

# Optical Metrology for the Characterization of Fluids Relevant for Hydrogen Storage and Transport

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## Summary:

This contribution demonstrates the application of light scattering and related optical techniques for the characterization of fluids relevant for hydrogen (H<sub>2</sub>) storage and transport, with emphasis on the accurate determination of thermophysical properties. Conventional dynamic light scattering (DLS), surface light scattering (SLS), and the shadowgraph method were employed for broad ranges of fluid classes, temperatures, and H<sub>2</sub> pressures. By Raman spectroscopy, approaches for measuring H<sub>2</sub> concentrations in the liquid phase and the hydrogen loading of liquid organic hydrogen carriers (LOHCs) were validated.

**Keywords:** dynamic light scattering, hydrogen carriers, Raman spectroscopy, shadowgraph method, surface light scattering

## Background and Motivation

For establishing a H<sub>2</sub>-based energy economy, efficient and safe ways for its storage and transport are required. In the context of chemical H<sub>2</sub> storage, LOHCs are of increasing interest. Here, bi- or tricyclic compounds such as diphenylmethane (DPM, H0-DPM), benzyltoluene, and dibenzyltoluene are discussed. Also methanol is considered as a hydrogen carrier. For corresponding process design and optimization, thermophysical properties at process-relevant conditions including the presence of physically dissolved H<sub>2</sub> are necessary, but only sparsely available. Since the thermophysical properties and, thus, the reaction kinetics depend on the actual composition, knowledge on the liquid composition during the process is of special interest, too. For the large-scale storage of H<sub>2</sub> produced from off-shore wind energy, subsea caverns are currently discussed. Here, e.g., the mutual diffusion coefficient of H<sub>2</sub> in brine at storage conditions is relevant.

## Light Scattering Techniques

The experimental determination of thermophysical and especially transport properties over a broad range of thermodynamic states represents a considerable challenge. For this task, optical

metrology features the advantage of investigating fluids in a contactless way in or out of equilibrium. The analysis of quasi-elastically scattered light via photon-correlation spectroscopy allows for the simultaneous and accurate determination of several thermophysical properties without the need of calibration. DLS from the bulk of a binary fluid mixture gives simultaneous access to the Fick diffusion coefficient  $D_{11}$  and the thermal diffusivity  $\alpha$ . Similarly, SLS analyzes the temporal behavior of capillary waves at fluid interfaces. For the studied fluids, the simultaneous determination of the dynamic viscosity  $\eta$  and surface or interfacial tension  $\sigma$  is possible by SLS. Contrary to many conventional methods, both DLS and SLS are applied in macroscopic thermodynamic equilibrium and can be used to study mixtures containing dissolved gases at saturation conditions. The shadowgraph method studies long-range fluctuations in the bulk of the fluid in the presence of a macroscopic temperature gradient and can enable the measurement of various thermophysical properties in one experiment. By Raman spectroscopy, intensity ratios of characteristic lines associated with vibrational modes of the functional groups in the individual scattering molecules can be studied. This allows the contactless optical determination of

the composition of fluid mixtures as well as the detection of changes in the fluid structure.

## Results

By DLS,  $\alpha$  and  $D_{11}$  in binary LOHC mixtures of  $H_2$ -lean and  $H_2$ -rich species have been studied. In a mixture of H0-DPM with dicyclohexylmethane (H12-DPM),  $\alpha$  and  $D_{11}$  could be determined simultaneously at temperatures  $T$  up to 473 K. Investigations on the same mixture using the shadowgraph method allowed to access  $\alpha$ , where good agreement with the values from DLS was found. For quasi-binary dibenzyltoluene/perhydrodibenzyltoluene mixtures, DLS allowed to obtain effective  $D_{11}$  values covering four orders of magnitude for  $T$  from (264 to 571) K [1]. Furthermore, DLS was successfully applied for the accurate determination of  $\alpha$  and  $D_{11}$  of various fluids relevant for  $H_2$  storage and transport containing dissolved  $H_2$  at saturation conditions. Here, diffusivities in binary mixtures of  $H_2$  in the LOHC compounds H12-DPM [2] and ortho-perhydrobenzyltoluene, in methanol as well as in water or brine were determined over a broad range of  $T$  up to 572 K and  $H_2$  pressures  $p_{H_2}$  up to 20 MPa. Fig. 1 shows  $\alpha$  and  $D_{11}$  obtained by DLS for the example of binary mixtures of H12-DPM or methanol containing dissolved  $H_2$  close to infinite dilution of  $H_2$  as a function of  $T$ .

With SLS, the influences of LOHC composition and of pressurized  $H_2$  at  $p_{H_2}$  up to 7 MPa and  $T$  up to 573 K on  $\eta$  and  $\sigma$  of several LOHCs was studied [3]. For instance, measurements with DPM-based solvents as well as ortho-perhydrobenzyltoluene in the presence of dissolved  $H_2$  revealed nearly constant  $\eta$  values and a slight decrease of  $\sigma$  by up to  $-6\%$  with increasing  $p_{H_2}$  for all solvents, independent of the studied  $T$ . Investigations on binary mixtures of methanol with dissolved  $H_2$  at up to 8 MPa and 393 K by SLS showed very similar behaviors of  $\eta$  and  $\sigma$ .

To connect the information on  $\eta$  and  $\sigma$  of methanol in the presence of pressurized  $H_2$  with the actual amount of dissolved  $H_2$ , Raman spectra from the liquid phase recorded during SLS experiments were evaluated. For calibration, spectra recorded for methanol with dissolved  $H_2$  in a solubility apparatus with known liquid phase compositions determined from conventional solubility measurements by the isochoric saturation method were used. Here, the transfer of the calibration to the SLS setup for the determination of  $H_2$  concentrations thereon via Raman spectroscopy was successfully demonstrated.

In a similar manner, an approach for the contactless measurement of the hydrogen loading of LOHCs, i.e. the degree of hydrogenation ( $DoH$ ), which represents the share of reversibly bound

hydrogen compared to the total uptake capacity of the LOHC, was tested and validated for the DPM-based LOHC system up to 573 K [4]. Using Raman spectra from binary mixtures of H0- and H12-DPM, a  $T$ -independent calibration was obtained and successfully applied to determine the  $DoH$  of partially hydrogenated reaction mixtures containing also cyclohexylphenylmethane (H6-DPM) as well as of pure H6-DPM. For the studied systems and  $T$ , the known  $DoH$  values could be reproduced by Raman spectroscopy with an average absolute deviation of 0.018.

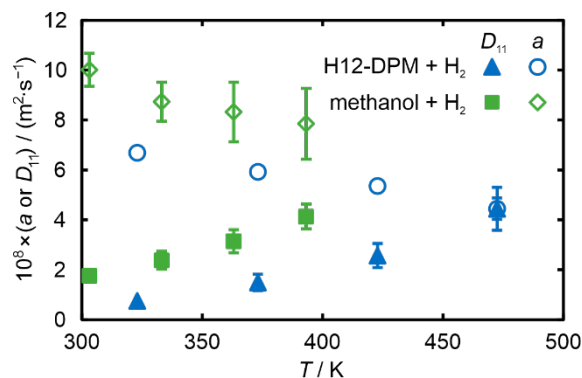


Fig. 1. Thermal diffusivities  $\alpha$  and Fick diffusion coefficients  $D_{11}$  as a function of temperature  $T$  measured by DLS in the saturated liquid phase of binary mixtures of H12-DPM [2] or methanol with dissolved  $H_2$  in the regime of infinite dilution at pressures  $p$  of about (3 or 8) MPa, respectively.

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