Remote quantification of the composition of multi-component high pressure systems using Raman spectroscopy

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ABSTRACT

For the development, design and optimization of high pressure processes the knowledge of numerous physical properties at elevated pressure conditions is essential. These also include the phase equilibrium compositions of the used substance system under the respective process conditions, since they influence mass transport phenomena. Gathering phase equilibrium data using conventional techniques is challenging and time-consuming, due to an invasive sampling step and a subsequent analysis. Especially the sampling step always leads to a perturbation of the equilibrium and thus is suspected to be the main error source of measuring phase equilibria. The non-invasive Raman spectroscopy avoids the above mentioned drawbacks.

The major challenge in analyzing multi-component Raman spectra is the unambiguous assignment of the signal intensities to the comprising components. Therefore, an evaluation routine was implemented to reconstruct the measured spectra, by applying the least-square method. The strategy is based on the combination of fitting weighted Raman spectra of the pure compounds to the measured spectra and deconvoluting Raman peaks in Gaussian and Voigt profiles. This allows considering also effects of intermolecular interactions onto the Raman spectra of the mixtures and additionally provides the opportunity of extracting further information, e.g. the temperature of the mixture, from the measured spectra. The evaluation strategy was successfully applied to ternary mixtures of carbon dioxide, water and organic solvents and will be presented in this contribution.

INTRODUCTION

Various benefits can be accomplished by operating chemical processes at elevated pressures, as improvements in reaction rate and selectivity lead to advanced product properties and qualities [1]. Recent developments in the high-pressure process technology are often based on the use of supercritical or near critical fluids, because they simplify the solvent removal, enhance the mass transport and increase the yields [2]. Especially carbon dioxide is a promising solvent in the production of thermal sensitive substances, due to its mild critical parameters (304.13 K and 7.39 MPa). Despite these mentioned advantages, the full capacity of supercritical fluids is by far not used. A reason therefore is, that for the development and

appropriate design of new processes, numerous thermodynamic properties have to be known, including the phase equilibrium data of the applied substance system [3].

Basically, methods for the determination of phase equilibrium data are distinguished between synthetic and analytical ones [4]. In synthetic methods commonly a phase transition is observed, as it is true for the vanishing point and the cloud point method [5-7]. Using these methods to determine reliable data, the exact composition inside the experimental apparatus has to be known. A hindrance of synthetic methods is the impossibility to determine tie lines in multicomponent systems without further experiments. More information can be gained using analytical methods. However, these methods usually include sampling and require a subsequent analysis leading to an additional experimental effort. Furthermore, the invasive sampling step disrupts the equilibrium and is quoted as the main error source in the determination of phase equilibrium data [8]. For that reason a non-invasive measuring technique is desired. In 2002, Stratmann and Schweiger [9] applied the Raman spectroscopy for the determination of high-pressure phase equilibria of binary mixtures containing CO_2 and organic solvents. In this contribution the technique is successfully extended to ternary mixtures containing CO_2, water and organic solvents.

MATERIALS AND METHODS

Acetone from Merck KGaA with a purity of 99.9 %, ethyl acetate (CHROMASOLV® Plus for HPLC) from Sigma Aldrich with a purity of 99.9 % and CO_2 from Linde with a purity exceeding 99.5 % were used as delivered.

For the determination of the phase equilibrium data the ternary mixtures were filled in a high pressure phase equilibrium cell, which is shown schematically in Figure 1 and described in detail elsewhere [10]. The volume of the cell can be adjusted by means of a moveable piston between 25 and 56 ml to ensure isobaric conditions. The temperature of the cell is controlled by a heating jacket. Furthermore, the cell provides an optical access through four borosilicate windows. Agitation is realized with a magnetic stirrer inside the cell to enhance the mass transport.

In order to measure the phase diagrams of ternary systems, firstly, a binary mixture of known composition was set inside the cell by high precision syringe pumps. Then, the third component was added to the mixture under isobaric conditions, until a phase separation occurred. Afterwards, the ternary mixture was stirred until the temperature and pressure inside the cell remained constant, which indicates the thermodynamic equilibrium. Then, the compositions of the obtained phases were measured with a self-made Raman-sensor, which detects the backscattered Raman-signals. As excitation source a frequency doubled, continuous wave-(cw)-Nd:YAG laser with a wavelength of 532 nm and an output power of 250 mW was used. The Raman signals were detected with an Ocean Optics spectrometer QE 65000, which features a back illuminated CCD chip. More details to the sensor can be found in [11].

By a stepwise addition of the third component, the two phase region is successive characterized.
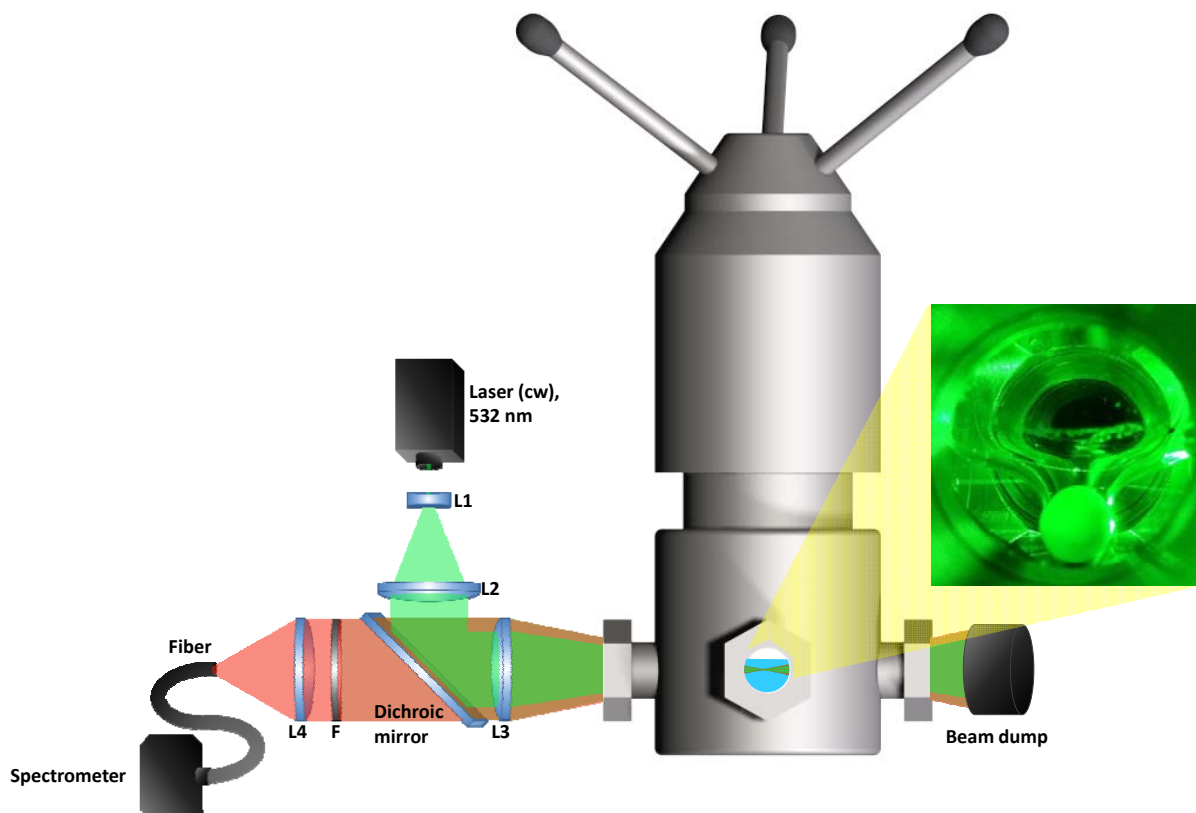
Figure 1: Schematic of the high pressure phase equilibrium cell and the optical setup; L1: Concave lens; L2: Convex lens; L3,4: Achromatic convex lenses; F: Long pass filter (532 nm)

RESULTS

In order to correlate the detected Raman signal with the molar composition of the mixture a calibration is essential. For the unambiguous description of a ternary system, two sub-systems have to be calibrated. A detailed derivation of the applied equations can be found in [11, 12]. The major challenge in evaluating Raman spectra of multicomponent mixtures is the clear and distinct assignment of detected Raman-signals to the containing components, due to the frequently appearing spectral overlap between different Raman peaks. Molar interactions like hydrogen bonds and dipole-dipole interactions affect the positions and the shapes of Raman bands and peaks in the mixture spectra compared to the spectra of the pure substances and made the evaluation even more difficult [13-15].

To isolate the Raman signals of the individual components the measured mixture spectrum is reconstructed by means of the Levenberg-Marquardt algorithm, which solves a set of non-linear equations using the least-square method [16]. Thereby, the contribution of water to the mixture spectrum is calculated as convolution of overall seven Gaussian peaks, two in the OH-bending vibration Raman region and five in the OH-stretching vibration Raman region. Additionally, for the contribution of CO_2 the envelope of the Fermi dyad is calculated as convolution of two Voigt profiles. The contribution of the organic solvent is determined by means of fitting a pure substance spectrum of the respective solvent to the mixture spectrum by adjusting position and amplitude. All mentioned adaptations of the components spectra to

the mixture spectrum are performed simultaneously by the algorithm. The algorithm stops when the residual between measured and calculated spectrum reaches a global minimum.

The strategy of the evaluation of a ternary mixture is illustrated in Figure 2. In the background the baseline corrected mixture spectrum is shown. In the center plane the isolated components spectra proportional to their contribution to the mixture spectrum can be seen, while the forefront exhibits the calculated fit and the difference between fit and measured spectrum.

In order to validate the presented routine, the ternary system acetone, water and CO_2 was evaluated and compared with literature values obtained by Traub and Stephan [17]. The achieved ternary phase diagram at 313 K and 10 MPa is presented in Figure 3. The figure shows that the data evaluated in this work are in good agreement with the literature data. Only at relatively high molar compositions of acetone, small deviations between the two data sets occur.
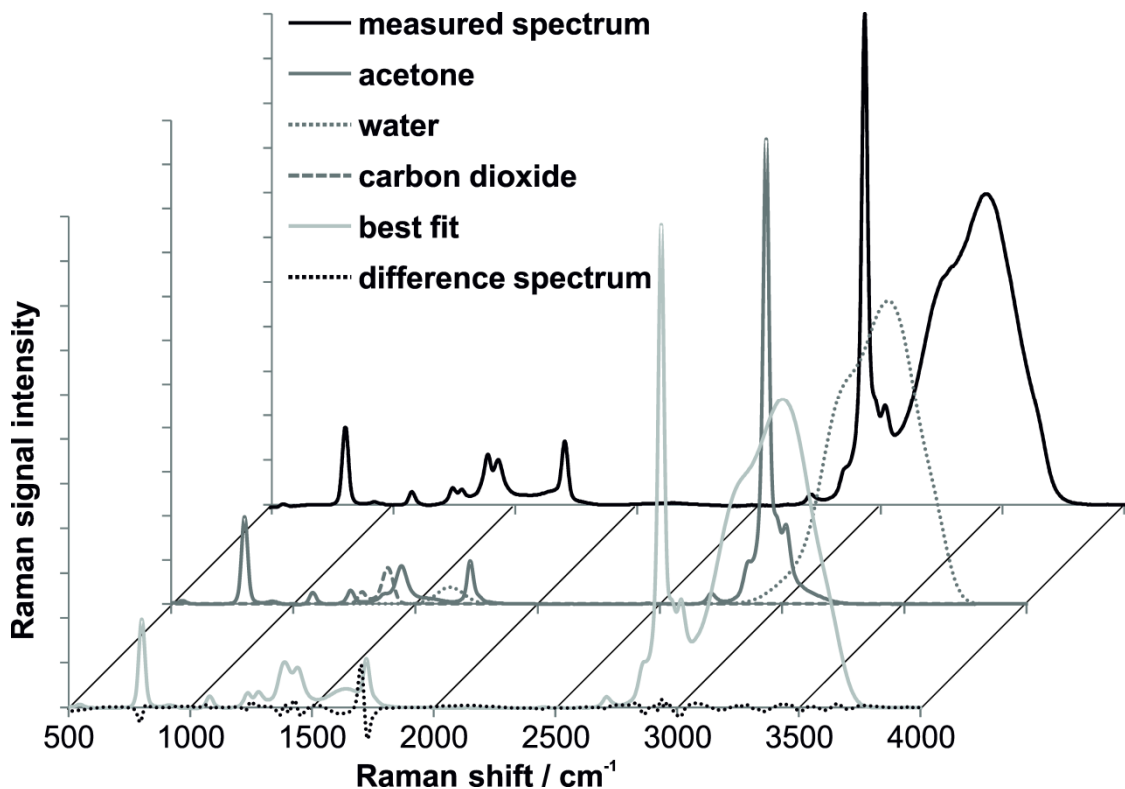

Figure 2: Illustrated strategy for the evaluation of a ternary mixture spectrum of acetone, water and carbon dioxide
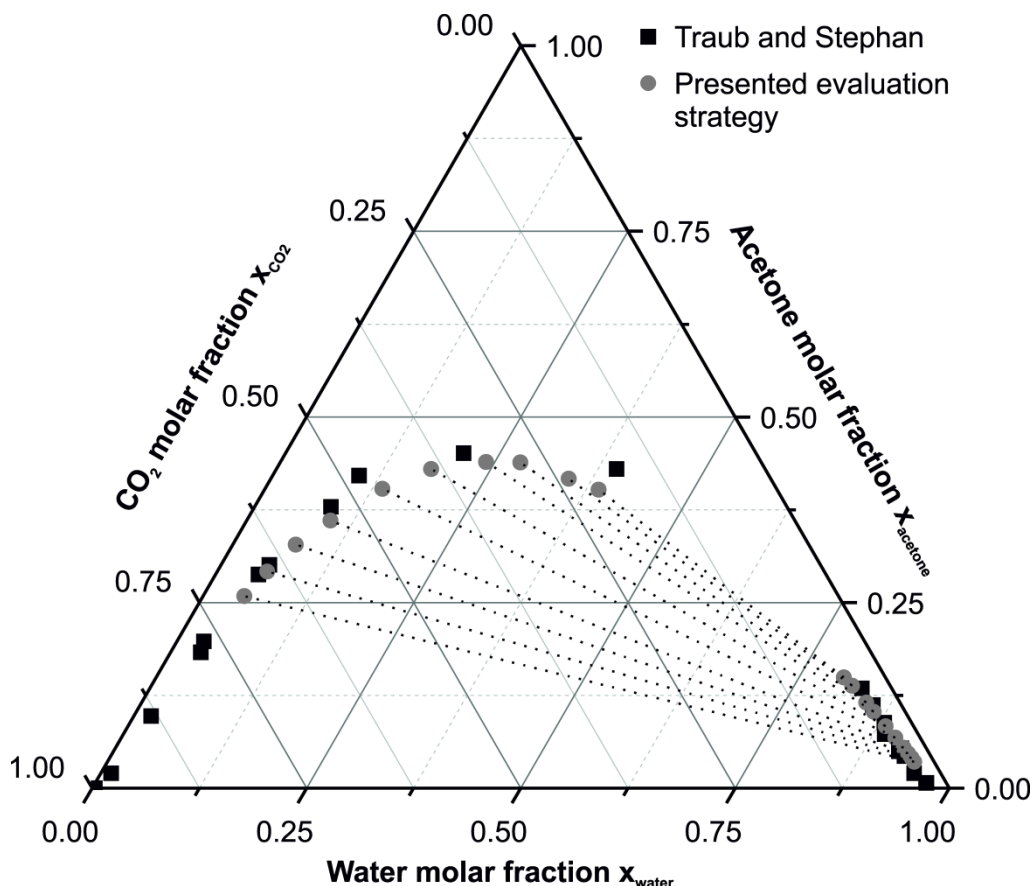
Figure 3: Ternary phase diagram of the system acetone, water and carbon dioxide at 313 K and 10 MPa; comparison between data obtained by the presented evaluation strategy and literature data from Traub and Stephan [17]

CONCLUSION

The adaptability of the Raman spectroscopy as a non-invasive measurement technique for the quantification of the composition of multi-component high pressure systems was shown. For the unambiguous assignment of the Raman signal intensities to the comprising components, which is the major challenge in analyzing multicomponent Raman spectra, an evaluation routine was implemented. This routine is based on the consideration of partially pure substance spectra and partially deconvoluted spectra and is in general applicable to evaluate the composition of multi-component mixtures. This includes also the analysis of mixtures containing more than one organic solvent. Applying the presented evaluation routine, the Raman spectra of the ternary system acetone, water, CO_2 was evaluated and the high pressure phase equilibrium data are presented, indicating a good agreement with literature data. A more detailed explanation can be found in [18].

ACKNOWLEDGEMENT

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