

Chapter 16

Experimental Measurement and Modeling of the Vapor–Liquid Equilibrium of β -Diketones with CO_2

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Isothermal bubble points and saturated liquid molar volumes for binary mixtures of the β -diketones: pentane-2,4-dione, 2,2,6,6-tetramethylheptane-3,5-dione, 2,2,7-trimethyloctane-3,5-dione, 1,1,1-trifluoropentane-2,4-dione, and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione + carbon dioxide have been measured in the temperature region 30°C–45°C and at pressures up to 80 bar. The fluorinated ligands showed a higher affinity for CO_2 than the alkylated ligands at lower pressures, with this trend diminishing at higher pressures. The Peng–Robinson equation of state with van der Waals-1 mixing rules and estimated critical properties predicted liquid phase compositions and liquid molar volumes quite well.

Introduction

Supercritical CO_2 has rapidly been gaining attention as a viable replacement for many traditional organic solvents used for the extraction of metal ions from contaminated soils, sludges, and wastewater streams due to increasing

environmental legislation regulating the use of organic solvents. This is because CO₂ is non-toxic, non-flammable, readily available, inexpensive, and has moderate critical properties, $T_c=31^\circ\text{C}$ and $P_c=73.8$ bar. Additionally, supercritical fluids in general, unlike liquid solvents, have tunable solvation power, with small changes in pressure and/or temperature producing large changes in density, viscosity, and diffusivity. Therefore, a solute extracted into the CO₂ phase can be easily recovered and the CO₂ recycled by just reducing the system pressure which precipitates the solute. Additionally, liquid extraction processes can result in cross contamination of the solid matrix, aqueous solution or sludge stream with the organic solvent, thus requiring additional unit operations such as steam-stripping or distillation to recover this residual solvent. The use of supercritical CO₂ as an extraction solvent ameliorates this problem.

Research has already been conducted examining the solubility of pre-formed metal chelate complexes, as well as the efficacy of a variety of chelating agents in extracting metal ions from solid and liquid phases, using supercritical CO₂. Dithiocarbamates, crown ethers, organophosphorous compounds, functionalized picolylamines, dithiols, and dithiocarbamates, and β -diketones are some of the major classes of chelating compounds investigated. Smart *et al.* (1) presents a comprehensive review of the solubilities of chelating agents and metal chelates in supercritical CO₂ that have been presented in the literature. Erkey (2) reviews research on the supercritical fluid extraction of metals from aqueous solutions using CO₂. Additional reviews on the subject of supercritical fluid extraction of metal ions are presented by Ashraf-Khorassani *et al.* (3) and Wai and Wang (4).

It should be noted that very little phase behavior data is available for ligands with CO₂. Since β -diketones have been shown to be viable for the supercritical fluid extraction of a variety of metals, ranging from transition metals to lanthanides and actinides, we will focus on this set of compounds. In particular, the goal of this research is to determine the binary phase behavior of several β -diketones with CO₂ because the phase behavior of the ligand/CO₂ systems is necessary for the design of *in-situ* chelation processes. Table I lists the IUPAC and abbreviated names for the β -diketones investigated here. These particular β -diketone ligands were chosen because they could be obtained commercially and have been used in a number of supercritical fluid extraction studies (1-4).

To date little or no thermodynamic modeling of the phase behavior of the ligand/CO₂ or metal chelate/CO₂ systems has been conducted. However, in order for supercritical fluid extraction to be considered as a possible replacement for organic solvent extraction, accurate models must be developed to predict the phase behavior of these systems to allow for both equipment and process design. Equation of state (EOS) modeling was chosen here to model the vapor-liquid equilibrium of the β -diketone/CO₂ systems studied. Cubic EOSs are the most widely used in modeling high pressure and supercritical fluid systems. This is

due to the fact that cubic EOSs are fairly simple, flexible, and have the ability to capture the correct temperature and pressure dependence of the density and all density-dependent properties, such as solubility (5,6).

Table I. IUPAC and Common Names of β -Diketones Studied

<i>IUPAC Name</i>	<i>Abbreviation</i>
Pentane-2,4-dione	ACAC
2,2,6,6-Tetramethylheptane-3,5-dione	THD
2,2,7-Trimethyloctane-3,5-dione	TOD
1,1,1-Trifluoropentane-2,4-dione	TFA
6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyloctane-3,5-dione	FOD

Experimental

Liquid phase solubility and molar volume measurements were taken using a static equilibrium measurement apparatus, which is described in detail by Lubbers (7). Liquid β -diketone samples were loaded into a high pressure, graduated borosilicate glass cell with a teflon stir-bar coupled to an external magnet for agitation. The glass cell was immersed in a constant temperature water bath. Carbon dioxide was metered into the sample cell using a positive displacement pump. The liquid phase compositions were determined by stoichiometry knowing the pressure and temperatures (density) in the cell and tubing, and the volumes of the lines, headspace and liquid volume.

Materials

Pentane-2,4-dione (CAS 123-54-6), 1,1,1-trifluoropentane-2,4-dione (CAS 367-57-7), 2,2,6,6-tetramethylheptane-3,5-dione (CAS 1118-71-4), and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione (CAS 17587-22-3) containing 0.1% 2,6-di-*tert*-butylphenol were purchased from Aldrich Chemical Co. with purities of 99.8, 99+, 97.8, 98+, and 98%, respectively. They were used without further purification. 2,2,7-trimethyloctane-3,5-dione (CAS 69725-37-7) was purchased from Oakwood Products, Inc. with a purity of 96.5% and it was used without further purification, as well. Coleman instrument grade CO₂ was purchased from Mittler Supply, Inc. with a purity of 99.99% and it was used as received.

Modeling

Modeling of the ligand/CO₂ phase behavior is one of the key areas that must be addressed when considering the design of a full-scale extraction process. For process design calculations, cubic EOSs are widely used in modeling high-pressure fluid systems. In this study, the Peng-Robinson equation of state (EOS) (8) was employed with the simple van der Waals-1 (vdW-1) mixing rules to extend the EOS to mixtures (8). The Peng-Robinson EOS with vdW-1 mixing rules has only one adjustable interaction parameter, k_{ij} , for each binary mixture. This parameter should be small ($-0.2 < k_{ij} < 0.2$) and, in most cases, it can be regressed from experimental data to provide quantitative agreement with the data.

The equation of state uses corresponding states theory to determine the attractive and volume parameters of each species. Therefore, the pure component critical temperature, T_c , and critical pressure, P_c , are required. The EOS uses a third parameter, *viz.* Pitzer's acentric factor, ω (9)

$$\omega = -\log P_r^{vap} \Big|_{T_r=0.7} - 1 \quad (1)$$

where subscript r represents reduced properties, to enhance the prediction. However, no critical property data exists for any of the ligands studied. Therefore, the critical properties were estimated using either the Gani (10) or Joback (11) group contribution method. These methods use the chemical groups or substituents to predict many different physical properties. A detailed description of how we used available physical property data and these group contribution methods to estimate critical properties and acentric factors for the β -diketone compounds can be found elsewhere (12).

In this study, a modified Simplex method was used to regress the binary interaction parameter, k_{ij} , using a packaged algorithm, *DBCPOL* (13). The objective function minimized by the optimization routine was the percent absolute average relative deviation (%AARD)

$$\%AARD = \frac{100}{n} \sum_{i=1}^n \frac{|x_{1,i}^{exp} - x_{1,i}^{pred}|}{x_{1,i}^{exp}} \quad (2)$$

where n is the number of experimental points, and x_l^{exp} and x_l^{pred} , respectively, are the experimental and calculated compositions of CO_2 in the β -diketone rich liquid phase for each of those points.

The vapor-liquid equilibrium was computed from the EOS model using the reliable and robust method of Hua *et al.* (14-16) based on interval analysis. Their method can find the correct thermodynamically stable solution to the vapor-liquid equilibrium problem with mathematical and computational certainty. Additionally, the tangent plane distance method (17,18) was used to test the predicted liquid and vapor phase compositions for global thermodynamic phase stability.

Results and Discussion

In this section the experimental liquid phase compositions and liquid molar volumes determined for the β -diketone/ CO_2 systems studied will be presented coupled with the modeling results using the Peng-Robinson EOS with van der Waals-1 mixing rules. Table II lists the estimated critical constants, T_c and P_c , and the acentric factor, ω , needed for modeling these systems.

Table II. Estimated Critical Properties of β -diketones

Ligand	T_b	$\ln P^{vap}[\text{Pa}] = A - B/T[\text{K}]$		T_c	P_c	ω
	[°C]	A	B	[K]	[bar]	
ACAC	140.4 ^a	21.885 ^c	4303.0 ^c	619.71 ^g	30.82 ⁱ	0.406
THD	215 ^a	22.074 ^d	5149.5 ^d	686.02 ^g	21.21 ⁱ	0.397
TFA	107 ^a	23.308 ^a	4478.9 ^a	519.53 ^h	23.90 ⁱ	0.711
TOD	238	24.891 ^c	6697.2 ^c	670.47 ^h	24.15 ^h	0.770
FOD	167.5 ^b	24.649 ^f	5778.7 ^f	580.89 ^h	24.23 ⁱ	0.852

a Ref. (19), b Ref. (20), c Regressed from ref. (21), d Regressed from ref. (22) and references therein, e Regressed from refs. (12,23,24), f Regressed from refs. (20,23) g Ref. (10), h Ref. (11), i Extrapolation of P^{vap} to T_c , j Equation 1.

β -Diketone/ CO_2 Vapor-Liquid Equilibrium

Experimental liquid phase compositions and liquid molar volumes for all β -diketone/ CO_2 systems studied are listed in Table III. Figure 1 shows the

Table III. Liquid Phase Compositions and Molar Volumes for β -diketone/ CO_2 Systems

<i>System with CO_2</i>	<i>T [°C]</i>	<i>P [bar]</i>	<i>Liquid Mole Fraction, x_i</i>		<i>\bar{V}^L [cm³/mol]</i>
			<i>Ligand</i>	<i>CO_2</i>	
ACAC	30.0	28.1	0.571	0.429	79
		41.9	0.391	0.610	68
		54.1	0.233	0.768	61
		60.2	0.143	0.857	57
		62.8	0.104	0.896	56
	35.0	26.6	0.619	0.381	82
		40.7	0.444	0.556	70
		54.9	0.285	0.716	62
		62.6	0.196	0.805	58
		68.1	0.137	0.864	57
	45.0	71.8	0.103	0.898	57
		28.6	0.657	0.343	87
		43.7	0.505	0.495	77
		57.4	0.368	0.633	68
		70.5	0.244	0.756	62
		77.1	0.185	0.815	59
		81.7	0.136	0.865	58
THD	30.0	29.9	0.522	0.478	127
		44.1	0.356	0.644	103
		57.6	0.198	0.802	80
		64.5	0.101	0.899	66
		67.9	0.043	0.957	60
	35.0	69.1	0.030	0.970	60
		28.6	0.609	0.391	150
		44.4	0.422	0.578	119
		57.8	0.274	0.726	93
		70.0	0.123	0.877	70
	45.0	74.5	0.059	0.941	63
		28.8	0.634	0.366	154
		43.4	0.494	0.506	131
		58.4	0.356	0.645	108
		72.0	0.233	0.767	87
		78.2	0.173	0.827	75

Table III. *Continued*

<i>System</i>	<i>T</i>	<i>P</i>	<i>Liquid Mole Fraction, x_i</i>		V^L
TOD	30.0	29.7	0.530	0.470	132
		43.4	0.362	0.638	103
		57.0	0.204	0.796	80
		64.6	0.088	0.912	64
		67.0	0.046	0.954	60
	35.0	29.5	0.566	0.435	141
		43.5	0.420	0.580	115
		56.9	0.282	0.718	93
		69.5	0.138	0.862	71
		72.8	0.088	0.912	64
	40.0	29.5	0.593	0.407	145
		43.3	0.450	0.550	120
		57.3	0.327	0.673	100
		71.5	0.191	0.809	78
		79.9	0.098	0.903	64
TFA	30.0	28.9	0.505	0.496	86.6
		42.4	0.331	0.669	72
		54.6	0.179	0.821	62
		62.0	0.092	0.908	57.8
		64.6	0.067	0.933	57.5
	35.0	28.6	0.544	0.456	89.6
		42.4	0.379	0.622	76
		55.3	0.235	0.765	66
		62.3	0.161	0.839	62
		67.5	0.111	0.889	60
	40.0	29.1	0.578	0.422	92
		43.1	0.411	0.589	80
		56.5	0.272	0.728	70
		73.0	0.112	0.888	61
FOD	30.0	43.6	0.267	0.734	98
		57.0	0.132	0.868	73
		64.8	0.058	0.943	63
		67.8	0.031	0.969	61
	35.0	21.2	0.597	0.403	164
		29.5	0.479	0.521	140
		43.0	0.321	0.680	110
		57.0	0.185	0.815	85
	40.0	29.5	0.505	0.495	141
		43.0	0.352	0.649	114
		56.7	0.228	0.772	92
		71.2	0.130	0.870	81
		76.9	0.073	0.927	66

isothermal bubble point data for the ACAC/CO₂ system at 30.0°C, 35.0°C, and 45.0°C, coupled with the modeling results using the Peng-Robinson EOS with van der Waals-1 mixing rules. Additionally, the bubble point data of Anitescu *et al.* (25) for this system at 25.0°C are included for comparison. This is the only other liquid phase solubility data for a β -diketone/CO₂ system that could be found in the open literature. Note that a rigorous analysis of the systematic error indicated that the liquid phase compositions could be measured to within ± 0.002 mole fraction; consequently, the error bars are smaller than the size of the symbols in the figure. There is significantly more error, on the order of ± 5 –10 cm³/mol, in the measurement of the liquid molar volumes. As expected, the solubility of CO₂ in ACAC decreased with increasing temperature at a fixed pressure. This same trend was observed for all of the β -diketone/CO₂ systems.

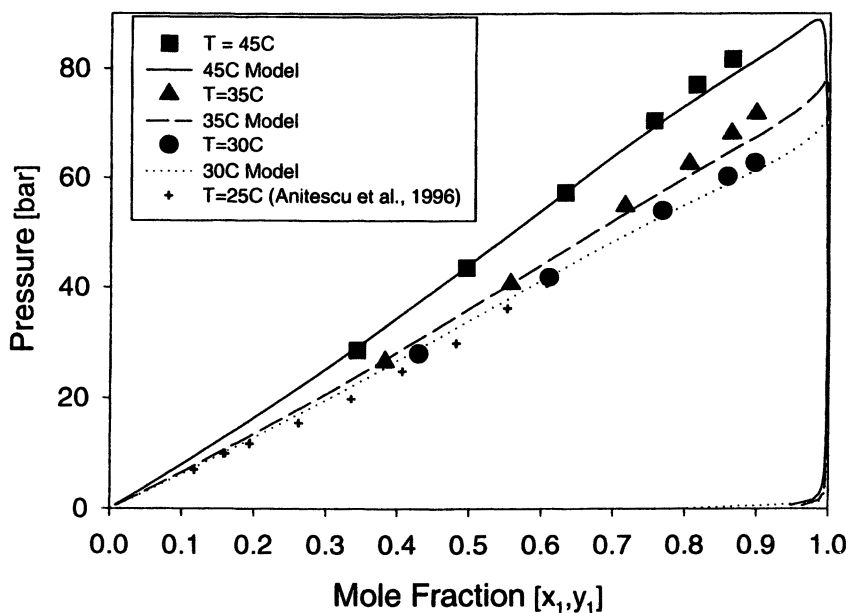


Figure 1. Vapor-liquid equilibrium of the ACAC/CO₂ system.

The Peng-Robinson EOS, with only one adjustable parameter, k_{ij} , and estimated critical properties, was able to reproduce the experimental liquid phase compositional data for this system quite well, with the relative deviation between

the experimental values and the model ranging from 1.87% to 7.17%. Modeling results for all the β -diketone/ CO_2 systems studied are presented in Table IV.

The %AARD values for all the other β -diketone systems ranged from only 0.86% to 4.59%, further showing the ability of the Peng-Robinson EOS to accurately model these systems using estimated critical properties. Figure 2 shows the experimental saturated liquid volumes for the THD/ CO_2 system at 30.0°C, 35.0°C, and 45.0°C. Note that the Peng-Robinson EOS tends to overpredict the liquid molar volumes for this system with relative deviations ranging from 9.44% to 10.41%. This is not entirely unexpected as the adjustable parameter in the model was only fit to the liquid phase compositions (see equation 2).

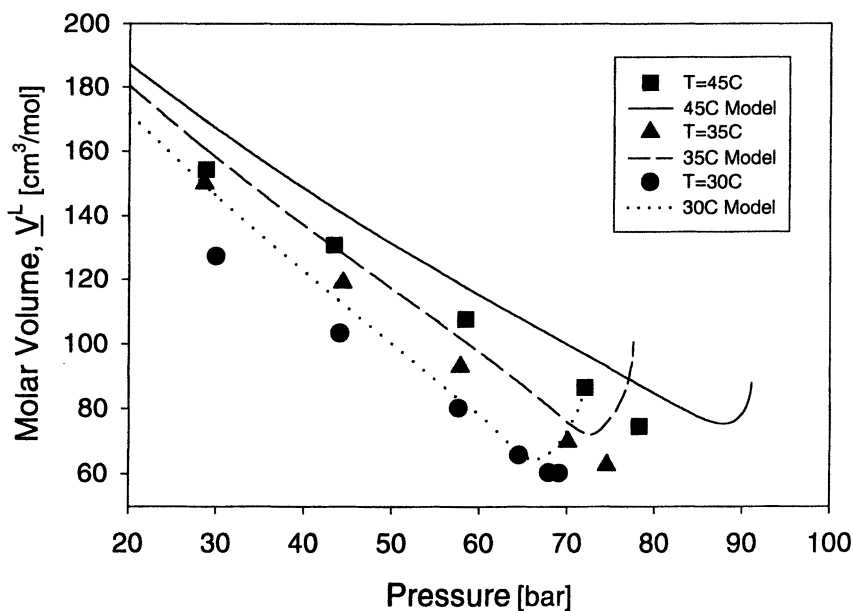


Figure 2. Liquid molar volume vs. pressure for the THD/ CO_2 system

Figure 3 shows the isothermal bubble point data for the aliphatic β -diketone/ CO_2 systems at 35.0°C. This figure clearly shows that the type of alkyl substituent on the β -diketone moiety has little effect on the liquid phase behavior. Similar bubble point compositions were seen for all these systems at 30.0°C as well.

Table IV. Peng-Robinson EOS Modeling Results

<i>Ligand</i>	<i>T</i> [°C]	<i>k₁₂</i>	%AARD	
			<i>x_{CO₂}</i>	<i>V^L</i>
<i>ACAC</i>	30	0.0517	7.17	23.93
	35	0.0460	2.97	24.36
	45	0.0570	1.87	26.59
<i>THD</i>	30	0.0423	2.18	10.41
	35	0.0602	1.11	9.44
	45	0.0565	0.86	11.34
<i>TOD</i>	30	0.0127	4.59	6.06
	35	0.0182	1.56	5.44
	40	0.0140	1.13	5.87
<i>TFA</i>	30	0.0323	1.46	18.38
	35	0.0454	2.98	21.50
	40	0.0378	1.46	22.55
<i>FOD</i>	30	-0.0191	0.12	8.35
	35	-0.0222	1.02	21.61
	40	-0.0290	0.91	15.97

Figure 4 shows a comparison of the experimental and predicted liquid phase compositions for the β -diketone/CO₂ systems studied at 35.0°C. This plot reveals all the salient features of the equilibrium phase behavior of these alkylated and/or fluorinated ligand/CO₂ systems. Namely, the bubble point compositions of the TFA and FOD/CO₂ systems are higher at lower pressures; i.e., at a given pressure more CO₂ dissolves in the two fluorinated ligands, TFA and FOD, than in the other β -diketones. However, at higher pressures the TFA and FOD equilibrium compositions are very similar to those of the ACAC, THD, and TOD/CO₂ systems.

With the liquid phase compositions and liquid molar volumes determined for these β -diketone/CO₂ systems, it is now possible to specify operating conditions and dimensions of a pre-extraction ligand saturation vessel such that a one-phase mixture of ligand and CO₂ is delivered to the extraction vessel. Again, it cannot be overstated that knowledge of the phase behavior of the ligand is essential when designing a complete extraction process. Furthermore, it has been shown that the Peng-Robinson EOS, with estimated critical properties and acentric factor for the ligand and incorporating standard van der Waals-1 mixing rules, is a viable model that could be used for the process design and control of this section of an *in-situ* extraction process using β -diketones as the chelating agents.

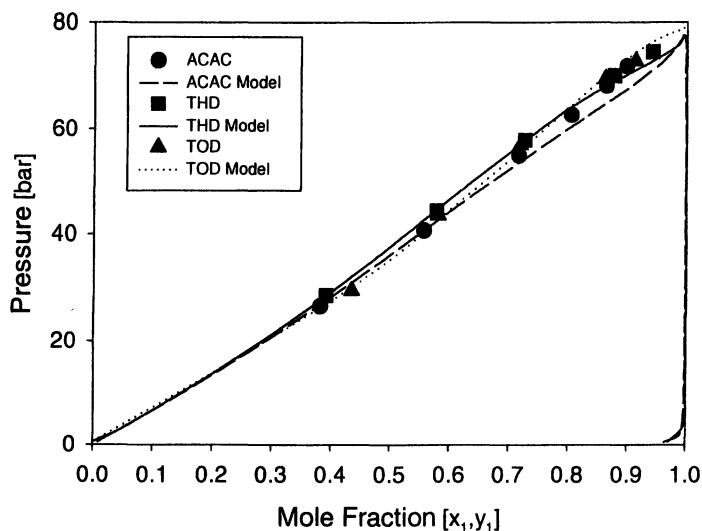


Figure 3. Vapor-liquid equilibrium of aliphatic β -diketone/ CO_2 systems at 35.0°C

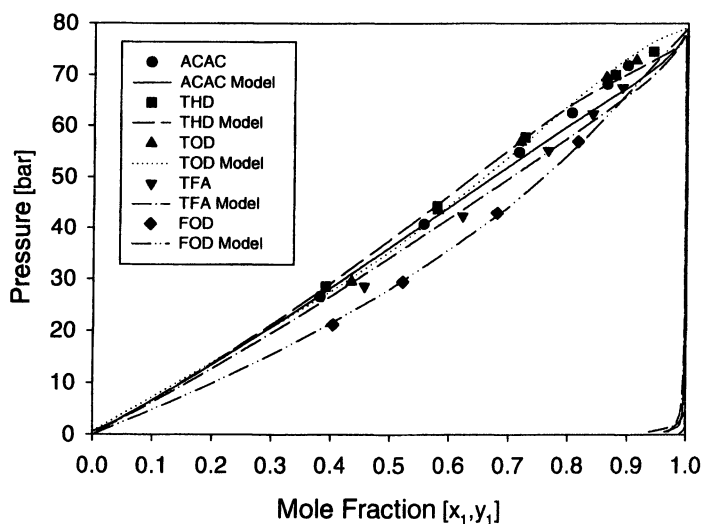


Figure 4. Vapor-liquid equilibrium of all β -diketone/ CO_2 systems at 35.0°C

Summary

We have presented isothermal bubble points and saturated liquid molar volumes for three alkylated β -diketones (pentane-2,4-dione, 2,2,6,6-tetramethylheptane-3,5-dione, and 2,2,7-trimethyloctane-3,5-dione) and two fluorinated β -diketones (1,1,1-trifluoropentane-2,4-dione and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione) with CO_2 at temperatures between 30°C and 45°C and at pressures up to 80 bar. As anticipated, the fluorinated ligands showed a higher affinity for CO_2 than the alkylated ligands at lower pressures, but surprisingly this trend diminished completely at higher pressures so that the mixture critical points appear to be virtually identical. Thus, the pressure needed to form a single phase ligand/ CO_2 mixture of any desired composition is no greater for the alkylated ligands. However, other factors, such as the solubility of the metal chelate complexes in CO_2 or the binding constants may make some of these ligands more attractive than others for supercritical fluid extraction of metals. We have also found that the Peng-Robinson equation of state with van der Waals-1 mixing rules and estimated critical properties modeled liquid phase compositions and liquid molar volumes quite well and, thus, can be used for process design of β -diketone/ CO_2 systems.

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