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Measurement and modelling of tracer diffusivities of gallic acid in liquid ethanol and in supercritical CO_2 modified with ethanol

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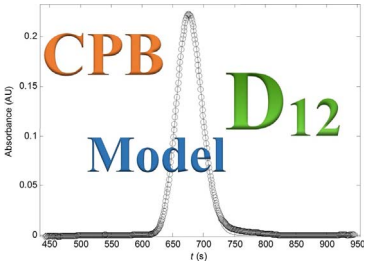
GRAPHICAL ABSTRACT



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ABSTRACT

The tracer diffusion coefficients, D_{12}, of gallic acid in liquid ethanol and in supercritical carbon dioxide (SC-CO_2) modified with 16 mol.% ethanol were measured using the chromatographic peak broadening technique of Taylor-Aris. The diffusivity in ethanol ranged $0.485 \times 10^{-5} - 0.905 \times 10^{-5} cm^2 \cdot s^{-1}$ (303.15–333.15 K and 1–100 bar) and in SC-CO_2/ethanol $3.256 \times 10^{-5} - 4.978 \times 10^{-5} cm^2 \cdot s^{-1}$ (313.15–333.15 K and 150-250 bar). The dependencies of D_{12} upon temperature, pressure and Stokes–Einstein coordinates were examined in detail. With respect to modelling, lower deviations were achieved in both systems by: four 2-parameter correlations of Magalhães *et al.* (error 0.9–3.0%;); the 1-parameter $TLSM_d$ model (5.8% and 2.9% of error); and the 2-parameter Dymmond-Hilbrand-Batchinski (DHB) expressions (5.7% and 1.6% of error). The Wilke-Chang correlation cannot be applicable, due to consistent overpredictions of 133.0% (gallic acid/ethanol) and 114.0 % (gallic acid/SC-CO_2/ethanol).

1. Introduction

The diffusivity can be defined in terms of a system response to a concentration disturbance, and relates the flow of particles with the resulting concentration gradients [1,2]. It is a transport property of great interest not only to study the structure and thermophysical behaviour of fluids, to capture information at microscopic level with regard to the interactions between molecules, but also for practical engineering applications [1–6]. The design of equipment depends on the physical properties of fluids, since an appropriate knowledge of equilibrium data together with viscosity, thermal conductivity and diffusion coefficients is required for modelling processes involving momentum, heat and mass transfer [2,7], such as separation units and chemical reactors, particularly in the case of multiphasic systems.

Gallic acid (3,4,5-trihydroxybenzoic acid) is a natural compound obtained from the hydrolysis of tannins [8], and possesses anti-inflammatory [9], antioxidant [10], antifungal [11]) and carcinogenic [8] properties. It has proven to be one of the components with the highest bioactivity, enabling the fight against amyloid fibrils (fibril protein), which result from the aggregation of misshapen proteins that

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Nomenclature

AARD	Average absolute relative deviation
B_{DHB}	Parameter of the interaction solute-solvent in the DHB model
BPR	Back pressure regulator
C^{app} (z,t)	Calculated average concentration of solute
C^{exp} (t)	Solute concentration at exit column
CO_2	Carbon dioxide
CPB	Chromatographic Peak Broadening method
D	Dispersion coefficient
D_{12}	Tracer diffusion coefficient of solute 2 through solvent 1
De	Dean number, $De = Re/\sqrt{\xi}$
DHB	Dymond-Hildebrand-Batchinski
H	Height of theoretical plate
k_B	Boltzmann constant, $k_B = 1.380658 \times 10^{-23} J \cdot K^{-1}$
$k_{12,d}$	Binary interaction diameter
L	Length of the column
m	Total mass of solute injected
M	Molecular weight
M_{12}	Reduced molar mass
N_{av}	Avogadro's number, $N_{av} = 6.022 \times 10^{23}\ mol^{-1}$
NDP	Number of data points
NP	Number of parameters
P	Pressure
P_c	Critical pressure
r	Radial coordinate
R	Inner column radius
R_c	Tube coil radius
Re	Reynolds number
R_g	Universal gas constant, $R_g = 8.3144 J \cdot mol^{-1} \cdot K^{-1}$
Sc	Schmidt number
S_{10}	Asymmetric factor (ratio between peak half-widths at 10% peak height)
SC—CO_2	Supercritical carbon dioxide
t_i	Time at 10% peak height in the fitting method
T	Absolute temperature
T_{bp}	Normal boiling temperature of the component i
T_c	Critical temperature
TLSM	Tracer diffusion coefficient model of Liu, Silva and Macedo
$\bar{u}$	Average linear velocity
V_c	Critical molar volume
V_D	Maximum packaging volume of the solvent in the DHB model
V_m	Molar volume
$V_{TC,bp,2}$	Molar volume of the solute at its normal boiling point estimated by the method of Tyn and Calus
$W_{0.607}$	Peak half-width measured at 60.7% of total peak height
y_i	Molar composition of the component i
z	Axial coordinate

Greek letters

ε	Root mean square deviation (rms)
λ	Wavelength
μ_1	Solvent viscosity
ξ	Curvature ratio
ρ_1	Solvent density; solvent number density
σ_i	Molecular diameter of component i
$\sigma_{LJ,i}$	Lennard-Jones diameter of component i
ϕ	Dimensionless solvent association factor in the Wilke-Chang equation
ω	Acentric factor

Subscripts

1	Solvent
2	Solute
12	Binary
bp	Property evaluated at normal boiling point
c	Critical property
eff	Effective hard sphere diameter
i	Component i
LJ	Lennard-Jones
mix	Mixture

Superscripts

*	Reduced quantity
calc	Calculated value
exp	Experimental value

deposit up in the tissues of the human body organs. Hence it plays an important role in treating diseases like Alzheimer and Parkinson [12].

Gallic acid is present in plants such as green tea and black tea [13], pomegranate peel [14], oak bark [15], and grape seed extracts [11]. This compound and its ester derivatives are important chemicals used in both pharmaceutical and food industries [14,16], from which one may cite the synthesis of *trimethoprim* (antibiotic used for infections) and propyl gallate, respectively [14].

In this work, tracer diffusion coefficients, D_{12}, of gallic acid in pure ethanol and in supercritical CO_2 (SC-CO_2) modified with ethanol were measured and modeled. The usage of ethanol as SC-CO_2 modifier is important under the context of biorefinery, taking into account that small amounts of a polar entrainer are frequently introduced to increment solubility and improve selectivity in separations [17]. However it is recognized the lack of diffusivity data in the case of multicomponent mixtures [18].

The diffusivities of the binary system gallic acid/ethanol were determined at 303.15, 313.15, 323.15 and 333.15K, and pressures of 1, 20, 40, 60, 80 and 100bar. In the case of the supercritical ternary system gallic acid/CO_2/ethanol, the measurements were carried out at 313.15, 323.15 and 333.15 K, and pressures of 150, 200 and 250 bar. In both cases the chromatographic peak broadening (CPB) method of Taylor-Aris [19–21] was applied. A preliminary study of the most adequate detection wavelength was performed, and the influence of temperature, pressure, and viscosity on the obtained diffusion coefficients is also discussed.

The structure of the article is as follows: In Section 2, a brief theoretical background of the lab methodology and modelling approaches is presented; in Section 3, the chemicals, equipment and experimental procedure are described; Section 4 is devoted to discuss the experimental and calculated results, while the main conclusions are compiled in Section 5.

2. Theoretical background

2.1. Chromatographic peak broadening (CPB) method

The CPB method originally derived by Taylor and Aris [22–25] can be applied to measure diffusion coefficients (D_{12}) of solutes (component 2) at infinite dilution in pure or mixed solvents (component or pseudo-component 1) [21,26–29]. When a pulse of a solute is injected into a laminar flow of solvent through a capillary tube of circular cross section, that pulse will broaden due to the combined action of axial convection and radial molecular diffusion. The approximate average