Solubility of vegetable cuticular waxes in supercritical CO_2 isothermal calorimetry investigations

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Abstract

Vegetable cuticular waxes have to be separated from the more valuable essential oils in extraction processes carried out with supercritical fluids (namely CO_2), allowing a solvent selectivity by modification of temperature and pressure. The solubility of these waxes in supercritical CO_2 can be adequately represented by that of solid n-octacosane. The present work shows that isothermal investigations, carried out with a differential flux calorimeter with adequate cells, allow the solubility and solubilization enthalpy of n-octacosane to be determined. The results concern investigations either at constant pressure and variable supercritical CO_2 flow-rate, or at zero flow-rate and increasing pressure. The latter conditions allow the solubility–pressure trend to be obtained, in satisfactory agreement with literature data derived from standard dynamic methods.

Keywords: Calorimetry; Carbon dioxide; Cuticular wax; Isothermal; Solubility; Supercritical fluid; Vegetable; Wax

1. Introduction

The cuticular waxes coating leaves, beans and berries belong to the long-chain (24–36 carbon atoms) n-paraffins and can form most of the extracted matter when vegetable matrices are processed with common solvents (n-hexane, ethyl ether, acetone) to obtain much more valuable products, such as essential oils which are ingredients for pharmaceutical and/or cosmetic preparations. In the last decade, supercritical CO_2 (SC-CO_2) has been recognized as a suitable solvent for the production of essential oils on an industrial scale, because it allows selective

extractions and is ecologically safe. In the plant extraction chamber, SC-CO_2 permeates the packed vegetable matrix and strips away any soluble (more or less) compound: the poorly volatile waxes are separated in the next plant chamber, where either the temperature or the pressure is lowered to reduce the solvent power of the supercritical phase which, nonetheless, still contains the dissolved essential oil compounds and can be conveyed to a subsequent separator.

A knowledge of the solubility of the waxes in SC-CO_2 is therefore necessary in order to pre-set the pressure and temperature conditions in the first separator. Fortunately, the entire family of these hydrocarbons shows similar solubility and can be adequately represented by solid *n*-octacosane [1] which is commercially available in the pure state.

The solubility in supercritical fluids (SCF) is assessed by determination of the solute mass recovered after a thorough separation from the solvent at subcritical T and p levels. To ensure the attainment of an actual thermodynamic equilibrium at a given T, either "static" or "dynamic" procedures can be followed: in the latter, the SCF flow slowly through the packed substrate that hosts the solute, whereas the former requires saturation of the SCF phase in a closed batch. In either case, strict control of the experimental conditions is mandatory, because the reliability of the results obtained is based on the assumption that thermodynamic equilibrium has been actually attained. When the solubility Y is plotted against the pressure p, part of the border-line of a two-phase (solid $\rightleftharpoons$ SCF) isothermal region of the relevant bindary phase diagram is revealed.

The solubility of a pure poorly volatile solid B in a supercritical fluid A, which is unsoluble in B, may be drawn from the general equilibrium condition

$$\mu(B_S) = \mu^\circ(B_{SCF}) + RT \log[f(B_{SCF})]$$

and

$$f^\circ(B_S) = f(B_{SCF})$$

where μ and f represent chemical potential and fugacity, respectively. If $p^\circ(B)$ is the vapour tension of the pure solid B, one gets the simple expresssion

$$Y(B_{SCF}) = \frac{p^\circ(B)}{p} \frac{\gamma^\circ(B_S)}{\gamma(B_{SCF})}$$

where p, Y and γ are the overall pressure, the molar fraction of B in the SCF, i.e. its solubility, and the fugacity coefficient, respectively. It can be shown that when the excluded volume V_{AB} is independent of Y in the narrow range of the expected values, the solubility at a given T and p is adequately represented by the expression

$$Y = \alpha \exp(-\Delta_{sol}H/RT)$$

where α is a function of p. This is the Chrastil [2] equation which has proved to describe adequately the solubility of a number of solids and liquids in SCF in narrow temperature ranges, at a given constant pressure.

In this work, the SC-CO_2 solubilization process took place within a specially designed cell of a differential flux calorimeter. The isothermal calorimetric signal

was detected either at constant p and variable CO_2 flow rate F, or at zero F and increasing p.

2. Experimental

A twin Calvet calorimeter (Setaram C80 D) was employed. Special cells (4 ml capacity) were designed to allow gas flow through a packed sample (see Fig. 1). The inlet and outlet routes are along coaxial tubes that run to each cell, the inner tube conveying fresh SC-CO_2, the outer providing the removal of supercritical fluid from the cell.

The CO_2 feeding line (the inner tube) is conveyed into the calorimeter through a hole in the refractory cover; before reaching the cells, it is wound into a 3-m-long coil, very close to the inner wall of the calorimeter: this allows CO_2 preheating. At the end of the coil, the line is split into equal flow for the measuring and reference cells, respectively. Along this path, the feeding line meets a countercurrent CO_2 flow conveyed from the calorimetric cells into the outer tube (Fig. 2).

The inner tube pierces the cover of the relevant cell and reaches its bottom. The escape route, i.e. the wider coaxial tube, is sealed to the cell cover. The CO_2 out-flow from either cell is conveyed to a single exit line at the same split-point of the feeding line. The cell covers are therefore sealed with the inlet–outlet tubing. Thus the cells are assembled with their covers: a long-fold screw sealing allows pressures as high as 100 MPa to be exploited.
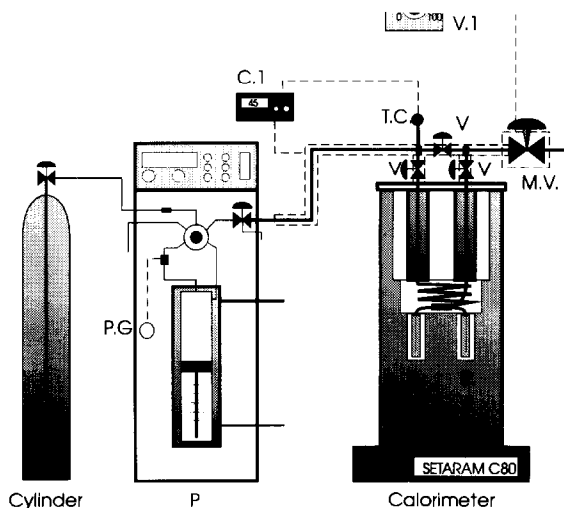

Fig. 1. Scheme of the plant used for calorimetric investigations. Cylinder of liquid CO_2; P, SCF 300 pump; P.G., pressure gauge; V, valve; C1, temperature control of the line; T.C., thermocouple; S and R, sample and reference calorimetric cells, respectively; M.V., micrometric valve; V.1., variac coil to keep the M.P. at ambient temperature.
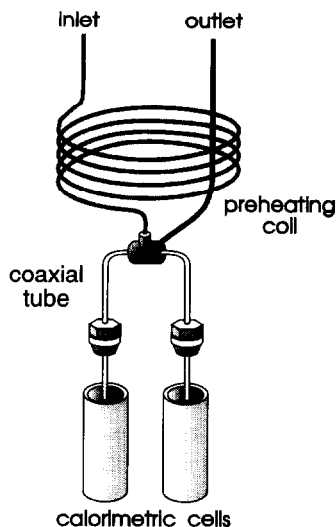
Fig. 2. Details of the inlet and outlet tubing conveying supercritical CO_2 into and out of the calorimetric cells.

The inlet gas line is fed by a pump for supercritical fluid chromatography (Fisons SFC 300) acting on liquid CO_2, which runs either at constant flow rate or at constant pressure.

The reference cell was filled with glass spheres. In the measuring cell, slices of n-octacosane (97% pure, Aldrich Chemie) were tightly packed to minimize the free volume. All the determinations were carried out under isothermal conditions at 35, 40 and 45°C. A set of runs was carried out at a constant pressure (25 and 30 MPa), the flow-rate F being pre-set from time to time: to obtain a stable calorimetric signal it was necessary to operate at very low flow-rates ($F < 1.5$ mg s^{-1}). In other investigations, pressure was regularly increased from 14 to 30 MPa with $F = 0$ (the out-flow line was closed).

3. Results

Runs at constant p and variable F gave calorimetric traces characterized by a series of horizontal steps, each of which was relevant to an F value (Fig. 3): once F was fixed, it was necessary to wait for signal stabilization. These stable s values represented the experimental data. For any operating condition, a preliminary run with empty cells was necessary to account for the unavoidable asymmetries of the system. The relevant trace was then subtracted from that obtained with filled cells. These "corrected" data were used to evaluate Y and $\Delta_{sol}H$.
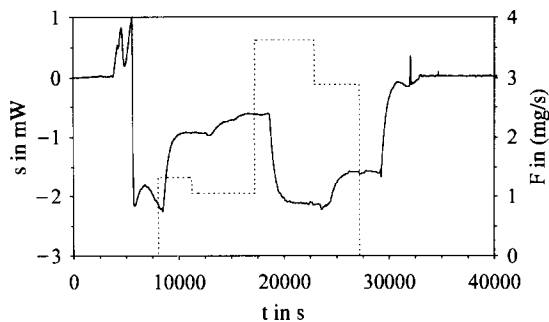
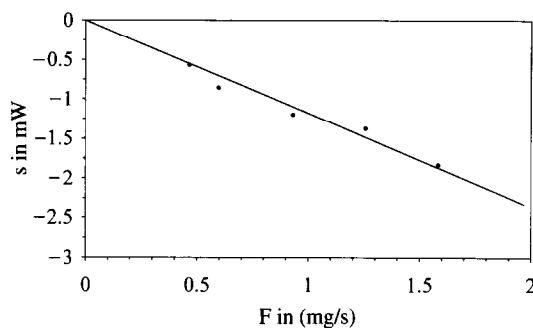Fig. 3. Typical isothermal DSC trace (full line) obtained when various CO_2 flow-rates (dotted line) were imposed.

Fig. 4. Correlation between calorimetric signal s and flow-rate F. Data concern the investigation at 30 MPa and 313 K.

When $\Delta_{sol}H$ is determined experimentally using calorimetric investigations at constant p and variable F, the observed signal $s = dQ/dt$ can be justified [3] with the relationship

$$s = -Y\Delta_{sol}H\frac{F}{M(CO_2)}$$

where s is in mW and $M(CO_2)$ is the molar mass of the solvent. Because $Y \ll 1$, it was approximated here by the ratio between the number of moles, $n(B, SCF)/n(CO_2, SCF)$.

For $p = 25$ and 30 MPa and $T < 320$ K, the signal is endothermic, $\Delta_{sol}H > 0$, which corresponds to an increase in Y with increasing T. The $s-F$ trend was fitted with a straight line passing through the origin (Fig. 4), the slope of which corresponds to $Y\Delta_{sol}H$. Using Y data from the literature [1,4], the $\Delta_{sol}H$ values of Table 1 were obtained.

Table 1
$\Delta_{sol}H$ from calorimetric investigations and Y data from the literature [4]

p in MPa	T in K	$-s/F$ in J g^{-1}	$\Delta_{sol}H$ in kJ mol^{-1}
25	308	0.12	100
	313	0.41	81
	318	1.18	134
30	313	0.52	210
	318	0.99	253

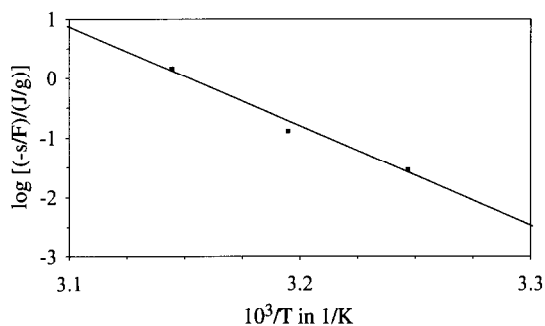Fig. 5. Semi-log plot of calorimetric data obtained at 25 MPa at various temperatures.

Table 2
Solubility of n-octacosane at 25 MPa and various T; $\Delta_{sol}H$ was calculated via the Chrastil equation [2]

T in K	Solubility $\Delta_{sol}H = 139$ kJ mol^{-1} $Y_{calorim} \times 10^{-4}$	$\Delta_{sol}H = 114$ kJ mol^{-1} $Y_{solubil} \times 10^{-4}$
308	0.68	0.95
313	1.42	2.22
318	3.74	3.88

When combined with the Chrastil equation, the above expression gives

$$-\frac{s}{F} = \frac{\alpha \Delta_{sol}H}{M(CO_2)} \exp\left(-\frac{\Delta_{sol}H}{RT} \right)$$

which is a straight line in the plane $[\log(-s/F), 1/T]$ with slope equal to $-\Delta_{sol}H/R$, as shown in Fig. 5. This allowed α, Y and $\Delta_{sol}H$ to be evaluated. In Table 2, these Y data are compared with those derived from chemical analyses [1].

Determinations carried out with closed out-flow, i.e. with increasing p, must be determined in a different way. The relevant calorimetric signal is shown in Fig. 6.
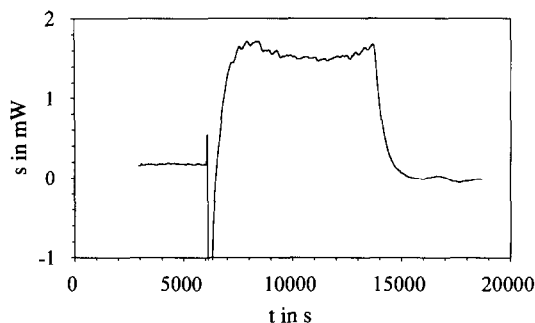
Fig. 6. Calorimetric signal vs. increasing pressure observed at $T = 318$ K in zero flow-rate conditions.

When the pump is activated to increase the pressure, the out-flow valve being closed, the signal jumps to a more or less steady level, from where it drops down to zero when the pump is switched off. The pressure scan exploited can be empirically described as

$$p/\text{MPa} = 10.437 + 7.631 \times 10^{-3}\, t + 1.602 \times 10^{-7}\, t^2$$

The compression work is responsible for less than 10% of the observed signal and has therefore been neglected. Because $F = 0$, the calorimetric signal is mainly related to changes in Y with p. Given

$$Y \approx \frac{n(\text{B,SCF})}{n(\text{CO}_2,\text{SCF})}$$

$$dY = \frac{dn(\text{B,SCF})}{n(\text{CO}_2,\text{SCF})} - \frac{n(\text{B,SCF})}{n(\text{CO}_2,\text{SCF})}\frac{dn(\text{CO}_2,\text{SCF})}{n(\text{CO}_2,\text{SCF})}$$

by replacing $n(\text{CO}_2,\text{SCF})$ with the product ρV, where V and ρ are the actual cell volume occupied by and the density of the supercritical phase, respectively, one obtains

$$dY = \frac{dn(\text{B,SCF})}{\rho V} - Y\frac{d\rho}{\rho}$$

which can be rewritten as

$$d(\rho Y) = \frac{dn(\text{B,SCF})}{V} = \frac{dQ}{V\Delta_{\text{sol}}H} = -\frac{s\,dt}{V\Delta_{\text{sol}}H}$$

and integrated

$$Y = Y*\frac{\rho^*}{\rho} - \frac{1}{\rho V}\int_{t^*}^{t} \frac{s\,dt}{\Delta_{\text{sol}}H}$$

Because the density of the supercritical phase is very close to that of pure CO_2, a suitable equation of state (Peng and Robinson) was used to calculate ρ; V was assumed to be practically independent of T and p, solid n-octacosane being poorly
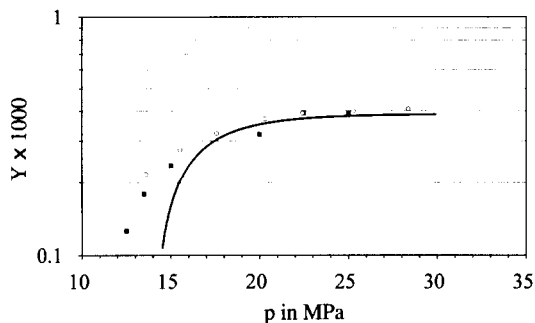
Fig. 7. Solubility of n-octacosane vs. p at 318 K. For the sake of comparison, Y data from chemical analysis of the extracts, ■ [1] and ○ [5] are also reported.

compressible. The value of V, namely 250 μl, could be achieved using the above results from determinations with variable F

$$-\frac{\displaystyle\int_0^t s\,\mathrm{d}t}{\Delta_{\mathrm{sol}}H} = Y\rho V$$

s being the constant signal observed at a given flow rate.

The isothermic Y vs. p curves cross one another at a point in the plane (Y, p) named the cross-over point ($p = p_{\mathrm{co}} = 10.5$ MPa for n-octacosane [1]), where the solubility is the same at any temperature; for $p > p_{\mathrm{co}}$, it increases with T, whereas for $p < p_{\mathrm{co}}$ it decreases with T. Accordingly, $\Delta_{\mathrm{sol}}H$ is zero at the cross-over and increases with increasing p. If this trend is assumed to be represented by a straight line in the pressure range exploited, then

$$\Delta_{\mathrm{sol}}H(p) = \frac{\Delta_{\mathrm{sol}}H(p^*)}{(p^* - p_{\mathrm{co}})} \times (p - p_{\mathrm{co}})$$

where $p^* = 25$ MPa has been chosen because at this pressure Y, $\Delta_{\mathrm{sol}}H$ and ρ are known with a greater confidence [1].

Fig. 7 shows the Y vs. p trend drawn accordingly (at $T = 318$ K); it is in satisfactory agreement with literature data [1,4,5] which derive from standard dynamic methods.

4. Conclusions

Isothermal calorimetric investigations were proven adequate to assess the solubility and the solubilization enthalpy of n-octacosane in supercritical CO_2. Determinations are possible either at constant pressure and variable flow-rate, or at zero flow-rate and increasing pressure, and give results in accord with those derived from other methods.

Improvements to the plant are in progress in order to extend the investigations to extractions from liquid matrices.

Acknowledgement

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