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Hydrogen bonds in camphorsulfonic acid doped polyaniline

Summary — We conducted a set of computer simulations to explore in details the way polyaniline (PANI) interacts with its dopant molecules like camphorsulfonic acid (CSA) and with solvent like chloroform, *m*-cresol or a mixture of *m*-cresol and water. The simulated system was built of a single layer of polyaniline chains in protonated state with attached camphorsulfonic acid ions as dopants. The system of the size above 50 Ĺ was subject to the periodic boundary conditions. All atoms in simulated molecules were assigned to atom types from OPLS-AA force field. However the inter-ring torsion profile for polyaniline in protonated emeraldine state was modified according to the density functional theory simulations. Prepared systems were simulated for 1 ns under the constant temperature (293 K) and constant pressure (1000 hPa) conditions. The results of molecular dynamics simulation exhibit a broad variety of hydrogen bond patterns between PANI-CSA as well as solvent molecules. We observed high probability (36 %) of configurations where single CSA molecule is attached to a PANI chain *via* a single hydrogen bond. However, the high probability (44 %) of a configuration where single CSA molecule bridges two or more PANI chains *via* hydrogen bonds was quite unexpected. Our simulations show also that in the presence of solvent, PANI-CSA interaction slightly weakens. Nevertheless, in the case of solvents being able to form hydrogen bonds in which CSA molecule is involved.

Keywords: polyaniline, camphorsulfonic acid, hydrogen bonds.

WIĄZANIA WODOROWE W POLIANILINIE DOMIESZKOWANEJ KWASEM KAMFOROSULFONOWYM

Streszczenie — W celu lepszego zrozumienia wpływu wiązań wodorowych na strukturę polianiliny (PANI) domieszkowanej kwasem kamforosulfonowym (CSA), przeprowadziliśmy symulacje tego systemu metodą dynamiki molekularnej uwzględniając także cząsteczki rozpuszczalnika, tj. chloroform, *m*-krezol oraz *m*-krezol z dodatkiem wody. Symulowany układ był złożony z warstwy polianiliny, którą tworzyło 12 łańcuchów polimeru otoczonych 96 jonami CSA. Cały układ o wymiarach rzędu 50 Ĺ podlegał periodycznym warunkom brzegowym, tak że łańcuchy polianiliny mogły być efektywnie traktowane jak nieskończony polimer. Parametry oddziaływań międzyatomowych zostały dobrane w ramach pola siłowego OPLS-AA, przy czym parametry profilu torsyjnego dla łańcucha polianiliny w stanie sprotonowanym zostały obliczone na podstawie symulacji kwantowych metodą DFT/B3LYP/6-31G*. Tak spreparowane systemy były symulowane w temp. 293 K i ciśnieniu 1000 hPa przez 1 ns. Wyniki symulacji pokazują dużą różnorodność konfiguracji wiązań wodorowych. Zaobserwowaliśmy znaczny procent (36 %) oczekiwanych konfiguracji, w których jedna cząsteczka CSA łączy wiązaniem wodorowym jeden łańcuch PANI. Niespodziewanym wynikiem było duże prawdopodobieństwo (44 %, tabela 2) konfiguracji, w których cząsteczka CSA łączy za pomocą wiązań wodorowych dwa lub trzy łańcuchy PANI [wzór (III)—(V)]. W przypadku dodania rozpuszczalnika, symulacje odkryły dwa typy zachowań. Cząsteczki rozpuszczalnika zdolne do formowania wiązań wodorowych (*m*-krezol, woda) wbudowują się między CSA i PANI tworząc rodzaj mostków [wzór (I)] i nie wpływając w sposób istotny na całkowitą liczbę wiązań wodorowych, w których uczestniczy polianilina. To zachowanie powoduje znaczny wzrost liczby wiązań wodorowych między CSA i rozpuszczalnikiem, co usztywnia strukturę takiego układu i powoduje, że jest on mniej podatny na zmiany. Z drugiej strony, cząsteczki dowolnego rozpuszczalnika osłaniają cząsteczki CSA [wzór (VII)] i redukują liczbę wiązań wodorowych PANI-CSA (tabela 3).

Słowa kluczowe: polianilina, kwas kamforosulfonowy, wiązania wodorowe.

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Long term studies of polyaniline led to discovery of many interesting materials such as polyaniline doped with sulfonated organic protonating acids used to produce highly conducting freestanding films [1].

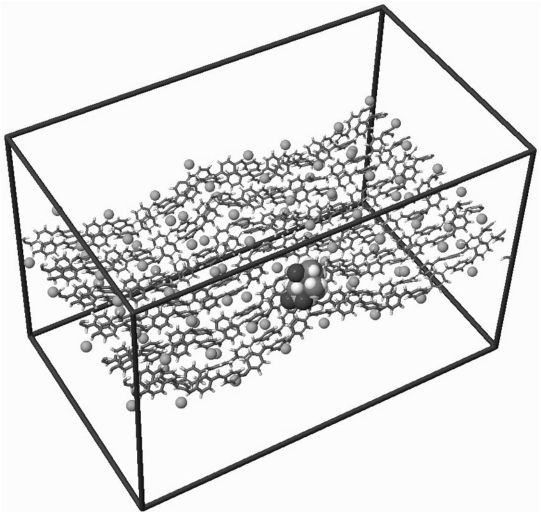
Even after so many years of investigations it is still not clear what structural properties and mechanisms are responsible for the high conductivity of doped polyaniline [1—4].

Some authors suggested that hydrogen bonds between polyaniline chains and dopant as well as solvent molecules play important role in forming polyaniline structure [5, 6].

We conducted a set of computer simulations to explore the way polyaniline interacts with its dopant molecules and with solution. To observe molecules in the real space we used molecular dynamics algorithm, which generates molecular trajectory by integrating the Newton equation. Meaningful physical quantities are obtained further by averaging the specific variables evaluated during simulation for a time range where we can assume simulation ergodicity.

MOLECULAR DYNAMICS SIMULATIONS

We simulated a system of polyaniline (PANI) layer doped by camphorsulfonic acid (CSA) ions surrounding the layer. The system cannot be related to a known structure; however it has been proven to be a good model to study interaction between polyaniline and dopant with respect to possible molecular configurations.



(I)

Formula (I) illustrates the simulated system, which was subject to periodic boundary conditions and contained a layer of thickness of one molecule of PANI in protonated state with attached camphorsulfonic acid ions as dopants. The layer consisted of 12 polyaniline chains. Each polyaniline chain was made of 4 emeraldine salt units which, under periodic boundary conditions and without endings can be interpreted as infinite polymers. The dimension of simulation box were as follows: width equal to the polyaniline chain width (75 Ĺ), depth of polyaniline layer depth (50 Ĺ) and fixed height (50 Ĺ) big enough to avoid molecule self-interactions.

The width and depth of simulation box were allowed to adjust and the box could skew to accommodate for chain relative motion. In this way we allow the structure of polyaniline layer to change.

Table 1. Protonated PANI inter-ring torsion profile coefficients for OPLS torsion potential function

Profile coefficients	C_1	C_2	C_3	C_4
Values, kJ/mol	4.92407	77.85621	-4.92407	0.00000

All atoms in all simulated molecules have been assigned atom types from OPLS-AA force field [7]. Atom types had either standard or derived parameters. *E.g.* inter-ring torsion profile for polyaniline in protonated emeraldine state was derived based on quantum simulations (DFT using 6-31G* basis and B3LYP as exchange-correlation functional). Consult Table 1 for calculated coefficients of the inter-ring torsion potential that in case of OPLS force field has the following form:

$$V(\phi) = \frac{1}{2}\sum_{n=1}^{4} C_n\,(1-\cos n\phi) \qquad (1)$$

where: *$V(\phi)$ — inter-ring torsion potential dependent on the inter-ring torsion angle ϕ, C_n — n-th expansion coefficient of the potential V where n goes from 1 to 4.*

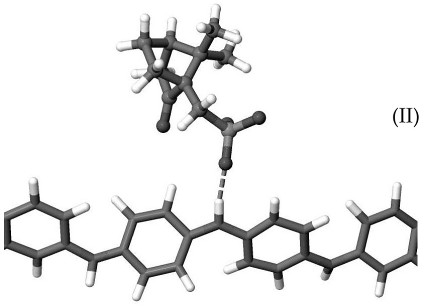
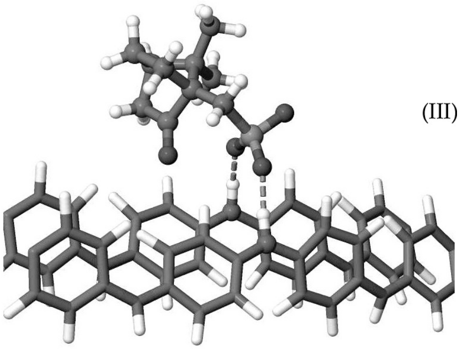
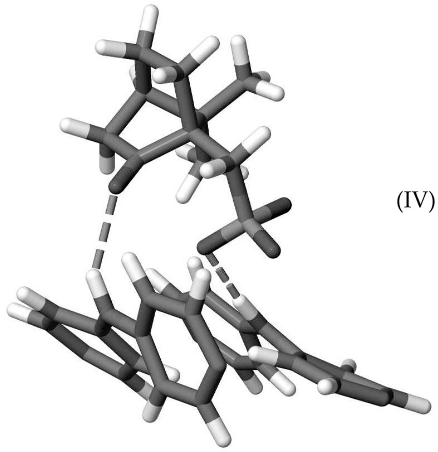
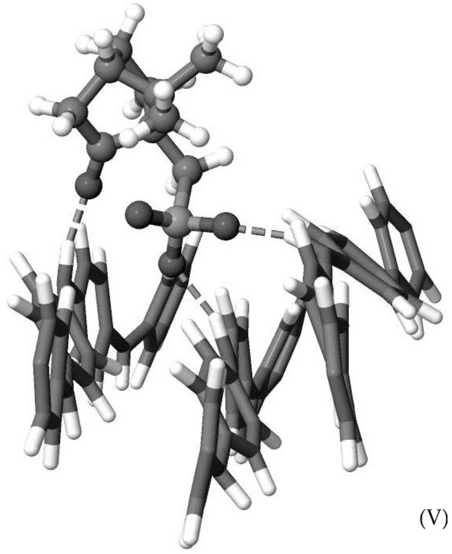
All charges were derived from quantum simulations for tetramer ion in doped state (PANI) or for whole molecules or ions for the rest of species using RESP algorithm [8] as implemented in the NWCHEM simulation package [9].

SIMULATION SETUP

To reduce computational load, a neighbour-list method was applied with cut-off radius at 14 Ĺ for Van der Waals forces as required by OPLS-AA force field and 16 Ĺ for Coulomb forces. Coulomb long tail beyond cut-off was calculated with Particle-Mesh-Ewald algorithm.

Firstly the prepared PANI/CSA system was minimized to reduce artificially large forces. Than it was relaxed at temperature 293 K and normal pressure for 0.5 ns. During relaxation, "Nose-Hoover" thermostats were used separately for PANI and CSA molecules to control temperature and "Parrinello-Rahman" barostat was used to control pressure. After relaxation, the stable system was simulated at the same conditions for another 0.5 ns. Alternatively we derived other molecule configurations based on the stable PANI/CSA systems by adding specific solvent: *m*-cresol, chloroform or water. Derived

T a b l e 2. Most representative configurations of hydrogen bonds between PANI and CSA

Description	Formula	Probability
Camphorsulfonic acid cation (CSA) attached to a single polyaniline (PANI) chain	 (II)	36 % (4)
CSA molecule bonding two PANI chains by double hydrogen bonds between single CSA and two PANI chains. Structure known in literature [5]	 (III)	44 % (4)
CSA molecule bonding two PANI chains by hydrogen bonds between sulfonate residue, carbonyl oxygen and PANI chains	 (IV)	7 % (2)
Three PANI chains bonded by single CSA molecule by hydrogen bonds between sulfonate residue, carbonyl oxygen and PANI chains	 (V)	6 % (2)
Several remaining, least representative structures treated as a whole	—	3 % (2)

systems were further simulated in the same conditions for 0.5 ns.

All systems were built using Tinker [10] and pacmol [11] tools. Simulations were carried out by Gromacs package v4.0.7 [13].

SIMULATIONS RESULTS

PANI layer adjusted its dimensions and structure during simulations and remained stable without solvent and with small amount of solvent. For configurations that reproduce solvent density for given temperature and pressure, the PANI layer quickly become unstable and breaks.

During simulations, CSA ions were attached to PANI layer only by Van der Waals and Coulomb interactions and changed their starting position while remained attached to the layer. It proves that the layer-dopant interaction is strong with respect to thermal energy. The radius of gyration for CSA molecules is 24.06(4) Ĺ or in other words 3 to 4 % of the simulation dimensions.

Hydrogen bonds in PANI-CSA system

In this paper analysis we concentrated on hydrogen bonds investigation, previously known to appear in corresponding systems and examined to some extent [6, 13]. Hydrogen bonds were identified by geometric condition applied to triples of donor-hydrogen-acceptor. PANI amino group, *m*-cresol and water hydroxyl group were donors and all oxygen atoms were acceptors. The expected geometry of hydrogen bond was: acceptor-hydrogen distance not larger than 4 Ĺ and angle formed by hydrogen-donor-acceptor not larger than 20°. The limiting values of hydrogen distance and angle are based on statistical investigation of crystal structures made by Mills and Dean [14].

A broad variety of hydrogen bond configurations between PANI chains and CSA and solvent molecules was observed. Table 2 and Formulas (I)—(IV) present the most common four configurations of CSA-PANI hydrogen bonds and their respective probabilities in our simulations. The probabilities were calculated as an average fraction (over time and system) of given configuration with respect to the total number of CSA molecules, since this number limits the number of all configurations:

$$p_{configuration} = \frac{\sum\limits_{time\ frames} \sum\limits_{CSA} n_{configuration}}{n_{time\ frames} \cdot n_{CSA}} \qquad (2)$$

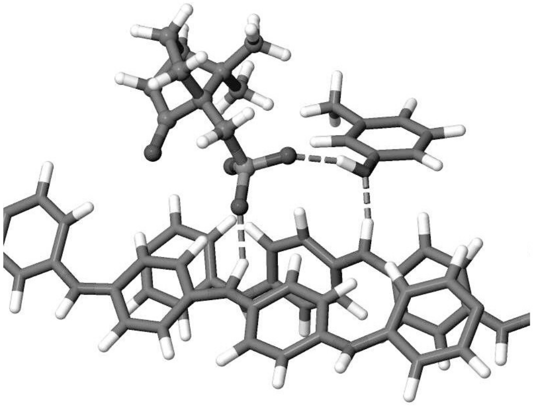
where: $p_{configuration}$ — *probability of given CSA-PANI configuration, where configuration goes from 1 to 4 as in the Table 2,* $\sum\limits_{time\ frames}$ — *sum over different time-frames of simulated system,* $\sum\limits_{CSA}$ — *sum over all CSA molecules within each time-frame,* $n_{configuration}$ — *equals 1 if given CSA molecule in the given time-frame form the configuration with any PANI chain and 0 otherwise,* $n_{time\ frames}$ — *the total number of time frames of the simulation,* n_{CSA} — *the total number of CSA molecules in the system (96).*

When we change the perspective and calculate the average number of hydrogen bonds per CSA molecule (counting appropriate number of hydrogen bonds for configurations above), we obtain the number 1.62. This means that in average each CSA molecule is attached to the PANI chain by one or more hydrogen bonds (Table 2).

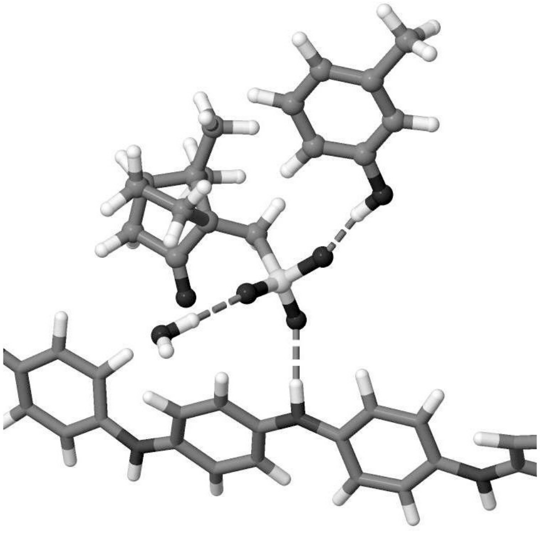
Hydrogen bonds in PANI-CSA in solution

We simulated configurations of PANI-CSA in presence of solution molecules like *m*-cresol known for excellent support for creation of very well conducting films and chloroform which produces poorly conducting films.

Since configurations with solvent/CSA ratio that reproduced solution density resulted in unstable polyaniline layer, we chose an arbitrary small number of solvent molecules for our study. The studied configurations were as follow: CSA:*m*-cresol in the ratio 2:3, CSA:*m*-cresol:water in the ratio 2:1:3 and CSA:chloroform in the ratio 2:12, respectively. The *m*-cresol/water mixture was simulated as the role of water in PANI systems can be important as investigated in the work of Luzny *et al.* [15]. Solution simulations proved to be stable during 0.5 ns and resulted in



(VI)



(VII)

number of interesting configurations of molecules involving solvent molecules.

We observed two kinds of behaviour in the presence of solvent. Solvent molecules that are able to form hydrogen bonds with CSA or PANI (*m*-cresol or water) are localized between CSA and PANI molecules forming a kind of a bridge [Formula (VI)]. While this reduces the number of direct PANI-CSA interactions, it does not change significantly the total number of hydrogen bonds where PANI is involved.

Table 3. Fractions for different hydrogen bond configurations in PANI-CSA and PANI-CSA-solvent structures

Hydrogen bonds configuration	Molecule configurations			
	PANI/CSA	PANI/CSA + *m*-cresol	PANI/CSA + *m*-cresol + water	PANI/CSA + chloroform
PANI…CSA	1.62(4)	1.53(5)	1.50(5)	1.39(5)
PANI…solvent	—	0.03(1)	0.05(2)	—
CSA…solvent	—	0.54(3)	0.51(4)	—
PANI…any molecule (1 + 2 row)	1.62(4)	1.56(5)	1.55(5)	1.39(5)
CSA…any molecule (1 + 3 row)	1.62(4)	2.07(6)	2.01(6)	1.39(5)

On the other hand any solvent molecules including chloroform tend to shield CSA molecules from PANI [Formula (VII)] which also contributes to slight reduction of CSA-PANI hydrogen bonds number (see first row of Table 3). This behaviour is also responsible for large increase in the total number of hydrogen bonds between CSA and solvent molecules. For given CSA:solvent ratios CSA-PANI interaction was however strong enough so we did not observe CSA detach (see Table 3).

CONCLUSION

Our molecular dynamics simulations show a broad variety of hydrogen bond patterns between PANI-CSA as well as solvent molecules. For PANI-CSA system without solvent molecules, we observed high probability of configurations where single CSA molecule is attached to PANI chain *via* a single hydrogen bond. Surprising an especially interesting results is the high probability of single CSA molecule bridging two or more PANI molecules *via* hydrogen bonds. Moreover our simulations revealed three possible CSA alignments that lead to bridging of two and even three PANI chains. Formula (III) shows the first configuration where CSA sulfonate group participates in two hydrogen bonds. Formula (IV) presents less probable but still significant alignment, where hydrogen bonds are formed separately by sulfonate and carbonyl group of CSA bridging two polymer molecules. Formula (V) shows similar configuration with three polymer molecules being bridged.

All described configurations that lead to PANI chains bridging may drive alignment between PANI chains that can further contribute to the high crystallinity of this polymer.

Our simulations show also that in the presence of solvent, PANI-CSA interaction slightly weakens. However, for solvents being able to form hydrogen bonds the total number of hydrogen bonds in which CSA molecule is involved increases making the system less prone to changes.

We think that our results for a model of PANI-CSA layer deserve for further deep examination of a real PANI-CSA system from the structural and electronic transport perspectives.

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