A DFT Assessment of the Environment Polarity Effect on Polyaniline-Water Coupling

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Abstract

Crystallization water plays an important role for the self-organization of oligomer chains in conducting polyaniline. In order to quantify the interaction between emeraldine salt and such a water, models containing a tetramer in bipolaronic or polaronic form, chloride counterions and an explicit water molecule are used. Different initial positions of water with respect to the oligomer chain – tangential and vertical, are considered. Various media are simulated by introducing implicit solvent continuum of decreasing polarity. The DFT-D3/PCM computational approach is employed to examine the behavior of the systems in several aspects – the role of the explicit water position and the effect of the environment polarity on the spatial structure, energetics, charge distribution, and the frontier molecular orbitals energy. The strength of hydrogen bonding and the patterns of charge redistribution invoked by the water molecule are discussed. The study establishes trendlines in the variation of the molecular characteristics upon change of milieu as a tool for control of the self-assembly process.

The results show that chains interact more efficiently with tangentially placed water. The influence of the environment polarity is minor and is mainly expressed in slight shortening of the intermolecular distances and mild decrease of the group charges of the system components with reduction of polarity.

Introduction

Encapsulated (residual or absorbed) solvent may have a critical effect on a variety of desired macroscopic properties of the materials crucial for their potential commercial applications. That defines the necessity of more knowledge at the microscopic level about the impact of incorporated solvent on the materials characteristics. Although the topic has been long investigated,¹⁻³ the role of captured solvent is system-specific and in many cases not fully elucidated.

Naturally, the majority of studies exploring the effect of trapped solvent are focused on water. There are numerous investigations on water as a component or additive that assists or induces various processes – here are listed just a few of the more recent reports.⁴⁻¹¹ The process of water absorption and formation of hydrogels by some polymers is also a subject of interest.¹² Water molecules can mediate the self-organization in some materials.¹³ Microstructure emergence in a material can change the existing and introduce new observable macroscopic properties. Such is the case of polyaniline, where there is evidence that the water molecules play a central role in the formation of the highly crystalline and the liquid-crystalline (J-aggregates) states¹⁴⁻¹⁶ related to enhanced electric conductivity or to a redshift of the longest-wavelength absorption.

Nowadays, polyaniline (PANI) is still a very appealing target because of its easy and cheap processing, high stability, leading position among the organic conductors and broad promising applications in solar cells,¹⁷ LEDs,¹⁸ batteries,¹⁹ antistatic coatings,²⁰ etc. Polyaniline can exist in several stable oxidative forms – leucoemeraldine, emeraldine, and pernigraniline. All of them are neutral bases and can form salts upon protonation of the nitrogen atoms. The three bases can interconvert depending on the synthetic conditions. As a result, changes in color – from yellow to blue and purple and in conductivity – from insulator to semiconductor, occur with increasing degree of oxidation. Most attention receives the semiconducting emeraldine base (EB) consisting of aromatic and quinoid rings in ratio 3:1 connected by amine or imine nitrogens (Fig. 1, top). Protonic acid doping (typically with HCl) is frequently used for easy transformation of EB into the highly conductive emeraldine salt (ES), without changes in the number of electrons in the chain. As a result, the conductivity of the sample is increased by 10 orders of magnitude and values of 10^1 - 10^2 S.cm⁻¹ have been measured.²¹

The presence of hydrophilic fragments in EB allows intercalation of water molecules between the conjugated oligomer chains and formation of fibril-like mesophases, or the so-called J-aggregates. This liquid-crystalline state is characterized by the appearance of a J-band in the electronic absorption spectrum, i.e., a redshift of the longest-wavelength transition from 650 nm to about 800 nm, while the absorption band at 570 nm, typical for highly crystalline samples of PANI, disappears.^{14,15} The observed shift in the position of the longest-wavelength absorption is reversible and is registered only upon water absorption. The modification of the microstructure of the emeraldine base induced by the absorbed water invokes changes in the physical properties analogous to the effect of conversion between the oxidative forms of PANI. Atomistic molecular dynamics simulations^{14,15} confirmed that water aids the self-organization of the oligomer chains.

The important role of water for the self-assembly of the conjugated chains is reported also for the emeraldine salt (ES). Highly ordered and highly crystalline (> 70%) material is obtained just by partially drying the product as the only post-synthetic treatment.¹⁶ A certain amount of water, which is responsible for the rigorous chains arrangement, is always retained in the well-ordered thin polymer films and the sample loses its crystallinity if completely dried. The water intercalation and the enhanced self-organization of the oligomers is realized by highly hydrated counterions. Moreover, the type of the counterion is important in regard to the water structure perturbation that influences its interaction with the polymeric matrix.¹⁶

Some experimental evidence about the role of trace water in PANI-organic acid systems have been reported.²² The interactions of emeraldine base with dichloroacetic acid (DCAA) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) are studied by gel permeation chromatography and UV-vis spectroscopy. The effect of water is also examined. Even in low concentration, its quantity inside the {EB}_x·AMPSA clusters may be sufficient to initiate the protonation of some EB molecules. The results indicate that the water addition largely shifts the longest-wavelength absorption peak. Control of water concentration and temperature can minimize the protonation and regulate the stability of the solutions.

Hence, understanding the coupling of water molecules to the emeraldine chains will be a valuable first step towards the explanation of these non-conventional properties. Theoretical chemistry tools have been used for better apprehension at the microscopic level of the role of water in the polyaniline systems.²³⁻²⁵ Different computational approaches have been employed - mainly the DFT approximation, as well as MD atomistic simulations.

The important role of the solvent for the correct description of PANI molecular features is credibly demonstrated by modelling the solvent as an implicit polarizable continuum.²³ The effect of the presence of trace water on EB models characteristics has been addressed in a multifaceted study of Casanovas et al.²⁴ Quantum mechanical calculations are carried out in order to study the interactions between the reversibly and irreversibly absorbed water with amine or imine units of the emeraldine base modelled by an amino group end-capped oligomer. The calculations are performed in the gas phase at the B3LYP/6-31+G(d,p) level on models with one or two water molecules. The computed binding energies show slightly preferred interaction of water with the imine nitrogens. Atomistic MD simulations are performed in order to study at the microscopic level the organization of water absorbed in the polymeric matrix modelled by a simulation box containing four polymeric EB chains and water molecules corresponding to 15% w/w of absorbed water. Two types of interactions are considered: between an individual water molecule and the emeraldine base and between water aggregates (nanodrops) and the polymer. The second type of physisorbed water is deemed to feature higher activation energy due to binding to both EB chains and nanodrop waters.

At a hybrid QM/MM level, the AM1 method and the AMBER96 force field are used to study models of two solvated stacked tetramer chains of emeraldine salt that differ in their mutual alignment.²⁵ The solvent molecules are described with the TIP3P model. The counterions are included as well. The semiempirical calculations indicate a significant effect of the explicit account of water molecules and of the inter-chain coupling on the structure and optical properties of the system. It is also found that PANI interacts directly with a limited number of water molecules.

The present *ab initio* study is based on that conclusion and on the aforementioned experimental observation of a limited amount of water in the highly crystalline samples. It aims at gaining insight into the influence of the media polarity on ES-chain/explicit solvent molecule coupling and at evaluating the effect of the counterions configuration on this interaction. Three different solvents are simulated using an implicit polarizable continuum model. The focus is on the structure of the ES-water complex, on the strength of the hydrogen bonds, on the electron density redistribution and on the energy of the frontier molecular orbitals. Preferred water positioning along and against the chain is discussed. The results are an initial step of a systematic study aiming to shed light on the process of chains self-organization and on the factors that govern it.

Models and Methods

The model systems consist of three types of structural units: a dicationic emeraldine salt oligomer, two chloride anions, and a water molecule (Fig.1, bottom). The experimental data indicate that the ES chains in highly crystalline samples are octamers.¹⁶ However, in the current study the ES is represented by tetramers: being the smallest structural unit that can describe the emeraldine salt, this chain-length allows a feasible consequent expansion of the model size by introduction of more tetramers in order to study the intermolecular chain-chain interactions in the presence of explicit waters and counterions.

ES can exist in two forms that differ in their magnetic behavior.^{26,27} Therefore, in the computations each single chain is modelled as a singlet – describing a spin-silent bipolaron, and as a magnetically active triplet – corresponding to two polarons (Fig.1, middle). The geometry of the ES tetramers optimized earlier in implicit water²³ is utilized as a starting structure. In both cases the doped (protonated) chain possesses charge 2+, which is neutralized by two Cl⁻ counterions, as HCl is the most commonly used dopant. Each of the chloride ions is initially situated along the N-H bond of the **protonated nitrogens** (N2, N3 for the **bipolaron** and N1, N3 for the **polarons**, Fig. 1) at a distance of ~ 2 Å. The interaction of one explicit water molecule consecutively with each of the hydrophilic sites (N - containing groups) along the chain, is taken into account. According to the experimental estimates, the water content of the ES samples with the highest reported crystallinity corresponds to about 1 to 2 water molecules per tetramer,¹⁶ which vindicates the choice of models.

Two different water alignments to each of the fragments are modelled:

1) **Tangential position:** a water molecule is situated along the N-H bond in the plane defined by the tetramer backbone (Fig. 2, top). The amino group is a proton donor in the H₂O:....H-N hydrogen bond.

2) **Vertical position:** a water molecule is on top of a nitrogen along the tetramer chain (Fig. 2, bottom). The amino group is a proton acceptor in the HOH.....:N-H interaction.

These labels are used below to denote the model systems: the **magnetic state** - **B** (bipolaronic) or **P** (polaronic), followed by the **number of the nitrogen** along the chain (Fig. 1) and the type of the **initial placement of the water** molecule – **T** (tangential) or **V** (vertical) (Fig. 2). For the terminal nitrogen (N4), only one position – above the nitrogen, is considered; the proper tangential model without artificial loss of symmetry would require two water

molecules, but since all other models contain one H₂O, we preferred to refrain from including tangential structures at N4.

The environment around the described three-component supramolecular complexes is considered as an implicit continuum. Three solvents are simulated: water ($\epsilon=78.3553$), acetone ($\epsilon=20.4930$), and chloroform ($\epsilon=4.7113$). The non-equilibrium PCM^{28, 29} is applied for discrimination between the polarizing capacity of the three surroundings.

Fig. 1. Schematic representation of: emeraldine base (EB, top), emeraldine salt (ES) in the bipolaronic (middle, left) and polaronic (middle, right) tetrameric form, and an illustrative example of the three-component models (bottom). The numbering of the nitrogens used in the text is shown.

Fig. 2 represents an example of the initial structures of the tangential (top) and vertical complexes (bottom). All initial and optimized structures in water, acetone, and chloroform are summarized in Figs. S1-S3 of the Supporting Information (SI). The initial structures are constructed by positioning the water molecule intuitively in a way deemed to allow its maximum interaction with the respective functional group (for alternative water placement pattern see SI, Fig. S4).

Fig. 2. Top (left) and side (right) view of representative tangential (top) and vertical (bottom) initial structures of polaronic complexes with water at N1, illustrating the nomenclature employed.

All calculations are performed at the B3LYP-D3³⁰⁻³² level with 6-31G* basis set. The D3 empirical correction is used in order to take into account the dispersion interactions in the supramolecular/non-covalent complexes. The Gaussian 09³³ program package is utilized.

The bipolarons are calculated as singlets and the polarons – as triplets, as usually assumed and corroborated in our earlier study.³⁴ All models are subject to unrestrained geometry optimization followed by frequency analysis for confirmation of the minima. $\langle S^2 \rangle$ of the open shell systems is about 2.02 before and 2.00 after annihilation – based on these results it could be concluded that the triplet ground spin state is not spin contaminated. The stability of the ground state wavefunctions is verified, no instability is found. The electron density distribution of the optimized structures is characterized by natural (NBO) population analysis. The NBO scheme³⁵ as implemented in Gaussian 09 is used.

Results and Discussion

Structure of the complexes

The mutual orientation of the systems components in the optimized structures is dependent on the initial water molecule position. The lowest-energy geometries of the complexes in the three solvents are very similar (Figs. S1-S3 of SI). A small quantitative difference of the complexes in chloroform compared to the rest of the solvents can be delineated – in the least polar medium most of the intermolecular distances between the components are slightly shorter (Tables 1, S1, S2).

The main tendencies in the structure specifics of the complexes are summarized as follows:

At not protonated positions the N-H...:Cl⁻ distances are preserved unchanged after optimization in both tangential and vertical structures (Tables 1, S1, S2 of SI), while when the water molecule is inserted between the tetramer and the anion, the N-H...:Cl⁻ distance are already longer than 3.0 Å. The latter values do not depend on the chain multiplicity and are slightly influenced by the continuum polarity. In all cases the counterions retain their initial position with respect to the chain plane.

Table 1. Characteristic distances^{a)} in the systems optimized in implicit water.

Distance, Å	Bipolaronic						
	B_1_T	B_1_V	B_2_T	B_2_V	B_3_T	B_3_V	B_4_V
H ₂ O: H-N	1.80		1.69		1.69		
HOH :N-H							2.03
¹ Cl:.....H-N	2.06	2.06		2.04	2.05	2.05	2.03
² Cl:.....H-N	2.06	2.04	2.05	2.04		2.05	2.05
Cl:.....H-O-H			2.08		2.09		
Distance, Å	Polaronic						
	P_1_T	P_1_V	P_2_T	P_2_V	P_3_T	P_3_V	P_4_V
H ₂ O: H-N	1.72		1.79		1.72		
HOH :N-H		2.23					2.25
¹ Cl:.....H-N		2.13	2.09	2.07	2.08	2.08	2.07
² Cl:H-N	2.07	2.07	2.08	2.07		2.13	2.06
Cl:.....H-O-H	2.10	2.23			2.10	2.23	

^{a)} only distances corresponding to hydrogen bonds (<3.0 Å) are listed; the two chloride counterions in each model are denoted as ¹Cl⁻ and ²Cl⁻

It is interesting to analyze in more detail the interactions of the water molecule in the different types of complexes.

With tangential initial position: the water molecule preserves the same tangential orientation to the chain, along the respective N-H bond, as initially situated. A very strong H₂O: H-N hydrogen bond is formed with length varying in the range of ~1.68-1.86 Å. The counterion proximity does not affect the length and the strength (see below) of this type of H-bond. In the cases when water is placed at the protonated sites and a counterion is close as well, a second strong HOH:Cl⁻ hydrogen bond is registered with length in the range ~ 2.03 - 2.10 Å, irrespective of the chain spin state. Decreasing of the dielectric permittivity of the solvent results in a slight shortening of the latter hydrogen bond.

With vertical initial position: generally, the water tends to move away from the nitrogen on top of which it is initially positioned (except when placed at the terminal N4). It adsorbs either above the center of a neighboring ring (B_1_V, P_2_V) or in the vicinity of the closest counterion (P_1_V, P_3_V) where a HOH:Cl⁻ hydrogen bond is formed. This hydrogen bond distinguishes the polaronic systems from the bipolaronic ones and is of medium

strength (2.23 Å). It should be noted that in the latter structures the water acquires almost tangential alignment with respect to the tetramer plane. In the singlet systems, irrespective of the location along the chain, the water molecule remains in a vertical position. On the other hand, the preferred interaction of water molecule with the chloride ions in polaronic vertical structures agrees with the literature data and supports the provided interpretation that the hydration of crystalline ES films by means of intercalation of water molecules in the π -stacking direction is facilitated by the presence of highly hydrated counterions.^{14, 16}

B_4_V and P_4_V attract additional attention with qualitatively different structures that are realized in water, acetone, and chloroform. The vertical placement of the water molecule defined initially remains vertical after geometry optimization in the first solvent but converts to tangential – along one of the N-H bonds, into the other two. This delineates different characteristics of these complexes in water and in acetone and chloroform.

In summary, the interactions in each of the systems involve the formation of intermolecular hydrogen bonds. The stronger hydrogen bonding (Tables 1, S1, S2) in the tangential models explains why they are more stable (Table 3) than the respective vertical ones.

The system stability, the strength and type of the intermolecular interactions are discussed in terms of relative energy and interaction energy decomposition analysis in the next sections.

Energetic stability of the systems

The relative energy, summarized in Table 2, is considered as a measure of the system stabilization in the respective solvent. The results show that both the bipolaronic and polaronic structures are most stabilized in the most polar medium – water. A decrease of the solvent dielectric constant value leads to an increase of the total energies by ~ 3 kcal/mol in acetone and ~12÷16 kcal/mol in chloroform, almost independently of the water molecule position. This could be explained by the fact that the doped emeraldine oligomer in the presence of counterions is a polar system (Tables S3, S4). The only exception are the structures with water adsorbed above N4, where acetone is preferred. However, the shift of water at N4_V from vertical to tangential position in the less polar media has obviously a strong stabilizing effect, reflected in the negative values of $\Delta E_{\text{acetone-water}}$ and substantially lower values for $\Delta E_{\text{chloroform-water}}$ in B_4_V and P_4_V.

The solvent effect in terms of relative energy is quantitatively comparable for both forms of ES. This is unexpected because of the large difference in their dipole moments (Tables S3, S4). The polaronic species have much larger dipole moments (~38÷43 D) than the spinless forms (~7÷16 D). This is determined by the different configuration of the chloride anions with respect to the tetramer – in the polaronic systems the counterions are on the same side of the oligomer chain forming a hefty dipole (Fig. 1). In the bipolaronic configuration the anions are positioned on different sides of the chain, which reduces the dipole moment. Because of the similar degree of destabilization of polarons and bipolarons in the less polar solvents it may be concluded that the observed increase in energy is due mostly to the enhanced hydrophobic character of the solvent.

Table 2. Relative energy (ΔE , kcal/mol) for the model systems in different solvents calculated with respect to the total energy in water.

	$\Delta E_{\text{acetone-water}}$	$\Delta E_{\text{chloroform-water}}$		$\Delta E_{\text{acetone-water}}$	$\Delta E_{\text{chloroform-water}}$
B_1_T	2.5	12.7	P_1_T	3.2	16.3
B_1_V	1.9	10.5	P_1_V	3.1	15.0
B_2_T	2.5	13.6	P_2_T	3.2	16.0
B_2_V	2.8	10.4	P_2_V	3.4	13.0
B_3_T	2.6	13.2	P_3_T	3.2	15.9
B_3_V	3.0	13.2	P_3_V	3.2	15.2
B_4_V	-2.3	7.8	P_4_V	-3.3	9.3

The computed relative stability of each complex as a difference in the total energy of the system and that of the lowest-energy structure in the series is summarized in Table 3. The positive values are a numerical measure for energetic destabilization of the systems.

Table 3. Energy (kcal/mol) of the complexes, relative to that of the energetically most favorable system (B_1_T and P_2_T for bipolaronic and polaronic systems, respectively) in the three implicit solvents.

Bipolaronic Model	Water	Acetone	Chloroform
B_1_T	Reference (lowest energy) B -structure		
B_1_V	4.4	3.7	2.1
B_2_T	0.2	0.1	1.0
B_2_V	4.3	4.5	2.0
B_3_T	0.0	0.0	0.4
B_3_V	4.5	5.0	5.1
B_4_V	6.1	1.2	1.2

Polaronic Model	Water	Acetone	Chloroform
P_1_T	0.6	0.6	0.9
P_1_V	2.3	2.2	1.3
P_2_T	Reference (lowest energy) P -structure		
P_2_V	4.9	5.0	1.9
P_3_T	0.7	0.6	0.6
P_3_V	2.1	2.0	1.3
P_4_V	7.9	1.3	1.1

The energetically most favorable structures in the three solvents are B_1_T among the bipolaronic and P_2_T among the polaronic ones. However, all tangential complexes differ by less than 1 kcal/mol and can be presumed isoenergetic. This is probably due to the equal number (3) of relatively strong H-bonds (Tables 1, S1, S2) in this topology. Because of the smaller number of hydrogen bonds (2) all vertical structures have higher relative energy but the increase depends on the position of the water molecule along the chain. The P_1_V and P_3_V are comparatively more stable because of the additional intermediate-strength hydrogen bond (Table 1). The influence of the spin state on the relative stability of the complex is analyzed in the SI (Table S5).

Interaction energy

The strength and the type of interactions (or the absence of coupling) between the components are quantified in terms of the computed two-body interaction energy. For the purpose, it is assumed that the interaction between each pair of components (PANI, water molecule, and the two counterions treated as one entity) does not depend on the energy of the third one. Hence, in order to calculate the strength of coupling between them all model systems are divided into the following pairs of partners: tetramer chain – water ($\text{ES}^{2+} - \text{H}_2\text{O}$); tetramer chain – counterions ($\text{ES}^{2+} - 2\text{Cl}^-$); counterions – water ($2\text{Cl}^- - \text{H}_2\text{O}$). The interaction energy is evaluated as a difference of the dimer energy and the energy of the separate monomers, all computed with the basis set of the entire three-component system at the optimized geometry of the complex. The structures obtained after geometry optimization in water, in acetone, and in chloroform are used for the calculations.

Table 4. Interaction energy (kcal/mol) between the components of the systems optimized in implicit water.

System	$\text{ES}^{2+} - \text{H}_2\text{O}$	$2\text{Cl}^- - \text{H}_2\text{O}$	$\text{ES}^{2+} - 2\text{Cl}^-$
B_1_T	-15.6	2.4	-280.9
B_1_V	-0.8	-4.4	-281.8
B_2_T	-15.2	-14.6	-251.0
B_2_V	-4.3	2.7	-281.8
B_3_T	-14.1	-16.2	-260.2
B_3_V	-3.3	-3.3	-281.8
B_4_V	0.4	-0.8	-284.3
P_1_T	-13.1	-18.3	-259.9
P_1_V	0.7	-16.7	-263.2
P_2_T	-14.2	-1.2	-265.2
P_2_V	-3.8	2.2	-263.9
P_3_T	-13.8	-15.4	-241.6
P_3_V	-0.9	-13.8	-256.0
P_4_V	0.2	1.5	-266.3

The counterpoise procedure^{36, 37} as implemented in Gaussian 09 is applied to correct for the basis set superposition error. This implementation does not take into account the presence of a solvent in the computations, so the solvent effect on the interaction is accounted for indirectly through its effect on the structure upon optimization. However, the obtained values outline the contributions of the different dimer-interactions to the total interaction energy. The calculated energy values are collected in Tables 4, S6, S7.

In both tangential and vertical systems optimized in implicit water the strongest inter-particle interactions are between the ionic components – the oligomer chain, possessing ideally 2^+ charge, and the two counterions with the total of 2^- charge. Its magnitude in the three solvents is over 240 kcal/mol, irrespective of the spin state of the chain and of the water position (Table 4, S6, S7). These high energy values show that the interactions are realized not only by hydrogen bonds but that the electrostatic forces are dominant. In the structures where water is shielding a protonated nitrogen (B_2_T, B_3_T, P_3_T) the attraction is weaker because the tangential position of the water molecule screens the interaction between the tetramer and the respective counterion, as already discussed above. Apart from these structures, the $ES^{2+} - 2Cl^-$ interaction energies for a given spin state are very similar. As a whole, the ionic coupling is stronger in the bipolaronic structures than in the polaronic ones; on the other hand, the vertical positioning of water results in more enhanced (by ca. 20 kcal/mol) ionic interaction than the tangential placement.

The tangential position of water at the protonated nitrogens (B_2_T, B_3_T, P_1_T, P_3_T) favors its interactions with both the oligomer chain and with the closest counterion. The interaction energy of water with the ionic components, irrespective of their type (dicationic tetramer or anionic chloride) is very similar and greater than 10 kcal/mol (12÷18 kcal/mol). These interactions are realized by two types of relatively strong hydrogen bonds: $HOH \cdots :Cl^-$ of about 2.1 Å length and $H_2O \cdots H-N$ of ~1.8 Å, independent of the chain multiplicity. The latter distance is slightly longer (by 0.1 Å) in case the water is placed far from the anion (B_1_T, P_2_T). The distance of the water to the closest proton from the chain is slightly shorter than to the proximate anion but the interaction energy related to these bonds is the same. Just the larger radius of the anion defines an elongation of the hydrogen bond, but its strength is not influenced.

The tetramer-water ($ES^{2+} - H_2O$) and chloride-water ($2Cl^- - H_2O$) interaction energy is very similar for the vertical bipolaronic systems and indicate very weak coupling between the water molecule and the ionic fragments, much lower compared to the tangential systems. In the vertical polaronic ones the tetramer-water ($ES^{2+} - H_2O$) attraction is always weak, while the chloride-water ($2Cl^- - H_2O$) is substantial at the protonated positions. B_4_V and P_4_V are the exceptions due to the shift of the water molecule to the chain plane, i.e., the water molecule is attracted by the chain and does not sense the presence of the chloride ion due to spatial remoteness.

In the vertical systems the distances from water to the chloride ions and to the adjacent nitrogen are relatively large (Table 1) and exclude the possibility for hydrogen bonds formation. The calculated low interaction energy is a result mainly of ion-dipole and dipole-dipole interactions and is very similar for both bipolaronic and polaronic chains, regardless of the substantial difference in the computed dipole moments (Tables S3, S4 of the SI). In some

structures (B_2_V, B_3_V, P_1_V, P_3_V) the optimized position of water favors weak interaction (2.3 Å) with a hydrogen atom from the closest aromatic ring that also contributes slightly to the computed interaction energy.

In the systems (B_1_T, B_4_V, P_2_T, P_2_V, P_4_V) where the water molecule keeps away from the counterions in the optimized structure, the interaction energy between the two components ($2\text{Cl}^- - \text{H}_2\text{O}$) is negligibly small (-1 kcal/mol) or even positive: 2 kcal/mol. The latter may be due to the fact that in all such structures the water molecule is facing one anion with its oxygen atom, which should result in unfavorable ion-dipole interaction.

Three-body contribution to interaction has been neglected so far but in order to check its influence on the results the interaction energy was calculated with an alternative scheme, which includes it.³⁸ The values are provided in the Supporting Information (Table S8). The data show that the three-body interaction adds only a mild contribution to the interaction energy. The electrostatic attraction of the charged oligomer chain and counterions is undoubtedly dominant. As could be expected, the three-body term is relatively small – it never exceeds 10.9 kcal/mol. It is interesting how the decrease of medium polarity changes the balance of the three-body contribution as far as the spin state of the systems is concerned. In water, the magnitude of this term in the polaronic systems is on average much larger than that in the bipolaronic ones. In acetone this disparity is reduced, while in chloroform the two types of complexes have comparable three-body shares. This means that in the most polar medium the three-body coupling is stimulated in the high spin state.

Overall, the results for the interaction energy (Table 4, S6, S7, S8) disclose identical tendencies for the three solvents – not only qualitatively similar but also numerically close. They are in good agreement with the structural specifics found. The mild contraction of the inter-particle distances upon decrease of dielectric permittivity of the surroundings (Table 1, S1, S2) is reflected in the marginally growing values of all components of the interaction energy upon decrease of medium polarity.

Based on the computed interaction energy, it could be concluded that the chain-water interaction is not as much dependent on the spin state of the oligomer chain or on the water placement along the chain but rather on water position with respect to the oligomer plane. The tangential position is clearly energetically preferred (Table 3) and these are the systems where the interaction between water and tetramer is sizeable. The counterion proximity to water does not influence the strength of the water-tetramer interaction in the tangential systems. It could be speculated that the presence of water molecules will be favorable for the tangential interactions and tangential ordering of the emeraldine chains, irrespective of their spin state, while for the vertical ordering the role of water is less important. In all cases, the contribution of water is a perturbation complementing the dominating electrostatic interactions.

Charge distribution

The NBO charge distribution (Tables 5, S9, S10) of the systems in the different solvents is evaluated in order to outline the effect of environment polarity on the electron density distribution.

Table 5. NBO charges of the systems components in implicit water; **B** and **P** are the respective implicitly solvated models without explicit water.

Charge	B	B_1_T	B_1_V	B_2_T	B_2_V	B_3_T	B_3_V	B_4_V
Chain	1.750	1.701	1.735	1.777	1.731	1.773	1.731	1.766
Water	-	0.056	0.012	0.001	0.019	0.003	0.019	-0.025
¹ Cl ⁻	-0.876	-0.877	-0.874	-0.903	-0.874	-0.876	-0.876	-0.866
² Cl ⁻	-0.874	-0.880	-0.873	-0.875	-0.876	-0.899	-0.874	-0.875
Charge	P	P_1_T	P_1_V	P_2_T	P_2_V	P_3_T	P_3_V	P_4_V
Chain	1.778	1.795	1.779	1.726	1.761	1.796	1.778	1.780
Water	-	-0.002	-0.028	0.058	0.016	-0.002	-0.028	-0.007
¹ Cl ⁻	-0.889	-0.905	-0.862	-0.894	-0.888	-0.890	-0.890	-0.889
² Cl ⁻	-0.889	-0.889	-0.889	-0.889	-0.889	-0.904	-0.860	-0.885

In most of the optimized structures the water molecule is slightly charged, as it could be a donor or an acceptor of electron density. This is a clear indication of electron density redistribution between the components. The number of systems with a negatively charged water molecule is larger among the polaronic systems than amidst the bipolaronic ones, where in the majority of the complexes that molecule is positively charged.

A comparison between the systems with and without explicit water reveals slight charge redistribution assisted by the discrete water. The value and the direction of the charge transfer is defined largely by the water topology and is independent of the spin state of the chain. When the water molecule is placed tangentially at the positions of protonation (B_2_T, B_3_T and P_1_T, P_3_T), the direction of the transfer is from the chain to the proximate chloride ion. The charges of the water molecule and of the distant counterion are unaffected. The tangential placement of water at a non-protonated nitrogen fragment (B_1_T and P_2_T) invokes a transfer in the reverse direction - the water donates electron density to the chain. The counterions are spectators in these complexes.

The vertical bipolaronic systems feature identical redistribution of charge – from the chain to water; an exception is only the terminal case (B_4_V) where the chain and a chloride ion donate electron density to water. However, the direction is reverse in the less polar media, where B_4_V behaves as a tangential system with water far from the protonated imine nitrogens.

In the vertical polaronic systems, when water is at the protonated sites the charge exchange is between water and the closest counterion while at the non-protonated sites it is between the water and the chain. Naturally, the shift of water to a tangential position upon optimization of P_4_V in less polar environment makes them similar to P_2_T. In the least polar medium the direction of transfer in P_2_V and P_3_V is like in P_1_V, i.e., from counterion to water, defined by the spatial propinquity of these components in chloroform.

The most polar medium – water, invokes the strongest polarization of the charged components: the tetramer chain possesses the largest positive charge, the counterions – the largest negative charges compared to the same systems in the rest of the solvents where the

group charges of the separate components decrease slightly. Typically, the tangential structures feature stronger polarization than the vertical ones. The charge of the explicit water appears to be less sensitive to the surrounding polarity – overall, with the decrease of polarity its electron-accepting behavior enhances. The tendencies in the charge distribution between the system components and its variation by complex type are the same in the three solvents used.

Energy of frontier molecular orbitals

The process of protonic acid doping that converts the emeraldine base into the conducting emeraldine salt is accompanied by the emergence of electron accepting orbitals (AMOs) in the band gap that are vacant in the spinless bipolaron (one in a tetramer) and singly occupied for each polaron (two in a tetramer).^{39, 40} An antibonding AMO* corresponds to each bonding AMO. Electronic transitions involving the frontier molecular orbitals – HOMO, AMOs, LUMO, are of paramount importance for the optical characteristics of ES; the analysis of these orbitals reveals the presence/absence of charge transfer upon excitation. Therefore, these orbitals are primarily considered in the evaluation of the stabilizing/destabilizing effect of environment polarity (Fig. 3, Tables S11, S12).

Fig. 3. Energy (eV) of the frontier molecular orbitals of illustrative tangential bipolaronic (left) and polaronic (right) complexes, computed with B3LYP-D3/6-31G*/PCM in water, acetone, and chloroform.

Overall, the sensitivity of the frontier molecular orbitals to the solvent polarity is analogous for both the spin inactive and spin active forms. The decrease of solvent dielectric permittivity from water to acetone results essentially in down-shift of the energy of LUMO and AMOs and upshift of HOMO of each system. Upon decrease of solvent polarity, in bipolaronic systems the antibonding MOs are negligibly stabilized by identical decrement while the bonding ones undergo more substantial changes and draw nearer. In the polaronic systems the trends are similar but more pronounced – the shift of the orbitals is of the order of $\sim 0.09 \div 0.13$ eV; LUMO and AMO1*, as well as HOMO and AMO1 become quasidegenerate.

Conclusions

The interaction of a water molecule with the hydrophilic centers of emeraldine salt – the conducting form of polyaniline, is modelled quantum chemically. Two series of non-covalent complexes that contain a fully protonated tetrameric chain in bipolaronic or polaronic configuration, two chloride anions, and an explicit water molecule are considered. Two types of the explicit water alignments – tangential or vertical to each of the nitrogens along the chain, are simulated. The environment of these complexes – water, acetone, or chloroform, is modeled as an implicit polarized continuum. The B3LYP-D3/6-31G*/PCM computational protocol is employed. The influence of the environment polarity on the complexes characteristics is discussed.

After energy minimization of the *tangential* non-covalent complexes, water retains its initial orientation with respect to the chain. These complexes are characterized by a strong water-chain coupling realized by $\text{H}_2\text{O}:\dots\text{H-N}$ hydrogen bonds. When the chloride counterion is spatially close, the water molecule participates as a proton-donor in a second strong hydrogen bond. The computed interaction energies indicate the same strength of water coupling to each of the charged components.

For most of the *vertical* complexes weak or no coupling between water and the modelled emeraldine salt is typical, which allows larger mobility of the water molecule. The latter changes its initial position and is situated above the neighboring ring or just moves closer to the nearby counterion striving to interact with it. According to the interaction energies, the strength of water-counterion coupling is similar to this in the tangential systems.

Although the interaction is realized by hydrogen bonds, the computed energies indicate that the strongest coupling force is the electrostatic attraction between the positively charged chain and the negatively charged counterions.

The formation of hydrogen bonds within the complexes results in a small charge transfer between the fragments of the system. The two types of water topology define difference in the charge redistribution between the components. In most of the structures the water molecule donates electron density to the oligomer chain and acquires a small positive charge while the tetramer reduces slightly its total charge. There are examples (mainly among the polaronic systems) where the negative total charge outlines water as an acceptor of electron density. Tangential water at any protonated fragment mediates the charge transfer between the tetramer and the closest counterion, the water remaining neutral. In the vertical bipolaronic models only water-to-chain electron transfer is registered, while in some of the polaronic ones the redistribution includes also the proximate counterion.

There is no preferred position along the tetramer for interaction with water. The chain multiplicity and the configuration of the counterions are not formative for the system specifics. The tangential water placement is energetically more favorable than the vertical one.

The structure of the non-covalent complexes and the molecular characteristics of interest are basically identical in water and in acetone. Additional reduction of the environment polarity in chloroform causes a minor shortening of the intermolecular distances and a slight decrease of the total charges of the system components. The structural and energetic similarity of the systems in water and acetone allow the conclusion that the doped emeraldine salt complex with water is more stable in solvents of large or medium dielectric permittivity.

Next step of the study will focus on the effect of the amount of absorbed water on the characteristics of the complexes.

Supporting Information

The following supporting information is available: Fig. S1: Initial and optimized geometries in implicit water; Fig. S2: Optimized geometries in implicit acetone; Fig. S3: Optimized geometries in implicit chloroform; Fig. S4: Alternative initial and optimized geometry; Fig. S5: A sketch with notations of the various fragments for the counterpoise calculations from which the interaction energy components are estimated; Table S1: Characteristic distances in acetone; Table S2: Characteristic distances in chloroform; Table S3: Dipole moments of bipolaronic complexes; Table S4: Dipole moments of polaronic complexes; Table S5: Energy splitting between bipolaronic and polaronic systems; Table S6: Interaction energies in acetone; Table S7: Interaction energies in chloroform; Table S8: Interaction energies in the three solvents taking into account the three-body contribution; Table S9: NBO charges in acetone; Table S10: NBO charges in chloroform; Table S11: Frontier MOs energies of the bipolaronic structures; Table S12: Frontier MOs energies of the polaronic structures.

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TOC Graphic

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