# Molecular dynamics and phenomenological modeling of experimental diffusivities in supercritical mixtures

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## 1. Introduction

With the chemical industry moving towards a greener future, alternatives to conventional harmful organic solvents are required. Supercritical fluids such as supercritical $CO_2$ (SC-$CO_2$), pure or modified with a cosolvent, are widely used alternatives, especially in processes involving mass transfer, as for example, in extraction, multiphase reactors, and chromatography[1]. In extraction processes, the cosolvent allows to fine tune the solvent affinity towards specific solutes[2]. For more sustainable processes it is of utmost importance to obtain a complete understanding of transport properties, *e.g.*, diffusivities, for a large set of chemical compounds with industrial relevance for optimizing their extraction.

In this work, the diffusivities of gallic acid[3] and eucalyptol[4] in SC-$CO_2$ modified with ethanol will be presented and extensively analyzed with state-of-the-art phenomenological models, such as the predictive Multi-LSM and the classical Wilke-Chang[5] equations. These data will be further compared with diffusivities calculated from trajectories derived from classical molecular dynamics (MD) simulations.

## 2. Materials and Methods

The experimental $D_{m,i}$ measurements were carried out using the well-known chromatographic peak broadening (CPB) method[6] between 303.15 K and 333.15 K, and from 150 bar to 275 bar. Both gallic acid and eucalyptol were measured in SC-$CO_2$ modified with ethanol. Molar fractions of 16 mol.% or 8 mol.% of ethanol were used for gallic acid and eucalyptol, respectively.

The MD simulations have been carried with the general-purpose simulation software package GROMACS[7], using the canonical ensemble (NVT), which considers constant number of molecules, $N$, temperature, $T$, and system volume, $V$. The Elementary Physical Model (EPM2) force field was used for SC-$CO_2$ while the remaining species considered the optimized potentials for liquid simulation – all atoms (OPLS-AA) parameters. The $D_{m,i}$ was computed from the long-time limit of the mean square displacement obtained by the Einstein relationship.

## 3. Results and discussion

The experimentally determined $D_{m,i}$ values of gallic acid in $CO_2$ modified with 16 mol.% ethanol at $T$ = 313.15 –333.15 K and $P$ = 150–250 bar were between $3.3\times10^{-5}$ cm$^2$ s$^{-1}$ and $5.0\times10^{-5}$ cm$^2$ s$^{-1}$. As for eucalyptol in SC-$CO_2$ modified with 6 mol.% ethanol at $T$ = 303.15–333.15 K and $P$ = 150–250 bar the $D_{m,i}$ values were in the range $5.5\times10^{-5}$ – $1.0\times10^{-4}$ cm$^2$ s$^{-1}$. The dependencies on temperature, pressure, free-volume, and Stokes-Einstein coordinates were analyzed for both systems (Figure 1). The data were modeled with the previously mentioned equations, and the average absolute relative deviation (AARD) achieved for the Wilke-Chang model was 156.42 % for gallic acid and 5.31 % for

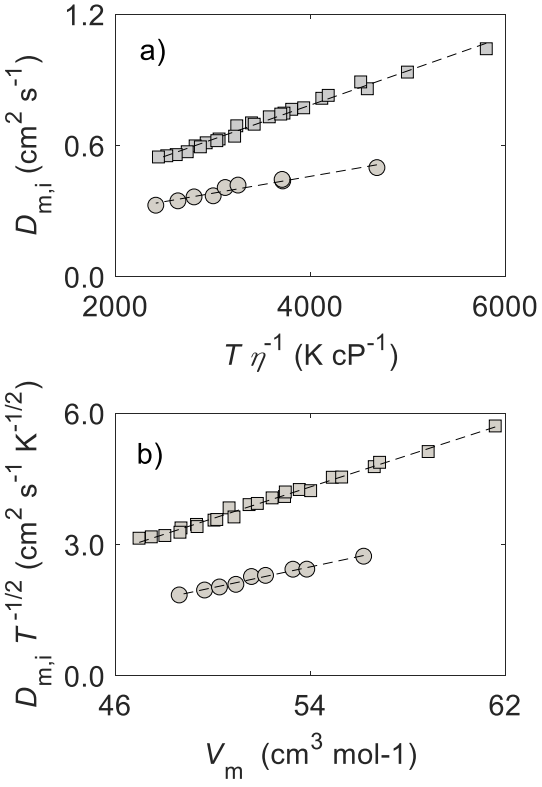


**Figure 1.** Stokes-Einstein (a) and free-volume representations (b) of gallic acid (●) and eucalyptol (■) diffusivities in supercritical mixture of $CO_2$ and ethanol.

eucalyptol. As for the Multi-LSM, the AARD values were lower than the ones achieved by the Wilke-Chang equation, with values of 23.14 % and 3.02 % respectively.

Regarding MD simulations, they have been carried out at the limit conditions of the experimental measurements in order to validate a newly developed procedure for $D_{m,i}$ estimation in supercritical mixtures of $CO_2$ and ethanol.

## 4. Conclusions

Experimental diffusivities of gallic acid and eucalyptol in $CO_2$ modified with ethanol under supercritical conditions have been successfully measured using the CPB method. The data was modelled with the Multi-LSM and Wilke-Chang equations. For the eucalyptol diffusivities, the results achieved by both equations were equivalent while in the case of the gallic acid there is a clear advantage in using the Multi-LSM equation despite being more complex. The MD simulations attained good results, being a successful tool for the computer calculation of these diffusion coefficients in alternative to the phenomenological models.

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