

Measurement and Modeling of Phase Equilibrium in a Reaction System Using Environmentally Benign CO₂

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Supercritical CO₂ has significant potential as an environmentally benign solvent to replace hazardous organic compounds in reactions. However, an important factor in doing reactions in CO₂ is the phase behavior. To address this issue we present phase equilibrium measurements and modeling of components in an epoxidation reaction that occurs with very high enantiomeric selectivity in CO₂. The two binary systems studied are trans-2-hexen-1-ol---CO₂ and (2R,3R)-(+)-3-propyloxiranemethanol---CO₂. The composition of the liquid phase was determined as a function of pressure for both binaries, at 303.15, 305.95, 313.15 and 323.15 K for trans-2-hexen-1-ol---CO₂ and 305.95, 313.15 and 323.15 K for (2R,3R)-(+)-3-propyloxiranemethanol---CO₂. Liquid/liquid immiscibility regions were found for both binaries. This region is located between 310.9 (LCST) and 315.3 K (type-k point) and the corresponding pressures of 79.5 and 86.7 bar for the trans-2-hexen-1-ol---CO₂. The (2R,3R)-(+)-3-propyloxiranemethanol---CO₂ liquid/liquid immiscibility region ranges from 315.1 K (type-k point) to below 293.7 K at the corresponding pressures of 86.1 to 55.8 bar. Modeling of the two phase regions with the Peng Robinson equation of state gave good results for the trans-2-hexen-1-ol---CO₂ system at 303.15 and 305.95 K and for the (2R,3R)-(+)-3-propyloxiranemethanol---CO₂ system at 305.95 K. The model does predict three phase regions but at conditions different from those observed experimentally.

Introduction

Supercritical fluids can be used to replace traditional organic solvents in industrially important reactions. Supercritical carbon dioxide (CO₂) has been used in the synthesis of polymers¹⁻³, formic acid⁴ and a variety of new compounds.⁵

Preliminary results have indicated that other reactions of industrial interest can be done successfully in liquid CO₂.⁶ These reactions can be further studied to determine whether the solvent properties of CO₂ can be used for both the reaction and separation stages. The first step is to find the solubility of the reactants and products in CO₂ to determine the feasibility of carrying out the reaction in this medium. The allylic epoxidation of trans-2-hexen-1-ol (alcohol) to (2R,3R)-(+)-3-propyloxiranemethanol (epoxy) is a representative example of an important synthesis reaction. This is performed traditionally in an organic solvent but also has been done in liquid CO₂ at 30°C.⁷ The reaction consists of the addition of an oxygen atom to the double ring of the alcohol (epoxidation), as shown in Fig. 1. The result is two stereochemical centers formed with high enantiomeric selectivity.⁸⁻¹³

Our objective is to present new data and modeling of the phase behavior of trans-2-hexen-1-ol and (2R,3R)-(+)-3-propyloxiranemethanol in high pressure carbon dioxide at temperatures similar to

those used by Tumas and coworkers to study the reaction selectivity.⁷ We present modeling results of the alcohol-CO₂ and epoxy-CO₂ vapor/liquid equilibria (VLE) using the Peng-Robinson equation of state (PREOS) with standard mixing rules and a temperature-independent interaction parameter k_{ij} computed to provide the best fit to experimental data. Also, we studied the three phase regions (LLV) for both systems, determined the compositions of the liquid phases and compared that data to the PREOS predictions of the three phase region.

Experimental Methods

Phase equilibrium measurements were carried out using a static measurement apparatus, which has been described previously.^{14,15} Briefly, the carbon dioxide was pumped into the cell using a Ruska pump readable with a precision of 0.002 cm³. Pressures in the carbon dioxide pump and experimental cell were measured with Heise gauges with a precision of 2 psi. The high pressure cell is made of borosilicate glass and its temperature was controlled by immersion in a water bath, whose temperature was monitored using a platinum resistance thermometer read with a Mueller Bridge to an accuracy of 0.02°C (Rubicon Instruments Co.).

Determination of liquid phase compositions was done by stoichiometry assuming that the gas phase

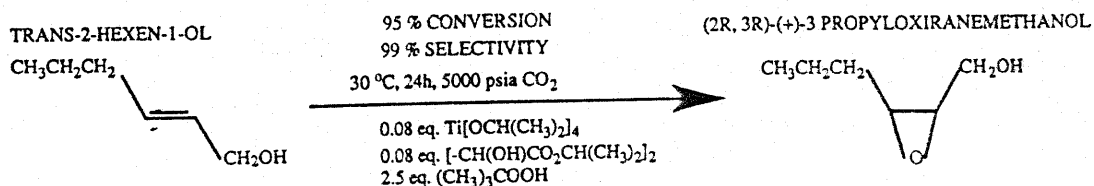


Figure 1 Titanium catalyzed epoxidation reaction.

was composed of only CO₂.^{14,15} In the three phase regions the composition of each phase was determined by conjugate runs, in which the dominant phase occupied no less than 75% of the cell volume (*ibid.*).

Modeling

The Peng-Robinson Equation of State was used to model the phase behavior of both binaries:¹⁶

$$P=RT/(v-b)-a/[v(v+b)+b(v-b)]$$

where the a and b parameters were determined from acentric factors, critical temperatures and pressures. The mixture parameters were determined using the conventional van der Waals mixing rules with a single binary interaction parameter: $a_{ij}=(a_{ii} a_{jj})^{0.5} (1-k_{ij})$.^{17,18} Since the critical properties of the alcohol and the epoxy were not available, they were estimated using the contribution method by Joback. Vapor pressures were estimated using the Riedel method.¹⁷ The two phase compositions were determined using the Michelsen algorithm, as implemented in LNGFLASH, which is part of the IVC-SEP Program Package.¹⁹ Although this code is usually extremely reliable, it did fail to give the correct answer at some points close to the LLV line so the three phase pressures were determined by direct examination of the Δg_{mixing} curves.

Materials

Trans-2-hexen-1-ol (CAS 928-95-0) and (2R,3R)-(+)-3-propyloxiranemethanol (CAS 92418-71-8) were purchased from Aldrich Chemical Co. with purities of 96 and 94%, respectively. The CO₂ was bone dry with a purity of 98% obtained from Mittler Gas Co. and further purified to exceed the Kuenen test.²⁰

Results

Trans-2-hexen-1-ol and CO₂

The liquid phase compositions were measured at 303.15, 305.95, 313.15 and 323.15 K. Experimental and estimated values using the PREOS are given in Table I and shown in Fig. 2. A vapor-liquid-liquid region (LLV) was found and is shown in Fig. 3. The LLV experimental compositions are given in Table II.

(2R,3R)-(+)-3-propyloxiranemethanol and CO₂

The liquid phase compositions were measured at 305.95, 313.15 and 323.15 K. Experimental and estimated values using PREOS for the liquid phase compositions are given in Table III. The pressure versus composition diagram Pxy is shown in Figure 4. A LLV region was found and is shown along with the LLV line for trans-2-hexen-1-ol and CO₂ in Figure 3. The LLV experimental compositions are given in Table II.

Table 1. Experimental and predicted compositions for the 2-phase region for trans-2-hexen-1-ol---CO₂.

x CO ₂ Experimental	x CO ₂ Estimated	Pressure (bar)
T=303.15 K		
0.99	0.68	70.2
0.98	0.68	69.0
0.97	0.68	68.9
0.93	0.66	67.5
0.93	0.66	67.5
0.92	0.66	67.4
0.85	0.66	67.0
0.73	0.65	66.7
0.64	0.61	63.2
0.60	0.60	62.4
0.51	0.52	55.3
0.46	0.49	52.5
0.35	0.39	41.2
0.22	0.26	26.8
0.12	0.14	14.6
T=305.95 K		
0.99	0.68	74.2
0.98	0.68	73.5
0.98	0.68	73.0
0.98	0.68	72.9
0.97	0.68	72.6
0.97	0.68	72.5
0.96	0.67	72.4
0.79	0.64	69.8
0.71	0.64	70.0
0.67	0.63	68.9
0.60	0.59	65.8
0.52	0.54	59.9
0.41	0.44	49.6
0.29	0.32	35.5
0.18	0.20	21.6
T=313.15 K		
0.75	0.67	85.7
0.71	0.65	83.4
0.60	0.61	78.4
0.51	0.55	70.0
0.35	0.41	51.4
T=323.15 K		
0.71	0.64	100.3
0.53	0.55	82.5
0.44	0.48	71.1
0.37	0.40	57.9
0.34	0.39	56.3

Table 2 Liquid/liquid equilibrium compositions.

TRANS-2-HEXEN-1-OL---CO ₂			
PRESSURE (bar)	TEMPERATURE (K)	L1 (Mole Fraction CO ₂)	L2 (Mole Fraction CO ₂)
85.3	314.38	0.92	0.32
83.1	313.40	0.92	0.34
82.2	312.40	0.93	0.34
80.5	311.44	0.90	0.37
(2R,3R)-(+)-3-PROPYLOXIRANEMETHANOL---CO ₂			
PRESSURE (bar)	TEMPERATURE (K)	L1 (Mole Fraction CO ₂)	L2 (Mole Fraction CO ₂)
81.9	312.01	0.93	0.75
80.1	309.96	0.93	0.75
77.0	307.97	0.93	0.77
73.4	305.95	0.95	0.78

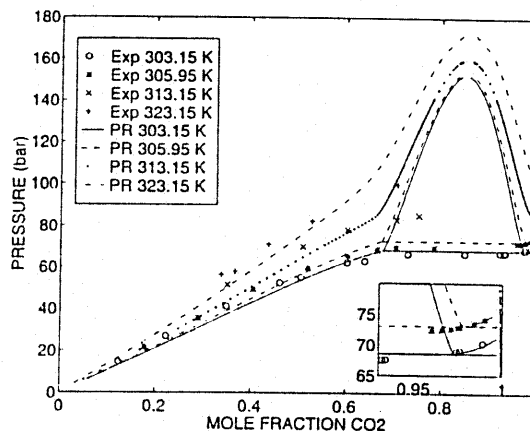


Figure 2. P-x diagram for trans-2-hexen-1-ol---CO₂.

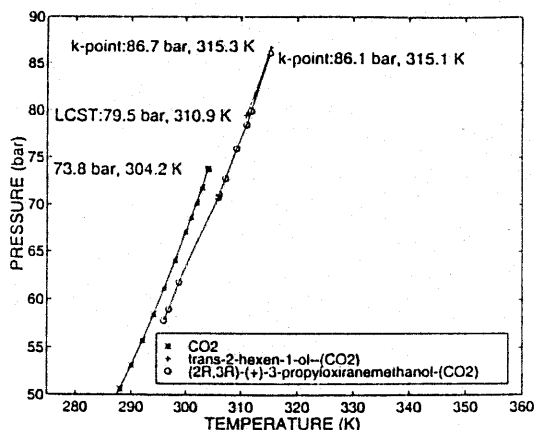


Figure 3. PT diagram showing LLV lines.

Table 3 Experimental and predicted compositions for the two phase VLE region for (2R,3R)-(+)-3-propyloxiranemethanol--CO₂.

x CO ₂ Experimental	x CO ₂ Estimated	Pressure (bar)
T=305.95 K		
0.23	0.33	31.5
0.37	0.44	43.7
0.37	0.46	45.6
0.47	0.59	60.3
0.63	0.60	62.4
0.63	0.61	63.0
0.74	0.66	68.9
0.74	0.69	72.5
T=313.15 K		
0.50	0.59	71.3
0.55	0.67	84.1
0.63	0.67	83.9
0.66	0.66	82.7
0.76	0.71	95.0
0.77	0.71	94.9
0.82	0.70	91.7
T=323.15 K		
0.33	0.44	59.3
0.42	0.54	77.5
0.57	0.65	100.0
0.82	0.68	110.2

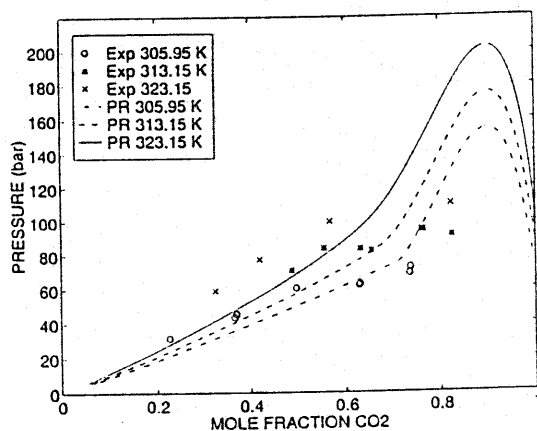


Figure 4. P-x diagram for (2R,3R)-(+)-3-propyloxiranemethanol--CO₂.

Discussion

Trans-2-hexen-1-ol and CO₂

As shown in Table 1 and Fig. 2, the amount of CO₂ dissolved in trans-2-hexen-1-ol increases with

increasing pressure, as expected.²¹ The range of CO₂ mole fractions in the liquid phase spans from 0.12 to 0.99. Modeling of the system was done with the PREOS and a temperature independent k_{ij} of 0.084, which is the value that best fit the liquid phase compositions in the VLE region. The modeling corroborated our assumption that the vapor phase was mainly CO₂, with the CO₂ mole fractions above 0.99. The experimental and predicted values for the liquid phase composition are shown in Fig. 2. There is excellent agreement of the experimental and estimated values below 66 bar.

The system trans-2-hexen-1-ol--CO₂ has a liquid-liquid immiscibility region and the pressure versus temperature diagram is shown in Fig. 3. The second liquid phase is found in the range of temperatures from 310.9 (LCST) to 315.3 K (type-k point) and corresponding pressures of 79.5 and 86.7 bar. The locus of this region is unusual since it appears to have a LCST above the T_c of the more volatile component, CO₂. This is not found in any of the five categories of high pressure binary phase behavior described by Scott and Konynenburg.²¹ The composition of the liquid phases are given in Table II. There are only small differences in the phase compositions in the LLV region.

Modeling with the PREOS predicts only two phases in most of the region where LLV was found experimentally. However, the PREOS does predict three phases for this system, as shown in Fig. 2. The three phase pressures from the PREOS at 303.15K and 305.95 K are 68.6 bar and 73.1 bar, respectively. You will note that the predicted three phase pressures match the experimental liquid phase compositions for two phase VLE quite well. The experimental measurements of large increases in the liquid phase mole fraction of CO₂ with very small increases in pressure does indicate the incipient formation of an additional liquid phase. However, we did not actually observe a second liquid phase until much high temperatures (310.9 K). The PREOS predicts the high temperature termination of the LLV region just below 313 K. The predictions indicate that the LLV region would extend to temperatures well below those studied experimentally. The PREOS predicts that there is a large LLE region above the three phase pressure, with both liquid phases rich in CO₂. The VLE envelope is very small, as shown in the inset in Fig. 2, with both the liquid and vapor phases having CO₂ mole fractions greater than 0.97.

(2R,3R)-(+)-3-propyloxiranemethanol and CO₂

The amount of CO₂ dissolved in the (2R,3R)-(+)-3-propyloxiranemethanol rich liquid phase increases with pressure. The measured liquid CO₂ mole fractions cover the spectrum from dilute (0.23) to concentrated (0.82) values. The solubility of CO₂ in the epoxy is lower than that in the alcohol, requiring higher pressures to achieve the same liquid

composition. This emphasizes that addition of a single atom and rearrangement of the atoms can drastically modify solubility properties, which may be used in subsequent separation steps.

Modeling was done in the same way as for the alcohol using the PREOS with one fit parameter, k_{ij} , whose optimal value was 0.0282. The modeling corroborated the assumption that the vapor phase is mainly CO_2 , with mole fraction greater than 0.99 at all conditions. The experimental and predicted values for the liquid phase compositions are shown in Fig. 4. There is good agreement between the experimental and estimated values at 305.95 K. However, the predictions at 313.15 and 323.15 K have a larger deviation from the experimental values, although the trend in both is the same. These deviations may be attributed to the wide temperature range of the data, which is not adequately fit with a temperature-independent k_{ij} , and impurities in the epoxy, which is only 94%.

The epoxy- CO_2 system presents a partial immiscibility region which we studied at temperatures from 293.65 to 315.13 K (type-k point) and pressures from 55.8 to 86.1 bar. The pressure versus temperature diagram is shown in Fig. 3. The immiscibility behavior is Type III in the Scott and Konynenburg classification.²¹ The compositions of each liquid phase are given in Table II. Modeling using the PREOS and a $k_{ij}=0.0256$ did not predict a second liquid phase over the pressure and temperature ranges studied experimentally.

Clearly, for both the alcohol- CO_2 and epoxy- CO_2 systems experimental information is necessary to validate the accuracy of the PREOS predictions, especially for the three phase region. While extrapolation of binary data to multicomponent mixtures is difficult, the presence of liquid/liquid partial immiscibility regions over different ranges of temperatures and pressures for the reactant (alcohol) and product (epoxy) indicates that it may be possible to choose operating conditions that result in the formation of a product-rich liquid phase.

Conclusions

We have presented the measurement and modeling of the high pressure phase equilibria of binary mixtures of trans-2-hexen-1-ol- CO_2 and (2R,3R)-(+)-3-propyloxiranemethanol- CO_2 . The experimental results indicate that there are substantial differences in the solubility behavior, with CO_2 being more soluble in the alcohol than in the epoxy. Modeling of the alcohol- CO_2 two phase region at 303.15 and 305.95 K using the PREOS was very good below 66 bar. However, at higher temperatures (i. e. 313.15, 323.15 K) the modeling of the epoxy- CO_2 and alcohol- CO_2 two phase behavior was less accurate. Both binaries exhibit regions of liquid/liquid immiscibility and it may be possible to use these features to devise efficient separation for the allylic epoxidation of the alcohol.

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