Our Research: Speciation, Structure and Dynamics in Complex Liquids

The group mainly uses dielectric relaxation spectroscopy, accompanied by conductivity and viscosity measurements, to probe transport properties, structure and cooperative dynamics of complex liquids. Our facilities are supplemented by external cooperation partners specializing in

- Terahertz spectroscopy (M. Walther, Freiburg, DE)
- Optical Kerr-effect spectroscopy (OKE; K. Wynne & D. Turton, Glasgow, UK)
- Time-resolved IR spectroscopy (H. Bakker, Amsterdam, NL)
- Thermodynamic measurements (G. Hefter, Murdoch, AU)
- Computer simulations (C. Schröder & O. Steinhauser, Vienna, AT)
- Small-angle X-ray scattering (T. Sato, Ueda, JP)

Current topics are

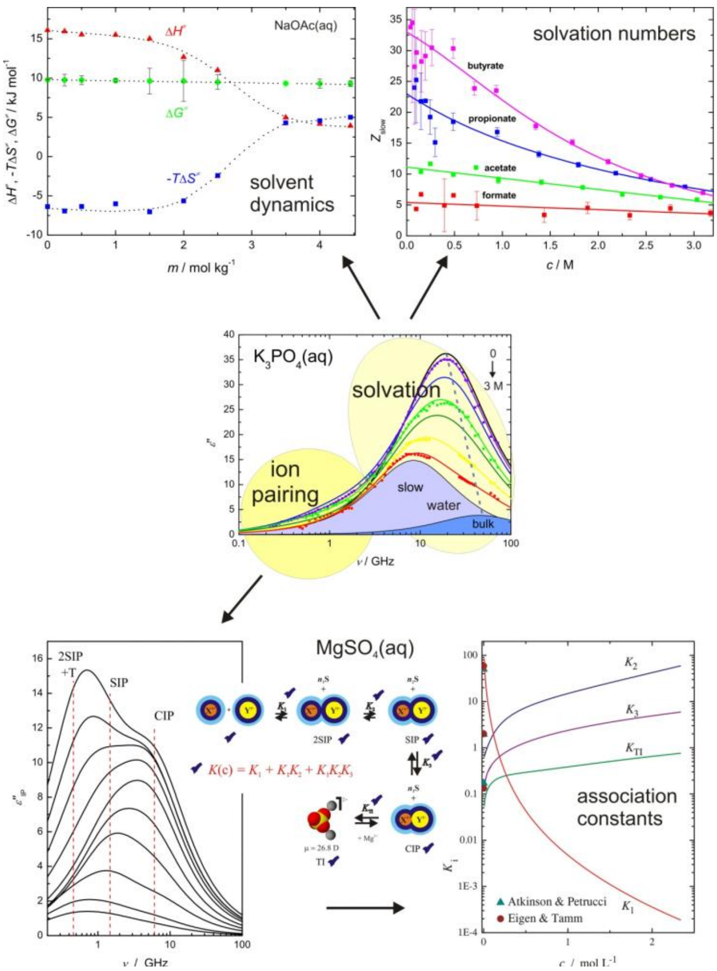
Electrolyte Solutions

Electrolyte solutions are relevant in many areas, ranging from biology and geochemistry to technical applications. We study for aqueous and nonaqueous solutions

- Solute & solvent dynamics ➲ relaxation mechanism, activation parameters
- Solute-solvent interactions ➲ solvation numbers
- Solute-solute interactions ➲ species present, ion-pair concentrations, association constants

We found

- Multi-step ion-pair formation common for strongly associating electrolytes
- Ion-cloud relaxation not negligible for weakly associating electrolytes
- Strongly and weakly bound hydration water can be distinguished
- Bulk solvent dynamics may be affected by solute



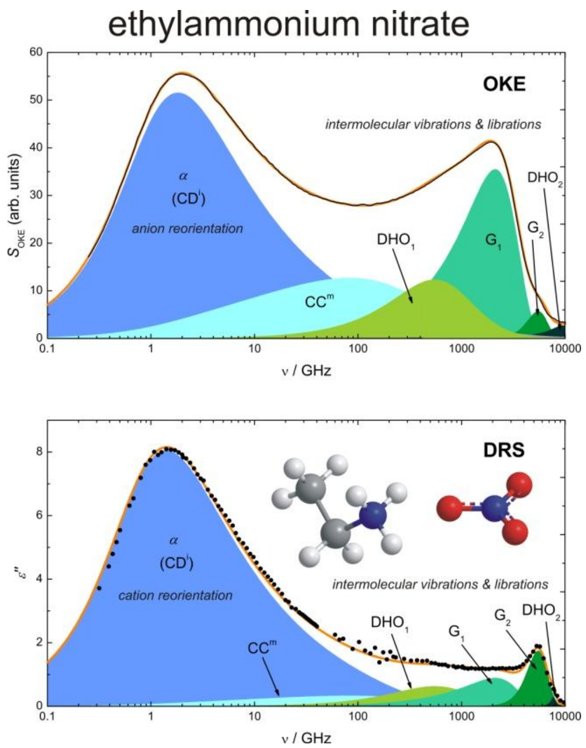
Recent publications:

- A. Eiberweiser and R. Buchner, *Ion-pair or Ion-cloud Relaxation? On the Origin of Small-amplitude Low-frequency Relaxations of Weakly Associating Aqueous Electrolytes*, J. Mol. Liq. DOI: 10.1016/j.molliq.2012.03.025
- H. M. A. Rahman, G. Hefter and R. Buchner, *Hydration of Formate and Acetate Ions by Dielectric Relaxation Spectroscopy*, J. Phys. Chem. B **116** (2012) 314-323. DOI: 10.1021/jp207504d

- A. Płaczek, G. Hefter, H. M. A. Rahman and R. Buchner, *Dielectric Relaxation Study of the Ion Solvation and Association of $NaCF_3SO_3$, $Mg(CF_3SO_3)_2$ and $Ba(ClO_4)_2$ in N,N-Dimethylformamide*, J. Phys. Chem. B **115** (2011) 2234-2242. DOI: 10.1021/jp1116307

Ionic Liquids

Ionic liquids are room-temperature molten salts with many potential applications, either in the pure state or mixed with conventional solvents.

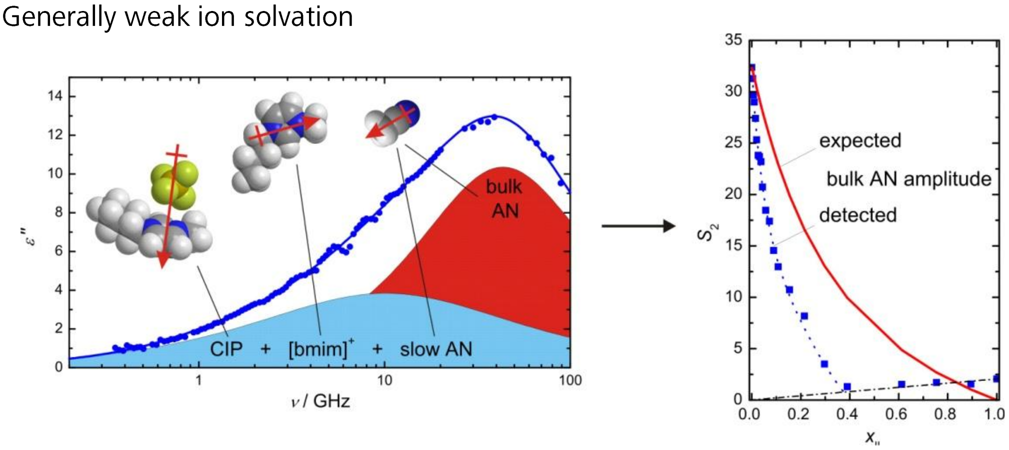


Pure ionic liquids exhibit

- Complicated dynamics extending from a few hundred femtoseconds to several nanoseconds (frequency range ~10 MHz to 10 THz)
- Significant THz-contributions from intermolecular vibrations and librations
- Ion reorientation through large-angle jumps
- Ion caging on nanosecond time-scale
- Aggregate formation for imidazolium ILs

IL+solvent mixtures show

- Smooth transition from electrolyte-solution like to molten-salt like behaviour at IL mole fractions $x_{IL} \approx 0.3$-0.5
- Compared to pure IL, dynamics in molten-salt like region accelerated (solvent "lubricates" IL)
- Solvent-dependent degree of ion pairing at low x_{IL}
- Generally weak ion solvation



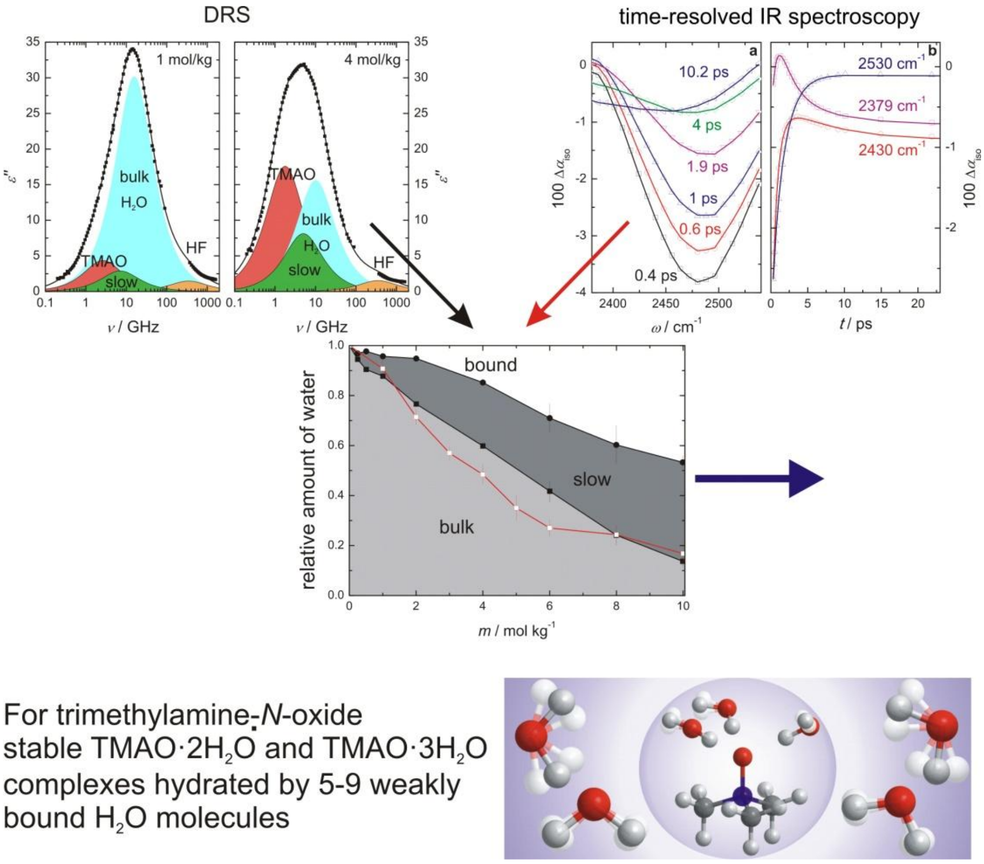
Recent publications:

- J. Hunger, T. Sonnleitner, L. Liu, R. Buchner, M. Bonn, and H. J. Bakker, *Hydrogen-Bond Jump Reorientation Dynamics in a Protic Ionic Liquid*, J. Phys. Chem. Lett. **3** (2012) 3034-3038. DOI: 10.1021/jz301247nH.
- A. Stoppa, J. Hunger, G. Hefter and R. Buchner, *Structure and Dynamics of 1-N-Alkyl-3-N-Methylimidazolium Tetrafluoroborate + Acetonitrile Mixtures*, J. Phys. Chem. B **116** (2012) 7509-7521. DOI: 10.1021/jp302067
- D. A. Turton, T. Sonnleitner, A. Ortner, M. Walther, G. Hefter, K. R. Seddon, S. Stana, N. V. Plechkova, R. Buchner and K. Wynne, *Structure and dynamics in protic ionic liquids: A combined ultrafast optical Kerr-effect (OKE) & dielectric study*, Faraday Discuss. Chem. Soc. **154** (2012) 145-153. DOI: 10.1039/C1FD00054C

Osmolytes

Osmolytes are compounds that counteract osmotic or hydrostatic pressure and stabilize proteins. Thus, they allow organisms to adapt to hostile environments, like highly saline waters. We study

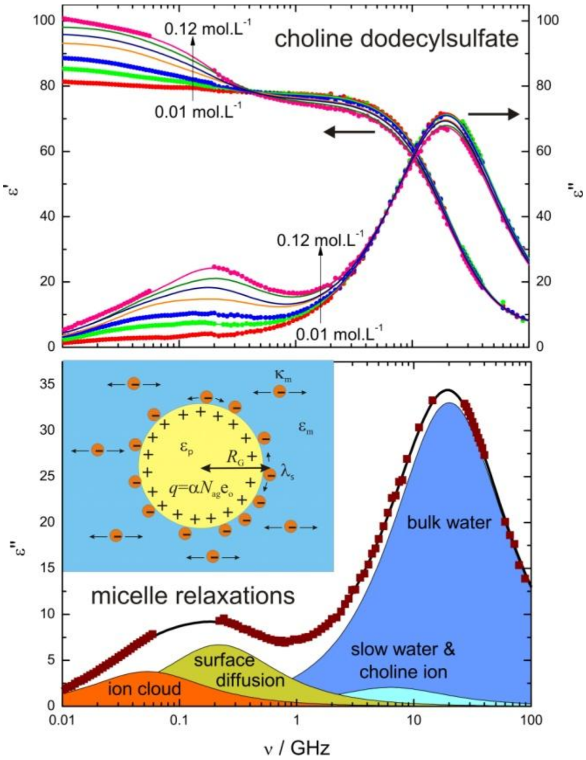
- Osmolyte hydration
- Osmolyte-osmolyte interactions
- The impact of osmolytes on bulk-water structure and dynamics



Recent publications:

- J. Hunger, K.-J. Tielrooij, R. Buchner, M. Bonn and H. Bakker, *Complex Formation in Aqueous Trimethylamine-N-oxide (TMAO) Solutions*, J. Phys. Chem. B **116** (2012) 4783-4795. DOI: 10.1021/jp12542q
- K.-J. Tielrooij, J. Hunger, R. Buchner, M. Bonn and H. Bakker, *Influence of concentration and temperature on the dynamics of water in the hydrophobic hydration shell of Tetramethylurea*, J. Am. Chem. Soc. **132** (2010) 15671-15678. DOI: 10.1021/ja06273w

Micelles, Microemulsions and Polyelectrolytes



Micelles, microemulsions and polyelectrolytes are ubiquitous colloidal systems with properties governed by long-range cooperativity. With DRS we study

- Headgroup hydration of ionic and nonionic surfactants
- Location and mobility of bound counterions
- Phase behavior

Recent publications:

- W. Wachter, G. Trimmel, R. Buchner and O. Glatter, *Dynamics of Water Confined in Self-Assembled Monoglyceride-Water-Oil Phases*, Soft Matter **7** (2011) 1409-1417. DOI: 10.1039/c0sm00681e
- T. Sato, T. Fukasawa, K. Arimaki, O. Glatter and R. Buchner, *Molecular to diffusion dynamics and static structures of aqueous micellar solutions: A SAXS/DLS/DRS study*, J. Mol. Liq. **159** (2011) 76-82. DOI: 10.1016/j.molliq.2010.06.001
- M. Lukšic, R. Buchner, B. Hribar-Lee and V. Vlachy, *Dielectric relaxation spectroscopy of aliphatic ionene bromides and fluorides in water. The role of the polyion's charge density and the nature of counter-ions*, Macromolecules **42** (2009) 4337-4342. DOI: 10.1021/ma900097c