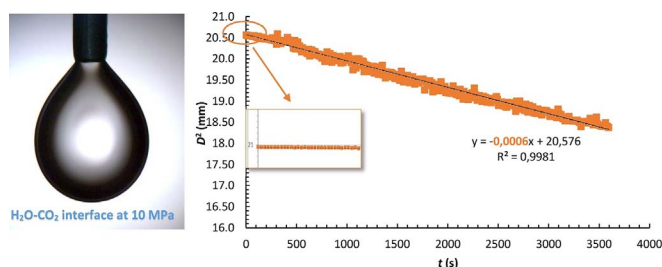# Diffusion coefficients of water and propylene glycol in supercritical CO$_2$ from pendant drop tensiometry

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GRAPHICAL ABSTRACT

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ABSTRACT

New optimized experimental setup based on pendant drop tensiometry was developed, and a mathematical model designed to fit the experimental data was used to determine the diffusion coefficients of binary systems at elevated pressures and temperatures. For the first time, the diffusion coefficients of propylene glycol in supercritical CO$_2$ were determined at temperatures of 398.2 and 423.2 K and at pressures from 5 MPa, up to 17.5 MPa.

Experimental procedure was validated by a comparison of the experimental data for the mixture water-CO$_2$ with data from the literature. For this purpose, the diffusivity of water in CO$_2$ was measured at 298.15 K in the pressure range from 5 MPa, up to 60 MPa. Accuracy of results was certified by measuring more than 1000 points of equivalent drop diameter. Droplet geometry was examined by using a precise computer algorithm that fits Young–Laplace equation to the axisymmetric shape of a drop.

1. Introduction

Accurate prediction of diffusion coefficients, D_{ab}, is fundamental in various engineering and industrial operations to design processes involving mass transfer (e.g. conventional and supercritical extractions, multiphase chemical reactions, distillation, carbon sequestration, membrane separation processes, absorption and adsorption) [1]. Mass transfer data, measured at ambient conditions, can be found in the literature for numerous binary and ternary systems. Data in the literature that reports on the diffusion coefficients of liquids in supercritical fluids are still relatively scarce [2]. In addition, most of the experimental techniques for determining diffusion coefficients at high

pressures are either expensive or time-consuming and have considerable scatter, with relative uncertainties [3,4]

Several methods have been developed to study mass transfer properties of different systems of components. Those are divided into direct, when the composition of the liquid samples with gas absorbed is analyzed during the test, and indirect, when the composition of the liquid phase after diffusion is correlated with a measured system property. The main disadvantages of such methods is that they are time consuming and require expensive equipment and subsequent analysis of the composition of system components. Besides, these methods are susceptible to experimental errors [5]. Therefore, there is a high interest to develop simpler, quick and economical methods that would

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give results of a high accuracy.

Frequently used experimental methods for measuring diffusion parameters that do not require to measure compositions comprise the pressure decay (PD) method, which took a long period of time to attain the equilibrium state of the mixture [6,7] and the similar, the constant pressure dissolving gas volumes (CPDGV) method, where volume–time data is recorded with constant pressure and temperature[8,9]. A method, based on NMR spectra changes caused by changes in the mixture's properties with the diffusion process has been termed as low-field nuclear magnetic resonance (NMR) method [10]. The X-ray computer assisted tomography (CAT) is used in reservoir rock characterization [11], however both methods, nuclear magnetic resonance (NMR) method and computer assisted tomography, require expensive devices. Gas permeation through immobilized liquid membrane (ILM) method is used to determine the pressure decay of gas entering in a closed chamber with a thin layer of ionic liquid [12].

The dynamic pendant drop volume analysis (DPDVA) method is used to calculate the swelling coefficient of the liquid phase and is based on measuring the change in volume of a pendant oil drop in a cell surrounded by a gas absorbed by the drop. This method has been used in the frame of the present study and modified to enable measurements at elevated pressures. The speciality of the model that has been developed by the authors is the possibility to determine diffusion of liquid in supercritical phase.

There is a possibility for studying the mass transfer phenomenon in a system, even under unconventional operating conditions, relatively economically, without the need for advanced equipment, but quickly, accurately and with less dependence on the nature of the fluid: this is drop tensiometry, which has already been recognized as a reliable technique that can be applied to determine surface and interfacial properties, swelling factors as well as dynamic changes in drop volume [13]. Furthermore, by applying the suitable mass transfer model for the observed changes in drop volume by time, diffusion coefficients for a specific system can be relatively easily calculated.

Diffusivity measurements using drop tensiometry have been done by Espinoza et al. [14], where a sessile droplet of water on substrate was surrounded by supercritical CO_2. The diffusion model was solved numerically using Crank-Nicolson implicit scheme for evaporating sessile droplets. Yang et al. [15] presented a method that determines the solvent diffusion coefficient and the oil swelling factor from dynamic measurements of pendant oil drop volumes. This model was numerically solved by applying the semi-discrete Galerkin finite element method. Bellen et al. [16] validated the diffusion coefficients and the thermal diffusion factors of naphthalene in CO_2 from levitated drops. Hirai et al. [17] estimated the diffusion coefficient in a CO_2-water system, where a liquid CO_2 droplet without CO_2 clathrate was placed in the flow of a uniform velocity profile. The diffusion coefficient was obtained by measuring the liquid CO_2 droplet-dissolution rate and using the empirical mass transfer coefficients. Erbil et al. [18] performed fully spherical liquid drop evaporation experiments in still air, where diffusion coefficients were calculated from the decreasing mass of the droplets.

Compared to the methods described above, the present investigation develops a simple, reliable, and widely applicable method for the estimation of gas-phase diffusion coefficients. Pendat drop tensiometry was primarily established for measurements of surface tensions of the system at ambient pressures. Recently, the pedant drop method has been applied to perform measurements at elevated pressures and the system of water and CO_2 has been frequently used as a model system to verify the reliability of the method and provide repeatability of the results [19–22]. The aim of the present study was to expand its applicability also for other systems of liquids and surrounding gas media, and additionally, to modify the method for the measurements of diffusivity at elevated pressures.

In the first step, a new experimental technique for obtaining diffusion coefficients by means of pendant drop tensiometry was developed.

Changes in evaporating drop geometry (volume and surface area) were determined by fitting the Young-Laplace equation to an experimental image using suitable software. The equilibrium solubility (phase equilibria) data required in the present mass transfer model were found in the literature or determined experimentally by our research group using a static–analytic method.

The experimental technique for obtaining the diffusion coefficients of liquids in supercritical fluids by means of pendant drop tensiometry was validated by measuring the diffusion coefficients of water in liquid CO_2 at 298.15 K and supercritical CO_2 at 318.15 K, in a pressure range up to 60 MPa. There is increasing need to develop new experimental techniques, enabling quick and accurate estimation of mass transfer properties under unconventional conditions, at elevated pressures and temperatures. Indeed, diffusivity in a mixture of water and CO_2 plays an important role in environmental and petrochemical processes, such as CO_2 sequestration in the ocean, saline reservoirs and oil reservoirs to enhance oil recovery.

In the frame of the present research, for the first time the diffusion coefficients of propylene glycol in supercritical CO_2 at temperatures of 398.2 K and 423.2 K in a pressure range from 5 MPa, up to 17.5 MPa were measured. Knowledge about the diffusivity of volatile liquids, such as propylene glycol in supercritical fluids, especially in CO_2, which is most widely applied, is essential for several applications. The results of the present research serve as a good framework for further development in the processing of poly (propylene fumarate)[23]. Propylene glycol is also used in various edible items, as a vaporizer in the delivery of pharmaceuticals or personal-care products and as an environmentally friendly automotive antifreeze.

The method is distinguished by its advantage of being simpler to apply than the more rigorous advanced techniques described above.

2. Experimental

2.1. Materials

Carbon dioxide 3.5 was obtained from Messer (Slovenia). Propylene glycol with 99.5% purity was purchased from Sigma (Germany) and was used without further purification. The needles (used in the pendant drop method) were made of stainless steel, with a nominal outer diameter of 1.56 mm.

2.2. High-pressure drop tensiometry apparatus

The central part of the experimental setup comprises an optical high-pressure cell (NWA GmbH, Germany) equipped with two stainless steel heaters (mod. Firerod, Watlow, USA). Liquid phase was injected by a high-pressure manual pump (mod. 750.1100, SITEC, Zurich, Switzerland). Pendant drops of adequate size were formed on a stainless steel tip that was placed vertically in the cell between two sapphire windows. Measurements of dynamic drop volume were filmed with a Basler Aca1300-200um digital camera equipped with a CCTV lens (Tamron, Japan), connected to a computer by using the OpenDrop algorithm [24]. To avoid optical aberrations and the fake reflections from other sources that can occur at the drop edge, the drop was lit from the other side with a diffusion light, which was achieved by placing a glass diffuser between the light source and the hanging drop. The undesirable effect of droplet oscillation was minimized with an anti-vibration table. Pressure inside the cell was increased with inlet gas by a high-pressure pump (NWA PM-101) or Gas Buster (DLE 75-1-GG-H2), depending on the type of gas. Pressure was monitored during the entire experiment by an electronic pressure gauge (WIKA Alexander Wiegand GmbH & Co. KG, Alexander-Wiegand-Straße, Klingenberg, Germany) with an uncertainty of 0.01 MPa. Total uncertainty of the temperature measurement was 0.1 K. The entire experimental setup is presented in Fig. 1.