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The application of a shear mode piezoelectric sensor to monitoring the high-pressure phase behaviour of asymmetric binary systems

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Abstract

We demonstrate for the first time that high-pressure phase diagrams can be measured in a simple, objective and fully automated manner for complex binary fluid mixtures. Supercritical CO_2 is becoming of increasing industrial importance. Many of the important binary systems with CO_2 are highly asymmetric, and exhibit a variety of the phase behaviour from liquid–liquid immiscibility to discontinuous critical loci. We investigate the possibility of mapping these different types of phase diagram using a single shear-mode piezoelectric sensor. We focus on two systems (1-octanol + CO_2 and 2-octanol + CO_2). We show that the existence of three phases (liquid–liquid–vapour) can be detected by the presence of two discontinuities when the impedance minimum of the sensor is measured as a function of fluid volume. This method is used to measure the three-phase coexistence curve quantitatively for the 1-octanol + CO_2 system and the result is in good agreement with literature data. By analyzing the impedance minimum along the *p*–*T* phase boundary, we have found that the vapour–liquid critical locus of 2-octanol + CO_2 is interrupted by the occurrence of a previously unobserved liquid–liquid immiscibility. For both systems, we have used the critical points, located either by the isochoric method or extrapolated from composition/*T*/*p* phase envelope to construct a *p*,*T*-projection with characteristic features which allow the particular mixture to be classified to its appropriate type (i.e., 1-octanol + CO_2, Type III; 2-octanol + CO_2, Type IV).

Keywords: Vapour–liquid-equilibrium; Critical points; Shear-mode piezoelectric sensor; Binary mixtures; Carbon dioxide; Octanol

1. Introduction

Supercritical carbon dioxide ($scCO_2$) has been shown to be one of the green solvents that can be used as reaction media in both laboratory and industrial scales [1–6]. Over the past 20 years, hundreds of chemical reactions have been well studies in $scCO_2$, including hydrogenation [7–10], hydroformylation [11–15] and polymerization [16–18]. Recently, interest has extended to more sophisticated reactions, e.g. oxidation [19–22], enantioselective reactions [23–25], and enzymatic-catalyzed reactions [26–28]. These reactions involve thousands of substrates, ranging from non-polar to high-polarity molecules. Also their molecular weight spans in several orders, e.g. from 2 for H_2 to ca. $10^{4–5}$ for polymers.

Often the miscibility of substrates and CO_2 is a crucial factor in achieving high-reaction rates and selectivity. There are a number of examples where a homogeneous single-phase is the more favourable condition for fast reaction rates and chemoselectivity. For instance, Bhanage et al. [29] studied the selective hydrogenation of α,β-unsaturated aldehydes towards unsaturated alcohols, finding the selectivity can be controlled by varying pressure. Later, it was suggested by Pereda et al. [30] that the reactions need to be operated under the homogeneous conditions to achieve the high selectivity (>90%). Our own group [31] showed that 1,6-hexenandiol can be selectively reacted with MeOH in $scCO_2$ to form mono-ether by merely increasing the pressure above 20 MPa. With a detailed phase study, it was proved that the selectivity switch from bis- to mono-ethers was related to the homogeneous condition of the reaction mixtures [31]. On the other hand, a heterogeneous state can in some circumstances dramatically increase the reaction rate or influence the outcome of a reaction. da Ponte and his co-workers [32] reported that, in the hydrogenation of α-pinene in $scCO_2$, much higher yields were obtained when the reaction mixture was under heterogeneous conditions than when the system became homogeneous at higher pressures.

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Nomenclature

LCEP	low critical end point
p	pressure
T	absolute temperature
UCEP	upper critical end point
V	volume
x	mole fraction
$\|Z\|_{\min}$	impedance minimum
Greek letters	
η	viscosity
ρ	density

Thus, there is no universally favourable phase-state for reactions in $scCO_2$ and we need to consider the effect of phase behaviour on reactivity for individual reactions. Synthetic chemists are often keen to know the phase behaviour of their reaction mixtures, which allows them to understand the relationship between the reactivity and the phase state, and hence even to tuning the reactivity by choosing the favourable phase state.

Unfortunately, the fluid phase behaviour of mixtures is inherently complicated at high pressures. Even for binary systems, there are six main types of phase diagrams according to the work of van Konynenburg and Scott [33]. Among the six types, Type I shows the simplest behaviour; it has a continuous vapour–liquid critical curve, connecting both critical point of pure components. Types II–VI have two or more critical curves, and exhibit the liquid–liquid–vapour (LLV) equilibrium over a certain temperature region [34–36]. For a wide variety of substrates, an accurate prediction of binary phase diagrams is not possible merely by using the-state-of-the-art thermodynamic models; hence, the phase behaviour of the mixtures needs to be measured experimentally.

Visual observation remains as one of the most widely used techniques for studying the phase behaviour of reaction mixtures in the critical region, but it is time-consuming, labour intensive, and often constrained by the subjectivity of the experimenter. In addition, the equipment used for such visual experiments is less reliable due to short life-time of the materials required for sealing windows, particularly under high temperatures. Furthermore, it is extremely difficult to automate a visual apparatus fully even with the help of the modern boroscopes and cameras.

Over the past few years, our research group has developed non-visual methods for studying high-pressure vapour–liquid equilibria using a variety of different sensor [37–41]. In particular, we have reported [42] that a shear-mode piezoelectric sensor can be used to measure the bubble-, dew-, and critical-point of binary mixtures. The piezoelectric sensor gives a significant difference in output depending on whether the sensor is in contact with gas or liquid. A key feature is that it responds only to the thin layer of fluid immediately contacting its surface. By recording the sensor output as a function of pressure along isotherms, we are able to determine whether the vapour–liquid phase transition belongs to bubble- or dew-point according to the shape of the isotherms. The critical point is then located by extrapolation to the point where the bubble- and dew-point curves meet. We have shown that our method is applicable to simple binary mixtures, e.g. MeOH + CO_2, a Type I mixture, for which the vapour–liquid critical point can be measured without the interference from the partial miscibility of two liquids. The critical point data obtained with the piezoelectric sensor are in good agreement with data published in the literature.

In this paper, we investigate whether the piezoelectric sensor can be applied to highly asymmetric binary systems, in which the polarity and size of the solute molecules are very different from the CO_2 molecule, resulting in more complicated phase behaviour, such as the coexistence of three phases, and discontinuous critical curves. Such systems are important because most substrates used in $scCO_2$ form highly asymmetric binary mixtures with CO_2. Therefore, there is a genuine need for an objective, reliable, and automated method for studying the phase behaviour of such systems. Also, there is the fundamental challenge of finding a method for monitoring three-phase equilibria with only a single sensor. We have chosen two binary systems (1-octanol + CO_2, and 2-octanol + CO_2) because: (i) the solutes are interesting substrates for oxidation reactions in $scCO_2$ [22,43–46]; (ii) they are not expected to form the Type I mixtures with CO_2. In addition, we performed some preliminary experiments with heptane + CO_2, a known Type II system.

2. Experimental

2.1. Apparatus, sensor, and sample preparation

All measurements were carried out using a high-pressure variable-volume cell made of steel and designed for temperatures from ambient to 360 K and pressures up to 35 MPa. Fig. 1 is a schematic diagram of the variable-volume cell, which is separated into two parts by a movable piston with three O-ring seals. The cylinder above the piston is filled with water, which is employed as a pressure transmission fluid to control the position of the piston; the volume of the cell is varied by pumping in or withdrawing water from the top of the cell. The experimental chamber below the piston accommodates a sensor and a stirrer. The sample is introduced into the chamber, and is stirred by a magnetic spin-bar, driven by an external magnet coupled to a motor.

The sensor used in this study was a shear mode piezoelectric sensor made from an AT-cut quartz plate. This type of sensor gives a linear response to the square root of (density × viscosity) of the fluid immediately in contact with its surface, see Eq. (1) [39,47].

$$|Z|_{\min} \propto (\rho\eta)^{1/2} \tag{1}$$

where ρ and η are the density and viscosity of the fluid. $|Z|_{\min}$ is the impedance minimum obtained by monitoring the impedance of the electrical equivalent circuit of the sensor. The details of the design of the variable-volume cell, the equipment used for mea-