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Carbon Nanotubes, New Material for Purification of Water–Ethanol Mixtures from Isomers of Propanol

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Abstract—The possibility of purification of water–ethanol mixtures from the unwanted admixtures of higher alcohol, in particular, of the isomeric propanols, with the help of carbon nanomaterial is discussed. Results of quantum-chemical calculations of *n*-propanol and isopropanol on the surface of the monolayer carbon nanotube of the "armchair" type are presented. Investigations are carried out within the frame of model of molecular cluster using semi-empiric quantum chemical MNDO method. The possibility of adsorption of molecules of propanol isomers on the outer surface of nanotubes of small diameter as well the absence of adsorption of ethanol molecules on them is shown. It indicates the possibility of selective sorption with carbon nanotubes. Main geometric, electronic, and energy characteristics of obtained adsorption complexes are evaluated. A conclusion is made on the possibility to use carbon nanotubes for superfine purification of water–ethanol mixtures from the unwanted admixtures of *n*- and isopropanol.

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Ethyl alcohol widely used in pharmaceutical, chemical, electronic, and food industry practically in all cases contains various admixtures. Many of them are present in ethanol in small concentrations, but they influence its organoleptic characteristics and toxic properties. Content of some admixtures is strictly controlled [1, 2]. Ethyl alcohol used in food industry notwithstanding the method of its manufacturing contains the admixture of propanol which is formed together with ethanol in the course of brewing of different plant materials. Propanol cannot be completely removed by rectification. It gives the alcohol-containing products (for example, vodka) the unpleasant taste. Propanol belongs to the third class of dangerous substances and negatively affects the human health.

As is known, organic admixtures can be removed by adsorption method. Natural minerals, charcoals and fibers are used as adsorbents. But filters on the basis of natural minerals do not provide effective purification of water–ethanol mixtures from fusel oil containing isopropyl and isoamyl alcohols. Therefore the application of carbon-based adsorbents is most effective due to their hydrophobity that prevents the competing adsorption of water while removing admixtures from ethanol solutions. For purification of water–ethanol mixtures activated carbons are widely used. They possess a sufficiently developed specific surface (up to 1200 $m^2\ g^{-1}$ [3]) and regulated porosity. Nowadays several hundreds of carbon-based sorbents differing in the method of production, starting material, shape, and size of grain, etc. are offered [4, 5]. Nevertheless, because of the necessity of using water–ethanol mixtures of high purity there exists actual necessity of developing new effective methods of purification of ethanol-containing liquids from undesired admixtures and of the search for new materials exhibiting better sorption properties compared to known carbon sorbents.

Nowadays special hopes in development of many fields of science and technique are connected with carbon nanotubes [6–11]. Nanotubes are prolonged structures looking like long (up to several microns) tubes having several nanometers in diameter. Their surface consists of regular six-membered carbon cycles (hexagons). Unusual properties of such structures underlie many daring technologic decisions. Outstanding specific feature of carbon nanotubes is connected with their unique sorption characteristics [12]. As nanotube is a surface structure all its mass is contained

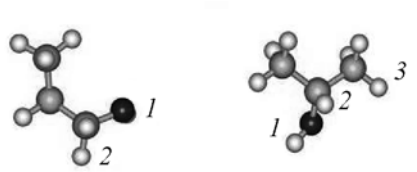

Fig. 1. Model of molecule of (a) *n*-propanol and (b) isopropanol with the indication of adsorption sites.

in the surface of its layers. Therefore the carbon nanotubes have extremely high specific surface (up to 2600 $m^2 g^{-1}$ [13]) which in its turn determines specific features of their sorption characteristics. So high specific surface and also large number of active adsorption centers provided by regular structure open the opportunity of carbon nanotubes application in filters and another apparatus of chemical technology. Besides, highly crooked surface of nanotube permits to adsorb on it sufficiently comlex molecules. Higher adsorption activity of carbon nanotubes as compared to graphite sorbents is proved experimentally with respect to a series of metals and their oxides [15,16], atoms and molecules of gaseous substances [12], organic molecules [14], among them monohydric alcohols of normal and iso structure [17]. In the patent [18] a method of extraction of isopropyl alcohol from water–ethanol mixtures by passing it through the adsorbent is described. The role of adsorbent is played by carbon nanotubes activated preliminary by heating at 120–150°C. The mixture purified was analyzed by GLC [19] and the degree of purification from isopropyl alcohol is calculated. This invention provides the increase in degree of sorption of isopropyl alcohol from water–ethanol mixtures at the preservation of high absorption properties of nanotubes after multiple regeneration.

Experimental results, demonstrating high sorption activity of carbon nanotubes with respect to isomeric propyl alcohols required a theoretical explanation which became the goal of this investigation. We carried out computer simulation of processes of adsorption interaction of ethanol, *n*- and isopropanol molecules with monolayer carbon nanotubes of the "armchair" type (6, 6). The choice of a nanotube of small diameter and hence of high surface curvature is determined by the previously proved effect of surface curvature on the effectiveness of adsorption interaction with large organic molecules by one-center normal interaction permitting to provide their multiple adsorption [14, 20] unlike the adsorption on flat surfaces of graphite sorbents.

Investigations were carried out within the framework of molecular cluster model using semiempiric NMDO method which had shown its worth in the calculations of molecules and solid bodies. We believe that in the structure of alcohol molecules several centers are present which are capable of formation of adsorption bond between the molecule and the surface of the carbon nanotube. As known, saturated mono-

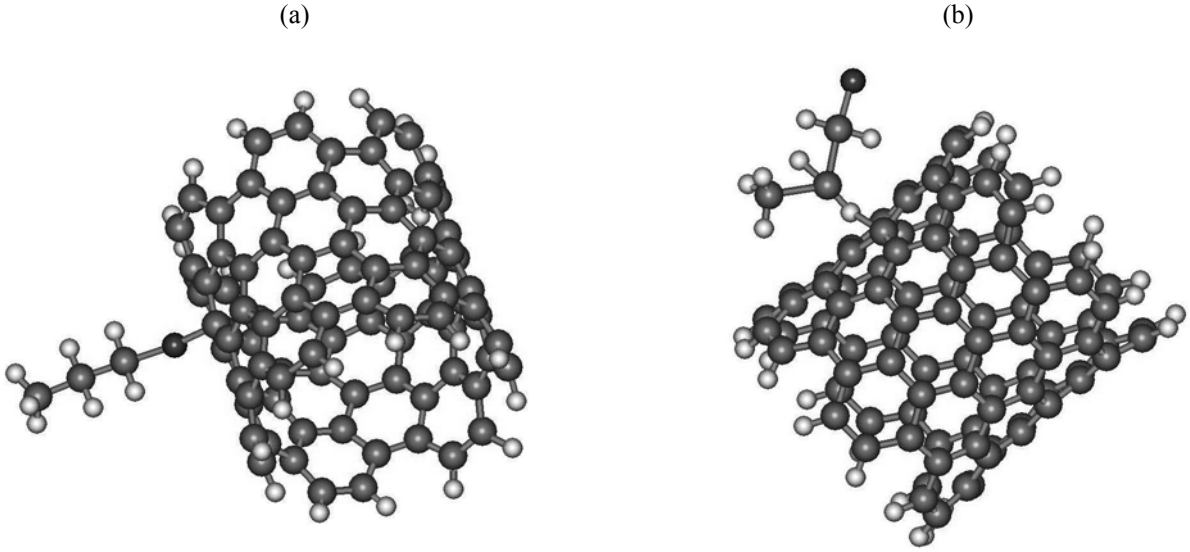

Fig. 2. Model of adsorption interaction of nanotube (6, 6) and the molecule of normal propanol with the addition through the (a) adsorption site 1 and (b) the adsorption site 2.

hydric alcohols have a general formula $C_nH_{2n}OH$ or in the general form R–OH [23]. Oxygen of hydroxy group possesses significant electronegativity and drives the electron density of O–H bond to its side providing polarization of the bond. Due to that the oxygen atom becomes one of the active sites of the alcohol molecule. Hydrogen atoms of hydrocarbon residue can interact with the surface of nanotube by dispersion interaction and hence play the role of active sites. Just these two types of sites were considered while simulating the process of adsorption interaction with the surface of a carbon nanotube.

We have studied the mechanisms of the adsorption interaction of *n*-propanol and isopropanol molecules with the carbon nanotube of (6, 6) type. The molecular cluster of nanotube contained 96 carbon atoms and dangling bonds on the boundary were locked with pseudoatoms. The role of the latter in this model was played by hydrogen atoms. The process was simulated by gradual approach of a chosen molecule of alcohol to the outer surface of the carbon nanotube along the normal passing through the surface carbon atom located in the center of the cluster with the step equal to 0.1 Å. Geometric parameters of the system were optimized in each step. One-center normal interaction in the following kinds of addition of isomeric propanols molecules to the carbon atom of nanotube surface was considered: (a) the molecule adds along the normal to the outer surface of carbon nanotube using active site 1, that is oxygen atom; (b) the molecule adds along the normal to the outer surface of carbon nanotube using sites 2 and 3, the hydrogen atoms of hydrocarbon residue of the alcohol molecule (Fig. 1). In Fig. 2 the model of the adsorption interaction of nanotube (6, 6) and the molecule of normal propanol with the addition through the adsorption center 1 is presented.

Performed calculations permitted plotting the profiles of the potential energy of interaction (Figs. 3, 4) and showing the geometric and energy peculiarities of the adsorption. The analysis of the results obtained showed that adsorption is possible for all kinds of interaction of nanotube with propanol isomers. It is illustrated by the presence of minima on the curves located in the range of negative values. The so-called physical adsorption takes place because the adsorption distances are relatively large. Main parameters of adsorption interaction are presented in Table 1.

Analysis of geometry of interacting systems showed that in the course of adsorption a distortion of

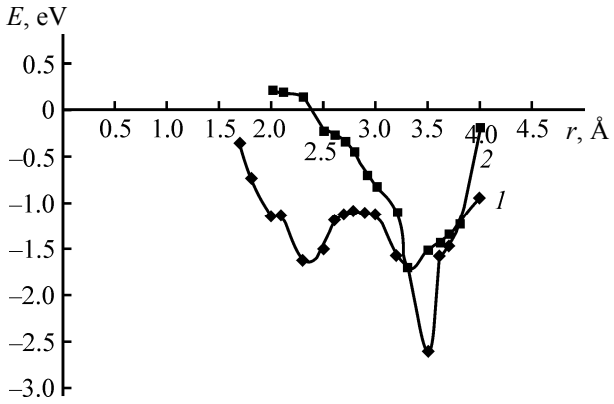

Fig. 3. Profiles of potential energy of interaction of *n*-propanol molecules with the surface of carbon nanotube (6, 6): (*1*) addition through the adsorption site 1 of the molecule and (*2*) addition through the adsorption site 2 of the molecule.

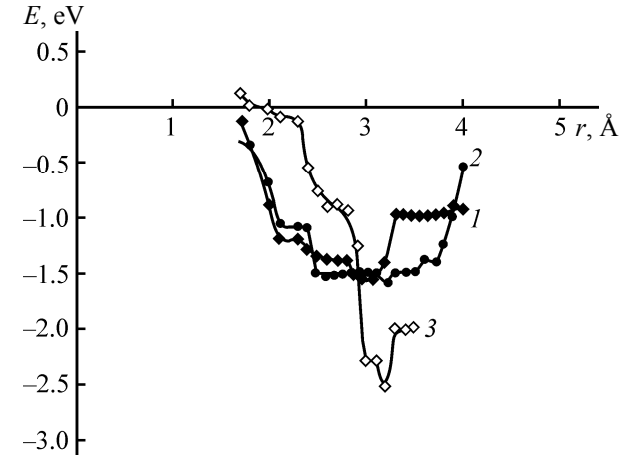

Fig. 4. Profiles of potential energy of interaction of isopropanol molecules with the surface of carbon nanotube (6, 6): (*1*) addition through the adsorption site 1 of the molecule and (*2*) addition through the adsorption site 2 of the molecule; addition through the adsorption site 3 of the molecule.

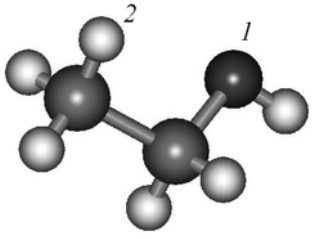

Fig. 5. Molecule of ethanol with the indication of active sorption sites.

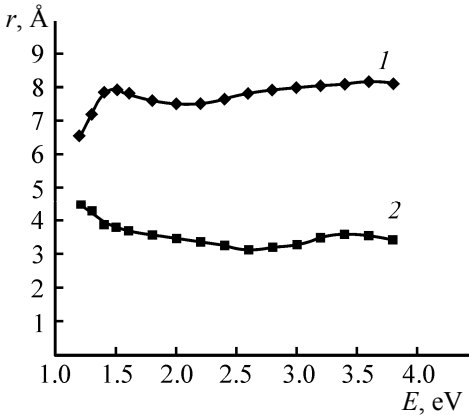

Fig. 6. Profiles of potential energy of interaction of ethanol molecules with the surface of carbon nanotube (6, 6): (*1*) addition through the adsorption site 1 of the molecule and (*2*) addition through the adsorption site 2 of the molecule.

Fig. 7. Model of the adsorption interaction of nanotube (6, 6) and two molecules of *n*-propanol.

cylindrical symmetry of carbon tubulene takes place. Interatomic C–C bonds of nanotube in the place of adsorption have 5% elongation which leads to the formation of convexity on the tube surface with the center located on carbon atom bound to the adsorbed propanol molecule.

The comparison of adsorption energies for different kinds of interaction of *n*-propanol and isopropanol molecules permitted the evaluation of the most active adsorption sites of these molecules. They occurred to be adsorption center 1 for *n*-propanol (E_{ad} –2.62 eV) and adsorption center 3 for isopropanol (E_{ad} –3.51 eV).

Computer simulation of adsorption interaction of ethanol molecule with the monolayer carbon nanotube of (6, 6) type was also carried out. MNDO calculations of one-centered mechanisms of adsorption of molecule on the surface of nanotube for following versions were carried out (Fig. 5): the molecule adds along the normal to the outer surface of nanotube using active site 1, oxygen atom (a); the molecule adds along the normal to the outer surface of nanotube using active site 2, the hydrogen atom of the hydrocarbon residue of the alcohol (b).

The process was simulated as follows. The molecule of ethanol gradually approached to the outer surface of carbon nanotube (6, 6) along the normal coming through the chosen carbon atom of surface of molecular cluster of nanotube with the step 0.1 Å. Performed calculations permitted obtaining the profile of potential energy of the interaction (Fig. 6). The analysis of the curves showed the absence of adsorption interaction between the ethanol molecule and carbon nanotube because the curves are located in the range of positive energy values.

Table 1. Main parameters of adsorption interaction of carbon nanotube (6, 6) with the molecules of propanol-1 and propanol-2 for different kinds of addition of molecules to the surface of nanotube

Variants of adsorption interaction	*r*, Å	E_{ad}, eV
n-Propanol: adsorption site 1	3.4	–2.62
n-Propanol: adsorption site 2	3.5	–1.71
Isopropanol: adsorption site 1	3.2	–1.58
Isopropanol: adsorption site 2	3.1	–1.56
Isopropanol: adsorption site 3	3.2	–2.51

Table 2. Main parameters of multiple adsorption interaction of molecules of *n*-propanol with the carbon nanotube (6, 6) and graphite plane[a]

Type of sorbent + number of adsorbed molecules	r_{ad}, Å	E_{ad}, eV	*n*
Nanotube (6, 6) + 1 molecule	3.4	–2.62	–
Nanotube (6, 6) + 2 molecules	2.5	–1.20	3
Graphite plane + 1 molecule	3.3	–1.19	–
Graphite plane + 2 molecules	5.6	–0.70	8

[a] (r_{ad}) adsorption distance, Å; (E_{ad}) adsorption energy, eV; (*n*) number of carbon hexagons on the surface of sorbent between the adsorbing molecules.

Hence, an important conclusion was obtained proving the selective adsorption activity of carbon nanotubes that permits their use for the selective adsorption of admixtures from water–ethanol mixtures.

For proving the positive effect of surface curvature on the effectiveness of sorption of alcohols MNDO calculations wer performed of adsorption of several molecules of *n*-propanol on the cylindrical surface of a carbon nanotube (6, 6) and the flat surface of a graphite sorbent. Cases of consecutive addition of two molecules of propanol to nanotube by its perimeter and on the graphite plane on equal distances from one another, in particular, over three carbon hexagons using the adsorption site 1 of the molecule, namely, the oxygen atom, are presented in Fig. 7. The analysis of obtained results showed that multiple adsorption on chosen distances between the adsorbed molecules is possible and effective on the cylindrical surface of carbon nanotube (Table 1) unlike the case of flat graphite surface where no adsorption was observed. It is found that molecules of *n*-propanol can adsorb on carbon atoms of graphite plane located from one another at a distance of no less than eight hexagons. Besides, the comparison of values of adsorption energy of the interaction of propanol molecule with carbon nanotube and with graphite plane showed higher sorption activity of carbon nanotube with respect to the chosen molecule of alcohol. Hence, it can be stated that high curvature of nanotube surface significantly decreases the effect of adding to the surface neighboring propanol molecules and positively influences the process of adsorption of large organic molecules. It leads to the appearance of more stable multi-center "nanotube-propanol molecules" system as compared to the system consisting of graphite and propanol molecules.

Results of the performed computer simulation of processes of interaction of ethanol, normal propanol, and isopropanol molecules present in composition of widely used water–ethanol mixtures permit the following conclusions. The adsorption interaction between the molecules of *n*- and isopropanol and the surface of carbon nanotube of small diameter proceeds according to the mechanism of one-center normal interaction for the active centers located on the edges of molecules. The adsorption interaction between the ethanol molecule and carbon nanotube is absent proving the selectivity of adsorption activity of carbon nanotubes and determining the possibility of their use for selective sorption of admixtures from water–ethanol mixtures without affecting ethanol, the main component of the system.

Multiple adsorption of isopropanol molecules on the cylindrical surface of carbon nanotube is possible and effective unlike the case of flat graphite surface, which is explained by the significant decrease in the effect of neighboring propanol molecules added to the surface in the process of interaction due to high curvature of nanotube surface.

The occurrence of the physical adsorption of molecules of propanol isomers on the surface of carbon nanotubes proves the possibility of effective and multiple regeneration of sorbent what provides the advantage of use of nanotube-based filter in the processes of purification of water–ethanol mixtures.

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