A NEW CONTINUOUS METHOD TO PERFORM QUICK PHASE EQUILIBRIUM MEASUREMENTS AT HIGH PRESSURES AND TEMPERATURES

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Introduction

Supercritical water (SCW) and carbon dioxide (scCO$_2$) have being exhaustively investigated in recent years as media for carrying out different reactions [1,2]. These two fluids are much cheaper and environmentally less hazardous than organic solvents. There is therefore a rising interest to implement these solvents in the chemical industry.

The dielectric constant of water at near- or super-critical conditions decreases enough to allow organic substances to dissolve in it; scCO$_2$ is also a good solvent for many organic compounds. In addition, reactive gases like oxygen and hydrogen are completely miscible with these supercritical fluids creating a homogeneous medium for carrying out oxidations and hydrogenations.

Knowledge of the phase behaviour of the mixtures involved in these reactions is of great interest in order to ensure that the reaction is actually taking place in a single phase. For this reason, experimental data for systems organic + water are demanded.

In this paper, a new device for quickly measuring phase equilibria at high pressures and temperatures is presented. The method has the characteristics of a synthetic dynamic device according to the criteria of Christov and Dohrn [3]. This method is similar to that presented by Wu et al. [4]. In that method, changes in the refractive index of a mixture of known composition are detected when a phase split occurs. Instead of refractive index, our method detects a change in the flame ionisation detector (FID) signal of a sample taken with a capillary.

An additional advantage of our method is that it could easily be coupled to a continuous process in order to obtain information on-line of the phase behaviour for reaction mixtures in the different stages of a process.

Materials and Methods

In our method a hollow fibre is used to take samples from a measuring chamber and then to lead that sample to a detection device in continuous flow. The detector gives signal related to what phase is in the measuring chamber and an abrupt change in signal indicates a phase transition. SEM pictures of two different hollow fibres are shown in Figure 1.

Figure 1. SEM photos of the ends of different "holey" fibres. In this paper, we have used fibre on the left which has 18 holes each 5 microns in diameter.

In our case a Flame Ionization Detector (FID) was used because, although our solvents (CO_2 and H_2O) are nonflammable and do not give signal, the second components of our mixtures give good signals. This should give us the opportunity to measure relative concentration of second component in the mixture.

The signal that the detector gives depends on the volumetric concentration of flammable compound in the carrier gas. That means that, if there is liquid phase in the chamber, the concentration of flammable compound per unit volume will be higher rather then if there is gas phase. When there are two phases in the chamber - both high and low signals will alternate giving a trace that looks like a noisy and spiky line. These three types of flow are shown in Figure 2.
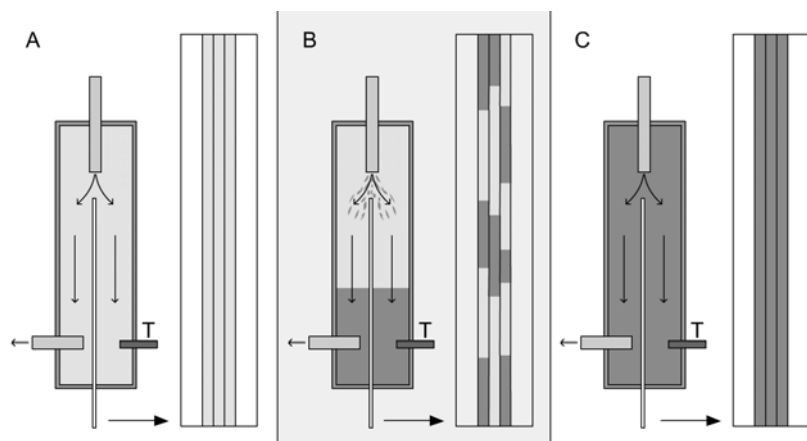

Figure 2. The key features of the holey fibre method. The left of Figs 2A, 2B and 2C show the measuring chamber with the inlet at the top and the outlet and thermocouple at the bottom. To the right is shown a short length of fibre, highly magnified to illustrate how the flow regime changes according to the phase in the chamber. A – gas phase only, B – two phases and C – liquid phase only.

All measurements were carried out using the continuous flow rig as shown in Figure 3. Similar rigs are used to carry out continuous reactions in $scCO_2$ and scH_2O [1, 2].
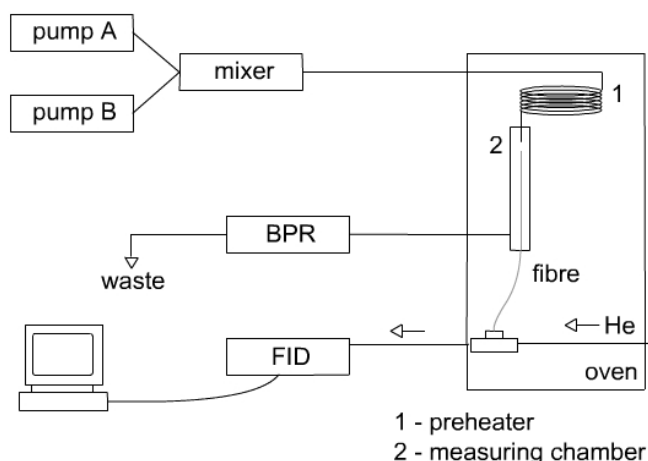

Figure 3. Block scheme of equipment that was used during recent experiments for $scCO_2$ system.

This is a dynamic measurement method; a mixture of known composition is pumped under different conditions and phase transition points are detected. The rig includes two liquid pumps for the two components of a binary mixture. The pumps are connected to a mixer which ensures that the mixture is homogeneous before entering the measuring chamber. Pump A is used to pump liquid CO_2 to make measurements of $scCO_2$ systems. To liquefy CO_2 before feeding it to

the liquid pump the special chiller and cooled syringe pump (ISCO 260D) were used. Pump B is used to deliver the organic compounds.

The preheater, coil and the measuring chamber are all situated inside a temperature-controlled oven. The preheater is made of a 3 meter long 1/16 inch stainless steel tubing, ensuring that, even at high flow rates, a mixture reaches thermal equilibrium before it enters the measuring chamber. In the measuring chamber, the flow is split into two; the main stream goes out via a Back Pressure Regulator (BPR) while a tiny amount of fluid is bled through the holey fibre. The BPR is used to adjust the pressure in the system; the temperature is controlled by an external controller.

The holey fibre is connected to the Flame Ionization Detector (FID) where all flammable compounds are detected. The flow from the fibre is mixed with a carrier gas (He or H_2) before entering the detector which is fuelled by H_2. Graphite-vespel ferrules are used to seal the holey fibre, because they are soft enough to avoid damaging the holey fibre while sealing; nevertheless there is still a possibility of crimping the fibre if it is overtightened. The apparatus can be used at temperatures up to $350^{\circ}C$ and pressures up to 300bar.

Results and conclusions.

The acetone + CO_2 system was used to validate our holey fibre method. This system was recently investigated at Nottingham using an optical fibre reflectometer [4]. As shown in Figure 4, the data that were collected during our experiments correlate well to the literature data for two different concentrations.
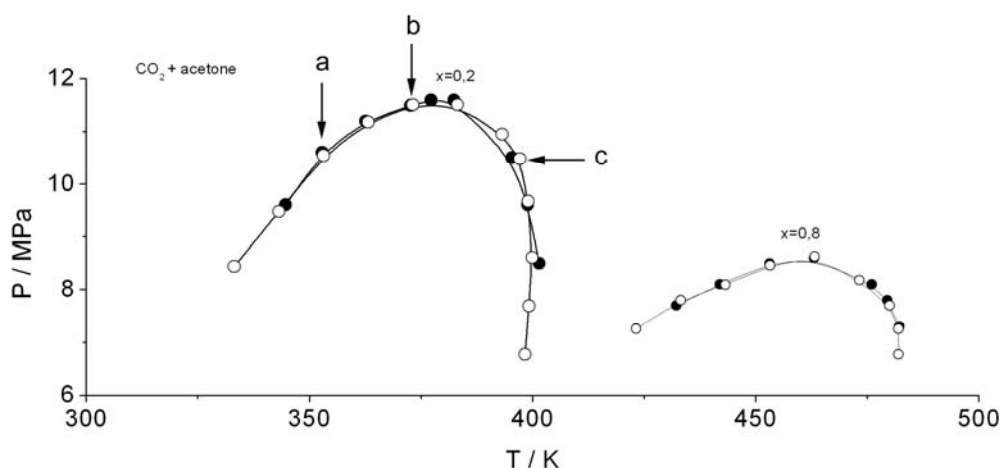

Figure 4. P, T phase diagram for binary mixtures of acetone + CO_2. White circles are literature data [5] measured using the optical fibre reflectometer and black circles are data measured using the holey fibre method. Two concentrations are presented, 0.2 and 0.8 mole fraction of acetone. Arrows show if either pressure or temperature was changed to cross phase boundary. a – bubble point region, b – approximate critical point, c – dew point region. These two envelopes were measured in less then 2 days each, more rapidly then by traditional methods.

Examples of raw data are presented in Figure 5. This experiment was carried out at constant temperature. As shown, when the pressure is reduced, a modest change in FID signal occurs due to changes in flow rate through the fibre. When the phase boundary is crossed, a big change in FID signal occurs.
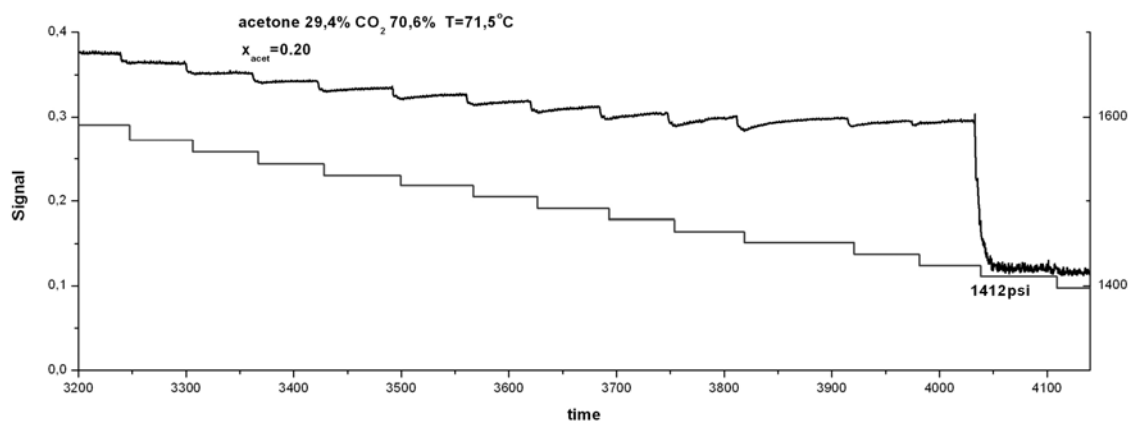
Figure 5. Signal, time and pressure, time plots are presented. The lower line is pressure plot, and the upper line is the FID signal. Measurements were done for the Acetone + CO_2 system; the mole fraction of acetone is 0.2 and the temperature of system was 71.5°C. 200 units = 1 minute.

The most challenging mixtures are those containing water because they involve higher temperatures and cause rapid degradation of optical components such as the optical fibre in the reflectometer by Wu et al. [4], which therefore cannot be applied to such mixtures. After confirming that our holey fibre method worked with a scCO$_2$ system, a water + ethanol (EtOH) system was studied as model for more difficult water-containing systems. However, we encountered several problems when working with them. In particular, the BPR causes large oscillations in the FID signal because the BPR is either open or closed; for CO$_2$-containing systems this open/closed operation is acceptable because CO$_2$ is highly compressible at room temperature and this compressibility dampens any pressure oscillations. On the other hand, liquid water is virtually incompressible at ambient temperatures with the result that the BPR induces large amplitude oscillations in both the pressure and the FID signal, see Figure 6.
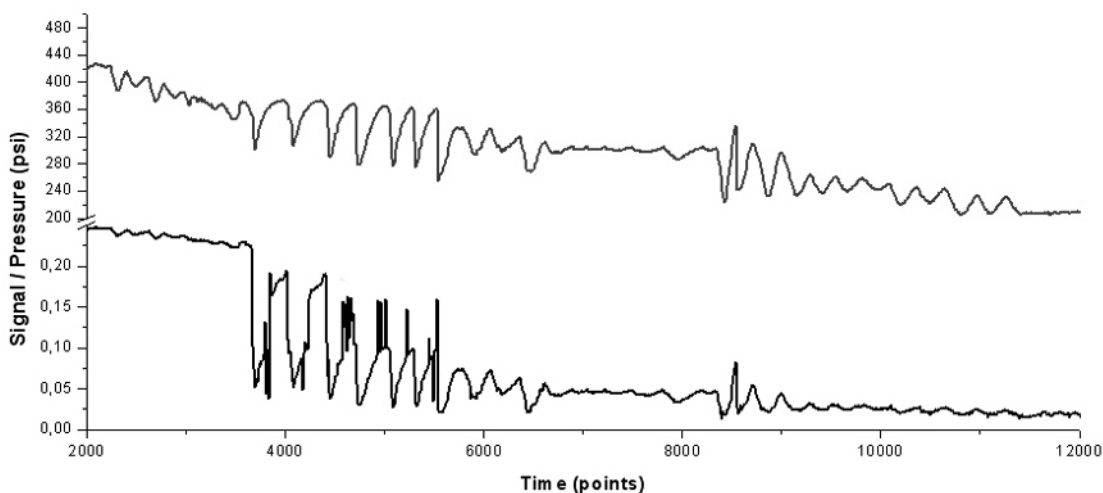

Figure 6. Oscillations induced by the BPR when using EtOH + H_2O. The upper trace is pressure, the lower is the FID signal. 200 units = 1 minute.

To avoid such oscillations, the equipment was modified as follows. The BPR was closed, and was used merely to monitor the pressure in the system. A capillary restrictor was used to maintain pressure in the main fluid stream. The HPLC pumps were replaced by a single syringe pump containing the premixed EtOH and H_2O, which not only controls the pressure in the system but also can be programmed to change the pressure. After the modifications shown in Figure 7, the apparatus worked without oscillations, even during pressure ramps.
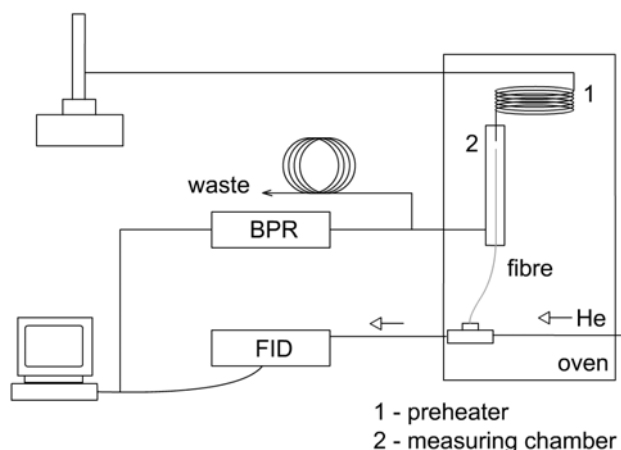
Figure 7. Block scheme of modified apparatus for use with water-containing system.

The EtOH + H_2O system was measured using the modified apparatus. Examples of P, T diagrams are presented in Figure 8. Results were obtained with good quality and reproducibility. As shown this system differs from the CO_2 + acetone system. Bubble and dew curves are completely separated by a two phase region. The envelopes are very sharp and the two phase region is very narrow between liquid and gas phase. Occasionally, it was not possible to locate the dew point either due to blockage of the fibre or very weak signal.
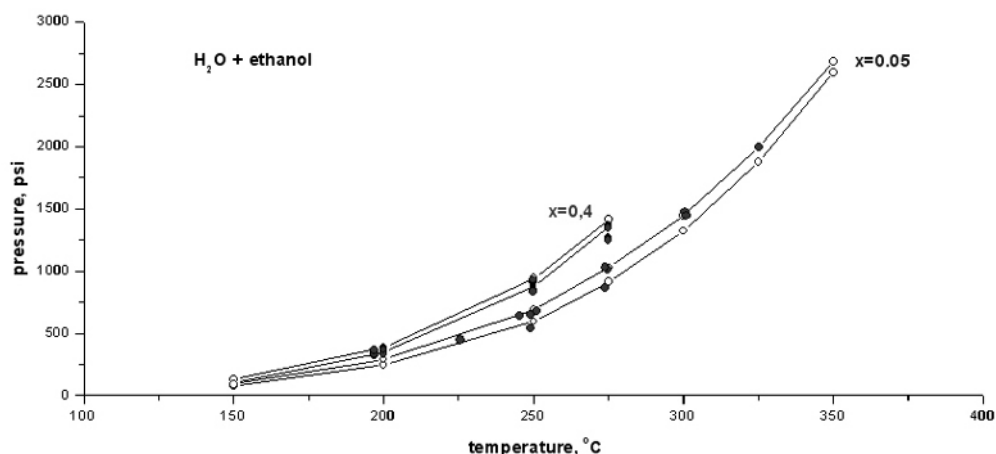

Figure 8. P, T phase diagram for binary mixture ethanol + H_2O. White circles represent the data interpolated from ref. [6] and black circles are data measured using the holey fibre method. Two concentrations are presented, 0.4 and 0.05 mole fraction of ethanol.

The raw data are presented in Figure 9. There is trace without noise at the beginning which shows that there is gas phase in the sample chamber. Then noise starts and trace goes up due to increasing of pressure, this is the two phase region; at the end the noise disappears when we cross bubble point curve and have only liquid.
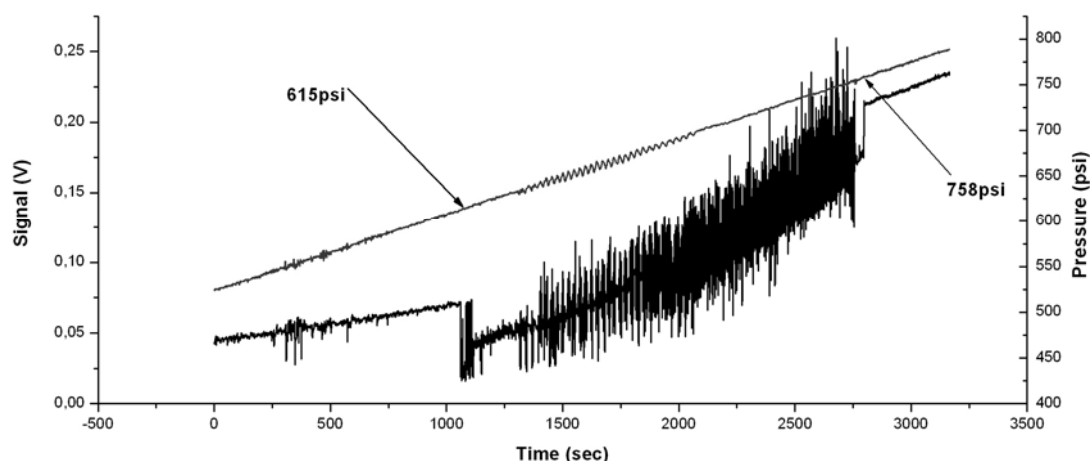
Figure 9. Signal vs. time and pressure vs. time plots are presented. The straight, sloping line is the pressure ramp, the black trace is the FID signal. Measurements are for EtOH + H_2O system; the mole fraction of EtOH is 0.1 and the temperature of system was 250 ^{o}C.

Conclusions

A new method for determining phase transitions at high pressure and high temperature has been developed. High pressure equipment has been constructed to deal with both CO_2 and H_2O-based systems and has then been optimized to avoid oscillations in pressure and temperature during the experiments. The model systems, acetone + CO_2 and then H_2O + EtOH have been used to validate the performance of this method against literature data. For both systems, data were collected and recorded on a PC. The data were processed and compared to literature. A good agreement was obtained.

References

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