MEASUREMENT, MODELING AND COMPUTATION OF THE PHASE BEHAVIOR OF CO_2-BASED REACTION SYSTEMS

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ABSTRACT

An important consideration in using CO_2 as an environmentally benign solvent to replace hazardous organic compounds in reactions is the phase behavior. We have used a two pronged approach to address this issue. First, we present phase equilibrium measurements and modeling of components in the allylic epoxidation of trans-2-hexen-1-ol (alcohol) to (2R,3R)-(+)-3-propyloxiranemethanol (epoxy), which occurs with very high enantiomeric selectivity in CO_2. We have investigated the high pressure phase behavior of the components in this reaction with CO_2 at temperatures between 303.15 and 323.15 K and pressures between 31.5 and 110.2 bar. The components include *trans*-2-Hexen-1-ol, (2R,3R)-(+)-3-Propyloxiranemethanol, Diisopropyl L-tartrate, Titanium (IV) isopropoxide, *tert*-Butyl hydroperoxide, and *tert*-Butyl alcohol. Modeling with the Peng Robinson equation of state gave reasonably good results for the two phase (vapor-liquid equilibrium) regions of all systems and did successfully predict three phase regions for both binaries that exhibited VLLE, but generally at conditions different than those observed experimentally. Second, we have developed a computational technique based on interval Newton generalized bisection method that is completely reliable for the determination of phase stability. We have implemented this technique for the general cubic equations of state that we use to model high pressure phase behavior.

INTRODUCTION

High pressure gases and supercritical fluids can be used to replace traditional organic solvents in industrially important reactions. Supercritical carbon dioxide (CO_2) is particularly attractive as an environmentally benign solvent and numerous reactions have been done successfully in liquid and supercritical CO_2, sometimes with rates and selectivities as good as or better than can be achieved in conventional liquids.[1,2] There is also the possibility that the solvent properties of CO_2 could be used to facilitate both the reaction and separation stages of the overall process. However, the solubility of many compounds is rather low in CO_2 and high pressures may be necessary to achieve reasonable concentrations or a one phase mixture, if that is necessary. Therefore being able to measure, model and accurately predict the high pressure phase behavior of CO_2 based reaction systems is important to the ultimate design and implementation of CO_2 as a replacement solvent in reactions.

Our general program to deal with this problem has been 1) to have available experimental methods to take the limited amount of phase equilibrium data that is needed to fit parameters in thermodynamic models, 2) to develop new general methods to reliably perform phase equilibrium computations, and 3) to choose a specific system of potential interest upon which to demonstrate the experimental and new computational techniques. In this paper, we report on the phase equilibrium measurements and modeling for a specific system, the allylic epoxidation of trans-2-hexen-1-ol (alcohol) to (2R,3R)-(+)-3-propyloxiranemethanol (epoxy). Traditionally, this important synthesis reaction has been performed in organic solvents but it also has been done in liquid CO_2 at 30°C.[3] The reaction consists of the addition of an oxygen atom to the double ring of the alcohol (epoxidation), as shown in Figure 1. The result is two stereochemical centers formed with high enantiomeric selectivity. Our objective is to present new data on the high pressure phase behavior of binary systems of carbon dioxide with the various components in the reaction, including temperatures similar to those used by Tumas and coworkers in their study of the feasibility and selectivity of this reaction in CO_2.[3] We will present liquid phase compositions, as well as identify the regions where three phase equilibria exist. In addition, we present modeling results of the binary systems using the Peng-Robinson equation of state (PREOS). Also, we give a brief description of the new computational techniques that we have developed to perform phase stability calculations.

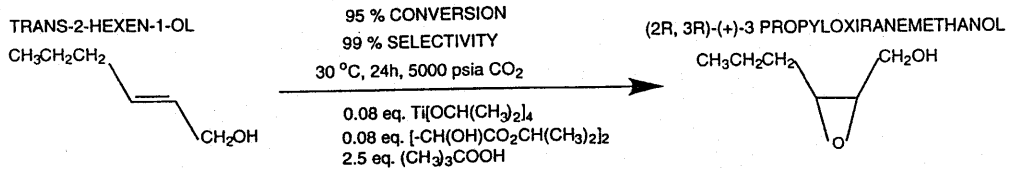

Figure 1 Titanium catalyzed epoxidation reaction.

EXPERIMENTAL METHODS

Phase equilibrium measurements were carried out using the static measurement apparatus, which has been described previously.[4] The liquid is loaded into a cell that can be observed visually and CO_2 carefully metered into the system. The liquid phase compositions were determined by stoichiometry, assuming that the gas phase was composed of only CO_2.[5,6]

MODELING

The Peng-Robinson equation of state was used to model the phase behavior of all the binaries systems, with conventional van der Waals mixing rules.[7-9] For each binary, one temperature independent binary interaction parameter, k_{ij}, was fit to the experimental liquid phase composition data [$a_{ij} = (a_{ii}\, a_{jj})^{0.5}\ (1-k_{ij})$]. Since the critical properties of most of the constituents were not available, they were estimated using the contribution method by Joback.[8] Vapor pressures were estimated using the Riedel method.[8] The values of the properties used in the modeling of the various binaries are given in Table I.

Table I. Properties of Components

Component Name	Formula	T_c(K)	P_c(bar)	ω	k_{ij}
trans-2-Hexen-1-ol	$C_6H_{12}O$	601.76	36.73	0.724	0.084
(2R,3R)-(+)-3-Propyloxirane-methanol	$C_6H_{12}O_2$	631.77	38.39	0.794	0.043
Diisopropyl L-tartrate	$[-CH(OH)CO_2CH(CH_3)_2]_2$	691.18	30.73	0.491	0.052
Titanium (IV) isopropoxide	$Ti[OCH(CH_3)_2]_4$	661.35	16.22	0.685	0.087
tert-Butyl hydroperoxide	$(CH_3)_3COOH$	505.16	40.42	0.303	0.199
tert-Butyl alcohol	$(CH_3)_3COH$	506.21	39.73	0.611	0.108

The two phase compositions were determined using the Michelsen algorithm, as implemented in LNGFLASH, which is part of the IVC-SEP Program Package.[10] Although this code is extremely reliable, it did fail to give the correct answer to some points close to the LLV line, thus, emphasizing the need for the new computational techniques described below.

INTERVAL NEWTON GENERALIZED BISECTION

The determination of phase stability and ultimately phase equilibrium is a very difficult computational problem for which conventional techniques often fail by converging to a trivial or incorrect solution corresponding to a local rather than global minimum in the Gibbs energy. Thus there has been much recent interest in developing more reliable solution methods. The only method available to date which can mathematically guarantee a correct solution in connection with cubic equation of state models of interest here is a technique that we have developed[11-13] based on an interval Newton/generalized bisection algorithm. This approach provides the power to find with confidence all solutions to a system of nonlinear

equations, and to find with total reliability the global minimum of a nonlinear objective function, provided only that upper and lower bounds are available for all variables. The technique is initialization independent and can be used in connection with any activity coefficient model or equation of state model for computing the Gibbs energy.

EXPERIMENTAL RESULTS

The high pressure vapor/liquid and vapor/liquid/liquid equilibria were measured for six different binary systems involved in the epoxidation reaction shown in Figure 1. The range of temperatures, pressures and mole fractions for each system are summarized below:

trans-2-Hexen-1-ol---CO_2. Liquid phase compositions for this system were measured at 303.15, 305.95, 313.15 and 323.15 K and pressures between 14.6 and 100.3 bar and are shown, along with compositions estimated with the PREOS, in Figure 2. This system exhibits a liquid-liquid-vapor region (LLV) which extends from 310.9 K and 79.5 bar (LCST) to 315.3 K and 86.7 bar (type-k point). The compositions of both of the liquid phases at conditions where LLV existed were rich in CO_2, with typical values of about 0.8 and 0.95 mole fraction CO_2.

(2R,3R)-(+)-3-Propyloxiranemethanol---CO_2. Liquid phase compositions for this system were measured at 305.95, 313.15 and 323.15 K and pressures between 31.5 and 110.2 bar and are plotted, along with compositions estimated with the PREOS, as pressure versus composition (Pxy) in Figure 3. A LLV region was found for this binary systems, as well, and extends from 315.1 K and 86.1 bar (type-k point) to below 293.7 K and 55.8 bar, which was the lowest temperature measured. The LLV experimental liquid phase compositions were about 0.77 and 0.93 mole fraction CO_2 and were fairly insensitive to pressure over the range investigated.

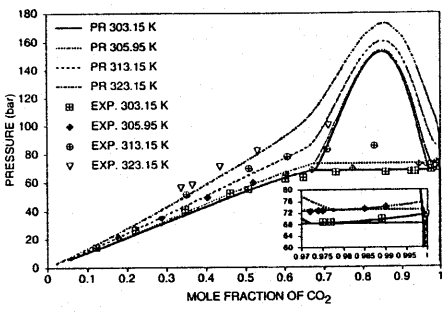

Figure 2. P-x diagram for trans-2-hexen-1-ol---CO_2

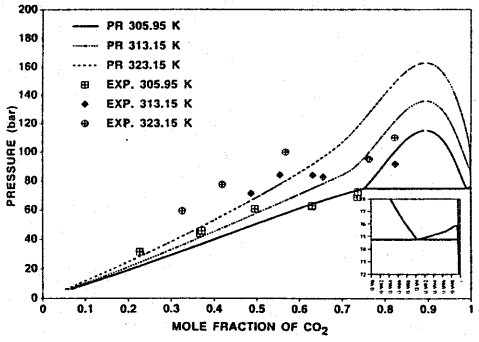

Figure 4. P-x diagram for (2R,3R)-(+)-3-propyloxiranemethanol---CO_2.

Diisopropyl L-tartrate---CO_2. Liquid phase compositions for this system were measured at 305.95 and 313.15 K and pressures between 46.6 and 87.2 bar. The compositions ranged from 0.50 to 0.97 mole fraction CO_2. Only two-phase VLE was observed experimentally and this was what was predicted by the PREOS except at 313.15K and pressures above 87 bar, where the PREOS predicted a single phase system.

Titanium (IV) isopropoxide---CO_2. Liquid phase compositions for this system were measured at 305.95 and 313.15 K and pressures between 42.8 and 84.7 bar. The compositions ranged from 0.43 to 0.97 mole fraction CO_2. Although only two-phase VLE was observed experimentally, the PREOS predicted two liquid phases at 305.95 at all pressures and at 313.15 at pressures up to 84.1 bar.

tert-Butyl hydroperoxide---CO_2. Liquid phase compositions for this system were measured at 305.95 and 313.15 K and pressures between 56.3 and 79.6 bar. The compositions ranged from 0.38 to 0.85 mole fraction CO_2. Only two-phase VLE was observed experimentally and this was what was predicted by the PREOS at 313.15 K. However for 305.95 K the PREOS predicted the presence of two liquid phases.

tert-Butyl alcohol---CO_2. Liquid phase compositions for this system were measured at 305.95 and 313.15 K and pressures between 40.5 and 75.7 bar. The compositions ranged from 0.34 to 0.89 mole fraction CO_2. Only two-phase VLE was observed experimentally and this was what was predicted by the PREOS.

COMPUTATIONAL RESULTS

An enhanced version of our original interval Newton/generalized bisection technique for cubic equations of state models[12,13] is currently being developed. The enhancements are based on obtaining tighter bounds on function ranges than possible when using ordinary interval arithmetic, thus providing significant improvements in computational efficiency. The new technique has been applied to phase stability computations for several binary and ternary systems using the Peng Robinson and SRK EOS models. In all cases the correct solution to the problem was obtained. The technique also proved to be quite efficient, with solution times ranging from about 5 to 0.1 seconds (on a Sun Ultra 1/170 workstation) over a wide variety of problems.

SUMMARY

We have presented phase equilibrium measurements for the binary components in the allylic epoxidation of trans-2-hexen-1-ol to (2R,3R)-(+)-3-propyloxiranemethanol in CO_2 and modeled the data with the PREOS. We have also developed a new completely reliable interval Newton/generalized bisection technique to perform phase stability computations for high pressure systems using any of a variety of EOS models. Future work will include prediction of the multicomponent phase behavior using the interaction parameters determined from the binary systems and comparison with multicomponent phase measurements. To perform the high pressure phase equilibrium computations we will use the newly develop IN/GB technique. This work is important because it develops techniques and procedures to identify and reliably predict appropriate operating conditions where reactant, product and catalyst solubilities are sufficiently high in CO_2 to make the use of CO_2 as an environmentally benign replacement solvent a viable alternative.

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