Presented at the DLSU Research Congress 2015
De La Salle University, Manila, Philippines
March 2-4, 2015

A Molecular Dynamics Investigation of Cyclohexane On Water for Oil Spill Mitigation

Dhonny Bacuyag[1,*], Al Rey Villagracia[1], Nelson Arboleda Jr.,[1, 2] and Melanie David[1]

[1]*Physics Department, De La Salle University, 2401 Taft Avenue, Manila*

[2]*De La Salle University-Science and Teachnology Complex, Binan Laguna.*

**Corresponding Author: dhonny_p_bacuyag@dlsu.edu.ph, dhonny_bacuyag@yahoo.com*

Abstract: The problem of oil spill that affects many aquatic environments is still considered a big challenge to different fields, government agencies and scientific communities alike. Different toxic water pollutants, like cyclohexane, can be released to bodies of water when this oil spill accident occurs. Efforts to reduce these water pollutants and to design an effective oil spill mitigation model is still a priority and a concern that needs immediate response. This study investigated the behavior of cyclohexane on water at different temperatures. It employed Molecular Dynamics (MD) simulation to investigate the different properties of cyclohexane on water with this varying temperature. The GROningen MAchine for Chemical Simulations (GROMACS) version 5.0 open source software was used for all calculations with the Martini course grained force field. The calculated cyclohexane cluster density agreed with an expected pattern of decrease as temperature increased. The significant rapid decrease in this density upon reaching a temperature of about 350 K matched with its expected density behavior at its boiling point of 353 K [1]. This result is supported by the calculated radius of gyration where slight changes were recorded below the boiling point and a sudden increase was calculated near 350K. The results of the calculations on the lateral diffusion and the root mean square deviation (RMSD) showed a pattern on the movement of cyclohexane on water at different temperatures. Increasing the temperature also increased the movement of cyclohexane cluster on water. This study is an attempt to examine the movement of cyclohexane on water in the atomic scale. The initial results from this investigation could lead to new techniques in reducing water pollutants and in designing new oil spill mitigation model.

Keywords: molecular dynamics; GROMACS; cyclohexane; oil spill mitigation

1. INTRODUCTION

The gravity of the effect of oil spill on aquatic environment has influenced many environmental advocates, politicians and scientist to think of a more improved way of mitigation. According to the Clean Energy Jobs and Oil Company Accountability Act (2010) of the United States Congress, oil companies are spending very little money, in comparison to their profits, in preventing and in responding to oil spills. This has motivated them to promote improvements in oil spill response technologies and mandate oil companies to have the ability to prevent and respond to domestic oil spills. Even if very serious incident such as this is rare, lessons must be learned and improved scientific approaches are very important especially in the early stages of mitigation (McIntosh and Nolan 2001). There are two methods of mitigating crude oil spill today, the bioremediation and the use of chemical

dispersants. Having a deeper understanding on the relationship between these two methods and the knowledge on modelling the mitigation design will lead to quicker and more effective decision-making for mitigation response (Carpio et al. 2013).

To understand any scientific mitigation design model, it is important to understand the molecular nature and properties of the components of crude oil. One of the natural components of crude oil is cyclohexane (C_6H_{12}). According to the United States Environmental Protection Agency (1994), this chemical is considered to be very toxic to aquatic organisms, and it can be released to the environment from places where petroleum products are refined, stored, used, and in serious cases of oil spills. This chemical is also slightly soluble in water (55 ppm) and has the potential to leach through soil into groundwater. The Toxic Chemical Release Inventory in 1992 reported an environmental release of this chemical by different industries in the United States a total of 21,039 pounds to surface water. The agency had identified *volatilization* as the primary route for its removal from water. The Clean Air Act Amendments of the United States Congress (1990) also list this chemical as hazardous air pollutant.

Understanding the behavior of cyclohexane on water in terms of different properties, like density, molecular movement or velocity of spread and discharge velocity from water are very important in designing a mitigation response model. An initial approach to this investigation is to apply a molecular dynamics (MD) simulation technique for the Cyclohexane and water system. MD simulation is one of the basic tools used in analyzing molecular systems which cannot be easily investigated by experiment. It provides deeper understanding on the interaction of different molecular systems (Manrique et al. 2014) like cyclohexane and water. This study provides initial theoretical explanation on the movement of cyclohexane on water at different temperatures with the use of MD simulation. Its general objective is to investigate the mechanism for the possible natural or mechanical extraction of cyclohexane from water surface and its specific objective is to obtain a nano-scale picture of cyclohexane dynamics in terms of cluster density, molecular compactness, and molecular deviation (molecular spread) on water at different temperatures.

2. METHODOLOGY

The GROningen MAchine for Chemical Simulations (GROMACS) version 5.0 open source software was used for all calculations with the MARTINI course grained force field (Martini et al. 2007). The initial structure of cyclohexane cluster was generated from random positions of 500 cyclohexane molecules (1500 beads) solvated with 1500 beads of water molecules. The structure was optimized by energy minimization at 298K temperature and 1 atm pressure for 100ns. To study the effects of varying the temperature on the density, radius of gyration, root mean square deviation (RMSD), and lateral diffusion of cyclohexane on water, the unit cell was placed in 6.98183 nm x 15.0000 nm x 6.98183 nm box with vacuum space along the y axis. The box dimensions were made fixed during system formations at different temperatures from 298 K to 378 K, in increments of 10 K, at 1 atm pressure for 400ns. An analysis on the cyclohexane density and its correlation to its radius of gyration was done to investigate the possible behavior of cyclohexane cluster on water with varying temperature. The changes in the density and radius of gyration near the known boiling point of cyclohexane were investigated to prove the validity of the calculation. To investigate the possible movement of cyclohexane cluster on water, calculations on the lateral diffusion and RMSD with varying temperature were done and the results were analyzed to see a possible trend. The Visual Molecular Dynamics (VMD) was used to visualize the optimized structures and the different simulations. Xmgrace plotting tool was used to plot the different parameters in this study.

3. RESULTS AND DISCUSSION

The molecular dynamics investigation of solvated cyclohexane in this study was focused on the analysis of the effect of varying temperature on cyclohexane cluster properties in terms of its density, radius of gyration, lateral diffusion, and root mean square deviation. These properties can give an initial description on the behavior and movement of cyclohexane on water. The results of the different calculations on these properties are discussed below.

3.1 Cyclohexane density versus the temperature

The optimized structure of cyclohexane-water system is shown in Figure 1. It can be seen in the figure that the hydrophobic cyclohexane formed a

heterogeneous biphasic system with water. The resulting unit cell size is 6.98183 nm x 6.98183 nm x 6.98183 nm. The unit cell was placed in a simulation box with a dimension of 6.98183nm x 15.00000 nm x 6.98183 nm as shown in Figure 2. The box height was increased to clearly observe the behavior of cyclohexane as the temperature is increased.

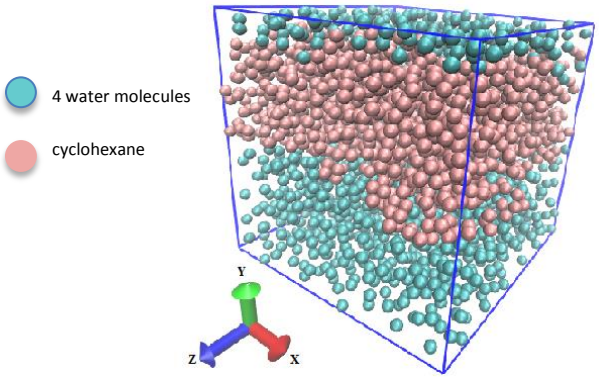

Fig. 1. Optimized structure of cyclohexane and water system showing a heterogeneous biphasic system.

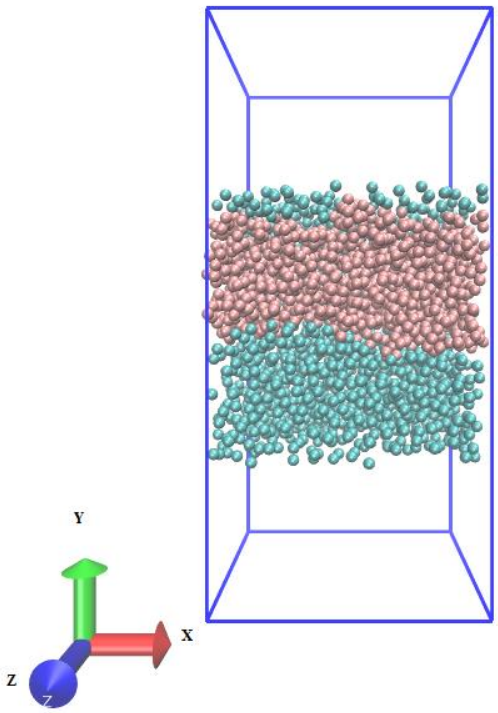

Fig. 2. The unit cell system of cyclohexane-water in a box with vacuum along the y-axis.

A general trend on the density of cyclohexane with the change in temperature can be observed from this graph. As the temperature is increased, the density, in general, decreases. A significant rapid decrease in the density at temperature range of 350 K to 358K is also observed. According to the chemical summary provided by the U.S. Environmental Protection Agency (1994), cyclohexane is known to have a boiling point of 353.9 K which falls at this temperature range. This decreased density of cyclohexane cluster is also brought about by the separation of some cyclohexane molecules from the cluster as the temperature is increased.

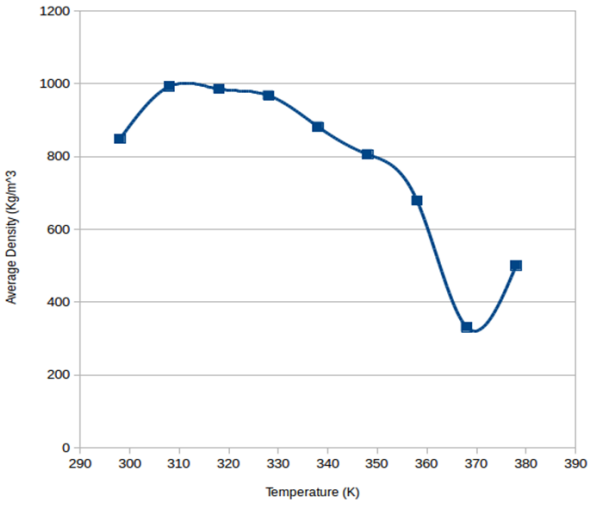

Fig. 3. Plot of the average density of cyclohexane as the temperature is increased in increments of 10 K.

3.2 Radius of gyration versus temperature

To support the temperature dependence of density of cyclohexane, a calculation on its radius of gyration, to measure the compactness of the structure, was done with varying temperature in the same incremental increase as before. The result of the calculation was plotted in Figure 4. Interestingly, the same slight change (increase) was observed from 298 K to 348 K and a significant change (increase) was also observed in the temperature range of 350K K to 358 K with 3.60 nm and 6.11 nm radius of gyration, respectively. Again, it is in this temperature range where the cyclohexane reached its boiling point.

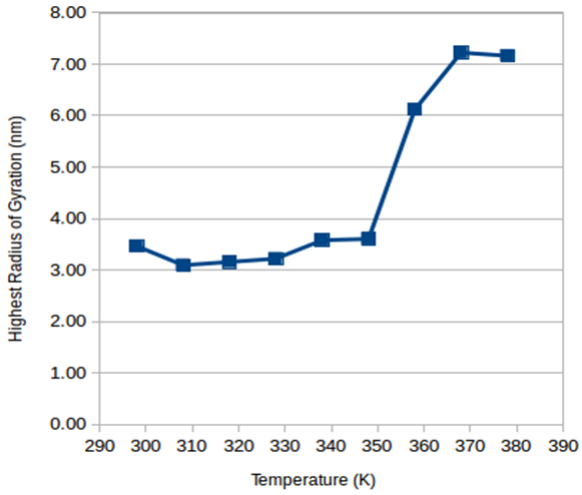

Fig. 4. Plot of the radius of gyration versus temperature showing the significant rapid increased at 353K.

3.3 Lateral diffusion and Root Mean Square Deviation (RMSD)

Calculations on lateral diffusion and RMSD were done to have an initial understanding on the movement of cyclohexane on water. The plot of the diffusion with respect to temperature can be seen in Figure 5.

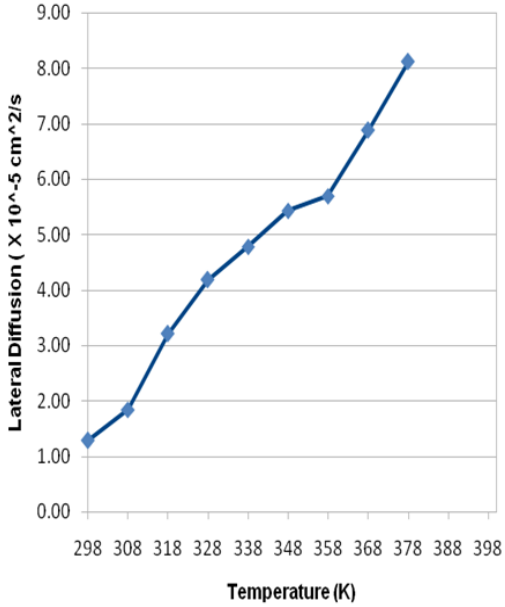

Fig. 5. Plot of the lateral diffusion of cyclohexane along the y-coordinate of the box upon the increase of temperature.

It can be observed that cyclohexane diffuses in an increasing manner as the temperature increases. A sharp linear increase in its lateral diffusion was observed when the cyclohexane attains its boiling point at 353 K. The result of RMSD calculations supports this movement where a more stable cyclohexane system is seen at temperature range below boiling point. Again the deviation from the clusters center of mass is seen to sharply increase at temperature above the boiling point. The plot of this RMSD is shown in Figure 6.

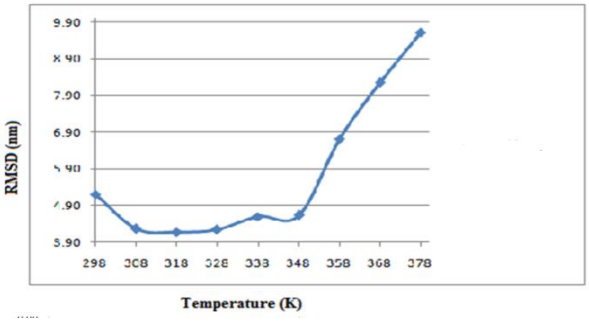

Fig. 6. Plot of the root mean square deviation of cyclohexane on water showing a significant rapid movement at temperature near the boiling point (353 K).

4. CONCLUSIONS AND RECOMMENDATIONS

In this paper, the molecular dynamics investigation of the different properties of cyclohexane solvated at different temperature was presented. Principles of MD simulation was applied to investigate and to understand the behavior of cyclohexane in water upon variations in temperature. The optimized structure of the biphasic cyclohexane-water system was presented and the result of the MD calculations show that properties like density, radius of gyration, lateral diffusion and root mean square deviation are all dependent in temperature. Plots of the density versus temperature showed the significant decrease in the cyclohexane density when it reaches its boiling point of 353 K. It was found out that the density decreases as the temperature increases. The results on the calculations of radius of gyration support this change in density with temperature. The plot of radius of gyration versus temperature shows decrease in the compactness of cyclohexane cluster as temperature increases. Consequently, the

movement of cyclohexane on water is also affected by this increased temperature. Calculations on the lateral diffusion and root mean square deviation show increasing values with the increasing temperature. A noticeable sharp increase is observed at temperature near the boiling point. The findings in this paper serve only as groundwork to deepen the understanding of macromolecular cyclohexane-water system for designing a more scientific oil-spill mitigation model. A detailed analysis in the discharge velocity of cyclohexane in water is recommended for future investigations.

5. ACKNOWLEDGMENTS

The authors wish to thank the Physics Department of De La Salle University for providing the necessary computers and software for all the calculations. We thank all the members of the Computational Material Design Research Group (CMDRG) of De La Salle University for the computational support. D. B. wishes to thank the Department of Science and Technology (DOST), for the financial support.

6. REFERENCES

Carpio M, Phillips M, Mottaleb N, Gabrielle (2011). Optimization of Remediation Efforts for Mitigation of Oil Spills, an Interplay Between Biodegradation and Chemical Dispersants. Proceedings of the National Beach Conference. Retrieved November 15, 2014, from http://water.epa.gov/type/oceb/beaches/meeting2011_posters.cfm

Congress of the United States. Senate Act No. 3663. Clean Energy Jobs and Oil Company Accountability Act of 2010. Retrieved October 30, 2014, from https://www.congress.gov/bill/111th-congress/senate-bill/3663

Congress of the United States. Senate Bill No. 1630. Clean Air Act 1990. Retrieved October 30, 2014, from http://thomas.loc.gov/cgi-bin/query/z?c101:S.1630

Dearden J. and Bresnen G. (2005). Thermodynamics of Water-octanol and Water-cyclohexane Partitioning of some Aromatic Compounds. International Journal of Molecular Science, 6, 119-129.

Giannootti C. and Richter C. (1999). Photocatalysed oxidation of cyclohexane by $W_{10}O_{32}^{4-}$ irradiation with natural sunlight. International Journal of Photoenergy. 1, 1-5.

Hess B, Spoel D, Lindahl E. GROMACS User Manual 2013. The GROMACS development team at the Royal Institute of Technology and Uppsala University. 7-9.

Manrique R, Ubando A, Villagracia A, Corpuz J, Padama A, David M, Arboleda N, Culaba A, Kasai H. (2014). A molecular dynamics investigation of water migration in a lipid bilayer for microalgae drying. Philippine Science Letters,7, 1, 138-145.

Marrink S., Risselada J., Yeefimov S., Tieleman P. and De Vries A. (2007). The MARTINI Force Field: Coarse Grained Model for Biomolecular Simulations. 7812 J. Phys. Chem., 111, p. 7812-7824

McIntosh R.D and Nolan P.F. (2001). Review of the selection and design of mitigation systems for runaway chemical reactions. Journal of Loss Prevention in the Process Industries, 14, 27-42.

Unites States Environmental Protection Agency-Office of Pollution Prevention and Toxics. Chemical Summary for Cyclohexane. 1994. Retrieved November 3, 2014, from www.epa.gov/chemfact/s_cycloh.txt