

FLUID PHASE BEHAVIOR OF SYSTEMS OF CARBON DIOXIDE AND CERTAIN ESSENTIAL OILS

E.M. Bittencourt Dutra de Sousa¹, V.A. Toussaint³,
O. Chiavone-Filho¹, Meireles, M.A.A.² and C.J. Peters^{3,*}

¹Universidade Federal do Rio Grande do Norte-UFRN, Departamento de Engenharia Quimica
Natal/RN-CEP 59072-970, Brasil

²Universidade Estadual de Campinas-UNICAMP, Faculdade de Engenharia de Alimentos
FEA, LASEFI, 13083-970, Campinas-SP, Brasil

³Laboratory of Physical Chemistry and Molecular Thermodynamics
Faculty of Applied Sciences, Delft University of Technology
Julianalaan 136, 2628 BL Delft, The Netherlands

Phone: +31-15-2782660; Fax: +31-15-2788047; E-mail: Cor.Peters@tnw.tudelft.nl

From numerous studies on binary and ternary mixtures with carbon dioxide as the near-critical component, it became apparent that the fluid phase behavior of these systems can be quite complex. For instance, with many solutes carbon dioxide shows a second liquid phase. In processing essential oils, we are dealing with complex mixtures of organic constituents of which many of them may show fluid multiphase behavior with carbon dioxide, of course, depending on temperature, pressure and composition of the system. Therefore, it has to be expected that also essential oils may show such a complex multiphase behavior. This study reports on phase equilibrium experiments of two essential oils, namely eucalyptus and alecrim oil in the presence of carbon dioxide as the near-critical solvent. It has been established that both oils show liquid-liquid immiscibility with carbon dioxide with all characteristics of type-III fluid phase behavior in the classification of Van Konynenburg and Scott. Although both essential oils have a completely different molecular composition, it was found that only minor differences occurred in their fluid phase behavior.

INTRODUCTION

Essential oils comprise a group of natural substances that are complex mixtures of molecules mainly composed of carbon, hydrogen and oxygen. Especially, the presence of oxygen in the molecules lead to functional groups like, for instance, -OR, -OH, =O, -COOH, etc., causing strong interactions (polar, hydrogen bonding, etc.) between the various species in the oils. Consequently, it is obvious that the phase behavior of these oils in the presence carbon dioxide, the most frequently used near-critical solvent, may be complex accordingly, be it, of course, depending on the specific composition of the oil, temperature and pressure. Compared to mineral oils and petroleum fluids, there are similarities, but also significant differences, for instance:

Mineral oils and petroleum fluids:

- Almost only hydrocarbons are present;
- Chemical structure and nature of the components are paraffinic, isoparaffinic, naphthenic and aromatic;
- Broad molecular weight distribution;

- Moderate intermolecular interactions.

Essential oils:

- Besides hydrocarbons also molecules containing oxygen are present;
- Chemical structure and nature of the components show very large differences;
- Molecular weight range of the components is in general limited;
- Because of the presence of all kind of functional groups, strong intermolecular interactions occur.

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 e.g. perturbed-hard-chain theory. In all, it turned out that the description or 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 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.

Table 1: Composition of eucalyptus oil obtained from CO₂- extraction.

Substance	(% area)	Substance	(% area)
para – cymene	1.03	1 - tetradecene	0.26
limonene	1.43	a – gurjunene	1.72
1.8 cineole	11.03	trans - cariophylene	1.89
? – terpinene	1.71	β - gurjunene	0.83
a – fenchol	0.18	aromadendrene	21.07
trans - pinocarveol	0.31	allo - aromadendrene	5.05
4 - terpineol	4.43	? – gurjunene	0.33
para - cimen-9-ol	0.58	β - selinene	0.64
cis - pinocarveol	0.81	a – selinene	1.76
? – terpineol	2.50	? – cadinene	0.46
para -cimen-7-ol	0.34	d - cadinene	0.36
carvacrol	0.46	globulol	13.83
eugenol	1.45	sesquiterpenes (not identified)	25.29
isodene	0.25		

From many phase equilibrium studies of model systems (see, for example, Peters et al. 1999 and Gauter et al., 2000) it became apparent that phenomena like liquid-liquid two-phase splits, immiscibility windows, holes, etc. may occur easily.

The development of adequate thermodynamic models for systems comprising essential oils need as input systematic studies on the phase behavior of the oils with the extracting solvent, in general, carbon dioxide. This study focuses on the fluid phase behavior of both eucalyptus and alecrim oil with carbon dioxide as the near-critical solvent. In a recent study, Bittencourt Dutra de Sousa (2001) provided CO₂-extracted eucalyptus and alecrim oil, along with a compositional analysis of the oils. Tables 1 and 2, respectively, summarize the composition of the two oils. From both tables it becomes apparent that the two oils consist of completely different constituents. Another observation that can be made from both tables is that at highest four components in the multi-component mixture are dominantly present in the studied essential oils extracted with near critical CO₂ (Bittencourt Dutra de Sousa et al., 2002).

Table 2. Composition of alecrim oil obtained from CO₂-extraction.

Substance	(% area)	Substance	(% area)
a - pinene	0.17	Thymol	48.32
1-octen-3-ol	0.37	Carvacrol	6.90
Myrcene	0.32	Eugenol	0.49
a - terpinene	0.12	a - copaene	0.26
para-cymene	1.38	trans -	13.77
1,8 cineole	8.62	caryophyllene	
(E) - β - ocimene	0.5	aromadendrene	1.81
? ? terpinene	0.58	a - humulene	0.65
trans - myroxide	1.32	? ? muurolene	0.26
umbellulone	0.22	a - selinene	1.72
4-terpineol	1.34	d - cadinene	0.59
a - terpineol	2.27	caryophyllene oxide	1.88
thymol, methyl ether	1.34	Not identified	4.8

CLASSIFICATION OF FLUID PHASE BEHAVIOR

Van Konynenburg and Scott (1980) introduced a classification of six types of binary fluid phase behavior encountered experimentally. With an exception of the closed loop immiscibility (type-VI fluid phase behavior) all types could be generated from the simple van der Waals equation of state.

Figure 1 shows the six types of fluid phase behavior as originally introduced by Van Konynenburg and Scott (1980). Type-I (Figure 1a) has a continuous critical locus between both critical points of the pure components. Figure 1b represents type-II fluid phase behavior. This type is characterized by the presence of a three-phase equilibrium l_1l_2g (dashed line) ending at higher temperature in a critical endpoint of the nature $l_1 = l_2 + g$, i.e., the two liquid phases are critical in the presence of a gaseous phase. Type-III fluid phase behavior, shown in Figure 1c, also has a three-phase equilibrium l_1l_2g (dashed line). However, its critical endpoint has the nature $l_1 = g + l_2$, i.e., the liquid phase l_1 and the gaseous phase g are critical in the presence of the liquid phase l_2 . Figure 1c also shows that one branch of the critical locus ($l_1 = g$) connects the critical point of pure component A to the critical endpoint of the three-phase

equilibrium l_1l_2g . A second branch of the critical locus ($l_1 = g$) originates from the critical point of pure component B and extends to higher pressures meanwhile gradually changing its nature from $l = g$ into $l_1 = l_2$. The latter critical locus in type-III systems may have a maximum and minimum in pressure, as shown in Figure 1c. At least three additional shapes of this critical locus are known, for example, see Rowlinson and Swinton (1982). The type of fluid phase behavior shown in Figure 1d (type-IV) has two separate three-phase regions l_1l_2g (dashed lines). The critical endpoint of the low-temperature three-phase region has the nature $l_1 = l_2 + g$.

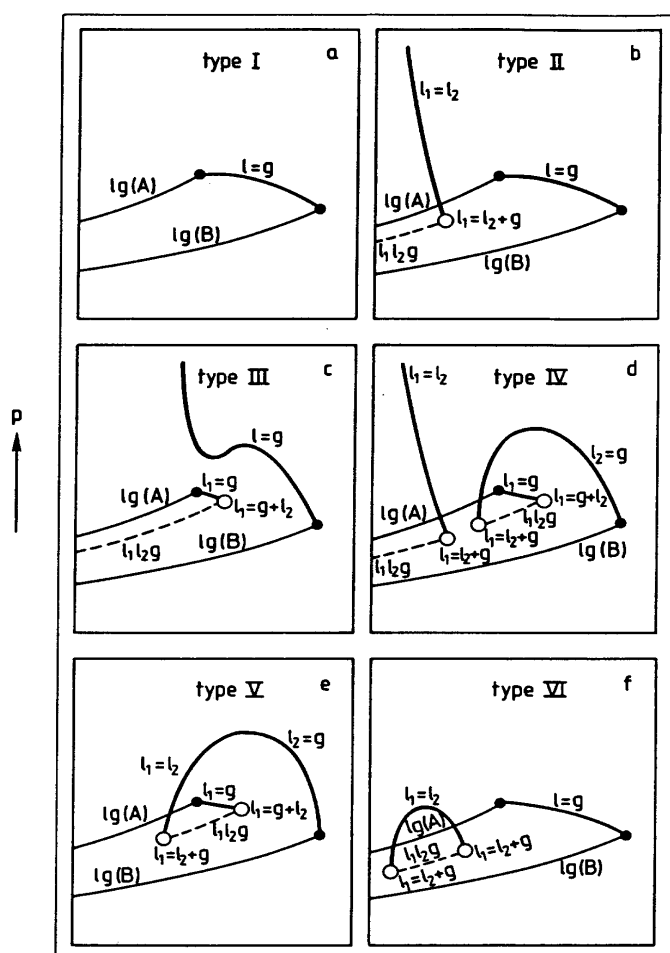


Figure 1: The classification of fluid phase behavior (Van Konynenburg and Scott, 1980).

The critical endpoint at the lowest temperature of the high-temperature three-phase equilibrium l_1l_2g also has the nature $l_1 = l_2 + g$, whereas the critical endpoint of this three-phase equilibrium at higher temperature has the nature $l_1 = g + l_2$. Figure 1d also shows the connectivity of the three critical loci to the critical points of the pure components and to the three critical endpoints. Removal in Figure 1d (type-IV fluid phase behavior) of the low temperature three-phase region l_1l_2g and of the related critical locus $l_1 = l_2$, results in type-V fluid phase behavior (Figure 1e). Both critical endpoints of type-V have the same nature as those of the high-temperature three-phase equilibrium as shown in Figure 1d. Also, the critical loci have schematically the same connectivity to the various characteristic points in this figure.

Finally, Figure 1f represents type-VI fluid phase behavior. It is the so-called closed-loop immiscibility. This type of fluid phase behavior is characterized by a three-phase region l_1l_2g , which is bounded by two critical endpoints of the same nature ($l_1 = l_2 + g$). Between both critical endpoints a continuous critical locus $l_1 = l_2$ is present.

However, from experiments it became apparent that in most cases this critical locus is not continuous but consists of two branches with a tube-like shape and a narrowing at somewhat higher pressures. The critical points of both pure components are connected by a continuous critical locus $l_1 = g$.

EXPERIMENTAL

For the measurements a Cailletet apparatus was used. In principle, this apparatus covers a temperature and pressure range of $250 < T/K < 450$ and $0.5 < p/\text{MPa} < 15.0$, respectively. Because this facility operates according to the synthetic method, samples of

known composition have to be dosed into the equilibrium cell. The accuracy of the Cailletet facility is better than 0.02 K and 0.002 MPa. The phase transitions are observed visually using a microscope. For details on the experimental facility and the experimental procedures, one is referred to Raeissi et al. (2001). Carbon dioxide (99.995 vol%) was supplied by Hoek-Loos and was used without further purification. Both essential oils were provided by the University Federal of Rio Grande do Norte-UFRN, Chemical Engineering Department, Natal, Brazil, using a near critical CO₂ extraction procedure (Bittencourt Dutra de Sousa et al., 2002).

RESULTS, DISCUSSION AND CONCLUSIONS

Because both oils studied in this work are viscous, especially at lower temperatures, it was decided to perform measurements at temperatures not lower than approximately 275 K. Viscosity of the sample may cause large equilibration times and enhanced inaccuracy of the data as well.

Figure 2 represents for five isopleths experimentally determined bubble-points for the system CO₂ + eucalyptus oil. As can be seen, with increasing weight fraction of CO₂ the various isopleths are shifted to higher pressure. For the locus located at the highest pressures (weight fraction of 0.562 in CO₂), the following phase transition was measured: $l_1 + l_2 + g \rightarrow l_1 + l_2$. This locus comprises a part of the three-phase region $l_1 l_2 g$. Also, it turned out to be possible to determine for this particular isopleth a critical endpoint of type $l_1 = g + l_2$, i.e., the two light phases (vapor and light liquid phase) are critical in the presence of the heavy liquid phase.

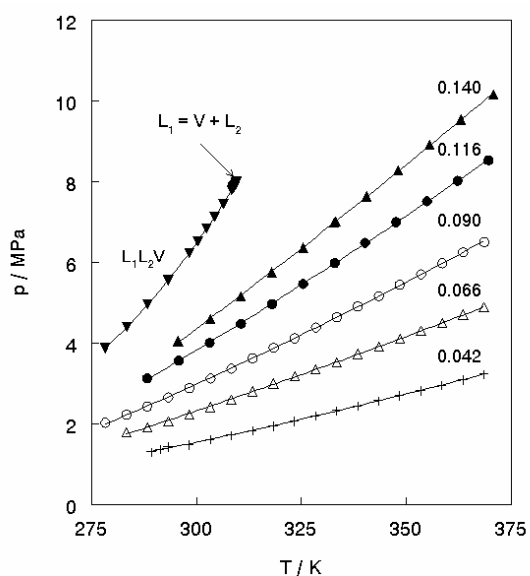


Figure 2: Experimentally determined isopleths for the system CO₂ + eucalyptus oil. Symbols are experimental data and full curves are best fits to the experimental data.

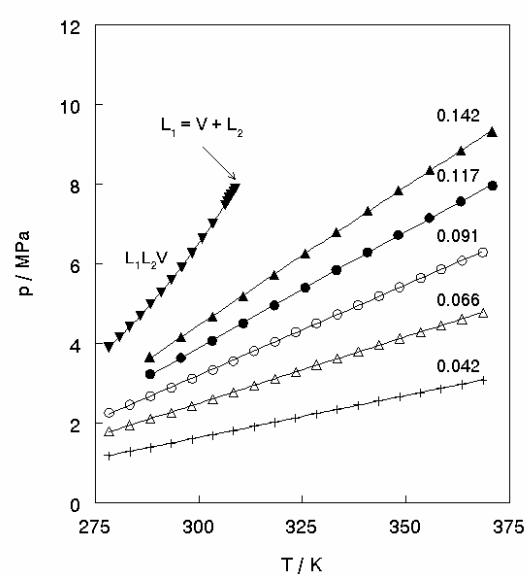


Figure 3: Experimentally determined isopleths for the system CO₂ + alecrim oil. Symbols are experimental data and full curves are best fits to the experimental data.

For the system CO₂ + alecrim oil, almost completely similar experimental results were obtained. Again for five isopleths bubble-points were measured along with an isopleth at higher CO₂ weight fraction (also 0.562 weight fraction in CO₂). For the latter isopleth also phase transitions of the kind $l_1 + l_2 + g \rightarrow l_1 + l_2$ were determined, i.e., this system also shows three-phase behavior $l_1 l_2 g$. Similarly, also a critical endpoint of type $l_1 = g + l_2$ was

established. For the system CO₂ + alecrim oil, all experimental results are depicted in Figure 3. Although both oils have completely different compositions, their fluid phase behavior with CO₂ is almost similar. This is clearly shown in Figure 4, where the fluid phase behavior of both systems is compared. It is shown that all isopleths of the same overall composition almost coincide.

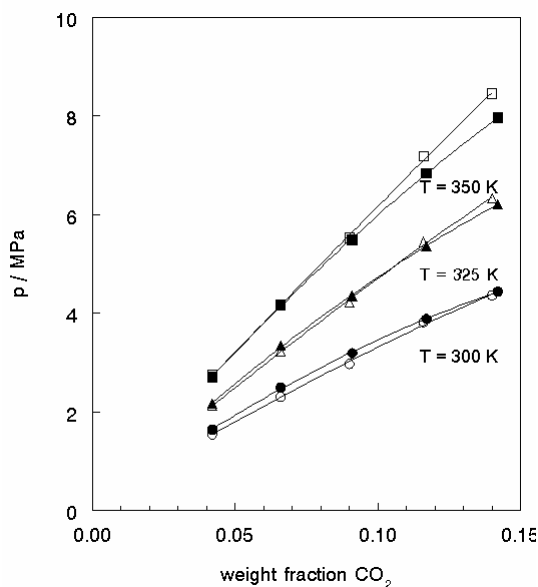


Figure 4: Comparison of the fluid phase behavior of the two CO₂-systems with eucalyptus and alecrim oil. Symbols are experimental data and full curves are best fits to the experimental data.

At higher weight fractions of CO₂, both systems show a three-phase region l_1l_2g in which both critical endpoints for the same overall composition are located at almost the same temperature and pressure. From the experimental results obtained, it becomes apparent that the fluid phase behavior of both critical endpoints is of type $l_1 = g + l_2$.

From the classification of Van Konynenburg and Scott (see Fig. 1) it is known that only in the systems belonging to type-III, -IV or -V, such a behavior is possible. Since in literature no CO₂-systems showing type-V fluid phase are known, this type for the investigated systems in this work should be excluded.

As pointed already, since measurements could not be extended to lower temperatures due to the viscosity of the systems, additional critical endpoints at lower temperatures have not been found. The latter is a prerequisite for type-IV fluid phase behavior. However, taking into account that type-IV is rarely met at the conditions of this study, it is to be expected that both systems will show type-III phase behavior.

In summary it can be concluded that from this study it became apparent that, although both eucalyptus and alecrim oil differ significantly in composition, leading to completely different intermolecular interactions in both fluids, it does not seem to affect the fluid phase behavior with CO₂, which most likely will belong to type-III, although type-IV should not be excluded.

REFERENCES:

- SOUSA, E.M.B.D., Ph.D. thesis, **2001**, Federal University of Rio Grande do Norte – UFRN, Natal, Brasil.
- SOUSA, E.M.B.D., CHIAVONE-FILHO, O., MORENO, M.T., SILVA, D.N., MARQUES, M.O.M. AND MEIRELES, M.A.A., Braz. Journal of Chem. Eng., Vol. 19, **2002**, p. 229.
- GAUTER, K., PETERS, C.J., SCHEIDGEN, A.L. AND SCHNEIDER, G.M., Fluid Phase Equilibria, Vol. 171, **2000**, p. 127.
- PETERS, C.J. AND GAUTER, K., Chemical Reviews, Vol. 99, **1999**, p. 419.
- ROWLINSON, J.S., SWINTON, F.L., Liquids and Liquid Mixtures, Butterworths Monographs in Chemistry, **1982**, London.
- RAEISSI, S., PETERS, C.J., Journal of Supercritical Fluids, Vol 20, **2001**, p. 221.
- VAN KONYNENBURG, P.H.; SCOTT, R.L., Phil. Trans. of the Royal Society (London), Vol. 298, **1980**, p. 495.