# Solubility Behaviour and Fractionation of Essential Oils in Dense Carbon Dioxide

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Large quantities of essential oils are used in food industries as well as in perfume industries. The aroma and flavour substances often differ substantially in their chemical composition and especially in their sensory properties depending on their production procedures.

In steam distillation which is still the most often used process, the material is exposed to a relatively high temperature stress which can lead to artefacts of the essential oil components, especially due to the hydrolytic influence of the water. Extraction with low boiling organic solvents is used, too. Here, a very important step in the process is the complete removal of the solvents from extracts and its residue as they are in part toxicologically objectionable. In addition, the organic solvents have only a low selectivity. Apart from the desired substances, higher molecular, non-volatile components are also extracted, such as fatty oils, resins, waxes and colouring matters.

The extraction with dense gas proves to be a true alternative to the conventional procedures. To obtain essential oils or aroma substances which are used in perfume industries, in the pharmaceutical sector or in the food and human nutrition field, carbon dioxide offers itself as an extractant which is physiologically unobjectionable and leaves the obtained products free of solvents. Another advantage is the mild operational process. Under exclusion of oxygen and at temperatures around 40° C, even thermally unstable substances can be won undecomposed with dense carbon dioxide; thus, essential oils genuinely present in the plant material are obtained.<sup>1-3</sup> The extraction of essential oils can easily be carried out.48 Problems are, on the one hand, the quantitative recovery of the easily volatile components, and on the other hand that the

undesired substances may be partly coextracted. For an optimal regulation of the two process parameters, pressure and temperature, the knowledge of the solubility behaviour of the essential oils in dense carbon dioxide is a precondition.

#### **Experimental Section**

# Materials

The pure substances which were used for the solubility determinations were isolated as follows:

- -limonene, from the oil of sweet orange (Oleum Aurantii dulcis "Florida")
- -carvone, from the essential oil of caraway seed (Carvi fructus)
- -anethole, from the essential oil of anise seed (Anisi fructus)
- -eugenol and caryophyllene, from the essential oil of cloves (Caryophylli flos)
- -valeranone, from the essential oil of spikenard (Nardostachys jatamansi)

Further details concerning the isolation of the tested substances will be published.<sup>9</sup> The carbon dioxide gas, purity 99.9 vol %, was used for extraction.

#### **High Pressure Equipment**

The measuring arrangement for the solubility determination of essential oil components is schematically shown in figure 1. The solubilities are determined by means of the dynamic flow principle from the weight of the solved substance in proportion to the amount of gas flow. To carry out an experiment, the substance (approximately 3 g) is applied on glass wool in the lower part of the autoclave E (effective volume =  $20 \text{ cm}^3$ ). Packing material (glass balls) is filled on top of



Figure 1. Measuring arrangement for the solubility determination of essential oil components in dense carbon dioxide: G dense gas supply, M manometer, T thermo-sensor and -indicator, H heat exchange, E sample autoclave, A separation unit, K freeze mixture, D Dewar vessel, F charcoal filter, S flow meter, RV micrometering valve, V1 and V2 shut-off valves.

the glass wool to prevent the entrainment of liquid drops of essential oil components in the gas stream. The dense gas flows slowly from the base to the top of the sample chamber (E) under defined conditions of pressure and temperature. The gas-depending on its state-takes up a certain amount of the substance and transports it to the separating unit A (cooling trap and washing bottle). The separation of the solved substances is achieved by expansion to atmospheric pressure on the micrometering valve RV. The substances are collected at  $-30^{\circ}$  C in a cooling trap (freeze mixture: methanol-dry ice). Substance remnants which are not completely separated are collected in a suitable solvent, e.g. n-pentane, in a washing bottle, connected in series. The uncharged gas then passes the flow meter S where the amount of gas flow is measured. The substances collected in the separation unit are determined quantitatively. To carry out tests with water-saturated CO2, the dense gas first flows at a constant temperature through an autoclave which is partly filled with water and then through the sample chamber E.

#### **Analytical Methods**

The determination of the solved and trans-

ferred substances was carried out in the case of the high solubility values by weighing after evaporation of the solvent which was contained in the washing bottle. Smaller amounts of the compounds, that is at lower solubilities, were determined photometrically, as was the case for anethole and eugenol, or for all other compounds, by gas chromatography with flame ionization detector (FID) after establishing calibration curves with authentic reference substances.

#### **Results and Discussion**

#### Physical Properties of Essential Oil Components

The essential oil components can be classified according to their differing properties in four groups:

- -monoterpene hydrocarbons
- -oxygen containing monoterpenes and phenylpropane derivatives
- ---sesquiterpene hydrocarbons
- ---oxygen containing sesquiterpenes.

Vapour pressure and polarity have a special in-

fluence on the solubility behaviour in dense carbon dioxide. The compounds are the better extractable the lesser polar they are and the smaller the molar mass and the larger the vapour pressure. The presence of polar functional groups causes a diminished solubility in dense carbon dioxide.

In figure 2, the vapour pressure curves of some typical components of essential oils are plotted as functions of the temperature.<sup>10,11</sup> The monoterpene hydrocarbons, e.g.  $\alpha$ -pinene, limonene, show the highest volatility. The vapour pressures of the sesquiterpene hydrocarbons, e.g., caryophyllene, are somewhat smaller and in the same size range as those of the oxygen containing monoterpenes, e.g. carvone, geraniol, and phenylpropane derivatives, e.g. eugenol. The oxygen containing sesquiterpenes, e.g. valeranone,  $\alpha$ -bisabolole, are of considerably lower volatility.

#### **Solubility Behaviour**

All components of essential oils are very well soluble in dense carbon dioxide at already relatively low gas densities (figure 3). Due to the strong increase in density of the extractant in the pressure range between 70 and 100 bar at 40° C, solubilities increase exponentially. Solubilities of 100 mg/NL\* CO<sub>2</sub> are reached at a pressure of 90 bar, that is at a gas density of only 0.5 g/cm<sup>3</sup>.

At higher gas densities, that is in higher compressed supercritical or in liquefied carbon dioxide<sup>4</sup> there is even unlimited miscibility. As figure 3 shows, the monoterpene hydrocarbons, e.g., limonene, have the highest solubility values. Carvone and caryophyllene have almost the same solubility in supercritical carbon dioxide at 40° C, somewhat lower than that of the monoterpene hydrocarbons.

A solubility behaviour similar to that of carvone can be seen in the phenylpropane derivatives anethole and eugenol. The solubility curve of valeranone is in the lower pressure range markedly lower than those of the remaining components, that is the somewhat higher molecular, oxygen containing sesquiterpenes are less soluble under these conditions. With increasing gas density their solubility also increases very much. At pressures above 90 bar at 40° C, the solubility curve of valeranone approaches those of the other essential oil components.

#### Separation Behaviour

The extracting gas is circulated in a preparative extraction. With the aim of ensuring a recovery of

\*1 NL CO<sub>2</sub> = 1000 cm<sup>3</sup> CO<sub>2</sub> at 1 bar and 20° C = 1,78 g



Figure 2. Vapour pressure curves of typical essential oil components: 1  $\alpha$  -pinene, 2 limonene, 3 carvone, 4 geraniol, 5 caryophyllene, 6 eugenol, 7 valeranone, 8  $\alpha$ -bisabolole



Figure 3. Solubility isotherms of essential oil components in dense carbon dioxide at 40° C



Figure 4. Separation isobars (left) and isotherms (right) for typical essential oil components

the essential oils as complete as possible, the solubilities of characteristic compounds were investigated and the separation isobars and isotherms constructed (figure 4). As can be seen from figure 4 (left) the isobars pass through a minimum, and when pressure is lowered the separation minima are displaced to lower temperatures and solubility values. Thus, it follows that the separation should be done at low pressure and temperature. Attention must be paid to the fact that the separation temperature is above the liquefaction temperature of carbon dioxide, depending on the respective pressure, as the liquefied gas has a high solving capacity for these substances.

Another remarkable fact is that at a given temperature the separation pressure cannot be chosen in any low range since the isotherms also pass through a minimum (figure 4, right). At low pressures the high vapour pressure of the essential oil components causes a certain solubility. With increasing pressure, the part of the vapour pressure on the system pressure becomes smaller; as consequence hereof the solubility decreases. The isotherms progress to a minimum to finally reach a marked increase due to the higher gas density, that is due to solvatation effects. The lower solubility of caryophyllene and of eugenol

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as compared with limonene in the discussed pressure and temperature range is based on their markedly lower volatility.

# Fractionation of Essential Oils

To separate essential oils in substance groups of differing volatility or polarity the solubilities of the compounds in the dense gas should vary as much as possible. Due to the higher vapour pressures, due also to the lower polarity and to the smaller molar masses the monoterpene hydrocarbons are better soluble in dense carbon dioxide than the other essential oil components. The solubility isobars of limonene and carvone (figure 5) show that at gas densities above  $0.4 \text{ g/cm}^3$ , that is, at temperatures below 35° C at 80 bar, fractionation is impossible. At isobaric temperature increase the solubility curves pass through a minimum. On the one hand, the solving capacity of the gas decreases due to the lower density, and on the other hand, the higher temperature causes an increase in the vapour pressure. At higher temperatures, the different volatility, together with the solving capacity of the supercritical carbon dioxide, cause a markedly different solubility of the essential oil components that have to be separated. The solubility curves take a similar course at higher pressures, but higher temperatures are required to cause a difference in the

solubilities and therefore a separating effect. In this case, the higher loading of the dense gas phase is of advantage.

The separation of sesquiterpene hydrocarbons and oxygen containing monoterpenes is difficult as their solubility behaviour in  $CO_2$  is alike and moreover their vapour pressures are almost the same. A fractionation due to various polarities is, however, possible if the selectivity of the extractant is enhanced by increasing the polarity, for



Figure 5. Solubility isobars for limonene and carvone as function of temperature and density of the compressed CO<sub>2</sub>

instance, by saturation with water.<sup>12</sup> This causes a solubility increase of the polar components and a decrease of the hydrocarbons. This effect is most marked in the strong increase of the solubility isotherms, at pressures between 80 and 90 bar at 40° C (figure 6). At 85 bar, for instance, anethole is better soluble than caryophyllene by the factor of 8 (interrupted arrow in figure 6) in water-saturated supercritical CO<sub>2</sub> whereas their solubilities are almost alike in the pure supercritical gas. At gas densities above 0.5 g/cm<sup>3</sup>, that is at pressures above 90 bar at 40° C, the solubility of the components increases at the cost of selectivity so much that a separation is getting more difficult.

As figure 3 already shows, the solubility of the oxygen containing sesquiterpenes in supercriti-



Figure 6. Influence of the water saturation of carbon dioxide on the solubility of anethole and caryophyllene

A, B: solubilities in pure CO<sub>2</sub>

A\*, B\*: solubilities in water-saturated CO<sub>2</sub>



Figure 7. Solubility isobars of caryophyllene and valeranone in dense carbon dioxide

# Solubility Behaviour

cal carbon dioxide of low density (<  $0.5 \text{ g/cm}^3$ ) is worse than that of the other essential oil components. Consequently, a fractionation is possible in the way that the better soluble monoterpenes, their derivatives and the sesquiterpene hydrocarbons can be selectively extracted with supercritical carbon dioxide, for instance at pressures of 70 to 80 bar at 40° C. The low charging of the extraction gas, however, presents a disadvantage.

Another possibility of a separation shall be discussed with the help of figure 7. At high gas densities, that is, at low temperatures and 90 bar, caryophyllene and valeranone are very well soluble. With increasing temperature the solubilities decrease. The curves pass through a minimum and steepen again due to the volatility of the substances. Here, the solubility curve of valeranone decreases more steeply. If extraction takes place at 90 bar and 35° C, all components can be solved very well. At isobaric temperature increase, for instance at 60° C, the lesser soluble sesquiterpene derivatives are mainly precipitated whereas the other essential oil components remain in solution and can be separated in a second receiver.

#### Conclusion

As low molecular lipophilic substances with high vapour pressure, the essential oils are well soluble in dense carbon dioxide. The extracted oil should be free of undesirable substances and no fractionation effects within the essential oil should occur. Supercritical  $CO_2$  with densities around 0.5 g/cm<sup>3</sup>, e.g., at 90 bar and 40° C, is suitable for this purpose. The  $CO_2$  extraction of spices under thermally mild conditions yields concentrates which, in their sensory qualities, are superior to steam distillates or classical solvent extracts.<sup>7</sup>

Further examples of the selective extraction are shown with the separation of the essential oil genuinely present in calamus rhizomes<sup>2</sup> and the detoxification of wormwood herb.13 The essential oil of wormwood herb, especially the  $\beta$ -thujone, is known for its toxicity. In its extraction, the content of the bitter principles which determine the value of the herb, remain practically unchanged, especially in the case of the dimeric sesquiterpene lactone absinthine. At higher gas densities, that is with liquefied or higher compressed supercritical carbon dioxide, undesirable lipophilic principles, such as fatty oils, waxes and other substances, are extracted in addition to the essential oil, and have to be precipitated separately.3,14 The knowledge of the solubility behaviour of essential oils, of fatty oils,15 of the waxes, and of further lipids<sup>16</sup> in dense carbon dioxide is a prerequisite for the optimal choice of fractionation conditions. The complete recovery of essential oils from the circulated gas requires the simultaneous application of low pressures and temperatures due to the high volatility of these substances; the liquefaction of the extractant, however, must be prevented.

For the separation of the essential oils into certain substance groups, it is necessary to further increase the selectivity of the dense carbon dioxide contrary to the extraction in which fractionation effects are deliberately prevented. A higher selectivity is reached at lower gas densities. In addition, an enhanced polarity leads to a further increase in selectivity. A lower gas density is obtained at low pressures, e.g., 70 to 80 bar at 40° C. This, of course, leads to an uneconomically low loading of the dense gas phase. In working at higher temperatures, the differing vapour pressures of the substances can be utilized for separation besides the solvent properties of the supercritical CO<sub>3</sub>.

The continuous deterpenation of citrus oils in a high pressure countercurrent column is a very interesting sample for the application of the fractionation of essential oils.<sup>17</sup> A separation is reached by the higher volatility of the hydrocarbons as well as by their lower polarity compared with the other oil components.

#### Acknowledgement

We thank the Deutsche Forschungsgemeinschaft Bonn-Bad Godesberg and the Fonds Chemie of the German Chemical Industry for granted financial help.

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