Video Article

High-pressure Sapphire Cell for Phase Equilibria Measurements of CO_2/ Organic/Water Systems

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Abstract

The high pressure sapphire cell apparatus was constructed to visually determine the composition of multiphase systems without physical sampling. Specifically, the sapphire cell enables visual data collection from multiple loadings to solve a set of material balances to precisely determine phase composition. Ternary phase diagrams can then be established to determine the proportion of each component in each phase at a given condition. In principle, any ternary system can be studied although ternary systems (gas-liquid-liquid) are the specific examples discussed herein. For instance, the ternary THF-Water-CO_2 system was studied at 25 and 40 °C and is described herein. Of key importance, this technique does not require sampling. Circumventing the possible disturbance of the system equilibrium upon sampling, inherent measurement errors, and technical difficulties of physically sampling under pressure is a significant benefit of this technique. Perhaps as important, the sapphire cell also enables the direct visual observation of the phase behavior. In fact, as the CO_2 pressure is increased, the homogeneous THF-Water solution phase splits at about 2 MPa. With this technique, it was possible to easily and clearly observe the cloud point and determine the composition of the newly formed phases as a function of pressure.

The data acquired with the sapphire cell technique can be used for many applications. In our case, we measured swelling and composition for tunable solvents, like gas-expanded liquids, gas-expanded ionic liquids and Organic Aqueous Tunable Systems (OATS)[1-4]. For the latest system, OATS, the high-pressure sapphire cell enabled the study of (1) phase behavior as a function of pressure and temperature, (2) composition of each phase (gas-liquid-liquid) as a function of pressure and temperature and (3) catalyst partitioning in the two liquid phases as a function of pressure and composition. Finally, the sapphire cell is an especially effective tool to gather accurate and reproducible measurements in a timely fashion.

Video Link

The video component of this article can be found at https://www.jove.com/video/51378/

Introduction

When reactions are being conducted with a hydrophilic catalyst and a hydrophobic substrate to form a hydrophobic product, it is quite common to employ mixed solvents in order to provide a homogeneous reaction system. For example, THF-water and acetonitrile-water are commonly mixed solvent vehicles for these homogenous reaction processes. Ideally, it would be advantageous to develop a process in which the reaction is performed under homogeneous conditions followed by an induced phase split to separate the aqueous and organic solvent components. The hydrophilic catalyst would then be located in the aqueous phase and the hydrophobic product in the organic phase. The overall process would enable a facile separation/isolation of product and a means to recycle the catalyst. Organic Aqueous Tunable Solvents (OATS) provide a vehicle to accomplish this strategy. The first step in developing OATS was to understand the phase behavior of the organic-aqueous solution as a function of organic/water proportion, CO_2 pressure and temperature. The efficiency of the phase separation upon addition of CO_2 (*i.e.* the cross-solubility in each phase) is important to quantify. In fact from a process standpoint, cross-solubility can translate directly to product and catalyst losses in the undesired, respective phases. Therefore, knowing phase composition as a function of pressure is key information for "real-world" applications. Sampling methods are available;[5-7] however, direct sampling from high pressure systems may alter the equilibrium of the system and result in phase separation or flashing as a result of abrupt changes in pressure or temperature in the sample line. Therefore, a method that does not disturb the system and enables fast acquisition and reproducible data was preferable. The high pressure sapphire cell apparatus is indeed a versatile tool to measure phase behavior without sampling. Using a cathetometer, very precise volume measurements can be recorded. These experimental volume measurements are then used with the Peng-Robinson cubic equation of state (modifications of Stryjek and Vera) and modified Huron-Vidal mixing rules to effectively calculate volume expansion and phase compositions as a function of temperature and pressure[8-10]. This technique was specifically designed to measure phase equilibria of vapor-liquid-liquid systems. It should be highlighted that the sapphire cell is not suited to study systems that involve solids. The data acquired with the high-pressure sapphire cell guided the choice of experimental conditions for OATS mediated reactions, separations and catalyst recycling. Furthermore, the sapphire cell was also used to (1) measure solvent expansion (or swelling) as a function of CO_2 pressure with organic solvents and ionic liquids, (2) determine catalyst

partitioning in multiphase systems as a function of pressure, solvent system and temperature and (3) understand phase behavior in complex reaction systems conducted under pressure. Herein, we report (1) the description of high- pressure sapphire cell apparatus, (2) the possible limitations and safety precautions, (3) its operating protocol, and (4) specific proof of principle results.

The high-pressure sapphire cell discussed above was custom made (**Figure 1**). The equilibrium cell consists of a hollow sapphire cylinder (50.8 mm O.D. x 25.4±0.0001 mm I.D. x 203.2 mm L). The cell is divided into two chambers separated by a piston. The bottom cell contains water used as a pressurizing fluid (dyed blue for demonstrative purposes) and the top cell contains the equilibrium components (**Figure 2**). The air bath was custom-constructed of Plexiglas to fit specific setting and hood-size. The cell is placed inside a temperature controlled airbath, which is maintained with a digital temperature controller. The temperature of the airbath is monitored with thermocouples (Type K) and digital readouts. There is an additional thermocouple (Type K) inside the sapphire cell that is also monitored with a digital readout. The pressures were measured with a pressure transducer and digital readout. Two high pressure, 500 ml, syringe pumps capable of maintaining pressure up to 10 MPa were required for operation. The first high pressure syringe pump contains water that is used to pressurize the system. The second high pressure pump was used to introduce CO_2 (or other gas) to the system. The gas inlet is at the top of the sapphire cell. The pressure is controlled with the high pressure syringe pump to achieve equilibrium pressure on both sides of the piston. The cell is mounted on a rotating shaft, and mixing is achieved by manually rotating the entire cell.

Liquid and vapor volumes are calculated by measuring the height of the meniscus with a micrometer cathetometer. For displacements less than 50 mm, the accuracy is 0.01 mm; for larger displacements, the accuracy is 0.1 mm.

Protocol

1. Assembly of the Sapphire Cell

1. Place a 116 size backing ring and 210 size O-ring onto the piston. Verify that O-ring material is compatible with chemicals used during the experiment ***prior*** to assembly.
    1. Some backing rings have a flat and a curved edge. If this is the case, place the flat edge down and the curved edge against the O-ring.
2. Thread rod into the bottom of the piston using a rod with a threaded tip (**Figure 3**).
3. Wrap the rod with a layer of lab towel (or other nonabrasive lab wipes) to prevent scratching while inserting the piston into the cell.
4. Insert the piston in the cell. This step can be difficult, so force must be used. However, it is important to ensure that only the O-ring comes in contact with the cell wall.
5. Place an 8210 size backing ring and 210 size O-ring onto the top and bottom end cap (**Figure 4**). Note: the bottom end cap is the water side with the fitting attached. Be careful that while inserting the end caps, only the O-ring comes in contact with the cell wall.
6. Align end caps and insert two bolts through the mounting bracket and through the aluminum spacers.
7. Loosely attach nuts.
8. Insert the remaining two bolts through aluminum spacers and end cap holes.
9. Loosely attach nuts.
10. Tighten all nuts to 8-10 ft/lbs torque.
11. Mount assembled cell to bracket on rotating shaft by screwing bolts through the bottom of the sapphire cell and then through the rotating shaft.
    Safety Notes:
    1. Mount assembled cell so that the opening of the valve on the top end cap (for sample addition) is facing away from the user should a catastrophic failure occur.
    2. Place the top of the needle valve specifically to face away from the user.
12. Attach all high pressure fittings, tubing and the thermocouple to top and bottom end cap. Attach high pressure tubing to include a pressure relief valve on the pressurizing side of the sapphire cell. Located the pressure relief valve away from the user and electrical equipment (pressure relief will result in the release of water).

2. Safe Handling of the Sapphire Cell

Note: **Do not handle the sapphire cell with bare hands.** The transfer of oil from skin can result in micro-cracks or scratches. **Do not place the sapphire cell on the lab bench unprotected**. The hard surface will likely scratch the cell, or there is risk of the cell rolling. **Always inspect the cell for any cracks or defects prior use**. **Place the air-bath in the down position when operating the cell under pressure.** The airbath serves two purposes: (1) to control temperature when necessary and (2) to provide a barrier between the individual and the pressurized contents of the cell in case of catastrophic failure.

1. **Pressure-test the sapphire cell every 12 pressure cycles.** A pressure cycle is increasing the pressure above atmospheric and then depressurizing. If not used frequently, pressure-test the cell every four months. Complete pressure testing with the operating side full of water.
   Safety Note: Pressure testing must be completed with an incompressible fluid (*e.g.* water) should the apparatus fail while under pressure.
    1. Attach water-filled high pressure syringe pump to the sample inlet connection (top of the cell) and fill the cell completely.
    2. Close the sample inlet valve.
    3. Run the syringe pump so that a few drops of water leave the high pressure tubing. This is to ensure no air is in the line prior to connection.
    4. Attach the tubing to the sapphire cell fitting at the bottom of the sapphire cell.
    5. Fill the bottom cell with water to pressurize and monitor pressure to detect any possible pressure drop.
    6. Gradually increase pressure 0.1 MPa over the setting of the pressure relief valve. Collect water that is released from the pressure relief valve in a small container.

7. Reduce pressure to atmospheric.
8. Reset the pressure relief valve and high pressure syringe pumps.

3. Operation of the Sapphire Cell Apparatus

1. Fill the high pressure syringe pump approximately half full with water. The amount of water that will be required will be determined by the pressures at which the experiment will be run. Note: Do not completely fill the high pressure syringe pump so that the system may be depressurized if required.
2. Run the high pressure syringe pump so that a few drops of water leave the tubing. This is to ensure no air is in the line prior to connection.
3. Attach the tubing to the sapphire cell fitting.
4. Open the gas inlet valve.
5. Fill the cell with water until the piston is at a level that liquid height may be measured with the cathetometer. Note: If the gas inlet valve is not open the system will become pressurized.
6. Close the gas inlet valve.
7. Attach an air-tight syringe to the sample inlet connection (open) and evacuate the cell by pulling back 10 ml.
8. Close the sample inlet valve.
9. Apply slight pressure on the airtight syringe while slowly opening the sample inlet valve
10. Inject a volume of sample by again using an airtight syringe attached to the sample inlet. Note: depending on the syringe size, the sapphire cell may need to be inverted on the rotating shaft as the airbath cannot be raised completely above the cell.
11. Close the valve.
12. Mass the syringe before and after addition of the sample. Measure the amount of sample by recording the mass of the syringe before and after addition. There is a small error associated with this method due to an unknown amount of sample left in the tubing and fittings.
13. Set air bath at the desired temperature.
14. Allow sample to come to equilibrium prior to taking first height measurement with the cathetometer. To ensure equilibrium was reached repeat measurements until no change is observed for at least 3x. The time to reach equilibrium is highly dependent on the system and may range from minutes to hours. Complete a preliminary study in which the system is observed for an extended period of time (24 hr) to ensure equilibrium has been achieved.
15. Prime the line with CO_2. Add CO_2 by first running the high pressure syringe pump to eject any air from the line (not attached the inlet valve).
16. Attach the tube to the gas inlet valve.
17. Open the gas inlet valve to the sapphire cell. Measure the amount of CO_2 added to the system by recording the volume of the high pressure syringe pump before and after CO_2 addition.
18. Check that the flow-rate on the water high pressure syringe pump is zero (after equilibrium is reached) to ensure there are no leaks.
19. Bring pressure to desired value by adjusting the pressurizing fluid (water) with the high pressure syringe pump.

4. Cleaning the Sapphire Cell

Following the completion of the experiment, clean the sapphire cell. Clean the cell by repeatedly washing with solvents. Disassemble cell (see Protocol 5) to clean if needed.

1. Inject approximately 10 ml of solvent in which the sample is soluble.
2. Shake the cell on the rotating shaft to clean the walls and piston.
3. Invert the sapphire cell and open the sample inlet valve to empty the contents of the cell.
4. Repeat procedure.
5. Repeat procedure with acetone as solvent.
6. Dry cell: open all valves and heat the airbath.

5. Disassembling the Sapphire Cell

1. Remove the tubing from the fittings. Note: Water will drain from the bottom of the sapphire cell. Removing the piston from the sapphire cell is difficult if it is halfway up the cell once the system is dismantled.
2. Run back the water into the high pressure syringe pump.
    1. Close the sample inlet valve and pressurize the cell with CO_2.
    2. Refill high pressure syringe pump (<5 ml/min).
    3. Do not refill the high pressure syringe pump if the cell is not pressurized. If the cell is still pressurized after running the water back to the high pressure pump: open the gas inlet valve to vent into the hood.
    4. Remove the tubing supplying the water from the sapphire cell.
3. Loosen the nuts and the spacer bolts.
4. Take out the bolts. Ensure that no metal comes in contact with the cell.
    1. If the bolts do not come out easily, tap the bolts.
    2. Take the end caps straight off without touching the cell.
5. Remove the piston with the threaded rod wrapped in a towel.

Representative Results

The schematic of the high-pressure sapphire cell is shown in **Figure 2**, along with a picture of the cell. The sample is in the top cell and in the bottom cell is water with blue dye for demonstration purposes. The liquid components are fed via a syringe and valve, while the CO_2 (gas component) is pumped through a high pressure syringe pump. The pressure can be controlled through the piston (the water is also fed via high pressure syringe pump in our setup). The liquid and gas phases can be clearly seen in the cell, above the piston. The assembly of the piston is described in the protocol, and is basically constructed with the threaded rod (**Figure 3**), the backing ring and associated O-ring (**Figure 3**). The thermocouple measures the temperature in the cell. The whole cell is encased into an air bath to precisely control temperature. The level of each liquid and vapor phase is precisely measured using the cathetometer located on the left hand side of the diagram.

Ternary phase diagrams have been calculated using the measurements recorded using the sapphire cell technique[11-13]. Using the following material balances, two specific ternary phase diagrams were constructed as shown in **Figures 5** and **6**.

$$N_T = \frac{V^\alpha}{v^\alpha} + \frac{V^\beta}{v^\beta} + \frac{V^v}{v^v}$$

Equation 1

$$N_1 = \frac{x_1^\alpha V^\alpha}{v^\alpha} + \frac{x_1^\beta V^\beta}{v^\beta} + \frac{x_1^v V^v}{v^v}$$

Equation 2

$$N_2 = \frac{x_2^\alpha V^\alpha}{v^\alpha} + \frac{x_2^\beta V^\beta}{v^\beta} + \frac{x_2^v V^v}{v^v}$$

Equation 3

In the above equations, *N* is the number of moles, known from loading the sapphire cell and V is the volume of phases α, β or measured using the cathetometer. The molar volumes, and the mole fraction of component *i* in phase α, β or are unknown variables. For a multicomponent, multiphasic system, the nine unknown terms are solved by using three different cell loadings to establish nine material balances[14,15].

A ternary diagram of water + CO_2 + THF at 25 °C obtained with two distinct techniques is shown in **Figure 5**. The synthetic method refers to the data obtained with the sapphire cell protocol. The analytical method refers to sampling method, in which samples of each phase were taken and analyzed separately (this was conducted in a Parr reactor equipped of dip-tubes and sampling loops). Clearly, the data obtained by the two methods compare well, establishing the sapphire cell as an accurate technique. In contrast with the sampling technique however, the sapphire cell is much less experimentally intensive than the analytical method and minimizes measurement error and improves repeatability. In **Figure 6**, the ternary phase diagram of CO_2 + THF + water is shown along with calculated phase behavior. The table of data at 3 different temperatures is also shown (**Table 1**). Experimentally, the ability to have a direct visual on the phase behavior was essential. This is particularly evident in **Figure 7**, which shows a water/THF solvent system in the absence and in the presence of CO_2. Again the blue liquid is simply the water (with a blue dye) that controls pressure by moving the piston. A homogeneous mixture of THF/ water (70/30) containing a red, hydrophilic dye in the absence of CO_2 is shown on the right in **Figure 6**. The addition of 2 MPa of CO_2 causes a striking phase split with the aqueous rich phase at the bottom and the THF-expanded phase on the top. The hydrophilic red dye partitions exclusively in the aqueous phase-the UV measurements indicate a partition coefficient higher than 10^6 (the limit of detection of our instrument).

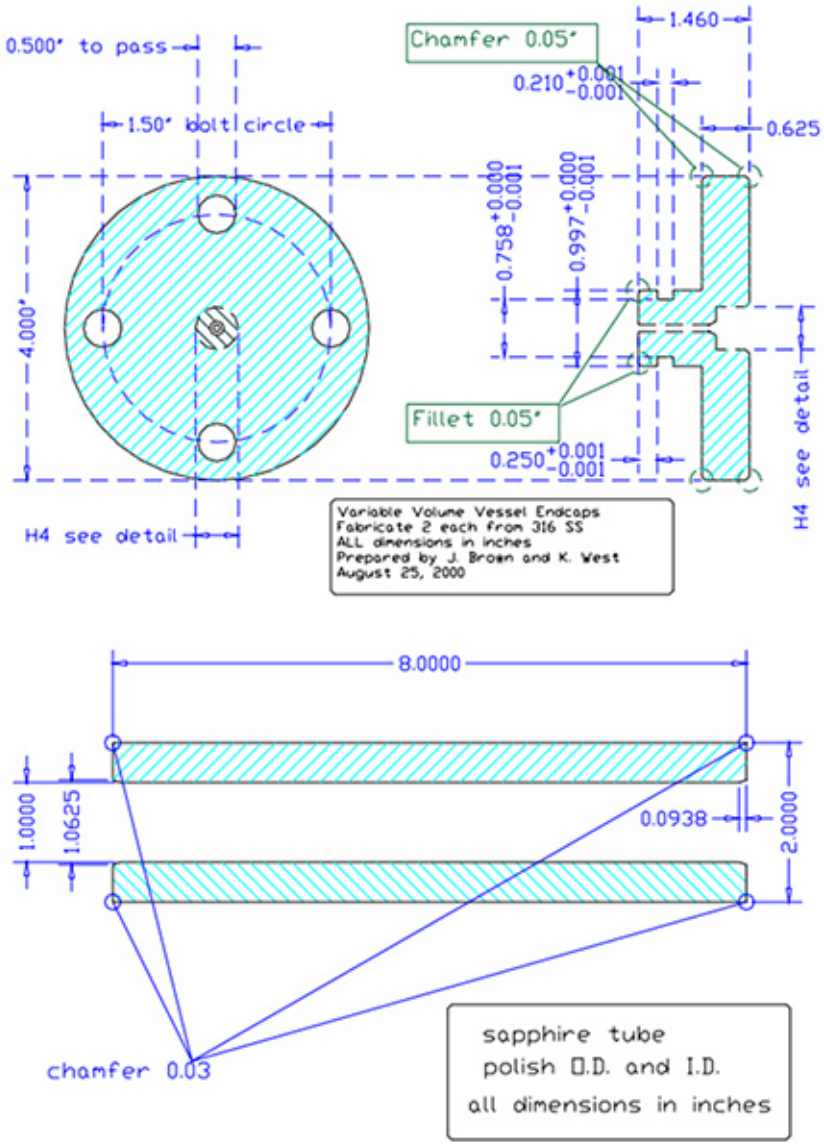

Figure 1. Schematic with dimensions of the body of the sapphire cell. Click here to view larger image.

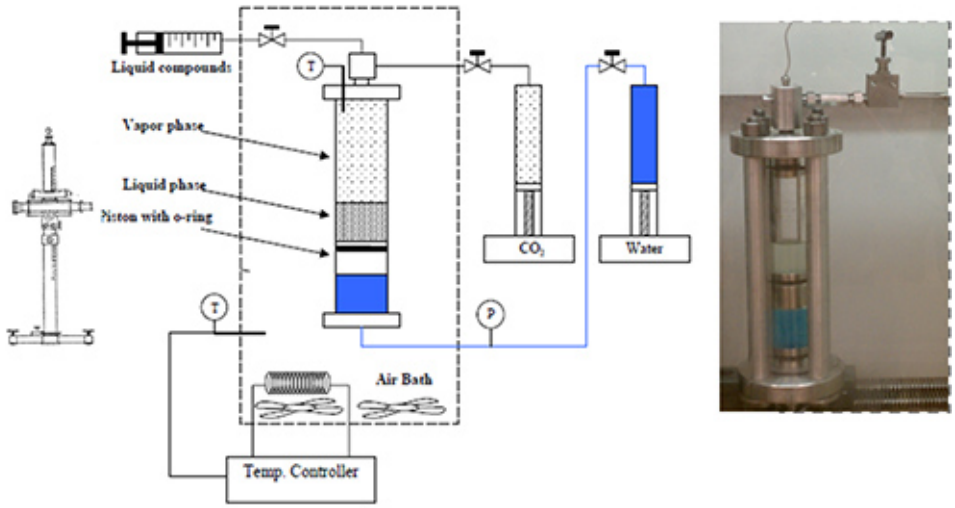

Figure 2. Schematic and picture of the sapphire cell apparatus. Click here to view larger image.

Figure 3. Threaded rod for piston removal.

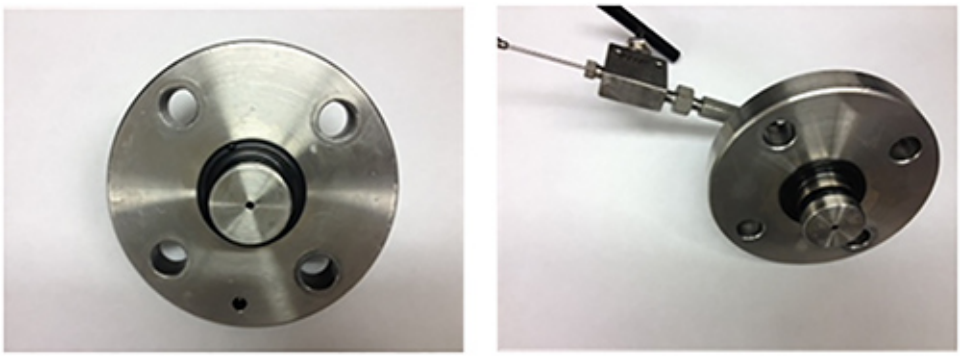

Figure 4. Bottom (left) and top (right) end caps fitted with backing rings and O-rings.

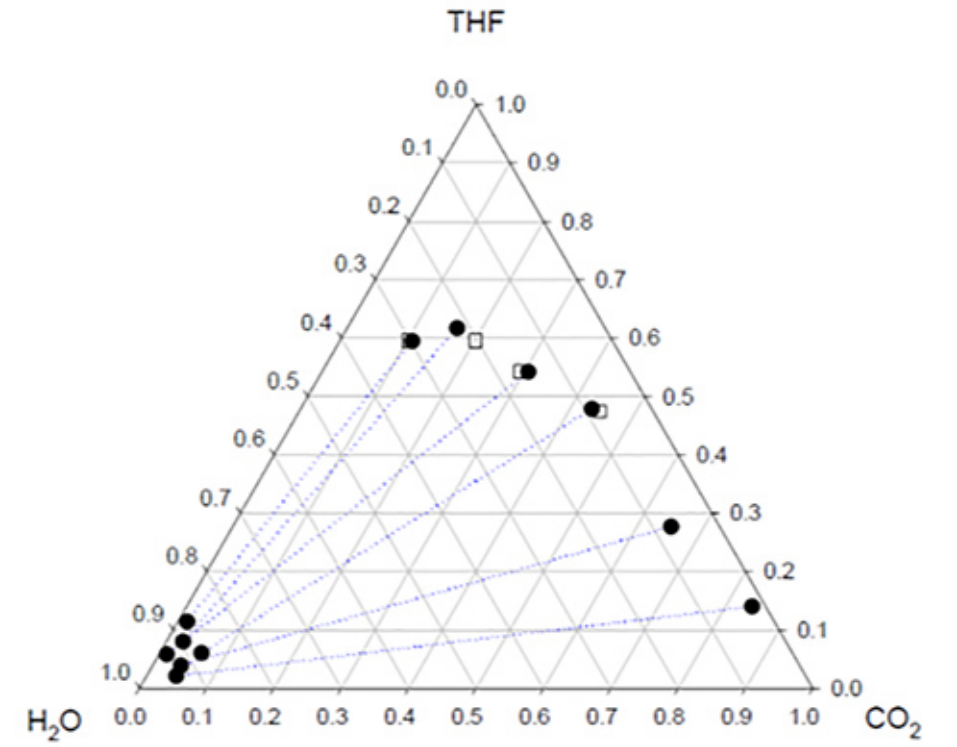

Figure 5. Ternary diagram of the system THF/Water/CO_2 at 25 °C. Comparison of experimental methods (●) Synthetic method (Sapphire cell). (□) Analytical method[8].

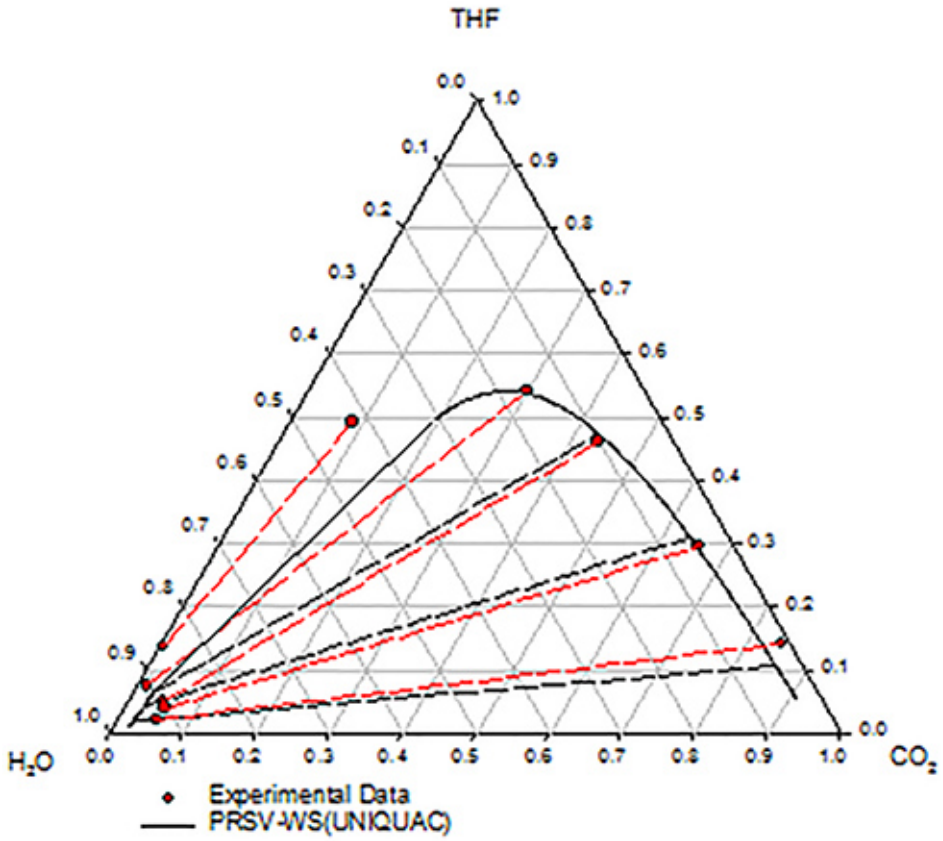

Figure 6. Ternary diagram of the system THF/Water/CO_2 at 25 °C, showing the liquid-liquid equilibrium at various CO_2 pressures, experimental and predicted data[16].

Figure 7. Water-THF-CO_2 Equilibria. Left: No CO_2, a single phase. Right: 2 MPa of CO_2, two liquid phases with dye partitioning >10^6.

		Liquid phase 1 (L_1)				Liquid phase 2 (L_2)				Vapor
T (K)	P (MPa)	x_{CO2}	x_{THF}	x_{H2O}	v_L (cm^3/mol)	x_{CO2}	x_{THF}	x_{H2O}	v_L (cm^3/mol)	v_V (cm^3/mol)
298	1.03	0.014	0.114	0.872	23.7	0.107	0.595	0.298	55.5	2269.1
298	1.55	0.025	0.080	0.895	21.8	0.163	0.617	0.220	61.0	1467.6
298	2.07	0.012	0.058	0.930	20.2	0.306	0.542	0.152	58.9	1065.2
298	3.10	0.062	0.060	0.878	18.7	0.432	0.479	0.089	79.8	658.8
298	4.14	0.042	0.039	0.919	19.4	0.651	0.277	0.072	54.1	449.4
298	5.17	0.044	0.021	0.935	18.1	0.839	0.140	0.021	53.3	316.0
313	0.99	0.013	0.117	0.870	25.1	0.045	0.511	0.444	53.4	2512.6
313	2.42	0.028	0.072	0.900	21.7	0.230	0.545	0.225	62.0	957.9
313	3.86	0.015	0.047	0.938	20.2	0.421	0.464	0.115	60.0	549.5
313	4.49	0.005	0.038	0.957	20.7	0.557	0.381	0.062	58.0	451.9
313	5.21	0.030	0.033	0.937	19.9	0.625	0.324	0.051	59.1	367.4
333	1.03	0.002	0.102	0.896	24.0	0.055	0.535	0.410	58.0	2581.3
333	2.07	0.006	0.064	0.930	22.3	0.116	0.559	0.325	55.5	1240.7
333	3.10	0.003	0.042	0.955	21.0	0.225	0.573	0.202	59.2	791.1
333	4.14	0.021	0.040	0.939	20.5	0.308	0.546	0.146	64.6	565.3
333	5.17	0.018	0.025	0.957	20.4	0.407	0.454	0.139	58.0	428.6

Table 1. LLE of CO_2+THF+Water System at 298, 313 K [8].

Discussion

The sapphire cell apparatus is a unique tool for measuring phase behavior without sampling, and thus equilibrium is not disturbed. To ensure accurate repeatable data, there are critical steps in the protocol (Protocol 4 entitled “Operation of the Sapphire Cell Apparatus”) that must be followed. For any system in which phase composition is measured, it is critical to reach equilibrium prior to measurement. The sapphire cell is placed on a rotating shaft that facilitates mixing to more rapidly achieve equilibrium. The ternary system consists of three components and three phases (vapor-liquid-liquid) at a fixed temperature and pressure. Through a series of material balances, the composition and molar volumes of the three phases is measured. Measurement repetition is required to ensure repeatable and accurate visual data collection.

As mentioned, solids are not easily handled with this technique. First, it renders visual measurement almost impossible. Second, it requires that the cell be disassembled for cleaning. Literature provides a means for troubleshooting[14,17]; however, the technique is straightforward and without significant potential for difficulties. Limitations of the presented technique must also be considered for extension to highly nonideal systems.

Modifications to the outlined technique may be made to accommodate additional phase behavior studies. Using the sapphire cell apparatus, volume measurements of binary systems (VLE) and phase behavior measurements may be used to describe accurately the effect of the solvent system on the reaction kinetics in a multicomponent system. The method described herein to determine VLL phase equilibria at low and high pressures is precise and efficient. The effect of pressure on phase composition can be obtained visually and without the need of sampling - and thus without disturbing the system. It is a versatile technique and has been used in our laboratory for additional applications including the determination of catalyst partitioning, volume expansion, or ionic liquid swelling as a function of CO_2 pressure.

Disclosures

The authors do not have competing financial interest or conflicts of interests.

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