Solubility of Echium, Borage, and Lunaria Seed Oils in Compressed CO_2

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The solubility of borage, echium, and lunaria oils in compressed CO_2 was measured using the dynamic method. Pressure and temperature were varied from (60 to 300) bar and (10 to 55) °C, respectively. The solubilities were compared to those of other vegetable oils and were correlated using the density-based model proposed by Chrastil. As predicted by the model, a linear relationship between the logarithm of solubility and the logarithm of solvent density was obtained. Average deviation between measured and calculated solubility did not exceed 14%.

Introduction

Extraction of seed oils with compressed CO_2 has received considerable interest as an alternative method to cold pressing, hot expelling and hexane extraction. Its main advantages include the outstanding quality of the extract,[1,2] the safe and environmentally friendly operation, and, in some cases, the lower operational costs of the plant.[3] On the other hand, the capital investment cost is higher as a result of the high-pressure equipment involved. In addition, the continuous transport of solids in to and out of pressure vessels is still not possible at the operating pressure required.[4] In the case of novel seed oils with a high market value, extraction by compressed CO_2 is very promising, as extraction yield and quality of the oil are very important factors in the economic feasibility of the process.

The extraction rate from seed material with high oil content is often limited by the solubility of the oils within the compressed CO_2,[5,6] and therefore, oil solubility data are important for the development and optimization of the process. Solubility data of vegetable oils in carbon dioxide are mainly available for commodity oils, such as rapeseed,[7] soybean oil,[8] sunflower seed oil,[8] palm oil,[9−11] and sesame.[11] The aim of this work is to measure the solubility of echium, borage, and lunaria seed oils in compressed CO_2 and to provide an easy-to-use correlation for their estimation. These seeds are novel in that they are not, as yet, widely cultivated but contain important polyunsaturated fatty acids some of which are in very short supply or not yet available to industry. Echium seeds are a source of steriadonic acid (18:4) and γ-linolenic acid (18:3 $n - 6$). Borage oil is rich in γ-linolenic acid, and lunaria seeds contain substantial amounts of nervonic acid (24:1). The solubilities of these three seed oils were measured for pressures between (60 and 300) bar and temperatures between (10 and 55) °C. The data were then correlated using the density-based equation proposed by Chrastil.[12]

Table 1. Fatty Acid Composition in Echium, Borage, and Lunaria Oils (% by mass)

		echium	borage	lunaria
C16:0	palmitic	6−8	9−12	1−3
C18:0	stearic	3−5	3−5	1−2
C18:1	oleic	15−19	15−20	16−20
C18:2	linoleic	14−18	30−40	8−10
C18:3 (n-3)	α-linolenic	28−33		2−4
C18:3 (n-6)	γ-linolenic	9−12	18−25	
C18:4	stearidonic	10−14		
C22:1	erucic			38−48
C24:1	nervonic			22−25

Experimental Section

Materials. Seeds of borage (*Borago officinalis*), echium (*Echium plantaginuem*), and lunaria (*Lunaria annua*) were supplied by John K. King & Sons Limited. Oil content in echium, borage, and lunaria seeds was 28, 30, and 37% (by weight), respectively. The fatty acid composition of the three oils, supplied by John K. King & Sons Limited, is given in Table 1. Carbon dioxide was supplied by BOC with a purity of 99.995% (BOC grade N4.5(CP)).

Equipment and Procedure. The solubility tests were carried out in the single pass flow apparatus presented in Figure 1. A 150-g sample of finely comminuted seeds (average particle size of 0.65 mm) was charged to the extraction vessel (E), which has a diameter and height of 45 mm and 210 mm, respectively. Carbon dioxide was supplied from the storage cylinders (SC) and cooled in WT1 before pressurization by a liquid pump. Pressure and temperature were controlled by the back-pressure regulator (BPR) and the heat exchangers (WT2 and WT3), respectively. Temperature (at the inlet and exit of the extractor) was controlled within 0.5 °C of the set temperature, before dynamic extraction was started. Vessel E was maintained at the extraction temperature by a water jacket and an air

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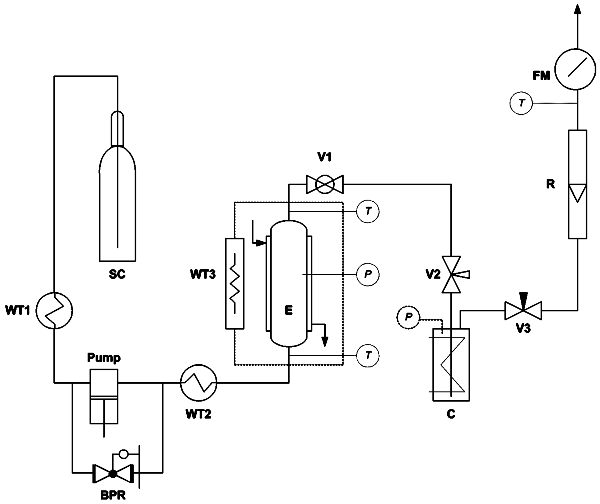

Figure 1. Apparatus for CO_2 solubility measurements.

bath (WT3). Pressure fluctuation during dynamic extraction was less than 1 bar. The solvent was fed at the bottom of E and passed through the bed of seed material. The stream containing the dissolved oils left E and was expanded to (8 to 10) bar at V2 before entering the oil collector (C). The latter was maintained at near ambient temperature by a heating cord. The stream leaving C was further expanded to atmosphere at valve V3. V3 was adjusted to the desired flow rate, 0.25 kg·h^{-1}, which was monitored by a rotameter (R) and a gas flow meter (FM), accurate within 0.5 g at operating conditions, before the discharge of the CO_2. (In preliminary tests, flow rates between (0.1 and 0.8) kg·h^{-1} were found to provide the same values of oil load in the compressed CO_2, indicating that within this range the measured solubility was not affected by contacting time and solvent velocity.)

For each pressure and temperature, a new charge of sample was used. The oil extract was collected at (60, 120, and 180) min, and for each interval, the mass of oil in CO_2 was determined. Oil solubility was then calculated from the ratio between mass of oil and mass of CO_2 used at each interval. The average and maximum deviation between the three solubility measurements at each pressure and temperature was 4% and 9%, respectively. Only the mean values of the three measurements are presented here.

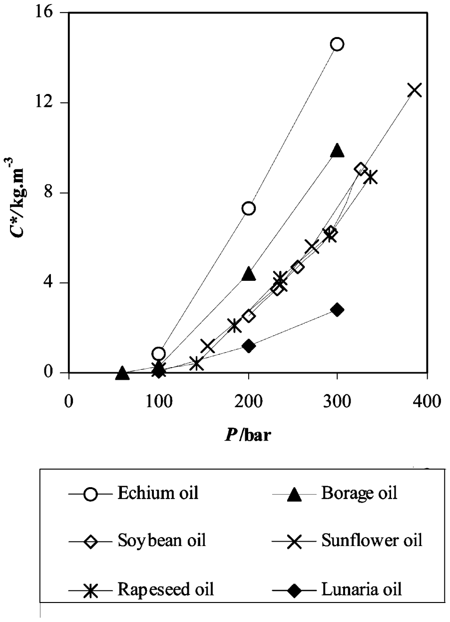

Figure 2. Solubility of vegetable oils in carbon dioxide at 40 °C. Sunflower seed oil and soybean oil;[8] rapeseed oil;[7] echium oil, borage oil, and lunaria oil (this work).

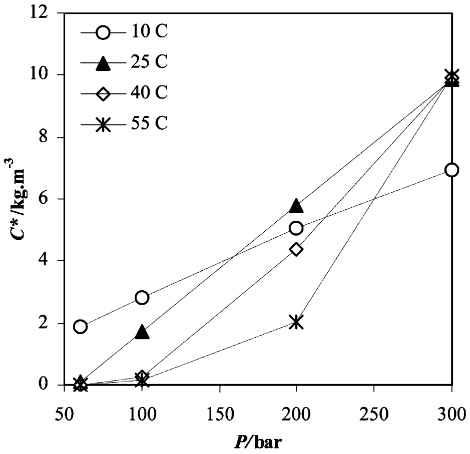

Figure 3. Effect of pressure and temperature on the solubility of borage oil in compressed CO_2.

Table 2. Experimental Solubility of Seed Oils (C^*_{exp}) in Compressed CO_2

P	T	ρ		C^*_{exp}/kg·m^{-3}	
bar	°C	kg·m^{-3}	echium	borage	lunaria
60	10	883.8	3.17	1.90	0.49
	25	190.5		0.11	
	40	149.2		0.00	
	55	129.6		0.00	
100	10	921.9	4.78	2.80	0.64
	25	819.5	3.01	1.75	0.52
	40	629.3	0.81	0.26	0.09
	55	327.1	0.02	0.13	0.00
200	10	980.8	7.72	5.07	1.10
	25	915.2	8.61	5.77	1.70
	40	840.8	7.31	4.39	1.21
	55	755.5	5.27	2.05	0.65
300	10	1020.2	10.20	6.93	1.40
	25	966.8	13.44	9.87	2.88
	40	910.3	14.56	9.90	2.84
	55	850.6	16.35	9.96	3.23

Results and Discussion

Effect of Pressure and Temperature in Oil Solubility. The measured solubilities of echium, borage, and lunaria oils in compressed CO_2 at different pressures and temperatures (and, consequently, solvent densities) are presented in Table 2. (As mentioned in the Experimental Section, the solubility values presented are the mean of three measurements.) It is clear from Table 2 and Figure 2 that echium and lunaria oils are the most and the least soluble in CO_2, respectively. This trend is observed at all conditions studied, and the differences in solubilities from different seed oils are considerable. Figure 2 also shows that, when compared to other vegetable oils, echium and borage oils are more soluble, but lunaria oil is clearly less soluble. The effect of pressure and temperature on the oil solubility remains consistent for the three seeds under study. At a given temperature, the solubility increases with the increase of pressure, as a direct result of the increased solvent density. The effect of extraction temperature is also similar for all oils. At low pressures (60 bar and 100 bar), an increase of temperature leads to a decrease of solubility, and the opposite is observed at the highest tested pressure (300 bar). At 200 bar, there is an improvement in solubility when increasing the temperature from (10 to 25) °C.

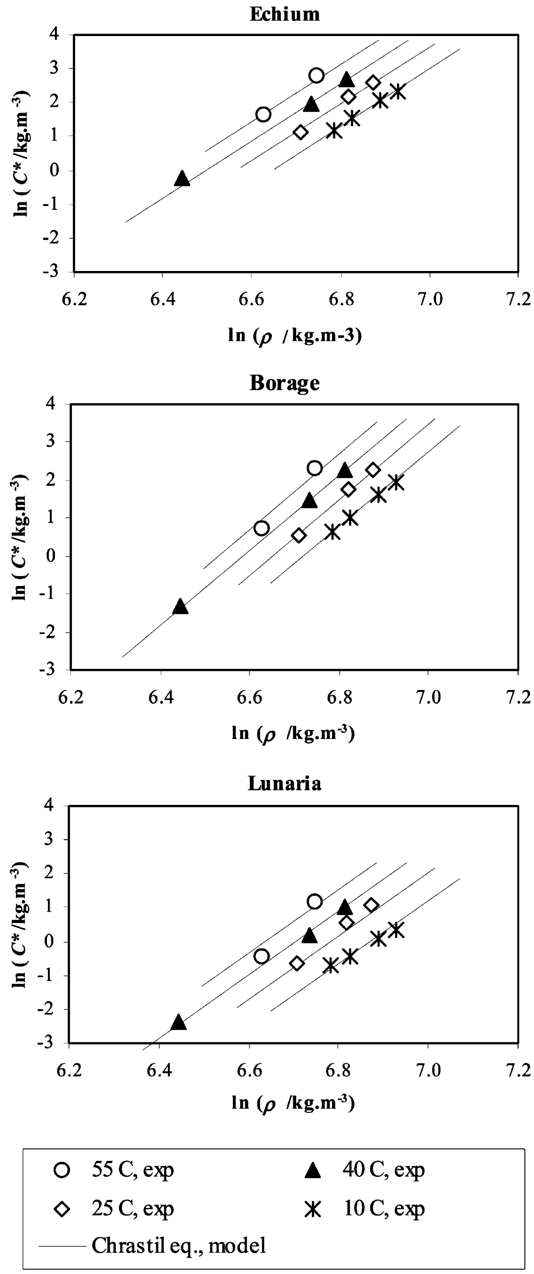

Figure 4. Comparison of experimental data (expt) with Chrastil model (k, a, and b as shown in Table 3).

However, with the increase of temperature to (40 and 55) °C, a drop in solubility is observed at 200 bar. This is better seen in Figure 3, where the effect of pressure and temperature on the solubility of borage oil is illustrated. These pressure and temperature trends are due to the competing effects of temperature on the solvent density and on solute vapor pressure. At very low pressures, the former effect dominates, resulting in reduced solubility, whereas at higher pressures, the decrease in solvent density is compensated by the enhanced oil volatility. At 200 bar, the increase on oil volatility does not compensate for the decrease on solvent density when raising the temperature to (40 and 50) °C.

Solubility−Density Correlation. Empirical density-based correlations are very useful to determine the solubility of solids and liquids in compressed fluids, as they are both simple and do not require physicochemical properties of the solute. The measured solubility data, in the high-density range ($629.3 \le \rho/\text{kg}\cdot\text{m}^{-3} \le 1020.2$), are well correlated by the Chrastil model.[12] The Chrastil model relates the solubility (C^*) to the solvent density (ρ) at each temperature (T) through (1).

Table 3. Best-fit Values of Chrastil Model Parameters and Average Absolute Deviation from Experimental Data

	echium	borage	lunaria
k	8.43	9.95	9.37
a	−3777.5	−3984.9	−4491.9
b	−42.68	−52.8	−48.5
AAD (%)	5.0	7.4	13.5

$$\ln(C^*) = k\ln(\rho) + \frac{a}{T} + b \qquad (1)$$

In (1), C^* and ρ are expressed in kilogram per cubic meter and T is expressed in Kelvin. k represents the number of solvent molecules associated with one molecule of solute in the solvato complex, a is related to the heat of solvation and heat of vaporization of the solute, whereas b depends on the molecular mass and melting points of solvent and solute. At a given temperature, a linear relation between logarithm of solubility and logarithm of solvent density is obtained. Figure 4 shows that (1) fit the experimental data well. The values of k, a, and b for the three oils were adjusted to minimize the sum of the square deviations between measured and calculated solubilities. For each seed oil, 12 experimental solubilities were adjusted using the 3-parameter model proposed by Chrastil. The best-fit values of k, a, and b and the average absolute deviation (AAD) between experimental and modeled solubilities are shown in Table 3.

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