

MODELING THE PHASE EQUILIBRIUM OF THE CLOVE OIL + CO₂ SYSTEM

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The phase equilibria for the mixture clove oil + CO₂ was modeled as a pseudo-binary system. Clove oil is a multicomponent mixture formed by eugenol, β -caryophyllene, α -humulene and eugenol acetate that was reduced to a pseudo-single component. For the modeling of experimental data the Peng-Robinson equation of state with the quadratic mixing rule (two temperature independent adjustable parameters: k_{ij} and l_{ij}) was employed through the methodology described for Michelsen. Experimental phase equilibrium data was used to fit the interaction parameters using the Maximum Likelihood Method. Two different procedures were used: i) the phase stability was calculated using the Helmholtz free energy employing the interval analysis, and ii) the phase equilibria was calculated using the Gibbs free energy solved with the Simulated Annealing. Both methods provide a mathematical and computational guarantee that no roots would be missed. The calculations were performed at 303.15 K, 308.15 K, 313.15 and 318.15; VLE and LLE were considered.

Keywords: Phase equilibrium, clove oil, phase stability, Interval analysis

INTRODUCTION

Interest on natural products has increased in the last years, above all in substances used by pharmaceutical and chemical industries. Over the years much attention was given to the thermodynamic description of mineral oils and petroleum fluids, both at normal and up to very high pressures. Because of the, in general, essentially limited number of molecular structures and moderate intermolecular interactions, this turned out to be feasible. For that purpose, methods were developed to characterize the heavy tail of the hydrocarbon fluids in terms of well-chosen pseudo-components. Also application of continuous thermodynamics has been used for that purpose. Although size differences between the various molecules are large, certain equations of state were able to account for that, e.g., equations originating from perturbed-hard-chain theory. In all, it turned out that the description / prediction of thermodynamic properties, including phase behavior, of these fluids by means of the individually detectable components and of some pseudo-components, in principle, was feasible, at least qualitatively. Considering the similarities and differences between both types of fluids, it is not surprising that the thermodynamic description and / or prediction of the phase behavior and other related thermodynamic properties of systems with essential oils will be much more problematic. The large differences between the chemical and structural nature of the constituents in these fluids may cause complex phase behavior. This complexity may increase even more when we are dealing with mixtures of interest for supercritical fluid technology, i.e., mixtures where carbon dioxide is used as the near-critical solvent [1], [2].

In recent decades, a great deal of literature has been focused on the prediction of multiphase flash equilibrium calculation. Convergence of these algorithms depends on the initial estimates of the distribution of the components between the different phases. A very important issue in phase equilibrium calculations is how to check if the solution of these algorithms is correct. This issue may rely on the stability analysis of the phase equilibrium results.

Since the number of phases present at equilibrium may not be known *a priori*, the computation of phase equilibrium is often considered in two stages, as outlined by Michelsen [3], [4]. The first involves the *phase stability* problem, that is, to determine whether or not a given mixture will split into multiple phases. The second involves the *phase split* problem that is to determine the amounts and composition of the phases assumed to be present. After a phase split problem is solved; thus, it is necessary to make a phase stability analysis on the results in order to determine whether or not the number of postulated phases was correct, and if not the phase split problem must be repeated. Both the phase stability and phase split problems can be formulated as minimization problems, or as equivalent nonlinear equation solving problems.

Conventional minimization or equation solving techniques for solving the phase stability problem are initialization dependent, and may fail by converging to trivial or nonphysical solutions or to a point that is a local but not a global minimum, thus there is no guarantee that the phase stability problem has been correctly solved. Because of the difficulties that may arise in solving such problems by standard methods [3], [4], there has been significant interest in the development of more reliable methods.

Two alternative approaches for solving the phase stability problem are the use of interval analysis and Simulated Annealing method, which are not dependent on initialization.

The aim of this work was to model experimental data for clove oil + CO₂ system using an equation of state coupled with the stability analysis. This was done to verify the performance and capacity of the model (equation of state) to correlate the experimental data for a particular system. Also, interval analysis and Simulated Annealing routines were used with the Nagarajan's methods [5] and [6] and tangent plane distance of Gibbs free energy [7] to overcome the global uncertainty, latter on applied to model multi-phase equilibrium to the mixture CO₂ + clove oil.

METHODOLOGY

Stability Analysis and Flash Calculation

The stability analysis was performed using two different methodologies: **M1**) minimization of tangent plane distance to Helmholtz free energy is tried [5], [6]. For this, it is used interval analysis based in interval Newton/generalized bisection technique (INBIS [8] / INTLIB [9]); **M2**) At the second, minimization of tangent plane distance to Gibbs free energy is tried [1], through a Simulated Annealing routine (Amebsa – Numerical Recipes in Fortran [10] Both using Peng–Robinson equation state and van der Waals mixing rule. For both methodologies, the determination of the phase equilibrium and phase stability combines local methods for doing phase-split calculations with one of and two global methods for verifying phase stability (INTBIS/INTLIB with Broydn method [**M1**] or Simulated Annealing with Broydn [**M2**]). The results for the phase stability are used as the initiation for the flash calculation. The key is the use of technique based on interval analysis or Simulated Annealing in performing the phase stability analysis. By incorporating this for global phase stability, can guarantee that correct phase equilibrium results are obtained.

Some calculations with two methodologies (**M1** and **M2**) above presented were done and compared at results presented in literature [11], which are showed in the Table A1 (Appendix 1).

Modeling of Experimental Data

The Peng-Robinson equation of state with the van der Waals quadratic mixing rule (two temperature independent adjustable parameters: k_{ij} and l_{ij}) was used to model of the experimental data. Experimental phase equilibrium data was used to fit the interaction parameters. The minimized objective function (OF) was of the square minima, through the Maximum Likelihood Method.

$$OF = \Delta P^2 = \sum_i^{NEP} (P_i^{calc} - P_i^{exp})^2$$

RESULTS AND DISCUSSION

In this work, was studied only on the high-pressure phase behavior of CO₂ with clove oil. The critical temperature T_c , critical pressure P_c , acentric factor ω , with CO₂ (component 1) of these two compounds are given in Table 2.

Table 2. Properties of Compounds

Compound	T_c (K)	P_c (bar)	ω	PM (g/gmol)
CO ₂	304.21	73.83	0.2236	44.01
Clove Oil*	758.33	30.97	0.6286	172.02

* Estimated by Constantini and Gani method of second order.

The phase equilibrium experiments were performed in a high-pressure variable-volume view cell. The Table 3 shows the values of the fitted parameters for different temperatures.

Table3. Values of the fitted parameters

T (K)	k_{12}	l_{12}	ΔP (bar)	NU
303.15	0.03626	-0.03341	3.51	9
308.15	0.03379	-0.02060	5.39	9
313.15	0.03112	-0.03850	4.85	8
318.15	0.02945	-0.04411	1.69	9

NU: number of points used in the fit.

In the temperatures of 313.15 K and 318.15 K, there is not formation of the three-phases, only transition vapor-liquid was visualized, phase equilibrium calculations were then done with these model parameters in order to compare the model predictions to experimental measurements, as observed in the Figures 1 (a) and (b).

At 303.15 K and 308.15 K, the model predicts a three-phase line at 71.25 and 80.15 bar, respectively. Above this pressure exists a region of liquid-liquid and below there is a region of vapor-liquid. This can be showed in the Figures 2 (a) and (b).

For the diagrams that followed (Figures 2 (a) and (b)), the vapor-liquid envelopes were calculated using the values of the parameters (k_{12} , l_{12}) fitted to liquid-liquid.

CONCLUSIONS

Several difficulties were encountered when standard tools were used to model the

phase behavior of the compounds present. The major problems occurred near the three-phase boundary and in the region with retrograde behavior. Conventional tools for modeling phase behavior may become unreliable, for example, convergence failures, computing the wrong number of phases, and computing incorrect phase compositions. By using a technique based on interval mathematics, which eliminates the need for initial guesses, these difficulties were eliminated and correct results obtained, turning a completely reliable method.

The experimental data were very well modeled with the Peng-Robinson equation of state and van der Waals quadratic mixing rule either LVE or LLE. And, a computation of interval analysis is a useful tool for calculation of the phase equilibrium, principally for mixtures with higher non-ideality, as such clove oil + CO₂.

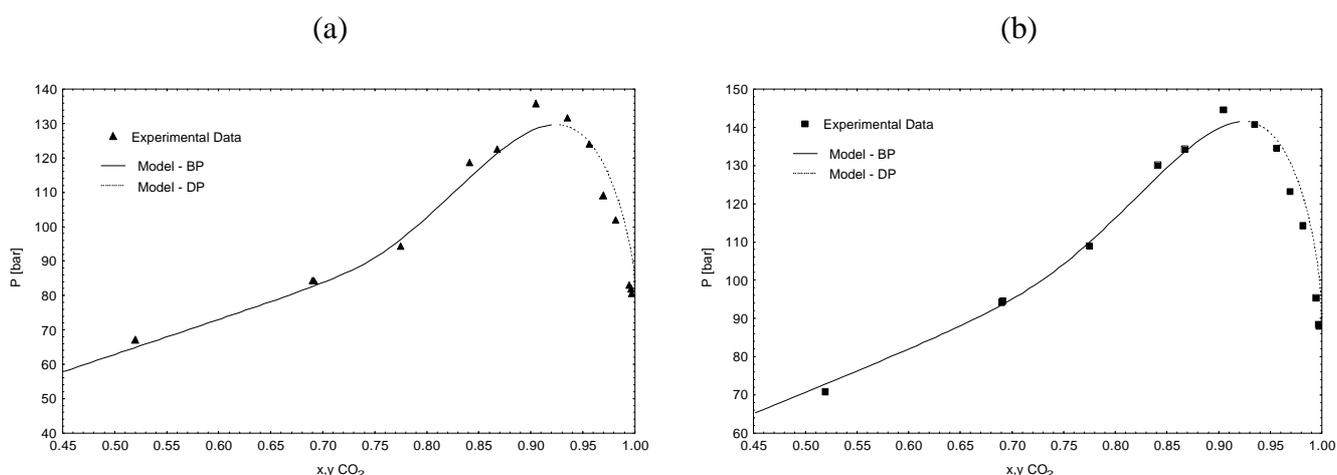


Figure 1: P-x-y plot for CO₂-clove oil at 313.15 K (a) and 318.15 K (b) (BP = Bubble Point; DP = Dew Point).

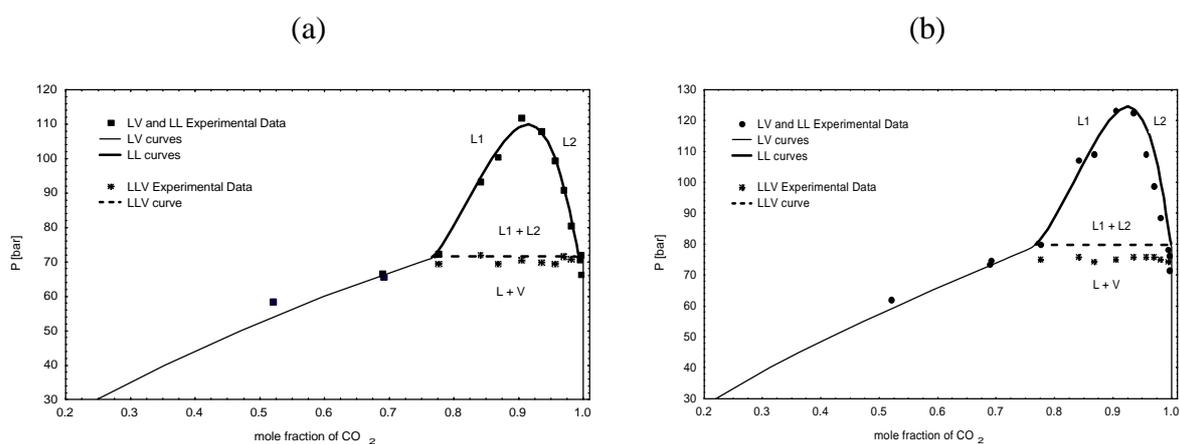


Figure 2: P-x-y plot for CO₂-clove oil at 303.15 K (a) and 308.15 K (b).

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Table A1. Examples showing the results of the different flash programs for trans-2-hexen-1-ol/CO₂.

Binary Mixture				*P1	*P2		*P3		*P4		M1		M2		
Case	Feed	T (K)	P (bar)	x_{CO_2}	y_{CO_2}	x_{CO_2}	y_{CO_2}	x_{CO_2}	y_{CO_2}	x_{CO_2}	y_{CO_2}	x_{CO_2}	y_{CO_2}	x_{CO_2}	y_{CO_2}
1	0.800	303.15	71.00725	0.7315	0.9986	0.7310	0.9987	0.7309	0.9987	0.6846	0.9690	0.6850	0.9689	0.6850	0.9689
2	0.700	303.15	70.09	NPS		NPS		NPS		0.6828	0.9702	0.6833	0.9701	0.6833	0.9701
3	0.970	323.15	97.75	NC1	0.6267	0.9948	0.6267	0.9949	0.6281	0.9947	0.6283	0.9945	0.6284	0.9947	
4	0.742	323.15	135	0.7345	0.9490	NPS		0.7347	0.9515	0.7352	0.9489	0.7356	0.9488	0.7356	0.9488

The mole fraction x_{CO_2} and y_{CO_2} in each phase are given. Entries in bold indicate incorrect results. The notation NPS indicates that no phase split was predicted. NC1 indicates that the program predicted a phase split, but that the phase split calculation did not converge after 1000 iterations.

*Results presented in [11].

P1 - LNGFLASH

P2 – FLASH3

P3 – RGIBBS

P4 – INTFLASH

M1 – Methodology 1 presented in this work

M2 - Methodology 2 presented in this work