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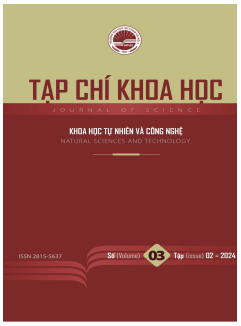

Article type: Research article

Study on the adsorption L- and D- proline on MKN-MWCNT-P5000 carbon nanotubes from aqueous solutions

Dinh-Tuan Le*, Anh-Van Chu

Hanoi Pedagogical University 2, Vinh Phuc, Vietnam

Abstract

Carbon nanotubes (CNTs) are a new type of nano-adsorbent material with unique properties, which are promising adsorbents for the separation of enantiomers. Information regarding the interaction mechanism of enantiomers with carbon nanotubes has not yet been fully explored yet. In this work, we studied the adsorption of L and D-proline on carbon nanotubes in aqueous solution. Adsorption isotherms of enantiomers proline on multi-walled carbon nanotube MKN-MWCNT-P5000 from aqueous solution at 25℃ were constructed. The results of the experiments show that the adsorption capacity of the D-isomer is higher than that of the L-isomer. The separation coefficient of enantiomers on carbon nanotubes is in the range of 1.88–7.92. L-proline was adsorbed on CNTs as zwitterions and clusters of 62 molecules; and D-proline - in the form of zwitterions and clusters of 33 molecules. The results of quantum chemistry show that the adsorption energy of the D-proline monomer on carbon nanotubes is greater than that of the L-isomer. The nature of the bond between enantiomers and nanotubes was Van der Waals force.

Keywords: Carbon nanotubes, enantiomers of proline, adsorption, computer simulation

1. Introduction

A carbon nanotube (CNT) is visualized as a rolled graphene sheet. This is a new nano-adsorbent material with unique adsorption, mechanical, optical, and electrical properties [1]. Because of these properties, carbon nanotubes have become important materials in biomedical technology, such as developing new generation biosensors, targeted drug delivery platforms, and tissue engineering [2]–[4]. The chiral nature of carbon nanotubes and their high adsorption properties make it possible to consider nanotubes as promising adsorbents for the separation of enantiomers. However, in practice, there is very little research, which has been published on this issue. One of them is our work [5]–[7].

* Corresponding author, E-mail: ledinhtuan@hpu2.edu.vn

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Realizing the properties of nanotubes in biotechnology requires understanding the nature of the interactions between biomolecules and CNTs [8]–[15]. Therefore, studying the interaction of amino acids with CNTs is necessary because amino acids are the simplest structural units of many biological molecules. Proline is one of the basic amino acids that make up proteins. No studies on the interaction mechanism of this amino acid with multi-walled carbon nanotube MKN-MWCNT-PT5000 have been published. Therefore, proline and carbon nanotube MKN-MWCNT-PT5000 were chosen as research objects.

This work aims to study the adsorption interaction of L- and D- proline with MKN-MWCNT-P5000 carbon nanotubes in an aqueous solution at 25℃.

2. Experimental

2.1. Construction of adsorption isotherm

In this experiment, multi-walled carbon nanotube MKN-MWCNT-P5000 brand Sigma-Aldrich, originating from Canada with 95% purity, tube length over 50 μm, and outer diameter from 10–30 nm was used as the adsorbent. These are a mixture of nanotubes with different chirality. L- and D-proline are chemicals from Sigma-Aldrich with purity over 99% (pK-COOH = 1.99; pK-NH-= 10.60; pI= 6.30). To determine the adsorption capacity of amino acids on carbon nanotubes, 0.01 g of MKN-MWCNT-P5000 CNT was added to amino acid solutions with different concentrations. Then, the resulting solution was subjected to ultrasonic treatment for 3 minutes using a MEF91 ultrasonic unit. The resulting suspension was shaken well in an ES-20 incubator-shaker until equilibrium was established at 25℃ according to the kinetic investigation time (15 h). The resulting solutions were then filtered through a pleated filter and centrifuged. The proline concentration in the supernatant was determined by measuring the optical density of the solution using a Shimadzu UV-1800 spectrophotometer at 520 nm. The adsorption isotherm was built using the volume method combined with the concentration change method. Under experimental conditions, the pH value of the solution ranges from 5.43 to 5.60. Proline in aqueous solution exists at these pH values in the zwitterion form (Figure 1.).

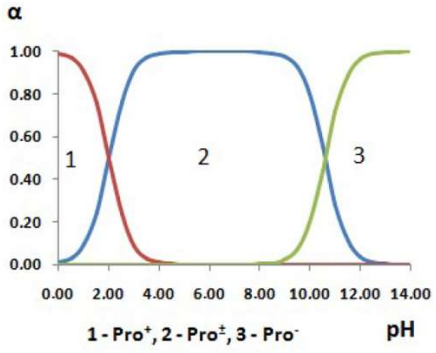


Figure 1. Distribution diagram of proline's ion forms according to pH [16].

2.2. Quantum modelling

Quantum modeling of the L- and D-proline–CNT system was performed using the Gaussian 09 program with the B3LYP/6-31G(d,p) GD3 method, which allows calculating the energy of these structures, takes into account dispersion correction [17]. The influence of the solvent is taken into

account using the Tomasi PCM continuous polarization method. The interaction energies between amino acids and CNTs are calculated according to the formula:

$$E_{ad} = E_{CNT} + E_{AA} - E_{AA+CNT} \quad (1)$$

Here, E_{ad} is the adsorption energy; E_{CNT} is the energy of CNT; E_{AA} is the energy of the amino acid; E_{AA+CNT} is the energy of the system "amino acid – CNT".

A dextrorotatory nanotube with chiral indices (7, 5) with a length of ~13 Å was used as a model nanotube in a computer experiment. Since in the experiment, nanotubes with a length-to-diameter ratio of approximately 2500 were used in the experiment, most of the AA will be adsorbed on the lateral surface of the CNT. Therefore the contribution to the isotherm due to adsorption at the CNT tips being negligible compared to the contribution of adsorption at the side surface. The nanotubes used have a small defect concentration, so AA is unlikely to penetrate inside the CNT. Therefore, when performing quantum modeling, the adsorption process is performed on the outer surface of the nanotube. The use of open-ended tubes in calculations is due to the complexity of the procedure for closing the ends of nanotubes and the influence of the end of the tube on the adsorption of the side surface is negligible. Calculations were performed at the VSU Supercomputing Center and the Siberian Supercomputing Center.

2.3. Cluster adsorption model

The isotherms are interpreted based on the cluster adsorption model. This model was developed in [18], for the case where adsorbate molecules A exist in solution as monomers, thereby forming clusters of different sizes on the surface of the adsorbent S according to the equilibriums:

$$\begin{cases} S + A \rightleftarrows SA \\ S + 2A \rightleftarrows SA_2 \\ \quad ... \\ S + nA \rightleftarrows SA_n \end{cases} \quad (2)$$

The adsorption equation in this case has the form [18]:

$$q = q_m \cdot \frac{K_1 C_e + \frac{2}{m_2} K_2 C_e^2 + ... + \frac{n}{m_n} K_n C_e^n}{1 + K_1 C_e + K_2 C_e^2 + ... + K_n C_e^n} \quad (3)$$

Here q - adsorption capacity, C_e - equilibrium concentration, K_i - equilibrium coefficient of the adsorption reaction $S + iA = SA_i$, i = 1, 2, ..., n - number of adsorbate molecules; m_i - the number of adsorbate molecules (ions) in the first layer since the cluster contains i molecules (ions), q_m - the monolayer adsorption capacity, n - the maximum size of the adsorbate cluster.

3. Results and discussion

The adsorption isotherms of L- and D-proline on MKN-MWCNT-P5000 CNTs are shown in Figure 2. Figure 2. shows that, for L-proline, when the equilibrium concentration of the external solution is small (Ce < 0.017 M) if increasing the AA concentration, the adsorption increases steadily. In the region of 0.017 M ⩽Ce ⩽0.019 M, if the equilibrium concentration of L-proline increases, the isotherm is almost vertical, showing a sudden increase in adsorption. When continuing to increase the concentration of L-proline, the isotherm has a very small slope, almost parallel to the horizontal axis, proving that the adsorption level is almost unchanged. For the D-proline, when Ce < 0.007 M, the value of q gradually increases with increasing concentration of D-proline. In the region 0.007 M ⩽ Ce

⩽ 0.008 M, the isotherm is almost a vertical line parallel to the vertical axis. This shows a sudden increase in the adsorption value at this concentration range. When Ce > 0.008 M, as Ce increases, the value of q increases very little, and the slope of the graph gradually decreases.

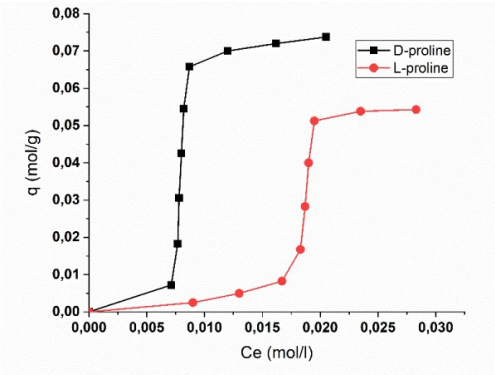


Figure 2. Adsorption isotherm of L- and D-proline from aqueous solution on CNT MKN-MWCNT-P5000.

Experimental results show that CNT MKN-MWCNT-P5000 adsorbs the D-proline better than the L-proline at 25℃, proving that the affinity of CNT for D-proline is higher than its enantiomer. This will be explained based on quantum modeling results in the following section. The higher adsorption capacity of D-proline on CNT is due to the different interactions of enantiomers with chiral carbon nanotubes. To evaluate the ability to separate L- and D-proline on nanotubes, the distribution coefficient of proline isomers between CNTs and solutions - K_L and K_D, as well as the separation coefficient of enantiomers "α" on these CNTs calculated according to the formula:

$$\alpha = \frac{K_D}{K_L} \tag{4}$$

where K_D is the distribution coefficient of D-proline on carbon nanotubes in aqueous solution, and K_L is the distribution coefficient of L-proline on carbon nanotubes in aqueous solution. The distribution coefficients K_D and K_L are equal to the ratio between the equilibrium concentrations of D- and L-proline in the adsorbent and the solution:

$$K_{D(L)} = \frac{C_{ads}}{C_e} \tag{5}$$

The results obtained are shown in Figure 3. Figure 3. shows that the separation coefficient gradually increases when the initial concentration of AA increases to 0.02 M (respectively α = 7.92). Then, this value gradually decreases with increasing initial concentration. The α value obtained is higher than the data presented in the literature for other adsorbents [19]–[21] (α =1.82-3.74). The data in Figure 3. allow us to conclude that the MKN-MWCNT-P5000 nanotube is a promising adsorbent for proline separation. The parameters of the cluster adsorption isotherm equation (3) are determined from the condition of the smallest deviation of the experimental isotherms compared to the model (3). Calculations show that the best agreement between experiment and theory occurs if the adsorption isotherm equations take the form:

$$q = q_m \cdot \frac{K_l C_e + \frac{n}{m_n} K_n C_e^n}{1 + K_l C_e + K_n C_e^n} \tag{6}$$

This equation describes the adsorption of monomers and clusters made up of the maximum possible number of molecules (ions). The formation clusters with the largest possible size are energetically favorable since larger clusters include a larger number of AA-AA bonds, contributing to lowering the energy of the system during the adsorption process. Numerical values of model parameters (6) for D- and L-proline on CNT are presented in Table 1.

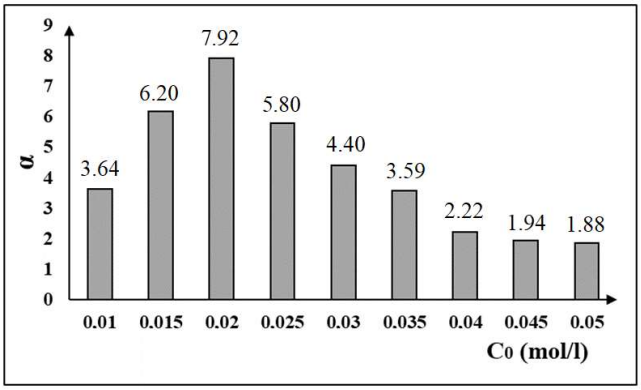


Figure 3. Chart of separation coefficient α at different initial concentrations of amino acids.

Table 1. Parameters of adsorption isotherm equation (6) of L- and D-proline on CNT.

Isomer	q_m (mol/g)	K_1 $(mol/l)^{-1}$	K_n^*	n m_n	R^2
L	5.43×10^{-2}	8.94	1.97×10^{107}	62 62	0.999
D	7.13×10^{-2}	10.00	1.31×10^{70}	33 33	0.996

**The dimension of the coefficient K_n corresponds to the condition that the quantity $K_n C_e^n$ is dimensionless.*

Isothermal equation (6) includes parameters that characterize the structure of AAs on CNTs. Specifically, the number of adsorbed zwitterions bound together into clusters is equal to the exponent of concentration (n) in the isotherm equation (6) and the number of zwitterions in the first adsorbate layer of the n-cluster equals m_n. This is the physical meaning of the parameters of the cluster adsorption equation [5]–[7], [22]. This helps determine the structure of clusters from experimental isotherms by determining the parameters n and m_n using the least squares method. The values of structural parameters of n and m_n adsorption clusters on the CNT surface are presented in Table 1. From the value of n (Table 1), it follows that L-proline is adsorbed on CNT in the form of individual zwitterions and clusters consisting of 62 molecules, and D-proline - in the form of individual zwitterions and clusters of 33 molecules. Thus, all monomers of L- and D-proline clusters are located on the surface of CNT (monolayer adsorption). This conclusion is made because the number of molecules in the first layer m_n equals the number of molecules in cluster n (m_n= n), Table 1. The physicochemical reasons for cluster formation are explained in the work of us [5]–[7], [22]. Note that monolayer cluster adsorption is the most favorable adsorption process if the adsorbent surface area is sufficient to cover one layer because in this case the interaction between not only the adsorbate and adsorbent but also adsorbate-adsorbate, contributing to reducing the energy of the system during the adsorption process [22]. The monolayer cluster adsorption isotherm equation is a generalization of Langmuir's theory in the case of taking into account the adsorbate-adsorbate interaction between the molecules of the first layer [22]:

$$q = q_m \frac{K_l C_e + K_n C_e^n}{1 + K_l C_e + K_n C_e^n} \quad (7)$$

Isothermal equation (7) can be expressed as the sum of two terms:

$$q = q_m \frac{K_l C_e + K_n C_e^n}{1 + K_l C_e + K_n C_e^n} = q_l + q_n \quad (8)$$

$$q_l = q_m \cdot \frac{K_l C_e}{1 + K_l C_e + K_n C_e^n}; \quad q_n = q_m \cdot \frac{K_n C_e^n}{1 + K_l C_e + K_n C_e^n} \quad (9)$$

Here q_l – The contribution to the adsorption process of individual zwitterions; q_n - The contribution to the adsorption process of clusters containing n molecules.

Setting up the equation (9) with specific parameters - describing the contribution to the adsorption of individual zwitterions (q_1) and their clusters (q_n), allows us to decompose the isotherm into its contributions through building graph q(Ce), q_1(Ce) and q_n(Ce), are shown in Figure 4. and Figure 5.

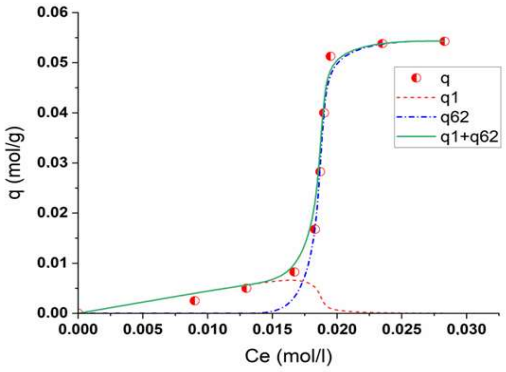


Figure 4. Adsorption isotherm of L-amino acid on carbon nanotubes and contributions of monomers and clusters to the adsorption process.

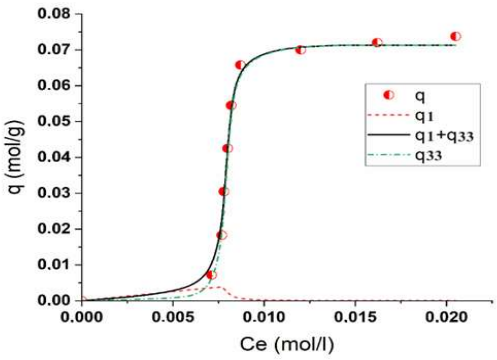


Figure 5. Adsorption isotherm of D-amino acid on carbon nanotubes and contributions of monomers and clusters to the adsorption process.

From the plot of the q_1(C) function, it is inferred that adsorption in the form of individual zwitterions makes the main contribution to the isotherm at low concentrations. However, at high concentrations, when there are many molecules of AA on the CNT surface, there is practically no adsorption of AA as individual monomers. Then, on the CNT surface, there are only adsorbate

clusters, which are energetically favorable due to the contribution of sorbate-sorbate interaction to the adsorption energy. The contribution of the clusters is determined by the sigmoid curve and concave at low concentrations. Cluster adsorption is the main adsorption process in the high-concentration region of amino acids.

Three characteristic concentration zones can be distinguished on the isotherm:

1. Concentration range in which only sorbate monomers are immobilized on the nanotube surface (low concentration).

2. The concentration range in which sorbate molecules are immobilized on nanotubes is only in clusters (high concentration).

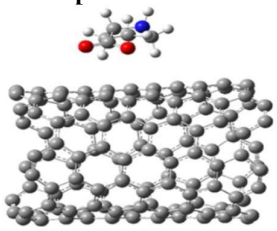
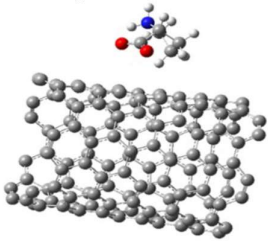
3. The concentration range in which monomers and clusters are present on the adsorbent surface. In this region, there is a concentration at which the adsorption participation of monomers and clusters is equal.

Characteristic concentration values for the adsorption isothermal regions of L- and D-proline on CNTs are presented in Table 2.

Table 2. Characteristic concentration values Ce (mol/l) for the 3 adsorption isothermal regions of L- and D-proline on CNT.

Isomer	On CNT there are only monomers	Clusters begin to form	The contribution of monomer reaches the largest value	The contributions of monomers and clusters are equal	On CNT there are only clusters
L	< 0.0150	0.0150	0.0170	0.0175	> 0.0200
D	< 0.0050	0.0050	0.0075	0.0071	> 0.0083

Table 3. Optimal structure of AA-CNT system and characteristic parameters.

Visually optimized structure	E_{ads}, kJ/mol	R_{CO1}, R_{CO2}, Å	R_{CN}, Å
L-proline – CNT 	42.54	3.18 3.24	4.84
D-proline – CNT 	49.10	3.16 3.17	4.79

The results of quantum chemical modeling of the adsorption process of proline isomers on the side surface of the CNT model are presented in Table 3. The results show that the adsorption energy of an individual zwitterion of D-proline on CNT is higher than the adsorption energy of the L- isomer:

E_{ads} (L) < E_{ads} (D), which is due to the exposed carbon nanotube closer to the O- and N-atoms of D-proline. This is consistent with the three-point interaction theory. Indeed, the distance from the N- and O- atoms of AA to the nearest C-atom of the nanotube is smaller for the D-isomer than for the L-isomer, leading to larger adsorbate-adsorbent interaction energy. Therefore, nanotubes have more affinity for the D-isomer and enantiomeric separation can be performed.

Analysis of the shortest distance from the O- and N-atoms of the enantiomers to the C-atom of the CNT also allows us to conclude that there is no covalent bond between the adsorbate-adsorbent. Indeed, according to calculations, these distances exceed 3.1 Å (Table 3.), which is significantly longer than the lengths of the covalent bonds C-O (1.43 Å) and C-N (1.47 Å) that appear in chemical compounds. The total charge on the atoms of CNT and AA in the optimal structure of the adsorption complex (according to Mulliken) is close to zero. This allows us to conclude that during the adsorption process, there is practically no charge transfer from the adsorbate to the adsorbent, and no electrostatic interactions occur due to charge transfer occurs. Therefore, the most likely mechanisms for attachment of amino acids to CNTs are Van der Waals forces.

4. Conclusion

The adsorption isotherms of enantiomers of proline on MKN-MWCNT-P5000 carbon nanotubes from aqueous solution at 25℃ were constructed. The adsorption capacity of the D-isomer is higher than that of the L-isomer, which may underlie their separation. The separation coefficients of enantiomers on CNT are in the range of 1.88–7.92 and are higher than the coefficient of other adsorbents. We determined that L-proline is adsorbed on CNTs as zwitterion and clusters of 62 molecules; D-proline – is adsorbed in the form of a zwitterion and cluster of 33 molecules. For D-proline, sorbate cluster formation begins at lower concentrations than for L-proline. The work presents the results of quantum modeling of the adsorption interactions of enantiomers of proline on the dextrorotatory CNT surface with chirality index (7, 5) and analysis of the optimal structure of the monomer system L- (D-) proline - CNT. The shorter distances of the nitrogen and oxygen atoms of the D-isomer with the dextrorotatory CNT were established, determining the larger adsorption energy of the monomer of D-proline on the CNT compared to the L-isomer. The results also showed that the enantiomers are attached to the nanotube mainly by Van der Waals forces.

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