



Study of the diffusion coefficient of solute-type extracts in supercritical carbon dioxide: Volatile oils, fatty acids and fixed oils



Alexis López-Padilla, Alejandro Ruiz-Rodríguez, Guillermo Reglero, Tiziana Fornari*

Institute of Food Science Research CIAL (CSIC-UAM) CEI UAM+CSIC, C/Nicolás Cabrera 9, Campus de Cantoblanco 28049 Madrid, Spain

ARTICLE INFO

Article history:

Received 13 August 2015

Received in revised form

17 November 2015

Accepted 18 November 2015

Available online 23 November 2015

Keywords:

Diffusion coefficients

Carbon dioxide

Correlation

Volatile oils

Fatty acids

Triglycerides

ABSTRACT

Supercritical carbon dioxide (SCCO₂) extraction is an innovative and efficient method to recover valued substances from vegetal materials. The diffusion behavior of the extract in the supercritical solvent is an important parameter to understand the mass transfer behavior of the process. In this work, experimental data from the literature were utilized to analyze the diffusivity of lipophilic chemically similar solutes in SCCO₂.

Substances with similar chemical structure, molecular weight and volatility, have also very similar diffusion coefficients, which are mainly determined by temperature, pressure and, in turn, by the corresponding physicochemical properties of the supercritical solvent (density and viscosity). Based on this premise, general correlations were derived to represent the diffusion coefficient of volatile oils, fatty acids and its esters, and fixed oils (triglycerides) in SCCO₂ as a function solely of pressure and temperature. The diffusion coefficients obtained were satisfactory compared with those calculated with theoretical and semi-empirical models from the literature, which require pure component parameters.

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1. Introduction

The supercritical fluid extraction (SFE) of vegetable materials is a semi-continuous process in which the high pressure solvent dissolves and extracts substances, while flowing through a fixed bed of particles of the solid raw material. This technology is being extensively applied using supercritical carbon dioxide (SCCO₂) to extract lipophilic substances such as carotenoids, fatty acids, fatty acid esters, volatile oils, fixed oils, antioxidants, etc. from a wide variety of plants and herbs, seeds, algae and microalgae, wastes and by-products of the agrochemical and food industry.

One important parameter to describe mass transfer in SFE is the diffusion coefficient of the different substances extracted (solutes) in SCCO₂. Most of experimental data so as predictive and/or correlative models were determined for binary systems [1,2]. Equations available in the literature, demand pure solute parameters (molar mass, critical volume, molar volume at normal boiling point, surface tension, etc.), the physicochemical properties of the supercritical solvent (density, viscosity, critical parameters) and sometimes specific correlation parameters. The higher the accuracy of the model, the higher the number of parameters required.

Wilke–Chang equation [3] is one of the most popular correlations to calculate the diffusion coefficient of a pure solute in SCCO₂, with average deviations around 10% for 600 experimental data points including different type of solutes [1]. Lately, Magalhães et al. [4] proposed two modified Stokes–Einstein equations and proved their accuracy using a large database comprehending extremely distinct molecules in terms of size, shape, molar mass and polarity. The global deviations achieved by these equations were lower than 7%. In general, temperature, solvent viscosity and solute size (introduced in equations via molar volume at normal boiling point and critical volume) were explicit parameters in this type of correlations. More recently, Magalhães et al. [5] developed novel correlations for the diffusion coefficient of a pure solute in liquids and supercritical fluids over wide ranges of temperature and density, which are based on expressions that depend only on temperature, and/or solvent density, and/or solvent viscosity. Also, the equations involved two fitting parameters specifically for each pure compound. The accuracy of these correlations was tested with a large database (539 binary systems and 8219 data points) with average deviation around 3%.

Even though good correlations are available in the literature to represent the diffusion of a pure solute in SCCO₂, supercritical plant extracts are in general multicomponent mixtures. Furthermore, depending on the vegetal material and the process conditions, the resulted extract may mainly contain certain type of solutes,

* Corresponding author. Tel.: +34 910017927.
E-mail address: tiziana.fornari@uam.es (T. Fornari).

Table 1
Diffusion coefficient correlations from the literature and pure component solute parameters required.

Equation		Parameters	Ref.
Scheibel	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = \frac{8.2 \times 10^{-8} T}{\mu_1 V_{bp,2}^{1/3}} \left[1 + \left(\frac{3V_{bp,1}}{V_{bp,2}} \right)^{2/3} \right]$	$V_{bp,2}$	[21]
Reddy-Doraiswamy	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = \beta x \frac{T \sqrt{M_1}}{\mu_1 (V_{bp,1} V_{bp,2})^{1/3}} \beta = 1.0 \times 10^{-8} (V_{bp,1}/V_{bp,2} \leq 1.5); \beta = 8.5 \times 10^{-8} (V_{bp,1}/V_{bp,2} > 1.5)$	$V_{bp,2}$	[22]
Lusis-Ratcliff	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = \frac{8.52 \times 10^{-8} T}{\mu_1 V_{bp,1}^{1/3}} \left[1.40 \left(\frac{V_{bp,1}}{V_{bp,2}} \right)^{1/3} + \left(\frac{V_{bp,1}}{V_{bp,2}} \right) \right]$	$V_{bp,2}$	[23]
Lai-Tan	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = 2.50 \times 10^{-7} \frac{T \sqrt{M_1}}{(10x\mu_1)^{0.688} V_{c,2}^{1/3}}$	$V_{c,2}$	[24]
Wilke–Chang	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = 7.4 \times 10^{-8} \left(\frac{T \sqrt{M_1}}{\mu_1 V_{bp,2}^{0.6}} \right); \left\{ \begin{array}{l} x = 1 \text{ for nonassociated solvents} \\ x = 2.6 \text{ for water} \end{array} \right.$	$V_{bp,2}$	[3]
Modified Stokes–Einstein Equation 1	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = A \left(\frac{T}{\mu_1} \right)^\alpha \frac{1}{(M_2 V_{bp,2})^\beta}$	$M_2, V_{bp,2}$	[4]
Modified Stokes–Einstein Equation 2	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = A \left(\frac{T}{\mu_1} \right)^\alpha \frac{1}{(M_2 V_{bp,2} \sigma_{bp,2}^{1/4})^\beta}$	$M_2, V_{bp,2}, \sigma_{bp,2}$	[4]
Modified Schiebel	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = A \left(\frac{T}{\mu_1} \right)^\alpha \frac{1}{V_{c,2}^\beta} \left[1 + \left(\frac{3V_{c,1}}{V_{c,2}} \right)^{2/3} \right]$	$V_{c,2}$	[20]
Modified Lusis–Ratcliff	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = A \left(\frac{T}{\mu_1} \right)^\alpha \left[\beta \left(\frac{V_{c,1}}{V_{c,2}} \right)^{1/3} + \left(\frac{V_{c,1}}{V_{c,2}} \right) \right]$	$V_{c,2}$	[20]
Modified Wilke–Chang	$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = A \left(\frac{T}{\mu_1} \right)^\alpha \frac{1}{V_{c,2}^\beta}$	$V_{c,2}$	[20]

1: solvent (CO₂); 2: solute; T: temperature; P: pressure; μ : viscosity; σ : surface tension; V_{bp} : molar volume at normal boiling point; M: molar mass; V_c : molecular critical volume; x: association parameter in Wilke–Chang equation; A, α , β and γ : specific constants in the corresponding correlations.

such as volatile oils, fatty acid esters or triglycerides. Information in the literature regarding the diffusion behavior of these multicomponent extracts is scarce. In this work, the diffusivity of these families of lipophilic compounds in SCCO₂ was analyzed and represented.

Volatile oil plant extracts comprise monoterpenes and sesquiterpenes with normal boiling points from 150 °C to 230 °C and molecular weights are in the range of 100–250 g mol⁻¹. On the other hand, fatty acid chains in vegetal oils are between C13 and C21 carbon number. Their molecular weights are around 220–350 g mol⁻¹ and have very low volatility (normal boiling points around 250–450 °C). Similarly to fatty acids, triglycerides or fixed oils have high normal boiling points (low volatility) but considerable larger molecular weights, around 750–950 g mol⁻¹.

Significant different diffusion coefficients at a given temperature and pressure were measured for volatile oil compounds, fatty acids and triglycerides. For example, the diffusion coefficient of citral at 313 K and 20 MPa is $8.10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is rather similar to the diffusion coefficient of other volatile oil substances such as eugenol ($7.69 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) or α -pinene ($8.90 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) [6–8]. Nevertheless, at the same conditions of pressure and temperature, these values are $6.13 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $6.06 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $5.45 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for respectively, linolenic, oleic and docosahexaenoic acids [9–11], i.e., around 40% lower than those of volatile oil compounds. Regarding the diffusion coefficient of fixed oils at 313 K and 20 MPa, the value reported for e.g., triarachidonin is $3.96 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (around 30% lower than those corresponding to fatty acids) [12].

Thus, substances of the same chemical family, with similar molecular mass and volatility, have very similar diffusion coefficients. Yet, substantial differences were observed among the diffusion coefficient of a volatile oil, a fatty acid and a triglyceride. Based on these observations, three general and simple correlations were derived in this work to estimate the diffusion coefficient of type-extracts, namely (i) volatile oils, (ii) fatty acids and derived fatty acid esters and (iii) fixed oils, as a function solely of pressure and temperature. The equations obtained are based on the regression of experimental data from the literature. A total of 30 different solute-SCCO₂ binary systems (1191 data points) were considered to assess the capability of the correlations developed and deviations lower than 13% were obtained.

2. Overview of diffusion coefficient correlations

The diffusion coefficient of a solute in a supercritical fluid (D_{i-SCF}) is affected by the size and shape of the solute, the intermolecular interaction with the supercritical solvent and the temperature and pressure conditions. In general, solutes with large molecular mass and solutes which can present chemical interactions diffuse more slowly. Additionally, pressure and temperature define solvent density and viscosity, which have an important effect on the solute diffusion. In general, the diffusion coefficient increases with increasing temperature at constant pressure, being the effect less important at higher pressures. And with respect to pressure, D_{i-SCF} decreases with increasing pressure. High pressure means high solvent density, and if solvent density increases diffusion becomes more difficult due to an increased number of molecular collisions. Furthermore, intermolecular interactions also increase because the average intermolecular distance is reduced as density increases.

Predictive and correlative models and equations available in the literature follow the above observed experimental behavior of diffusion coefficients with respect to temperature, pressure, solute and solvent properties. Table 1 show several mathematical expressions derived from the Stokes–Einstein formula which were frequently used in the literature. In general, the supercritical fluid properties in these equations are viscosity, molecular weight, molar volume at normal boiling point and critical volume. Particularly, the supercritical solvent viscosity is a strategic variable in all equations given in Table 1, connecting the effect of temperature and pressure on the solute diffusion coefficient. Despite the goodness of correlations available in the literature, all equations demand pure component solute physicochemical parameters or even fitting parameters, which are problematic to estimate in the case of multicomponent and complex SFE extracts.

Recently, Magalhães et al. [5] investigated the effect of the supercritical solvent viscosity and density by defining several equations in which the term D_{i-SCF}/T depends explicitly on solvent viscosity, on solvent density and both viscosity and density. All equations demand two specific fitting parameters for each pure compound and, in general, presented excellent correlative capability. Particularly, the equation:

$$D_{12} \text{ (cm}^2 \text{ s}^{-1}\text{)} = T \left(a \cdot \rho + \frac{b}{\mu} \right) \quad (2.1)$$

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