

**THERMOPHYSICAL PROPERTY RESEARCH ON IONIC LIQUIDS AT THE  
ERLANGEN GRADUATE SCHOOL IN ADVANCED OPTICAL TECHNOLOGIES  
(SAOT)**

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**Introduction:** Due to an almost unlimited number of potential combinations of cations and anions, ionic liquids (ILs) can be tailored to a specific application. Yet, for identifying their usefulness, e.g., as solvents, the knowledge about physical and chemical properties is required. The properties of every conceivable IL cannot be obtained by carrying out appropriate measurements, which is a more substantial investment. In this context, it would be helpful to predict the composition of an IL with a desired set of properties. For this, however, knowledge about the origins of the fundamental properties of ILs is necessary resulting in a better understanding of structure-property relationships. Until now, for the design of new ILs with particular characteristics, trial-and-error methods are used. For overcoming this limit, quantitative prediction methods with reasonable certainty must be developed. Yet, all prediction methods can only be as accurate as the experimental data used for the evaluation of their performance.

Although a large number of data including transport properties is available for numerous pure ILs as well as in the meantime also for their mixtures with solvents, one impediment for the progress in the field of ILs is the lack of reliable data. It is fairly common to find differences between published data sets which are more than one order of magnitude larger than the combined uncertainties of the measurements. This situation holds for equilibrium data and is even more pronounced for transport properties.

Present research activities at SAOT- and LTT-Erlangen are aimed to contribute to the structure-property relationships of pure ILs by an accurate and reliable determination of thermophysical properties by dynamic light scattering (DLS) and conventional measurement techniques. Here, thermophysical properties of interest are, e.g., viscosity, surface tension, thermal conductivity, density, and refractive index [1-4]. Furthermore, our activities within the priority program "Ionic Liquids" (DFG – SPP 1191) of the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) should contribute to the characterization of the nature of interactions in IL solvent mixtures from thermophysical property research by DLS [5-8].

**Experimental:** Beside conventional methods, e.g., the vibrating U-tube method, the parallel plate method, and the pendant drop technique, dynamic light scattering (DLS)

from bulk of fluids and its application to fluid surfaces, also called surface light scattering (SLS), are applied for the characterization of ILs and their mixtures with solvents. In the following, only the underlying theory of DLS from bulk fluids and SLS is briefly summarized.

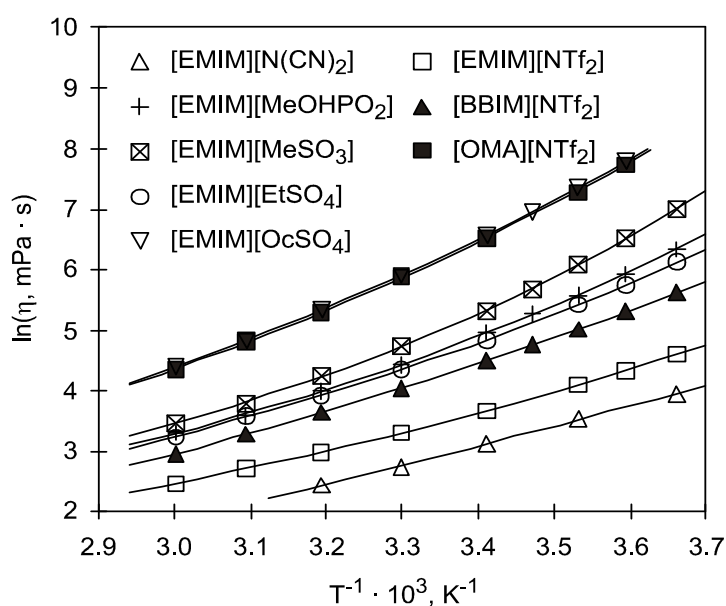
When a fluid sample in macroscopic thermodynamic equilibrium is irradiated by coherent laser light, light scattered from the sample can be observed in all directions. The underlying scattering process is governed by microscopic fluctuations of temperature (or entropy), of pressure, and of species concentration in mixtures. The relaxations of these statistical fluctuations follow the same rules that are valid for the relaxation of macroscopic systems. The decay of temperature fluctuations is governed by the thermal diffusivity. Pressure fluctuations in fluids are moving with the sound speed and their decay is governed by the sound attenuation. In a fluid mixture, the decay of concentration fluctuations is related to mass diffusivities by a more or less complex way, depending on the number of single species. This is represented in the simplest case of a binary fluid mixture by the binary diffusion coefficient. In light scattering experiments, the above-mentioned equalization processes result in a temporal modulation of the scattered light intensity. Information about these processes and hence the thermophysical properties can be derived by a temporal analysis of the scattered light intensity using photon correlation spectroscopy (PCS).

The method of SLS is very similar to that of light scattering from bulk fluids (“conventional” DLS). The major difference relies on the fact that, in SLS, fluctuations are analyzed on the surface of a liquid or, in general, on boundary layers between two different phases. Surface waves, whose energy quanta are referred to as “ripples,” form on interfacial boundary layers as a consequence of thermal molecular motion. For the temporal decay of surface fluctuations, two cases may be distinguished. In the case of large viscosity and/or small surface tension, the amplitude of surface waves is damped exponentially, while in the case of small viscosity and/or large surface tension, the amplitude decays in the form of a damped oscillation. The frequency and damping of surface waves are determined by the viscosity and surface tension. In SLS, scattered light emerging from the interaction between light and the fluctuating surface structure is analyzed. As in “conventional” DLS, this can be done by a temporal analysis of the scattered light intensity using PCS.

**Results and discussion:** A compilation of thermophysical property data obtained until now at SAOT- and LTT-Erlangen for ILs is given. Measurement results are presented for selected thermophysical properties accessible for ILs both by DLS (e.g., thermal diffusivity, mutual diffusivity, viscosity, and surface tension) and conventional techniques (e.g., density, thermal conductivity, and surface tension).

In the following, results for the dynamic viscosity (uncertainty of less than 2% to 3%) of pure ILs investigated by SLS from 273.15 K to 333.15 K are exemplarily discussed. Within experimental uncertainty, the dynamic viscosity can well be represented in form of a Vogel equation. The investigations could point out the influence of the anion on the viscosity of [EMIM]-based ILs and the effect of the cation structure for ILs with the [NTf<sub>2</sub>]-anion. In general, the viscosity of ILs is governed beside the entanglement between the molecules by Coulomb forces like van der Waals interactions and hydrogen bonding. Charge delocalization within the anion weakens intermolecular hydrogen bonding with

the cation, leading to lower viscosities if not overcompensated by van der Waals interactions. For the ILs containing the [EMIM]-cation, the highest viscosity found for [EMIM][OcSO<sub>4</sub>] can be explained with the long side chain of the anion, which increases the contributions to viscosity by entanglement and van der Waals interactions. It is worth mentioning that the ILs [EMIM][MeSO<sub>3</sub>] and [EMIM][MeOHPO<sub>2</sub>] exhibit higher viscosities compared to [EMIM][EtSO<sub>4</sub>]. For the latter, a higher viscosity would be expected, because the ethyl side chain is larger than the methyl side chain, enhancing van der Waals forces. Yet, also the basicity, the strength of the negative charge of the anion, has an effect on the thermophysical properties. In [EMIM]-based ILs, more basic anions lead to tighter ion pairing of the cation with the anion, which also increases intermolecular forces like hydrogen bonding. The [EtSO<sub>4</sub>]-anion exhibits the lowest basicity, followed by the [MeOHPO<sub>2</sub>]- and the [MeSO<sub>3</sub>]-anion, which is in agreement with the order of the viscosity of the three ILs. The IL [EMIM][NTf<sub>2</sub>] shows the lowest viscosity of the [EMIM]-based ILs investigated. This can be explained with the disability of the [NTf<sub>2</sub>]-anion to interact in form of hydrogen bonding and a randomized aggregation of ions caused by very low anionic basicity. Also for the comparison of different ILs containing the [NTf<sub>2</sub>]-anion, [EMIM][NTf<sub>2</sub>] exhibits the lowest viscosity, followed by [BBIM][NTf<sub>2</sub>] and [OMA][NTf<sub>2</sub>]. It is evident that a higher viscosity is caused by an increasing alkyl chain length of the cation.



**Figure 1.** Arrhenius plots of dynamic viscosity  $\eta$  for pure ILs [1,3].

**Conclusions:** During the last five years, at SAOT and LTT Erlangen DLS and conventional techniques were applied for the determination of thermophysical properties of pure ILs and their mixtures with solvents. The experimental results provide not only a reliable database but also allow an insight into the structure-property relationships.

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