BINARY DIFFUSION COEFFICIENT OF CAROTENOIDS IN SUPERCRITICAL CARBON DIOXIDE AND COSOLVENTS

Mª Dolores Macías-Sánchez*, Casimiro Mantell, Miguel Rodríguez, Enrique J. Martínez de la Ossa Fernández
Department of Chemical Engineering, Food Technology and Environmental Technologies. Science Faculty. Avda. República Saharaui, s/n, 11510 - Puerto Real (Cádiz), Spain.* e-mail: dolores.macias@uca.es

INTRODUCTION

In pharmaceutical or food industries, natural antioxidant compounds have increasingly become significant. For example, beta-carotene has been identified as important antioxidants for human beings and plays a key role as provitamina [1-4]. Due to its properties, it is used as a colorant and a healthy food ingredient. Deficiencies of this compound in the human body may cause many diseases such as anemia, neurilogical dysfunction, and myopathies.

The use of the supercritical fluid extraction technique in the food industry is now commonplace due to the number of studies that have appeared in the last decade. The application of this technique to the production of food additives —such as aromas, antioxidants, and dyes— is highly competitive in comparison to conventional methods owing to the excellent properties shown by supercritical fluids. In the modelling and subsequent design of industrial processes, it is necessary to ascertain the values of the mass transfer parameters of the system. So binary diffusion coefficients are significantly important.

A wide range of techniques have been reported in the literature for the determination of the binary diffusion coefficient in supercritical fluids [5]. The most commonly used method is undoubtedly the chromatographic peak-broadening technique, which is also called Taylor's dispersion technique. This method is based on the work carried out by Taylor [6, 7] and later extended by Aris [8]. The application of this technique to the determination of the diffusion coefficient of solutes in CO2 at high pressure has been demonstrated in a large number of studies [9]. However, the application of this technique to the system CO2–cosolvent has not been developed to the same extent. There are only a few reports that describe the study of the diffusion coefficient of solutes, including acridine, benzene, phenanthrene, benzoic acid, in the system CO2–cosolvent [10–12].

In this study the objective was to measure the binary diffusion coefficient for beta-carotene by the chromatographic peak-broadening technique, using supercritical carbon dioxide.

MATERIALS AND METHODS

The diffusion coefficients of beta-carotene in the system carbon dioxide+ethanol were determined using a modified series 602 supercritical chromatograph from 'LEE

SCIENTIFIC'. The modifications consisted of replacing the original pump of the equipment with two syringe pumps supplied by 'ISCO' (Lincoln, Nebraska). This change was required for the determination of the diffusion coefficient of the solute in the carbon dioxide and ethanol system.

The main items are the two syringe pumps—models 100DX (for ethanol) and 260D (for CO2); a valve for the sample injections ('Rheodyne' serial number 7725i) equipped with an external loop of 20 ml volume; a coiled column for the diffusion of the solutes (30 m length, 0.25 mm internal diameter and 20 cm coil diameter); an oven to maintain the diffusion column at constant temperature—the oven had a maximum temperature of 450 °C; a variable wavelength UV detector (DIONEX model 'UV detector') with two cells of 60 and 200 ml, respectively, that were able to support a maximum pressure of 500 bar and operate at ambient temperature; and finally, a thermostated restrictor (ISCO) situated at the exit of the UV detector to regulate the flow rate. The body of the valve and the tip of the restrictor were maintained at 80 °C during all experiments.

It was prepared a disolution of 25 mg of beta-carotene by mL of chloroform for being injected. This is recommended by the bibliography [13, 14].

It was designed a number of experiments as it is presented by the table 1. The maximum pressure used was 400 bar because the equipment is not able to support higher pressure.

Table 1: Values of studied parameters in the determination of binary diffusion coefficient of beta-carotene.

Solvent	CO_2+5% ethanol
Temperature	40°C, 50°C and 60°C
Pressure	100, 200, 300 and 400 bar

CONCLUSION

The diffusion coefficient data for beta-carotene versus temperature in carbon dioxide with 5 % molar of ethanol, at different operating pressures, are plotted in figure 1.

At 100 and 200 bar it was not possible to obtain reproducibility in the values, so it can be said that the chromatographic peak-broadening technique is not suitable to obtain diffusivity values of beta-carotene at the studied temperatures.

The graph shows that the diffusion coefficient increases with temperature. This fact is in full agreement with the conclusions reported in the literature for the diffusion coefficients of a range of substances in supercritical CO_2 [13, 14, 15-20].

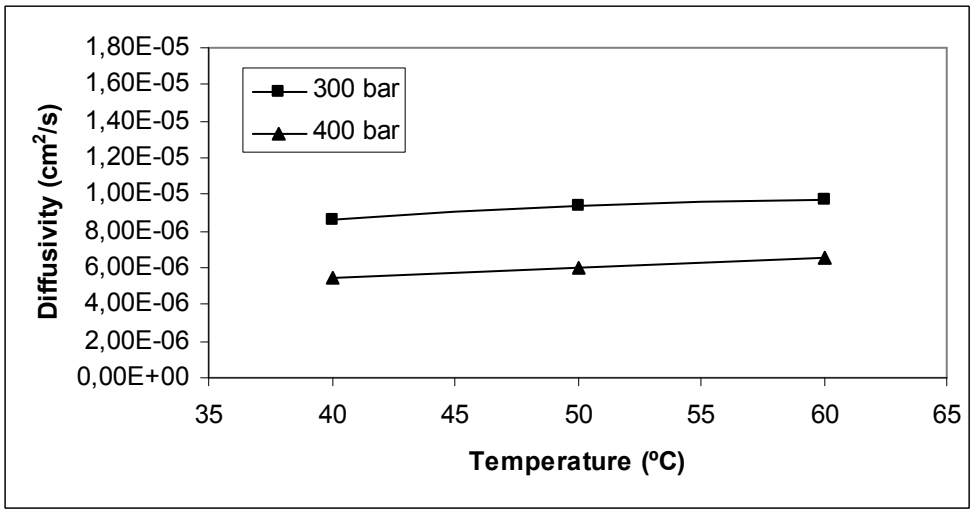

Figure 1: Variation of the diffusion coefficient of beta-carotene in the CO_2 + 5% ethanol system vs. temperature

REFERENCES

[1] Crevatin A., Zwahlen A., Kikic I., J. Supercritical Fluids Vol. 12, **1998**, p. 99.
[2] Mendes R.L., Nobre B.P., Coelho J.P., Palavra A.F., J. Supercritical Fluids Vol. 16, **1999**, p. 99.
[3] Baysal T., Ersus S., Starmans D.A.J., J. Agric. Food Chem. Vol. 48, **2000**, p. 5507.
[4] de Lucas A., Martínez de la Ossa E., Rincón J., Blanco M.A., Gracia I., J. Supercritical Fluids Vol. 22, **2002**, p. 221.
[5] Liong K.K., Wells P.A., Foster N.R., J. Supercritical Fluids Vol. 4, **1991**, p. 91.
[6] Taylor G., Proc. R. Soc. (London) Vol. 225, **1953**, p. 473
[7] Taylor G., Proc. R. Soc. (London) Vol. 219, **1954**, p. 186
[8] Aris R., Proc. Roy. Soc. (London) Vol. 235, **1956**, p. 67
[9] Suarez J.J., Medina I., Bueno J., Fluid Phase Equilibria Vol. 153-1, **1998**, p. 167.
[10] Smith S.A., Shenai V., Matthews M.A., J. Supercritical Fluids Vol. 3, **1990**, p. 175.
[11] Souvignet I., Olesik S.V., Anal. Chem. Vol. 70, **1998**, p. 2738.
[12] Sassiat P.R., Mourier P., Caude M.H., Rosset R.H., Anal. Chem. Vol. 59, **1987**, p. 1164.
[13] Funazukuri T., Kong C.Y., Kagei S., Fluid Phase Equilibria Vol. 194-197, **2002**, p. 1169.
[14] Funazukuri T., Kong C.Y., Kagei S., Journal of Supercritical Fluids Vol. 27, **2003**, p. 85.
[15] Smith S.A., Shenai V.M., Matthews M.A., J. Supercritical Fluids Vol. 3, **1990**, p. 175.
[16] Liong K.K., Wells P.A., Foster N.R., Ind. Eng Chem. Res. Vol. 30, **1990**, p. 1329.
[17] Liong K.K., Wells P.A., Foster N.R. J. Supercritical Fluids Vol. 4, **1990**, p. 91.
[18] Molero A. Tesis Doctoral, **1998**, Universidad de Cádiz.
[19] Souvignet I., Olesik S.V. Anal. Chem. Vol. 70, **1998**, p. 2738.
[20] Fu H., Coelho L.A.F., Mathews M.A. Journal of Supercritical Fluids Vol. 18, **2000**, p. 141.