Simultaneous study of molecular and micelle diffusion in polyol-based microemulsions with CO_2-swollen micelles by dynamic light scattering

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Microemulsions are of interest for many technical applications, *e.g.*, in the form of polyol-based systems with nanometer-sized supercritical carbon dioxide (CO_2)-swollen micelles as a starting point for the production of high-performance insulation foams. In such systems investigated in the present study, dissolved CO_2 as well as CO_2-swollen micelles formed by surfactants diffuse inside the polyol-based continuous phase of the microemulsion. These processes can be described with a molecular and a micelle diffusion coefficient, respectively.

While the determination of molecular diffusion coefficients of gases dissolved in various kinds of liquids by dynamic light scattering (DLS) is well-established at our institute since about five years, we have shown only recently that a proper use of this method also gives access to the translational micelle diffusion coefficient for such systems. In the given technical example, the latter diffusion coefficient is of particular interest for the insulation foam production because it can be used to derive information on the micelle size *via* the Stokes-Einstein relation.

In the present contribution, it is shown for the first time that the simultaneous study of both diffusion processes in microemulsions can be realized successfully by DLS. As the diffusion process of micelles is much slower than that of molecular solutes, the corresponding DLS signals analyzed in the form of intensity correlation functions appear on different time scales and can be separated by an appropriate data evaluation procedure. To determine the correct diffusion coefficient values from the obtained correlation times, it is necessary to identify the detection schemes for the different hydrodynamic modes. For the contribution from translational micelle diffusion, a homodyne detection scheme could be ensured, which means that sufficiently pure scattered light from the micelles was analyzed. For the contribution from molecular diffusion, it was proven with the help of an additional model system that light scattered by strong scatterers such as particles or micelles superimposes the much weaker scattered light modulated by fluctuations in species concentration on a molecular scale. Thus, it acts as sufficiently strong reference light to achieve heterodyne conditions for the hydrodynamic mode related to molecular diffusion.

Besides other experimental details, it is demonstrated that also absorbing samples can be investigated by implementing a newly developed technique analyzing scattered light in reflection direction as well as by a careful selection of the laser wavelength and power to minimize the effect of local sample heating caused by laser light absorption.

All determined diffusion coefficients for a given system show an increasing trend with increasing temperature. The presence of CO_2 increases the translational micelle diffusion coefficient despite the detectable swelling of the micelles. This can be related to the decreasing viscosity of the polyol mixture when CO_2 is dissolved therein. Hydrodynamic diameters of the non-swollen and CO_2-swollen micelles determined from the translational diffusion coefficients are in good agreement with literature data. The effective diffusion coefficient related to the molecular diffusion processes only observable in the presence of CO_2 in the microemulsion is in agreement with that measured without the presence of micelles and in the same order of magnitude as binary diffusion coefficients reported for similar systems without inhomogeneities. Additionally, it is shown that the surfactant concentration affects the hydrodynamic diameter of non-swollen micelles for the systems studied.