

## Supercritical Carbon Dioxide Extraction of Lemon Oil

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In 1983-1984, Arizona and California produced annually over 10<sup>6</sup> kg of cold-pressed lemon oil. After being concentrated by distillation or liquid extraction, lemon oil is used as flavoring and/or fragrance agent in beverages and cosmetics. Distillation thermally degrades lemon oil. Extraction with organic solvents only partially reduces thermal degradation (since the solvents must be recovered by distillation) and introduces solvent contamination. Extraction with nonfermentative supercritical carbon dioxide near its critical point (304.3 K, 7.38 MPa, 0.467 g/cm<sup>3</sup>) offers a cheap, nontoxic solvent that does not impart flavors nor thermally degrade the product. It can handle feedstocks with high wax content because these constituents can be solubilized in supercritical carbon dioxide. Supercritical extraction is a hybrid unit operation in the domain between extractive distillation and liquid extraction. Solvent recovery is accomplished by depressurization at ambient temperature.

Processes for supercritical extraction of oils have been described in numerous literature references. Several recent ones are Paulaitis et al. (1983), Ely and Baker (1983), Gerard (1984), Stahl et al. (1984), and Robey and Sunder (1984). The literature lacks detailed data on multicomponent essential oils with supercritical solvents in the proximity of the solvent critical temperature. Accurate prediction of data in this region by equations of state is limited to binary and ternary systems.

The purpose of our research is threefold: evaluate the feasibility of supercritical carbon dioxide extraction of lemon oil near ambient temperature, generate equilibrium data with carbon dioxide and multicomponent essential oil constituents, and evaluate the ability of the Peng-Robinson equation of state to model a reduced multicomponent supercritical system.

### CONCENTRATING LEMON OIL

Staroscik and Wilson (1982) have quantitated various lemon oils and identified 38 compounds. These compounds can be subdivided into three major classifications: terpenes (C<sub>10</sub> hydrocarbons), oxy's (oxygenated C<sub>8</sub>-C<sub>12</sub> hydrocarbons), and sesquiterpenes (C<sub>15</sub> hydrocarbons). A usual goal in concentrating lemon oil is to remove the terpenes and sesquiterpenes from the desired oxy fraction.

When concentrating the lemon oil by multistage fractional distillation under vacuum, column operability coupled with condenser pressure, column pressure drop, reboiler design, and mode of operation (batch or continuous) dictate the degree of thermal exposure. Overhead temperatures increase in the range of 320 to 340 K, reboiler temperatures increase in the range of 330 to 370 K, and exposure times of 15 to 20 hours may be expected during batch distillation. In continuous distillation, exposure times are lower but reboiler temperature may be higher.

In extractive distillation with supercritical solvent, volatility amplification by the solvent rather than vacuum is used to get the components into the extract or vapor phase. Operating temperature can be made lower than in conventional distillation, and the heart-cut product will have been subjected to less thermal degradation. Carbon dioxide has a critical temperature that meets this goal.

In order to make data correlation tractable in supercritical carbon dioxide extraction, it is convenient to represent each major chemical classification by a single compound. Each select compound should have available good vapor pressure data and should be a predominant constituent in its group with regard to structure and concentration. For correlation purposes, we selected limonene, geranial, and  $\beta$ -caryophyllene. Their structures are shown in Figure 1.

Stahl et al. (1984) presented solubility data for limonene and caryophyllene with carbon dioxide; Gerard (1984) included carvone. Temperatures in the range of 279 to 377 K, and pressures in the range of 1.5 to 11 MPa were covered. Robey and Sunder (1984) provided solubility and relative volatility data for carbon dioxide with folded lemon oil and with limonene and citral (geranial/neral) at 323 to 353 K and 9.4 to 10.6 MPa.

Gerard (1984) describes a continuous multistage column process for carbon dioxide extraction (distillation) of essential oils at ambient temperature and 8 MPa, with solvent recovery at 273 K and 3 MPa. Robey and Sunder (1984) propose a lemon oil fractionator operated at 333 K and 10 MPa with an efficiency equivalent to 12 stages, with solvent recovery at 293 K and 5.5 MPa.

#### EXPERIMENTAL SECTION

Cold-pressed oil from Arizona early desert lemons was supplied by A. M. Todd Company, Kalamazoo, MI. Degassed lemon oil and dry carbon dioxide were charged into the one-liter isothermal constant volume cell shown in Figure 2. After the operating temperature was reached, the system was stirred for one hour, then allowed to settle for 15 minutes before sampling. Experiments were performed at 303 to 313 K and 4 to 9 MPa. Parallel phase visualization experiments were conducted in a sight gauge to insure operation in the two-phase region.

A sample of the equilibrated liquid phase was removed (after purging) by depressurization through a valve and hypodermic tubing into a two-stage trap cooled by dry ice - acetone. A wet test meter measured the carbon dioxide off-gas. A sample of the vapor phase was then similarly removed. Purge and sample sizes were kept small to minimize disturbance of equilibrium. Pressure changes in the cell were 0-0.1 MPa during sampling of liquid phase and 0-1.2 MPa during sampling of vapor phase. Special high-pressure sample valves with microliter-sized traps were tried in an effort to reduce pressure disturbance, but reliability was inadequate.

Estimated relative errors are 0.2% for temperature, 5% for pressure, 4% for carbon dioxide mole fraction in the liquid phase, and 10% for lemon oil mole fraction in the vapor phase.

The recovered lemon oil samples were analyzed by gas chromatography. A 0.5 mm i.d. x 30 m thin film (0.1  $\mu$ m) SE-30 glass capillary column (Supelco, Inc., Bellefonte, PA) was used with a flame ionization detector in a F&M 810 chromatograph. The unit was fitted with a temperature programmer (F&M Scientific Model 240), glass-lined inlet splitter (J&W Scientific, Inc.), and integrator (Hewlett-Packard Model 3370B). No reference column was used. The following conditions were employed: 27 cm/s He carrier gas; 250 cm<sup>3</sup>/min air, 40 cm<sup>3</sup>/min N<sub>2</sub>, and 55 cm<sup>3</sup>/min H<sub>2</sub> to detector; 0.4  $\mu$ l sample size, 27/1 split ratio; temperature program 348 K hold 8 minutes, 4 K/min, 473 K hold 15 minutes; injection port temperature 523 K; detector temperature 523 K; attenuation X1, range 10 $\times$ ; slope sensitivity 0.01 mV/min; manual baseline reset; chart speed 1.3 cm/min. Baseline drift was 0.02 mV/125 K. Peak areas from the integrator were within 5% of those determined by cutting and weighing the peaks.

Peak identification was based on information of Supelco, Inc., A. M. Todd Company, and Staroscik and Wilson (1982). Staroscik (1984) provided us with the response values used in his work and we assumed that our detector would give proportionate response. Staroscik found in his work that relative standard deviations were generally less than 3%.

## RESULTS

Lemon oil-carbon dioxide equilibrium was measured at 303, 308, and 313 K and in the pressure range of 4 to 9 MPa. Below 6 MPa, there was insufficient lemon oil in the vapor phase to attain good samples for analysis. Above 9.0 MPa at 313 K, above 7.8 MPa at 308 K, and above 7.4 MPa at 303 K, the system reverted to a single phase. Nine experiments provided two-phase, vapor-liquid equilibrium data suitable for correlations and generating coefficients for the Peng-Robinson equation. Detailed experimental data can be found in Coppella (1985).

The results of an experiment at 308 K and 6.98 MPa are detailed here. The liquid phase contained 48 wt% (74 mole %) carbon dioxide and the vapor phase contained 99.5 wt% (99.8 mole %) carbon dioxide. A gas chromatogram for the lemon oil from the liquid phase sample is shown in Figure 3. A chromatogram for the lemon oil in the vapor phase is shown in Figure 4. Peak identification, retention, response value, and concentration for these traces are given in Table I. Average molecular weight of lemon oil is 137.9 in liquid and 136.4 in vapor.

The relative volatility in the presence of carbon dioxide, or selectivity factor, for each component with respect to limonene is also given in Table I. Relative volatility is defined as the ratio of equilibrium vaporization  $K$  for component 1 to equilibrium vaporization  $K$  for limonene. Equilibrium vaporization  $K_1$  is defined as mole fraction 1 in the vapor (extract) phase to mole fraction 1 in the liquid (raffinate) phase.

By comparing the relative volatilities of various components, the ease of separation between these components can be determined. The chromatographic column employed separates components in the order of volatility; thus, the first cut point in the separation should be between terpinolene and adjacent oxygenated compounds. The chromatograph doesn't separate terpinolene from linalool or nonanal, so the separability of these compounds couldn't be determined. The next adjacent separation involves terpinolene with a relative volatility with respect to limonene of 0.7 and citronellal with a relative volatility with respect to limonene of 0.4. The relative volatility of terpinolene to citronellal is then 0.7/0.4 or 2. For the limonene/geranial pair, the relative volatility is 1.0/0.2 or 5. These separation factors for the terpene-oxy split are adequate.

The second cut point in the separation is between geranylacetate and  $\beta$ -caryophyllene. This separation factor is 0.06/0.07, or 0.9. This is opposite that of 0.2/0.07 or 3 for geranial to  $\beta$ -caryophyllene.

There is some overlap in the volatilities of  $C_{12}$  oxy and sesquiterpenes, which means that for extractions of lemon oil with supercritical carbon dioxide, some  $\beta$ -caryophyllene will be extracted into the heart-cut oxy product. This is the result of the nonpolar carbon dioxide preferentially extracting the less polar of the lemon oil constituents.

## SOLUBILITY AND SELECTIVITY

Solubility diagrams were prepared for the phases that separated in the lemon oil extractions performed in this study with carbon dioxide. Such diagrams can serve

only as guides, since solubility is composition-dependent and is a function of extraction severity. The data are shown in Figures 5, 6, and 7 at 303, 308, and 313 K, respectively.

Extractions or extractive distillations with supercritical solvent need to be performed at as high as possible a solubility of oil in the extract or vapor phase in order to reduce the solvent or carrier gas requirement. From our lemon oil-carbon dioxide phase diagrams, it appears that the highest practical solubility level is 0.9 mole % (2.8 wt.%) essential oil. This is attainable at 313 K. At lower temperature, sensitivity of solubility to pressure requires that solubility be lower (e.g., 0.3 mole % at 308 K).

At 313 K and 8.4 MPa, slope of extract phase solubility versus pressure is 0.06 weight fraction oil/MPa. For a 15 m tall extraction tower operated at a density of 0.5 g/cm<sup>3</sup>, the pressure at the bottom is higher than that at the top by 0.025 MPa. The solubility at the bottom will then be 0.15 wt.% higher at the bottom (ignoring composition effects). At 308 K and 7.69 MPa, an increase in pressure of 0.14 MPa causes the two-phase system to revert to a one-phase system. It is imperative that temperature and pressure profiles in the supercritical extraction tower be maintained accurately. Windows are recommended to confirm that operation remains in the two-phase domain.

The selectivities in supercritical carbon dioxide extraction of terpenes from oxs, and oxs from sesquiterpenes, for lemon oil are shown in Figures 8 and 9, respectively. Figure 8 shows the relative volatility, or selectivity factor, of limonene to geranial as a function of oil solubility in the vapor phase. Operation of the extractor at 308 K and 1 wt.% solubility provides a relative volatility of 2. Operation at 313 K provides a relative volatility of 1.4. The selectivity factors, though adequate, are an order of magnitude lower than the vapor pressure ratio.

Figure 9 shows the relative volatility of geranial to  $\beta$ -caryophyllene as a function of oil solubility in the vapor phase. At 313 K and 1 wt.% volatility, relative volatility is 1.4. At 308 K and 1 wt.% solubility, these constituents are inseparable by supercritical carbon dioxide extraction. The ratio of vapor pressures for this pair is in the vicinity of 2.

#### MODELING OF EQUILIBRIA

The carbon dioxide:lemon oil P-x behavior shown in Figures 5, 6, and 7 is typical of binary carbon dioxide:hydrocarbon systems, such as those containing heptane (Im and Kurata, 1971), decane (Kulkarni et al., 1972), or benzene (Gupta et al., 1982). Our lemon oil samples contained in excess of 64 mole % limonene; so we modeled our data as a reduced binary of limonene and carbon dioxide. The Peng-Robinson (1976) equation was used, with critical temperatures, critical pressures, and acentric factors obtained from Daubert and Danner (1983), and Reid et al. (1977). For carbon dioxide,  $\omega = 0.225$ ; for limonene  $\omega = 0.327$ ,  $T_c = 656.4$  K,  $P_c = 2.75$  MPa. It was necessary to vary interaction parameter with temperature in order to correlate the data satisfactorily. The values of  $d_{12}$  are reasonable (0.1135 at 303 K, 0.1129 at 308 K, 0.1013 at 313 K). Comparisons of calculated and experimental results are given in Figures 5, 6, and 7.

Attempts to model the relative volatilities of the minor organic constituents to limonene using the Peng-Robinson equation proved unfruitful.

### PROPOSED PROCESS

Lemon oil can be concentrated by supercritical carbon dioxide extraction in the temperature range of 308 to 313 K. Pressure in the extractor will be in the range of 7.7 to 8.5 MPa. Solubilities of oil in the extract, or vapor, phase will range from 1 to 3 wt.%. Selectivity factors near 1.4 will be attained for the terpene-oxy split and oxy-sesquiterpene split. The operation is performed in a multistage extractor with reflux. Operation can be either in the batch or continuous mode. Solvent recovery is performed at conditions slightly below the critical point of carbon dioxide.

Solubility limitations require that the solvent treat be high; an economic analysis is needed to establish process feasibility.

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TABLE I  
LEMON OIL VAPOR-LIQUID ANALYSES AT EQUILIBRIUM IN CO<sub>2</sub>

PEAK NO.	COMPOUND	RETENTION <sup>a</sup> RELATIVE TO LIMONENE	WEIGHT <sup>b</sup> RELATIVE RESPONSE	MOLE %		VOLATILITY RELATIVE TO LIMONENE
				VAPOR	LIQUID	
ref	acetone	0.00	-	-	-	-
1	$\alpha$ -thujene	0.55	0.75	0.61	0.35	1.8
2	$\alpha$ -pinene	0.58	0.75	2.80	1.68	1.7
3	camphene	0.63	0.70	0.09	0.06	1.6
4	sabinene } $\beta$ -pinene }	0.76	0.74	17.27	13.06	1.34
5	myrcene	0.79	0.73	1.87	1.59	1.2
6	octanal } phellandrene }	0.86	1.17	0.09	0.07	1.3
7	$\alpha$ -terpinene	0.92	1.19	1.21	1.10	1.1
8	limonene	1.00	0.75	67.14	68.22	1.0
9	$\gamma$ -terpinene	1.09	0.78	7.59	8.45	0.91
10	terpinolene } linalool } nonanal }	1.19	0.78	0.47	0.67	0.7
11	citronellal	1.40	1.06	0.02	0.04	0.4
12	terpinenen-4-ol	1.51	0.92	0.02	0.04	0.4
13	$\alpha$ -terpineol	1.55	0.92	0.06	0.20	0.3
14	decanal	1.60	0.97	0.01	0.08	0.1
15	neral	1.70	0.96	0.24	0.92	0.3
16	geranial	1.80	0.96	0.29	1.45	0.2
17	nonylacetate	1.95	0.24	0.00	0.03	-
18	nerylacetate	2.12	1.02	0.03	0.25	0.1
19	geranylacetate	2.18	1.02	0.009	0.15	0.06
20	$\beta$ -caryophyllene	2.36	0.78	0.013	0.18	0.07
21	<i>trans</i> - $\alpha$ -bergamotene	2.40	0.78	0.016	0.26	0.06
22	$\alpha$ -humalene	2.53	0.71	0.00	0.05	-
23	$\beta$ -bisabolene	2.60	0.77	0.013	0.38	0.03

<sup>a</sup> Retention time for limonene averaged 8.7 minutes

<sup>b</sup> Peak area multiplier

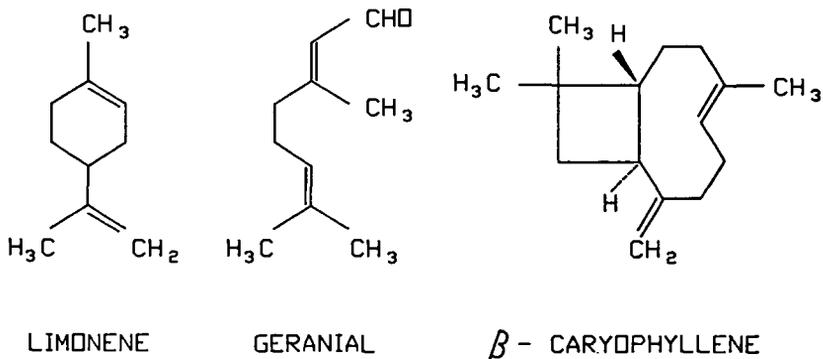


Fig. 1. Key constituents in lemon oil.

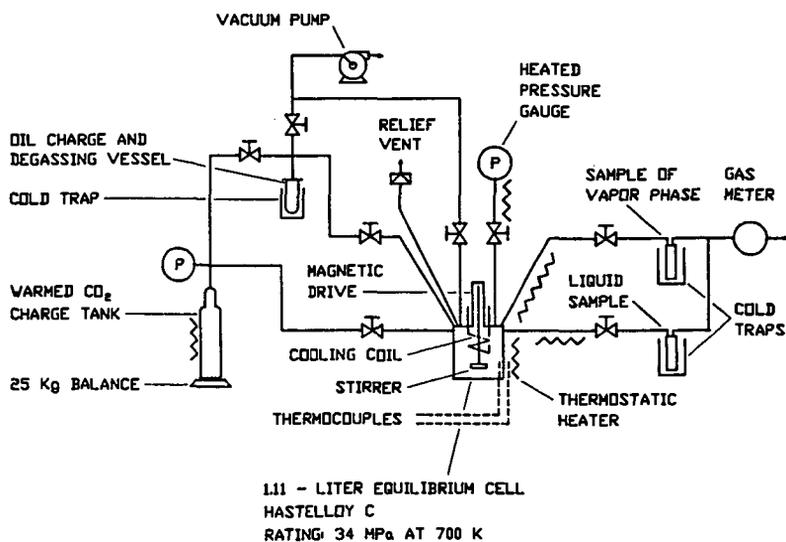


Fig. 2. Vapor-liquid equilibrium apparatus

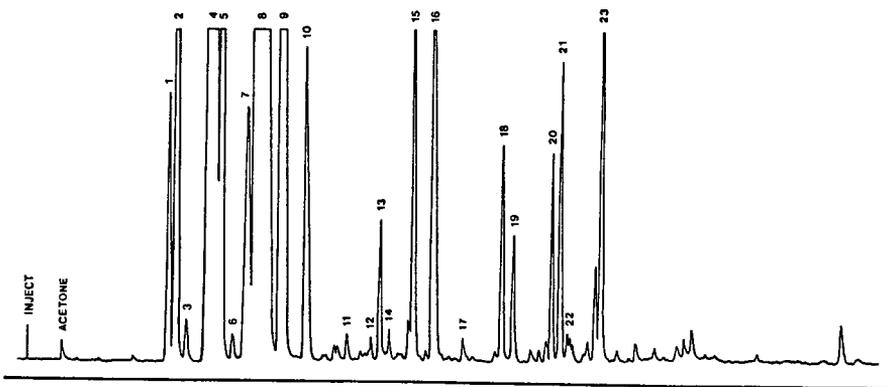


Fig. 3. Gas chromatogram of lemon oil in liquid phase sample

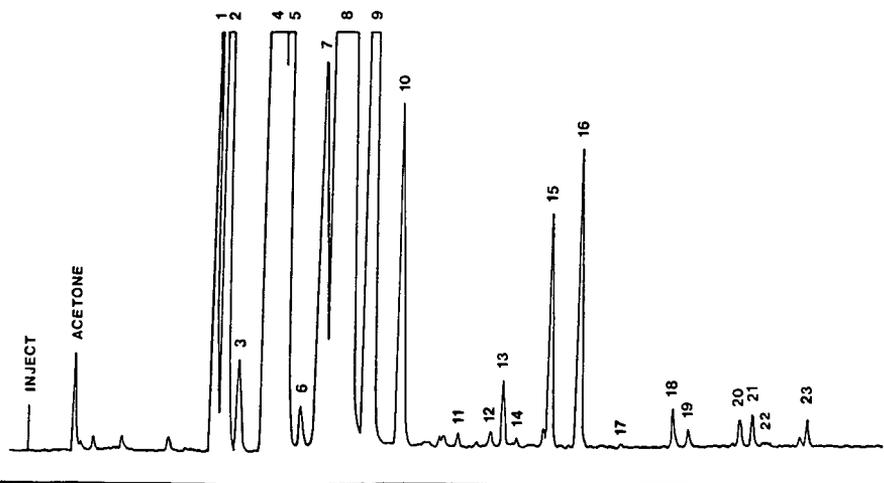


Fig. 4. Gas chromatogram of lemon oil in vapor phase sample

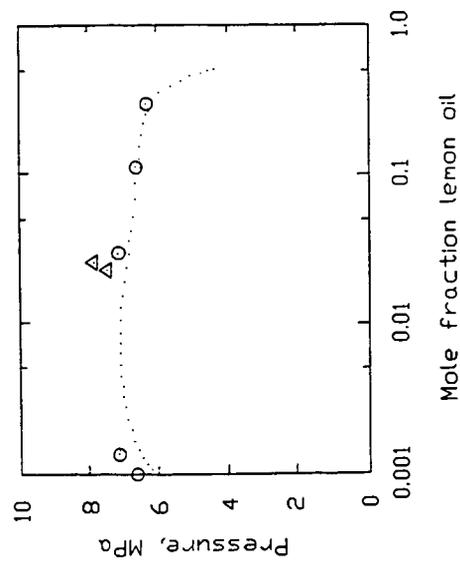


Fig. 5. Phase equilibrium for carbon dioxide : lemon oil at 303 K.  
 o - experimental two-phase  
 Δ - experimental one-phase  
 . . . Peng-Robinson eq.

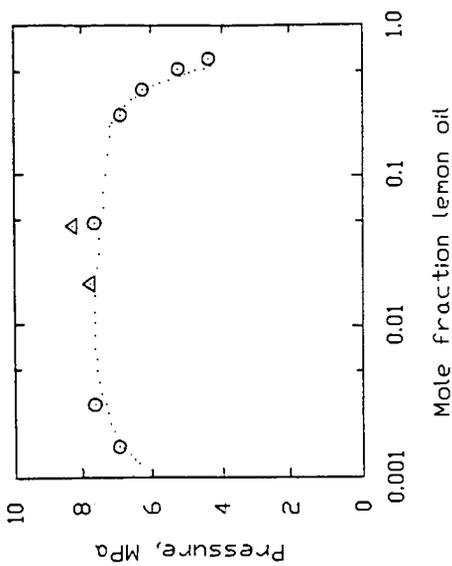


Fig. 6. Phase equilibrium for carbon dioxide : lemon oil at 308 K.  
 o - experimental two-phase  
 Δ - experimental one-phase  
 . . . Peng-Robinson eq.

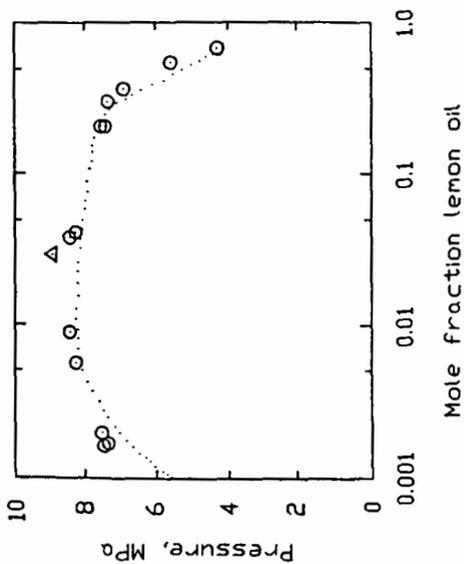


Fig. 7. Phase equilibrium for carbon dioxide : lemon oil at 313 K.  
 o - experimental two-phase  
 Δ - experimental one-phase  
 ... Peng-Robinson eq.

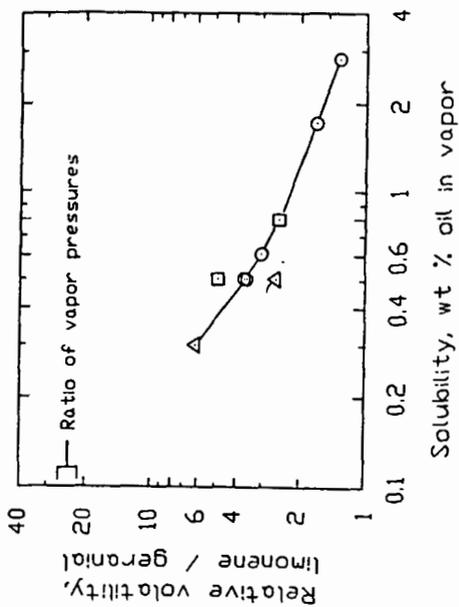


Fig. 8. Lemon oil : carbon dioxide vapor-liquid equilibria. Δ - 303 K.  
 □ - 308 K. o - 313 K.

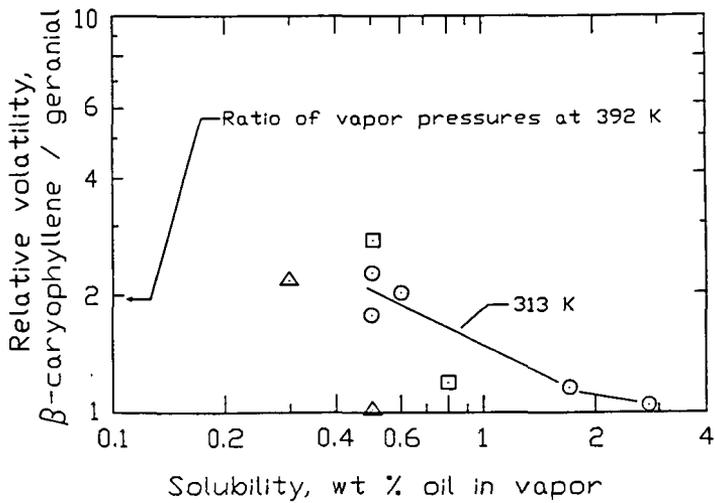


Fig. 9. Lemon oil : carbon dioxide vapor-liquid equilibria.  $\Delta$  - 303 K.  $\square$  - 308 K.  $\circ$  - 313 K.