INTERACTION BETWEEN NUCLEOSIDE AND NUCLEOTIDE WITH CARBON NANOTUBES

Maryna V. Manilo[1,2*], Igor A. Ar`ev[2], Nikolai I. Lebovka[2], Grigorii S. Lytvynov[1]

1 College of Biotechnology and Bioengineering, National Technical University of Ukraine, Prospect Peremogy 37, 03056, Kiev, Ukraine
2 F.D. Ovcharenko Institute of Biocolloidal Chemistry The National Academy of Sciences of Ukraine, Blvr Acad. Vernadskoho 42, 03142, Kyiv, Ukraine

ABSTRACT

Carbon nanotubes (CNTs) possess a number of unique properties; they are successfully applied as fillers for improving the mechanical, electric, thermophysical, and optical properties of composite materials. At present, CNTs are intensively used in the development of biosensor devices and materials designed for pharmaceutics and diagnostics. Functionalization of CNT surfaces with molecules playing important roles in biological processes, including proteinforming peptides, nucleic acids, etc., makes it possible to produce new systems capable of identifying biological objects. CNT surface can serve as a platform for the targeted transport of different molecules, including drugs (antibiotics or protein). Efficiency of this transport is governed by the unique adsorption ability of CNTs and the specific interaction of molecules with their surface.

The idea of this work was to investigate the adsorption of a number of biological molecules with different numbers of phosphate groups from aqueous solutions onto the surface of multiwall CNTs. Adsorption isotherms for adsorbate concentration range $C = 0$–10^{-3} mol/dm^3 were plotted.

Experimentally observed positive adsorption of adenosine (AN), adenosine triphosphate (ATP), and adenosine monophosphate (AMP) from aqueous solutions onto the surface of multiwall CNTs takes place because of the presence of adenine fragments in the studied com-pounds. At the same time, the data obtained indicate that, in the case of monomolecular adsorption, the molecular packing is rather loose and the packing density is higher for compounds containing phosphate groups. The observed behavior of the adsorbates seems to reflect the intensification of lateral interactions in the adsorption layers. In the region of polymolecular adsorption at high adsorbate concentrations in solutions ($C > (5$–$6) \times 10^{-4}$ mol/dm^3), the adsorption reduced in a series AN > AMP > ATP, i.e., with the enhancement of the hydrophilicity and the solubility of these compounds in water.

Key words: adenosine, AMP, ATP, carbon nanotube, adsorption isotherm

INTRODUCTION

Carbon nanotubes (CNTs) possess a number of unique properties; they are successfully applied as fillers for improving the mechanical, electric, thermo-

* e-mail: assol_M@i.ua, tel: (+38)0975453655

physical, and optical properties of composite materials [1]. At present, CNTs are intensively used in the development of biosensor devices and materials designed for pharmaceutics and diagnostics [2–4]. The functionalization of CNT surfaces with molecules playing important roles in biological processes, including proteinforming peptides, nucleic acids, etc., makes it possible to produce new systems capable of identifying biological objects [5]. A CNT surface can serve as a platform for the targeted transport of different molecules, including drugs (antibiotics or protein). The efficiency of this transport is governed by the unique adsorption ability of CNTs [7] and the specific interaction of such molecules with their surface [2].

EXPERIMENTAL

AN, AMP, and ATP produced by Sigma-Aldrich Co. (the United States) were applied in the experiments.

Multiwall CNTs (Spetsmash, Ukraine) had a specific surface area of 190 m^2/g, a diameter of 10–30 nm, a length of 1–10 μm, and a content of mineral impurities of less than 1% [9]. AN, AMP, and ATP were adsorbed from an aqueous physiological solution (infusion solution with NaCl concentration of 0.9 wt %, Novofarm-Biosintez, Ukraine). Initial samples of adsorbate solutions were prepared by the gravimetric method with following dilution. The adsorption was performed in dark at 293 K and were continuously stirred on a water bath shaker.

The concentration of biomolecules was measured spectrophotometrically with a Specord UV Vis spectrophotome ter (Germany). Spectra were registered in the wavelength $\lambda = 250–357$ nm with the absorption maximum at $\lambda = 260$ nm.

The initial region of a adsorption isotherms (in the range of the monolayer filling) was approximated by the Langmuir equation.

The surface area per a molecule was found from the relation $s = A/a_m N_A$, where A is the specific surface area of nanotubes occupied by an adsorbate and N_A is Avogadro's number.

RESULTS AND DISCUSSION

Typical time dependences of the normalized values a/a_∞ for AN, AMP and ATP adsorption on CNTs are presented in *Fig. 1*. Here, a_∞ corresponds to the adsorption value at $t \to \infty$, and all dependences are obtained for initial solution concentrations C of approximately 2.3×10^{-4} mol/dm^3. Similar $a(t)/a_\infty$ dependences were observed for other C values.

As a rule, adsorption equilibrium was established within 1 h. Note that, during 2 h, the equilibrium of the reversible hydrolysis of AMP and ATP remained nonshifted, thus indicating a relative stability of the examined biomolecules in aqueous solutions.

Figure 2 illustrates the isotherms of AN, AMP and ATP adsorption measured at room temperature. The initial regions of the isotherms correspond to the process of the formation of adsorbate monolayers on the CNT surface. When equilibrium concentration i is increased to the value that corresponds to the complete CNT surface coverage with the monolayer of a substance, a horizontal region is observed. As the adsorbate concentration in a solution is further increased, all three substances exhibit the behavior typical of polymolecular adsorption [10] (*Fig. 2*).
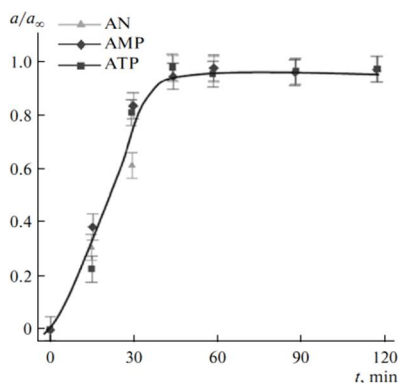

Fig. 1. Normalized adsorption values a/a_∞ of AN, AMP, and ATP on CNT surface as functions of time t (a_∞ is the adsorption value at $t \to \infty$). All dependences are obtained at an initial solution concentration C of approximately 2.3×10^{-4} mol/dm^3.
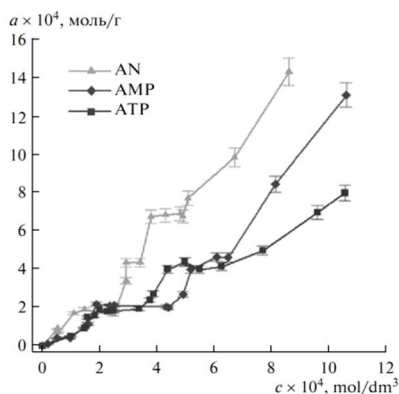
Fig. 2. Isotherms of AN, AMP, and ATP adsorption from aqueous solutions on CNT surface.

In the case of AN, the onset of the monolayer formation is observed at lower concentrations than for AMP and ATP. Polymolecular layers of AN, ATP and AMP are formed at $C > 2.5 \times 10^{-4}$, 3.5×10^{-4} and 4.5×10^{-4} mol/dm^3. The longest horizontal region of the monomolecular adsorption is observed for AMP (n = 1), thus indicating the most complete coverage of the CNT surface with the adsorbate monolayer; for AN (n = 0) and ATP (n = 3) shorter regions are seen. Table 1 presents the calculated values of the surface areas per a molecule s and free energy G, which characterize the monomolecular adsorption of the examined biomolecules.

Table 1. Surface areas *s* per *a* molecule and standard adsorption free energies *G* for AN, AMP, and ATP molecules on CNT surface

Adsorbate	s, nm^2	$k \times 10^{-5}$	$-G$, kJ/mol
AN	1.80±0.17	4.13±0.21	31.5±0.1
AMP	1.50±0.12	1.71±0.18	29.4±0.2
ATP	1.71±0.15	1.65±0.20	29.3±0.1

After the CNT surface is completely covered with an adsorbate layer, the adsorption value spliked. A further increase in C causes the appearance of additional horizontal regions that seem to reflect the formation of adsorption bilayers, etc. (*Fig. 2*). At higher C values, a increases with C.

The studied compounds are amphiphilic, and their hydrophobic–hydrophilic balance is governed by the size ratio between adenosine and phosphate fragments. Hence, AN, AMP, and ATP are adsorbed on the hydrophobic surface via the adenine fragments, which have a relatively high hydrophobicity parameter $\log P = -0.3$ [11]. The decrease in the adsorption free energy in the aforementioned series of the biomolecules in the initial regions of the isotherms (*Table 1*), which is symbate to the increase in the solubility, confirms this conclusion.

At high concentrations of adsorbate solutions ($C > (5–6) \times 10^{-4}$ mol/dm^3), the adsorption diminished in a series AN > AMP > ATP, with the weakest $a(C)$ dependence being observed for ATP. This character of the polymolecular adsorption absolutely corresponds to the enchance in the hydrophilicity and solubility of these compounds in the aforementioned series.

Note that the obtained surface areas s per molecules of AN and AMP exceed the theoretically estimated value of the total area of the largest molecule (ATP), which is equal to nearly 1.0–1.2 nm^2 [12]. Hence, the molecular packing of AN and AMP on the CNT surface in the case of the monomolecular coverage is rather loose. This fact seems to reflect the peculiarities of the interaction between adenine fragments of these biomolecules and the aromatic surface of CNTs.

Taking into account that AN molecules have the smallest areas, it may also be concluded that that the packing of this adsorbate molecules on the CNT surface is loosest. The analysis of the chemical shifts in the ^{1}H NMR spectra of adenine and D-ribose fragments [8] led us to conclude that hydrophobic and π-π interactions take place between adenine fragments and CNT surface. The denser packing of AMP and ATP molecules in the adsorption monolayers may be assumed to reflect a stronger lateral attraction between molecules of these adsorbates compared to AN molecules due to the appearance and elongation of the phosphate fragment. The differences in the character of the polymolecular adsorption that are observed for AN, ATP, and AMP (Fig. 2) are likely to reflect the differences in the character of their molecular association in aqueous solutions.

CONCLUSIONS

The experimentally observed positive adsorption of AN, ATP, and AMP from aqueous solutions on the surface of multiwall CNTs takes place because of the presence of adenine fragments in the studied compounds. At the same time, the data obtained indicate that, in the case of monomolecu-lar adsorption, the

molecular packing is rather loose and the packing density is higher for compounds containing phosphate groups. The observed behavior of the adsorbates seems to reflect the intensification of lateral interactions in the adsorption layers. In the region of polymolecular adsorption at high adsorbate concentrations in solutions ($C > (5–6) \times 10^{-4}$ mol/dm^3), the adsorption reduces in a series AN > AMP > ATP, i.e., with the enhancement of the hydrophilicity and the solubility of these compounds in water.

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