

## Liquid–vapor and liquid–liquid–vapor equilibria in the ternary system ethane + limonene + linalool

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Received 27 June 2004; accepted 25 August 2004

### Abstract

To investigate the potential of replacing supercritical carbon dioxide by supercritical ethane in the deterpenation of citrus essential oils, the phase behavior of the ternary system ethane + limonene + linalool was determined experimentally. The measurements were made with a synthetic method in which at any desired temperature, the pressure was varied for a mixture of fixed overall concentration, until a phase change was observed visually. The molar concentration of ethane was fixed at a constant value of 98% in all the experiments, leaving the ratios of limonene to linalool as variables ranging from 0 to 1. Equilibria between the vapor and liquid phases were measured within temperature and pressure ranges of 293–363 K and 3–9 MPa, respectively. It was observed that limonene had higher solubility than linalool in supercritical ethane, with the difference in solubility increasing with temperature. In contrast to the ternary system with carbon dioxide, the ternary system with ethane, limonene and linalool exhibited liquid–liquid phase splitting, resulting in the presence of a three-phase liquid–liquid–vapor region. This occurred in the linalool-rich side of the phase diagram. Experimental values of the upper and lower critical endpoints of the three-phase region, in addition to normal critical points of two-phase equilibria are presented. From the experimental results, it can be concluded that the system ethane + linalool + limonene shows type-V fluid phase behavior according to the classification of van Konynenburg and Scott.

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**Keywords:** Citrus oil; Orange peel oil; Essential oil; Solubility; Phase behavior; Liquid–liquid immiscibility; Bubble point; Dew point; Critical point; Supercritical; High pressure

### 1. Introduction

During the past two decades, there has been an intensive interest in the application of supercritical fluids to a great variety of chemical processes. Among the available literature in the supercritical field, supercritical extraction of essential oils is one of the most widely discussed applications. In this respect, Reverchon [1] presented a comprehensive and critical overview of the analytical, processing and modelling aspects of essential oil supercritical extraction. One of the most, if not the most, industrially significant essential oils, are the citrus peel oils. The citrus oils are used in a wide variety of applications in major industries such as flavor, food,

cosmetic, pharmaceutical, and chemical industries, but the major consumption by far is in the flavor industry.

Citrus oils are obtained from the small balloon-shaped glands or vesicles located in the flavedo or colored portion of the citrus peel. The quality of these oils depend on factors such as soil, climate, extraction method of the oil, weather, maturity and, variety of the fruit [2].

Citrus oils are complex mixtures of over 200 chemical compounds, of which more than one hundred have been identified [2]. These include high-volatile components such as terpenes, sesquiterpenes and oxygenated compounds, and non-volatile compounds, such as pigments and waxes. The terpene fraction can constitute from 50% up to more than 95% of the oil. However, this fraction gives little contribution to the flavor and fragrance of the oil. Since terpenes are mostly unsaturated compounds, they are easily decomposed by heat, light, and oxygen to unpleasant off-flavors and aro-

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mas. Therefore, it is common industrial practice to remove some of the terpenes and, as a consequence, to concentrate the oxygenated compounds which are mainly responsible for the characteristic citrus flavor and fragrance. This procedure is known as “deterpenation” or “folding” and is carried out to improve oil stability, increase oil solubility, and to reduce storage and transportation costs [3].

Deterpenation is currently done by distillation, solvent extraction, or chromatographic separation. The main drawbacks of these conventional processes are low yields, formation of thermally degraded undesirable by-products, and/or solvent contamination of the products [3]. The necessity of developing alternative refining processes has given rise to extensive research in the field of supercritical CO<sub>2</sub> extraction (for example [3–25]). Carbon dioxide would seem to be the supercritical fluid of choice as it is cheap, readily available, non-toxic, and non-flammable. It is a clean solvent that leaves no residue in the product. Its low critical temperature allows operation at temperatures lower than thermal degradation limits for many thermally labile natural products. However, since all the components of essential oils are very soluble in dense carbon dioxide [6,11], it is not possible to obtain good deterpenation of citrus oils using supercritical CO<sub>2</sub>. In other words, it is difficult to optimize the operating conditions in terms of both the extraction yield and separation selectivity [4]. The current study is part of a general research [26–28] attempting to increase the efficiency of supercritical fluid deterpenation of citrus oils by replacing CO<sub>2</sub> with a better supercritical fluid. Earlier work investigated the phase behavior of binary systems of ethane and major citrus oil constituents. In the binary system of ethane + limonene [26], no liquid–liquid phase split was observed and hence, the fluid phase behavior is classified as type-I, according to Scott and Van Konyenburg. The binary system ethane + linalool [27] on the other hand, most likely belongs to type-V phase behavior as a region of liquid–liquid immiscibility was experimentally observed within a limited concentration range. This work presents experimental phase behavior data for the ternary system ethane + limonene + linalool within a temperature and pressure range of 293–363 K and 3–9 MPa, respectively.

## 2. Choice of solutes and solvent

In essential oil research, it is very common to represent the very complex natural mixtures by representative components. In this study, the oil is assumed to be a mixture of limonene (an unsaturated hydrocarbon monoterpene of 10 carbons) to represent the terpene fraction, and linalool (an oxygenated monoterpene of 10 carbons) as a representative of the aroma fraction. The choice of components is based on the following considerations:

- Limonene is the major constituent (more than 95) of the oil and it is also the undesired terpene, which must be separated from the aroma components.

- Limonene and linalool are the most difficult to separate. If separation of linalool is achieved, the whole flavor fraction is obtained.

In the quest to find a replacement for CO<sub>2</sub> as supercritical solvent, preliminary calculations, as explained earlier [26], were carried out on a number of non-toxic and low-critical temperature solvents, and ethane was ultimately selected as the potential solvent for further investigation.

## 3. Experimental

The d-Limonene (purity  $\geq 99\%$ ) from Fluka, linalool (purity  $\geq 97\%$ ) from Fluka, and ethane (99.95 vol%) from Messer Griesheim were used without further purification. Throughout all the experiments, the molar concentration of ethane was kept at an approximately constant value of 98.00%, while the ratio of limonene to linalool was varied from 0 to 1.

The Cailletet apparatus, used for performing the phase behavior experiments, operates according to the synthetic method. At any desired temperature, the pressure is varied for a sample of constant overall composition until a phase change is observed visually. A sample of fixed known composition is confined over mercury in the sealed end of a thick-walled Pyrex glass tube. The open end of the tube is placed in an autoclave and immersed in mercury. Thus, mercury is used for both sealing and transmitting pressure to the sample. Continuous stirring of the sample is facilitated by an enclosed stainless steel ball, of which the movement is activated by reciprocating magnets. The autoclave is connected to a hydraulic oil system, generating the pressure by means of a screw type hand pump. A dead weight pressure gauge is used to measure the pressure inside the autoclave with an accuracy of 0.03% of the reading. The temperature of the sample is kept constant by circulating thermostat liquid through a glass thermostat jacket surrounding the glass tube. The thermostat bath is capable to maintain the thermostat liquid at the desired temperature with a constancy better than  $\pm 0.01$  K. A platinum resistance thermometer, located close to the sample-containing part of the Cailletet tube, records the temperature of the thermostat liquid with a maximum error of 0.02 K. Further details of the apparatus and experimental procedure may be found elsewhere [29,30].

## 4. Results and discussions

Table 1 summarizes the experimentally measured temperatures and pressures for the different types of liquid–vapor phase transitions involved in the ternary system ethane + limonene + linalool at 15 selected overall compositions. Fig. 1 shows these results graphically. The bubble point curves of all the compositions more or less overlap one another. This is expected since bubble points are mostly influenced by the light component, which is kept at an ap-

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