Doctoral Dissertation Summary

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Ionic liquids and ionic liquids-solvent mixtures have attracted scientific interest and become the research focus as solvents in the green chemistry field and in surface science and physical chemistry due to their remarkable properties and features such as wide electrochemical and thermal stability, low vapor pressure, and the ability to mix them in order to tune specific properties. One of the most important applications of ILs is in the development and design of energy storage devices such as fuel cells, batteries, and supercapacitors, where ILs are usually in contact or confined by porous materials. Nevertheless, thermodynamic and structural properties of ILs/IL- mixtures near charged surfaces are not sufficiently understood. Moreover, these systems in the vicinity of their phase transformations exhibit some remarkable features, yet there is no theory able to describe the phase behavior of confined ionic liquids correctly. These difficulties in theoretical modeling are due to inhomogeneities and the interplay of entropic effects, dispersion, and long-range interactions.

This thesis is devoted to the theoretical description of ILs-solvent mixtures close to demixing. We have developed a mean-field model suitable for the IL-solvent mixtures confined by selective electrodes to fulfill this purpose. We have taken into account electrostatic forces, short-range dispersion interactions, and entropic effects in which we have implemented two approximations for describing excluded volume interactions, namely Carnahan-Starling and lattice-gas. Additionally, we have assumed selective electrodes within the parameter called *ionophilicity* that accounts for the surface's preference to ions or solvent. Thus, we have derived a grand-potential functional and minimized it to obtain the Euler-Lagrange (EL) equations for the excess density of ions and the charge density profiles. Then, we have proposed analytical and numerical approaches to solve the EL equations and found that the comparison between the analytical and numerical results is just valid at low voltages. Therefore, to study a wide range of voltages, we considered numerical results for further analysis.

We consider two cases. In the first case, the ILs-solvent mixture is in contact with a single electrode, and we demonstrate that, besides the well-known camel and bell-shaped capacitance, there is a *bird-shaped* capacitance that exhibits three peaks as a function of voltage, which emerges due to the proximity to demixing. Additionally, we find that although the camel-shaped capacitance is a signature of dilute electrolytes, such a shape can appear at high IL densities provided the electrode has a strong preference for solvent. Regarding the temperature effects, we find that the capacitance increases as the system's

temperature is lowered to demixing, and an enhancement of the energy storage accompanies such an increase.

In the second case, we study the IL-solvent mixture confined by a slit-shaped nanopore wider than a few ion diameters and reveal that such systems can undergo a capillary ionization transition where the pores spontaneously ionize or de-ionize upon infinitesimal changes of temperature, slit width, or voltage. We show that capillary ionization could be voltage-induced, and interestingly, such transition is followed by a subsequent de-ionization as the voltage increases. We find that ionization transitions produce sharp jumps in the accumulated charge and stored energy, finding practical applications in energy storage and heat-to-energy conversion.

Finally, we perform molecular dynamics simulations where we investigate the concentration fluctuations in a simple model of electrolyte, that is, two charged Lennard-Jones spheres in a solution of an uncharged Lennard-Jones liquid, confined between electrodes formed by parallel graphene layers. Using two approaches: constant potential and extensive constant charge simulations, the effect of the proximity to the demixing transition on the electric double layers is analyzed. In agreement with our previous theoretical findings, we find there is a considerable enhancement of the capacitance when approaching the demixing transition for dilute ionic solutions. This enhancement tends to disappear when the ionic concentration is increased. We also find that the "bird-like" capacitance, predicted by our theory, appears when Lennard-Jones interactions are taken into account and may lead to phase separation.