

Phase equilibria of the ternary system R,S-1-phenylethanol / vinyl acetate / carbon dioxide at high pressure conditions.

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INTRODUCTION

The need of technologies that allow separating optical isomers is increasing. Enzymes can distinguish substances on the molecular level very efficiently. They can catalyze a bio-transformation, where basically one of the enantiomers is preferably chemically modified. As a result, the reaction products differ in their physical behaviour more than the educts. This difference can be adjusted to the needs of subsequent separation processes by choosing appropriate compounds for modification of the enantiomers.

Using supercritical carbon dioxide as a reaction medium would be advantageous to utilize the solvent power of carbon dioxide to separate the reaction products immediately after the reaction.

It is important to study not only the reactions themselves but to extend the research to what appends before and after the reaction takes place. This involves the phase equilibrium measurements and calculations of the reactants and products of the reaction.

For this work the model reaction of the separation of the enantiomers R,S-1-Phenylethanol by means of a biocatalytical reaction catalyzed by a lipase was chosen.

The reaction will take place in a supercritical environment, which means that supercritical carbon dioxide will also act as the carrier of the reactants, 1-R,S-Phenylethanol and vinyl acetate, to the reaction media [1]. For that the knowledge of the phase equilibrium for the ternary system R,S-1-phenylethanol / vinyl acetate / CO₂ was studied.

Since chemical process design is often concerned with separation of fluid mixtures, the reliable knowledge of the phase equilibrium behaviour as function of T , P , x of multicomponent mixtures is a prerequisite for the synthesis and optimization of separation processes. It's frequently necessary to estimate the phase behaviour of the system at hand. In the cases where phase equilibrium data are available such estimations can usually be done with ease. In many other cases however, where the required experimental data are not available it is difficult to make even rough estimates on a rational basis.

In the cases where no data is available and/or the interaction parameters of the mixture are not known its necessary take on a different approach. The predictive, group-contribution methods like UNIFAC [2] can predict vapour-liquid equilibria of systems with high non-idealities but they are unable to treat those containing gaseous components.

Methods combining equations of state with group-contribution predictive equations (the so called G^E mixing rules) can treat any type of system, including those with gaseous compounds, at high pressures and at near-critical conditions.

In this work phase equilibrium measurements were made at temperatures of 323 K, 333 K and 343 K and pressures between 7 MPa and 12 MPa using a high pressure visual cell with variable volume. Simulation of phase equilibrium of the system and its subsystems has been carried out using the program package PE [3].

The experimental pTxy data were correlated using the Peng-Robinson equation of state [4] with the Mathias-Klotz-Prausnitz mixing rule [5]. The method combining the equations of state, Soave-Redlich-Kwong and Peng-Robinson, using the Mathias-Copeman equation with the predictive mixing rule MHV1 [6] were used in order to obtain optimum condition for operation and separation with a minimum of experimental data.

I - MATERIALS AND METHODS

The (R,S)-1-Phenylethanol was supplied by Fluka and has a purity of 98%. The Vinyl acetate was supplied by Merck and has a purity of 99%. CO₂ was supplied by KWD Kohlen säurewerk Deutschland GmbH (Bad Hönningen) and has a purity of 99.95%.

The phase equilibrium measurements were made by analytical method using a visual high pressure cell with variable volume. Samplings are taken both from the liquid and vapour phases.

A schematic of the phase equilibrium cell used is represented in Figure 1.

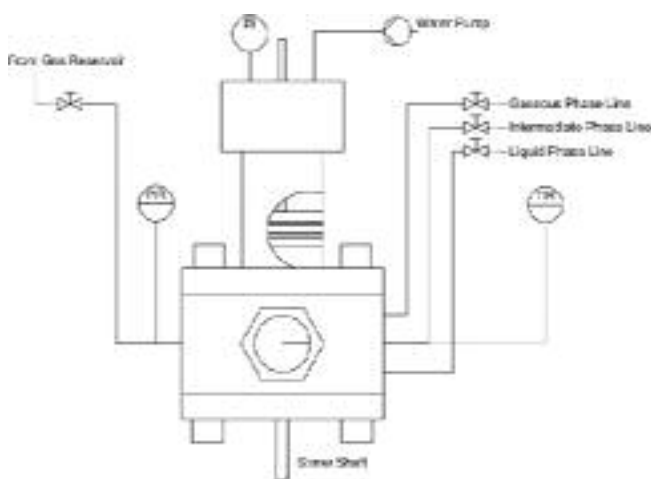


Figure 1 –
Schematic of the experimental visual cell with variable volume

First vacuum is made so that a previously prepared mixture of 1-Phenylethanol and Vinyl acetate can be loaded into the cell. Afterwards CO₂ is inserted into the cell to the desired pressure. Before each sample the system inside the cell is stirred for 45 min and then it's let to rest for 20 min. During the sampling the pressure inside the cell is maintained constant by moving the piston and decreasing the volume. The piston moves by pumping water to it's back using an automatic water pump, so by increasing the pressure of water the piston moves forward and by decreasing the pressure of water the piston moves backwards.

The samples are taking to a glass trap in vacuum and cooled with dry ice plus acetone and where the liquid is separated from the CO₂. The CO₂ amount in the sample is then measured by a flowmeter.

The liquid composition of each sample is measured by GC.

Isothermal vapour-liquid phase equilibria were measured at 323, 333, 343K for the ternary system Vinyl acetate / 1-Phenylethanol / CO₂, in the pressure range of 7–12MPa. Four different feed compositions were studied: 0,154; 0,397; 0,753; 0,898 mass fraction 1-Phenylethanol.

The experimental pTxy data were correlated using the Peng-Robinson equation of state with the Mathias-Klotz-Prausnitz mixing rule. The pure component parameters for the PR-EOS are calculated by the following expressions, where the parameter *a* is made temperature dependent:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 2bv - b^2} \quad (1)$$

$$a(T) = a(T_c) \cdot a(T_r, \omega) \quad (2)$$

$$a(T_c) = 0,45724 \frac{R^2 T_c^2}{P_c} \quad (3)$$

$$a(T_r, \omega) = \left(1 + k(1 - \sqrt{T_r})\right)^2 \quad (4)$$

$$k = 0,37464 + 1,5422\omega - 0,26992\omega^2 \quad (5)$$

$$b = 0,0778 \frac{RT_c}{P_c} \quad (6)$$

The Mathias–Klotz–Prausnitz mixing rule has three adjustable binary interaction parameters, k_{ij} , λ_{ij} and l_{ij} :

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) + \sum_{i=1}^N x_i \left[\sum_{j=1}^N x_j \left(\sqrt{a_i a_j} \lambda_{ij} \right)^{\frac{1}{3}} \right]^3 \quad (7)$$

With $k_{ij} = k_{ji}$ and $\lambda_{ij} = -\lambda_{ji}$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}), \quad \text{With } l_{ij} = l_{ji} \quad (8)$$

| Compound | T_c (K) | P_c (MPa) | ω |
|-----------------|-----------|-------------|----------|
| Vinyl acetate | 518.71 | 3.958 | 0.351 |
| 1-Phenylethanol | 668.00 | 3.990 | 0.706 |
| CO2 | 304.10 | 7.380 | 0.225 |

Table 1 - Pure component physical properties

pure component parameters used in the correlation of experimental data are presented in table 1. Fitting the PR-EOS to the ternary system was made by finding the best set of interaction parameters that minimized the deviations between the calculated and experimentally determined liquid and vapour phase compositions, as well as the distribution factors of all components of the mixture. The fitting of the VLE data led to an average absolute deviation of 6.25%. Experimental and correlated phase boundary lines for the ternary system at 333 K are presented Figure 2, and the interaction parameters are presented in table 2.

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| | 1-2 | 1-3 | 2-3 |
|----------------|------------|------------|---------|
| k_{ij} | -0.0660 | 0.0117 | -0.0097 |
| λ_{ij} | 0.0988 | 0.0407 | -0.0989 |
| l_{ij} | 0.0346 | -0.0011 | 0.0369 |
| AAD | x 6,25% | y 0,86% | |

Table 2 – Optimized interaction parameters of the ternary system with PR-EOS and MKP-MR and the average absolute deviation for the liquid and vapour phase

$$deviation = \sqrt{\frac{1}{n} \sum_{i=1}^n (z_i^{\text{exp}} - z_i^{\text{EOS}})^2} \quad (9)$$

With $z = x, y$

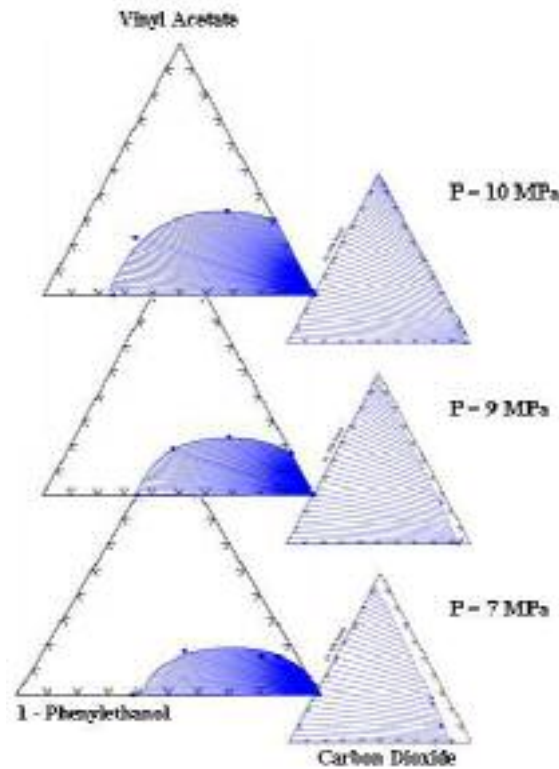


Figure 2 - Correlation of the pTxy experimental data with the Peng-Robinson EOS with the Mathias–Klotz–Prausnitz mixing rule using phase equilibria program PE, at 333 K. Points represent experimental data.

The vapour-liquid phase equilibria of the system Vinyl acetate / 1-Phenylethanol / CO₂ was predicted using the Peng-Robinson EOS and the Soave-Rendlich-Kwong EOS, both with the Mathias-Copeman equation for the temperature dependence of the pure component parameter $a(T_r)$ [7]:

$$a(T_r) = \left[1 + c_1(1 - \sqrt{T_r}) + c_2(1 - \sqrt{T_r})^2 + c_3(1 - \sqrt{T_r})^3 \right]^2 \quad (10)$$

In the equation of state a parameter for a mixture is calculated by an expression for the mixture excess Gibbs energy by means of the MHV1 mixing rule:

$$q_1 \left[\alpha - \sum x_i \alpha_i \right] = \frac{g_0^E}{RT} + \sum x_i \ln \frac{b}{b_i} \quad (11)$$

Pure component parameters of Vinyl acetate and 1-Phenylethanol used for the prediction methods were estimated by adjusting both the PR-MC EOS and the SRK-MC EOS to the vapour pressure curve of each pure compound. Data for CO₂ were already available in literature [8].

The pure component parameters are presented in table 3.

| Compound | EOS | T _c (K) | P _c (MPa) | c ₁ | c ₂ | c ₃ |
|-----------------|--------|--------------------|----------------------|----------------|----------------|----------------|
| Vinyl acetate | PR-MC | 527.71 | 43.84 | 0.865 | -0.284 | 1.071 |
| | SRK-MC | 521.30 | 42.77 | 1.051 | -0.121 | -4.246 |
| 1-Phenylethanol | PR-MC | 669.62 | 39.25 | 1.467 | -0.984 | 0.697 |
| | SRK-MC | 662.21 | 42.33 | 2.156 | -4.000 | 5.016 |
| CO ₂ | PR-MC | 304.10 | 73.80 | 0.727 | -0.604 | 2.936 |
| | SRK-MC | 304.10 | 73.80 | 0.586 | -0.220 | 0.000 |

Table 3 – Estimated pure component physical properties with the Peng-Robinson Mathias-Copeman /PR-MC EOS and the Soave-Rendlich-Kwong Mathias-Copeman EOS

Predictions were made using the two equations referred above for the binary systems Vinyl acetate / CO₂ and 1-Phenylethanol / CO₂, and for the ternary system Vinyl acetate / 1-Phenylethanol / CO₂.

The comparison between the predictive methods SRK-MC – MHV1, PR-MC – MHV1 and the correlation with the PR – MKP for the two binary systems can be seen in Figure 3, where the phase boundary at 333 K and 9 MPa is presented. The comparison between the predictive method PR-MC – MHV1 and the correlation with the PR EOS and the MKP mixing rule for the ternary system at 333 K and 9 MPa is presented in Figure 4

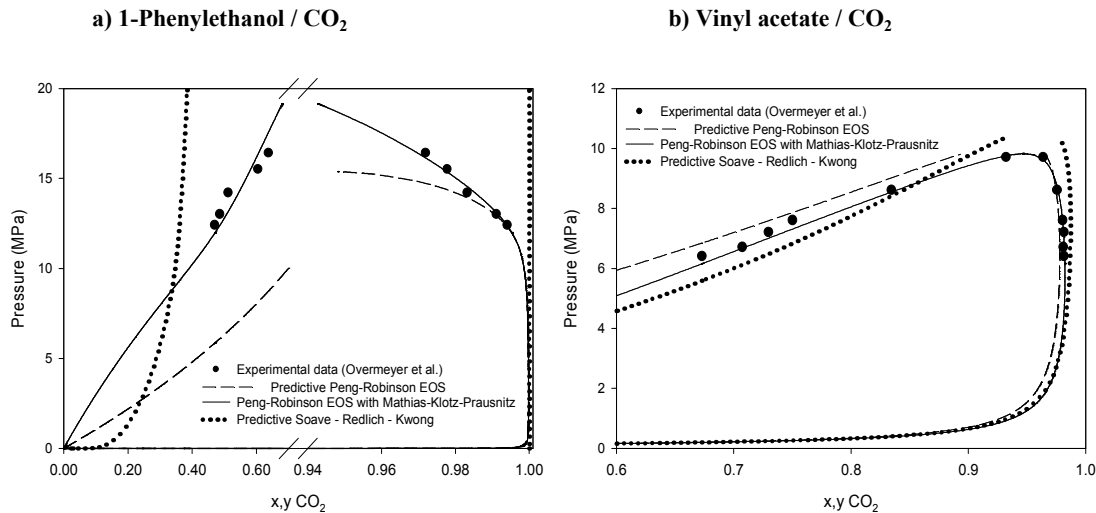


Figure 3 – Correlation of the binary experimental data with the PR EOS with the MKP mixing rule and prediction with the PR-MC – MHV1 and SRK-MC – MHV1 using phase equilibria program PE, at 333 K. Points represent experimental data.

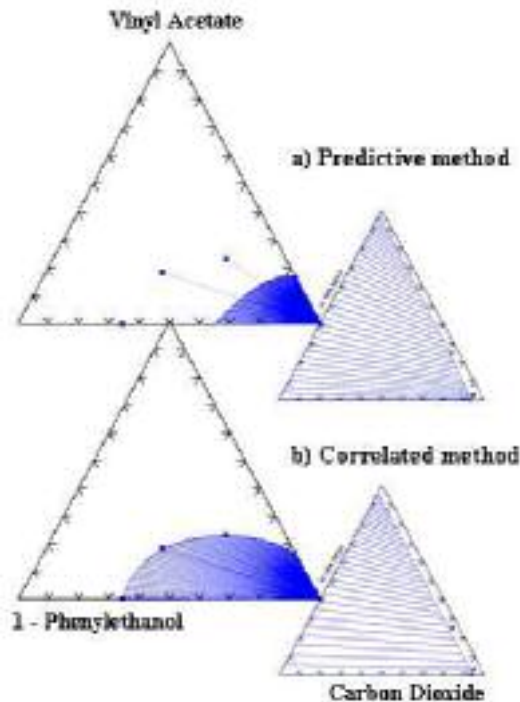


Figure 4 –
a) Prediction of pTxy data with PR-MC EOS and MHV1 mixing rule at 333K and 9 MPa using phase equilibria program PE
b) Correlation of the pTxy experimental data with the PR EOS with the MKP mixing rule at 333 K and 9 MPa using phase equilibria program PE

CONCLUSIONS

Vapour-Liquid equilibria were determined for the ternary system Vinyl acetate/1-Phenylethanol/CO₂ at 323, 333 and 343K with a pressure range of 7 – 12 MPa. The experimental measurements were made by an analytical method using a high pressure visual cell with variable volume.

Experimental pT_{xy} data were correlated using the Peng-Robinson equation of state and the Mathias-Klotz-Prausnitz mixing rule with an AAD of 6.25%. This EOS with the referred mixing rule showed to accurately represent both liquid and vapour phases of the ternary system.

The phase equilibria of the ternary system and of the binary sub-systems were predicted using two group contribution methods. The Peng-Robinson - Mathias-Copeman EOS with the MHV1 predictive mixing rule and the Soave-Rendlich-Kwong - Mathias-Copeman EOS with the MHV1 predictive mixing rule.

While both methods were able to predict the binary system Vinyl acetate/CO₂ with an AAD of 2.58% for the PR-MC EOS and with an AAD of 24.10% for the SRK-MC EOS, the same was not observed for the binary system 1-Phenylethanol/ CO₂, where both methods used gave poor predictions for the system at hand.

For that reason is to be expected that the prediction for the ternary system will not be completely accurate. In fact the method using the SRK-MC EOS was not even able to predict the phase equilibria and the method using the PR-MC EOS gave good predictions for the vapour phase but not for the liquid phase.

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