352 *J. Chem. Eng. Data* **2004,** *49,* 352−356

# Phase Equilibrium Measurements for the System Clove (*Eugenia caryophyllus*) Oil + $CO_2$

**Alexandre T. Souza,[†] Marcos L. Corazza,[‡] Lúcio Cardozo-Filho,[‡] Reginaldo Guirardello,[†] and M. Angela A. Meireles*[,§]**

DPQ-FEQ (College of Chemical Engineering)/UNICAMP (State University of Campinas), Cx. Postal 6066, 13081/970 Campinas, São Paulo, Brazil; Universidade Estadual de Maringá (UEM), Department of Chemical Engineering, Av. Colombo, 5790 Bloco D-90, 87020-900 Maringá, Paraná, Brazil; and LASEFI-DEA/FEA (College of Food Engineering)/UNICAMP, Cx. Postal 6121, 13083-970 Campinas, São Paulo, Brazil

Phase equilibria data for the system formed by clove oil + $CO_2$ were measured at pressures from 58.3 to 108.1 bar and temperatures of 303.2, 313.2, and 328.2 K. The phase equilibrium experiments (cloud points) were performed using a high-pressure variable-volume view cell. The phase transitions were visually recorded as bubble or dew points. The clove oil used in the present work was extracted with carbon dioxide at 150 bar and 298.2 K, and it consisted of a mixture of the following mass fractions: eugenol (75.5%), $\beta$-caryophyllene (12.1%), eugenol acetate (11.0%), and $\alpha$-humulene (1.40%). Liquid−liquid−vapor equilibria were observed at 303.2 and 308.2 K, and liquid−vapor equilibria were observed at 313.2, 318.2, and 328.2 K. The phase equilibria data were modeled assuming the system to be a pseudobinary system. The Peng−Robinson equation of state with the quadratic mixing rule was used. The experimental data were fitted using the simulated annealing minimization method. Two different procedures were employed: (i) the phase stability was calculated using the Helmholtz free energy and the interval analysis, and (ii) the phase equilibrium was calculated using the Gibbs free energy, which was solved with the simulated annealing method. The model described quantitatively the experimental data.

## 1. Introduction

Supercritical fluid extraction (SFE) from a solid substratum, especially from aromatic, medicinal, and spice plants, is an important technology due to its classification as a green technology and its capability of extracting valuable substances at intermediate temperatures. Despite the reduction observed in the investment costs in the past decade, the manufacturing costs of SFE extracts are still considered prohibitive by many in industry. To achieve a reduction in these costs, it is mandatory to gather all the information related to a particular system. In that respect, the knowledge of phase equilibria can benefit the design of SFE systems, specifically in the separation step. Although relevant data on phase equilibria of several binary and ternary systems of interest have been published in the literature, the use of phase equilibria data for real systems, such as the true mixture that forms clove oil, is more appropriate for process design.

Over the years, much attention has been focused on the thermodynamic description of mineral oils and petroleum fluids, both at normal and high pressures. Because of the generally limited number of molecular structures and moderate intermolecular interactions, methods have been developed to characterize the heavy tail of the hydrocarbon fluids in terms of either well-chosen pseudocomponents or the application of continuous thermodynamics. Although size differences between the various molecules are large, certain equations of state were able to account for that characterization, that is, equations originating from perturbed-hard-chain theory. All in all, it turned out that it was feasible to obtain the description and the prediction of the thermodynamic properties and the phase behavior of these fluids by means of the individually detectable components and of some pseudocomponents, at least qualitatively. The volatile oils (or essential oils) are a multicomponent mixture of terpenoids (mono-, sesqui-, and diterpenes, various alcohols, ketones, and aldehydes of terpenoids[1]). Considering the similarities and differences between both types of fluids (mineral oils and volatile oils), it is not surprising that the thermodynamic description and/or prediction of the phase behavior and other related thermodynamic properties of systems with volatile oils is much more problematic. The large differences between the chemical 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, that is, mixtures where carbon dioxide is used as the near-critical solvent.[2,3]

In recent decades, several papers focusing on the prediction and calculation of multiphase flash equilibria have been published. The convergence of these algorithms depends on the initial estimates of the distribution of the components in 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.[4,5] The first involves the *phase stability* problem,

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* To whom correspondence should be addressed. E-mail: meireles@fea.unicamp.br. Phone: +55 19 3788.4033. Fax: +55 19 3788.4027.

[†] DPQ-FEQ (College of Chemical Engineering)/UNICAMP (State University of Campinas).

[‡] Universidade Estadual de Maringá (UEM).

[§] LASEFI-DEA/FEA (College of Food Engineering)/UNICAMP.

10.1021/je034190f CCC: $27.50

**Table 1: Composition of the Clove Oil and the Thermophysical Properties of the Pure Components and Pseudocomponents**

| component[a] | mass fraction | molar mass/kg·kmol$^{-1}$ | molar fraction | $T_{\text{boiling}}$/K | $T_{\text{crit}}$/K | $P_{\text{crit}}$/bar | $10^3 V_{\text{crit}}$/m$^3$·kmol$^{-1}$ | $\omega$ |
|---|---|---|---|---|---|---|---|---|
| eugenol | 0.755 | 164.20 | 0.794 | 545.07 | 763.20 | 33.42 | 500.90 | 0.6545 |
| CN: methoxy-4-(2-propenyl)phenyl; CAS no.: 97-53-0 | | | | | | | | |
| $\beta$-caryophyllene | 0.121 | 204.36 | 0.102 | 519.23 | 714.73 | 18.98 | 701.30 | 0.4799 |
| CN: trimethyl-8-methylenebicyclo(7.2.0)undec-4-ene; CAS no.: 87-44-5 | | | | | | | | |
| $\alpha$-humulene | 0.014 | 204.36 | 0.012 | 524.50 | 719.00 | 17.09 | 743.00 | 0.4502 |
| CN: tetramethyl-1,4,8-cycloundecatriene; CAS no.: 6753-98-6 | | | | | | | | |
| eugenol acetate | 0.110 | 206.24 | 0.092 | 556.92 | 767.01 | 22.97 | 668.10 | 0.5735 |
| CN: phenol, 2-methoxy-4-(2-propenyl)-, acetate; CAS no.: 93-28-7 | | | | | | | | |
| $CO_2$ | | 44.01 | | | 304.21 | 73.83 | | 0.2236 |
| clove oil | | 172.02 | | | 758.33 | 30.97 | | 0.6286 |

[a] CN: systematic name and CAS no. as given by Adams.[1]

which aims at determining whether a given mixture will split into multiple phases. The second involves the *phase split* problem, in which the amounts and composition of the phases assumed to be present are determined. After a phase split problem is solved, it is necessary to make a phase stability analysis on the results in order to determine whether the number of postulated phases was correct. In the case when it was not, the phase split problem must be reworked. Both the phase stability and the 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. Therefore, there is no guarantee that the phase stability problem has been correctly solved. Because of the difficulties that may arise in solving such problems using standard methods,[4,5] 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 the interval analysis and the use of simulated annealing methods, which are not strongly dependent on initialization. Both methods converged on the same numbers and values of roots. However, the convergence time using the method of interval analysis was greater than that of the simulated annealing method.

The purposes of the present work were to measure the phase equilibria for the system formed by clove oil + $CO_2$ and to model the experimental data using an equation of state coupled to the phase stability analysis.

## 2. Materials and Methods

***2.1. Preparation and Characterization of the Clove Oil.*** Clove oil was obtained by supercritical extraction using commercial clove buds (*Eugenia caryophyllus*) and $CO_2$ in a SFE unit (Applied Separations, Allentown, PA). The oil was obtained at 25 °C and 150 bar. The clove oil formed a quaternary mixture of eugenol (75.5%, mass), $\beta$-caryophyllene (12.1%, mass), eugenol acetate (11.0%, mass), and $\alpha$-humulene (1.4%, mass).

***2.2. Phase Equilibrium Apparatus and Procedure.*** Phase equilibrium experiments (cloud points) were performed through a static method without sampling,[6] in a high-pressure variable-volume view cell. The apparatus is very similar to the one used to measure the phase equilibria of orange peel oil + $CO_2$,[7] and it is also the equipment used to measure the phase equilibria of binary mixtures of $CO_2$ + acetonitrile, dichloromethane, carvone, and 1,2-limoneneoxide.[8] Phase transitions were visually recorded as bubble or dew points. Carbon dioxide, 99.99% (AGA, Brazil), was used. The temperature was measured with a precision of ±0.5 K. The amount of solvent charged was monitored by the change in the total volume of the transfer vessel of the pump. The uncertainty was around 0.001 for the molar fraction. The cell content was continuously agitated with the aid of a magnetic stirrer and a Teflon-coated stirring bar. After the desired temperature was reached, the cell pressure was increased to the point of the observation of a single phase. At this point, the system was allowed to stabilize for at least 30 min and the cell pressure was slowly decreased until the incipient formation of a new phase; after repetition of the experimental procedure at least three times, the equilibrium pressure was then recorded, leading to an average reproducibility of 0.7 bar. After completing the test at a given temperature, the cell temperature was stabilized at a new value, and the experimental procedure was repeated. Experimental data were measured at 303.2, 308.2, 313.2, 318.2, and 328.2 K.

***2.3. Modeling of Experimental Data.*** The thermophysical properties of the pure components were estimated using the method of Constantinou and Gani;[9] the acentric factor was calculated with the Lee and Kesler method.[9]

The Peng−Robinson equation of state, together with the van der Waals quadratic mixing rule (two adjustable parameters: $k_{ij}$ and $l_{ij}$), was used to model the experimental data. However, at the temperatures where liquid−liquid−vapor was observed, only the experimental data of liquid−liquid equilibrium were used to estimate the model parameters.

The phase stability analysis was performed using a procedure that is a modification of the one described by Xu[10] and Xu et al.[11] The analysis used two different methodologies: (i) minimization of the tangent plane distance of the Helmholtz free energy[12,13] was done using the interval Newton/generalized bisection technique (INBIS[14]/INTLIB[15]); (ii) minimization of the tangent plane distance of the Gibbs free[16] energy was done using the simulated annealing routine.[17] The modified procedure was validated using the examples of Hua et al.[18] and Stradi et al.[19] The results for the phase stability problem were used as the initialization for the flash calculation. In both cases, the model for multiphase equilibrium of the system $CO_2$ + clove oil used the Peng−Robinson equation of state with the van der Waals mixing rule.

## 3. Results and Discussion

Table 1 shows the mass fractions, molar fractions, and thermophysical properties of carbon dioxide and the substances that form clove oil. The systematic names and the CAS nos. of the substances were also indicated to avoid the usual mistakes that happen when the common name is used to indicate terpenoids. Despite the structural differences among these substances, their estimated ther-

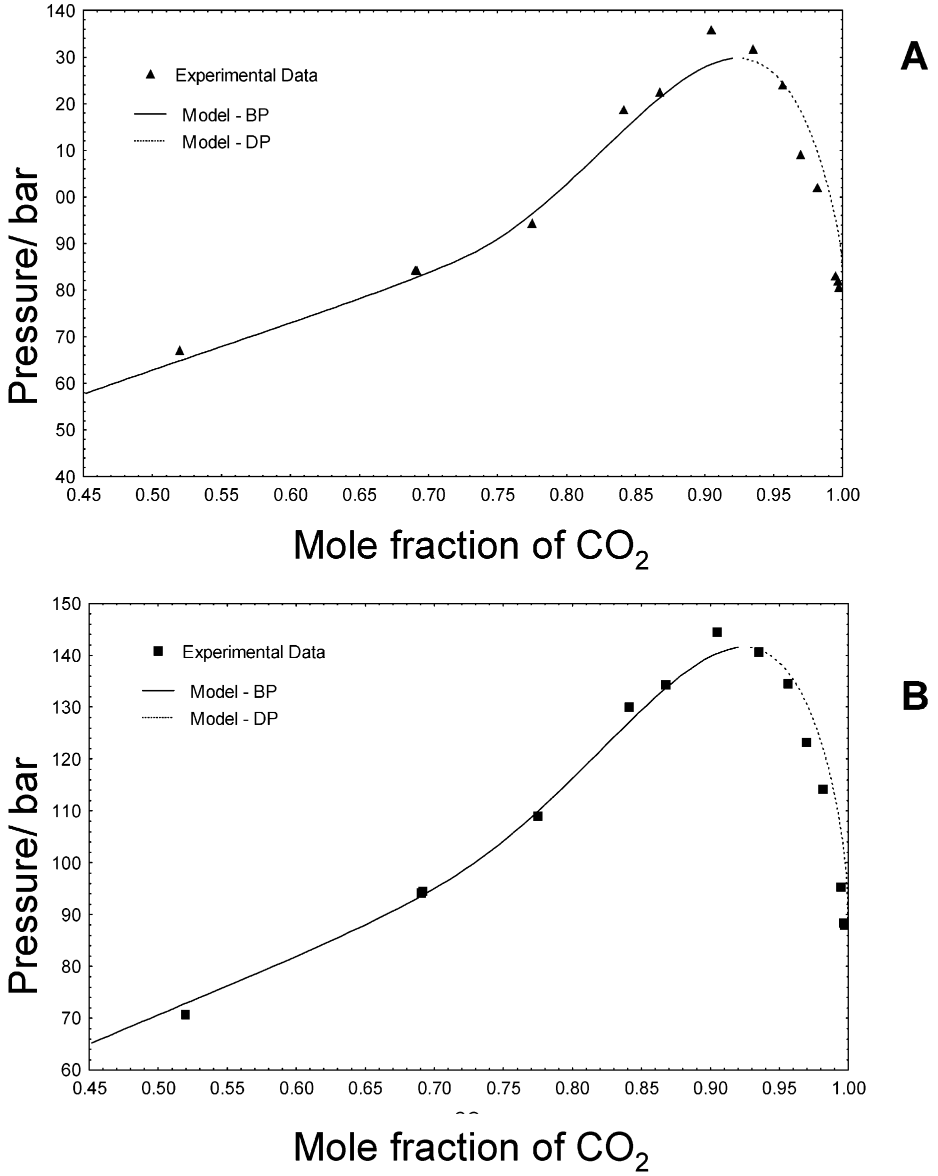

**Figure 1.** *P*−*x*−*y* plot for $CO_2$−clove oil at 313.2 K (A) and 318.2 K (B) (BP = bubble point; DP = dew point).

**Table 2: Bubble Point and Dew Pressures of the System $CO_2$ + Clove Oil at Specified Temperatures**[a]

| molar fraction of $CO_2$/% | pressure/bar at the following values of *T*/K | | | | |
|---|---|---|---|---|---|
| | 303.2 | 308.2 | 313.2 | 318.2 | 328.2 |
| 51.97 | 58.32* | 68.22* | 67.14* | 70.76* | 80.680* |
| 69.03 | 66.48* | 73.60* | 84.32* | 94.17* | 112.46* |
| 69.16 | 65.74* | 74.72* | 84.28* | 94.45* | 110.90* |
| 77.51 | $72.51^{LL}$<br>$69.46^{LLV}$ | $79.94^{LL}$<br>$75.03^{LLV}$ | 94.39* | 108.97* | 131.73* |
| 84.14 | $93.18^{LL}$<br>$71.84^{LLV}$ | $107.25^{LL}$<br>$75.96^{LLV}$ | 118.71* | 130.06* | 154.93* |
| 86.76 | $100.45^{LL}$<br>$69.58^{LLV}$ | $109.13^{LL}$<br>$74.19^{LLV}$ | 122.52* | 134.28* | 158.30* |
| 90.49 | $111.89^{LL}$<br>$70.70^{LLV}$ | $123.21^{LL}$<br>$75.06^{LLV}$ | 135.86* | 144.52* | 167.70* |
| 93.52 | $108.06^{LL}$<br>$69.82^{LLV}$ | $122.50^{LL}$<br>$76.01^{LLV}$ | 131.71 | 140.65 | 161.80 |
| 95.64 | $99.47^{LL}$<br>$69.42^{LLV}$ | $109.13^{LL}$<br>$75.90^{LLV}$ | 124.04 | 134.51 | 158.29 |
| 96.96 | $91.02^{LL}$<br>$71.76^{LLV}$ | $98.63^{LL}$<br>$75.77^{LLV}$ | 109.12 | 123.17 | 150.47 |
| 98.16 | $80.69^{LL}$<br>$70.93^{LLV}$ | $88.56^{LL}$<br>$74.94^{LLV}$ | 102.01 | 114.22 | 137.00 |
| 99.47 | 70.40 | 78.21 | 83.080 | 95.33 | 114.01 |
| 99.66 | 66.29 | 71.62 | 81.970 | 88.36 | |
| 99.72 | 72.04 | 76.12 | 80.640 | 87.97 | 100.10 |

[a] An * indicates a bubble point; all others points are dew points.

mophysical properties are quite similar. The thermophysical properties of the pseudopure component denoted by “clove oil” were calculated using the Kay’s rule.[9]

Table 2 shows the bubble and dew points measured for the system $CO_2$ + clove oil. The system exhibited two liquid phases in equilibrium with a vapor phase at 303.2 and 308.2 K, while at 313.2, 318.2, and 328.2 K only the liquid−vapor transition was visualized.

Table 3 shows the parameters fitted to the Peng−Robinson equation of state. The comparisons between experimental and fitted equilibria are shown in Figures 1 and 2. Several difficulties were encountered when standard tools were used to model the phase behavior of the system. The major problems occurred near the three-phase boundary and in the region with retrograde behavior. By using a technique based on interval mathematics, which elimi-

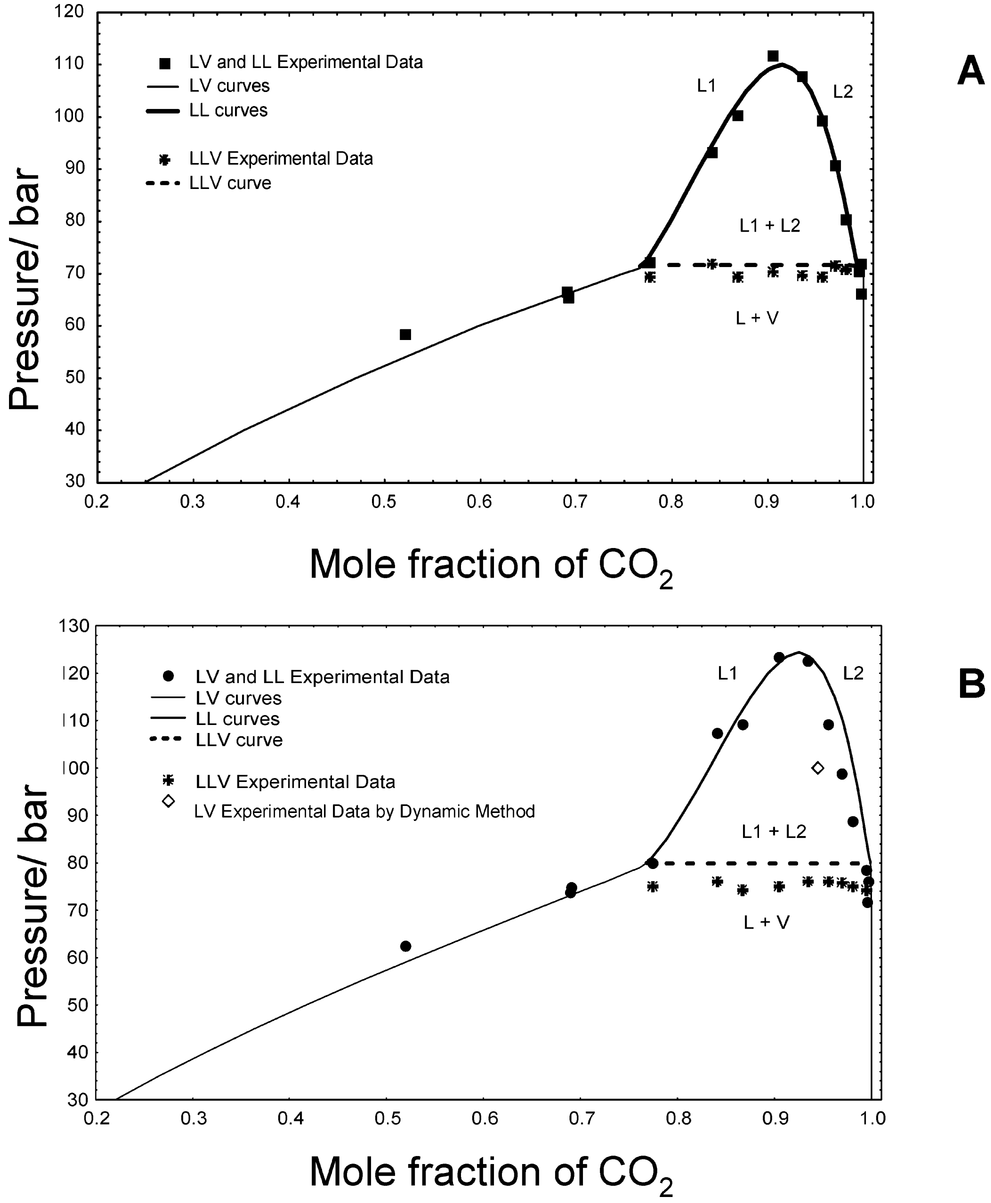

**Figure 2.** $P-x-y$ plot for $CO_2$−clove oil at 303.2 K (A) and 308.2 K (B).

**Table 3: Values of the Fitted Parameters**[a]

| $T$/K | $k_{12}$ | $l_{12}$ | $\Delta P$/bar | NU[b] |
|---|---|---|---|---|
| 303.2 | 0.036 26 | −0.033 41 | 3.51 | 8 |
| 308.2 | 0.033 79 | −0.020 60 | 5.39 | 8 |
| 313.2 | 0.031 12 | −0.038 50 | 4.85 | 8 |
| 318.2 | 0.029 45 | −0.044 11 | 1.69 | 9 |

[a] At 303.2 and 308.2 K, only experimental data of the LLE were used. [b] NU = number of experimental points used in the parameters' fitting.

nates the need for initial guesses, these difficulties were eliminated and correct results were obtained, producing a completely reliable method.

At the temperatures 313.2 K and 318.2 K, only the vapor−liquid transition was visualized, and the phase equilibrium calculations were then done with these model parameters, to compare the model predictions with experimental measurements (Figure 1). At 303.2 K and 308.2 K, the model predicted a three-phase line at 71.3 and 80.3 bar, respectively. There is a region of liquid−liquid above this pressure and a region of vapor−liquid below it (Figure 2). The diagrams for the vapor−liquid envelopes were calculated using the values of the parameters ($k_{12}$, $l_{12}$) fitted to the liquid−liquid equilibria.

Cheng et al.[20] reported equilibrium data for the system eugenol + $CO_2$ at the temperatures 308.2, 318.2, and 328.2 K. The values of pressure obtained at 328.2 K and $CO_2$ mole fraction ($x_{CO_2}$) in the range 0.13−0.71 varied from 16 to 125 bar. These values are slightly higher than the values measured for the system $CO_2$ + clove oil as shown in Table 2. Rodrigues et al.[21] reported solubility values measured for the system clove buds + $CO_2$. Therefore, these authors have measured the solubility of clove oil in $CO_2$ in the presence of the cellulosic structure, thus, resulting in a very simplified view of a ternary system formed by the cellulosic structure + clove oil + $CO_2$. The value measured at 308.2 K is indicated in Figure 2 as the open symbol. Considering the differences between the system studied here (binary system) and that of Rodrigues et al.[21] (a ternary system in which $CO_2$ interacts with clove oil but not with the cellulosic structure), the two values are very close.

## 4. Conclusions

The system $CO_2$ + clove oil exhibited transitions of the type liquid−vapor at 313.2, 318.5, and 328.2 K, liquid−

liquid at 303.2 and 308.2 K, and liquid−liquid−vapor at 303.2 and 308.2 K. The experimental data were very well modeled with the Peng−Robinson equation of state and the van der Waals quadratic mixing rule for each type of phase transition. The interval analysis and the simulated annealing proved to be useful tools for the calculation of the phase equilibrium, particularly for mixtures with higher nonideality, such as clove oil + $CO_2$.

## Acknowledgment

This work is part of a cooperation network denoted SuperNat.

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Received for review September 30, 2003. Accepted December 1, 2003. Financial help was provided by CAPES/PROCAD (0081/01-9) and FAPESP (1999/01962-1). M.L.C. and A.T.S. thank CAPES and FAPESP (00/02566-1) for the Ph.D. assistantships, respectively.

JE034190F