NEW METHODS FOR THE DETERMINATION OF THE PHASE BEHAVIOUR OF SUPERCRITICAL REACTION MIXTURES

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Phase behavior provides a fundamental knowledge of understanding chemical reactions in supercritical fluids. We describe two types of sensors for probing phase transitions: shear-mode quartz sensors and fibre optic sensors. The application of such sensors has been demonstrated by measuring the phase boundaries of carbon dioxide and its mixtures with *n*-heptane and cyclohexane.

INTRODUCTION

In recent years, there has been growing interest in the use of supercritical fluids as a reaction medium.[1-3] The phase behaviour of reaction mixtures plays a key role because it can frequently affect the yields and selectivities of reactions.[4] Traditionally, vapour-liquid equilibria have been studied either by analysis methods or by visual methods. However, both methods have disadvantages. It is difficult to apply analysis methods closing to the critical point of mixtures. This is due to the fact that a small variation of temperature and / or pressure in the critical region could make two coexisting phases become one. Therefore, taking samples from both of the gas and liquid phases is not always achievable. Visual methods are suitable for measuring phase equilibrium data in the critical region, but they are time consuming, less subjective, and difficult to automate.

Developing sensors for studying phase equilibria in the near-critical and supercritical region may be an alternative way to solve the problems arising from traditional techniques. However, phase separations are complicated processes. Bubbles or liquid drops could initially appear anywhere, and then a meniscus is formed between the gas and liquid phases. A meniscus could be at the very top, or the bottom of the cell, or somewhere in the middle. Therefore, the challenge is how to probe the phase transition by using a single sensor or just a few sensors, which contact only a limited portion of the fluid.

In this paper, we describe two types of sensors for probing phase transitions: shear-mode quartz sensors and fibre optic sensors. The quartz sensor gives a response related to the product of density and viscosity of the fluid contacting its surface, and the fibre measures the difference in refractive index between the fluid and the fibre itself. In addition, the sizes of these two sensors are very different. The quartz sensor has a relatively large active area, which could monitor the meniscus in a small-diameter equilibrium cell. But the optical fibre has a total diameter of 100 μm including cladding, and it is hence possible to install an array of such sensors in the different places of the cell. The quartz and fibre sensors have been tested with pure carbon dioxide and its mixtures with organic solvents either in a static variable-volume cell or using a flow system. We show that phase boundaries for both pure fluids and fluid mixtures can be obtained in the critical region by applying such sensors.

THE SHEAR-MODE QUARTZ SENSOR

Shear-mode quartz sensors consist of thin quartz plates with metallic coating over the opposing faces. When the plate is immersed in a fluid, the resonance is affected by both the density and viscosity of the fluid contacting the sensor surface. Therefore, the fluid properties can be determined from the impedance analysis of the electrical equivalent circuit of the sensor.

Figure 1a shows sensor geometry of a 6 MHz AT-cut quartz plate with a coated area of the gold electrodes of 0.145 cm^2. The sensor is operated in the impedance minimum mode, which has been proved to have a wider range of linearity than the frequency shift mode. An electrical circuit consisting of a function generator, a rectifier, and a digital multimeter is used to measure the sensor impedance (Figure 1b). The relationship between the impedance minimum, $|Z|_{\min}$, and fluid properties is given by

$$|Z|_{\min} = \left(\frac{q_0}{w_{\min} C_0 K^2} \right) g \tag{1}$$

with

$$g = [(rhw)/(2C_s r_s)]^{½} \tag{2}$$

where r and h are the density and viscosity of the fluid, and $(C_s r_s)^{½}$ is the acoustic impedance of the sensor material.[5,6] Further details of the sensor linearity analysis, and the calibration procedure are described elsewhere.[7]

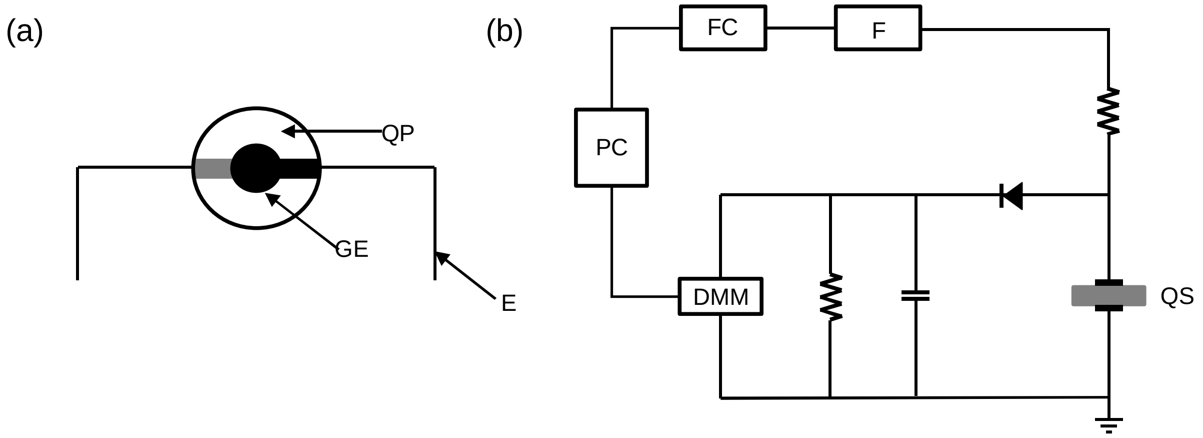

Figure 1 (a) Sensor geometry: E, electrical contact; GE, gold electrode; QP, quartz plate. (b) Schematic diagram of the arrangement used to measure the sensor properties: DMM, digital multimeter; F, filter; FC, function generator; PC, personal computer; QS, quartz sensor.

The quartz sensor was placed vertically inside a high-pressure variable-volume cell, which is a fully automated apparatus for the investigation of phase behaviour. After the sample was made, the cell was electrically heated to the required temperature, and was maintained at this temperature during the measurements. Then the cell volume was slowly increased or decreased by a computer-controlled pump. The contents in the cell were stirred to ensure that equilibrium was achieved after changing the volume. The temperature, pressure, and $|Z|_{\min}$ were automatically recorded during the experiment.

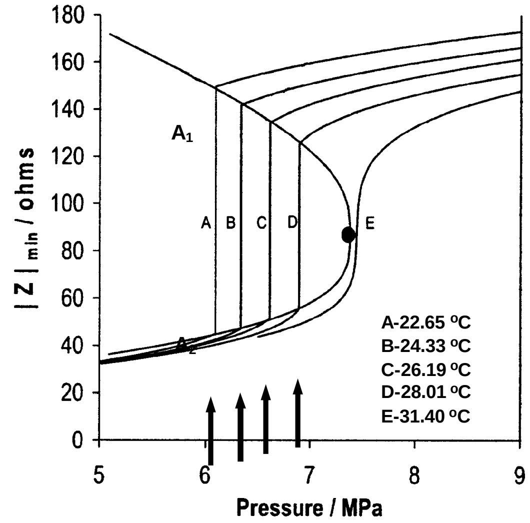

Figure 2 Experimental $|Z|_{\min}$ of pure CO_2. • critical point. The tie lines A-D are actually measured data, not interpolated lines.

The quartz sensor was initially tested using pure carbon dioxide. Figure 2 shows the experimental $|Z|_{\min}$ as a function of pressure along five isotherms close to the critical temperature (31.1°C).[8] Isotherms A-D correspond to those temperatures below the critical temperature. It can be seen from the Figure that the phase transition pressure at a given temperature (indicated by the arrows in Figure 2) is easily detected by the quartz sensor. Before the phase transition pressure, $|Z|_{\min}$ decreases as pressure decreases because the system is in a homogeneous liquid-phase. Just after reaching the phase transition pressure, bubbles form inside the cell, and the sensor works in heterogeneous conditions. Therefore, the measured $|Z|_{\min}$ is located between the values of the coexisting liquid and gas phases (e.g. vertical line A_1A_2 in Figure 2). After all of the liquid is vapourized, there is only a homogeneous gas-phase existing in the cell. Again, $|Z|_{\min}$ decreases as pressure decreases. Therefore, the two abrupt changes in gradient define the boundary of the two-phase region. However, isotherm E shows no abrupt change in gradient, which suggests that the system is always in a single-phase state.

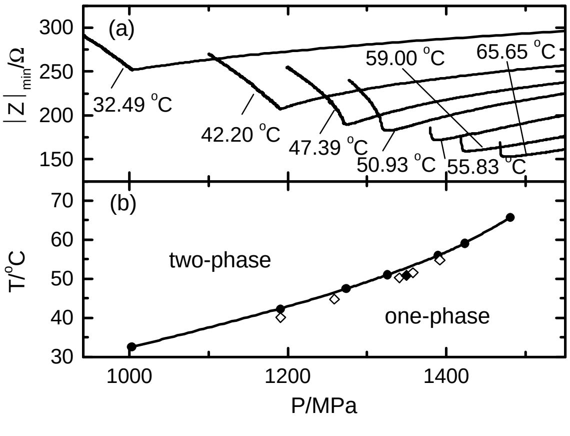

Figure 3. A binary mixture of n-heptane and CO_2 with 0.0463 mole fraction of *n*-heptane. (a) the impedance minimum ($|Z|_{\min}$) versus pressure along seven isotherms. (b) the *P*-*T* phase boundary ; •, from this work ($x_{\text{n-heptane}} = 0.0463$); ◇, reported by Choi *et al.*, ($x_{\text{n-heptane}} = 0.042$) [9] ; ♦, critical point for a similar composition measured by Choi *et al.* [9]

Our second interest has been the investigations of the behaviour of the quartz sensor in mixtures. Here we present results for a binary mixture of *n*-heptane and CO_2 ($x_{\text{n-heptane}} = 0.0463$). The impedance minimum has been measured as a function of pressure for seven isotherms ranging from 32.49 °C to 65.65 °C. It can be seen from Figure 3a that $|Z|_{\min}$ decreases as pressure decreases when pressure is above the phase-transition pressure. After the occurrence of the phase transition, $|Z|_{\min}$ increases as pressure decreases. In the case of the bubble point, the gas phase appears at the top of the pressure vessel. Since the quartz sensor is placed close to the bottom of the vessel, it measures only the properties of the liquid phase. In the case of the dew-point, liquid droplets condense on the surface of the sensor after the phase separation. Although the sensor is in the gas phase, a thin film of liquid forms on its surface. Therefore, a large increase in $|Z|_{\text{min}}$ is found when the pressure is just below the dew-point pressure. For both cases, the phase-transition point is marked by the minimum point of $|Z|_{\text{min}}$ on each curve. The results of the bubble and dew points are shown in Figure 3b together with the data reported by Choi *et al.* [9] for a mixture with a similar composition ($x_{\text{n-heptane}} = 0.042$). Considering the slightly different composition of two mixtures, there is a good agreement between our data and the data of Choi *et al*.

THE FIBRE OPTIC SENSOR

Fibre optic sensor technology has been applied to measure a wide range of physical properties, such as temperature, pressure, electric and magnetic field, strain, and humidity. Its inherent advantages over conventional sensor systems include lightweight, small size, inertness and corrosion resistance.[10] We have recently developed a fibre optic sensor for measuring refractive index under high-temperature and high-pressure conditions, and even in flammable gases. Based on this sensor, coexistence boundaries of the single-/multi-component systems could in principle, be determined due to the difference in refractive index for gases and liquids.

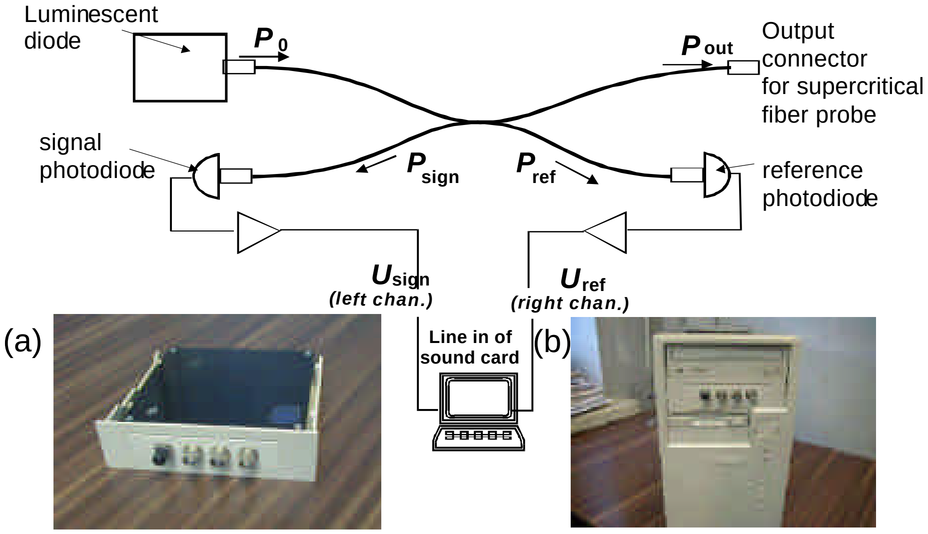

Figure 4 The fibre-optic sensor. (a) The optical unit and (b) the unit installed in a standard PC.

The schematic arrangements of the fibre-sensor source and detector are shown in Figure 4. Light from a luminescent diode (1.3 μm) is launched into a single-mode optical fibre (10 μm core diameter). The light is then split by a "X-shape" coupler. One arm is connected to the optical fiber probe, and another is used as the reference arm to monitor the instability of the luminescent diode. The fourth arm is used to measure the intensity of the light reflected back from the end of the fibre probe. The outputs from the photodiodes is amplified and converted to digital signals by using a sound card as A/D device. The whole system was wrapped in a box with a dimension of 4 cm high, 15 cm wide, and 21 cm deep, and was installed into a free 5-1/4" bay of a personal computer, as shown in Figure 4.

The measuring principle is as follows: in the case of using a simple flat-end fiber sensor, light propagates through the core of the fibre and hits the fibre end. If the refractive index of the fibre is not identical to that of the medium contacting the fibre, light is reflected back into the fibre. The reflectivity (R) at the interface between the fluid and the fibre is given by

$$R = \left(\frac{n_{fibre} - n_{fluid}}{n_{fibre} + n_{fluid}} \right)^2 \qquad (3)$$

where n_{fluid} and n_{optic} are the refractive index of the fluid and the fibre, respectively. R is proportional to the ratio of U_{sig} to U_{ref}. ($U_{sig} / U_{ref} = kR$, k is a constant.) We note that the refractive index of the silica fibre (n_{fibre} = 1.45) is greater than that of the pure supercritical fluids and their mixtures with the organic compounds which we have studied. Therefore, the smaller value of U_{sig} / U_{ref} corresponds to high values of refractive index, while the larger value of U_{sig} / U_{ref} represents the opposite.

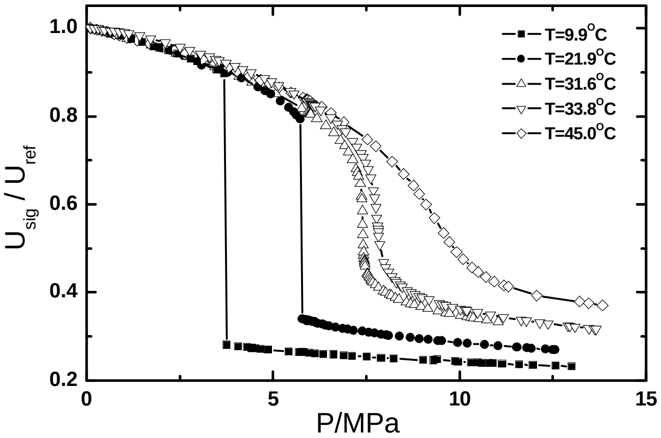

Figure 5 Normalised U_{sig} / U_{ref} v.s. pressure for near critical isotherms of pure CO_2 in the temperature range 9.9 ^oC~45.0 ^oC. Note that the physics of the sensor means that this diagram is inverted with respect to Figure 2.

Again, pure CO_2 was chosen as the initial test of the fibre-optic sensor. Figure 5 shows the normalised U_{sig} / U_{ref} as a function of pressure along five isotherms. For those subcritical isotherms (marked with solid symbols), we can see a sudden decrease in signal with increasing pressure. This corresponds to the phase transition from gas to liquid. The top of the vertical line corresponds to the dew point, and the bottom of the vertical line is the bubble point. The supercritical isotherms, marked with open symbols have no abrupt change in gradient since there is no phase transition at these temperatures. However, the points of inflection can be found from these isotherms. By tracing these inflection points, the critical point could be in principle located for pure substances using the condition $[\partial P / \partial (U_{sig} / U_{ref})]_T = 0$.

Additionally, we have calculated the density (r) of pure CO_2 from refractive index (n) according to the Lorentz-Lorentz equation:

$$\frac{n^2-1}{n^2+2}=Ar \qquad (4)$$

where the parameter A is constant for a given wavelength of light. The results show good agreement between the NIST data[11] and the experimental density data obtained from fibre-optic sensor.

We have now extended our studies to the binary system of cyclohexane + CO_2. The experiments were carried out in a flow system along three isobars. The composition of the inlet flow was kept at constant, and temperature was increased from 20 °C to 100 °C for each experiment. Three peaks, shown in Figure 6 indicate the phase-separation temperature. When the temperature is below the phase-separation temperature, the sensor works in a homogenous liquid phase, and above this temperature, two-phase-fluid flows simultaneously through the vessel. Although such a system is rather complicated, we believe that our sensor picks up the signals from the liquid phase even when both gas and liquid are present in the vessel. This is possible due to the wetting properties of the fibre.

CONCLUSIONS

We have demonstrated the use of the shear-mode quartz and the fibre optic sensors in monitoring of vapour-liquid phase transitions and determining the bubble-point, dew-point lines of fluids and fluid mixtures. The sensors are based on measuring the physical properties of fluids (the product of density and viscosity or refractive index). They offer a convenient and objective way of identifying the formation or disappearance of a phase. Furthermore, both sensors have an excellent chemical resistance, and also are able to be operated over very wide ranges of temperature and pressure. The small size of the fibre optic sensor makes it a useful tool for the in-situ monitoring of the phase behaviour of chemical reactions in supercritical fluids.

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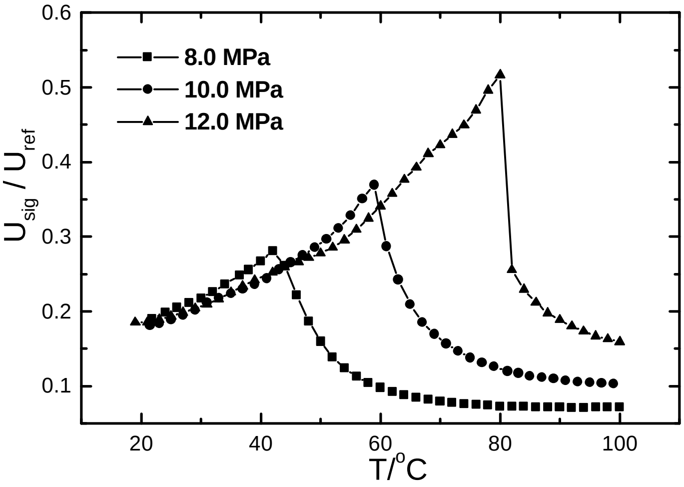

Figure 6 U_{sig} / U_{ref} v.s. temperature for three isobars of the mixture of cyclohexane + CO_2.

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