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A modified continuous flow apparatus for gas solubility measurements at high pressure and temperature with camera system

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ABSTRACT

A continuous flow apparatus with a camera system was modified for high-pressure gas–liquid equilibrium measurements. The continuous flow method is suitable for phase equilibrium measurements of heat-sensitive materials, such as heavy oils and bio-based feedstocks, which are refined in hydroprocesses at high temperatures and pressures. Benefits of the modified apparatus are a short residence time of a sample in the heated zone and no sampling is required. In contrast, the static method is usually impractical with the heat-sensitive materials due to the long residence time of sample in the equilibrium cell. In this study, the continuous flow apparatus and the measurement method was adopted and validated. The validation was conducted by measuring hydrogen solubility in toluene and *n*-hexadecane at high temperatures and pressures ($T = 461–575$ K, $P = 5–10$ MPa) and comparing the results with the literature values. Relative average pressure deviation was found to be 3.8% for measurements of this work when the PC-SAFT equation of state was optimized against literature values while the relative average pressure deviations for the literature data sets varied from 0.9% to 4.7%. Thus, the quality of measurements was shown to be excellent. In addition, hydrogen solubility was also measured in *n*-octadecane in order to obtain new data for this system. All measured systems were modeled with the PC-SAFT and the original and modified Peng–Robinson equations of state in order to simplify the validation of the measurement method and to compare the performance of the selected models. PC-SAFT was found to predict phase behavior of the systems precisely whereas the predictions of the Peng–Robinson modifications were less precise.

1. Introduction

Phase equilibrium data is required in order to improve and validate the thermodynamic models. Gas–liquid equilibrium is difficult to measure at high pressures and temperatures, especially if one of the measured components decompose at elevated temperatures. Amount of suitable measurement methods is scarce for measuring systems consisting of decomposing components [1]. One of the suitable methods for decomposing systems is synthetic continuous flow method [2] where the mixture of known composition is pumped through the equilibrium cell and the temperature and the pressure of the system are measured. The residence time of sample at the high temperature zone is short making the method appropriate for heat sensitive materials, like heavy oils or bio-based feedstocks.

Catalytic hydrocracking is one of the most used processes for refining heavy oil in the petrochemical industry. In hydroprocesses, the solubility of hydrogen is one of the major factors affecting the operation of the process. In addition, it is a key parameter in process models. Reliable data of hydrogen solubility in heavy oil are scarce at elevated temperatures and pressures in the literature. Challenges to the measurements and inaccuracy of the hydrogen solubility data is caused by the demanding measurement conditions, the thermal instability of the oils, the complex phase behavior of the systems and the low hydrogen solubility in oils [3].

Recently, Saajanlehto et al. [4] have developed a novel continuous flow measuring method and constructed apparatus for bubble point pressure measurements. To extend the application possibilities of the equipment, this paper presents the modified continuous flow apparatus and measurement method suitable for gas solubility measurements. In this study, the apparatus and the method was adopted and validated by measuring hydrogen solubility in known solvents: toluene and *n*-hexadecane. The measured bubble points were compared to the literature values

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Nomenclature

A	parameter in the density correlation (Eq. (2))
AAD	average absolute deviation
B	parameter in the density correlation (Eq. (2))
C	parameter in the density correlation (Eq. (2))
D	parameter in the density correlation (Eq. (2))
EoS	equation of state
F	flow rate ($\text{cm}^3\,\text{min}^{-1}$)
k	binary interaction parameter in the PC-SAFT equation of state
l	binary interaction parameter in the Peng–Robinson equation of state with the original alfa-function
m	binary interaction parameter for the Peng–Robinson equation of state with the Boston–Mathias modification
M	molar mass ($\text{g}\,\text{mol}^{-1}$)
N	number of data points
OF	objective function in the regression
P	pressure (MPa)
RAD	relative average deviation
T	temperature (K)
V_m	molar volume of ideal gas (22 414 $\text{cm}^3\,\text{mol}^{-1}$)
x	liquid mole fraction

Greek letters

ε/κ	segment energy parameter (K) in PC-SAFT equation of state
ρ	density ($\text{kg}\,\text{m}^{-3}$)
σ	segment diameter (Å) in PC-SAFT equation of state

Subscripts

2-P	two-phase region
C	critical property
calc	calculated value
H_2	hydrogen
i	component i
j	component j
L	liquid sample
LI	liquid phase region
lit	value from the literature
meas	measured value

[5–8]. In addition, hydrogen solubility in *n*-octadecane was measured in order to obtain new data for this system. The gas solubility of the measured systems was also modeled with the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [9] and the Peng–Robinson [10] equations of state (EoS). The calculations using Peng–Robinson were performed with original α-function (PR) [10] and with Boston–Mathias (PR-BM) modification [11]. Modeling was performed in order to make the validation of the measurement method simplier and to compare a new generation EoS, PC-SAFT, with classic cubic EoS for predicting hydrogen solubilities.

2. Experimental

2.1. Materials

The purities and the suppliers of the used components are listed in Table 1. The components were used without further purification.

2.2. Apparatus

The hydrogen solubility in toluene, *n*-hexadecane and *n*-octadecane were measured with the continuous flow apparatus developed based on the previous work by Saajanlehto et al. [4]. The modifications needed for present work were mainly conducted for feeding specific amounts of gas continuously into the system. The experimental set-up is shown in Fig. 1. The system consisted of four sections: feeding the liquid, introducing the gas, the measurement and the stabilization parts. In the liquid adding section, there was a line for filling the pump with the liquid sample from the flask and a syringe pump (Teledyne Isco, model 260D) for feeding the sample to the system. The gas was introduced to the system through a mass flow controller (Bronkhorst Hi-Tech; F230MI-AAD-11-V). The liquid and gas lines were connected through the μ-mixer (Institut für Mikrotechnik Mainz GmbH, HPIMM) placed in the oven. The measurement part consisted of an oven (HP 5890 Series II) where the μ-mixer was located in addition to the optical cell (Sitec-Sieber, <673 K and <30 MPa) equipped with the sapphire glass windows, and another syringe pump (Teledyne Isco, model 500D), which received the fluid from the system. The third syringe pump (Teledyne Isco, model 260D) was located in the stabilization section. Moreover, nitrogen gas was fed into the oven for accomplishing a nitrogen atmosphere for safety reasons, and another nitrogen gas line was connected to the system in order to flush the lines. The video camera recorded events in the equilibrium cell through the window. The camera system was located outside of the oven. A small hole was drilled (diameter about 15 mm) to the side of the oven for visual access of the camera system, and illumination of the cell was provided through a second hole from the opposite side of the oven. The holes were insulated with a piece of glass. All the lines were constructed of stainless steel (AISI 316) tubes with an inside diameter of 1 mm. In addition, the lines were equipped with resistance wires in order to heat the lines if needed. The data acquisition was implemented with NI LabVIEW software and NI cDAQ-9174 module.

Temperature was measured with K-Type thermocouples (Nokeval) in the line through a T-piece that was located in the oven. Thermocouples were calibrated against a Tempcontrol F200 thermometer equipped with a Pt-100 temperature probe calibrated at the Finnish National Standards Laboratory (MIKES). The uncertainty for temperature measurements was estimated to be ±0.2 K, which includes the uncertainty of the thermocouple and the measurement method.

Table 1
Suppliers and purities of pure components.

Component	CAS number	Supplier	Purity[a]	Purification method
Hydrogen	1333-74-0	AGA	0.99995[b]	None
Toluene	108-88-3	Sigma–Aldrich	$\geq$0.997[c]	None
n-Hexadecane	544-76-3	Sigma–Aldrich/Merck	0.99/ $\geq$ 0.99[c]	None
n-Octadecane	593-45-3	Sigma–Aldrich	0.99[c]	None

[a] Purity as reported by the supplier.
[b] Mole fraction.
[c] Mass fraction.