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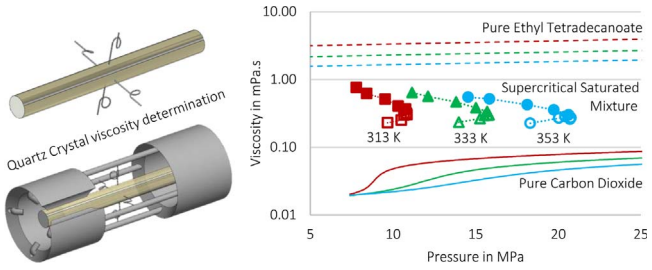
Concurrent measurement of high-pressure binary phase equilibrium, density and dynamic viscosity

H.H. Franken, J.H. Knoetze, C.E Schwarz*

Department of Process Engineering, University of Stellenbosch, Private Bag X1, Matieland, 7602, South Africa

GRAPHICAL ABSTRACT



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ABSTRACT

New equipment offering a novel combination of concurrent binary phase equilibria, saturated fluid density and dynamic viscosity determination, was developed. The setup (P_{max} 30 MPa; Tmax 393 K) includes a variable volume view cell to determine bubble/dew points and density, with a quartz-crystal resonator to measure dynamic viscosity. Phase equilibrium is determined visually, using a synthetically known composition (SynVisVar). Uncertainties in measurements are 0.06 MPa in pressure, < 0.0005 in mass fraction, and 0.2 K in temperature. Density is calculated to within < 0.003 of the value. The dynamic viscosity is determined by measuring the frequency shift over the quartz crystal, to within < 0.01 of the value. Equipment verification was done using n-dodecane and benzene at 0.1–30 MPa and 313–353 K while contributing to available benzene literature. Binary equilibrium measurements were verified using CO2 + ethyl tetradecanoate while presenting new data on the dynamic viscosity and density of the saturated binary phase.

1. Introduction

A need for comprehensive equipment sizing and design methods for supercritical processes has become ever more pronounced. To develop these methods a fundamental understanding of the mass transfer and transport phenomena in supercritical systems is required, each discussed separately below. Potential mass transfer in a system is determined by the system's phase equilibria, indicating the viability of separation and, if separation is possible it quantifies the driving force behind said separation. Mass transfer addresses design concerns such as the operating pressure, temperature and method specific considerations, such as the required number of separation stages in a separation column [1]. Mass transfer alone is, however, not sufficient when accounting for the physical size and geometry of equipment. To address this, the transport phenomena are investigated, with a particular focus in this study on physical properties and the dependent fluid dynamics. Fluid dynamic properties (e.g. density and viscosity), along with the potential equipment size and geometry, can be used to calculate the operating regime/range and the efficiency of a system. Efficiency and operating range are essential in design considerations, highlighting the

* Corresponding author.
E-mail address: cschwarz@sun.ac.za (C.E. Schwarz).

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associated importance of the fluid properties of density and viscosity [2]. In the supercritical regime, these fluid properties undergo substantial changes with small changes in temperature and pressure, significantly affecting fluid dynamics, which in turn requires revision and adjustment of design methodology and equipment geometry. These properties can also not easily be predicted using standard models [3].

Preciously little research on fluid properties and fluid dynamics under supercritical conditions has been done to date [4]. When investigating fluid dynamics with equipment sizing and design methods in mind, the fluid properties must be known and other transport phenomena, such as mass- and heat transfer, should be eliminated or fully quantified. This implies that phase equilibria and fluid property data are required to make informed decisions and reasonable deductions, necessitating their combined accurate measurement.

This paper aims to present and verify a new piece of equipment, proposing a novel combination of an established phase equilibrium determination method (dew/bubble point), supplemented with density and viscosity measurement at the point of equilibrium. To validate the equipment, the viscosity and density methods are used to gather pure component data for n-dodecane and benzene for comparison with the literature, while contributing a higher resolution of data points at comparatively low temperatures and pressures. The equipment is then validated for the measurement of binary phase equilibria, using CO_2 + ethyl tetradecanoate, with new density and dynamic viscosity data for this binary system. The developed equipment simplifies and accelerates data acquisition towards further study into fluid dynamic properties by the concurrent measurement of properties. This ultimately provides a basis for equipment sizing and design methods to be developed, with future work aimed at fluid dynamics in packed columns operating under supercritical conditions.

Each of the measurement aspects of the equipment is discussed separately below.

1.1. Phase equilibria

Many different methods are used to measure high-pressure phase equilibria with no single method being superior [5]. The measurement of phase equilibria is typically divided into analytical and synthetic methods. In analytical methods, the composition of the equilibrium phases is determined through a qualitative measurement at a defined state. Synthetic methods investigate a mixture with a known composition, by manipulating the system's intensive properties to achieve equilibrium. Both methods are further subdivided into several subcategories. Interested readers are directed to the work of Dohrn, et al. [5].

For this study, a high-pressure, variable volume cell was selected. This cell is comparably inexpensive to manufacture and simple to operate, providing a robust, flexible, and above all, tried and tested solution. The cell is equipped with a sight glass to visually observe and determine phase changes, in accordance with a synthetic-visual (SynVisVar) method. The operating procedure for such a cell is described in full by Schwarz and Nieuwoudt [6] and more recently in brief by Fourie, et al. [7].

1.2. Viscosity

Viscosity is measured by applying a shear force to a fluid and measuring the resultant rate of deformation. Knowledge of a fluid's viscosity provides insight into the frictional forces during fluid transport, the turbulence of and mixing behaviour in a fluid, and falling film thickness, to name a few.

Viscosity measurement technology for the equipment has to conform to a few requirements. Firstly, the method must be capable of measuring saturated fluids under high pressure/supercritical conditions. Secondly, a nondisruptive measurement method is required, as any significant disturbance may potentially upset the phase equilibrium at the point of measurement [8]. Thirdly, the measurement method has to be integrated into a device concurrently measuring the phase equilibria and density of the same fluid state.

Applying these metrics, most of the commonly used techniques can be dismissed out of hand. Capillary tube viscometers can measure under high pressures but present several practical challenges. A rotational rheometer can provide high accuracy, but presents mechanical sealing problems. Falling body or falling ball viscometers are commonly used, but present challenges to the accurate release, timing and detection of the falling body, with the range of shear rates limited by the size and geometry of the falling objects available. This leaves vibrational viscometers, such as the vibrating wire and crystal [9].

The vibrating wire technique requires a wire, of known mass and dimensions, to be clamped between two fixed supports. The wire is suspended in a permanent magnetic field and excited by passing an AC signal through the wire, as per Faraday's Law. The wire can measure both viscosity and density through knowledge of the wire density, −geometry and −tension and the resonance frequency and bandwidth generated [10].

The vibrating crystal technique exploits the converse piezoelectric effect of a quartz crystal, with a mechanical vibration induced in the crystal by a changing electrical field. The measurement principle is similar to that of a quartz microbalance (used in high accuracy scales), with the crystal resonance frequency shifting when a load, such as mass or viscous drag, is applied to the crystal. This method has been proven reliable up to 1000 MPa and 373 K for pure organic liquids [11], with method variables and constants effectively independent of pressure in the region of interest [12]. Density can also be derived from the crystal setup if the resonance bandwidth is measured, although this requires precise impedance analysis.

After consideration, the quartz crystal technique was selected. Firstly, it provided less variability compared to the vibrating wire, with the crystal dimensions fixed and finely machined by suppliers. In contrast, the wire geometry and mass are typically derived using a known viscosity, following the assumption of a perfect cylinder. Secondly, the wire was deemed to be more difficult to install into a removable unit, a requirement for easy cleaning, while keeping the wire tension constant. In contrast, the crystal setup provided a simple solution, with mobile, though sensitive connections to the crystal, immune to small distortions in the surrounding materials. To summarise, the crystal presents a more straightforward implementation and a more robust physical solution while providing a similar degree of accuracy.

Several different crystal types and techniques are available in the literature, but will not be discussed here for brevity's sake. For this work, a large, torsional crystal was selected. A larger crystal possesses a lower resonant frequency and larger surface area, which in turn minimises the energy transmitted into the fluid. This fulfils the prescription of minimising the disturbance of the phase equilibria during measurement. Additionally, a lower frequency is also less likely to violate the assumption of a no-slip boundary condition at the interface between the fluid and the crystal.

1.3. Density

The importance of density is self-explanatory, with the fluid property playing a central role in fluid dynamics and physical sizing. Density, per definition as mass per volume, is easily measured.

By loading a known mass into a known volume, the density of the system is known. This would imply precise mass measurement and the determination or calibration of the volume, both easily possible with the selected high-pressure cell.

As an alternative, the quartz crystal viscometer has the added advantage of being capable of determining the density. This, however, requires additional equipment to determine the bandwidth such as impedance analysers and is beyond the scope of the current work.