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EQUILIBRIUM DISTRIBUTIONS OF KEY COMPONENTS OF ORIGANUM OIL IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Equilibration-time, temperature and solvent density effects on relative distribution coefficients of eight key components of origanum oil (essential oil of *origanum vulgare*) in supercritical CO_2 are investigated at 95 atm. Monoterpene-hydrocarbons fraction of the origanum oil exhibit similar equilibration-time, temperature and solvent-density dependence. The degree to which the key compounds are affected by the equilibration-time, temperature and solvent density are correlated with their concentration in the original origanum oil charged to the equilibrium cell. Decrease in solvent density (solvent power) with increasing temperature causes the relative equilibrium distribution coefficients of the monoterpene hydrocarbons to decrease. Temperature dependence of selectivity of supercritical carbon dioxide to monoterpene hydrocarbons may be capitalized on to increase quality of essential-oil extracts in supercritical deterpenation operations.

Keywords: *solubility of origanum oil in supercritical CO_2, deterpenation, solvent power*

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INTRODUCTION

Essential oils are the volatile oils derived from plants. They are mixtures of organic compounds which carry the essential odor and flavor of the parent plant. Essential oils are important raw materials in food, pharmaceutical, cosmetics and other related industries. Therefore, extraction of essential oils from plants, isolation and concentration of their valuable compounds/fractions are of industrial importance.

Essential oils are separated from the cellular structure of various parts of plants via a number of conventional methods. Among these methods are the hydro-/steam-distillation, expression, enfleurage, adsorption, and liquid-solvent extraction [Memory, 1968]. These conventional separation techniques, as well as ensuing operations performed on raw essential oils for the purpose of isolation and concentration of desired compounds/fractions, have some important disadvantages (e.g., high operating temperatures and/or the use of possibly toxic liquid solvents) which impair product quality.

As an attractive alternative to the conventional techniques, supercritical-fluid-aided extraction of essential oils from plants as well as fractionation of extracted oils into desired products have received great interest [Stahl et al., 1987]. Advantageous properties of supercritical-fluids (particularly those of supercritical CO_2) which make them favorable solvents especially for essential-oil applications are well known [Stahl et al., 1987; McHugh and Krukonis, 1986; Brogle, 1982]. Supercritical CO_2 with its low critical temperature (31 ^oC) and moderate critical pressure (73 atm) is an exceptional non-toxic solvent which permits extraction and fractionation operations on gentle essential oils to be carried out at relatively mild conditions.

Experimental results prove the technical feasibility of supercritical-fluid-aided extraction of essential oils from plants and fractionation of essential-oil extracts into desired products (e.g., deterpenation). For the successful design, operation and optimization of such supercritical-fluid-aided operations it is necessary to know the phase behavior of the

essential-oil/supercritical-solvent system over wide range of operating conditions. Solubilities of several characteristic essential-oil compounds (e.g., limonene, citral, caryophyllene, eugenol) in supercritical CO_2 can be found in literature [Stahl et al., 1987; Giocomo, 1989]. Most of the available solubility data, however, are for the binaries of the characteristic essential-oil compounds (e.g., limonene-citral-CO_2 phase-equilibrium). Being complex multicomponent mixtures, phase behavior of essential oils is affected by both solute-solute and solute-solvent interactions. Typical essential-oil extracts obtained from plants contain over 100 components; 10-20 of which constitute the bulk and thus characterize the essential oil. Undoubtedly, solubility of an isolated single essential-oil component in a supercritical fluid would be different than its solubility in the presence of other components of the essential oil due to solute-solute interactions. For the success of future industrial applications of supercritical-fluid technology to essential-oils extraction and processing, knowledge on the relative distributions of at least the key components of essential oils in supercritical solvents is more valuable than the knowledge on the solubility of an isolated single essential-oil compound (selectivity information is as important as the solubility information).

In this work, the effect of temperature on relative distribution of the eight key components of origanum oil (essential oil of *origanum vulgare*) at equilibrium in supercritical CO_2 is investigated. The effects of various physicochemical properties (molecular weight, vapor pressure, polarity) of the key components on their equilibrium distributions in supercritical CO_2 are also discussed.

EXPERIMENTAL

The equilibrium cell used in this study [Platin, 1993] (shown in Figure 1) was a bolted-closure type (six cap-screws) high-pressure vessel manufactured from 316 stainless-steel. The cell had 255.5 cm^3 effective volume (12 cm height, 6 cm ID, 8 cm OD). Sealing of the

cell was provided by an O-ring gasket made of Teflon. The sampling system consisted of a high-pressure on-off valve (V-1) with 1/4" ID and two high-pressure flow-regulating valves (V-2 and V-3) with 1/8" ID. The valves were connected to each other (4.5 cm between V-1 and V-3) and to the body of the equilibrium cell (5 cm between V-1 and the cell body) with stainless-steel tubing of 0.4 cm ID. The pressure of the cell was monitored within ±1 atm accuracy by a pressure gauge connected to the tubing between the cell body and the valve V-1.

At the beginning of each experiment, 15 cm^3 of Origanum Oil (essential oil of *origanum vulgare*) was put into the equilibrium cell. Depending on desired pressure, the cell was then packed with a predetermined amount (90-250 g) of crushed dry-ice (manufactured from 99.9% CO_2). The lid of the cell was closed quickly and the cell was placed on a cradle in a water bath which was being maintained at the preset temperature within ±1 ^oC. Thorough mixing of the cell contents were provided through motor-driven horizontal movements of the cradle in the water. The temperature of the cell contents was continuously measured by a thermocouple within ±0.1 ^oC. As the cell temperature approached to the preset temperature of the water-bath, the cell pressure also increased to the desired level (it took about 15 minutes to reach thermal equilibrium). Mixing of the cell contents was accomplished via the motor-driven horizontal movements of the cradle.

The effect of the extent of equilibration time was studied by varying the total equilibration time (mixing time + settling time) as 10, 20, 60, 120, and 360 min (after the system reached thermal equilibrium in 15 min). In each experiment, 50% of the total equilibration time was allowed for mixing and 50% was allowed for settling so as to eliminate possibility of essential-oil entrainment within the gas phase.

During sampling, the valve V-1 was quickly opened and closed to trap a sample of the gas phase within the space between the valves V-1, V-2 and V-3 without significantly disturbing the equilibrium. After taking the cell out of the water bath, a glass test-tube as a

sample collector was attached to outlet of the valve V-3. The valve V-3 was then opened slowly and thus CO_2 was released out of the space between the valves V-1, V-2 and V-3, and was vented to atmosphere through exit of the sample collector. 1 cm^3 of ethyl alcohol was then injected through the valve V-2 to wash out the essential-oil precipitated within the sampling system during depressurization. In each experiment, about 1.5 cm^3 of sample (ethyl alcohol plus essential oil) was collected in the sample collector. Variations in the results of the experiments performed with two different sample-collector temperatures (15 and 0 ^oC) were not significant and were within the overall experimental error.

At the end of each experiment, analyses of the oil-ethanol mixtures collected in the sample collector were done using 1μl samples on a gas chromatograph (HP5890 Series II; FID detector at 250 ^oC; Carbowax 20M capillary column: 30m × 0.25cm × 0.25μ; carrier gas: N_2 at 1 cm^3/min rate and 1/100 split; temperature programming: 8 min at 70 ^oC, 8 ^oC/min to 130 ^oC, 1 min at 130 ^oC, 3 ^oC/min to 190 ^oC, 1 min at 190 ^oC, 8 ^oC/min to 220 ^oC, 10 min at 220 ^oC). Origanum oil originally charged to the equilibrium cell was also analyzed in the same way at the beginning of each experiment. Chromatograms of the original origanum oil showed about 140 peaks.

The key components of the origanum oil originally charged to the equilibrium cell were identified by a gas chromatograph equipped with mass-selective detector (HP5890 Series II; HP5971 MS detector at 250 ^oC; Carbowax 20M capillary column: 50m × 0.32cm × 0.30μ; carrier gas: He at 1 cm^3/min rate and 1/50 split; temperature programming: 8 min at 70 ^oC, 8 ^oC/min to 130 ^oC, 1 min at 130 ^oC, 3 ^oC/min to 190 ^oC, 1 min at 190 ^oC, 8 ^oC/min to 250 ^oC, 10 min at 250 ^oC). The characteristic 8 components [Guenther, 1967] constituted the bulk of the origanum oil (about 95% of the total area count of about 140 peaks belonged to the selected eight key components).

The details of the set-up, experimental procedure, raw data, chromatographic analyses, and component-identification procedure can be found in [Platin, 1993].

RESULTS AND DISCUSSION

Figure 2 shows the chromatogram of the original origanum oil charged to the equilibrium cell at the beginning of each experiment. Table 1 gives the selected major components of the original origanum oil and their normalized area counts. Components labeled as *a,b,c,e* are *monoterpene hydrocarbons*, component labeled as *d* is a *benzene derivative*, and components labeled as *f,g,h* are *monoterpenic alcohols*. Carvacrol and linalool constitute bulk of this origanum oil.

Practically, it is not possible to determine the actual solubility values of the key components in the CO_2-rich phase since this requires elaborate calibration of the chromatographic analysis. However, distributions of the key components in the CO_2-rich phase relative to those in the original origanum oil charged to the equilibrium cell can be determined. Relative distribution coefficient R_i of a key component is defined as: $R_i = C_i^{eq} / C_i^{o}$; where, C_i^{eq} is the normalized concentration (normalized area count) of key component *i* in the sample taken from the CO_2-rich phase, and C_i^{o} is the normalized concentration (normalized area count) of key component *i* in the original origanum oil charged to the equilibrium cell. Hence, an R_i value greater than unity indicates that dense CO_2 preferentially dissolves key component *i*, or vice versa.

Figure 3 shows the effect of the equilibration time on the relative distributions coefficients of the eight key components of the origanum oil in supercritical CO_2 phase at 55 ^{o}C / 95 atm (0.31 g/cm^3 pure-CO_2 density) conditions. As can be seen, minimum 60 min of total equilibration time (30 min for mixing + 30 min for settling) is necessary for the system to reach thermodynamic equilibrium. All monoterpene hydrocarbons (α-pinene, myrcene, α-terpinene, γ-terpinene) and p-cymene (a benzene derivative) exhibit similar behavior; their relative distributions in supercritical CO_2 are sensitive to the extent of equilibration time. It is interesting to note that all monoterpenic alcohols (carvacrol, α-terpineol, linalool) are readily soluble in supercritical CO_2 even though CO_2 is a non-polar solvent (polarity of the

monoterpene hydrocarbons is much lower than that of monoterpenic alcohols [Stahl et al., 1987]). The degree to which the key compounds are affected by the equilibration time seems to be correlated with their concentration in the original origanum oil charged to the equilibrium cell.

Figure 4 shows the effect of temperature on the relative equilibrium distributions coefficients of the eight key components of the origanum oil in supercritical CO_2 at 95 atm (60 min total equilibration time). Pure-CO_2 densities corresponding to 50, 55, and 60 ^oC are 0.33, 0.31, and 0.26 g/cm^3, respectively. All monoterpene hydrocarbons and p-cymene exhibit similar behavior; relative equilibrium distribution coefficients decrease with increasing temperature. Relative equilibrium distribution coefficients of carvacrol and linalool are not sensitive to temperature. On the other hand, relative equilibrium distribution coefficient of α-terpineol increases with temperature. Among the key components, the monoterpene hydrocarbons have distinctly the highest vapor pressures [Stahl et al., 1987]. It is known that, at relatively low pressures (below critical pressure of the solvent), high vapor pressure of monoterpene hydrocarbons has a dominating effect on their solubility in dense gases; their relative distribution coefficients increase with temperature due to increase in their vapor pressures [Stahl et al., 1987; Platin, 1993, Özer, 1993]. However, as Figure 4 demonstrates, at elevated pressure above the critical pressure of the solvent the dominating effect is not the vapor pressure of the compounds but the density (solvent power) of the supercritical phase. The relative equilibrium distribution coefficients of the monoterpene hydrocarbons and p-cymene decrease with decreasing density (increasing temperature) of the supercritical phase. The degree to which the key compounds are affected by temperature seems to be correlated with their concentration in the original origanum oil charged to the equilibrium cell.

As can be seen from Figure 4, selectivity of supercritical CO_2 to monoterpene hydrocarbons and p-cymene varies significantly with temperature. It is known that the quality of essential-oil products decreases with increasing fraction of the monoterpene hydrocarbons.

These hydrocarbons are unstable substances and their decomposition generates compounds which impair the quality of the essential-oil products [Stahl et al., 1987]. Furthermore, the real aroma of essential oils is not due to monoterpene hydrocarbons. The results of this work show that deterpenation (extraction or fractionation) of origanum oil using supercritical CO_2 is possible at slightly elevated temperatures by capitalizing on the decreasing selectivity of the supercritical solvent to monoterpene hydrocarbons with increasing temperature. The extracts of a deterpenation process (e.g., carried out at 60 ^oC / 95 atm conditions) will be low in monoterpene-hydrocarbons fraction (better product quality).

CONCLUSIONS

Temperature and equilibration-time effects on the relative distribution coefficients of the eight key components of origanum oil (essential oil of *origanum vulgare*) in supercritical CO_2 were investigated at 95 atm. All monoterpene hydrocarbons and p-cymene exhibit similar equilibration-time and temperature dependence. The degree to which the key compounds are affected by the equilibration time and temperature seems to be correlated with their concentration in the original origanum oil charged to the equilibrium cell. Decrease in the relative equilibrium distribution coefficients of the monoterpene hydrocarbons is due to decrease in solvent density (solvent power) with increasing temperature. Decrease in selectivity of supercritical CO_2 to monoterpene hydrocarbons with increasing temperature may be capitalized on to increase quality of essential-oil extracts in supercritical deterpenation operations.

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FIGURE CAPTIONS

1. The Equilibrium Cell and the Sampling System

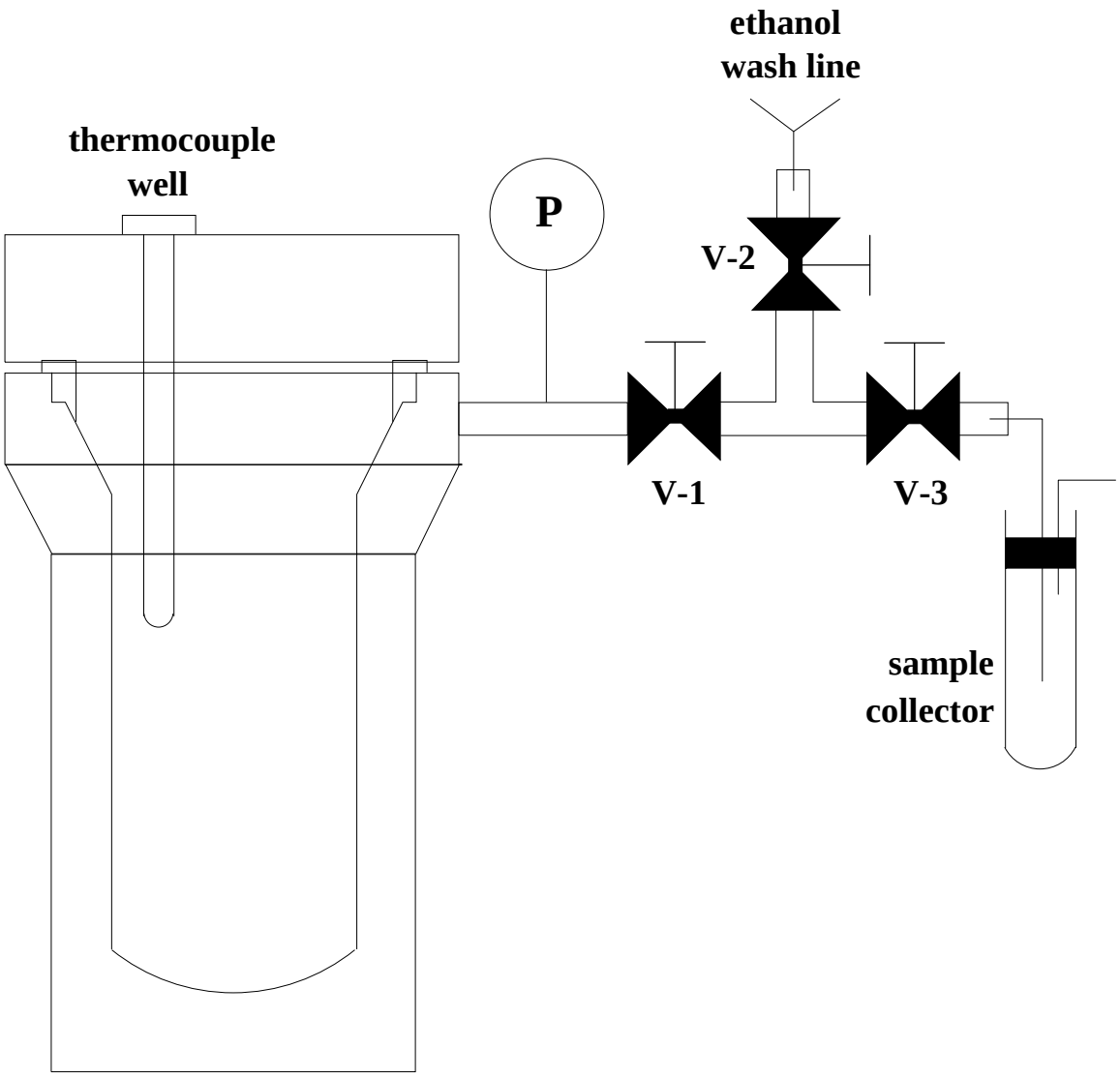
2. Chromatogram of the Original Spearmint Oil Charged to the Equilibrium Cell

3. Effect of the Equilibration Time on the Relative Distribution Coefficients of the Key Components

4. Effect of the Temperature on the Relative Distribution Coefficients of the Key Components

Table 1. Key Components of the Origanum Oil

Peak ID	Component	Retention Time (min)	Molecular Weight	Temperature (°C) at which Vapor Pressure is 100mmHg / 760mmHg	Normalized Area Count (%)
a	α-pinene $C_{10}H_{16}$	3.9	136.24	90/155	1.16
b	myrcene $C_{10}H_{16}$	6.5	136.24	106/171	0.93
c	α-terpinene $C_{10}H_{16}$	7.1	136.24	-/-	0.77
e	γ-terpinene $C_{10}H_{16}$	10.4	136.24	-/-	2.25
d	p-cymene $C_{10}H_{14}$	9.5	134.22	111/177	3.77
f	carvacrol $C_{10}H_{14}O$	18.2	150.22	170/237	67.68
g	α-terpineol $C_{10}H_{18}O$	19.3	154.26	150/218	1.81
h	linanool $C_{10}H_{18}O$	38.2	154.26	134/198	21.62


ethanol
wash line
thermocouple
well
P
V-2
V-1
V-3
sample
collector

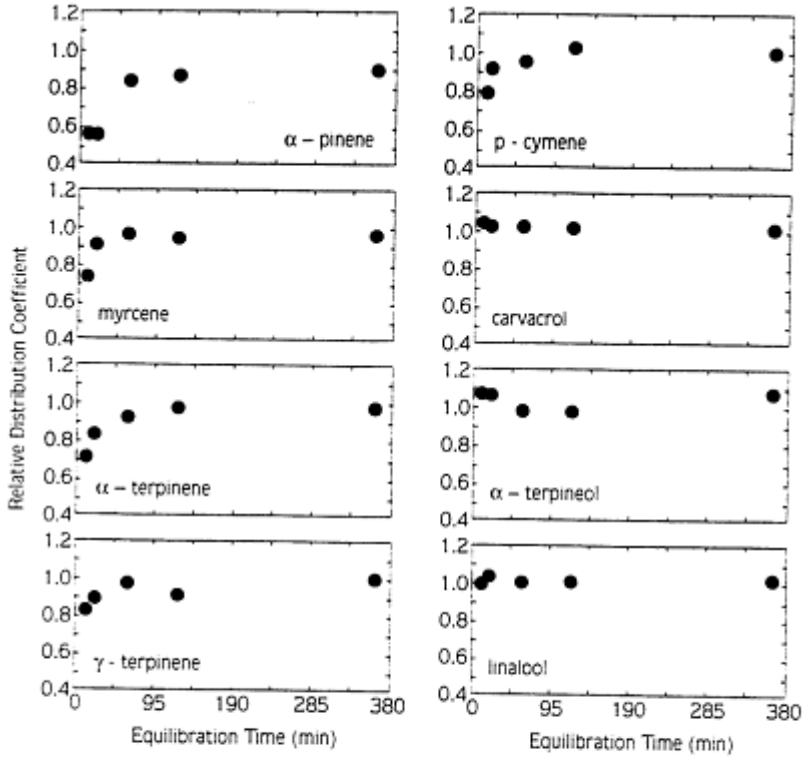


Figure 3.

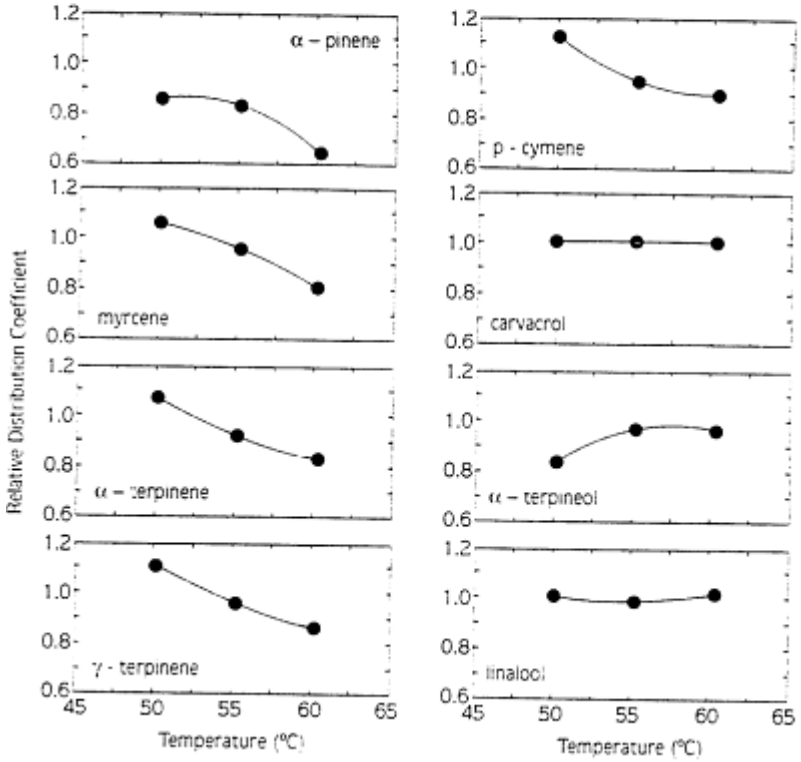


Figure 4.