



Diffusion coefficients of L-menthone and L-carvone in mixtures of carbon dioxide and ethanol

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ABSTRACT

The molecular diffusion coefficients of L-menthone and L-carvone in supercritical carbon dioxide (SCCO₂) and carbon dioxide containing 5 and 10 mol% ethanol as a modifier were measured by the Taylor–Aris chromatographic peak broadening (CPB) method over the ranges of temperature from 308.15 to 338.15 K and pressure from 15 to 30 MPa. It was found that the correlation relationships between diffusion coefficients and the temperature, pressure, viscosity, and density, such as the linear correlation between the D_{12} and ρ , and between the D_{12} and T/η , which were valid in binary systems, were also suitable for ternary systems of carbon dioxide containing modifier. The diffusion coefficients in modified SCCO₂ decreased with increasing the ethanol mole fraction due to the chemical association between the two solutes and ethanol. Of several models used to predict experimental data in pure carbon dioxide, the two models of Funazukuri–Ishiwata–Wakao and He–Yu–1998 were the best with the AAD less than 3.2%. Furthermore, the models of modified Wilke–Chang, Scheibel, Reddy–Doraiswamy, Lusi–Ratcliff, Hayduck–Minhas, Tyn–Calus, and Lai–Tan overestimated the diffusion coefficient in ethanol modified SCCO₂ with the AAD values increasing with the percentage of ethanol, which were probably due to the increase of the volume of solvation sphere as a true diffusion unit with the percentage of ethanol. Moreover, the free volume model of Dymond is good for predicting the experimental data in pure carbon dioxide and ethanol modified SCCO₂ with the AAD values range from 3.21 to 1.90%.

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1. Introduction

Diffusion coefficients are important physical properties to evaluate mass transfer rates in designing, scaling up and optimizing reactors and separators for extraction or chromatography with supercritical fluids. Therefore, binary diffusion coefficients for single solute in supercritical fluids have been studied extensively. Several methods such as the solid dissolution technique, photon correlation spectroscopy (PCS), light scattering, the nuclear magnetic resonance technique, Stefan tube, and the Taylor–Aris chromatographic peak broadening (CPB) method can be used to measure diffusion coefficients in supercritical carbon dioxide [1]. Of these methods the CPB method has been claimed to be relatively accurate and less time-consuming [2], which is suitable for determining diffusion coefficients for non- and weak-polar liquid compounds.

Usually, a small amount of modifier can be added to carbon dioxide to increase the solubility of solutes and improve the selectivity and resolution in separation. However, the studies on diffusion

coefficients in multicomponent systems are relatively scarce. Some researchers measured the diffusion coefficients of some solutes such as benzene [3], benzoic acid, phenanthrene and acridine [4], malvidin 3,5-diglucoside [5] in the CO₂ and methanol mixture. Olesik and Woodruff [6] measured the diffusion coefficients of benzene and m-cresol in two supercritical fluids (carbon dioxide and propane) containing acetonitrile, propylene carbonate, and water. Lee and Olesik [7] measured the diffusion coefficients of benzene and anthracene in the CO₂–methanol–H₂O mixture. Souvignet and Olesik [8] compared the diffusion coefficients of benzene, anthracene, m-cresol, and p-nitrophenol in the CO₂–ethanol–H₂O mixture. Funazukuri et al. [9,10] reported the diffusion coefficients of linoleic acid methyl ester, Vitamin K3, and indole in the mixture of carbon dioxide and n-hexane. González et al. [11] measured the diffusion coefficients of 2-nitroanisole, 1,2-dichlorobenzene, and tert-butylbenzene in carbon dioxide containing methanol and n-hexane. Suarez-Iglesias et al. [12] determined the diffusion coefficients of benzyl acetate, 2-phenylethyl acetate, 3-phenylpropyl acetate, and dibenzyl ether over the full concentration range of the CO₂ and ethanol mixture. However, in those papers, the studies on correlation relationships between diffusion coefficients and the temperature, pressure, viscosity, density in system of CO₂–modifier are relatively scarce. At present, there are not any models in ternary

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Nomenclature

a_p	fitting constant of Eqs. (8) and (9)
a_T	fitting constant of Eqs. (10)–(12)
a_η	fitting constant of Eqs. (17) and (18)
a_ρ	fitting constant of Eqs. (14)–(16)
AAD	average absolute deviation
b_p	fitting constant of Eqs. (8) and (9)
b_T	fitting constant of Eqs. (10)–(12)
b_η	fitting constant of Eqs. (17) and (18)
b_ρ	fitting constant of Eqs. (14)–(16)
B	fitting constant of Eq. (21)
c	fitting constant of Eq. (13)
CPB	chromatographic peak broadening
d_{coil}	coiled diameter of the dispersion column (m)
d_{tube}	inner diameter of the dispersion column (m)
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
$D_{c,22}$	self-diffusion coefficient of CO_2 at the critical point ($\text{m}^2 \text{s}^{-1}$)
De	Dean number
D_{12}	binary diffusion coefficient at infinite dilution ($\text{m}^2 \text{s}^{-1}$)
H	theoretical plate height (m)
L	length of the dispersion column (m)
M	molar mass (kg mol^{-1})
P	pressure (MPa)
r_0	inner radius of the dispersion column (m)
RHS	Rough–Hard–Sphere
Sc	Schmidt number
SE	Stokes–Einstein
t_r	retention time (s)
T	absolute temperature (K)
U_0	average linear velocity of the mobile phase (m s^{-1})
V	molar volume ($\text{m}^3 \text{mol}^{-1}$)
V_D	minimum free volume of diffusion ($\text{m}^3 \text{mol}^{-1}$)
$W_{1/2}$	half-height peak width(s)
x	mole fraction
ΔH_V	heat of vaporization (kJ mol^{-1})

Greek letters

η	viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
ρ	density (kg m^{-3})
σ^2	peak variance (m^2)
$\varepsilon_{LJ/k}$	Lennard–Jones energy parameter
φ	association factor

Subscripts

b	normal boiling point
c	critical point
i	component i
LJ	Lennard–Jones
VdW	van der Waals
1	solute
2	solvent

Superscripts

*	atmospheric pressure condition
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system of supercritical carbon dioxide containing modifier. Hence, it is essential to measure diffusion coefficients in the mixtures of carbon dioxide and modifier to develop accurate models.

Terpenoids as the major components in essential oil are fat-soluble and heat-labile compounds. Extraction, fractionation and purification of these compounds can be accomplished by supercrit-

ical fluid extraction and chromatography, which have advantages over the conventional liquid extraction process with organic solvents due to relatively low operation temperature, nontoxicity, and almost no contact to oxidant. Literature data on binary diffusion coefficients of terpenoids in supercritical carbon dioxide are limited. Only those for linalool [13], citral and β -limonene [14], and pinene [15] are available. L-Menthone is the major component of essential oil extracted from peppermint and Schizonepeta tenuifolia Briq [16,17], and L-carvone is the major component of essential oil extracted from Mentha spicata and caraway [18]. They are monoterpenoids and primarily used as flavouring in foods and beverages and as fragrance in detergents and cosmetics. Moreover, they have some biological activities, such as sedative, anti-fungal, anti-inflammation and anti-tumour properties. Therefore, in this study, infinite dilution diffusion coefficients of L-menthone and L-carvone in pure and ethanol modified CO_2 were measured by the Taylor–Aris chromatographic peak broadening (CPB) method over the ranges of temperature from 308.15 to 338.15 K and pressure from 15 to 30 MPa. The influences of temperature, pressure, density, and viscosity on the diffusion coefficients in the pure and ethanol modified SCCO_2 were discussed. It is found that the correlation relationships between diffusion coefficients and the temperature, pressure, viscosity, and density, which are valid in binary systems, are also suitable for ternary systems. The diffusion coefficients of solute in binary mixtures of supercritical carbon dioxide and solute characterize the nature of solute–carbon dioxide interactions, whereas the diffusion coefficients of solute in ternary mixtures include the influence of solute–modifier interactions as well [11]. It is for this reason that the modifiers can affect diffusion coefficients of the solute. Therefore, in present study, determining diffusion coefficients in ternary systems with ethanol as a modifier can help to get an insight into the effect of interactions among solute, modifier, and SCCO_2 on the diffusion coefficients of the solute in the microscopic aspect. Moreover, the validity of several available models based on the Stokes–Einstein (SE) equation and Rough–Hard–Sphere (RHS) equation was also investigated with the experimental data in the pure and ethanol modified SCCO_2 .

2. Theoretical background

The diffusion coefficients were measured by the Taylor–Aris chromatographic peak broadening (CPB) method. When a pulse of solute is injected into a solvent moving in laminar flow through a capillary tube or column, this pulse will disperse due to the combined action of axial convection and radial molecular diffusion. After a sufficient residence time, the pulse of solute becomes a Gaussian-like curve at the end of tube. The variance of the concentration profile may be written as follows:

$$\sigma^2 = \frac{2D_{12}L}{U_0} + \frac{r_0^2 U_0 L}{24D_{12}} \quad (1)$$

In chromatography, the theoretical plate height H is defined as:

$$H = \frac{\sigma^2}{L} \quad (2)$$

Substituting Eq. (1) into Eq. (2), the D_{12} can be expressed as:

$$D_{12} = \frac{U_0}{4} \left[H - \left(H^2 - \frac{r_0^2}{3} \right)^{1/2} \right] \quad (3)$$

H can be calculated from the following expression proposed by Cloete et al. [19]:

$$H = \frac{LW_{1/2}^2}{5.54t_r^2} \quad (4)$$

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