SOLUBILITY AND PARTITION COEFFICIENTS OF FISH OIL ESTERS IN SUPERCRITICAL CARBON DIOXIDE

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Introduction

The design of supercritical counter-current fractionation processes for fish oils and derived products requires knowledge of the phase equilibria with supercritical solvents and pilot-plant operation data[2]. In this work we present and compare the experimentally measured partition coefficients (K-values) of fatty acid ethyl esters (FAEEs) derived from sand launce (Ammodytes lancea) oil[8, 10] and from a urea fractionation of the same oil in supercritical (fluid) carbon dioxide. Multicomponent data of this kind have not been published previously[7], though Nilsson et al.[3] have reported similar results for menhaden oil ethyl esters by measuring the vapor-phase composition only.

1. Experimental

1.1 Phase equilibrium measurements

A combined gravimetric and volumetric method was used to determine the mutual solubilities of fish oil ethyl esters and carbon dioxide. The static cell is of the variable volume type, rated at 70 MPa and a working temperature range from 278 to 453 K. The pressure is measured with an accuracy better than ±30 kPa, and the

temperature within 0.2 K. Samples are withdrawn into high-pressure pycnometers. A gasometer is used to determine the volume of CO_2 at ambient conditions liberated from the pycnometer sample. The amount of FAEEs in the sample is determined from a mass balance. The apparatus and the experimental procedure have previously been described[5, 9].

1.2 Chromatographic analysis

The composition of the FAEEs in the samples was determined using a SFC-3000 (Carlo Erba Instruments, Milan, Italy) chromatograph in the gas chromatographic mode or a HP-5880A (Hewlett-Packard Company, Avondale, PA, USA) gas chromatograph, both with flame ionization detectors. The SFC-3000 chromatograph was equipped with a cold on-column injection port connected to a retention gap (1.5 m × 0.32 mm) and a HP-FFAP capillary column (25 m × 0.2 mm × 0.33 μm). The HP-5880A chromatograph employed the same capillary column, but with a manual split injection port using a split ratio of 1: 100. Further details of the chromatographic equipment are given elsewhere[5, 6].

1.3 Materials

The carbon dioxide was supplied by Linde AG. (München, Germany) having a stated purity of 99.995 %+. The ethyl esters from the fish oil of the sand launce
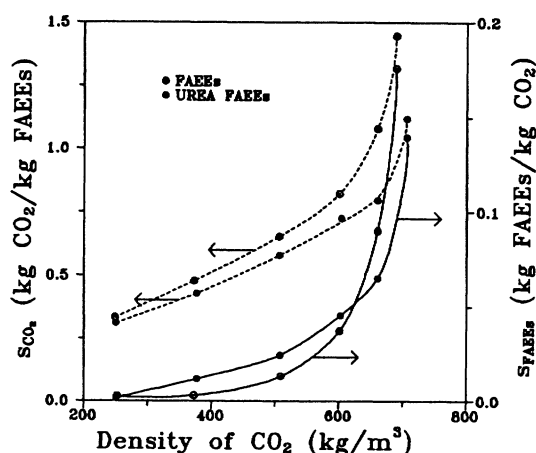
Fig. 1 Mutual solubility isotherms for the fish oil FAEEs and urea-fractionated FAEEs with carbon dioxide at 343.2 K as a function of pure CO_2 density

Table 1. Content (mass %) of some key components of the two FAEE mixtures

FAEE	Ordinary fish oil	Urea-fractionated fish oil
$C_{16:0}$	18.5	0.0
$C_{16:1\omega7}$	12.4	0.5
$C_{16:4\omega3}$	0.8	2.9
$C_{18:1\omega9}$	10.2	0.6
$C_{18:2\omega6}$	2.9	1.2
$C_{18:4\omega3}$	3.8	12.7
$C_{20:1\omega9}$	4.2	0.6
$C_{20:5\omega3}$	10.0	35.9
$C_{22:1\omega11}$	6.5	0.3
$C_{22:6\omega3}$	9.6	33.2

were supplied by Grindsted Products A/S (Århus, Denmark) with a stated purity of 98 %. The urea fractionation of the fish oil was performed by The Technological Laboratory, Danish Ministry of Fisheries (Lyngby, Denmark) by a method similar to that described by Haagsma et al.[1] The materials were used without further purification.
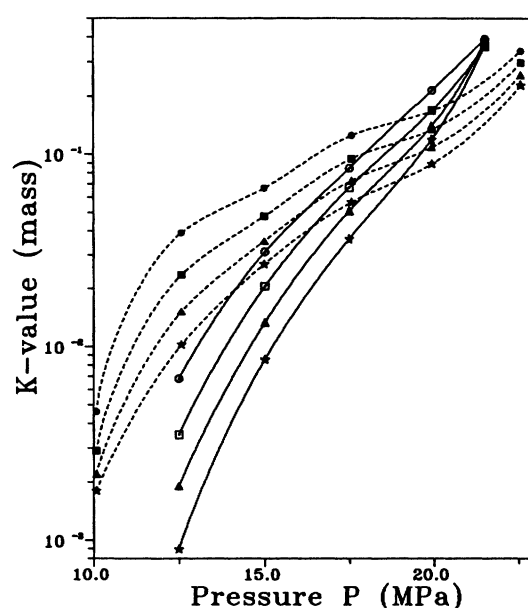
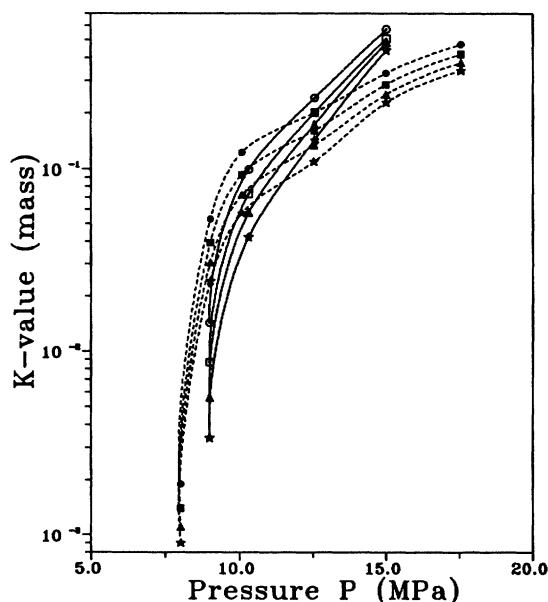## 2. Results and Discussion

2.1 Phase equilibrium and composition

The solubilities and partition coefficients of the ureafractionated FAEEs from sand launce were determined for a number of components at 313.2 and 343.2 K at pressures between 8 and 26 MPa. The results of the carbon dioxide + sand launce FAEE system have previously been published[8, 10].

The solubility isotherms of the two systems at 343.2 K are presented in **Fig. 1** as a function of the pure carbon dioxide density. Figure 1 displays a solubility behavior in carbon dioxide similar to that of other natural products like soybean oil[4].

The urea-fractionated mixture has a higher average molecular weight than the initial FAEE mixture, but consists mainly of poly-unsaturated FAEEs as shown in **Table 1**. The higher average molecular weight enhances

Fig. 2 K-values of: $\bigcirc$, $\bullet$ $C_{16:4\omega3}$; $\square$, $\blacksquare$ $C_{18:4\omega3}$; $\triangle$, $\blacktriangle$ $C_{20:5\omega3}$; $\star$, $\bigstar$ $C_{22:6\omega3}$ at 343.2 K in the mixtures of: — the fish oil FAEEs and - - - the urea-fractionated FAEEs

Fig. 3 K-values of: $\bigcirc$, $\bullet$ $C_{16:4\omega3}$; $\square$, $\blacksquare$ $C_{18:4\omega3}$; $\triangle$, $\blacktriangle$ $C_{20:5\omega3}$; $\star$, $\bigstar$ $C_{22:6\omega3}$ at 313.2 K in the mixtures of: — the fish oil FAEEs and - - - the urea-fractionated FAEEs

the critical pressure.

2.2 Partition coefficients

The K-values are given as the mass fraction, y in the vapor phase divided by the mass fraction, x in the liquid phase:

$$K_i = y_i / x_i \tag{1}$$

of the ethyl esters of hexadecatetraenoic acid, $C_{16:4\omega3}$, octadecatetraenoic acid, $C_{18:4\omega3}$, EPA, $C_{20:5\omega3}$, and DHA, $C_{22:6\omega3}$, from the two mixtures at 343.2 and 313.2 K are presented in **Figs. 2** and **3**, respectively. Three chromatographic analyses of each equilibrium phase

were performed.

The relative difference between the K-values of the components from the FAEE mixture presented in Fig. 2 becomes greater by reducing the pressure, but the absolute size of the K-values becomes very small corresponding to a decreasing solubility. The K-values of the components of the urea-fractionated FAEE mixture show a trend similar to that of the original FAEE mixture, but the influence of the increased critical pressure and the change in feed composition is obvious.

Conclusions

The partition coefficients of a natural mixture and a urea-fractionated mixture of fish oil FAEEs in supercritical carbon dioxide were measured. The K-values of the esters depend strongly on the operating pressure and temperature, the chain length, and the composition of the feed material.

The optimal extraction conditions in respect to solubility are at high pressures, while at low pressures the highest selectivity is achieved. The data presented indicates that the optimal extraction conditions at 343.2 K would be 16 to 18 MPa, corresponding to a CO_2 density of 500 to 615 kg/m^3.

Acknowledgments

Nomenclature

$C_{16:\,4\omega3}$	=	Hexadecatetraenoic acid ethyl ester	[-]
$C_{18:\,4\omega3}$	=	Octadecatetraenoic acid ethyl ester	[-]
$C_{20:\,5\omega3}$	=	Eicosapentaenoic acid ethyl ester	[-]
$C_{22:\,6\omega3}$	=	Docosahexaenoic acid ethyl ester	[-]
K	=	Partition coefficient	[-]
P	=	Pressure	[MPa]
s	=	Solubility	[kg/kg]
X	=	Overall mass fraction	[mass %]
x	=	Mass fraction in liquid phase	[mass %]
y	=	Mass fraction in vapor phase	[mass %]

\<Subscripts\>

i	=	component in sample
CO_2	=	carbon dioxide
FAEEs	=	fatty acid ethyl esters

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