A New Continuous Method for Performing Rapid Phase Equilibrium Measurements on Binary Mixtures Containing CO_2 or H_2O at High Pressures and Temperatures[†]

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Apart from paying a deserved tribute to Professor Schneider, a new synthetic dynamic method for rapid determination of phase boundaries at high pressures and temperatures is presented. This device is based on the change in the Flame Ionization Detector signal given by a small amount of sample taken by a capillary fiber from an equilibrium cell through which a mixture of known composition is continuously flowing. To validate the method, the phase boundaries for the system acetone + CO_2 are measured at (0.2 and 0.7) acetone mole fraction and at (350 to 380) K. We also measured the phase boundaries for the system ethanol + H_2O at compositions ranging from (0.05 to 0.4) ethanol mole fraction and temperatures up to 600 K. The results agree well with literature data, showing the feasibility of this method to measure the phase behavior of binary mixtures containing CO_2 and H_2O at extreme conditions.

Introduction

Supercritical water (SCW) and carbon dioxide ($scCO_2$) have been extensively investigated in recent years as media for carrying out chemical reactions.[1−5] The dielectric constant of water at near- or supercritical 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 homogeneous media for carrying out oxidations and hydrogenations. CO_2 and H_2O are much cheaper and environmentally less hazardous than many organic solvents. There is therefore an increasing interest in using these solvents for reactions in the chemical industry.

Knowledge of the phase behavior of the mixtures involved in these reactions is of importance to determine whether the reaction is actually taking place in a single phase. For this reason, experimental data for systems organic + water or organic + CO_2 are crucial. The study of phase behavior is one of the areas which was led for many years by Professor Schneider.[6−9]

There are many methods for measuring phase equilibria at high pressures. These methods have been extensively reviewed and classified by Christov and Dohrn.[10] Some of the research carried out by our group[11,12] is focused on the development of new synthetic dynamic methods. In this class of methods, a sample of known composition is prepared by mixing streams of components in a given ratio, and then that mixture is pumped into an equilibrium cell at a fixed temperature. The pressure is controlled at the end of the system by a back pressure regulator or similar device. In this way, the phase behavior of the sample can be studied under different conditions by means of a sensor which can detect the phase-transition point, located inside the equilibrium cell. Advantages of synthetic dynamic methods include the small size of the equilibrium cell, short equilibration times, and rapid measurements. Furthermore, such equipment could easily be coupled to a continuous process to obtain online phase behavior data for reaction mixtures at different stages of a process.

In a previous paper, Wu et al.[11] described a synthetic dynamic device developed jointly in Nottingham and Moscow using a fiber-optic probe. This sensor has been used to detect phase split[13] or interface levels[14] because it responds to changes in the refractive index of the sample depending on if it is in contact with high or low density fluids. However, this sensor has an important limitation: it is not stable in supercritical water which corrodes the optic fiber of the sensor.[15] This prevents the sensor from monitoring phase equilibria in SCW or water-rich mixtures. In this paper, we present a related method, but instead of refractive index, we detect a change in the signal from a Flame Ionization Detector (FID) which is fed a small amount of sample taken via a capillary. This capillary is a so-called "Holey" optic fiber which has a number of very narrow channels running throughout its length. This sensor is suitable for measuring systems containing either CO_2 or water at high temperatures and high pressures. To validate this new method, liquid−vapor boundaries for the acetone + CO_2 and ethanol + water systems are determined.

Experimental

Ten years ago, at a NATO Summer School in Turkey, Professor Schneider introduced one of M. Poliakoff's lectures by saying that his group built equipment from pieces that other groups had thrown away. Nowhere is this truer than in the present work where the apparatus is based on an old gas chromatograph (PYE UNICAM).

A set of pumps and mixer are used to prepare a mixture of known composition and to drive it through an equilibrium cell.

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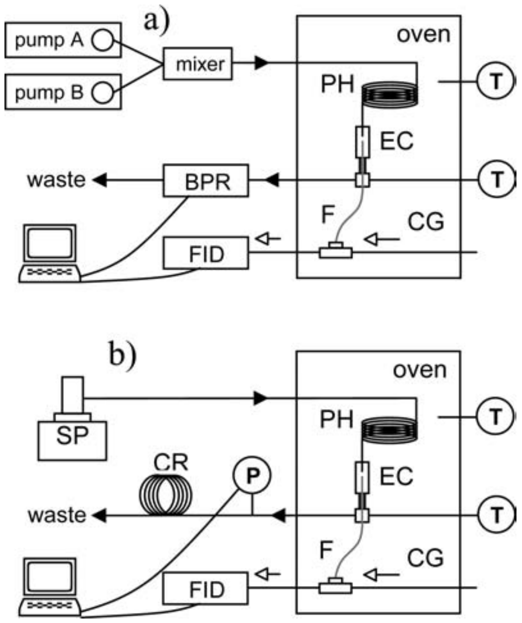

Figure 1. (a) Arrangement used for measuring the acetone + CO_2 system. (b) Arrangement used for measuring the H_2O + EtOH system. Components are labeled as follows: F, Fiber; P, Pressure transducer; T, Thermocouple; PH, Preheater; EC, Equilibrium cell; CG, Carrier gas; FID, Flame ionization detector; BPR, Back pressure regulator; SP, Syringe pump; CR, Capillary restrictor.

Upstream of the cell, the mixture is passed through a preheater which consists of a 3 m long coil of 1/16 in. stainless steel tubing. Both the preheater and equilibrium cell are located in the GC oven fitted with a modern temperature controller that can be kept at constant temperature within ± 0.2 K. The preheater ensures that, even at high flow rates, the mixture reaches thermal equilibrium before it enters the equilibrium cell. The overall flow rate depends on the measurement conditions, and it usually lies within (0.4 and 0.8) $mL\cdot min^{-1}$. At the equilibrium cell, the mixture is sampled by the hollow capillary fiber, and a tiny amount of sample is fed to the flame ionization detector (FID). Two slightly different approaches were used depending on the measured system, and they are represented in Figure 1 and explained in detail below.

The hollow fiber is a thin capillary made of silica that can have one or more holes of different sizes. They can be used to take small samples from high-pressure vessels[16] without significant perturbation of the system because the flow along them is so small. This flow depends on the pressure difference between the two ends, the length of the fiber, the inner diameter of the holes, and their number. Two different fibers were used in this work: for the system acetone + CO_2, an optical fiber with 18 holes, each of 5 μm in diameter, was used. This fiber was made by the group "Photonic, Electronic and Plasmonic Microstructured Optical Fibres" at the University of Southampton (UK). For the system ethanol + water, a capillary with a single 20 μm hole (POSTNOVA ANALYTICS) was used. The narrow holes in the multihole fiber tended to block with the aqueous system. The capillary is much more stable for measuring this system and, because it does not block, it has a much longer lifetime. The optimum flowrate along the fiber is ca. 0.05 $mL\cdot min^{-1}$ so the lengths of the fibers were about 15 cm for the 18-hole and 40 cm for the single hole fiber.

A FID responds to the quantity of ions generated when a flammable organic compound is burnt in an ionizing flame. The sample is mixed with hydrogen as carrier gas at a flow rate of 40 $mL\cdot min^{-1}$ and then fed into the original FID of the gas chromatograph. Only flammable material gives signal, so neither CO_2 nor H_2O is detected by the FID. When these fluids are mixed with organic compounds, the signal depends on the mass flow of the fluid within the fiber and on the composition of organic material in the fluid. Since in an LV equilibrium each phase has different composition and density, the FID signal allows us to distinguish between liquid and vapor and, therefore, to detect the phase transition point.

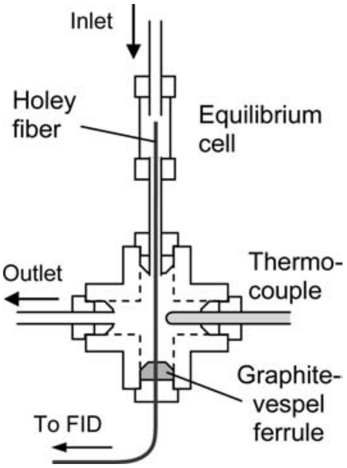

Figure 2. Detail of the equilibrium cell and fiber arrangement.

The temperature of the outgoing flow is measured by a type K thermocouple, with an uncertainty of ± 0.1 K immediately downstream of the equilibrium cell. Figure 2 shows a more detailed view of the equilibrium cell which is constructed entirely using Swagelok and HIP commercial components and seals. The only exception is the Graphite-Vespel ferrule (SIGMA) used to seal the fiber because Vespel is soft enough to prevent damage to the fiber. The inlet pipe projects ca. 1 cm into the equilibrium cell so that it acts as a nozzle, and any liquid is sprayed into the body of the cell. The reason for such a projection was discussed in some detail in our design of a fiber-optic reflectometer.[11] It is important that the fiber is located close to the end of the inlet pipe so that the cut end of the capillary is the first surface which the liquid encounters, but our earlier work with the reflectometer suggests that the precise distance is not very important.

After the equilibrium cell, the fluid leaves the oven, and it is cooled down. The pressure is reduced to atmospheric by either a back pressure regulator or a restrictor depending on the nature of the mixture.

Two binary systems were studied to validate this synthetic dynamic method: acetone + CO_2 and ethanol (EtOH) + H_2O. These mixtures are convenient models for CO_2- and water-containing reaction mixtures, and there are published data available for comparison. The acetone + CO_2 system was investigated earlier using our fiber-optic reflectometer method.[12] The EtOH + H_2O mixtures allow us to test our method at high temperatures and pressures where corrosion of the fiber-optic reflectometer occurred so rapidly that measurements could not be made. EtOH + H_2O has been previously studied by Barr-David and Dodge.[17] Slightly different strategies were followed for measuring the two systems. The way of pumping the components and depressurizing the sample needs to be different depending on whether the fluid is a liquid or a gas under ambient conditions.

Measurement of Acetone + CO_2. Two high-pressure reciprocating pumps (Gilson 308) drive the components through a

1.5 mL dynamic mixer (Gilson 811C) that ensures that the mixture is homogeneous before entering the equilibrium cell. (We assume that the compounds are mixed completely because few oscillations in FID signal are shown in single-phase regions. If the mixture was not complete, bigger oscillations would be observed.) The CO_2 is cooled and liquefied before being pumped. The volume delivered by each pump is measured with an uncertainty of ± 0.01 $mL\cdot min^{-1}$. The desired composition in mole fraction can therefore be achieved with an uncertainty of ± 0.01. A back pressure regulator (BPR) (JASCO 880-81) is placed at the exit of the oven to control and record the pressure of the system (Figure 1a).

Measurement of EtOH + Water. Due to the low compressibility of the liquids, a BPR cannot be used for this system. The volume fluctuations generated by the operation of the BPR lead to large oscillations in pressure. A 3 m capillary of 0.125 mm inner diameter was therefore used as a restrictor. A single syringe pump is used to drive a previously prepared mixture of water and ethanol. The pressure is now controlled by the pump and measured by a pressure transducer just upstream of the restrictor with an uncertainty of ± 0.01 MPa. The mixture is prepared by mass giving a composition with an uncertainty of ± 0.001 in mole fraction.

In a typical experiment, the mixture is pumped through the equilibrium cell at temperature and pressure conditions under which only the vapor phase exists. Then, the pressure is isothermically and slowly increased at 0.03 $MPa\cdot min^{-1}$ until a second phase appears as indicated by a change in the FID signal. The pressure and the temperature at that moment determine the dew point on the phase boundary. The pressure can then be increased to detect the bubble point. If the procedure is carried out in reverse with the pressure being decreased from a liquid phase region, similar signals are obtained from the FID, and bubble and dew points are observed at the same values. The uncertainty in the measurement of the boundary points is estimated to be ± 0.05 MPa. However, if the phase transition boundary curve is steep, it is more convenient to carry out an isobaric experiment. The pressure is kept constant, and temperature is slowly changed at 0.5 $K\cdot min^{-1}$ to cross the boundary. The uncertainty in the measurement of the boundary following this isobaric method was estimated to be ± 0.1 K. This procedure was used to measure some points of the acetone + CO_2 system.

The materials used were: acetone (Aldrich, ≥ 99.9 %), CO_2 (CRYOSERVICE, 99.95 %), ethanol (Aldrich, ≥ 99.8 %), and bidistilled water. Commercial materials were used without further purification.

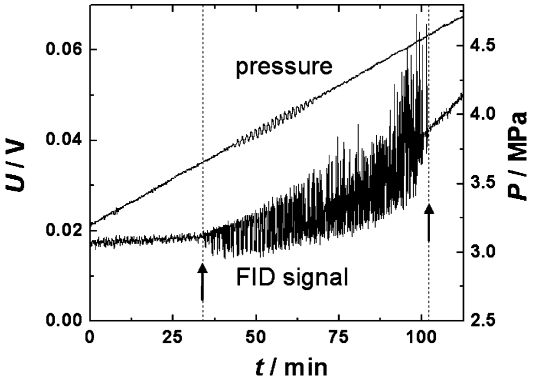

Figure 3. Plot of the FID signal and the pressure against time for the system EtOH + H_2O at 0.05 EtOH mole fraction and 523.2 K. At the start of the pressure ramp, the FID signal is stable at 0.17 V only increasing slightly. Suddenly, at t = 34 min (3.7 MPa), the signal becomes noisy (arrowed), and both signal and noise continue to increase until t = 102 min (4.6 MPa), when the noise suddenly disappears (right-hand arrow). The two pressures are the dew and the bubble point, respectively.

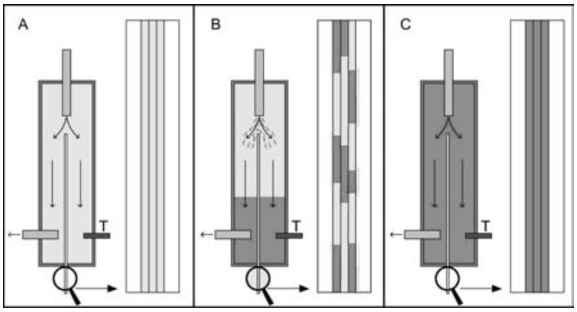

Figure 4. Three schematic views of the equilibrium cell to illustrate how the flow regime changes according to the phase behavior. A greatly magnified view of the fiber is shown on the right-hand side of each box. (A) Vapor phase. (B) Vapor−liquid equilibrium. (C) Liquid phase.

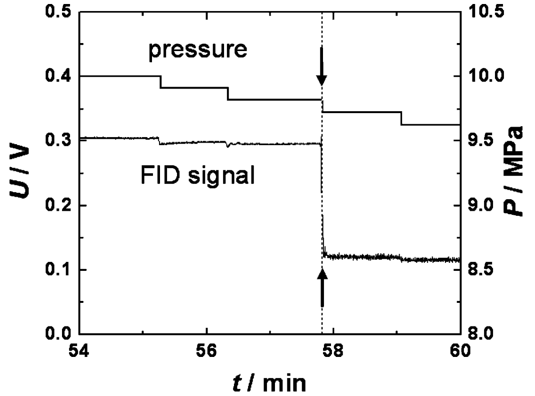

Figure 5. Plot of the FID signal and the pressure against time for the system acetone + CO_2 at 0.2 acetone mole fraction at 344.7 K. At 9.6 MPa (arrow), the FID signal jumps to a much lower value than usual. This pressure is the bubble point.

Results and Interpretation

Typical FID signals for EtOH + H_2O are shown in Figure 3. The FID signal depends on the amount of the flammable compound reaching the detector. This amount depends on the flow of fluid through the hollow fiber, the density, and the composition of the sample. At lower pressures, there is only a gas phase in the equilibrium cell. Therefore, the sample flowing through the fiber consists of a low-density fluid, and the FID signal has a low value. On the other hand, at the highest pressures, a high FID signal is observed because the density of the liquid phase is much higher than that of the vapor phase. Between these two situations, a two-phase region is expected, when droplets of liquid phase are sprayed onto the edge of the fiber. The FID detects alternately liquid and vapor phase and gives a spiky noisy line for the signal. A schematic representation of these three flow situations is given in Figure 4.

Notice that the slope of the signal in the single phase region is positive. The reason for this is that the flow rate through the capillary depends on the pressure difference between the equilibrium cell and the end of the fiber. Since the pressure increases during the experiment, the flow rate also increases, and hence, the concentration of organic material in the carrier gas also rises.

The plots for FID signal and pressure for the acetone + CO_2 system are somewhat different as shown in Figure 5. Due to the characteristics of the BPR, both the pressure and the FID signal decrease stepwise. However, at the phase transition,

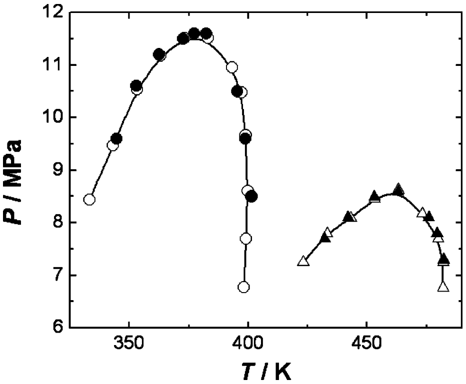

Figure 6. P, T phase diagram for the acetone (1) + CO_2 (2) system. This work: ●, $x_1 = 0.2$; ▲, $x_1 = 0.7$. Wu et al.:[12] ○, $x_1 = 0.2$; △, $x_1 = 0.7$.

Table 1. Phase Boundary for the Acetone (1) + CO_2 (2) System As Measured by Our Holey Fiber Method[a]

T/K	P/MPa	phase transition[b]	T/K	P/MPa	phase transition[b]	T/K	P/MPa	phase transition[b]
$x_1 = 0.2$								
344.7	9.6	b	352.9	10.6	b	362.6	11.2	b
372.7	11.5	d	377.3	11.6	d	382.4	11.6	d
395.4	10.5	d$^{\mathrm{ib}}$	398.9	9.6	d$^{\mathrm{ib}}$	401.5	8.5	d$^{\mathrm{ib}}$
$x_1 = 0.7$								
432.2	7.7	b	442.0	8.1	b	453.1	8.5	b
463.1	8.6	b	476.0	8.1	d$^{\mathrm{ib}}$	479.5	7.8	d$^{\mathrm{ib}}$
482.2	7.3	d$^{\mathrm{ib}}$						

[a] The uncertainty in the isothermal measurements is estimated to be ± 0.05 MPa and for the isobaric measurements ± 0.1 K, marked $^{\mathrm{ib}}$. [b] b: bubble point, d: dew point.

arrowed, the FID signal decreases by a much larger step, indicating that a bubble point is crossed. Just as before, a noisier line is observed in the two-phase region.

Comparison with literature data

Acetone + CO_2 System. As shown in Figure 6, the acetone (1) + CO_2 (2) system has wide phase boundary envelopes. The dew points were collected using the isobaric procedure, as explained above because of the steepness of the boundary. Two compositions, $x_1 = 0.2$ and $x_1 = 0.7$, were covered using our new method. The results are presented together with the literature data in Table 1 and represented in Figure 6. To evaluate the agreement between them, the standard deviation, σ, is calculated

$$\sigma = \left[\frac{1}{N-1}\sum_{i=1}^{N}(Y_i^{\mathrm{exp}} - Y_i^{\mathrm{lit}})^2\right]^{1/2} \qquad (1)$$

N is the number of experimental points and Y^{exp} is the magnitude changed during the measurement (either P or T, depending on the steepness of the phase transition boundary). Y^{lit} are values obtained from literature data by interpolation. The following values for standard deviation are obtained: 0.07 MPa for the pressure measurements and 1.3 K for the temperature measurements. Thus, this is an acceptable agreement between the literature data and those obtained in this work.

EtOH + H_2O System. The points collected using our method for the system ethanol + H_2O are gathered in Table 2 and represented in Figure 7 along with data from ref 17. The value for the standard deviation is 0.18 MPa calculated using eq 1. Again, the data obtained in this work agree well with those reported in the literature.

Table 2. Phase Boundary for the EtOH (1) + H_2O (2) System As Measured by Our Holey Fiber Method[a]

T/K	P/MPa	phase transition[b]	T/K	P/MPa	phase transition[b]	T/K	P/MPa	phase transition[b]
$x_1 = 0.05$								
523.1	3.7	d	523.1	4.6	b	548.1	6.0	d
548.1	6.9	b	573.1	8.8	d	573.1	10.0	b
598.1	13.7	b						
$x_1 = 0.1$								
473.1	1.8	d	473.1	2.3	b	523.1	4.3	d
523.1	5.2	b	548.1	6.3	d	548.1	7.6	b
573.1	9.5	d	573.1	10.8	b			
$x_1 = 0.2$								
423.1	0.5	d	423.1	0.8	b	473.1	2.0	d
473.1	2.4	b	523.1	4.9	d	523.1	5.8	b
548.1	7.3	b						
$x_1 = 0.3$								
473.1	1.9	d	473.1	2.7	b	523.1	5.5	d
523.1	6.2	b	548.1	8.1	d	548.1	9.0	b
573.1	12.0	d	573.1	12.6	b			
$x_1 = 0.4$								
423.1	0.7	d	423.1	0.9	b	473.1	2.3	d
473.1	2.6	b	523.1	5.8	d	523.1	6.3	b
548.1	8.7	d	548.1	9.3	b			

[a] The uncertainty in the measurements is estimated to be ± 0.05 MPa. [b] b: bubble point, d: dew point.

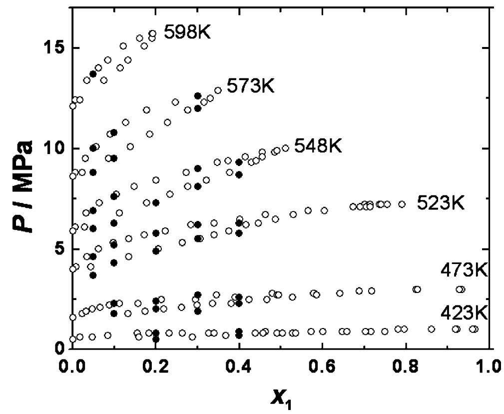

Figure 7. P, x phase diagram for the binary mixture ethanol (1) + H_2O (2). ●, this work; ○, Barr-David and Dodge.[17]

Conclusions

A new dynamic synthetic method has been developed to perform rapid phase equilibrium measurements. This method consists of detecting the change in FID signal of a sample taken with a capillary hollow fiber. This method is suitable for carrying out measurements on systems containing supercritical water. To validate our method, phase boundaries for binary mixtures acetone + CO_2 and EtOH + H_2O have been measured at temperatures up to 600 K. The good agreement between our measurements and the literature data support our view that our apparatus allows full equilibration of the phases.

A Toast to Professor Schneider. Our new method permits us to pay a unique tribute to Professor Schneider and his outstanding contribution to the fields of supercritical fluids, thermodynamics, and phase behavior.

One of the authors found an intact bottle of soviet vodka (STOLICHNAYA, 40 % vol. ca. 1991). To drink the toast to Professor Schneider with the precision that the occasion requires, we had to ensure that this vodka had actually the strength claimed on the bottle and that it had not deteriorated with age. Therefore we decided to test the phase behavior of the vodka. Points were taken at (423.2, 473.2, 523.2, and 548.2) K. Both dew and bubble points were found in every case. The vodka

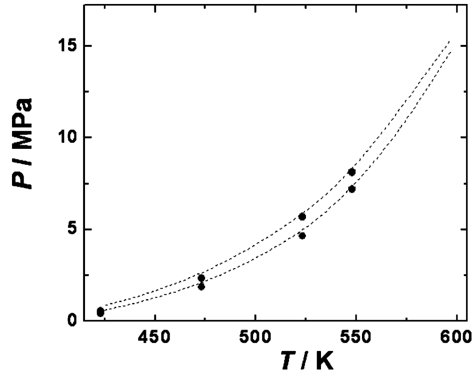

Figure 8. $P-T$ phase diagram for Stolichnaya vodka 40 % vol. ●, experimental data; ------, phase boundary for a mixture of ethanol (1) + water (2) with $x_1 = 0.17$.

with 40 % EtOH can be approximately considered as a mixture of EtOH (1) + water (2) with $x_1 = 0.17$. Figure 8 shows our points measured for the vodka overlaid with the boundary for EtOH (1) + water (2) ($x_1 = 0.17$) interpolated from data by Barr-David and Dodge.[17] It can be seen that a good agreement was found between them, showing that the vodka was as good as ever, so we had confidence when toasting Professor Schneider's good health!

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Literature Cited

(1) Bermejo, M. D.; Cocero, M. J. Supercritical water oxidation: a technical review. *AIChE J.* **2006**, *52*, 3933–3951.
(2) Savage, P. E. Organic chemical reactions in supercritical water. *Chem. Rev.* **1999**, *99*, 603–621.
(3) Fraga-Dubreuil, J.; Poliakoff, M. Organic reactions in high-temperature and supercritical water. *Pure Appl. Chem.* **2006**, *78*, 1971–1982.
(4) Licence, P.; Ke, J.; Sokolova, M.; Ross, S. K.; Poliakoff, M. Chemical reactions in supercritical carbon dioxide: from laboratory to commercial plant. *Green Chem.* **2003**, *5*, 99–104.
(5) Bourne, R. A.; Stevens, J. G.; Ke, J.; Poliakoff, M. Maximising opportunities in supercritical chemistry: the continuous conversion of levulinic acid to γ-valerolactone in CO_2. *Chem. Commun.* **2007**, 4632–4634.
(6) Deiters, U.; Schneider, G. M. Fluid mixtures at high pressures. Computer calculations of the phase equilibria and the critical phenomena in fluid binary mixtures from the Redlich-Kwong equation of state. *Ber. Bunsenges. Phys. Chem.* **1976**, *202*, 153–218.
(7) Deiters, U. K.; Schneider, G. M. High pressure phase equilibria: Experimental methods. *Fluid Phase Equilib.* **1986**, *29*, 145–160.
(8) Schneider, G. M. The continuity and family concepts: Useful tools in fluid phase science. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2285–2290.
(9) Brunner, E.; Thies, M. C.; Schneider, G. M. Fluid mixtures at high pressures: Phase behavior and critical phenomena for binary mixtures of water with aromatic hydrocarbons. *J. Supercrit. Fluids* **2006**, *39*, 160–173.
(10) Christov, M.; Dohrn, R. High-pressure fluid phase equilibria. Experimental methods and systems investigated (1994−1999). *Fluid Phase Equilib.* **2002**, *202*, 153–218.
(11) Wu, W.; Ke, J.; Poliakoff, M. New design of fiber-optic reflectometer for determining the phase boundary of multicomponent fluid mixtures at high pressures and high temperatures. *Rev. Sci. Instrum.* **2006**, *77*, 023903.
(12) Wu, W.; Ke, J.; Poliakoff, M. Phase Boundaries of CO_2 + Toluene, CO_2 + Acetone, and CO_2 + Ethanol at High Temperatures and High Pressures. *J. Chem. Eng. Data* **2006**, *51*, 1398–1403.
(13) Avdeev, M. V.; Konovalov, A. N.; Bagratashvili, V. N.; Popov, V. K.; Tsypina, S. I.; Sokolova, M.; Ke, J.; Poliakoff, M. The fibre optic reflectometer: A new and simple probe for refractive index and phase separation measurements in gases, liquids and supercritical fluids. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1258–1263.
(14) Mueller, S. G.; Werber, J. R.; Al-Dahhan, M. H.; Dudukovic, M. P. Using a Fiber-Optic Probe for the Measurement of Volumetric Expansion of Liquids. *Ind. Eng. Chem. Res.* **2007**, *46*, 4330–4334.
(15) Fournier, R. O.; Rowe, J. J. The solubility of amorphous silica in water at high temperatures and high pressures. *Am. Mineral.* **1977**, *62*, 1052–1056.
(16) Brunner, G. *Gas Extraction*; Steinkopff Darmstadt: New York, 1994.
(17) Barr-David, F.; Dodge, B. F. Vapor-liquid equilibriums at high pressures: systems EtOH-water and 2-propanol-water. *J. Chem. Eng. Data* **1959**, *4*, 107–120.

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