Institute Colloquium

Wednesday, 9 March 2016 4:00 p.m. Fermion

Speaker:

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Title:

Dielectric spectroscopy - a versatile tool in solutions chemistry

Abstract:

The key issue of solution chemistry is to understand the delicate balance between solvent-solvent, solute-solvent and solute-solute interactions as it governs solvation phenomena and solute aggregation processes and thus determines the macroscopic properties of solutions. This requires molecular level information on the structure and dynamics of solutions as well as accurate thermodynamic and transport data to benchmark computer simulations and theoretical calculations. Accordingly, a plethora of powerful techniques are used now in solution chemistry [1]. Spectroscopic techniques, such as NMR, Raman or time-resolved infrared spectroscopy, have provided valuable information on solvation and ion-binding phenomena [2]. However, these powerful methods are generally only sensitive to next-neighbour interactions and/or the reorientation dynamics of individual molecules so that mesoscopic structural correlations, including already solvent-shared ion pairs, or cooperative dynamical processes elude detailed investigation. Here dielectric relaxation spectroscopy (DRS) can step in. DRS probes fluctuations of the macroscopic dipole moment and thus yields information on the cooperative and molecular dynamics of the sample on a timescale ranging in principle from ~10-13 to 103 s [3]. Processes relevant in solution chemistry typically are in the pico- to nanosecond range and encompass the reorientation and libration of permanent dipole moments (e.g. solvent molecules, ion pairs), intermolecular vibrations (e.g. of anions and cations relative to each other), and motions of counterions bound to micelles

or polyions. In this contribution a short introduction into the principles of dielectric relaxation spectroscopy will be given before proceeding to examples from our laboratory on applications of this technique in solution chemistry. The focus will be on the solvation and ion binding of electrolytes and non-electrolytes in aqueous solutions, highlighting the different behavior of hydrophilic and hydrophobic solutes. The merits of DRS for the investigation of counter-ion condensation on charged micelles will be briefly discussed, as well as its use for studying the dynamics of ionic liquids.

References:

1. J.O'M. Bockris and A.K.N. Reddy, Modern Electrochemistry 1, 2nd ed., Plenum, New York (1998).
2. H.J. Bakker, Chem. Rev., 2008 (108) 1456-1473.
3. R. Buchner and G. Hefter, Phys. Chem. Chem. Phys., 2009 (11), 8984-8999.

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