DIELECTRIC SPECTROSCOPY OF SOLUTIONS

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Abstract: This contribution gives a short introduction into the basic principles of dielectric spectroscopy and its application in solution chemistry. Exemplified by recent results it is shown that precise complex permittivity spectra obtained by the use of time domain and frequency domain methods in the mega- to gigahertz range yield specific information on solvent dynamics as well as on ion-solvation and ion-association phenomena that is not readily accessible with other techniques.

1. Introduction

Solvation and association of ions are the dominating features of aqueous and nonaqueous electrolyte solutions and determine their physicochemical properties. The importance of these phenomena in many fields, from geochemistry via biological processes to technical applications, leads to the development of solution chemistry as the interdisciplinary science between chemistry, physics, biology and chemical engineering devoted to the investigation of ion-solvent and ion-ion interactions [1-3]. Although important new insights were also coming from thermodynamics, transport studies, various spectroscopies and theory, it is probably fair to say that in the last decade the major impetus for our current understanding of electrolyte structure came from the rapid development of scattering methods and computer simulations [4,5].

However, many open questions remain. First of all, one has to note that x-ray and neutron scattering, but also (at least up to now) many simulation studies, give an essentially static picture of the solutions. The
coordination numbers (CN) determined by these techniques often differ considerably from the so-called primary solvation numbers (PSO [1]) determined from thermodynamic or transport properties. This is understandable because CN are essentially obtained by counting the number of solvent molecules within a certain distance from the ion, whereas PSO reflect the balance between ion-solvent and solvent-solvent interactions and thus monitor the 'fluid' character of the solutions. Of course, the difference between CN and PSO is not a mere flaw of one or the other approach, but significant information for the understanding of solutions and in the next decade a major task of solution chemistry will be to find a coherent description which accomodates CN and PSO and thus allows a prediction of the concentration and temperature dependence of thermodynamic and transport properties. The second focus will be on chemical speciation. The investigation of complex formation to e.g. ion pairs has always been a major field of solution chemistry, but due to experimental problems was usually restricted to association constants \( K_A \geq 20 \). However, equilibria involving weak complexes are widespread, ranging from the importance of sodium oxalate ion pairs on kidney stones [6] to the Bayer process for the recovery of purified \( \text{Al(OH)}_3 \) from bauxitic ores [7,8], and there will be an increasing demand in the determination of the stability constants and the identification of the involved species.

In this review I would like to show what contributions can be expected from dielectric [relaxation] spectroscopy (DRS) on ion solvation and association. After a short introduction to the basic principles of the technique, the major features of the dielectric spectra of electrolyte solutions will be presented. Mainly exemplified with results from recent investigations of aqueous systems, the focus will be on equilibrium properties, that is effective solvation numbers and ion-pair concentrations. But also some of the accessible dynamic information will be highlighted. For a comprehensive review of dielectric relaxation studies of solutions the reader is referred to Ref. [9]; an encompassing compilation of literature data in this field is available with Ref. [10].

2. Principles of Dielectric Spectroscopy

DRS monitors the response of a sample, its polarization \( \vec{P}(t) \), towards an applied time-dependent electric field, \( \vec{E}(t) \), as a function of time, \( t \), or (alternatively) the dependence of \( \vec{P} \) on the frequency, \( \nu \), of harmonic fields. The technique is able to probe dynamical processes on a time scale ranging from tens of femtoseconds to hours and is therefore a widely used tool in material science to characterize solids [11], polymers [12],