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Particle Diffusion Coefficient and Dynamic Viscosity in Non-Ideal Liquid Mixtures by Dynamic Light Scattering

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1. Introduction

Dynamic Light Scattering (DLS) has been successfully applied in the past for the determination of a significant variety of thermophysical properties of transparent fluids [1]. Besides the Brillouin- and Rayleigh-scattering processes, which provide access to the thermal diffusivity, sound attenuation, sound velocity, and to the binary diffusion coefficient, particle scattering can be used for the determination of the tranlational particle diffusion coefficient D_P and thus of the dynamic viscosity of the fluid. DLS is an alternative to conventional viscometers, provided that a stable suspension of seed particles can be formed in the liquid, as it has been achieved in the past for selected pure liquids. In contrast to conventional methods, however, DLS has the advantage of allowing measurements in thermodynamic equilibrium. In this contribution, the possibility of measuring the viscosity via the particle diffusion coefficient of liquid mixtures manifesting strong deviations from ideal mixture behavior will be discussed, based on experimental results for mixtures of ethanol and water at room temperature as well as for more complex systems of current interest.

2. Methodological Principles

If a particle suspension is irradiated with coherent laser light, the intensity of the scattered light fluctuates in time according to the underlying relaxation of microscopic statistical fluctuations in the particle concentration, which grant access to D_P. The analysis of the scattered light is carried out through calculation of the correlation function of the scattered light intensity. For light scattered by a stable suspension of monodisperse, freely diffusing particles, the correlation function takes, in the case of homodyne conditions, the form of an exponential [2]

$$G^{(2)}(\tau) = A + B\exp(-2\tau/\tau_C)\,, \qquad (1)$$

where A and B are experimental constants. The mean lifetime τ_C of the observed fluctuations is related to D_P through

$$D_P = 1/(\tau_C q^2)\,. \qquad (2)$$

The modulus of the scattering vector q in equation (2) is determined both by the laser wavelength in *vacuo* and by the scattering geometry.

For the dense fluid phase in the hydrodynamic regime, the dynamic viscosity can be subsequently calculated from the particle diffusion coefficient with the aid of the Stokes-

Einstein relation according to [3]

$$D_P = k_B T/(3\pi\eta d) \quad (3)$$

with dynamic viscosity η, particle diameter d, Boltzmann's constant k_B, and temperature T.

3. Results

Despite being implemented in the past near ambient conditions over an extended temperature range including investigations of the critical consolute point, DLS has been so far limited either to pure liquids or to mixtures with quasi-ideal mixture behavior [4].

In this contribution, DLS has been implemented for the first time, to the best of our knowledge, for measuring the dynamic viscosity of liquid mixtures which cannot be described *a priori* by a general theoretical model due to the non-ideality of their viscosity behavior. Especially at low temperatures, the viscosity of such mixtures is sensitive to molecular interactions between mixture components, such as hydrogen bonding, molecular associations, charge transfer, dipole-dipole, and dipole-induced dipole interactions [5]. First, as a reference, mixtures of ethanol and water were investigated at room temperature at different compositions and a viscosity maximum was found to exist at a volume fraction of ethanol of about 0.4, which is in agreement with the literature [6] and thus proves the applicability of the technique. Other investigations on more complex systems included mixtures involving ionic liquids, where the viscosity was found to be reduced dramatically by the addition of methanol.

4. Conclusion

The application field of DLS can be extended to the determination of the dynamic viscosity of liquids if the particle diffusion coefficient is measured. The current investigation has proven the applicability of DLS to non-ideal liquid mixtures like ethanol in water, whose viscosity cannot be predicted theoretically due to molecular interactions between the mixture partners. The measurement of dynamic viscosity via the particle diffusion coefficient by DLS can therefore provide valuable information about molecular structures and also assist the construction of theoretical models.

References

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