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

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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_2) has been the principal solvent of interest on account of its best combination of properties.[1,2]

Solubility of compounds in SCF- CO_2 is one of the most extensively investigated areas of SCF research as it establishes the technical and economic viability of a particular supercritical process.[3] 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[4,5]

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.[6] 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.[7]

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_2, 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_2, 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.

Background

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 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

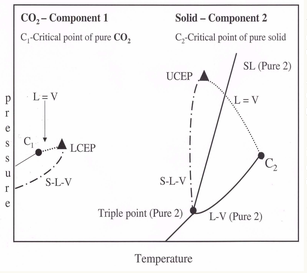


Figure 1. P-T projection of a binary system.[7]

The solid-liquid-gas (S-L-V) line interrupts the critical mixture curve at two points, the lower critical end point (LCEP) and the upper critical end point (UCEP).

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 phase.

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 this region of the phase diagram.

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 point in the presence of SCF.

P-T projection of a ternary system

There is very little experimental information available on the phase behavior of ternary systems consisting of two solids and a SCF.[8-10]

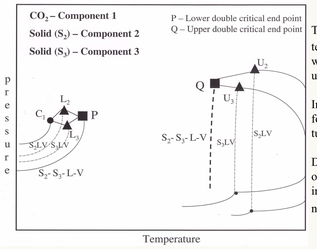


Figure 2. P-T projection of a ternary system.

The lower temperature branch of the S_2-S_3-L-V line 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 significant.[7]

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.

Experimental

Apparatus

The phase behavior was studied using a Phase Monitor (Supercritical Fluid Technologies, 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.

Experimental

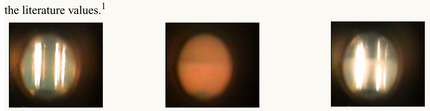
Method

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_2 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_2 with the literature values.[1]



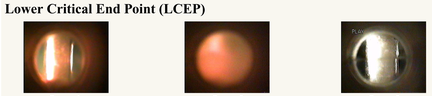
Supercritical state | Critical Point | Subcritical state

Critical point of CO_2	T_c / K	P_c/bar
Literature	304.2	73.8
This work	304.1	73.6

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).

Results and Discussion

Lower Critical End Point (LCEP)

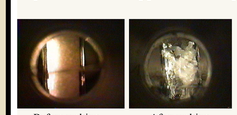


Stage 1 | Stage 2 | Stage 3

Figure 5. Phase transition of a ternary system from a supercritical state through LCEP to a subcritical state.

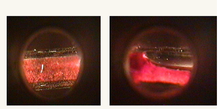
Stage 1. represents S_2-S_3-V equilibrium conditions, where the two solid solutes are in equilibrium with the supercritical fluid phase. Stage 2. is at the LCEP, where the contents of the cell become cloudy caused by scattering of light due to the large density fluctuations (**critical opalescence**). Stage 3. represents S_2-S_3-L-V equilibrium, where the two solid solutes are in equilibrium with L-V of CO_2.

Depression in melting point under high pressure CO_2



Before melting | After melting

Figure 6. Depression in melting point of 2,5-dimethyl phenol + 4-tert-butyl phenol solute mixture in a glass tube inside the view cell. (Ternary system)



Before melting | After melting

Figure 7. Depression in melting point of 2,3-dimethyl phenol binary system. Solute packed in a glass tube placed horizontally in the view cell.

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

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

System	LCEP T (K)	LCEP P (bar)
Binary		
Benzoic acid + CO_2	303.8	73.6
Salicylic acid + CO_2	303.8	73.8
Acetylsalicylic acid + CO_2	303.9	74.0
2,3-dimethyl phenol + CO_2	305.5	74.4
2,4,6-trimethyl phenol + CO_2	305.6	74.5
4-tert-butyl phenol + CO_2	304.8	74.4
Ternary		
Salicylic acid + Benzoic acid + CO_2	303.8	75.0
Acetylsalicylic acid + Benzoic acid + CO_2	304.5	74.0
2,5-dimethyl phenol + 4-tert-butyl phenol + CO_2	*	*
2,3,5-trimethyl phenol + 4-phenyl phenol + CO_2	304.7	74.0
2,4,6-trimethyl phenol + 4-phenyl phenol + CO_2	304.6	74.5
Quaternary		
Acetylsalicylic acid + Salicylic acid + Benzoic acid + CO_2	304.1	74.2

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

System	S-V Equilibrium (Under Conditions Studied)
Binary	
Benzoic acid + CO_2	S-V equilibrium; 101-280 bar at 308 K, 318 K and 328 K
Salicylic acid + CO_2	
Acetylsalicylic acid + CO_2	
2,3-dimethyl phenol + CO_2	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	S-V equilibrium; 101-280 bar At 308 K and 318 K
4-tert-butyl phenol + CO_2	
4-phenyl phenol + CO_2	
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	S-V equilibrium; 101-280 bar at 308 K, 318 K and 328 K
Acetylsalicylic acid + Benzoic acid + CO_2	
Acetylsalicylic acid + Salicylic acid + CO_2	
2,5-dimethyl phenol + 4-tert-butyl phenol + CO_2	Depression in melting point; Evidence of 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 + Salicylic acid + CO_2	S-V equilibrium; 101-280 bar 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_2. Under the conditions investigated the majority of the systems exhibited solid-fluid 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 eutectic 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 studied.

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

References

1. McHugh, M.A., and Krukonis, V. J. *Supercritical Fluid Extraction:* Butterworths: Boston, 1986; Chapter 1.

2.*Supercritical Carbon Dioxide Separations and Processes*; Gopalan, A. S.; Wai, C. M.; Jacobs, H. K.; Eds.; ACS Symposium series 860; American Chemical Society: Washington, DC, 2003.

3.Lucien, F. P.; Foster, N. R. *In Chemical Synthesis Using Supercritical Fluids*; Jessop, P. G.; Leitner, W.; Eds.; Wiley-VCH: Weinheim, 1999; Chapter 1.

4. Bartle, K. D.; Clifford, A. A.; Jafar, S. A.; Shilstone, G. F. J. Phys. Chem. Ref. Data **1991**, *20*, 713.

5. Hutchenson, K. W.; Foster, N. R. *In Innovations in Supercritical Fluids Science and Technology*; Hutchenson K. W.; Foster, N. R.; Eds.; ACS Symposium series 608; American Chemical Society: Washington, DC, 1995; Chapter 1.

6. McHugh, M. A.; Yogan, T. J. J. Chem. Eng. Data **1984**, *29*, 112.

7.Lucien, F. P.; Foster, N. R.; J. Supercrit. Fluids. **2000**, *17*, 111.

8. Zhang, D.; Cheung, A.; Lu, B. C. Y. J. Supercrit. Fluids **1992**, *5*, 91.

9. White, G. L.; Lira, C. T. In Supercritical Fluid science and Technology; ACS symposium series 406; Johnston, K.P., Penninger, J. M. L.; Eds. American Chemical Society: Washington, DC, 1989; Chapter 9.

10. Lemert, R. M.; Johnston, K. P. Fluid Phase Equilib. **1990**, *59*, 31.