# **Study on Critical Points of Carbon Dioxide + Single and Multicomponent Solid Solute Systems**

### Introduction

Supercritical fluids (SCFs) are gaining increasing attention as attractive alternatives for traditional solvents in green chemistry. The unique potential of SCFs to adjust solvent power by simply varying temperature and pressure offers a plethora of possibilities for selective extraction, purification and precipitation processes. Among supercritical fluids, carbon dioxide (CO<sub>2</sub>) has been the principal solvent of interest on account of its best combination of properties.<sup>1,2</sup>

Solubility of compounds in SCF- CO<sub>2</sub> is one of the most extensively investigated areas of SCF research as it establishes the technical and economic viability of a particular supercritical process.<sup>3</sup> Over the last few decades, a considerable amount of solubility data has appeared in the literature. However, lack of reliable phase equilibrium data has been one of the major obstacles in the progress of SCF technology.<sup>4,5</sup>

The phase behavior of solutes in SCF is an important aspect, which is often overlooked in the solubility determinations. In the presence of the solute the vapor pressure curve for pure  $CO_2$  is shifted ending in a critical end point. Also, solid solutes when in contact with supercritical  $CO_2$  can exhibit complex phase behavior such as depression in melting point resulting in multiple phases.<sup>6</sup> This depression in melting point can considerably influence the determination of solid solubility. In addition, density inversion may occur leading to erroneous solubility data. This emphasizes the need for checking the phase equilibria when measuring solid solubility data.<sup>7</sup>

The knowledge of phase behavior of solutes of interest under the SCF conditions is also essential for the development of any SCF process. Despite its importance there is very limited data on the phase behavior of solid solutes in supercritical CO<sub>2</sub>, which is particularly true for multicomponent systems. The reasons for lack of phase behavior data can be attributed to the fact that specialized equipment is required and the experiments are generally tedious and time consuming.

In conjunction with our research on solubilities of aromatic carboxylic acids and substituted phenols in SCF- CO<sub>2</sub>, the phase behavior of single (binary) and multicomponent (ternary and quaternary) systems was studied to ensure that only solid - fluid equilibria existed under the experimental conditions used for the solubility studies. The phase behavior study involved the determination of lower critical end point (LCEP) for each system and checking the possible depression in the melting point of the solutes at the temperature of interest.

# Experimental

#### Method

Determination of LCEP- The solute/mixture of solutes were packed in a small glass tube and placed inside the view cell. The system was pressurized and filled with liquid CO<sub>2</sub> until the liquid meniscus separating the liquid and gas phases was clearly seen. The LCEP was then determined visually by observing the disappearance and the appearance of the meniscus accompanied by critical opalescence, which is intense at the critical point. The LCEP of the systems presented here have an estimated experimental error of +/- 0.5 K and +/- 0.7 bar respectively. The first critical endpoints for ternary and quaternary systems have also been termed as LCEP in this work for convenience.

Depression in the melting point- Depression in the melting point of the solutes/ mixture of solutes at the temperature of interest was checked visually. The solute was placed in a glass tube inside the view cell and filled with  $CO_2$ . The system was then pressurized slowly from 101 bar to 240/280 bar over a period of several hours and was then held under static conditions for at least 2 hours.

#### Validation

The accuracy of the experimental method was validated by comparing the experimentally determined critical point for pure CO<sub>2</sub> with the literature values.<sup>1</sup>







Critical	poiı
	T <sub>c</sub>
Literature	30
This work	30

Supercritical state

**Critical Point** 

Subcritical state

**Figure 4.** The gradual phase transition of carbon dioxide from a single phase supercritical state through the critical point to a two phase subcritical state. (The view cell shown here has a glass tube inserted in the cell).

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#### Solid - Fluid (S-V) Phase Equilibrium

Solid solubility in SCF refers to its composition in the vapor phase. The solids of interest in most SCF processes have low volatility and differ greatly from the SCF in chemical nature. In these systems the phase behavior is complex, especially if multiple of two solids and a SCF.<sup>8-10</sup> solutes are present. The limiting case of a binary system consisting of single solid in a SCF offers a basis for understanding the phase behavior in multicomponent systems.

#### **P-T projection of a binary system**



upper critical end point (UCEP).

this region of the phase diagram.

point in the presence of SCF.



Back	ground
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- The solid-liquid-gas (S-L-V) line interrupts the critical mixture curve at two points, the lower critical end point (LCEP) and the
- At both the LCEP and the UCEP a liquid and a vapor phase critically merge into a single vapor phase in the presence of a solid
- The region between the LCEP and UCEP is of much commercial interest as it defines the temperature range in which S-V equilibrium exist for all values of pressure. Solid solubility is measured in
- The higher temperature branch of the S-L-V line lies at lower temperatures than the S-L coexistence curve, indicating that the solid will melt at temperatures lower than its normal melting

#### **P-T** projection of a ternary system

There is very little experimental information available on the phase behavior of ternary systems consisting



Figure 2. P-T projection of a ternary system.

Solubility measurements in the regions very close to the critical end points can be misleading due to the existence of multiple phases and may not represent S-V equilibrium conditions. Hence, phase equilibria need to be checked for measurement and interpretation of solubility data.

# **Results and Discussion**

### **LCEP and S-V equilibrium of binary, ternary and quaternary systems**

**Table 1.** LCEP data of binary, ternary and quaternary

· LCEP	
T (K)	P (bar)
303.8	73.6
303.8	73.8
303.9	74.0
305.5	74.4
305.6	74.5
304.8	74.4
	19 19 19 19 19 19 19 19 19 19 19 19 19 1
303.8	75.0
304.5	74.0
*	*
304.7	74.0
304.6	74.5
304.1	74.2
	LA T (K) 303.8 303.8 303.8 303.8 303.8 305.5 305.6 305.6 304.8 304.8 * 304.5 * 304.7 304.7 304.7 304.6

Table 2. S-V equilibrium of binary, ternary and quaternary

System	S-V Equilibrium (Under Conditions Studied)	
Binary		
Benzoic acid $+ CO_2$		
Salicylic acid $+ CO_2$	S-V equilibrium; 101-280 bar	
Acetylsalicylic acid $+ CO_2$	at 308 K, 318 K and 328 K	
2,3-dimethyl phenol + CO <sub>2</sub>	S-V equilibrium; 101-240 bar at 308 K and 318 K Depression in melting point; Evidence of liquid phase ~150 bar at 328 K	
2,5-dimethyl phenol + $CO_2$		
4-tert-butyl phenol + CO <sub>2</sub>	S-V equilibrium; 101-280 bar	
4-phenyl phenol $+ CO_2$	At 308 K and 318 K	
2,3,5-trimethyl phenol + $CO_2$		
2,4,6-trimethyl phenol + $CO_2$	S-V equilibrium; 101-280 bar at 308 K	
Ternary (1:1 Wt%)		
Salicylic acid + Benzoic acid + $CO_2$		
Acetylsalicylic acid + Benzoic acid + $CO_2$	S-V equilibrium; 101-280 bar	
Acetylsalicylic acid + Salicylic acid	at 308 K, 318 K and 328 K	
$+ CO_2$		
2,5-dimethyl phenol + 4-tert-butyl phenol	Depression in melting point; Evidence of	
$+ CO_2$	liquid phase under subcritical conditions	
2,3,5-trimethyl phenol + 4-phenyl phenol $+ CO_2$		
2,4,6-trimethyl phenol + 4-phenyl phenol $+ CO_2$	S-V equilibrium; 101-280 bar at 308 K	
Quaternary (1:1:1 Wt%)		
Acetylsalicylic acid + Benzoic acid +	S-V equilibrium; 101-280 bar	
Salicylic acid $+ CO_2$	at 308 K, 318 K and 328 K	

### Discussion

The experimental LCEP data for single and multicomponent systems of aromatic benzoic acids and substituted phenols are presented in Table1. The LCEP determined in this work are close to the critical point of pure CO<sub>2</sub>. Under the conditions investigated the majority of the systems exhibited solidfluid equilibrium with no liquid phase present (Table 2.). Thus solubility determinations under these conditions represent true solid solubility.

The solid solutes used in this study are nonvolatile. For solutes of low vapor pressure solubility in supercritical fluid  $CO_2$  is relatively low, hence the LCEP lies close to the critical point of pure  $CO_2$  and the depression in melting point is low.

In the case of 2,3-dimethyl phenol (normal melting point- 348 K), liquid phase was observed at 328 K. However, S-V equilibrium conditions existed at 308 K and 318 K in the pressure range studied (101-240 bar).

In the case of 2,5-dimethyl phenol + 4-tert- butyl phenol (normal eutection melting ~ 331 K), the depression in melting point was significant. Liquid phase was observed under subcritical conditions. The LCEP for this system could not be determined because of the complex phase behavior. There was no evidence of liquid phase in either 2,5-dimethyl phenol (melting point 347 K) or 4-tert butyl phenol (normal melting point-374 K) binary systems under the conditions stud-

The melting of the two systems under the conditions studied was also confirmed by solubility studies, which gave unusually high solubility data.

terminates at a lower double critical end point (P) while the higher temperature branch terminates at the upper double critical end point (Q).

In the region between P and Q, S-V equilibrium exists for all values of pressure. Solubility of the solute mixture is measured in this region of the phase diagram

Depression of the eutectic point of a solid mixture can occur in the same way as the depression of the melting point of a pure solid but could be even more sig-

### Experimental

#### Apparatus

The phase behavior was studied using a Phase Monitor (Supercritical Fluid Technolo gies, Inc.) consisting of the following components- a view cell (maximum capacity of 30 mL) with two quartz windows, a mixer, a light source, a video camera and a television monitor with VCR.



Figure 3. High-pressure view cell apparatus.

The quartz window of the view cell allows the visual observation of phase transitions and the camera placed against the outside of the quartz window allows collection of video images in addition to providing safety by avoiding having to look directly into the cell.

A high-pressure pump was used to introduce pressurized  $CO_2$  into the view cell. The cell was electrically thermostated with a heating jacket and the system temperature was measured by an RTD sensor probe inserted into the cell. The system pressure was measured using a pressure transducer, which was calibrated using a NIST-certified pressure gauge.

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