

Theoretical and computational characterization of dilute ionic solutions under the effects of external electric field.

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The rapid technological advances in electronics and computing that occurred over the last half century are based on the progressive miniaturization of the components involved [1]. This is particularly true speaking about computers' memories where the last goal is to obtain smaller and smaller calculators but, at the same time, more and more powerful ones. Structures of dimension in the range 1-100 nm are of great interest for possible applications; in fact they allow to realize better and smaller miniaturized components. In order to obtain these products the “top-down” approach, that means to work macroscopic materials with special techniques, is generally used. However, this process will soon reach a physical limit; with the lithographic techniques, for example, it can't get down a size smaller than the working light wavelength. In order to obtain an even smaller structure it is necessary to use the so called “bottom-up” approach that is actually real engineering at the molecular level, as shown in Figure 1.

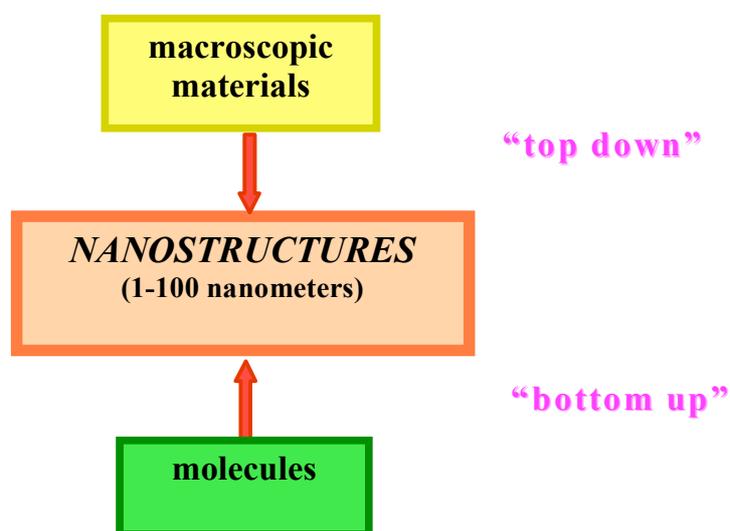


Figura 1

A main goal of "supramolecular chemistry", is to build devices and machines at molecular level, that can perform useful functions [2].

A molecular device, as shown in Figure 2, is an ordered assembly of molecular components (supramolecular structure) that is able to carry out a complex function resulting from the cooperation of simple acts performed by each

component.

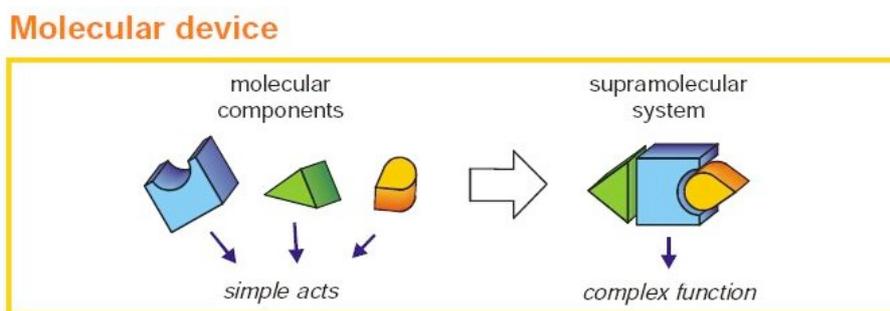


Figure 2.

These nanoscopic devices will take advantage of the greatest possible degree of miniaturization with benefits such as low cost of manufacture, low energy requirements and high speed of operation.

Our research group has completed a theoretical-computational study on the organic molecule, π -conjugated oligo(phenyleneethynylene) systems (OPE), that could be inserted into these molecular devices [3,4,5]. By means of molecular dynamics (MD) and quantum mechanics (QM) calculations, it was possible to describe in details the electric field induced intramolecular charge transfer in two π -conjugated oligomers (OPE1 e OPE2, Figure 3).

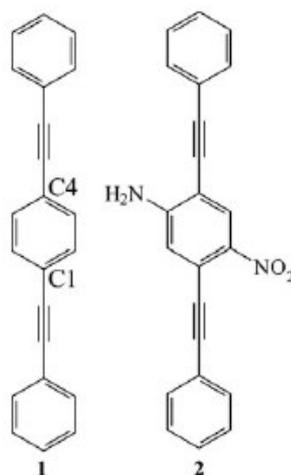


Figure 3. Schematic view of OPE1 and OPE2

These two molecular systems, in an external homogenous electric field, show a relevant relationship between molecular conformation and conductivity. The electric field causes the molecular switching between two structures, the one more conductive than the other.

Aim of the present study is to describe, using molecular dynamics (MD) simulations and the quasi-Gaussian entropy (QGE) theory, the thermodynamics of dilute ionic solutions under the effects of an external electric field. We took into account the sodium/water solution as a model system because it is largely used as a benchmark in thermodynamic computational studies [6,7].

Classical Molecular Dynamics is a computational technique that allows to study, through computer simulations, the time evolution of models of molecular systems by solving the Newton equation of motion. Two different sets of MD simulations were performed. Each set was simulated at eight different temperature in the range (280–1000K) and at three different external electric fields (1–3–5 V/nm) [10,11]. In the first set we simulated a cubic box of 256 simple point charge (SPC) water molecules, at 55.32 mol/l. In the second set we simulated the same SPC box, adding a single sodium ion. All the simulations were performed using the GROMACS software package modified to use the isokinetic temperature coupling. For all the simulations the number of steps was 3000000 with three different time step: 2 fs for simulations in the temperature range 280–370K, 1 fs in the temperature range 420–800K and 0.5 fs at T=1000K, respectively. Hence the corresponding simulation time lengths were about 6, 3 and 1.5 ns. Thermodynamic properties were calculated by the use of the quasi-Gaussian entropy theory (QGE). QGE, described elsewhere [8,9], allows the calculation of thermodynamic properties by means of the potential energy fluctuations.

In this methodology the basic statistical mechanical relations are rewritten in terms of the distribution of the fluctuations of a macroscopic property instead of the partition function. In fact, for each statistical mechanical ensemble it is possible to define a proper reference state such that the free energy difference between the actual condition and the reference one can be expressed exactly in terms of the moment generating function, defined by the distribution of a macroscopic fluctuation. Such an approach has two main advantages. First, the thermodynamics of the system is typically modeled via the fluctuation pattern of a rapidly relaxing mechanical property (e.g. the potential energy).

Moreover, because the QGE models are largely analytical, once obtained the model moment generating function via a few thermodynamic state point simulations, the complete thermodynamics as a function of a thermodynamic state variable is achieved. The Helmholtz free energy of a system at fixed volume, temperature and number of molecules is:

$$A = -kT \ln Q$$

where Q is the overall partition function. For all the systems, we can define a reference state at the same temperature and density, but without inter and intramolecular potential energy:

$$A_{\text{ref}} = -kT \ln Q_{\text{ref}}$$

Therefore, the excess Helmholtz free energy is

$$A' = A - A_{\text{ref}} = -kT \ln (Q/Q_{\text{ref}})/N$$

$$= -kT \ln \langle e^{-\beta U'} \rangle_{\text{ref}} - kT \ln \varepsilon = kT \ln \langle e^{\beta U'} \rangle - kT \ln \varepsilon$$

where ε is the fraction of the available configurational space. The entropic term due to a possible confinement of the system in configurational space, $k \ln \varepsilon$, is usually associated with hard-body excluded volume. The ensemble averages, as shown in the previous equation, can also be expressed as:

$$\begin{aligned} \langle e^{-\beta U'} \rangle_{\text{ref}} &= \int \rho_{\text{ref}}(U') e^{-\beta U'} dU' \\ \langle e^{\beta U'} \rangle &= \int \rho(U') e^{\beta U'} dU' \end{aligned}$$

where $\rho_{\text{ref}}(U')$, $\rho(U')$ are the probability distribution functions of the excess energy U' in the reference and actual conditions, respectively, for the elementary system. The use of ρ_{ref} or ρ is fully equivalent and, for a given model distribution, they provide identical results.

The Gamma distribution [9], one of the simplest distribution, yields a fully physically acceptable theoretical model (Gamma state) providing an excellent description of the fluid state thermodynamics over a wide range temperature and density, including solute-solvent systems. We can rewrite the excess free energy as

$$A'(T) = n_s a'_s + a'$$

where a'_s is the partial molecular excess (Helmholtz) free energy of the solvent and clearly a' is the partial molecular excess (Helmholtz) free energy of the solute. Assuming that A' can be well modeled by a single Gamma state, we can write

$$\begin{aligned} U' &= U'_0 + (T-T_0) c'_{v0} T_0 / T (1-\delta_0) + \delta_0 T_0 \\ A' &= U'_0 - T_0 C'_{v0} \Lambda(T) - kT \ln \varepsilon \\ \Lambda(T) &= 1/\delta_0 + T/T_0 \delta_0^2 \ln \{1-\delta(T)\} \\ \delta(T) &= T_0 \delta_0 / T (1-\delta_0) + T_0 \delta_0 \end{aligned}$$

with $U'_0 = U'(T_0)$ and $C'_{v0} = C'_v(T_0)$ the excess internal energy and heat capacity of the elementary system at the reference temperature T_0 . δ_0 is a dimensionless intensive property independent of the temperature, that in our case (high dilution) is determined by the solvent. Assuming a Gamma state behavior for the solute-solvent system as well of the pure solvent one, from the previous equations we can obtain the solute partial molecular properties via the excess chemical potential:

$$\mu' = \Delta A' = u'_0 - c'_{v0} T_0 \Lambda(T) - kT \ln \varepsilon + p'v$$

where u'_0 , c'_{v0} and $\ln \varepsilon$ correspond to the partial molecular excess internal energy and heat capacity, evaluated at the reference temperature T_0 , $-kT \ln \varepsilon$ is the partial molecular excess free energy due to the confinement, p' is the excess pressure and v the solute partial molecular volume. Finally $\Delta A'$ is the change of the excess free energy between the solute-solvent and the pure solvent systems. Note that the excess free energies of the solute-solvent system as well as of the pure solvent one, were obtained by fitting the average excess (potential) in temperature, provided by the simulations, with the corresponding Gamma state models.

We parametrized our theoretical models, using only the average potential energy (excess internal energy) and pure solvent pressure in the whole temperature range, i.e., by fitting these values with the corresponding theoretical models. The partial molecular properties of the solute are obtained, according to the theory, via $\mu' = \Delta A'$.

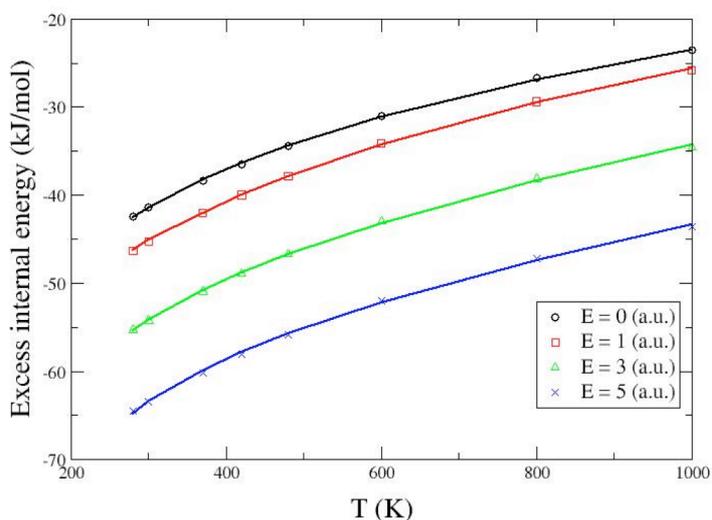


Figure 4. Excess internal energy of pure SPC water at different external electric field intensity as a function of temperature. Symbols represent the values obtained by simulation; the continuous lines are the values obtained by the QGE theory.

In Figure 4 The “experimental” (i.e. obtained by simulations) excess internal

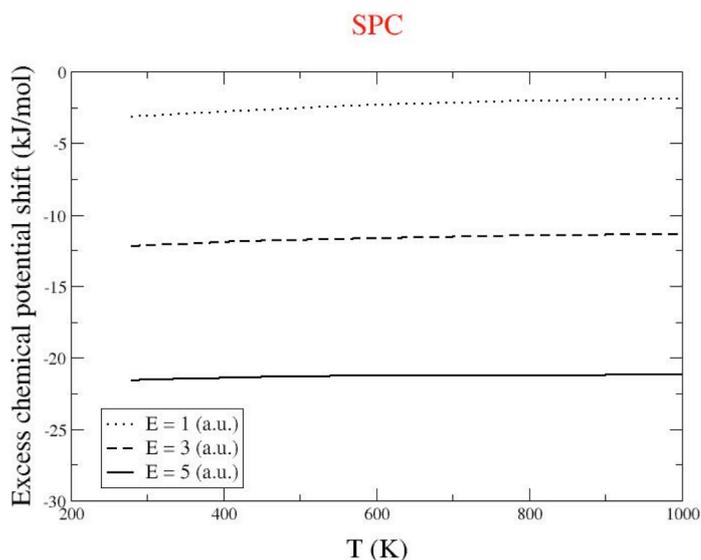


Figure 5. Excess chemical potential shift of pure SPC water as a function of temperature. Solid line: values obtained applying an electric field of intensity 5 a.u.; dashed line: values obtained applying an electric field of intensity 3 a.u.; dotted line: values obtained applying an electric field of intensity 1 a.u.

energy values and the values predicted by the QGE theory are shown for the pure SPC system at different external electric field values. It is important to note that the excess internal energy values decrease at low temperature and by increasing the electric field intensity.

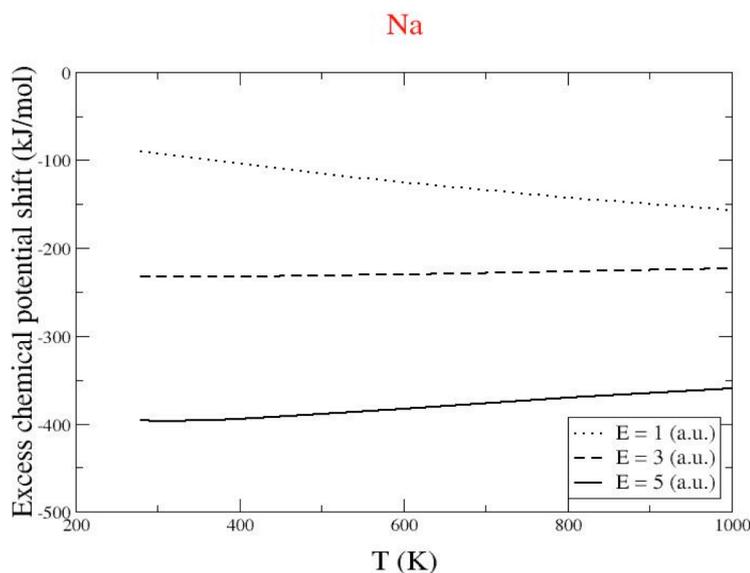


Figure 6. Excess chemical potential shift of sodium ion as a function of temperature. Solid line: values obtained applying an electric field of intensity 5 a.u.; dashed line: values obtained applying an electric field of intensity 3 a.u.; dotted line: values obtained applying an electric field of intensity 1 a.u.

Figure 5 and 6 show the excess chemical potential of pure SPC and the excess chemical potential of sodium ion respectively at different electric field intensity. It can be noted the decrease of the chemical potential upon increasing the electric field intensity. As the figures show, the effect of the external electric field results in a stabilization of the solvent-solute system from a thermodynamic point of view.

Figure 7 shows the partial molar internal energy variation $\Delta u'_0$ as a function of the external electric field intensity, both of pure water and of the system water+sodium at the reference temperature $T=300\text{K}$. It is important to note that, in the case of pure water, the values of the partial molar internal energy remain constant when increasing the intensity of the external electric field, while in the case of water+sodium it is evident a strong variation.

Figure 8 shows the partial molar heat capacity variation $\Delta c'_{v0}$ as a function of the external electric field intensity, both of pure water and of the system water+sodium at the reference temperature $T=300\text{K}$. As in the previous figure, also here the partial molar heat capacity of pure SPC remains constant; while the system containing the sodium ion shows a different behavior in the presence of the external electric field. It can be observed an initial decreasing of the values of partial molar heat capacity at “weak” electric fields, while as the electric field becomes stronger the values of partial molar heat capacity increase.

We can conclude that, under the effect of “weak” electric fields, the solubility of the sodium ion in water increases, while under the effect “medium” electric fields,

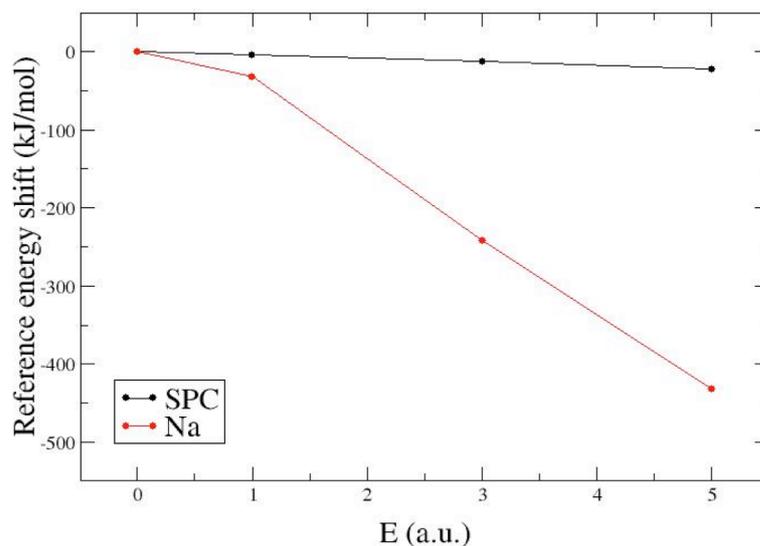


Figure 7. Partial molar internal energy change as a function of different electric field intensities. Black line: QGE model of SPC; red line: QGE model of Na in the SPC box. Reference is $T_0=300$ K.

the solubility of the sodium ion in water decreases.

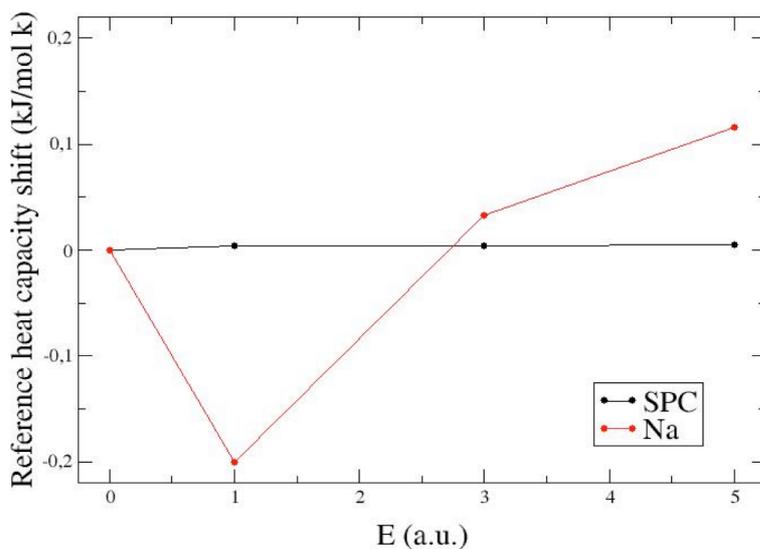


Figure 8. Partial molar heat capacity change as a function of different electric field intensity. Black line: QGE model of SPC; red line: QGE model of Na in the SPC box. Reference is $T_0=300$ K.

This behavior can be attributed to the different polarization of water in the presence of the external electric field. In the absence of electric fields, water molecules arrange themselves around the sodium ion minimizing the electrostatic interaction. The application of a “weak” electric field does not still change the position of the water molecules; but when the intensity of the field increases the

arrangement of water molecules changes. Some of the water dipoles will be oriented along the direction of the external electric field, while the others will be oriented along the lines of force of the electric field generated by the sodium ion. In this report it is shown that the combined use of the QGE theory with MD simulations can provide the whole thermodynamics of a solvent-solute system, including all the partial molar properties.

Starting from the theoretical and computational characterization of dilute ionic solutions under the effect of an external electric field, the present research project aimed to investigate particular molecular systems which could be used to design electronic devices of nanoscopic dimension. According to this purpose, the next step of this work will be to simulate the effect of different electric fields on a system containing an organic molecule as solute.

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