CHEMISTRY LETTERS, pp. 1789-1792, 1985.

EFFECTS OF ENTRAINERS ON THE EXTRACTION OF TRIGLYCERIDES WITH SUPERCRITICAL CARBON DIOXIDE

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The extraction of triglycerides with supercritical carbon dioxide (SC-CO_2) was carried out at pressures of 9.8-27.0 MPa and temperatures of 313 K and 333 K. The addition of ethyl acetate to CO_2 was found to produce a supercritical fluid that had an efficiency for the separation of triolein from triolein-tristearin mixtures.

A supercritical fluid (SCF) method, as can be operated at a relatively low temperature, is suitable for extracting thermolabile substances. Its specific advantages have been extensively described and discussed.[1-3] In food and pharmacy industry, it is recently noticed as the extraction method for valuable materials contained in natural products.[4-8] Some kinds of fishes, including mackerel (Scomber Japonicus), contain significant amount of glycerides,[9] which are of pharmaceutical importance.[10,11] Therefore, extraction of these substances from fishes of low price is anticipated to be of great value.

The purpose of the present work is to investigate the solubility of such model substances as triolein, tristearin and their mixtures, which are constituents of fish oils, in SC-CO_2 and particular attention is drawn to the effects of entrainers on its extraction efficiency.

The commercial-grade carbon dioxide was used. Triolein and tristearin were obtained from Wako Pure Chemical Ind., Ltd. All chemicals were used without further purification. Schematic diagram of supercritical extraction apparatus is indicated in Fig. 1. Using a 0.1-L extractor maintained at 313 and 333 K, a weighed sample of the glycerides was extracted by

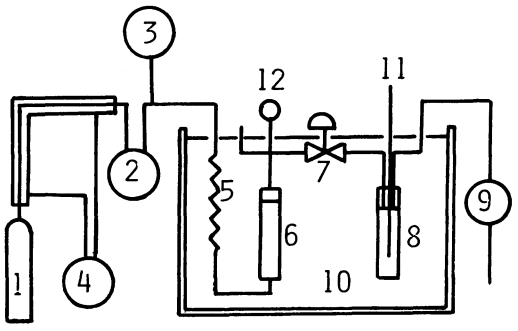


Fig. 1. Schematic diagram of supercritical extraction apparatus. 1: CO_2 cylinder, 2: High pressure pump, 3: High pressure pump for an entrainer, 4: Cooling circulator, 5: Preheater, 6: Extractor, 7: Back pressure regulator, 8: Reciever, 9: Flow totalizer, 10: Constant temperature bath, 11: Thermocouples, 12: Pressure gauge.

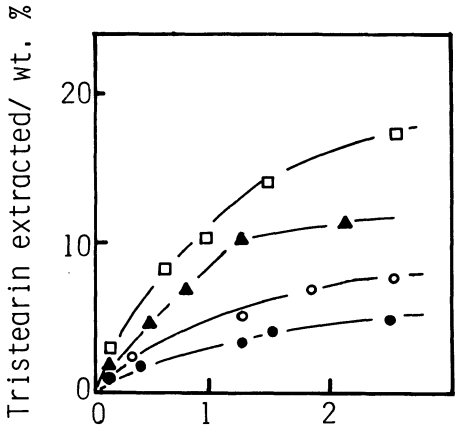


Fig. 2. Effects of pressure on the extraction efficiency of tristearin at 313 K.
●: 9.8 MPa, ○: 14.7 MPa, ▲:19.6 MPa, □: 27.0 MPa.

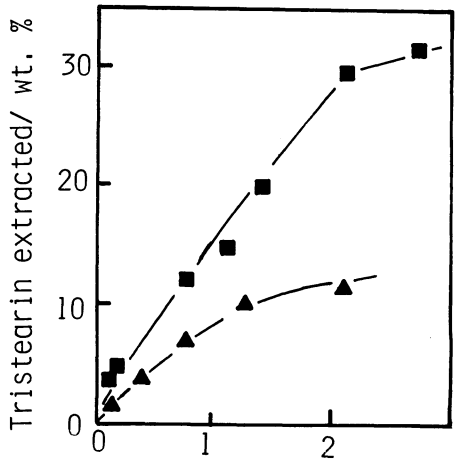


Fig. 3. Effects of temperature on the extraction efficiency of tristearin at 19.6 MPa.
▲: 313 K, ■: 333 K.

a supercritical fluid at a constant flow rate of 60 L/h. Liquid carbon dioxide and/or an entrainer were charged into each high-pressure pump, compressed to the desired pressure and then fed into the extractor. The effluent fluid was flashed to atmospheric pressure across a heated back pressure regulator and the components were collected in a trap. The amount collected was determined by weighing and the corresponding total volume of CO_2 used was measured with a flow tatalizer. The glycerides fractions were analyzed for each constituents. The glycerides were converted into methyl esters of fatty acids according to the usual method. The components of the esters were determined by a gas chromatography.

Figure 2 indicates.the effect of pressure on the extraction efficiency of tristearin at a temperature of 313 K. The weight of tristearin charged is 10 g. The solubility of tristearin in SC-CO_2 increases with the pressure. This effect is considered to be due mainly to interaction forces between molecules of tristearin and CO_2 induced by the increase of the density of CO_2. The rate of extraction remains nearly constant for its initial period of time, but then it gradually decreases under all the pressures examined.

The influence of temperature on the solubility of tristearin in SC-CO_2 at 19.6 MPa is shown in Fig. 3. The weight of tristearin charged is 10 g. The solubility at 333 K is remarkably greater and finally reaches 3.5 times than that at 313 K. In general, a rise in temperature at a constant pressure decreases the density of SC-CO_2, while it increases the vapor pressure of the low volatile components. Therefore, the results in Fig. 3 can be understood as follows: an increase of the vapor pressure contributes more to the increased solubility of tristearin, compared with a decrease of the density. It was reported that at high

pressures a rise in temperature caused an increase in the solubility of low volatile components in gaseous phase in a similar manner.[12] Further, the rate of extraction remains nearly constant similarly for its initial period of time, but then it decreases under the temperatures examined.

The relative volatilities of components to be extracted are little influenced by SCF used. Therefore, the addition of a third substance, which is the so-called entrainer, to the CO_2 is expected for increasing relative valatilities of components.[13] Namely, an entrainer is anticipated to have the function of rasing affinities between low volatile components and the gas. Figure 4 shows the extraction efficiency of triolein on the addition of some kind of solvents as an entrainer to the CO_2 at 19.6 MPa and 313 K. The weight of triolein charged is 10 g. The concentration of each entrainer in SCF is about 4 per cent by weight. As entrainers, ethanol, acetone, ether, ethylene dichloride and ethyl acetate are used. The addition of ethanol, acetone and ether to the CO_2 decreases the extraction efficiency of triolein, but the addition of ethyl acetate to the CO_2 greatly enhances the extraction efficiency of triolein. Further, the addition of ethylene dichloride to the CO_2 increases similarly the extraction efficiency of triolein, but as the extraction process progresses, the extraction efficiency becomes lower compared with that without an entrainer.

The triolein/tristearin mole ratios in the gaseous phase at 19.6

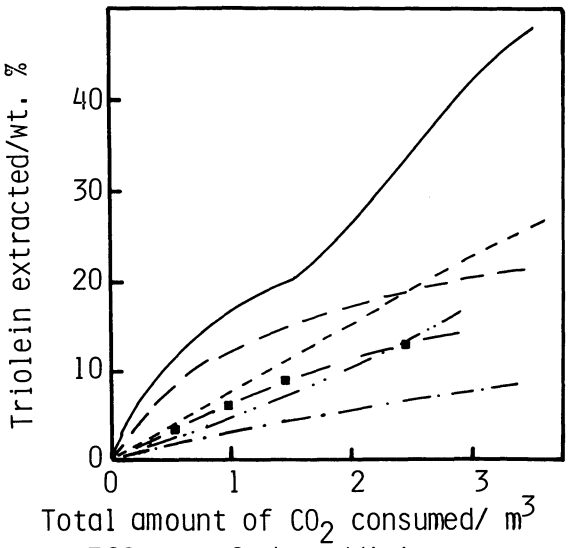
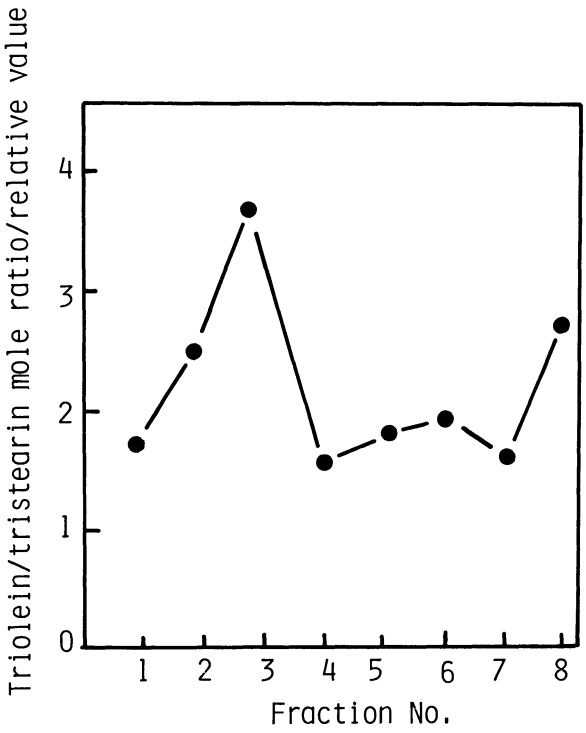


Fig. 4. Effects of the addition on entrainers on the extraction efficiency of triolein at 19.6 MPa and 313 K.
—·—:Ethanol, —··—:ether, —▪—:acetone, — —:ethylene dichloride, —:ethyl acetate, -----:without an entrainer.



Fi . 5. Separation efficiency of triolein with the CO_2-ethyl acetate relative to that with the CO_2 alone for a mixture of triolein and tristearin of 10 g each at 19.6 MPa and 313 K.

MPa and 313 K for the extraction of triolein-tristearin mixtures with the supercritical fluid of CO_2 and ethyl acetate are indicated in Fig. 5. A mixture of triolein and tristearin of 10 g each are used. The concentration of ethyl acetate in the supercritical fluid is about 4 per cent by weight. Evidently some fractionation takes place with the addition of ethyl acetate in the initial fractions. Separation efficiencies of triolein with ethyl acetate in the supercritical fluid relative to those with the CO_2 alone are larger than 1.5 over all fractions, especially, 2.5 for fraction 2; 3.6 for fraction 3. We have found that the addition of ethyl acetate to the CO_2 produces a supercritical fluid that has an enhanced extraction selectivity of triolein from triolein-tristearin mixture. However, the triolein/tristearin mole ratios in the latter part of the fractions do not greatly differ between both the extractions with and without the addition of ethyl acetate to the CO_2. It could be thought that since triolein is selectively extracted in the initial fractions, triolein content in the mixture decreases.

As described above, the supercritical fluid of CO_2 with ethyl acetate as entrainer can enhance both the extraction efficiency of triolein and the capacity for the fractionation of triolein from triolein-tristearin mixture. Furthermore, the fluid may enable some fractionation for glycerides of fatty acids of different degrees of saturation with the large number of carbon atoms.

References

1) L. G. Randall, Sep. Sci. Tech., 17, 1 (1982).
2) S. Saito, Petrotech, 5, 115 (1982).
3) K. Nagahama, Bunrigizyutsu, 11, 23 (1981).
4) Brit. Patent, 133651.
5) U. S. Patent, 3843824.
6) Brit. Patent, 1388581.
7) Japan Patent, 55-45391.
8) 8th Technical Seminar, The Society of Chemical Engineering, Japan, 1985.
9) P. G. Viswanathan Nair and K. Gopakuman, J. Food Sci., 43, 1162 (1978).
10) T. O. Lossonczy, Am. J. Clin. Nutr., 31, 1340 (1978).
11) A. Hirai, T. Hamazaki, T. Terano, T. Nishikawa, A. Tamura, A. Kumagai, and J. Sajiki, Lacent, 11, 1132 (1980).
12) Yu. Tsekhanskaja, M. B. Jomter, and E. V. Mashkina, Z. Fiz. Chim., 38, 2166 (1964).
13) S. Peter and S. G. Brunner, "Extraction with Supercritical Gases," ed by G. M. Schneider, E. Stahl, and G. Wilke, Verlag Chemie, Weinheim (1980), p. 145.

(Received August 7, 1985)