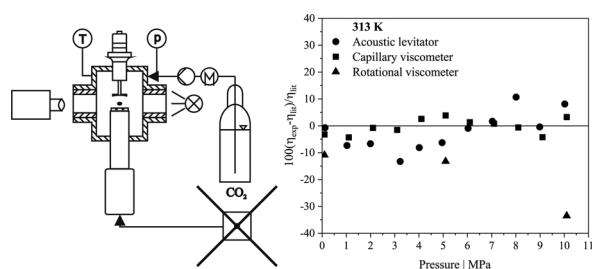# Viscosity of squalane under carbon dioxide pressure — Comparison of acoustic levitation with conventional methods

J. Kremer*, V. Bürk, S. Pollak, A. Kilzer, M. Petermann

Ruhr-University Bochum, Chair of Particle Technology, Universitaetsstr. 150, 44801 Bochum, Germany

GRAPHICAL ABSTRACT

ABSTRACT

Viscosity measurements with CO_2-saturated squalane with three different methods, a novel and two classical ones, are compared in a range of pressure from 0.1 MPa to 10.1 MPa at temperatures of 313 K, 333 K and 353 K. The dynamic viscosities were measured using an acoustic levitator developed for measurements under pressure, a capillary viscometer and a rotational viscometer. Squalane is saturated with CO_2 at each pressure and temperature measured. It is shown, that the measured data are in good agreement with the values published by Dilchert. With the comparatively fast measurement time, the acoustic levitation has been proven to be a promising method.

1. Introduction

The purpose of this work is to analyse and to compare three different experimental methods for measuring the viscosity of gas saturated liquids under pressure: a newly developed apparatus based on acoustic levitation, a self-built capillary viscometer and a customary rotational viscometer. Firstly squalane (2,6,10,15,19,23-hexamethyltetracosane) was chosen for several reasons: It is available with high purity of 99 % and it shows a Newtonian flow behaviour in the investigated region, which makes it an appropriate measuring fluid for the comparison of different viscosity measurement methods. Secondly the system of squalane and carbon dioxide was chosen because squalane is seen as representative for long-chain hydrocarbons. In addition,

the behaviour of the system squalane-CO_2 is well described through experimental data [1–3] and thermophysical models [2,4]. Nevertheless, viscosity of squalane in phase equilibrium with dense carbon dioxide is solely reported by Dilchert [1]. Such mixtures are of high interest e.g. for Enhanced Oil Recovery (EOR) processes or for the refrigeration industry, where hydrocarbons are used as compressor lubricants in cooling cycles with CO_2 as working fluid [2]. The focus of this work lays on the generation of data to compare the aforementioned methods to each other and to literature values while highlighting the merits and demerits of each method. The capillary viscometer, as a long known, well reliable technique, was selected as a reference for the acoustic levitation.

* Corresponding author.
  E-mail address: kremer@fvt.rub.de (J. Kremer).

2. Materials and methods

2.1. Materials

Squalane with a purity of 99 % purchased from Sigma Aldrich (Germany) is used for measurements and calibration. A share from the batch purchased was sent to an accredited laboratory (ZMK Wolfen, Germany) where the kinetic viscosity and the density were gauged from 293 K to 353 K in steps of 10 K. CO_2 is purchased from AirLiquide (France) with a purity of ≥ 99.95 %. All substances are used without any further purification and squalane is not degassed.

2.2. Methods

The viscosity of liquid squalane saturated with carbon dioxide is measured. Generally, the viscosity of liquids with dissolved gases depends on the amount of dissolved gas. For gas-saturated liquids, the amount of gas soluble is a function of pressure and temperature. The solubility of CO_2 in squalane increases as pressure is increased, which leads to a reduction in viscosity. Contrary, the solubility decreases with rising temperature. To calculate the viscosity of CO_2-saturated squalane using shape oscillations of acoustically levitated drops, the density is needed. Data for the density of the mixture at temperatures of 313 K, 333 K and 353 K and pressures from 0.1 MPa to 10 MPa are taken from Hiller [5]. To calculate the density at any conditions needed, the data points by Hiller [5] are interpolated with a model by Seifried [4]. Density (in kg/m^3) is described as a function of pressure (in MPa) and temperature (in K) using Eqs. (1)–(5). [4]

$$\rho(p, T) = \rho_0(T) + k_1(T)\cdot(p - 0.1 MPa) + k_2(T)\cdot\left(1 - e^{-k_3(T)\cdot(p-0.1 MPa)}\right) \tag{1}$$

$$\rho_0(T) = A_1 + A_2\cdot T \tag{2}$$

$$k_1(T) = A_3 + A_4\cdot T \tag{3}$$

$$k_2(T) = A_5 + A_6\cdot T + A_7\cdot T^2 \tag{4}$$

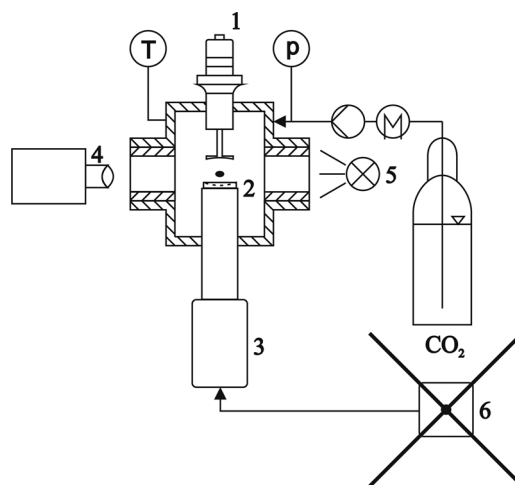$$k_3(T) = A_8 + A_9\cdot T \tag{5}$$

The parameters A_1 to A_9 are fitted using the solver implemented in the software Microsoft Excel. To estimate the accuracy of the fit, the absolute average relative deviation AARD (in %) is calculated by the following expression.

$$AARD = \frac{1}{n}\cdot\sum_{i=1}^{n}\frac{|x_{exp} - x_{calc}|}{x_{exp}}\cdot100\% \tag{6}$$

The parameters and the AARD values are given in Table 1. The density of CO_2-saturated squalane is well described by Eqs. (1)–(5) as shown by the low AARD value of 0.19 %.

Fig. 1. Acoustic levitator for high pressure systems: (1) transducer, (2) reflector, (3) swivel joint, (4) high speed camera, (5) LED light source and (6) screw press.

2.2.1. Acoustic levitation

Viscosity can be determined by analysing the freely decaying oscillation of an acoustically levitated drop. Fig. 1 shows a scheme of the high pressure acoustic levitator used for the experiments. A detailed description of the high pressure levitator can be found in Borosa [6].

The main components of the acoustic levitator are an ultrasonic transducer (1) and a reflector (2), which are both installed in a high pressure view cell (New Ways of Analytics, Germany) for pressures and temperatures up to 16 MPa and 433 K respectively. The view cell is equipped with two sapphire windows, which are positioned opposite another, and is heated by four heating cartridges, which are positioned in the walls of the cell. The transducer (1) emits ultrasonic waves with frequencies between 31 and 39 kHz, depending on temperature and pressure inside the view cell. Temperature and pressure are measured with uncertainties of $\pm$ 0.5 K and 0.03 MPa respectively. The waves are reflected at the surface of the reflector (2). Between the two, emitted and reflected waves interfere and, when the distance between transducer and reflector matches an integer multiple of half of the wavelength, resonance conditions are attained. In this case, the sound field is characterized by areas where sound pressure is zero, called nodes, alternating with areas of maximum pressure, called antinodes. Thanks to this pressure distribution, small liquid or solid samples can be positioned in the pressure nodes, where they are held contactlessly by two sound-induced forces: the axial force and the radial force. The axial force acts in the direction of gravity and counteracts the gravitational force of the sample. The radial force acts perpendicular to the axis of levitation and compensates displacements of the sample in radial direction.

For the analysis, the view cell is flushed with CO_2, heated up to the

Table 1
Parameters of the density model [4] (Eqs. (1)–(5)) and the viscosity model [14] (Eqs. (15)–(18)).

Density model			Viscosity model				
Parameter	Unit	Value	Parameter	Unit	Acoustic levitator	Capillary viscometer	Dilchert [1]
A_1	kg/m^3	1037.9	B_1	mPas	3.72	2.20	4.20
A_2	$kg/(m^3 K)$	−0.0774	B_2	mPas/K	$-7.99\ 10^{-3}$	$-4.41\ 10^{-3}$	$-10.3\ 10^{-3}$
A_3	$kg/(m^3 MPa)$	23.61	B_3	mPas	$-3.61\ 10^{-5}$	$-1.31\ 10^{-5}$	$-6.36\ 10^{-5}$
A_4	$kg/(m^3 MPaK)$	−0.061	B_4	K	3975.26	3601.93	3834.63
A_5	kg/m^3	1.143	B_5	1/MPa	74.00	39.66	104.94
A_6	$kg/(m^3 K)$	−0.052	B_6	1/K	$1.70\ 10^{-2}$	$1.54\ 10^{-2}$	$1.84\ 10^{-2}$
A_7	$kg/(m^3 K^2)$	0					
A_8	1/MPa	1					
A_9	1/(MPaK)	1					
AARD	%	0.19	AARD	%	4.20	1.66	3.62

desired temperature and filled with CO_2 to the desired pressure. Then a squalane drop is injected into the pressure node using a screw press (6) and a capillary, which reaches through a bore in the reflector (2). After injection, the capillary is removed from the sound field using a swivel joint (3). When the drop is stably levitated, amplitude modulation of the sound wave is used to excite shape oscillations of the fundamental mode, which is characterized by axisymmetric oblate-prolate oscillations. After cessation of the amplitude modulation, the drop fulfills a damped oscillation where the damping constant depends on the drop's viscosity. The set-up is backlit by a light-emitting diode (LED) light source (5) and recorded by a high speed camera (4) (CR3000x2, Optronis, Germany) equipped with a macro lens and a tele-converter (EX 2.8/105 DG Macro NAFD OS HSM and TC-2001, Sigma GmbH, Germany).

A self-written Matlab code is used to determine the damping constant from the record. Besides viscosity, which correlates with the damping constant, the algorithm also delivers the interfacial tension, which correlates with the oscillation frequency. Viscosity is calculated with Eq. (7), as proposed by Lamb [7] with the damping constant τ (in s^{-1}), the density of the liquid drop ρ (in kg/m^3) and the radius of a sphere R (in m), whose volume is equal to that of the acoustically levitated, deformed drop.

$$\eta = \frac{\tau \cdot \rho \cdot R^2}{5} \quad (7)$$

The detailed procedure is described elsewhere [8]. As long as a precise length scale is known for the image recordings, no further calibration is needed for the acoustic levitation method. To determine the length of one pixel in a high speed video, a reference picture of a precision ruby sphere with a diameter of 2 mm ± 0.0025 mm (Goodfellow, England) is used.

For the measurement of the viscosity of gas-saturated liquids, it has to be ensured that phase equilibrium is reached. For acoustically levitated squalane drops in a CO_2 atmosphere, Baer et al. [9] study phase equilibria of this system at a temperature of 315.15 K and pressures between 0.5 MPa and 5.61 MPa using an acoustic levitator coupled with a Raman spectrometer. They also investigate the time needed to reach full saturation of a droplet with a volume of 2 μl, as typically used for the acoustic levitation method. Even for a medium pressure of 2.64 MPa, phase equilibrium is reached in less than five minutes. [9] Own attempts indicate, that the phase equilibrium is reached in less than one minute after injection into the pressure node for all pressures investigated.

2.2.2. Capillary viscometer

The capillary viscometer is designed for a pressure range from 0.1 MPa to 30 MPa and a temperature range from 293.15 K to 373.15 K. The set-up of the apparatus and the calibration procedure are described elsewhere for a similar capillary viscometer built in the same working group [10,11]. For the measurement with gas-saturated liquids, the viscometer has been extended with an additional saturation autoclave and a piston pump to enhance the dissolution process. The following paragraph covers a short description of the capillary viscometer and the saturation section.

The capillary viscometer (Fig. 2) consists of an oven, autoclaves (A and SA), heating wires (HW), temperature (T) and pressure sensors (P), a high precision differential pressure sensor (ΔP), connection blocks (B) and the capillary (C). All piping except for the capillary has an inner diameter of at least 3 mm to minimise pressure losses before and after the capillary. Both autoclaves (A) contain a hydraulically operated metal bellow which is connected to an electrically driven spindle press. By this means, volume can be shifted from one autoclave to the other, flowing through the measuring capillary. The volume flow is adjustable from 1 ml/min to 25 ml/min. The connection blocks on both sides of the capillary are connected to a differential pressure gauge (PCX-AII, Fuji, France) with a working range of 5 mbar–5000 mbar. The entire

measurement procedure is controlled and recorded by a program written in the software LabView. The devices were calibrated for the chosen conditions and the maximal uncertainties were estimated to be 0.31 K at maximum temperature, 0.25 MPa in absolute and 500 Pa in differential pressure.

The PT100 resistance thermometers used, were calibrated with ice water and with a reference PT100. The differential pressure sensor was calibrated with a reference pressure sensor with an accuracy of 50 Pa and the absolute pressure sensor with a pressure sensor was calibrated with an accuracy of 0.008 MPa.

For fluid flow in a circular capillary, Hagen-Poiseuille's law allows to calculate the dynamic viscosity of the fluid from the volume flow rate Q (in m^3/s), the pressure loss Δp (in Pa) and the length l and radius r (in m) of the measuring capillary.

$$\eta = \frac{\Delta p \cdot \pi \cdot r^4}{8 \cdot Q \cdot l} \quad (8)$$

Eq. (8) is valid for a single-phase laminar flow. All measurements were performed at Re < 200. To take into account the energy dissipation at the in- and outlet of the capillary Eq. (8) is expanded with the Hagenbach-Couette correction which leads to Eq. (9). [12] The correction factor m for square cut ends was chosen to be 1.12. [13]

$$\eta = \frac{\Delta p \cdot \pi \cdot r^4}{8 \cdot Q \cdot l} - \frac{m \cdot \rho \cdot Q}{8 \cdot \pi \cdot l} \quad (9)$$

The maximal influence of the energy dissipation on the viscosity was calculated to be less than 0.25 %. The density of CO_2 saturated squalane was taken from [5].

For the filling and saturation procedure, squalane is fed into the saturation autoclave (SA) while the rest of the plant is evacuated. With opening the connecting valve between the saturation autoclave and the plant, the squalane is distributed in the whole system. Beforehand the measurements with CO_2, measurements with pure squalane are carried out to calibrate the capillary radius as described in [11].

In preparation for the measurements with squalane and carbon dioxide, the system is heated to the desired temperature and the remaining void volume in the autoclaves is filled with CO_2 up the desired pressure. After that, squalane is continuously pumped from the lower outlets of all autoclaves to the upper inlets to accelerate the saturation process. Thereby, the saturation is improved by the increased contact area between the falling squalane droplets and the gas phase. To assure that saturation is reached, the viscosity is regularly measured during the saturation process until it attains a constant value. At 313 K and 10 MPa, which corresponds to the highest solubility measured for this work, phase equilibrium is reached within six hours. After saturation, the mixing pump (P) is stopped and it is waited for more than one hour in order to enable complete separation of the phases in case of gas bubbles in the liquid phase. To maintain only liquid phase in the measuring system, the squalane from the saturation autoclave (SA) is shifted into the autoclaves (A) while the gas is shifted back by using the installed valve-system. The volume shift is generated with the use of the spindle presses (S) to maintain only liquid phase in the measurement autoclaves. Without gas left in the system, a solution at higher pressures is prevented.

Due to its working principle, a capillary viscometer demands for a pressure drop to be measured. As a consequence one has to decide, where exactly the set pressure shall be during operation. For pure liquids, this place usually is at the half length of the capillary. For mixtures with gases, the pressure drop Δp may lead to wrong or misleading results as degassing may occur when the pressure drops under the saturation pressure p_{sat}. To avoid bubble formation, measurements have to be performed at a slightly higher pressure than the pressure the liquid had been saturated at. In our case, to guarantee one-phase flow, the system pressure before the measurement is set to a pressure of at least
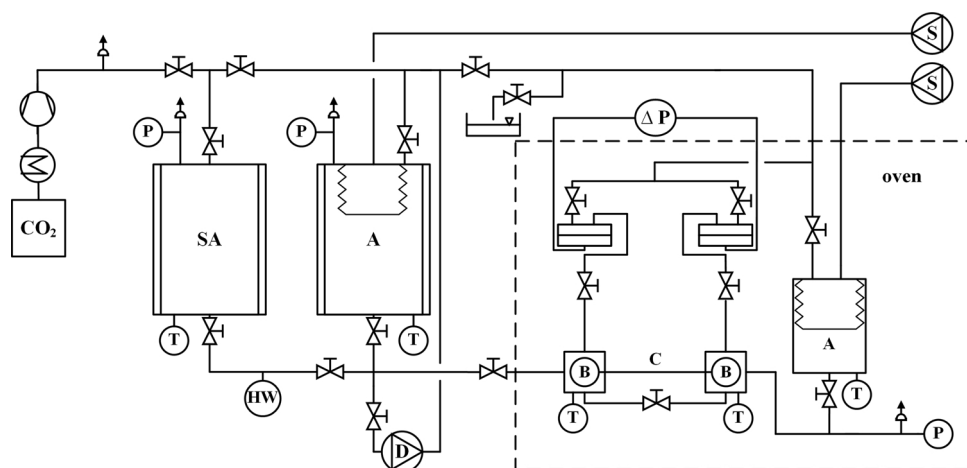
Fig. 2. Schematic principle of the capillary viscometer and the gas saturation section: (A) autoclave, (SA) saturation autoclave, (B) connection block, (C) capillary, (D) piston pump, (S) spindle press, (T) temperature sensor, (HW) heating wire, (P) pressure sensor, and (ΔP) differential pressure sensor.

$$p \geq p_{sat} + \frac{\Delta p}{2} \tag{10}$$

right before the spindle presses are started. The viscosity determined under these circumstances is not exactly the viscosity under saturation pressure, because even though the composition is not varied, viscosity slightly changes with the pressure. Therefore at least three measurements at different pressures slightly above p_{sat} are taken. The results of these three measurements are extrapolated to the saturation pressure using an e-function, which is typical for the dependency of viscosity on pressure, as shown in Fig. 5.

2.2.3. Rotational viscometer

The third apparatus used for viscosity measurements is a rotational viscometer (Rheostress RS75, Haake, Germany) equipped with a high pressure cell (PZ38b, Thermo Fischer Scientific, Germany) for pressures up to 40 MPa and temperatures up to approximately 573 K. The pressure cell has a bob and cup geometry with radii of 19 mm and 19.5 mm, respectively. The active length of the rotating cylinder is 80 mm. For a measurement, the pressure cell (cup) is filled with 32 ml of the sample, then the bob is inserted and the pressure cell is closed with a top lid. Two sapphire bearings at the bottom and top allow a rotation of the bob with very low friction. The top part is equipped with a magnetic coupling for a contactless connection of the enclosed bob with the viscometer. The two sapphire bearings must not be used without lubrication. Usually, a drop of the substance to be measured is used to lubricate the bearings.

Prior to the measurements, the pressure cell has to be calibrated to account for the unknown torque resulting from friction in the sapphire bearings, which depends on the viscosity of the lubricant. The viscosity of the lubricant depends on the temperature and, in the case of squalane in contact with CO_2, the amount of dissolved gas. The calibration is done according to the following procedure: The sapphire bearings are lubricated with a small amount of squalane. Then, the empty pressure cell is flushed with CO_2 for 30 s–60 s and afterwards heated up to the desired temperature. Then, CO_2 is filled into the pressure cell until the desired pressure is reached. After 12 h–14 h of rest, to account for the dissolution of CO_2 into the squalane used as lubricant, the torque is measured at different rotational speeds. The friction caused by the CO_2 in the pressure cell is neglected. This procedure is repeated for each temperature to be measured. A quadratic function (Eq. (11)) with parameters a, b and c is fitted to the torque data, which is used for the measurements to correct the torque M (in μN) as a function of rotation speed Ω (in min^{-1}).

$$M' = M - (a \cdot \Omega^2 + b \cdot \Omega + c) \tag{11}$$

For a measurement, 32 ml of squalane are filled into the pressure cell. Then, similar to the calibration procedure, the cell is filled with CO_2 and heated until the desired pressure and temperature conditions are reached. To speed up the saturation procedure, squalane is circulated from the bottom to the top of the cell by a HPLC pump (Waters 515 HPLC Pump, Waters, USA). When CO_2 dissolves in squalane, the pressure decreases and CO_2 has to be refilled. That way, the pressure is adjusted manually until it stays constant for several hours. This equilibration usually takes between 12 h and 24 h depending on temperature and pressure. Then, the HPLC pump is switched off. After one hour of rest, viscosity is measured. The measurement is repeated several times to test if viscosity and pressure stay constant. If changes in viscosity are smaller than 0.2 mPas between two measurements, which were made one hour apart, equilibrium is assumed to be reached and viscosity is measured in triplets at a shear rate of 200 1/s.

3. Results

To evaluate the reproducibility of viscosity measurement under high pressure, the expanded standard variation of the mean is used, which is calculated as follows. The arithmetic mean $\bar{x}$ of n individual measurements of the quantity x is calculated by the following expression.

$$\bar{x} = \frac{\sum\limits_{i=1}^{n} x_i}{n} \tag{12}$$

The experimental standard deviation s is determined using the following equation.

$$s(\bar{x}) = \sqrt{\frac{1}{n-1} \cdot \sum\limits_{i=1}^{n} (x_i - \bar{x})^2} \tag{13}$$

The expanded standard variation of the mean $U(\bar{x})$ is calculated with Eq. (13) using the Student's

t-distribution adjusted for the sample size and a level of confidence of 95.5 %.

$$U(\bar{x}) = t \cdot u(\bar{x}) = \frac{s \cdot t}{\sqrt{n}} \tag{14}$$

The standard variation of the mean calculated with Eqs. (12)–(14) will be applied in the following as the uncertainty of the measurement.

3.1. Acoustic levitation

Viscosity of CO_2-saturated squalane using acoustic levitation is measured at temperatures of 313 K, 333 K and 353 K and at pressures

between 0.1 MPa and 10 MPa. Every data point is the average of at least 15 individual measurements. To compare the experimental data to literature data and to interpolate viscosity to different temperatures and pressures, we used an empirical model proposed by Seifried [14] for the viscosity of CO_2-saturated fish oil and fitted the constants to our data. This model expresses the dynamic viscosity as a function of pressure and temperature using six parameters. The model consists of Eqs. (15)–(18), which are fitted to viscosity data (in mPas) as a function of pressure (in MPa) and temperature (in K) [14].

$$\eta(p, T) = \eta_\infty(T) + [\eta_0(T) - \eta_\infty(T)] \cdot e^{(-k(T) \cdot (p - 0.1 MPa))} \quad (15)$$

$$\eta_\infty(T) = B_1 + B_2 \cdot T \quad (16)$$

$$\eta_0(T) = B_3 \cdot e^{(B_4/T)} \quad (17)$$

$$k(T) = B_5 \cdot e^{-B_6 \cdot T} \quad (18)$$

The model is based on the assumption, that viscosity asymptotically reaches a constant value at high pressures, which is temperature dependent. This value depends on temperature with a linear relationship (Eq. (16)). Eq. (17) describes the exponential decrease of viscosity with temperature at atmospheric pressure. The viscosity is reduced exponentially as the gas-content is increased with the pressure. This decline is described with Eq. (18) [14].

The results of viscosity determination with the acoustic levitator are shown in Fig. 3. The points show the experimentally determined values, whereas the lines are functions fitted with the model (Eqs. (15)–(18)) at the respective temperatures. The error bars indicate the uncertainty of measurement calculated with Eqs. (12)–(14).

As expected, the viscosity decreases with increasing temperature. The results show that an increase in either temperature or pressure reduces the viscosity of the CO_2-saturated squalane. At 313 K, the viscosity decreases from initially 14.94 mPas at 0.1 MPa to 1.60 mPas at 10.0 MPa. The viscosity at 353 K changes from 4.57 mPas at 0.15 MPa to 1.57 mPas at 10.1 MPa. Obviously, the effect of temperature lessens with increasing pressure. The fitted curves match quite well with the measurements, as indicated by an AARD of 4.20 %. The parameters found for the model equations are summarized in Table 1.

3.2. Capillary viscometer

Squalane saturated with CO_2 was measured in the capillary viscometer at pressures from 0.1 MPa to 10.1 MPa and temperatures of 313 K and 353 K. The viscosities at saturation pressure, as shown in Fig. 4, were extrapolated from at least three measurements at higher pressures in the undersaturated region. Each point in the
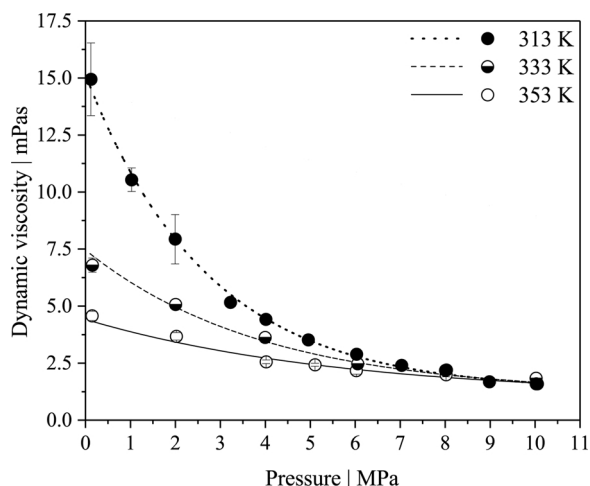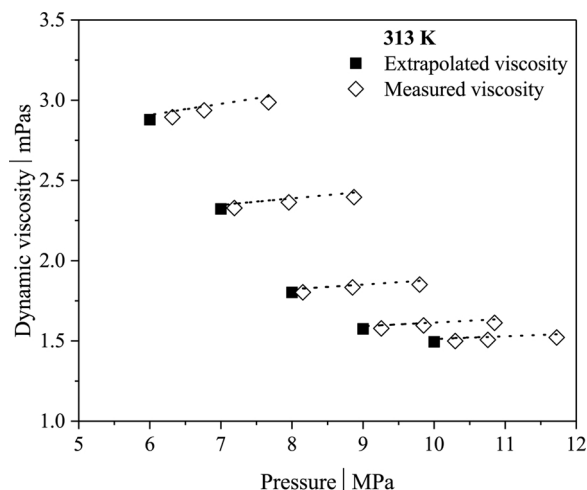

Fig. 4. Dynamic viscosity of undersaturated squalane with dissolved CO_2: undersaturated viscosities used for extrapolation to saturation pressure (open symbols) and calculated viscosities at saturation pressure (closed squares).

undersaturated region was calculated as the mean of three different measurements taken under the same conditions (p, T, Q).

Fig. 4 shows the measured points between 6 MPa and 12 MPa (open symbols) used for the extrapolation to the viscosity at saturation pressure (closed squares). The results from the extrapolations are shown in Fig 5.

The results in Fig. 5 show the decrease of the dynamic viscosity with increasing pressure. The uncertainty included is smaller than the symbols. The viscosity at 313 K ranges from 14.74 mPas at 0.185 MPa to 1.51 mPas at 10.1 MPa. At 353 K, the viscosity is lower, ranging from 4.65 mPas at 0.1 MPa to 1.36 mPas at 10.1 MPa. The values for this curve were measured using two different stainless steel capillaries. For viscosities above 11 mPas, a capillary with an inner diameter of 0.64 mm and a length of 345 mm was used. Viscosities smaller than 11 mPas were measured in a capillary with an inner diameter of 0.259 mm and a length of 350 mm.

The dotted and full lines represent the fitted curves at 313 K and 353 K, respectively. The fitted curves, with the parameters for the model equation summarized in Table 1, match the measurements with an AARD of 1.66 %.
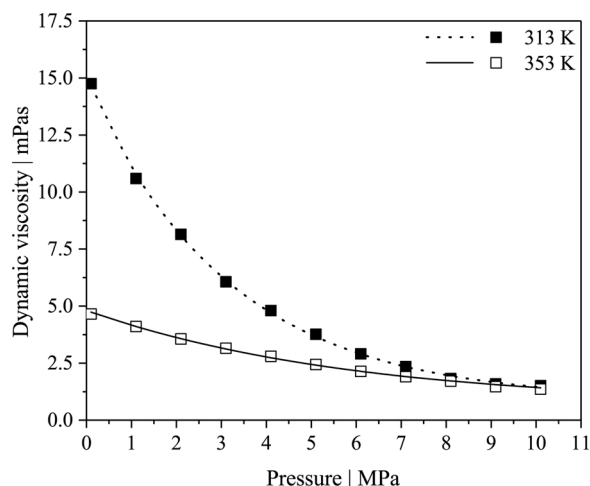

Fig. 3. Viscosity of CO_2-saturated squalane determined with acoustic levitation as a function of pressure at temperatures of 313 K, 333 K and 353 K.

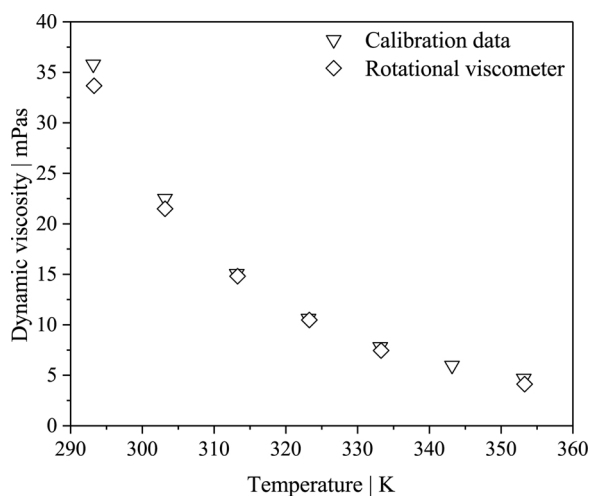**Fig. 5.** Dynamic viscosity of squalane saturated with CO_2 determined with a capillary viscometer.

Fig. 6. Dynamic viscosity of squalane measured with the rotational viscometer in comparison to calibration data.

Fig. 8. Dynamic viscosity of CO_2-saturated squalane: comparison of acoustic levitator (AL), capillary viscometer (CV) and rotational viscometer (RV) to literature data [1] at 313 K.

3.3. Rotational viscometer

Additionally, viscosity of CO_2-saturated squalane was measured at temperatures of 313 K and 353 K and pressures of 0.15 MPa, 5.1 MPa and 10.1 MPa using a conventional viscometer with a bob and cup geometry. Previously, the accuracy of the same geometry was evaluated under ambient pressure. The viscosity of pure squalane at different temperatures measured with the rotational viscometer is compared to calibration data at 293.15 K, 303.15 K, 313.15 K, 323.15 K, 333.15 K and 353.15 K obtained with a high precision Ubbelohde viscometer by a calibration institute (ZMK Wolfen, Germany) (Fig. 6).

As expected, the viscosity of pure squalane under ambient pressure decreases with rising temperature. The experimental values are in good agreement with the calibration data, because the data obtained with the rotational viscometer show deviations between 1.3 % and 7.5 % from the calibration data. With decreasing viscosity the percentage deviation between the measured and the calibration data increases up to 12 % for a viscosity of 4.6 mPas. The lower limit of the measurement range of the high pressure cell for the rotational viscometer is 1 mPas. If the measured viscosity approaches this limit, the error in viscosity measurement increases.

Fig. 7 shows the results for the viscosity of CO_2-saturated squalane at temperatures of 313 K and 353 K and pressures of 0.15 MPa, 5.1 MPa and 10.1 MPa. The error bars calculated with Eqs. (12)–(14) are too small to appear.
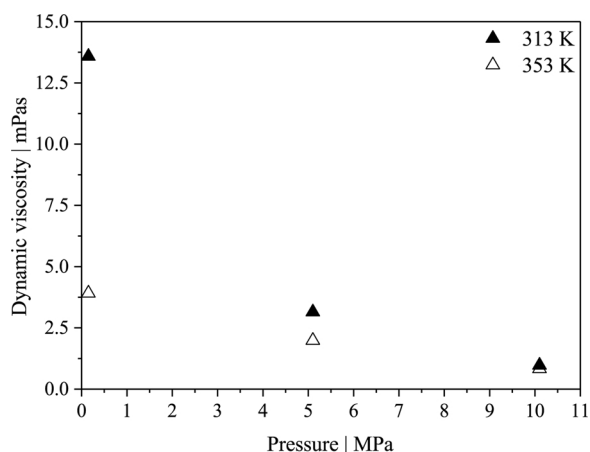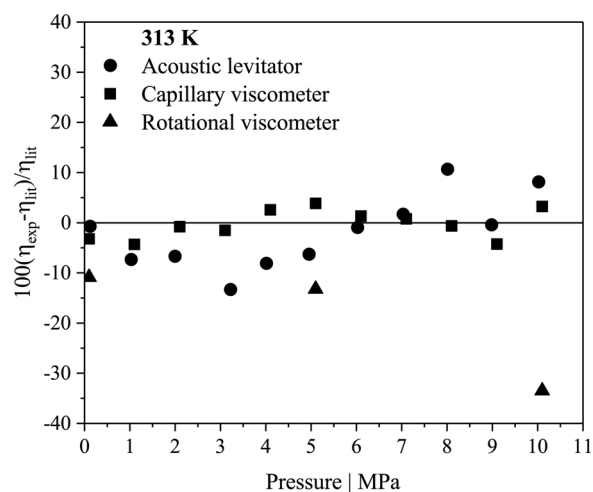

Fig. 7. Viscosity of CO_2-saturated squalane determined with the rotational viscometer as a function of pressure.

4. Discussion

Three different types of viscometers were used to determine the viscosity of liquid squalane saturated with CO_2 at temperatures of 313 K and 353 K and pressures between 0.1 MPa and 10.1 MPa. One of these methods, a new measurement method based on acoustic levitation, is compared to the other two conventional methods, a capillary and a rotational viscometer. To validate the generated data, literature values by Dilchert [1] for the same system are used. To interpolate between the data points by Dilchert, his data were approached with the model presented in Eqs. (15)–(18) with an AARD of 3.62 %. Fig. 8 shows the deviation of viscosity data as a function of pressure measured with the acoustic levitator (AL), the capillary viscometer (CV) and the rotational viscometer (RV) at a temperature of 313 K in comparison to literature data [1]. The data measured with the AL, CV and RV are compared to literature data by Dilchert [1], who studied the system squalane-CO_2 with a spring-bellows-capillary viscometer at 0.1 MPa, 5 MPa and 10 MPa.

Viscosity was measured in steps of 1 MPa from 0.1 MPa to 10.1 MPa with the AL and the CV. For comparison, measurements with the RV were taken at pressures of 0.15 MPa, 5.1 MPa and 10.1 MPa. All measured data show the same course of decreasing viscosity as the pressure, and thereby the mass fraction of gas, is increased. For pressures between 2 MPa and 6 MPa the data from the AL deviate by 6 % to 15 % from the measurements of the CV. For pressures lower than 2 MPa and higher than 6 MPa, this deviation is in the range from 0.5 % to 5.7 %. Therefore, the data measured with the AL and the CV are in good agreement. The deviations may result from the density values used. These were taken from Hiller [5] and interpolated using Eqs. (1)–(5). Hiller estimates the uncertainty in density measurement to be lower than 1 % in the liquid phase. The AARD for the density model is 0.19 %. The AL measurements are influenced by errors in density measurement with a linear dependency (Eq. (7)). For the CV data, the density of the liquid only appears in the correction term (Eq. (9)). Therefore, the influence of the error in density measurement on the AL data is higher than for the CV data, where the error in density is negligible. In addition, the uncertainty of the viscosity values measured with the AL is higher than for the other viscometers especially at pressures between 0.1 MPa and 2 MPa. This may result from temperature fluctuations caused by the sound field inside the high pressure view cell of the AL. For higher pressures, the uncertainty is in the same range for all three methods. The values made with the RV are lower than the measurements made with the AL for all pressures investigated. The deviations between the values of the RV and the AL increase with increasing
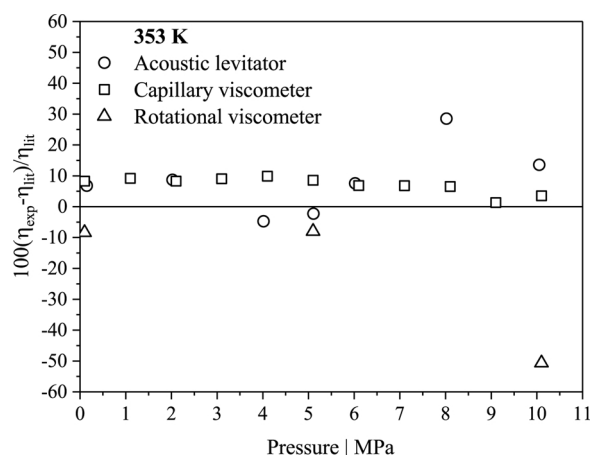
Fig. 9. Dynamic viscosity of CO_2-saturated squalane: comparison of acoustic levitator (AL), capillary viscometer (CV) and rotational viscometer (RV) to literature data [1] at 353 K.

pressure. For a pressure of 0.1 MPa the deviation between the viscosity results of the RV and the AL related to the value of the AL is 9.1 %. At a pressure of 10 MPa, this deviation amounts to 39 %.

Comparing the results of the CV and the RV, the viscosity measured with the RV is also lower than the viscosity measured the CV for all pressures investigated. The deviation is in the range of 8 % at 0.1 MPa to 35 % at 10 MPa related to the value of the CV. This shows that the high pressure cell used for the experiments with the RV does not work satisfactory for the determination of viscosities lower than 5 mPas.

The measured data and the model fitted to literature data show the same course over pressure. In average, the AL data deviate by 5.8 % from literature values. Therefore, these data are in good agreement. As for the comparison between the AL and the CV, the deviation between experimental and literature data has a maximum at medium pressures between 1 MPa and 4 MPa. This deviation can be explained by the temperature fluctuations in the high pressure view cell of the levitator. Deviations may also occur, because Dilchert [1] mentions the degassing of the squalane prior to the measurements, but the detailed procedure is not given. In this investigation, the squalane is used as received.

Fig. 9 compares the viscosity data generated with the acoustic levitator (AL), the capillary viscometer (CV) and the rotational viscometer (RV) with the viscosity data by Dilchert [1] at 353 K. The data measured with the RV were measured at pressures of 0.1 MPa, 5.1 MPa and 10.1 MPa.

The dynamic viscosity as a function of pressure measured by the AL, CV and RV in Fig. 9 shows a similar behaviour of the data measured at 313 K. The viscosities gauged with AL deviate from the curve fitted to the literature data by 10 % in average, which is higher than the deviation at 313 K (5.8 %). The CV data deviate by 7 % to literature values, which is higher than at 313 K (2.9 %).

5. Conclusions and outlook

Viscosity measurements of CO_2-saturated liquid squalane at temperatures of 313 K, 333 K and 353 K and pressures between 0.1 MPa and 10.1 MPa with a new method based on acoustic levitation are presented. Viscosity is determined under high pressure from decaying shape oscillations of acoustically levitated drops. To evaluate this method, comparative measurements using a capillary and a rotational viscometer are carried out at temperatures of 313 K and 353 K and at pressures between 0.1 MPa and 10.1 MPa. It has been shown, that the measurement of viscosity of gas-saturated liquids with the presented capillary viscometer yields reliable data. Nevertheless, measurements with this method are time-consuming due to the long saturation time of squalane with CO_2, which takes several hours although squalane is

pumped in a circle to accelerate saturation. Furthermore, an amount of 1 l of substance is needed to fill the three autoclaves. Prior to the measurements, the radius of the capillary has to be determined with high precision, which is time-consuming. The rotational viscometer equipped with the high pressure cell fails to measure low viscosities in the range of 1 mPas. The viscosities measured with the rotational viscometer are drastically lower than those determined with the capillary viscometer. The deviation between the capillary viscometer and the rotational viscometer is in the range of 7.9 % at 313 K and 0.1 MPa up to 42.6 % at 353 K and 10.1 MPa related to the value of the capillary viscometer. Measurements with the rotational viscometer are also time-consuming due to the saturation time, which is in the range of several hours, and the need for calibration prior to the measurements because of the additional torque caused by the sapphire bearings.

The results measured with the acoustic levitator are in good agreement with the values obtained with the reliable capillary viscometer with an average deviation of 6 % to 10 %. In addition, the viscosity results of the AL for the system squalane-CO_2 are in agreement with literature values [1]. As mentioned previously, the main advantage of an acoustic levitator for viscosity measurement of gas-saturated liquids under high pressure in comparison to capillary or rotational viscometers is the short saturation time of less than five minutes (usually hours to days). Measurement time is also reduced compared to conventional methods, because the acoustic levitator needs no calibration prior to the measurements. Only a reference picture of a reference sphere with precisely known diameter is required for the image analysis. Furthermore, the amount of required substance is very small (1 μl–5 μl) compared to conventional methods. As an additional benefit, interfacial tension of the system investigated can be deduced from the frequency of oscillation without further effort. Therefore, acoustic levitation offers the unique possibility to measure two important thermophysical properties simultaneously under high pressure. Regarding these advantages, it is concluded, that acoustic levitation is a promising method for the characterization of high pressure systems. Although the results deviate by about 6 % to 10 % from those made with the approved capillary viscometer, the measurement time is reduced. At the moment, viscosity measurement with acoustic levitation under pressure is restricted to Newtonian liquids due to the lack of knowledge about the shear rate in the drop. Some approaches regarding the measurement of viscoelastic liquids with acoustic levitation under ambient conditions are reported in literature [15–18]. In our future work, these methods will be adapted to high pressure systems to determine viscosity of viscoelastic liquids under pressure.

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