Measurement of Phase Equilibria States on Levitated Drops by Raman Spectroscopy

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Application Note

Introduction

The knowledge of phase equilibria states of multicomponent mixtures with supercritical solvents is still of interest in chemical engineering. As a new technique for concentration measurements with high accuracy we present Raman spectroscopy. With this method no probe extraction is needed, the investigated system will not be disturbed and furthermore the results are obtained in-situ in a few seconds. We can show that inter- and intramolecular interactions which may influence the Raman spectra are negligible.

In previous experiments the used autoclave with a volume of about 0,3 l takes many hours to get an phase equilibria state of multicomponent mixtures [A. Stratmann, In-Situ Raman Spektroskopie an Verdampfungsgleichgewichten, Shaker Verlag, Aachen, 2003]. The idea of our project is to miniaturize the volume of the mixtures. Therefore acoustic levitation is a useful technique for contactless handling of small liquid samples in a gaseous environment. Sample sizes are typically in the range of 5–5,000 nl corresponding to diameters of 0.2–2 mm, respectively. Because of the lack of containment, acoustic levitation inhibits wall effects and offers a contactless handling medium for microsized samples.

Experimental Setup

The experimental setup using Raman Spectroscopy is shown in Fig. 1. It consists of an acoustic levitation device, a frequency generator with a high frequency power supply, a commercial Czerny-Turner monochromator (Chromex 250is) with an adapted Peltier-cooled CCD-Camera (Andor iDus DU420A-OE) and the laser (Coherent Verdi Nd:YVO_4 laser, λ=532nm, P_{max}=5W).

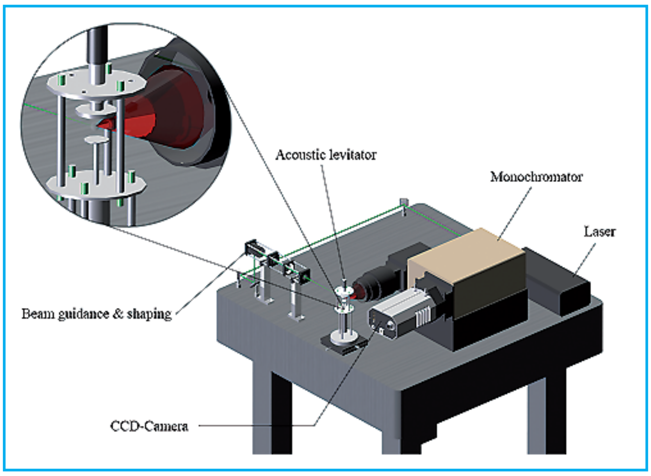

Fig. 1: Schematic representation of the experimental setup

A new acoustic levitation design for better levitation stability was investigated in the first period of this project [S. Baer, Design and Development of an Ultrasonic Levitation device for Raman spectroscopy investigations on single particles, Rev. Sci. Instrum., submitted 2010]. The levitator is working at a standard frequency of 38 kHz in ambient air and pressure, while the volumes of the droplet ranged between 0.4 µl to 5 µl corresponding to the levitated drop size of about 1 mm to 2 mm. The droplets were produced with a hypodermic syringe and were directly inserted into the pressure nodes of the stationary ultrasonic field. With increasing sound intensity the shape of the droplets will experience a deformation towards an oblate shape with a growing horizontal diameter. With an optimal setting of the HF power, a nearly spherical levitated drop can be achieved.

The levitated droplet was illuminated by a Coherent Verdi Nd:YVO_4 laser (λ=532 nm, power 0.1 W). The polarization of the laser beam was set to be perpendicular to the scattering plane. The laser beam was focused using a 300 mm lens to the center of the levitated droplet. The inelastic scattered light was measured under a scattering angle of 90° and imaged by an objective onto the entrance slit of a spectrograph (Chromex 250is). This instrument was used with a notch filter to eliminate the elastically scattered light and a 1800 l/mm diffraction grating. A Peltier-cooled CCD detector (Andor iDus DU420A-OE) was attached to the spectrograph. The spectrograph control and the spectra of the CCD detector were processed with the commercial software package Solis by Andor.

Results & Discussion

In order to check the possibility of direct spectroscopic determinations on levitated samples with Raman scattering, a standard experiment was carried out with $C_3H_8O_3$ (Glycerol). The measurements were done with a wavelength of 532 nm and a power of 100 mW. The levitated droplet had a size of about 1-2 mm and the measurement time was 30 s. The Raman signal was detected at a scattering angle of 90° and the laser beam was focused to the center of the levitated droplet.

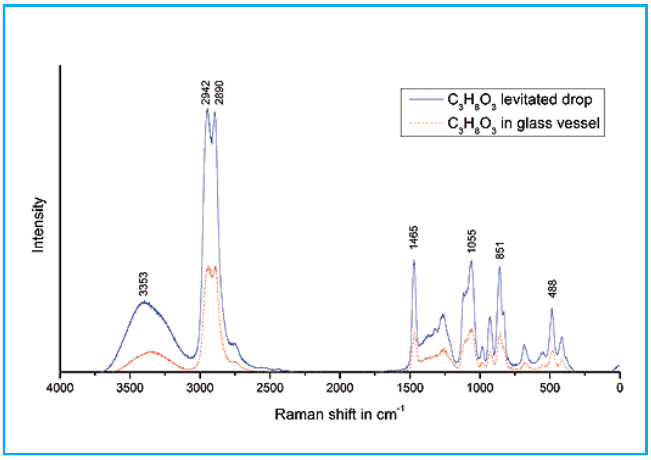

Fig. 2: Raman spectra of glycerol in an acoustically levitated drop under a scattering angle of 90°

In the case of levitated Glycerol drops, we observed much better Raman spectra on a single levitated drop with the new acoustic levitation device compared to a commercial levitator as a result of better levitation stability. As shown in Fig. 2, Raman bands positions and relative intensities of a glycerol drop and same liquid in a cuvette are in good agreement with the reference of Schrader [B. Schrader, *Raman/Infrared atlas of organic compounds*, VCH Verlagsgesellschaft mbH, Weinheim, 1989]. This enhancement in the spectra is a result of different experimental parameter. Measuring of the phase equilibria will be the next step in our investigation.

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