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:

Ionic Liquids

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

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:


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 timescale
- Aggregate formation for imidazolium ILs


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

For trimethylamine-N-oxide stable TMAO·2H₂O and TMAO·3H₂O complexes hydrated by 5-9 weakly bound H₂O molecules

Recent publications:
Recent publications:

- M. Lukšić, R. Buchner, B. Hribar-Lee and V. Vlachy, *Dielectric relaxation spectroscopy of aliphatic ionene bromides and fluorides in water. The role of the polion’s charge density and the nature of counter-ions*, Macromolecules 42 (2009) 4337-4342. DOI: 10.1021/ma900097c