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Studies of the reactivity of carbon nanotubes towards selected alkali cations and chlorides based on the HSAB theory

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ABSTRACT

Polycyclic curved aromatic fragments ($C_{24}H_{12}$) have been employed as models of SWNTs ((n,0), where n varies from 4 up to 30) in order to investigate the relation between the curvature and reactivity of the sidewalls. The flat coronene structure has been chosen as a molecular fragment topologically resembling the honeycomb lattice, and it is treated as the reference one. The intrinsic chemical reactivity in terms of the Fukui function, applying the principle of hard and soft acids and bases (HSAB) in the framework of the density functional theory (DFT), was investigated. In the current study we take into account the interactions of hard acids (Li^+, Na^+, and K^+) and isoelectronic ions (F^- and Cl^-, hard bases), treated as the probe molecules, with the exterior surface of mentioned above structures. The linear correlations between the adsorbate–adsorbent interactions and the both total as well as local hardness and/or molecular energy potential for studied ions were observed (increasing reactivity upon increasing curvature). Obtained results illustrate that the HSAB parameters can be a good measure for the reactivity if the influence of geometrical changes is considered.

1. Introduction

It is well known that in general, carbon surfaces (if unmodified with acids or bases) are amphoteric in nature, with the co-existence of acidic and basic centers. In view of experimental and theoretical results, different hypotheses about the both types of carbon sites have been widely considered [1–4]. Pearson's concept [5] has been widely used because the Lewis acid/base statement that "soft likes soft, hard likes hard" is easily understood, straightforwardly applied, and this idea rationalizes a range of otherwise very disparate facts. Some results demonstrated that for gases interacting with so-called "white" (i.e. non-carbonaceous) adsorbent surfaces, the reactions follow the HSAB (hard and soft acids and bases) principle [6–8]. It should be pointed out that the description of the properties of some polyaromatic compounds treated as carbon models using this theory is more and more popular [3,9–13]. Some results of the theoretical considerations in this field have been recently published also by us [14–18].

In order to investigate the reactivity of carbon nanotubes various "molecular probes" can be chosen (see [17] and reference therein). In the current studies we took into account the cations (Li^+, Na^+, and K^+) treated as hard acids accordingly to Pearson's classifications of hard and soft acids and bases [3,5]. We decided to study those ions due to widely theoretical and experimental interest ([3,13,19–23] and literature therein) in the research of the carbonaceous materials. Moreover, we considered isoelectronic ions (i.e., F^- and Cl^-, hard bases) together with the mentioned above cations.

The main goal of the current studies is the verification of the possibility of the application of the HSAB principles to interpret the adsorption properties of carbonaceous adsorbents for selected kinds of ions. Moreover, it is very interesting to investigate the relation between the curvature and reactivity of the sidewalls of SWNTs. We believe that the results of this study make the adsorption mechanism of the mentioned above ions more clear.

2. Computational method

It is well known that carbon nanotubes and activated carbons possess very complicated structure [24]. Therefore, it is very difficult to reconstruct their structure and, consequently the adsorption properties, porosity, reactivity, etc. Taking into account the computational costs, one can assume that studied models should be large enough (but not too much), in order to reproduce properly discussed above parameters [17,25,26]. Therefore, the polycyclic curved aromatic fragments can be treated as the models

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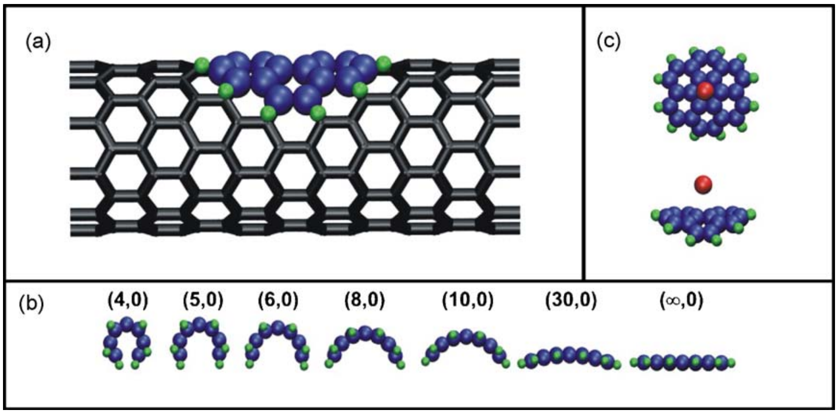

Fig. 1. (a) Illustration of the curved coronene-like ($C_{24}H_{12}$) structure (balls) treated as a part of (10,0) SWNT (tubes), (b) coronene-like structures, and (c) a unique positive charge or ions move towards the center of a six-membered ring ($C_{24}H_{12}$) excluding from (10,0) SWNT. The Figure was created using the VMD program [27].

representing the whole structure of both, carbon nanotubes and/or some activated carbons in the quantum chemical studies. We limited our considerations to five coronene-like ($C_{24}H_{12}$) structures (Fig. 1b) – parts of (n,0) SWNTs (where n varies from 4 up to 30). The graphene sheet (represented by flat coronene, i.e. $n \to \infty$) is treated simultaneously as the reference model. The (n,0) SWNTs were build using the Nanotube Modeler [28] with the assumption of the C–C bond equal to 1.42 Å. After excluding the coronene-like structure from the respective SWNT the C–H bond distance was fixed to 1.09 Å (Fig. 1).

The molecular electrostatic potential (MEP) was calculated along the line perpendicular to the central ring between a unique positive charge and the center of the C-hexagon (Fig. 1c) for various distances. MEP [29] represents the interaction energy of the system with a unique positive charge, and thus reflects mainly the hard–hard interactions. It was at first invoked to illustrate the reactivity towards an electrophile; however, its use as a descriptor of nucleophilic reactivity index is also well documented [30,31]. The local hardness ($\eta(r) = -0.5V_{el}(r)/N$, where N is the number of electrons of the system and $V_{el}(r)$ is the electronic part of MEP) in the context of the DFT-based reactivity descriptors [31], has already been successfully used as a negative charge accumulation index at defined points in the study of electrophilic attacks [32,33]. Additionally, the calculation of systems with N, $N-1$, and $N+1$ electrons is necessary to obtain the vertical IP (ionization potential) and EA (electron affinity) at constant external potential (the same geometries were studied). Then, these values are injected in the total hardness expression evaluated in a quadratic model and a finite difference approximation, i.e. $\eta = 0.5(IP - EA)$ [34]. Finally, the values of the binding energy (BE) of adsorbed ions were calculated while this molecule was moved perpendicularly towards the centre of a six-membered ring (similarly as for MEP, Fig. 1c). In the present calculations, we have adopted the same methodology of the location of ions as in [13] to ensure that the obtained molecular structures represent the accepted physical properties of these species accurately. The values of MEP and $\eta(r)$

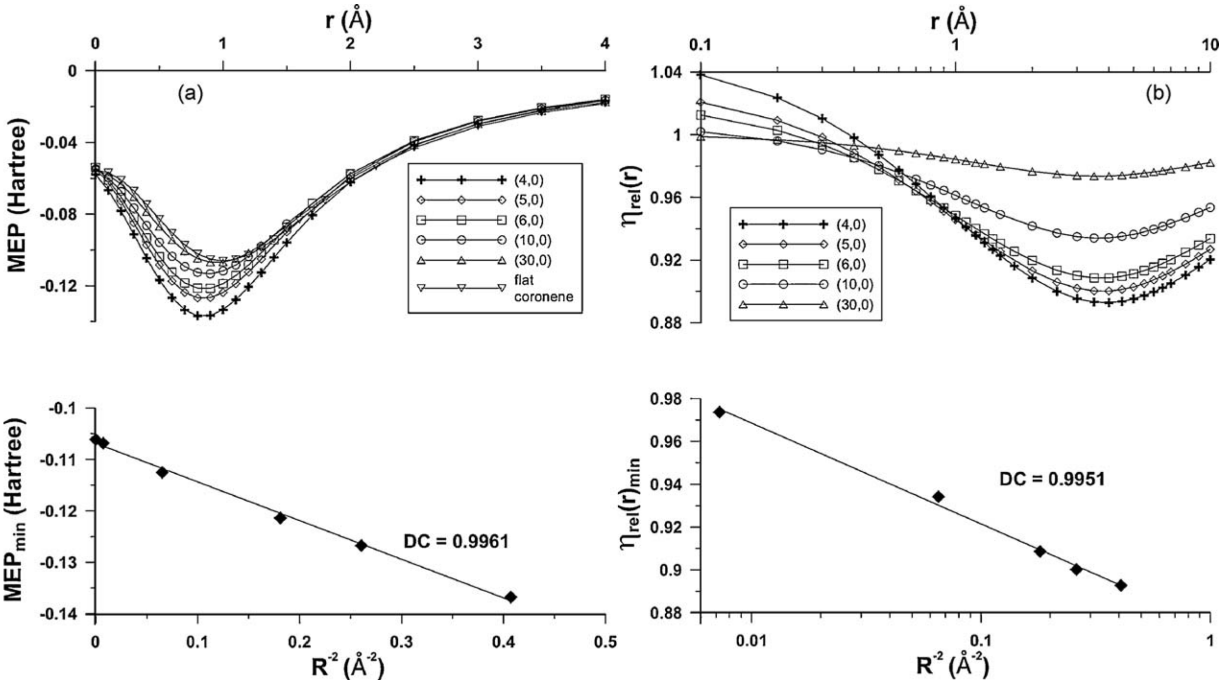

Fig. 2. (a) MEP for the curved coronene structures as the function of distance (r) between the center of the central ring of investigated structure and the probe positive charge, and the correlation between the calculated values of the minimum of MEP and inversed square of a nanotube radius (R^{-2}). (b) The same as for MEP but for the relative (with respect to flat coronene structure) local hardness.

are calculated for the optimized position of ions by replacing them by a unique positive charge (MEP_{inpos} and $\eta(r)_{inpos}$).

All calculations are performed (*via* Gaussian 03 [35]) at B3LYP level of DFT using 6-31G(d,p) basis sets.

3. Results and discussion

In Fig. 2 the linear dependences of the curvature of the studied adsorbents on MEP and the relative (with respect to flat coronene structure) local hardness ($\eta_{rel}(r)$) are shown. It is evident that the reactivity increases with the increasing curvature, since larger absolute value of tested index means also larger reactivity. Similar tendencies are observed for the relative local hardness. Analyzing Fig. 2 (i.e., MEP or ($\eta_{rel}(r)$, separately) one can conclude that the locations of the minimum are almost completely independent of the size of a nanotube. Moreover, the locations of the minimum are significantly various if the mentioned above reactivity parameters are compared. We previously stated studying the interaction of CO and $^{\bullet}NH_2$ with the sidewalls of SWNTs that $\eta_{rel}(r)$ better describes the physical adsorption; contrary to the MEP (chemisorption) [17].

The correlation between BE and MEP for all studied cations is shown in Fig. 3a. The similar tendency is observed for chlorides. Those phenomena can be explained by the increase in the ion radius and thus in the locations of the adsorbed ions. Analyzing the influence of the curvature of SWNTs on the correlations of the binding energy vs. the local and total hardness the linear dependences are observed for the respective ions (Fig. 3b and c). It is seen that the energy linearly increases with the decrease in the absolute values of the both types of hardness. Moreover, contrary to the adatoms or alkali metal clusters studied by Rytkönen et al. [22] single ions, due to electrostatic interaction, do not reveal the diffusion barrier. Thus BE increases with the rise in the atomic number. Summing up, it is seen that the reactivity parameters and the adsorption accessibilities are correlated and those parameters can be simultaneously used in the description of the reactivity of carbonaceous adsorbents.

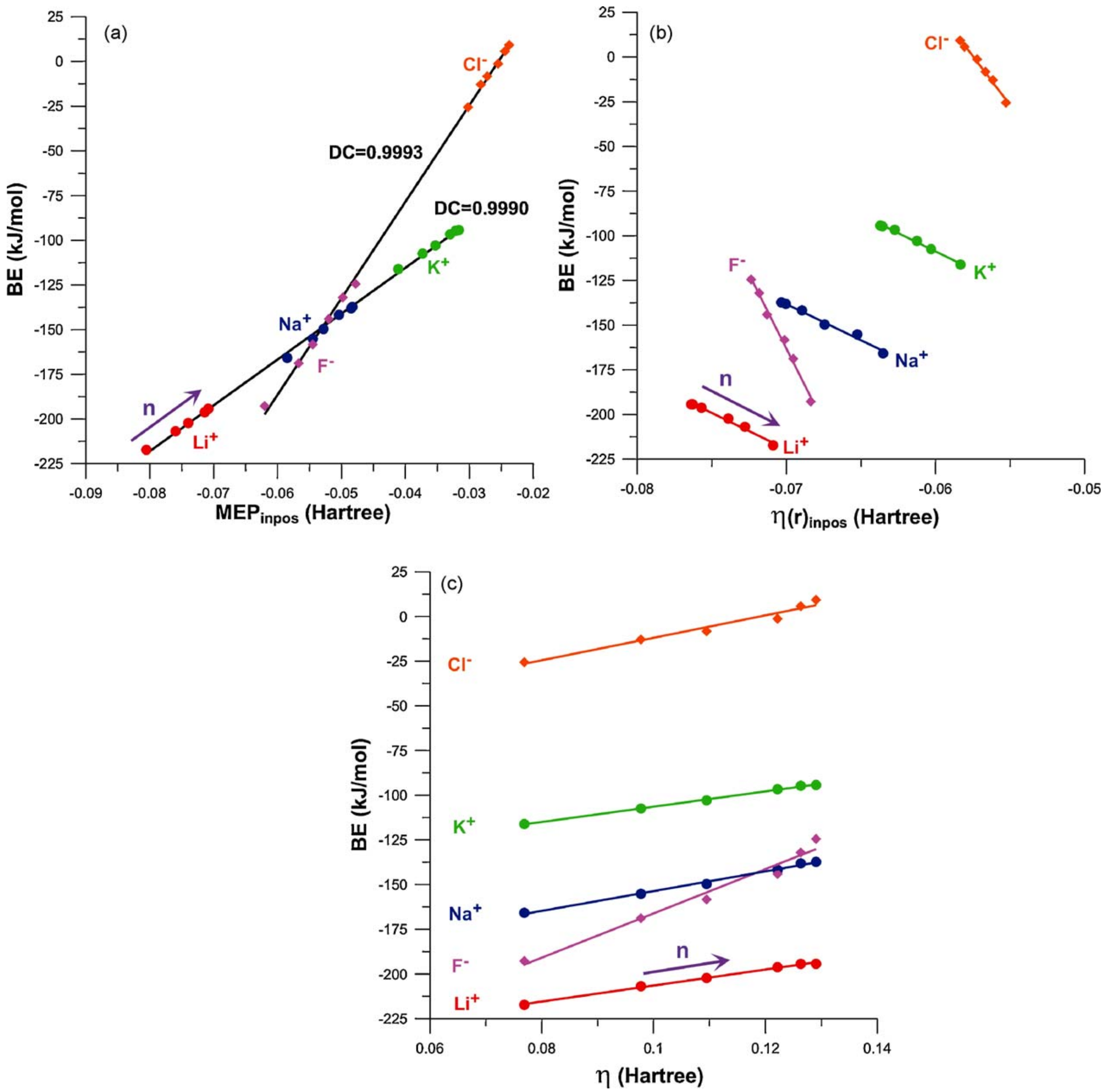

Fig. 3. The energy of adsorption of ions (BE) as the function of (a) MEP (a unique positive charge is in the position of adsorbed ion), (b) local hardness (for the same position of adsorbed ion as for (a)), and (c) total hardness. The coronene-like structures excluded from (n,0) SWNTs (where n varies from 4 up to 30) collected in Fig. 1 were studied.

4. Conclusions

DFT method was employed to intensively investigate the interactions of hard acids (Li^+, Na^+, and K^+) and hard bases (F^- and Cl^-) with coronene-like fragment of SWNTs. The intrinsic chemical reactivity in terms of the principles of hard and soft acids and bases (HSAB) in the framework of DFT was investigated. Obtained results illustrate that η and/or MEP can be a good measure for the reactivity if the influence of geometrical changes is considered. Moreover, those parameters can be useful in the understanding of adsorption mechanism of alkali ions and their isoelectronic counterions on carbonaceous materials. It is well known that the local hardness (from definition) is related to the MEP and the global hardness is claimed to be a measure of aromaticity. We believe that the local hardness through electrostatic potential is related in a similar way.

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