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Measurement of bubble point pressure in crude oils using an acoustic wave sensor

Jean Luc Daridon*, Ezequiel Orlandi, Hervé Carrier

Laboratoire des Fluides Complexes et leurs Réservoirs, UMR 5150, Université de Pau et des Pays de l'Adour, BP 1155, 64013 Pau Cedex, France

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ABSTRACT

An experimental method for the determination of the bubble point pressure of crude oils has been developed using an acoustic wave sensor that consists of a Quartz Crystal Resonator. The basis of the method has been developed and measurements have been carried out with different types of systems including a transparent synthetic mixture, a bottomhole oil from North Sea and a live crude oil with addition of nitrogen. The efficiency of the method has been tested by comparing the results with those obtained with traditional PVT techniques and with direct visual observation of the bubble conditions for the synthetic system.

1. Introduction

The experimental determination of multicomponent Vapor–Liquid Equilibria is essential for process design in many sectors of chemical engineering. In the oil industry, phase behavior of crude oils must be accurately acquired in order to optimize field developments and operations. Several methods have been proposed by chemical engineers for measuring phase behavior. These experimental approaches depend as much on the system as on the parameters measured and the pressure range investigated [1]. Depending on the variables measured, they can be classified as analytic or synthetic. Analytical methods involve the determination of the compositions of the phases once the system is brought to equilibrium. The composition of the phases is analyzed by either taking samples or by in-situ techniques like gravimetric or optical methods. At the opposite, synthetic methods do not need sampling and analyzing the phases but the exact feed composition of the system must be known prior to its loading into the equilibrium cell. Synthetic methods can operate with or without a phase transition. However synthetic methods with a phase transition detection are more often used than synthetic methods without a phase transition [2]. In this method, the appearance (or disappearance) of a phase can be detected either by direct visualization or by indirect methods using the change of a physical property (volumetric, calorimetric, acoustic, dielectric permittivity …). For gas condensates, vapor-liquid phase separation can be observed visually whereas for volatile oils, black oils and especially heavy oils phase transitions must be determined indirectly. In conventional *PVT* tests, constant mass expansion (CME) experiments are carried out to measure the bubble point of live crude oils at reservoir temperature. In this method a sample of an undersaturated oil is placed in a *PVT* cell at reservoir pressure. The pressure is then slowly decreased by an expansion of the cell volume at constant temperature. During the decompression, pressure and total volume are continuously monitored and the volume of cell is plotted against pressure. The bubble point is determined by noting the point at which a change in the slope of the pressure – volume (*PV*) curve occurs. CME test also provides information on the isothermal compressibility of the undersaturated oil and the bubble point density. Such experiments usually results in a sharp discontinuity in the derivative of the volume versus pressure at the bubble point. However, in some volatile oils, the discontinuity in the slope of the *PV* curve is not so pronounced and phase change only results in a small inflection in the *PV* curve. For such a fluid, the bubble point may not be determined with accuracy from *PV* curve as the method becomes subjective to the choice of points used to evaluate the slopes. Because of this difficulty, various methods have been proposed to highlight discontinuities in the volumetric behavior at the

* Corresponding author.
E-mail address: jean-luc.daridon@univ-pau.fr (J.L. Daridon).

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bubble point during flash expansion experiments. Some of them are based on the first derivative of the volume versus pressure by plotting the computed compressibility as a function of pressure or by calculating, from volumetric measurements, the so called Y-function link to the ratio of the change of pressure to the change in total volume [3,4]. Some others rest on the second derivative of volume versus pressure using a polynomial fit to compute the second order derivatives [5]. Changes in liquid properties can also be used to detect liquid vapor phase transitions if the monitored property is suitably selected. With this aim in mind, Hammami et al. [6] attained the bubble point from transmitted light measurements of a laser beam passing through a crude oil sample. Sivaraman et al. [7] measured bubble and dew point pressures for gas condensates and reservoir fluids using an acoustic resonator whereas Daridon et al. [8] and Ball et al. [9] measured speed of sound to evaluate bubble conditions.

It has been observed in an earlier work [10] that thickness shear wave sensors such as quartz crystal resonators (QCR) are extremely sensitive to changes in fluid properties and can therefore probe liquid-vapor phase changes in pure compounds and binary mixtures [11]. The overall aim of the present study is to show the capacity of using acoustic wave sensors in determining the bubble point of crude oils and to establish the experimental methodology that allows an optimal determination of bubble conditions. Thus, the first part of the work consists in studying the electrical response of a quartz resonator to liquid-vapor phase transition. For this purpose, measurements were carried out in a synthetic and transparent binary system for which bubble pressure determinations can be compared to direct visual observations. The second part aims at demonstrating the capability of the method for performing measurements in live crude oils. To this end measurements were carried out in two different crude oils.

2. Principe of quartz crystal resonator sensor

Quartz crystal resonator subjected to an alternating current suffers a thickness shear across its faces which can resound in different harmonic and inharmonic modes. The harmonic resonance depends upon on quartz properties as well as on the properties of the surrounding medium. Thus, changes in half band – half width (used to quantify dissipation) $\Delta\Gamma_n$ and resonance frequency Δf_n of an overtone n caused by full immersion of a quartz resonator in liquid under pressure, compared to the unloaded quartz (vacuum) response $f_{n,0}$ at same temperature, can be written as a sum of two different effects:

$$\Delta\Gamma_n = \Delta\Gamma_{n,liquid} + \Delta\Gamma_{n,P}.$$
$$\Delta f_n = \Delta f_{n,liquid} + \Delta f_{n,P}.$$

where, $\Delta\Gamma_{n,liquid}$ and $\Delta f_{n,liquid}$ are the changes in resonance bandwidth and frequency due to the contact of liquid with both quartz faces whereas $\Delta\Gamma_{n,P}$ and $\Delta f_{n,P}$ account for the sole effect of hydrostatic pressure. In a recent study, Cassiède et al. [12] have shown that dissipation is not modified by pressure variation ($\Delta\Gamma_{n,P} = 0$) whereas shift in resonance frequency varies proportionally to pressure change:

$$\Delta f_{n,P} = n\alpha f_0 \Delta P.$$

where f_0 is the fundamental resonance frequency measured in vacuum and α is a coefficient related to the change of the elastic modulus of quartz with respect to hydrostatic pressure. Its value is only a function of temperature. The shift in dissipation and resonance frequency caused by surrounding liquid also comes from various contributions including viscous damping, liquid trapping, quartz roughness, interfacial slipping. All these contributions do not add algebraically together but combine in a complex manner. In order to simplify the representation of all these effects, Cassiède et al. [13] have proposed a one-dimensional transmission line model in which a real quartz resonator is represented by ideal smooth quartz with a thin layer coated on both surfaces. By considering such simplified model, they expressed the shifts in resonance frequency due to surrounding liquid as the sum of two terms:

$$\Delta f_{n,Liquid} = -n2C_m\rho_{Liquid}h_{interface} - \sqrt{n}\,\frac{C_m}{\sqrt{\pi f_0}}\sqrt{\rho_{Liquid}\eta_{Liquid}}$$

where, C_m is Sauerbrey constant [14] defined as:

$$C_m = \frac{2\cdot f_0^2}{\sqrt{\rho_q \mu_q}}$$

The first term has the form of the Sauerbrey equation [14] with a theoretical thickness $h_{interface}$ that accounts for pure mass effects (liquid trapping or/and solid layer deposition) but also for interfacial effects such as roughness and slipping. This parameter can be either positive or negative as slippage acts like a theoretical negative mass [15]. The second term represents the effect of viscous friction. It has the exact form of the Kanazawa equation [10]. The model also leads to an expression of the change in dissipation due to surrounding liquid:

$$\Delta\Gamma_{n,Liquid} = \sqrt{n}\,\frac{C_m}{\sqrt{\pi f_0}}\sqrt{\rho_{Liquid}\eta_{Liquid}}\left(1 + R_{interface}\right).$$

It has the form of the Kanazawa equation with a correction factor ($R_{interface}$) that accounts for the roughness of quartz surfaces. It has been observed by carrying out various experiments [16] under pressure that $R_{\text{interface}}$ is independent of pressure. These equations show that $\Delta f_{n,Liquid}$ decreases linearly with $\sqrt{\rho_{Liquid}\eta_{Liquid}}$ whereas $\Delta\Gamma_{Liquid}$ increases proportionally to this quantity. Consequently, both $\Delta\Gamma_{n,Liquid}$ and $\Delta f_{n,Liquid}$ can be used to probe small changes in density and viscosity or any other phenomena associated with these changes.

3. Experimental apparatus and methods

3.1. High pressure cell

The main part of the experimental setup consists in a variable volume cell. This cell is made of thick wall cylinder able to operate from vacuum to 100 MPa in the temperature range from 273.15 to 423.15 K. The cell is closed at one end by a high pressure plug screwed to the cell (Fig. 1). Two hermetic feedthrough assemblies were accommodated in the cap for passing electrical pins. These electrical pins are also used to hold and plug the resonator inside the cell. All the experiments carried out in this study were performed with the same resonator. It consists in a highly polished AT-cut beveled quartz disk purchased from International Crystal Manufacturing Co. (Oklahoma City, Oklahoma, USA). It has a fundamental frequency of 3 MHz and a blank diameter of 13.6 mm. Two electrodes were deposited on its faces on the central plano-plano portion by vacuum evaporation of an adhesive layer of titanium of 10 nm thickness followed by a 100 nm thick layer of gold. The external parts of the pins are connected to a network analyzer thanks to coaxial cable with SMA connectors. The high pressure plug and the SMA connector are covered by a conductive housing that acts as a faraday cage, to shield radio frequency and electromagnetic disturbances. The cell is placed horizontally as well as the