EXPERIMENTAL SETUP FOR MEASURING THE THERMAL CONDUCTIVITY OF PRESSURIZED SOLUTIONS

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Knowledge about the thermal conductivity is expedient whenever heat transport is involved in a process. As pressure plays an important role in a multitude of treatments or reactions, conductivity measurements have also been carried out under pressure for various substances (e. g. lubricants, plant oils and several foods). Experimental data are needed as this property cannot be derived from equations of state. Nevertheless, data about thermal conductivity of pressurized fluid mixtures are scarce.

Hence, an apparatus appropriate for measuring thermal conductivities of dense and supercritical solutions under pressure was set up in this work. The applied principle of measurement is based on transient heat transfer. A line heat source was used as the probe and the maximum slope evaluation method without the need for calibration was applied.

The thermal conductivity of polydimethylsiloxane (Mw = 11000 g/mol) has been found to increase under helium pressure and the results were in good agreement with comparison values obtained by a hot-wire method. Consequently, first measurements on polydimethylsiloxane saturated with gaseous carbon dioxide were carried out at 25 °C. In this case, the conductivity decreased in the investigated pressure range up to 5 MPa.

INTRODUCTION

Information about the thermal conductivity of mixtures is not only important for different industrial processes but is also of scientific interest. Therefore, different measurement methods have been developed. As for fluids the accuracy of steady heat flow techniques is restricted due to natural convection effects, transient methods are widely used in this regard. In principle, an object is heated with a constant energy and at the same time its temperature increase is monitored. The thermal conductivity of the surrounding medium is then obtained by solving the instationary heat transfer equation according to Fourier's law. The maybe most popular probe based on this principle is the well-known transient hot-wire. The underlying idea is an infinitely long, straight and infinitely conducting continuous line source in an infinitely large specimen. A corresponding analytical solution to Fourier's law and detailed information about the application of the hot-wire can be found in the literature [1, 2].

As these probes are easily damaged and thus are difficult to apply in some cases due to physical constraints, the more robust line heat source was developed [3]. A commonly used assembly consists of a tubular housing which contains a heater wire and a separate thermocouple to measure the temperature rise. Examples for the application of the line heat source on fluids under ambient pressure are polymer melts [4] and ionic liquids [5]. Concerning elevated pressure, it has been used on several foods [6, 7].

To the authors' best knowledge no data about the thermal conductivity of gas saturated pressurized solutions is available in the literature. Therefore, it was the aim of the present work to establish and test a setup for performing measurements in this regard. To check the operational capability of the probe and data evaluation method, thermal conductivities of polydimethylsiloxane (PDMS) were determined at 25 °C at ambient pressure and under helium pressure up to 14.3 MPa without calibration. A comparison to hot-wire measurements under static pressure yielded absolute deviations of less than 4 %. Thus, it was assumed that the applied measurement method is capable of determining absolute thermal conductivities within an acceptable error range.

First measurements on PDMS which was saturated with gaseous carbon dioxide were carried out at 25 °C thereafter. In contrary to the results under helium pressure, the conductivity was found to decrease in this case with an increasing pressure.

MATERIALS AND METHODS

Materials. A PDMS sample with a viscosity of 145 mPas was obtained from Wacker (Munich/Burghausen, Germany) and used as received. Gel permeation chromatography with toluene as solvent was performed to determine both the molecular weight and the polydispersity. The analytic system was a Viscotek GPCmax equipped with a TDA 305 triple detector (refractive index, light scattering and viscosity). Absolute molecular weights were calculated by applying the typical value of -0.89 ml/g of the refractive index increment dn/dc for PDMS in toluene. The resulting molecular weight was 11000 g/mol and the polydispersity was 1.8.

Carbon dioxide was obtained from Yara Industrial (Dülmen, Germany) with a purity of 99.9 % v/v. It was dried using zeolites to reduce the water content to approximately 5 ppm v/v. Helium was supplied by Air Liquide (Düsseldorf, Germany) with a purity of 99.995 % v/v.

Probe and plant. A custom fabricated probe was applied in this work (East 30 Sensors, Pullman, USA). The probe's housing is a thin walled steel tubing with an outer diameter of 1.27 mm. The length to diameter ratio of the probe is 47.2. Inside the tube are a heater wire with a resistance of 1041.5 Ω/m and a thermocouple. The wires are fixed within the tube with thermally conductive epoxy resin. As the heater wire is made of Evanohm its resistance is assumed to be constant over the investigated pressure range [8]. The chosen thermocouple is of the type E because of its high Seebeck coefficient of 62 µV/K [9]. A Knick DC-calibrator J 152 (Knick, Berlin, Germany) was used as current source and connected to the heater wire. A Keithley 3706 data acquisition system with a type 3721 multiplexer card was applied to measure the thermocouple's voltage (Keithley, Munich, Germany). The thermocouple's reference junctions were immersed in an ice bath to achieve a higher accuracy of the temperature measurement.

Regarding the connection of the sensor to the pressure plant, it is soldered into a 1/8" steel tube. This allows it to be connected to a high pressure view cell with a commercially available gland (Hy-Lok, Oyten, Germany). The applied cell exhibits an inner diameter of 3 cm and an approximate volume of 500 cm³. Windows in the high pressure cell allow to assure visually that conduction and not natural convection is the controlling heat transfer mechanism during the test time. The probe was mounted at the bottom of the vessel (Figure 1).
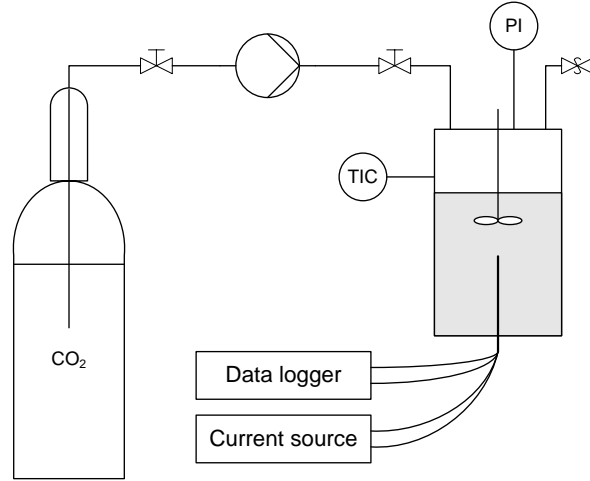
Figure 1. Experimental set-up

The cell is heated electrically by four heating rods which are placed vertically in its cylindrical shell. A PID controller is used to control the temperature. For applying the desired operating pressure, the cell is either charged with carbon dioxide or helium. In the case of CO_2, a diaphragm high pressure dosing pump (FIRMA, ORT, LAND?) was used to achieve the desired pressure. Helium was taken directly from the gas cylinder as the pressure was sufficiently high.

Measurement procedure. Before an experimental series the cell was charged with PDMS, evacuated for 20 minutes and heated to the operating temperature. Then, pressure was applied either with helium or CO_2. When CO_2 was used, the cell was stirred for approximately 5 minutes to mix the phases well. The following temperature equilibration and phase settling took about 20 minutes and the conductivity measurements were started thereafter. Helium was used to apply a quasi-static pressure. Thus, the cell was not stirred then to prevent dissolution of helium in the PDMS. The measurements began directly after the temperature became stable again.

For the conductivity measurement the current source was activated manually with a current value corresponding to the desired heating energy. At the same time, the temperature increase of the probe's thermocouple was recorded at 0.25 s intervals. The heating circuit's voltage was also monitored with the same frequency to determine the start time of heating. Heating energies between 0.5 and 3.0 W/m have been found to deliver smooth time-temperature responses during tests in PDMS at 25 °C and at ambient pressure.

Data reduction. The maybe most common method for determining the thermal conductivity from the measurement data is to evaluate the linear part of the temperature plotted against the natural logarithm of time. This method is based on the idea of an ideal line source for which the temperature rise is linear with the natural logarithm of time. A detailed derivation can be found in the literature [1]. Consequently, the following simplified working equation has been developed [3] to evaluate the linear portion of the plot in dependence of the heating energy Q to determine the thermal conductivity λ:

(1)

$$\Delta T = \frac{Q}{4\pi\lambda} \ln\left(\frac{t_2}{t_1}\right)$$

The disadvantage of this method is that it requires calibration and that the calibration factor depends on the ratio of the sensor's and the specimen's thermal masses. Best results are obtained with a calibration material of the same thermal mass ratio as the later specimen [10]. Due to pressure and gas dissolving effects, the thermal mass of the sample may change drastically and calibration with a single calibration material is hardly possible.

Thus, the maximum slope method developed by Asher et al. [11] was applied to determine the thermal conductivity in this work. It has been found that the method does not require calibration and evaluates the absolute thermal conductivity with an accuracy of better than 5 % for liquids with a viscosity of more than 3 mPas. It was also tested successfully on glycerol as a higher viscous sample for probes with a length to diameter ratio greater than 30 with an accuracy of 2 % [12, 13]. The viscosity of the sample and the length to diameter ratio of probe in this work are within these ranges.

As the method's name indicates, the maximum of the slope of the temperature plotted against the natural logarithm of time is evaluated. The following figure shows a sample temperature measurement curve and its according slope.
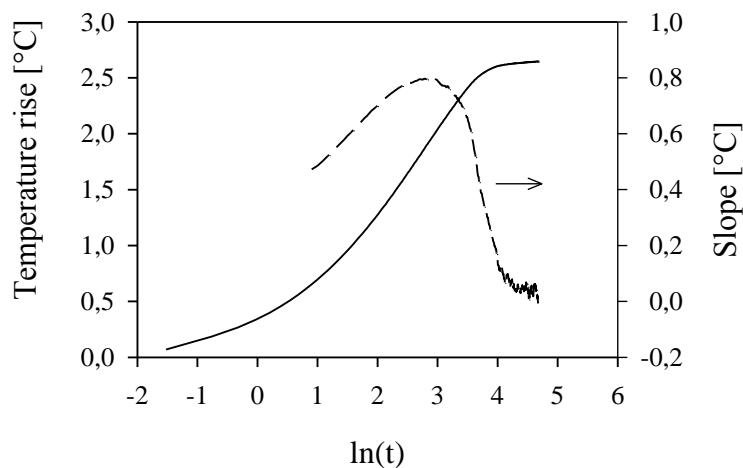

Figure 2. Sample measurement curve and slope recorded at 5 MPa and 25 °C in CO_2-saturated PDMS with a heating energy of 1.5 W/m

The slopes have been obtained through successive linear regression analysis with 19 data points to estimate each slope value. The thermal conductivity was then calculated with the maximum value according to equation 1. The slope appears there as temperature rise between two times in the natural logarithmic scale.

RESULTS

Generally, an increasing thermal conductivity was found in the measurements on PDMS under helium pressure. The maximum increase was 2.7 % at 7.5 MPa compared to the value at ambient pressure. The standard deviation of three subsequent measurements with a heating energy of 3.0 W/m was below 0.6 % for all pressure steps.

It is assumed that the helium amount which diffuses into the PDMS is negligible small and that the pressure can be considered as static. This assumption is supported through the fact that during the decompression from the maximum pressure of 14.3 MPa to ambient pressure gas nuclei emerged at the phase interface but not near the probe. This indicates that the sensor was sufficiently deep immersed in the oil phase to prevent notable helium diffusion effects.

Comparison measurements have been carried out on the same PDMS sample under static pressure using a hot-wire method (Flucon, Clausthal-Zellerfeld, Germany). The comparison values show the same dependency on pressure and deviate less than 4 % from the results of this work (Table 1). The applied absolute deviation (AD) is defined as the following:

(2)

$$AD = \frac{\lambda_{\text{experimental}} - \lambda_{\text{comparison}}}{\lambda_{\text{comparison}}}$$

Table 1. Measurement on PDMS under helium pressure at 25 °C with a heating energy of 3 W/m and comparison to hot-wire results under static pressure.

Pressure (MPa)	Exp. mean (W/(mK))	Standard deviation (W/(mK))	Comparison value (W/(mK))	AD (%)
0.1	0.1561	0.0002	0,1584	-1,5
5.0	0.1577	0.0009	0,1615	-2,4
7.5	0.1602	0.0008 [1]	0,1625	-1,4
10.0	0.1582	0.0009	0,1642	-3,6
14.3	0.1598	0.0007	0,1662 [2]	-3,8

[1] The standard deviation refers to four single measurements   [2] Interpolated value

The results suggest that the used probe and data reduction method allow determining absolute thermal conductivities within an accuracy of 5 % which is stated in the literature [11]. Subsequently, measurements on CO_2-saturated PDMS under pressure have been carried out. The measurement values and standard deviations under CO_2 pressure were obtained from three single experiments with a heating energy of 1.5 W/m. In contrast to the latter experiments, a decrease in conductivity with an increasing pressure was found (figure 3).
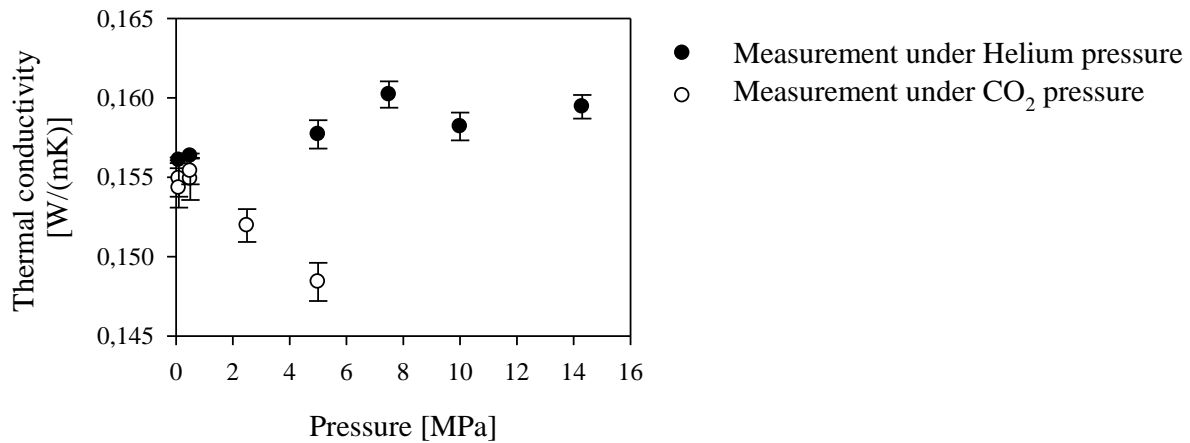

Figure 3. Influence of CO_2 and helium pressure on the conductivity of PDMS at 25 °C

Additional measurements with heating energies of 0.5 and 3 W/m were carried out at every pressure step and the resulting conductivities coincided within the standard deviation. Generally, higher heating energies cause natural convection to appear earlier and stronger. As the heat removal by natural convection is not considered in the underlying data evaluation method, these effects lead to a higher calculated thermal conductivity. Accordingly, the consistent results at different heating energies indicate that the influence of convective effects can be neglected in the investigated pressure range up to 5 MPa. Besides this fact, no visual indications of natural convection were observed.

Measurements with PDMS and CO_2 at pressures above 5 MPa were not successful due to convection and demixing effects in a boundary layer at the sensor. The calculated thermal conductivities depended on the heating energy for the reason as explained above. Therefore, it is planned to execute future experiments at even lower heating energies to prevent this effect.

CONCLUSION

A new experimental setup for determining the thermal conductivity of saturated solutions under pressure with a line heat source has been established. To check the measurement method, the results of this study on a PDMS sample ($M_W = 11000$ g/mol) under helium pressure have been compared to hot-wire measurements under static pressure. Both methods' results deviated less than 4 % and show the expected increase in conductivity with pressure. Subsequent measurements on the dense phase of mixtures containing PDMS and gaseous CO_2 revealed a decreasing thermal conductivity in the investigated pressure range up to 5 MPa at a temperature of 25 °C.
Investigations in a broader pressure and temperature range will be carried out in the near future. Furthermore, effort is currently underway to equip the apparatus with a hot-wire probe for a comparison of methods.

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