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Molecular dynamics simulation for self-diffusion coefficients of ginger bioactive compounds in subcritical water with and without ethanol

Nor Ilia Anisa[a,b], Noor Azian Morad[a,b,*], Yoshio Iwai[c], Mohd Halim Shah Ismail[d]

[a] Malaysia–Japan International Institute of Technology, Universiti Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia
[b] Center of Lipids Engineering and Applied Research (CLEAR iKohza), Universiti Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia
[c] Department of Chemical Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
[d] Department of Chemical and Environmental Engineering, Universiti Putra Malaysia, 43300 Serdang, Malaysia

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ABSTRACT

Molecular dynamics simulation was used to calculate the self-diffusion coefficients of ginger bioactive compounds (6-gingerol and 6-shogaol) in subcritical water with the presence of ethanol as an entrainer (0–10 mol%) at temperatures from 373.15 to 453.15 K. The all-atom optimised-potentials (OPLS/AA) were employed for the ginger bioactive compounds and ethanol. The extended simple point charge (SPC/E) model was adopted for water molecules. The self-diffusion coefficients increase from 1.00×10^{-9} to 2.70×10^{-9} m^2/s with increasing temperature from 353.15 to 453.15 K. The self-diffusion coefficients also increase from 1.71×10^{-9} to 3.00×10^{-9} m^2/s with increasing percentage of ethanol from 0 to 10 mol% at 413.15 K. The radial distribution functions between the ginger bioactive compounds and subcritical water (solvent) illustrate a weak interaction between the ginger bioactive compounds and solvent. The interaction increases with addition of ethanol as entrainer.

1. Introduction

The extraction of bioactive compounds from natural plants receive a great attention from researchers and industries due to market demands [1]. Solvent extraction is one of the conventional techniques to extract the bioactive compounds. However, this conventional technique which requires extended extraction duration and high production cost due to solvent recovery causes the researchers to use other alternative techniques. Subcritical water extraction is an environment friendly technique of utilizing water in its liquid state under pressurized condition at a temperature below the critical point. The subcritical water extraction is known as hot compressed water extraction as the process operates at elevated temperature (above boiling point of water at 373.15 K and below its critical value at 647.65 K and 22.09 MPa). The key point of operating at such elevated temperature is due to the decreasing polarity of the solvent hence improving suitability to extract non-polar compounds. Previous studies also introduce entrainer to subcritical water extraction in order to tune to the desired polarity of the solvent [2,3]. Ethanol is commonly used as an entrainer since it has low toxicity. Thus the contamination of ethanol in foods could be neglected. The extraction from natural plants using this technique has been applied on ginger [4], jabuticaba skin [5], and barberry fruits [6]. Despite the increasing demands in bioactive compounds, the application of hot compressed water technique for natural extract is still scarce.

The phenomena of extraction are important for optimising the recovery, which is commonly described through a mathematical study [7]. The phenomena of extracting the solute in solid matrix to bulk solvent involve mass transfer through solid–liquid interface. The transportation occurs due to the concentration gradient that is primarily controlled by effective diffusion coefficient, D_{eff} [8]. The D_{eff} is determined by taking into account the porosity, ε and tortuosity, τ of solid matrix [7]. In determining D_{eff}, the diffusion coefficient, D is firstly identified. The diffusion coefficient, D describes the movement of solute from the outer surface of solid matrix into the bulk of solvent, i.e. the movement of solute in solvent. In a complex matrix such as plant matrix, the effective diffusion coefficient, D_{eff} is by the following equation [9]:

$$D_{\mathrm{eff}} = \frac{\varepsilon}{\tau} D \quad (1)$$

Abbreviations: OPLS/AA, all-atom optimised-potentials; SPC/E, extended simple point charge; MD, molecular dynamics; NPT, isothermal–isobaric ensemble; NVT, canonical ensemble; MSD, mean squared displacement; SD, standard deviation; ANOVA, analysis of variance; RDF, radial distribution function.

* Corresponding author at: Center of Lipids Engineering and Applied Research (CLEAR iKohza), Universiti Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia. Fax: +60 3 26154317.

E-mail address: azian.morad@gmail.com (N.A. Morad).

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Nomenclature

Roman letters

V_1,V_2,V_3	Coefficients in the Fourier series (parameter in Eq. id=6#(2))
f_1, f_2, f_3	Phase angles (parameter in Eq.id=6#(2))
q	Charge, ^{-}e (parameter in Eq.id=6#(3))
D	Self-diffusion coefficient, (m^2/s)
D_{eff}	Effective diffusion coefficient, (m^2/s)
N	Number of time series
r	Position vector of molecule, (Å)
$g(r)$	Radial distribution function

Greek letters

φ_i	Dihedral angle
ε	Energy parameter, (kJ/mol) (parameter in Eq.id=6#(3))
σ	Size parameter, (Å) (parameter in Eq.id=6#(3))
$\rho(r)$	Local number density, (m^{-3})
ρ	Bulk number density, (m^{-3})

Subscripts

i, j	Sites
a, b	Molecules

As claimed by Takeuchi [8], the range of diffusion coefficients is 10^{-9}–10^{-10} m^2/s for food solutes in different types of solvent. Balachandran et al. [10] determined the diffusion coefficient of 6-gingerol in supercritical carbon dioxide as 7.20×10^{-9} m^2/s using an equation and D_{eff} by fitting concentration gradient against time. The calculated values of diffusion coefficients for gallic acid, catechin and procyanidin from grape pomace at 313.15 K are 2.22×10^{-9}, 1.42×10^{-9} and 0.79×10^{-9} m^2/s, respectively [11]. Srinivas et al. [12] found the determination of diffusion coefficients is difficult at temperatures higher than 352.15 K but still the diffusion coefficients can be predicted by Stokes–Einstein model.

A few techniques such as experimental, molecular dynamics simulation, empirical or theoretical approaches are used to determine the diffusion coefficients [13]. The experimental data such as by using Taylor dispersion can be found in the literature [13–17]. The literature data are limited to lower temperatures and mostly for smaller compounds only. The empirical or theoretical method often fails to predict reliable values of the diffusion coefficients especially when it dealing with highly polar or involving hydrogen-bonding [13].

Molecular dynamics (MD) simulation can be used to calculate the self-diffusion coefficients of solutes in solvents [18] and is a powerful tool with unique resolution down to Angstrom scale with picosecond calculation time [19]. However the application of MD simulation for food based solutes in water as solvent is limited at ambient temperature and to our knowledge it has never been applied to bioactive compounds at high temperature. Delgado [20] studied the effects of temperature on the self-diffusion coefficients of organic compounds such as 2-naphthol, benzoic acid, salicylic acid, camphor, and cinnamic acid in water below its boiling point using MD simulation. In another study of using MD simulation, Fioroni et al. [21] investigated the solvation phenomena of a tetrapeptide in water at ambient temperature. Paul and Patey [22] investigated the self-diffusion coefficients for urea in water also at ambient temperature and pressure. The other papers using MD simulation investigated the self-diffusion coefficients of methane in water at elevated temperatures from 296.15 to 650.15 K [23] and phenol in water in the range of 298.15–773.17 K [17].

In this work, MD simulation is employed to calculate the self-diffusion coefficients of the most abundant bioactive compounds in ginger extract; 6-gingerol and 6-shogaol in subcritical water with and without ethanol. The radial distribution functions which describe the interaction between the bioactive compounds and solvent are also studied. To the best of our knowledge, there are no previous data for the self-diffusion coefficients and radial distribution functions of larger compound + water and compound + water/ethanol at subcritical conditions. Thus, from this paper, the data can be expected to contribute to design the extraction parameters, especially when the entrainer (ethanol) is added in water at subcritical conditions.

2. Computational details

2.1. Intermolecular potential

The all-atom optimised-potential liquid simulation (OPLS/AA) has been used for describing the intermolecular potentials of phenol, ethanol and the ginger bioactive compounds (6-gingerol and 6-shogaol) since this force field is suitable for the organic and biomolecular systems [24]. The united-atom optimised-potential liquid simulation (OPLS/UA) was employed for CH_3 of anisole group in ginger bioactive compounds. This is because of the charge for CH_3 of anisole group are different from that for CH_3 of paraffins, and the charges of CH_3 of anisole group for OPLS/AA are not available in the literature. The SPC/E model [25] was adopted for water molecules.

The torsional energies were calculated by the following equation [24]:

$$E_{\text{torsion}} = \sum_i \frac{V_{1,i}}{2}[1 + \cos(\varphi_i + f_{1,i})] + \frac{V_{2,.i}}{2}[1 - \cos(2\varphi_i + f_{2,i})] + \frac{V_{3,i}}{2}[1 + \cos(3\varphi_i + f_{3,i})] \tag{2}$$

where ϕ_i is the dihedral angle, V_1, V_2 and V_3 are the coefficients in the Fourier series and f_1, f_2 and f_3 are the phase angles. The bond lengths and angles in the molecules were fixed to the equilibrium values to reduce the computation time.

The non-bonded interactions were explained by a combination of Coulomb with Lennard–Jones as follows [24]:

$$E_{ab} = \sum_i^{\text{on}a} \sum_j^{\text{on}b} \left[\frac{q_i q_j e^2}{r_{ij} + 4\varepsilon_{ij}} \left(\frac{{\sigma_{ij}}^{12}}{{r_{ij}}^{12}} - \frac{{\sigma_{ij}}^{6}}{{r_{ij}}^{6}} \right) \right] f_{ij} \tag{3}$$

where E_{ab} is the interaction energy between molecules a and b for sites i and j, respectively. The q, ε, σ and r are the charge, the energy parameter, the size parameter, and the site distance, respectively. Modification of Eq. (1) has been made by Jorgensen et al. [24] to authorize the usage of the same parameters for inter- and intramolecular interaction. Thus, the scaling factors f_{ij} for all cases is 1.0, otherwise $f_{ij} = 0.5$ for 1,4-interaction [24]. Lorentz–Berthelot (LB) mixing rules were applied in determining the mixing pair of sites [26]:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{4}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \tag{5}$$

The structure of ginger bioactive compound (6-gingerol) is shown in Fig. 1. The parameters and the charges are listed in Table 1.

2.2. Operating conditions

Molecular dynamics simulation was performed by the software SCIGRESS ME Compact 2.0 (Fujitsu Ltd., Japan). The simulation cell