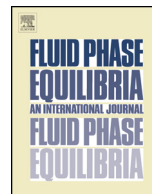




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Molecular dynamics simulations of the diffusion coefficients of light *n*-alkanes in water over a wide range of temperature and pressure

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ABSTRACT

The diffusion coefficients of the first five *n*-alkanes in water at infinite dilution have been obtained from molecular dynamics simulations over a wide range of temperatures at 0.1 MPa and additionally, for methane and *n*-butane, at higher pressures up to 200 MPa. Comparison with available experimental data provides confidence in the accuracy of the predictions using the TIP4P/2005 model for water and the TraPPE force field for *n*-alkanes. Additionally, a Speedy–Angell-type phenomenological equation that captures the pressure and temperature behavior of the methane and *n*-butane is provided which can be used for engineering calculations. Furthermore, it is shown that the diffusion coefficients of methane and *n*-butane obey the Stokes–Einstein equation. Finally, the molecular structure of water–*n*-alkane mixtures is examined.

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1. Introduction

Diffusion coefficients of the binary mixtures of water (H₂O) with light hydrocarbons are important for the study and design of numerous geological [1], petroleum [2–4] and chemical [5,6] engineering and environmental [7] applications. Light hydrocarbons are produced massively in the subsurface [8] either biogenically [9,10] or thermogenically [8], depending on the prevailing temperature and pressure conditions. Upon accumulation they can migrate upwards, as a result of buoyancy forces. If interstitial H₂O is encountered by the light *n*-alkanes, either during the production or the migration stages, dissolution and subsequent diffusion will take place. In oceanic sediments the migrating gases can encounter the hydrate stability zone (provided that the pressure and temperature conditions are appropriate), where they can remain trapped in the form of solid clathrate hydrates [11]. If hydrate formation is not possible, eventually the migrating gas can reach the ocean floor. The competition between advection and diffusion in the H₂O column will determine whether the light *n*-alkanes will eventually escape to the atmosphere [12]. Such processes can have a significant

effect to the global climate since methane (CH₄) is a strong greenhouse gas.

The diffusion coefficients of short *n*-alkane molecules in H₂O for temperatures up to approximately 400 K and atmospheric pressures have been repeatedly measured experimentally during the last 5 decades [13–21]. More recently, the diffusion coefficients of CH₄ in H₂O for temperatures up to 473 K and pressures up to 40 MPa have been measured by Guo et al. [22] by means of Raman spectroscopy. The authors proposed a Speedy–Angell power-law-type [23] correlation for the calculation of the diffusion coefficient of infinite diluted CH₄ in H₂O. Mutoru et al. [24] correlated the available experimental results and proposed a novel phenomenological model for the prediction of the mutual diffusion coefficients of the H₂O–CO₂ mixture, that performs equally well for binary mixtures of H₂O with light *n*-alkanes (CH₄, C₂H₆ and C₃H₈). A thorough discussion of various semi-empirical correlations, based either on the kinetic theory of Chapman–Enskog [25,26] or on the Stokes–Einstein hydrodynamic theory [27], is reported by Cussler [28], and Taylor and Krishna [29].

The experimental determination of thermodynamic properties and transport coefficients is usually costly and difficult to perform, especially when measurements at high pressures and/or temperatures are required. Alternative approaches like atomistic simulations have been proven reliable techniques for estimating thermodynamic or transport properties at temperature and

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pressure conditions that are experimentally unfeasible. To this purpose, various simple, yet efficient force-fields, for the representation of H₂O (as is discussed in detail in the reviews [30,31]), and *n*-alkane [32–35] molecules were developed.

Despite the significant effort that was put into the prediction of phase equilibria of mixtures of H₂O with *n*-alkanes [36–44] by many research groups, only one molecular simulation study exists in the literature for the diffusion coefficient of CH₄ in H₂O, while none for higher *n*-alkanes. Specifically, Shvab and Sadus [45] have performed an extensive series of molecular dynamics (MD) simulations for the calculation of a number of thermodynamic properties and diffusion coefficients of the H₂O–CH₄ mixture for various CH₄ compositions. The authors reported extended calculations that include the pressure–temperature behavior, isothermal and adiabatic compressibility, thermal pressure and expansion coefficients, heat capacity, speed of sound, and Joule–Thomson and diffusion coefficients.

From the above, it becomes clear that a comprehensive study of the diffusion coefficients of short *n*-alkane molecules in H₂O over the range of temperatures and pressures relevant to industrial and geological applications is still needed. The main objective of the current study is to report an extensive series of MD simulations for the diffusion coefficients of CH₄, C₂H₆, C₃H₈, *n*-C₄H₁₀, and *n*-C₅H₁₂ in H₂O at a wide range of temperatures (up to 623.15 K) and pressures (up to 200 MPa). The structure of this paper is as follows: In Section 2, a short description of the intermolecular potentials and the simulation methods used is given. In Section 3, a brief analysis of the molecular structure of H₂O–*n*-alkane mixtures is presented followed by presentation of the results for the diffusion coefficient and a comparison with the available experimental data, that are limited to pressures up to 40 MPa for the case of H₂O–CH₄, and to 0.1 MPa for all the other mixtures considered in the current study. Additionally, we present a phenomenological model for the calculation of the diffusivities of *n*-alkanes in H₂O as a function of pressure and temperature, which can be used for engineering calculations. Finally, we conclude with a brief summary of our findings.

2. Model and methods

2.1. Intermolecular potentials

For the representation of H₂O the TIP4P/2005 [46] force field was used. The TIP4P/2005 is a rigid 4-site model in which a Lennard–Jones (LJ) sphere is fixed on the oxygen site. The electrostatic contributions are implemented by positive partial charges located on each hydrogen atom and a negative partial charge fixed on an “M-site”, located on the bisector of the H–O–H angle at 0.1546 Å from the oxygen atom. For the *n*-alkanes, the TraPPE [32] model was employed. Since the TraPPE force field is based on a united atom (UA) description, different pseudoatoms are used to describe CH₄, CH₃ and CH₂ groups. The non-bonded interactions between the pseudoatoms separated by more than three bonds or belonging to different molecules were calculated by the LJ potential:

$$U^{\text{LJ}}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

where ε_{ij} , σ_{ij} , and r_{ij} are the LJ well depth, the LJ size, and the distance for the atoms i and j , respectively. The non-bonded interactions between H₂O molecules were calculated as the sum of the LJ repulsion–dispersion and the Coulombic interactions:

$$U^{\text{coul}}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (2)$$

where ε_0 is the vacuum permittivity.

The LJ parameters for the interactions between atoms belonging to different molecules were calculated using the standard Lorenz–Berthelot combining rules [47]:

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \quad (3)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (4)$$

In all cases studied, the pseudoatoms are connected by bonds with a fixed length and the bond angle bending is given by a harmonic potential:

$$U^{\text{bend}}(\theta) = \frac{k_\theta}{2}(\theta - \theta_0)^2 \quad (5)$$

where k_θ and θ_0 are the force constant [48] and the equilibrium angle, respectively. The 1–4 bonded interactions are described by the OPLS united atom torsional potential [35]:

$$U^{\text{tors}}(\phi) = c_0 + c_1[1 + \cos\phi] + c_2[1 - \cos2\phi] + c_3[1 + \cos3\phi] \quad (6)$$

where ϕ is the dihedral angle and c_i are constants. The values of the parameters of the force fields used in the present study are listed in Table 1.

2.2. Computational details

MD simulations were performed in the isothermal–isobaric (NPT) ensemble using the GROMACS open-source molecular simulation platform (version 4.6.5) [49,50]. A cubic box with periodic boundary conditions in all directions was used. The leap-frog integration scheme was used with a time step of 1 fs, while the temperature and pressure were maintained constant using the Nosé–Hoover [51,52] and Parrinello–Rahman [53] methods respectively. The coupling constants of the thermostat and barostat were set to 1 ps. Long-range Coulombic interactions were handled using the particle mesh Ewald (PME) method [54,55]. The cut-off distance was set to 14 Å, both for the LJ potential and the real space components of the PME summations, while tail corrections were applied for energy and pressure.

An equilibration period of 5 ns was carried out for each system examined, prior to any diffusion coefficient calculations. Subsequently, for each system, 25 production runs 2 ns long were performed. Monitoring the energy, pressure, and temperature during the production period showed that they were well stabilized, with small fluctuations present, typical for any MD simulation. The molecular trajectories were sampled every

Table 1

Force-field parameters for H₂O and *n*-alkanes examined in this study. The parameters between unlike atoms were calculated by the combining rules of Eqs. (3) and (4). Methyl (CH₃) and methylene (CH₂) pseudoatom parameters are common in C₂H₆, C₃H₈, *n*-C₄H₁₀, and *n*-C₅H₁₂. k_B is the Boltzmann constant.

TIP4P/2005		TraPPE	
H–O–H (°)	104.52	I _{C–C} (Å)	1.54
l _{O–H} (Å)	0.9572	θ _O (°)	114
σ _{O–O} (Å)	3.1589	σ _{CH₄} (Å)	3.73
σ _{H–H} (Å)	0	σ _{CH₃} (Å)	3.75
ε _{O–O} /k _B (K)	93.2	σ _{CH₂} (Å)	3.95
ε _{H–H} /k _B (K)	0	ε _{CH₄} /k _B (K)	148
q _O (e)	–1.1128	ε _{CH₃} /k _B (K)	98
q _H (e)	0.5564	ε _{CH₂} /k _B (K)	46
		k _θ /k _B (K/rad ²)	62,500
		c ₀ /k _B (K)	0
		c ₁ /k _B (K)	355.03
		c ₂ /k _B (K)	–68.19
		c ₃ /k _B (K)	791.32

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