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Estimation of Diffusion Coefficient of Benzene/Hexane Mixtures by Molecular Dynamics Simulation

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ABSTRACT

Molecular dynamics simulations have been performed in this study to predict the diffusion coefficient of benzene in hexane and vice versa by Materials Studio software. COMPASS force field has been applied to the system for optimization of the structures of benzene and hexane molecules. To model and calculate the van der Waals and electrostatic potential energies, a group-based summation method has been utilized. In order to predict the diffusion coefficient, firstly the simulation time and the force field have been optimized. In all simulations, Ewald and Atom-based summation methods were employed to calculate electrostatic and van der Waals potential energies. The optimized simulation times for the diffusion of benzene in hexane with the mole fraction of 0.2, and the diffusion coefficient of hexane in benzene with the mole fraction of 0.8, have been obtained to be 35 and 25 ps, respectively. In addition, the best force field to predict the diffusion coefficient has been identified to be *"Pcff"*.

Introduction

The diffusion in liquid mixtures is an important characteristic of complicated mass transfer processes and its accurate measurement is essential to design mass transfer equipment such as distillation, adsorption and extraction columns [1-3]. Diffusion is one of the most important properties among transport properties of binary mixtures [4, 5]. Bullerjahn et al. [6] presented a rigorous framework to obtain reliable estimates of the self-diffusion coefficient and its statistical uncertainty from molecular dynamics (MD) simulation.

Diffusion is characterized by diffusion coefficient of solute in solvent. Translational diffusion coefficients are routinely estimated from molecular dynamics simulations. Linear fits to mean squared displacement (MSD) curves have become the standard that is used in the MD simulations of different samples from simple liquids to complex biomacromolecules. Nonlinearities in MSD curves at short times are handled with a wide variety of practices, such

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as partial and piece-wise fitting of the data. Moradi et al. [7] predicted methane diffusion coefficient in water by molecular dynamics simulation to compare experimental and simulated results. The results showed that the model and the field force model which were used in MD were valid compared to experimental results.

Although many measured pressure dependent diffusion coefficients have been reported for one component liquids, not many studies have been devoted to the measurement of pressure and temperature dependent diffusion coefficients for two-component liquid mixtures [8-11]. In one study , Taheri et al. [12] estimated the diffusion coefficient of CH_4 molecules in graphene oxide by MD calculations. Hence, it was observed that, as the temperature increases, the calculated diffusion coefficient increases. In organic chemistry lots of molecules can form mixtures with alkanes, such as benzene that can completely mix with low n-alkanes at the atmospheric pressure. Therefore, the n-hexane/benzene system could be considered as an almost ideal solution. Experimental measurements of a solution diffusion are time consuming and expensive.

Also the empirical models, which are proposed to calculate the diffusion coefficient of liquids, cannot predict this parameter for all one-component liquid systems [7, 13]. The quality of a model can be obtained by comparing it with experimental data. A smaller difference between the predicted and the measured diffusion values infers more reliability for the model. In the recent years, the calculation of the diffusion coefficient via molecular dynamics simulation has been vastly investigated due to the higher accuracy of these methods.

MD method is based on the analysis of the interactions between atoms and molecules using Newton’s equations of motion during a specific period [14-16]. Taheri et al. [12] measured the slope of the MSD of CH_4 in the adsorbent versus time plot which used Einstein equation. Also, Lui et al. [17] demonstrated an approach for computing Fick diffusivities directly from equilibrium MD simulations for a ternary chloroform-acetone-methanol liquid mixture. They provided a way to predict multicomponent diffusion coefficients in liquids based on a consistent molecular picture and matched the simulation results with experiments.

By calculating the inter-particle forces and potential energies, MD models can provide the systems’ physical properties such as diffusivity, absorption, etc. [7, 18-22]. Jeeja Rani, et al. [23] used material studio software to calculate total energy of adsorbate and adsorbent and to recognize the type and interaction between materials. They visualized different configuration of the metal surface and inhibitor to demonstrate the best region of adherence between the three important fatty acids in CRE on mild steel surface.

Moreover, Barani Pour et al. [24] investigated the structural and dynamical properties of glucose-based Deep Eutectic Solvents (DESs) at different molar ratios. To understand effective interactions in the eutectic mixture formation they used the interaction energies, structural properties like atom–atom radial distribution functions (RDFs), the hydrogen-bonding network and spatial distribution functions (SDFs). They investigated on thermo-physical and dynamical properties. Dynamical properties were evaluated by calculating the MSD and the velocity autocorrelation function (VACF) in MD.

The purpose of this research is to investigate the possibility of application of MD simulations in calculation of the molecular diffusion coefficient of benzene in hexane and vice versa at various mole fractions. The simulation results are compared with the experimental results at the temperature and pressure of 298.15 K and 1 bar, respectively. In this study, firstly, the optimized simulation time is obtained for the mixture of benzene in hexane with two mole fractions of 0.2 and 0.8, and then the effect of the optimized force field is investigated in mixtures with mole fractions of 0.2, 0.4, 0.6 and 0.8.

Molecular Dynamics Simulation

To compute the diffusion coefficient of benzene/hexane mixtures, BIOVIA Materials Studio 2017 software has been used to perform the MD simulation. The potential energies of benzene and hexane molecules have been optimized before the cell construction, and then the optimized structures are used to construct the simulation box and to compute the diffusion coefficient. After generating the optimized molecular structures, COMPASS force field has been used for amorphous cell optimization. Ewald and Atom-based summation methods have been implemented to model the van der Waals and electrostatic potential energies at the temperature and pressure of 298.15 K and 1 bar, [7]. According to Zhao et al. [25], the cell dimension has an insignificant effect on the prediction of the diffusion coefficient. Therefore, the total number of benzene and hexane molecules are considered to be 100. Afterwards, the constructed cell was optimized at the temperature range of 200 – 400 K. For the system to reach the equilibrium state, first, the canonical ensemble (NVT) with scale velocity thermostat has been applied to the system for 50 ps. Finally, the micro-canonical ensemble (NVE) has been implemented. To calculate the diffusion coefficient, Eq. 1 (mean squared displacement (MSD)) has been used as follows [26]:

$$D = \lim_{t\to\infty} \frac{1}{6N_\alpha t}\langle\sum_{i=1}^{N}|r_i(t) - r_i(0)|^2\rangle \tag{1}$$

where N_a is the number of molecules in the system and r_i (t) is the displacement vector of the *i-th* molecule at time t. To calculate the diffusion coefficient (D), the MSD graph versus time is drawn and the best trend line ($y = ax + b$) is fitted to the data, and the diffusion coefficient (D) is computed from Eq. 2 [7, 27]:

$$D = a/6 \tag{2}$$

Moreover, for quantitative comparison of the MD predicted results with the experimental ones, the percent error has been defined as:

$$Erorr(\%) = \left(\frac{D_{AB}^{Exp} - D_{AB}^{sim}}{D_{AB}^{Exp}}\right) \times 100 \tag{3}$$

where D_{AB}^{Exp} and D_{AB}^{Sim} are the experimental and MD predicted diffusion coefficients of solute A in solvent B.

Results and Discussion

Optimum Simulation Time

To calculate the optimum simulation time, by bringing the cell to the equilibrium state using canonical ensemble (NVT) for calculating the simulation time, the microcanonical ensemble (NVE) has been used for the system with 5 to 40 ps simulation time, and the diffusion coefficient (D) has been calculated via Eq. 1. The variation of experimental and MD predicted diffusion coefficient at different simulation times has been represented for two mixtures of benzene in hexane (with benzene mole fraction of 0.2) and hexane in benzene (with benzene mole fraction of 0.8) in Figs. 1a and 1b, accordingly. To compute D at any simulation time, five runs have been executed and the average value has been reported. Regarding both Figs. 1a and 1b, it can be seen that increasing the simulation time gives rise to predicted values closer to the experimental ones. Predicted benzene/hexane D represents the least error of 23% at 35 ps, while predicted hexane/benzene diffusion coefficient represents the least error of 0.14% at 25 ps. As a result, thereafter, simulation times of 35 and 25 ps have been considered for the computation of diffusion coefficients at benzene/hexane and hexane/benzene systems, respectively.

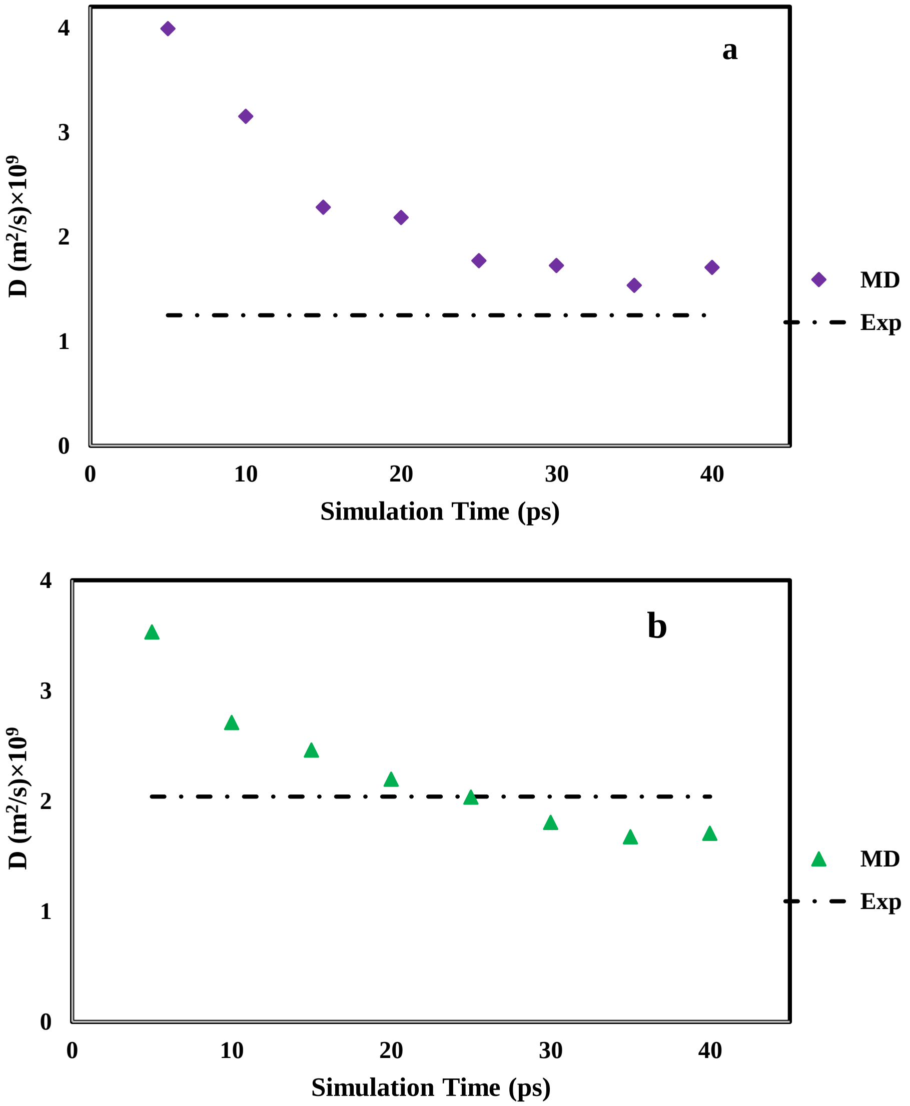
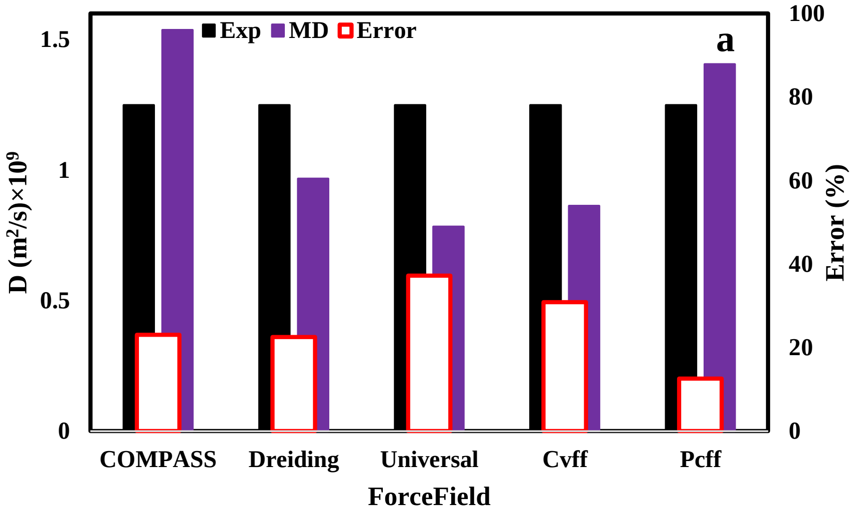


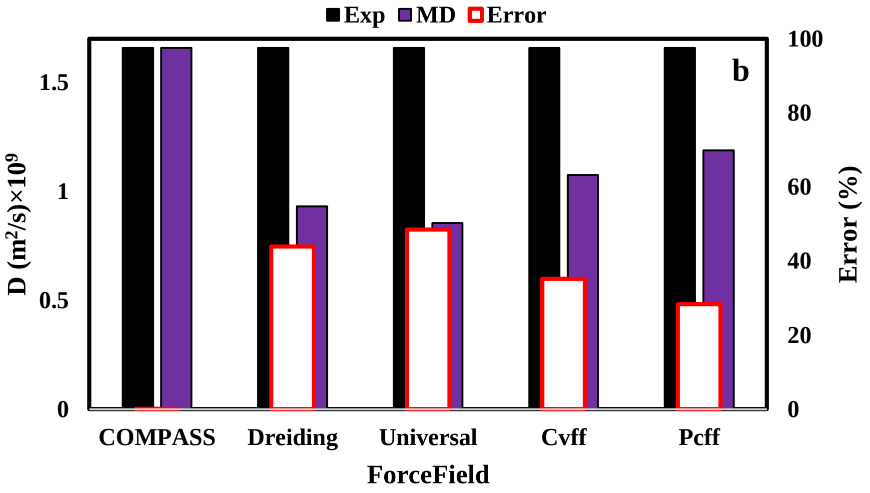
Fig. 1. Experimental and predicted MD diffusion coefficients of a) benzene in hexane with mole fraction of 0.2, and b) hexane in benzene with mole fraction of 0.8, at different simulation times

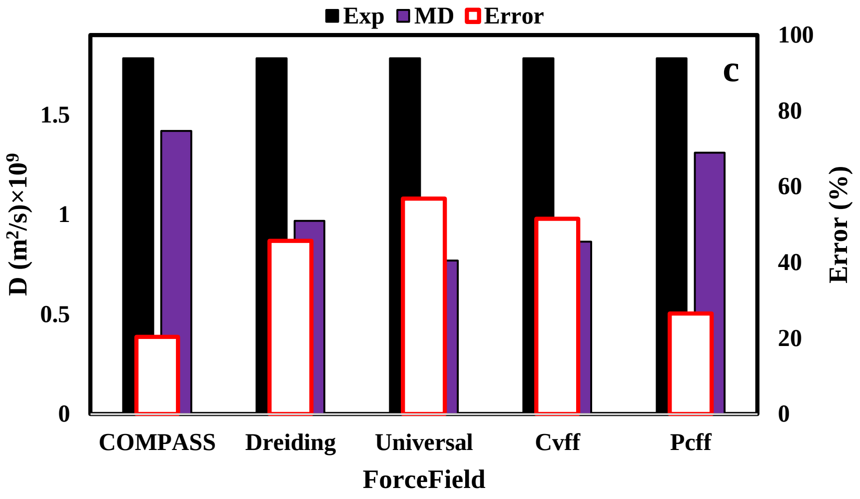
Optimum Force Field

After determining the optimum simulation time, to figure out the proper force field for obtaining the diffusion coefficient, more simulations have been performed using mole fractions of 0.2, 0.4, 0.6, and 0.8 with five force fields including COMPASS, Dreiding, Universal, Cvff and Pcff. Figs. 2a to 2d show the diffusion coefficients for benzene in hexane mixture and PE of the estimations, for different force fields and mole fractions of 0.2, 0.4, 0.6 and 0.8. As can be seen in Fig. 2a (plotted for mole fraction of 0.2), except for COMPASS and Pcff models, the other force fields estimate the diffusion coefficient less than the experimental values. For the other mole fractions, exhibited in Figs. 2b, 2c and 2d, the simulation data are less than the experimental ones in all models. The numerical modellings show the most discrepancy from the experimental data at the mole fraction of 0.8 in all the force fields and the obtained error is more than 50%. For all mole fractions the PE of COMPASS force field (25.37%) is less than the other force fields. This error is about 32.48% using Pcff force field.

Figs. 3a, 3b, 3c, and 3d show diffusion coefficients and percentage error (PE) values for the mixture of hexane in benzene, using different force fields and at various mole fractions of 0.2, 0.4, 0.6 and 0.8. The least PE for these settings has been obtained using Pcff force field as 14.64%. In addition, the errors using COMPASS, Dreiding, Universal and Cvff force fields have been estimated as 32.19%, 20.74%, 28.25% and 16.52% respectively. Based on the results of Figs. 2 and 3, the least relative error for the diffusion coefficient (about 24.55%) has been achieved using Pcff force filed. As a result, this force field can be used to predict the diffusion of benzene in hexane or hexane in benzene. Table 1 shows the diffusion coefficients and the attributed PE values of benzene in hexane and also hexane in benzene, using Pcff force field, for the mole fractions of 0.2, 0.4, 0.6 and 0.8.







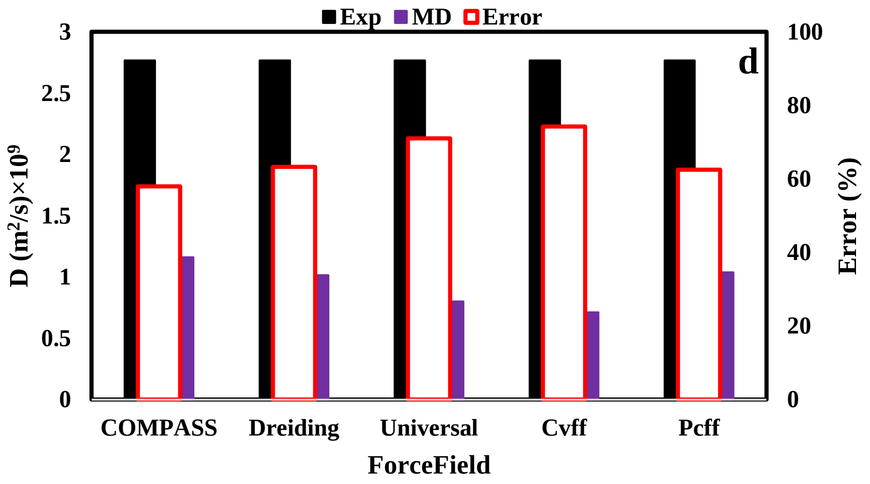
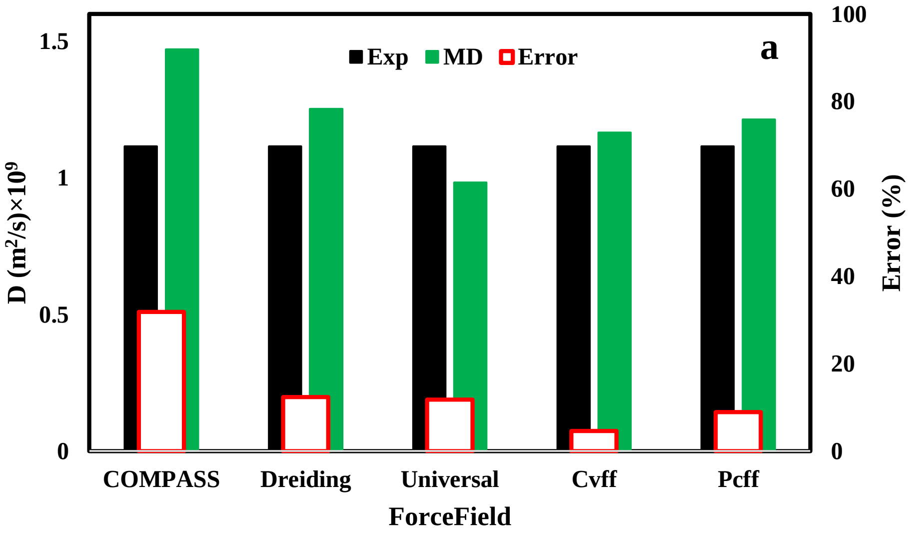


Fig. 2. Diffusion coefficients of benzene in hexane and the attributed errors compared to the experimental data, using different force fields and for the mole fractions of a) 0.2, b) 0.4, c) 0.6 and d) 0.8



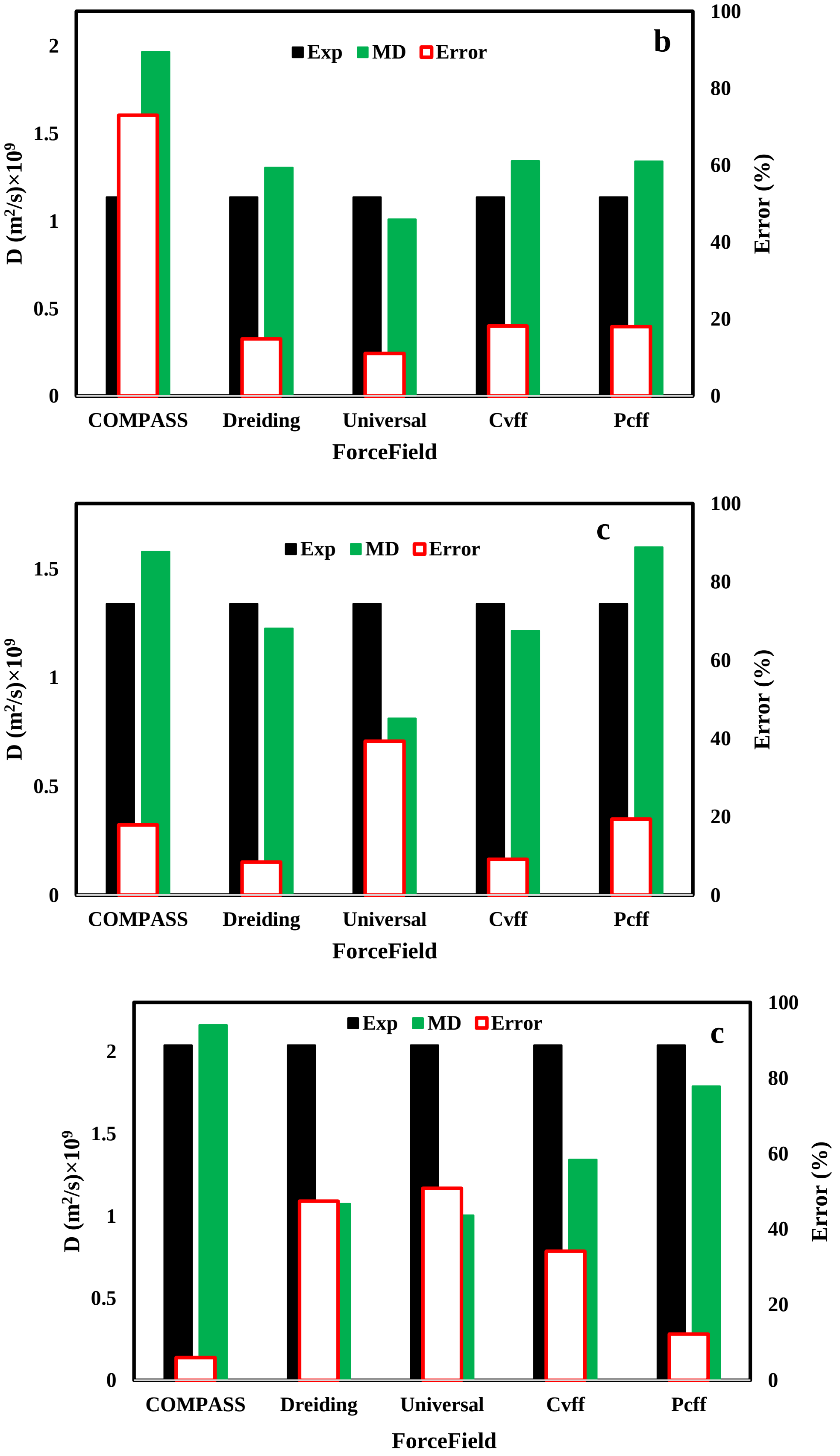


Fig. 3. Diffusion coefficients of hexane in benzene and the attributed errors compared to the experimental data, using different force fields and for mole fractions of a) 0.2, b) 0.4, c) 0.6 and d) 0.8

Table 1. Diffusion coefficients of hexane in benzene and corresponding errors using different force fields and at different mole fractions of 0.2, 0.4, 0.6 and 0.8

$\mathbf{(Benzene)_x(n-Hexane)_{1-x}}$				$\mathbf{(Benzene)_{1-x}(n-Hexane)_x}$		
Mole fraction (x)	D^{Exp} (m^2/s) $\times 10^9$	D^{MD} (m^2/s) $\times 10^9$	$\left\lvert\frac{D^{exp}-D^{MD}}{D^{exp}}\right\rvert \times 100$	D^{Exp} (m^2/s) $\times 10^9$	D^{MD} (m^2/s) $\times 10^9$	$\left\lvert\frac{D^{exp}-D^{MD}}{D^{exp}}\right\rvert \times 100$
0.2	1.2488	1.4062	12.61	1.1153	1.2144	8.89
0.4	1.6588	1.1885	28.35	1.1378	1.3429	18.02
0.6	1.7829	1.3104	25.50	1.3391	1.5990	19.41
0.8	2.7653	1.0379	62.47	2.0403	1.7906	12.24

Conclusion

In this work, COMPASS force field was applied to find the optimized structures of benzene and hexane molecules. In addition, in all the simulations, Ewald and Atom-based summation methods were used to compute van der Waals and electrostatic potential energies at 298.15 K and at atmospheric pressure for the cell construction. After the simulation cell was built, the system was developed by canonical ensemble (NVT) using velocity Scale thermostat for 50 ps to reach the equilibrium state and then it was controlled under the microcanonical ensemble (NVE) for 5 t 40 ps, to gain the equilibrium state. The optimum simulation times with the least errors, for the diffusion coefficient of benzene in hexane for mole fraction of 0.2, and the diffusion coefficient of hexane in benzene for mole fraction of 0.8 were studied and obtained to be 35 and 25 ps respectively. Finally, at the optimized simulation time for the NVE ensemble, various force fields were studied for different mole fractions of 0.2, 0.4, and 0.6. Pcff with the minimum error was considered as the optimum force field for the computation of diffusion coefficient of benzene/hexane and hexane/benzene mixtures for different mole fractions.

References

[1] Fei W, Bart H.-J. Predicting diffusivities in liquids by the group contribution method. Chemical Engineering and Processing: Process Intensification. 2001; 40(6): 531-535.

[2] Amirjalayer S, Tafipolsky M, Schmid R. Molecular dynamics simulation of benzene diffusion in mof- 5: importance of lattice dynamics. Angewandte Chemie International Edition. 2007; 46(3): 463-466.

[3] Winn E. B, The temperature dependence of the self-diffusion coefficients of argon, neon, nitrogen, oxygen, carbon dioxide, and methane. Physical review. 1950; 80(6): 1024.

[4] Shvab I, Sadus R. J. Thermodynamic properties and diffusion of water+ methane binary mixtures. The Journal of Chemical Physics. 2014; 140(10): 104505.

[5] Kimura Y, Kida Y, Matsushita Y, Yasaka Y, Ueno M, Takahashi K. Universality of viscosity dependence of translational diffusion coefficients of carbon monoxide, diphenylacetylene, and diphenylcyclopropenone in ionic liquids under various conditions. The Journal of Physical Chemistry B. 2015; 119(25): 8096-8103.

[6] Bullerjahn J. T, Bülow S. V, Hummer G., Optimal estimates of self-diffusion coefficients from molecular dynamics simulations. The Journal of Chemical Physics. 2020; 153(2): 024116.

[7] Moradi H, Azizpour H, Bahmanyar H, Mohammadi M, Akbari M. Prediction of methane diffusion coefficient in water using molecular dynamics simulation. Heliyon. 2020; 6(11): e05385.

[8] Brüsewitz M, Weiss A. Pressure- Temperature- Dependence of Mass Density and Self-Diffusion Coefficients in the Binary Liquid System n- Hexane/Benzene. Berichte der Bunsengesellschaft für physikalische Chemie. 1990; 94(3): 386-391.

[9] Caldwell C, Babb A. Diffusion in Ideal Binary Liquid Mixtures. The Journal of Physical Chemistry. 1956; 60(1): 51-56.

[10] Harris K. R, Pua C. K,, Dunlop P. J. Mutual and tracer diffusion coefficients and frictional coefficients for the systems benzene-chlorobenzene, benzene-n-hexane, and benzene-n-heptane at 25. deg. The Journal of Physical Chemistry. 1970; 74(19): 3518-3529.

[11] Guan Y, Chi M. H, Sun W. F, Chen Q. G, Wei X. L. Molecular dynamics simulations of molecular diffusion equilibrium and breakdown mechanism of oil-impregnated pressboard with water impurity. Polymers. 2018; 10(11): 1274.

[12] Taheri Z, Nakhaeipour A. Studying of the adsorption and diffusion behaviors of methane on graphene oxide by molecular dynamics simulation. Journal of Molecular Modeling. 2021; 27(2): 1-8.

[13] Akgerman A, Gainer J. L. Predicting gas-liquid diffusivities. Journal of Chemical and Engineering Data. 1972; 17(3): 372-377.

[14] Newsome D, Coppens M. O. Molecular dynamics as a tool to study heterogeneity in zeolites–Effect of Na+ cations on diffusion of CO2 and N2 in Na-ZSM-5. Chemical Engineering Science. 2015; 121: 300-312.

[15] Nalaparaju A, Khurana M, Farooq S, Karimi I. A, Jiang J. W. CO2 capture in cation-exchanged metal–organic frameworks: Holistic modeling from molecular simulation to process optimization. Chemical Engineering Science. 2015; 124: 70-78.

[16] Orozco G. A, Lachet V, Mackie A. D. A molecular simulation study of aqueous solutions of amines and alkanolamines: mixture properties and structural analysis. Molecular Simulation. 2014; 40(1-3): 123-133.

[17] Liu, X et al. Fick diffusion coefficients in ternary liquid systems from equilibrium molecular dynamics simulations. Industrial & engineering chemistry research. 2012; 51(30): 10247-10258.

[18] Moradi H et al. Molecular dynamics simulation of H2S adsorption behavior on the surface of activated carbon. Inorganic Chemistry Communications. 2020; 118: 108048.

[19] Moradi H, et al. Effect of Si/Al Ratio in the Faujasite Structure on Adsorption of Methane and Nitrogen: A Molecular Dynamics Study. Chemical Engineering & Technology. 2021; 44(7): 1221-1226.

[20] Emamian M et al. Performance of molecular dynamics simulation for predicting of solvation free energy of neutral solutes in methanol. Chemical Product and Process Modeling. 2021.

[21] Moradi, H., et al., Molecular dynamic simulation of carbon dioxide, methane, and nitrogen adsorption on Faujasite zeolite. Chinese Journal of Chemical Engineering. 2021.

[22] Moradi H et al. Enhancement of supercritical carbon dioxide solubility models using molecular simulation data. Korean Journal of Chemical Engineering. 2022: 1-7.

[23] Rani A. J, Thomas A, Joseph A. *I*nhibition of mild steel corrosion in HCl using aqueous and alcoholic extracts of Crotalaria Pallida–A combination of experimental, simulation and theoretical studies. Journal of Molecular Liquids. 2021; 334: 116515.

[24] Pour S. B, Sardroodi J. J, Ebrahimzadeh A. R. *Th*e study of structure and interactions of glucose-based natural deep eutectic solvents by molecular dynamics simulation. Journal of Molecular Liquids. 2021. 334: 115956.

[25] Zhao X, Jin H. Correlation for self-diffusion coefficients of H_2, CH_4, CO, O2 and CO_2 in supercritical water from molecular dynamics simulation. Applied Thermal Engineering. 2020; 171: 114941.

[26] Marry V et al. microscopic simulation of structure and dynamics of water and counterions in a monohydrated montmorillonite. The Journal of chemical physics. 2002; 117(7): 3454-3463.

[27] Zeebe R. E. On the molecular diffusion coefficients of dissolved CO2, HCO3-, and CO32- and their dependence on isotopic mass. Geochimica et Cosmochimica Acta. 2011; 75(9): 2483-2498.

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