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What is a Molecule?

By coarse-graining length- and time scales are defined that are appropriate for different fields in science as elementary particles, atoms, molecules, macroscopic physics, biology, sociology and so on. Molecules can be regarded as a certain region in the coarse-graining scales of matter. From the theoretical point of view the exact solutions for macroscopic systems would be given by the quantum mechanical solutions made up by electrons and nuclei. Usually we are interested only in certain solutions, which contain particular groups of atoms, the molecules we are interested in. Describing a macroscopic system as a system of interacting molecules is a most useful approximation. Using this approximation, the Schrödinger equation is solved for only one molecule and statistical mechanics is applied to take into account intermolecular interactions.

We review some historical aspects and discuss the statistical mechanical problem involved, when the intermolecular interactions become as strong as chemical bonds. This problem becomes particular important in ionic solutions, where ion pairs and higher associates are formed. The ion-association is a consequence of the strength of the Coulomb interactions at contact, which is of the order of 300 kJ/mol, thus with 100 kT much larger then the thermal energy and almost as strong as a typical chemical bond.

Molecules may be defined according to the Born-Oppenheimer approximation as groups of atoms with configurations of the nuclei that move on a much larger time scale than the electrons. On the other side, as pointed out by G. Hertz, the intramolecular motions are restricted. Intra molecular motions may be regarded as fluctuations about some averaged position on a macroscopic time scale.

If the strength of intermolecular interactions becomes comparable to that of chemical bonds, it is questionable if the distinction between chemical bonds and intermolecular interactions is meaningful. Two approaches are common in describe such system.

- In the "chemical picture" associates are treated as molecules in chemical equilibrium with other molecules.
- In the "physical picture" strong interactions are treated like other intermolecular interactions.

It is not clear by now if the two pictures are equivalent. If not, the predictions coming out from theoretical calculations may be rather different.

The partition functions for the two approaches and possible definitions for the association constants are discussed. The Bjerrum association constant involves the partition function of an ion pair and introduces an upper bound for the separation of the particles. Ebeling gives a formulation for the association constant that ensures agreement with the second virial coefficient obtained by evaluating the Helmholtz free energy by the cluster expansion for the physical model. As discussed by Fisher und Zuckerman, both approaches lead to thermodynamic inconsistencies. However, the definition proposed by the authors yield finite pair concentrations at high temperatures, while one would expect vanishing pair-concentrations.

By now, the most successful theory for describing the phase-separation and conductivity of ionic fluids in the near-critical region are based on the "chemical model". The theory is a generalization of the Debye–Hückel theory for electrolytes, which includes the formation of ion-pairs and takes into account mutual interactions of the ion pairs and ions. The numerical differences between the Ebeling- and the Bjerrum expressions for the association constant are negligible. The theory gives a good representation for the concentration dependence of the conductivity and of the phase diagrams, which, agree with simulation results based on the "physical picture". In the low density - low temperature region, where the critical point is located, both approaches appear to apply well. Quite likely, the low order cluster integrals evaluated for the Ansatz of a chemical equilibrium between ions and ion pairs, are reasonable approximations to high order cluster integrals corresponding to the "physical picture", which are much more difficult to evaluate.

Figures
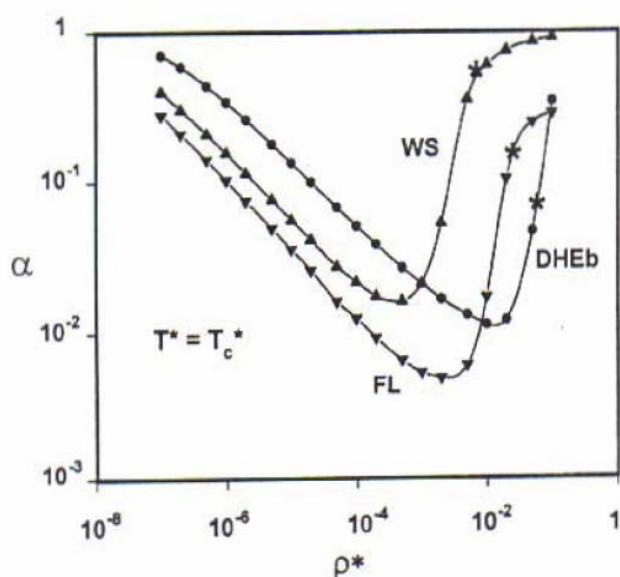
Degree of dissociation as calculated for the chemical picture. The theory DHEb (DebyeHückel-Ebeling) is the Debye Hückel theory and includes ionic association, FL (Fisher, Levin) includes also ion/ion-pair interactions, and WS (Weiss, Schröer) includes also ion-pair / ion-pair interactions. At low densities the degree of dissociation decreases with increasing concentration because of ion-pair formation;, at higher densities, when approaching the critical density (ξ) the ion-pairs redissociate.
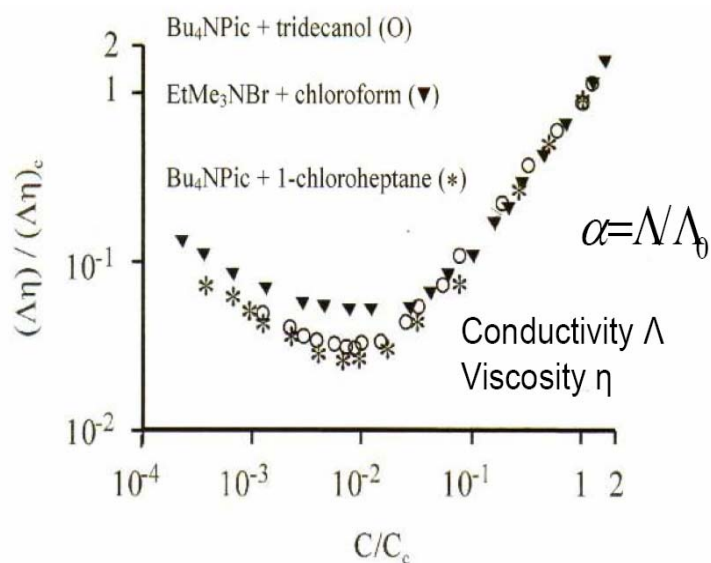
The Walden product corrects the conductivity for the influence of the viscosity and therefore is a better measure for the degree of dissociation α than the Arrhenius ratio of the molar conductivity to the figure at infinite dilution. The Walden product shows corresponding state behavior. The concentration dependence is in qualitative agreement with that estimated by theories.
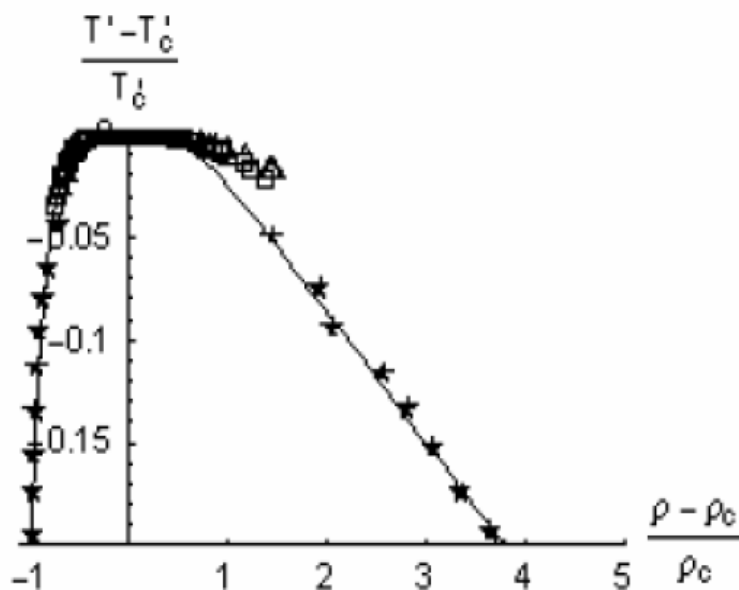
Corresponding state phase-diagram for the experimental coexistence curves for phosphonium ionic liquids (8∀ and the simulation results (ξ) for the model fluid of charged hard spheres.

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