following geometric parameters of the systems are calculated: “PAN cluster – oxygen molecule”, “PAN cluster – oxygen molecule – gas molecule”, “PAN cluster – water molecule – molecule of oxygen”, and “PAN cluster – a molecule of water – an oxygen molecule – a gas molecule”. It is concluded that PAN in atmospheric air in the presence of oxygen molecules is sensitive to carbon oxide (IV), sulfur (IV) oxide, chlorine, hydrogen sulfide and carbon oxide (II). In an anoxic environment, PAN films will show selective sensitivity to chlorine. The presence of water molecules in the investigated air should not affect the gas sensitivity of PAN films.

Keywords: polyacrylonitrile; steric energy; adsorption of gases; molecular modeling; the effect of a molecule of water (oxygen)

1. Introduction

It is known that polyacrylonitrile (PAN) under the influence of thermal heating can gradually change its structure [1–4]. PAN films have unique electrical, electrochemical and gas-adsorption properties and are used for various applications in electronic engineering [5,6].

Thin films of PAN that have passed infrared (IR) annealing at temperatures of 300–600 °C have semiconductor and gas sensitive properties already at room temperature [5,7–13]. Such materials can be used in energy-efficient gas sensors to monitor air quality [10,11]. The mechanism of interaction of molecules of simple gases with the surface of PAN was investigated using quantum chemical calculations. For this purpose, the authors of references [14,15] calculated the structure of a single-atomic PAN layer using a semiempirical quantum chemical calculation scheme MNDO (Modified Neglect of Diatomic Overlap). The PAN cluster consisted of five carbon rings in length and four in width. However, in one of the long rows, instead of five there were six rings. The mechanisms of adsorption of fluorine, oxygen and hydrogen molecules to the surface of the PAN cluster were investigated. The authors noted that on the surface of a single-layer cluster of PAN, molecules of gases are adsorbed by the mechanism of chemical adsorption. Here, a cluster was also modeled, consisting of two identical layers of PAN, which were located one above the other. It was shown that a physical adsorption of simple gas molecules can occur on a two-layer PAN cluster [16].

Adsorption of the triatomic nitrogen oxide molecule (NO_2) was considered in reference [7]. A single-layer PAN cluster consisting of seven rings, one of which is located at the center, with the other six around it, was obtained by quantum chemical calculations. During the adsorption of the NO_2 molecule, a surface adsorption complex was formed with the arrangement of the nitrogen dioxide molecule at a minimum distance of 2.37 Å from the nearest hydrogen atom of the PAN cluster. However, the coordination of the nitrogen atom of the molecule occurred over the center of one of the rings. Judging from the calculated distances between the gas molecule and the cluster, physical adsorption took place.

The mechanism of adsorption of a triatomic carbon monoxide (IV) molecule on the surface of a two-layer cluster of PAN was considered in reference [17]. Quantum-chemical calculations have shown that for a CO_2 molecule only physical adsorption at a distance of 2.5 Å from the center of the ring of the PAN cluster is possible.

The results of references [7,17] were confirmed in reference [18], in which it was shown that both molecules (CO_2 and NO_2) are actually adsorbed by the mechanism of physical adsorption. The calculated length ($l_{\min}$) of the bond formed was somewhat larger—3.7 and 4 Å for CO_2 and NO_2 , respectively. In both cases, the molecules of gases were adsorbed to the center of the ring. However, in reference [18] another two-layer cluster of PAN was simulated, consisting of two linear pentamers of PAN arranged one above the other [18]. A simpler form of the cluster made it possible to perform quantum-chemical calculations for a larger number of gas molecules. Adsorption of other molecules of pollutant gases (nitric oxide (IV), methane, ammonia, sulfur oxide (II), hydrogen sulfide, ozone, carbon oxide (II), chlorine) on the PAN surface was investigated. For all gas molecules, with the exception of the ammonia molecule, their location above the cluster surface at a distance of 3.4 to 4 Å was energetically advantageous. The binding energy ΔE for most gas molecules was not higher than 13 kJ/mol, which indicated physical adsorption due to van der Waals forces. The adsorption of the ammonia molecule proved to be energetically unfavorable. The steric energy of the PAN cluster (E_{PAN} , which was equal to 2795.7 kJ/mol) and the “PAN – gas molecule cluster” ($E_{\text{PAN}+\text{gas}}$) system were calculated. It was concluded that PAN films are selectively sensitive to chlorine, since only the “PAN cluster – chlorine molecule” system had a steric energy of $E_{\text{PAN}+\text{Cl}_2}$ equal to 2477.1 kJ/mol, that is, less than E_{PAN} .

At the same time, under real conditions, molecules of water and oxygen are always present on the surface of gas sensitive materials, which affects the mechanism of interaction of gas molecules with the surface of gas-sensitive materials [19]. In reference [20], the influence of the water molecule on the interaction of PANs with the molecules of these gases was estimated by analogous methods. It was shown that the water molecule is more advantageous at a distance of 2.7 Å from the center of the PAN cluster. However, the steric energy of the “PAN cluster – water molecule” system ($E_{\text{PAN}+\text{H}_2\text{O}}$) was significantly higher than the E_{PAN} , and was 6123.39 kJ/mol. In the interaction of a PAN cluster with molecules of pollutant gases in the presence of a water molecule, the steric energy of the “PAN cluster – water molecule – gas molecule” ($E_{\text{PAN}+\text{H}_2\text{O}+\text{gas}}$) system was estimated. The authors of reference [20] concluded that, in the presence of water molecules, PAN films can have a selective gas sensitivity to carbon oxide (II) molecules, since only when interacting with the CO molecule the steric energy $E_{\text{PAN}+\text{H}_2\text{O}+\text{CO}} = 6105.04$ kJ/mol was less than $E_{\text{PAN}+\text{H}_2\text{O}}$. The calculated values of ΔE (1–68 kJ/mol) and $l_{\min}$ (>3.2 Å) also indicated van der Waals interactions between the gas molecule and the PAN surface. High values of ΔE were characteristic of polar molecules, for which electrostatic forces are also possible [21].

However, in references [18,20] the effect of oxygen molecules on the processes of adsorption of gas-pollutant molecules on the PAN surface was not investigated. Oxygen, as is known, is constantly present in the environment. In addition, the simultaneous influence of oxygen and water molecules on adsorption of molecules of pollutant gases was not studied.

In connection with this, the aim of this paper is a theoretical study of the mechanisms of interaction of the PAN cluster with the molecules of the main pollutant gases (nitric oxide (IV), methane, ammonia,

sulfur oxide (II), hydrogen sulfide, ozone, carbon monoxide (IV), carbon monoxide (II), chlorine) in the presence of an oxygen molecule or with the simultaneous presence of an oxygen molecule and a water molecule.

2. Materials and Methods

The studies were carried out according to the method proposed in references [18,20,22]. The PAN cluster consisting of two macromolecules, PAN pentamers, arranged one above the other was obtained by the method of quantum chemical calculations in the HyperChem program using the semiempirical quantum chemical calculation scheme MNDO [23,24]. Spatial configurations of PAN macromolecules were obtained [22]. Further, in the GAUSSIAN09 software package, using the 6-31 G * basic set within the density functional theory (DFT), which allows the most accurate calculation of the energy of the correlated electron motion thermodynamic parameters of these macromolecules were calculated [22]. Then, by the molecular modeling method (the method of minimizing the potential energy of the system in the modified version of the force field (MM2) developed by Allinger, a model of the cluster of PAN was obtained in subroutine Chem3D of program Chemoffice. Using it, the possibility of interaction of PAN with molecules of gases–pollutants [18] and interaction of PAN with gas molecules–pollutants in the presence of water molecules was estimated [20]. Semiempirical calculations of the spatial configurations of macromolecules were carried out using the exchange correlation functional B3LYP (the correlation functionals LYP and VWN and the exchange functionals Becke + Slater + HF) include the dependence of the correlation energy of the electron density derivative and the exchange energy [18,20,22,25–28].

At the first stage, the interaction of the PAN cluster was modeled with the oxygen molecule, then with simultaneous presence of oxygen and water molecules. Figure 1 shows the positions that were set for the oxygen and/or water molecule or for the gas molecules. Position (1)—the gas molecule is located inside the cluster. The positions (2)–(12) of the molecule were above the surface of the middle of the cluster with distances from 2 Å to 10 Å.

Figure 1. Arrangement of gas molecules in interaction with the surface of a polyacrylonitrile (PAN) cluster.

Further, thermodynamic and geometric indicators of the systems include “cluster PAN – oxygen molecule” and “PAN cluster – water molecule – oxygen molecule”, namely, the steric energy of this system ($E_{\text{PAN}+\text{O}_2}$ and $E_{\text{PAN}+\text{O}_2+\text{H}_2\text{O}}$), the binding energy between the water molecule and the surface of the PAN cluster (ΔE), and the distance (l_{min}). Figure 2 shows the model of the “PAN cluster – water molecule – oxygen molecule” system.

Figure 2. The location of oxygen and water molecules in the “PAN cluster – water molecule – oxygen molecule” system.

At the last stage, molecular systems were used to study these systems: “PAN cluster – oxygen molecule – gas molecule” and “PAN cluster – water molecule – oxygen molecule – gas molecule”. Based on the results of comparison of thermodynamic parameters of the investigated systems, first of all their steric energies, the possibility of interaction of gas molecules–pollutants with PAN was estimated.

3. Results and Discussion

As a result of molecular modeling of the “PAN cluster – oxygen molecule – gas molecule” system, it was established that the location of the oxygen molecule at a distance of 3.4 Å above the surface in the middle of the PAN cluster is energetically favorable. This indicates a physical adsorption of the oxygen molecule and does not contradict the results of reference [16], which shows that the adsorption of an oxygen molecule on a two-layer PAN cluster, but of a larger size, occurs at a distance of 3 Å.

The results of calculations of the thermodynamic and geometric parameters of the “PAN cluster – oxygen molecule – gas molecule” system are presented in Table 1 and Figure 3. The steric energy of the system “PAN cluster – oxygen molecule” ($E_{\text{PAN}+\text{O}_2}$) is 2387.71 kJ/mol, which is less than E_{PAN} . This suggests that the effect of oxygen molecules on the interaction of gas molecules with the PAN surface can be significant.

Table 1. Parameters of the “PAN cluster – molecule of oxygen – molecule of gas” system.

No	Gas Molecule	E_{min} , (kJ/mol)	ΔE , (kJ/mol)	l_{min} , Å
1	NO ₂	8440.25	5.15	6
2	Cl ₂	2373.43	0.79	6
3	NH ₃	4729.17	15.04	3.2
4	CH ₄	3938.77	5.03	3
5	SO ₂	2371.96	56.69	3
6	H ₂ S	2373.72	4.52	2.5
7	CO	2376.69	2.30	3.2
8	O ₃	3235.73	5.03	3.2
9	CO ₂	2369.78	2.80	3.2

Figure 3. The location of the ammonia molecule in the “PAN cluster – oxygen molecule – gas molecule” system.

Comparing the values of the steric energies of the system $E_{\text{PAN}+\text{O}_2} + \text{gas}$ and $E_{\text{PAN}+\text{O}_2}$, it can be concluded that, in the presence of oxygen molecules, PAN films will exhibit a gas sensitivity to carbon monoxide (IV), sulfur (IV) oxide, chlorine, hydrogen sulfide and carbon monoxide (II). At the same time, in the “PAN cluster – oxygen molecule – SO_2 molecule” system, a high binding energy (56.69 kJ/mol) between the SO_2 molecule and the PAN surface is observed. This can be explained by the manifestation of electrostatic forces due to the high dipole moment of the SO_2 molecule of 1.61 D [28]. It is known that polar molecules of gases can interact with the surface of gas-sensitive materials with an interaction energy reaching 200 kJ/mol [29].

The calculated distances between the gas molecule and the oxygen molecule exceed 2.9 Å. This shows that the oxygen molecule does not affect the molecules of gases. The values of l_{min} (>2.5 Å) and ΔE (0.79–56.69 kJ/mol) also indicate van der Waals interactions between the gas molecule and the PAN surface.

Further, by the method of molecular modeling, the “PAN cluster – water molecule – molecule of oxygen – gas molecule” system was investigated. Here, the minimum distances between the gas molecule and the water molecule (L_1), and between the gas molecule and the oxygen molecule (L_2) were estimated. The results of the simulation are presented in Table 2 and in Figure 4. According to the results obtained, it is established that the steric energy of the “PAN – oxygen molecule – water molecule” system is $E_{\text{PAN}+\text{O}_2+\text{H}_2\text{O}} = 5092.65$ kJ/mol, which is higher than E_{PAN} and $E_{\text{PAN}+\text{O}_2}$, but less than $E_{\text{PAN}+\text{H}_2\text{O}}$.

Table 2. Thermodynamic parameters of the “PAN cluster – oxygen molecule – water molecule – gas molecule” system.

No	Gas Molecule	E_{min} , (kJ/mol)	ΔE , (kJ/mol)	l_{min} , Å	L_1 , Å (H_2O)	L_2 , Å (O_2)
1	NO_2	8874.96	208.75	2.5	3.6	5.2
2	Cl_2	5131.37	3.60	6	2.6	3.9
3	NH_3	8621.55	9.13	4	2.5	4.5
4	CH_4	7358.27	3.69	6	2.2	4.5
5	SO_2	4994.14	12.82	3	3.2	4.3
6	H_2S	4434.61	9.18	3.7	2.4	5.5
7	CO	5093.91	0.84	4	3	5.3
8	O_3	15,118.32	0.00	10	3.9	5.3
9	CO_2	4820.93	30.21	3.2	2.2	5.3

Figure 4. The location of the nitrogen dioxide molecule in the “PAN cluster – water molecule – oxygen molecule – gas molecule” system.

The calculated distances between the gas molecule and the water molecule (L_1) show the influence of the water molecule, which attracts molecules of gases such as CO_2 , H_2S , NH_3 , and Cl_2 due to its high dipole moment of 1.49 D [28]. L_1 in this case is in the range of 2.2–2.6 Å. At the same time, the distance between the molecules of these gases and the PAN surface ($l_{\min}$) is more than 3.2 Å.

The effect of the oxygen molecule in this system is low, since the distance between the gas molecule and the oxygen molecule (L_2) is above 3.9 Å. The calculated values of ΔE also indicate the action of van der Waals forces. Furthermore, simultaneous influence of water and oxygen molecules leads to the fact that the binding energy ΔE in the “PAN cluster – oxygen molecule – water molecule – nitrogen dioxide molecule” system is the highest ($\Delta E = 208.75$ kJ/mol), and $l_{\min}$ is the lowest ($l_{\min} = 2.5$ Å). This behavior may be due to the fact that the NO_2 molecule is polar with a dipole moment of 0.33 D [28], and a high value of ΔE is a consequence of the manifestation of electrostatic interaction forces.

A joint analysis of the results is presented in references [18,20], and the results of this paper showed that near the PAN surface, oxygen molecules are more likely to be located, since the steric energy of the “PAN – oxygen molecule” ($E_{\text{PAN}+\text{O}_2}$) system is the smallest of all the systems examined. The presence of water molecules in the investigated air should not affect the gas sensitivity of PAN films, since the steric energy of the “PAN cluster – water molecule – gas molecule” system is much higher. In this regard, the highest sensitivity in PAN in atmospheric air will be to carbon monoxide (IV), sulfur (IV) oxide, chlorine, hydrogen sulfide and carbon monoxide (II).

The theoretical results on the interaction of gas-pollutant molecules with PAN films that have passed IR annealing obtained in this paper were experimentally confirmed earlier in references [5,7,10,11,30]. It was shown in references [7,10,30] that the minimum measured concentration of chlorine was 0.14 ppm, and under the action of nitrogen dioxide it was 14 ppm. This means that the selective sensitivity of PAN films to chlorine is two orders of magnitude higher than that of nitrogen dioxide. In reference [10], the authors also noted the reaction of gas sensors based on PAN films to sulfurous gas at a concentration above 50 ppm. At the same time, the response of the sensors to the action of ammonia, carbon monoxide (II), and ozone was absent. In reference [5], a significant effect of carbon oxide (II) on the resistance of pyrolyzed PAN is shown. It was established in references [7,11] that, for gas sensors based on PAN films subjected to IR annealing, the effect of humidity in the range from 43 to 85% does not affect the gas sensitivity of the sensor.

As a result of quantum chemical calculations and molecular modeling, it has also been established that the introduction of molecules of gas-pollutants, water or oxygen molecules into the PAN structure is unlikely because of the relatively high steric energy of the system (2–3 times higher than $E_{\text{PAN/PAN+H}_2\text{O/PAN+O}_2/\text{PAN+O}_2+\text{H}_2\text{O}}$).

4. Conclusions

In this work, a theoretical study of the mechanisms of interaction of the PAN cluster with the molecules of the main pollutant gases (nitric oxide (IV), methane, ammonia, sulfur (II) oxide, hydrogen sulfide, ozone, carbon monoxide (IV), carbon monoxide (II), chlorine) in the presence of an oxygen molecule or with the simultaneous presence of an oxygen molecule and a water molecule was carried out.

As a result of quantum chemical calculations and molecular modeling, it was established that PAN in the presence of oxygen molecules has a sensitivity to carbon oxide (IV), sulfur (IV) oxide, chlorine, hydrogen sulfide and carbon oxide (II). The mechanism of interactions between gas molecules and the PAN surface is van der Waals interaction, since the binding energies of ΔE do not generally exceed 20–40 kJ/mol. In the case of polar molecules, the manifestation of electrostatic interaction forces is possible, then the binding energy can reach 200 kJ/mol. The presence of water molecules in the investigated air does not affect the gas sensitivity of PAN films.

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