

# Molecular dynamics simulations of CO<sub>2</sub> clathrate hydrate in the presence of organic components

S Sinehbaghizadeh<sup>1</sup>, and A Saptoro<sup>1</sup>

<sup>1</sup>Department of Chemical and Energy Engineering, Curtin University Malaysia, CDT 250, Miri 98009, Sarawak, Malaysia

agus.saporo@curtin.edu.my (A. Saptoro)

**Abstract.** As the major greenhouse gas emission, releasing CO<sub>2</sub> through human activities has already devastating consequences on the planet. In this context, hydrate-based (HB) techniques in favour of CO<sub>2</sub> capture, sequestration, or utilization (CCSU) are perceived to be a novel option to arrest increasing concentrations of CO<sub>2</sub> in the atmosphere. The end uses of captured CO<sub>2</sub> encompass its utilization for different realms of industry such as food and beverage manufacturing plants; water desalination; metal fabrication plants; and secondary refrigeration. To offset the cost of CO<sub>2</sub> capture as well as generating revenue, the increasing effectiveness of aforesaid techniques is crucial. Although HB approaches are faced with several limitations, the solution would be the inclusion of organic promoters which are classified as environmentally-friendly substances. However, the microscopic influences of such components on CO<sub>2</sub> hydrates are mostly unexplored. This work highlights the CO<sub>2</sub> clathrate hydrate stability and decomposition in the existence of organic additives through classical molecular dynamics (MD) simulations. The results can help to understand the molecular mechanisms involved in such CO<sub>2</sub> hydrate systems which may also aid to find the more efficient organic promoters for HB applications.

## 1. Introduction

CO<sub>2</sub> emissions from various industries have been accounted for as the main proportion of global warming while it can be removed from capturing techniques and then sequester or utilize to produce the valuable materials [1]. To date, several methods such as adsorption, absorption, membrane, and cryogenic have been employed. One of the new suggested technologies to split CO<sub>2</sub> from the gas mixture is the utilization of hydrate-based methods. Since the operating formation condition of CO<sub>2</sub> is less than other gas types, this component through the simple formation and dissociation stages can be eliminated from industrial emitted gases [2]. The CO<sub>2</sub> separation stage can be followed by transportation, sequestration, or utilization steps. In this regard, various methods for CCS have been developed. Moreover, hydrate-based methods can also be considered for the aforesaid steps after CO<sub>2</sub> separation. For example, these methods can be designed for secondary refrigeration systems [3]. To reduce the consumption of HFCs and HCFCs, the refrigeration industry has been led to seek new refrigeration possessing less destructive effects on the environment. Since the melting enthalpy of CO<sub>2</sub> hydrates are considerably higher than ice, the possibility of these materials as cold thermal energy storage is under the pilot design [4]. Such processes have also been offered for removing salt ions from wastewater. Applications of hydrate-based methodologies in the food industry would grab the attraction as this phenomenon remove extra water from juices without extra costs. In addition, processing volatile

compounds (e.g. aroma, vitamin C, and concentrated betanin) using traditional methods may impair product quality while with utilizing hydrate-based techniques would secure the outcome due to the proper operating conditions [5]. The strong characteristics of CO<sub>2</sub> hydrate, control the flames, and using it instead of conventional fire extinguishing would be the other alternative. It was evidently proved that this phenomenon possesses a higher capability than dry ice in vanishing hydrocarbon flames [6]. However, toward being industrialized of the suggested methods, the formation and dissociation of the above-mentioned hydrate-based methods need to be enhanced. For example, with the inclusion of organic additives, the formation and dissociation stages can be improved. Since these components are associated with the hydrate slurry, their impacts on the hydrate dissociation would be substantial. Although the organic components can play a positive role in gas hydrate applications [7], their impressions on gas hydrates at a molecular level are still poorly understood. Hence, in this work, the role of two organic additives on CO<sub>2</sub> hydrate stability using molecular dynamics (MD) simulation is investigated. This is the first MD simulation studying the effects of organic components on the CO<sub>2</sub> hydrate stability and dissociation.

## 2. Computational details

To perform all simulations, the classical MD same as our previous work for molecular investigations of CO<sub>2</sub> hydrates with different organic promoters was carried out [8]. To provide the initial clathrate hydrate structure, the water molecular positions were adopted from the Takeuchi et al. work that optimized the configurations with satisfying the ice rules [9]. Then the hydrate supercells were generated in all three dimensions followed by the geometrically optimization of the simulation box. To obtain the least energy between all molecules in the system, both conjugate gradient and steepest descent methods were used [10]. Also, long-range Coulomb as well as the van der Waals and terms were calculated by the Ewald summation algorithm, and the cut-off distance was set at 12 Å. CVFF force field was applied for all guest and host interactions of atoms in the simulation box. The NVT ensemble for 10 picoseconds (ps) was first performed to reach the desired temperature. Then the NPT ensemble for 100 ps was imposed to achieve the stable structure of CO<sub>2</sub> hydrates. These steps were implemented using the Berendsen thermostat and barostat technique. Also, considering the three-phase equilibrium curve of CO<sub>2</sub> hydrate, the simulation condition was 298 K and 1 MPa which can provide the dissociation condition for CO<sub>2</sub> hydrate.

## 3. Results and discussion

To analyze the effects of organic molecules on CO<sub>2</sub> hydrate dissociation, the parameters such as mean square displacement (MSD), radial distribution function (RDF), potential energy, and diffusion coefficient are evaluated. The initial and final snapshots of CO<sub>2</sub> hydrate with or without methylamine and glycine are depicted in Figure 1. The final configuration of cases (a), (b), and (c) is related to the operating condition of 273 K and 1MPa. As is evident, the clathrate in the presence of organic components can remain stable. Figures 1 (d), (e), and (f) show that by elevating the temperature to 293 K, the ordered structure lost its shape.

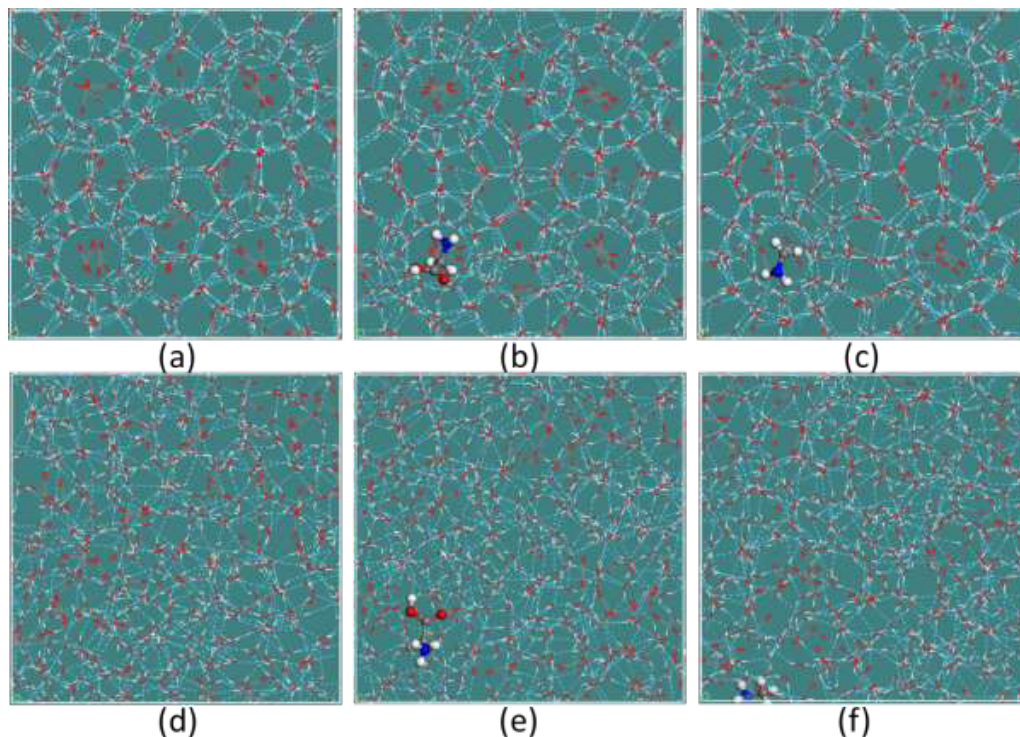


Figure 1: The final configuration of CO<sub>2</sub> hydrate in the presence of pure water (a) and (d); glycine, (b) and (e); methylamine, (c) and (f).

The hydrate cages can be created under the hydrogen bonds (H-bonds) of water molecules and the van der Waals interactions of CO<sub>2</sub> molecules inside the cavities. The amount of gas hydrate energy can be altered by the number of H-bonds and the quantities of host-guest interactions. The differential between the start and end configurations of simulated systems for CO<sub>2</sub> hydrate in the inclusion of organic molecules is displayed in Table 1. Under the stable condition, the inclusion of organic components slightly reduced the total energy but substantially increased the enthalpy. This indicates that these molecules in contact with CO<sub>2</sub> hydrate may destabilize the ordered water molecules. In contrast, the simulation results at 293 K show that although glycine or methylamine somewhat influences the kinetic energy, their presence can reduce the required energy during the dissociation step.

Table 1: Differential energy between the final and initial state of the simulation box.

Differential energy	1 MPa and 273 K			1 MPa and 293 K		
	pure water	glycine	methylamine	pure water	glycine	methylamine
Diff. total energy (kcal/mol)	7.0	-8.0	-3.3	557.6	573.1	610.1
Diff. potential energy (kcal/mol)	-3.8	-16.0	-0.4	565.3	587.3	630.8
Diff. kinetic energy (kcal/mol)	10.8	8.0	-2.9	-7.7	-14.2	-20.7
Diff. total enthalpy (kcal/mol)	0.6	100.8	245.5	744.7	537.4	613.6

To evaluate the stability of CO<sub>2</sub> hydrates either before the occurrence of hydrate decomposition or after that, the distance between water and guest atoms in phases can be monitored using the radial distribution function. RDFs denote the positions of water in the system during the decomposition phenomenon.

RDFs between oxygen atoms of water molecules are presented in Figure 2. According to this Figure, by increasing the temperature, the first peak's height of RDFs is dropped from 4.5 Å to nearly 3.5 Å. Also, the first peak by the inclusion of organic molecules is slightly declined which shows the lower ordered hydrate structure.

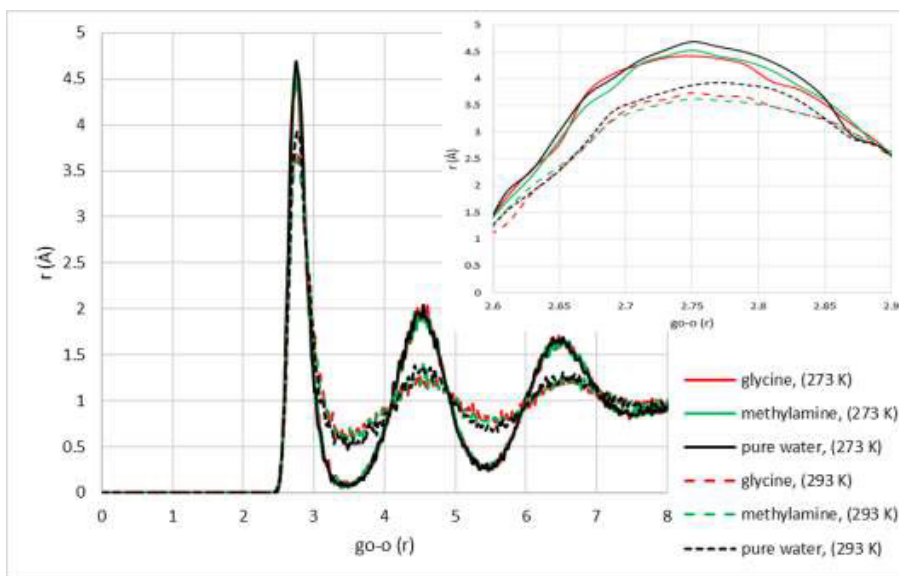


Figure 2: RDFs of water molecular oxygen pair atoms.

Analysis of the dynamical properties of CO<sub>2</sub> hydrate aids to comprehend the time evolution of guest molecules in the hydrate. Figure 3 exhibits the mean square displacement for CO<sub>2</sub> molecules within sI hydrate during the decomposition. Since the slope of MSDs for the system including methylamine and glycine is higher than pure water, it can be concluded that these molecules can enhance the water movements in the dissolved phase. In addition, the influences of glycine on water molecules are higher than methylamine.

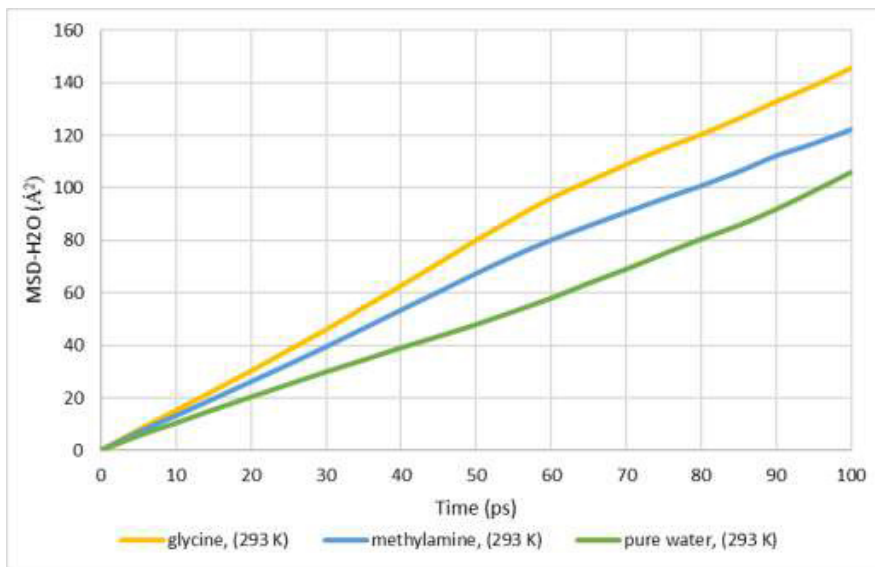


Figure 3: MSDs of water molecules in the simulations.

Table 2 summarizes the host and guest molecular diffusion coefficients of CO<sub>2</sub> sI hydrate in the inclusion of two organic components. Also, the obtained results are comparable with the diffusion coefficient of CO<sub>2</sub> in water that was measured from the conducted experiments. As is shown, after the conditions of thermodynamic stability, the diffusion coefficient of host and guest molecules is close to the dissolved CO<sub>2</sub> in the water phase. In addition, the existence of methylamine and glycine can increase the amount of diffusion coefficient of both water and CO<sub>2</sub> by around 23% and 58% respectively.

Table 2: Diffusion coefficients of water and CO<sub>2</sub> after the hydrate decomposition. (m<sup>2</sup>/s×10<sup>9</sup>).

System	P (MPa)	T (K)	D <sub>H2O</sub>	D <sub>CO2</sub>	Ref.
CO <sub>2</sub> in the presence of pure water	14.0	298	-	2.233	[11]
	31.6	298	-	2.256	[11]
	20.0	278	-	1.120	[12]
	20.0	298	-	1.910	[12]
	1.0	293	1.703	1.475	This work
CO <sub>2</sub> in the presence of methylamine	1.0	293	2.062	1.857	This work
CO <sub>2</sub> in the presence of glycine	1.0	293	2.468	2.512	This work

#### 4. Conclusion

In this work, the effects of two different organic components (methylamine and glycine) on CO<sub>2</sub> hydrate during the dissociation process were investigated. The obtained results indicated that the forces between organic components and the crystal of CO<sub>2</sub> gas hydrate increase the movements of both water and CO<sub>2</sub> molecules in the network of the hydrate crystal by two different mechanisms. At the initial stage of simulation, these molecules form a new hydrogen bond at the interface, and then by imposing disturbance movements to adjacent water and CO<sub>2</sub> molecules, they can induce changing orientations of all molecules in the crystal and weaken the hydrogen bonds. Hence, the presence of organic components may reduce the required energy for the dissociation process of hydrate-based technologies. Moreover, these molecules can facilitate the rate of mass transfer by increasing the diffusion coefficient of guest and host molecules in the system. Also, the inclusion of these components by accelerating the formation time of CO<sub>2</sub> hydrate and decreasing the dissociation energy can improve the efficiency of the hydrate-

based methods. Between the studied two organic substances, the effects of glycine on water and CO<sub>2</sub> molecules are higher than methylamine. It should be highlighted that due to the exponential correlation between the number of atoms in the system and the number of calculated interactions between them, this would be the main limitation of the present simulation which may influence the estimated dynamic parameters.

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### References

- [1] Ma ZW, Zhang P, Bao HS, Deng S. Review of fundamental properties of CO<sub>2</sub> hydrates and CO<sub>2</sub> capture and separation using hydration method. *Renew Sustain Energy Rev* 2016;53:1273–302.
- [2] Li L, Fan S, Yang G, Chen Q, Zhao J, Wei N, et al. Continuous simulation of the separation process of CO<sub>2</sub>/H<sub>2</sub> by forming hydrate. *Chem Eng Sci X* 2020;7:100067.
- [3] Xie N, Tan C, Yang S, Liu Z. Conceptual design and analysis of a novel CO<sub>2</sub> hydrate-based refrigeration system with cold energy storage. *ACS Sustain Chem Eng* 2019;7:1502–11.
- [4] Ngan YT, Englezos P. Concentration of mechanical pulp mill effluents and NaCl solutions through propane hydrate formation. *Ind Eng Chem Res* 1996;35:1894–900.
- [5] Rudolph A, El-Mohamad A, McHardy C, Rauh C. Concentrating model solutions and fruit juices using CO<sub>2</sub> hydrate technology and its quantitative effect on phenols, carotenoids, vitamin C and betanin. *Foods* 2021;10:626.
- [6] Hatakeyama T, Aida E, Yokomori T, Ohmura R, Ueda T. Fire extinction using carbon dioxide hydrate. *Ind Eng Chem Res* 2009;48:4083–7.
- [7] Bhattacharjee G, Linga P. Amino acids as kinetic promoters for gas hydrate applications: A mini review. *Energy & Fuels* 2021;35:7553–71.
- [8] Sinehbaghizadeh S, Saptorio A, Amjad-Iranagh S, Tiong ANT, Mohammadi AH. Molecular Dynamics Simulation Studies on the Stability and Dissociation of Clathrate Hydrates of Single and Double Greenhouse Gases. *Energy & Fuels* 2022;36:8323–39.
- [9] Takeuchi F, Hiratsuka M, Ohmura R, Alavi S, Sum AK, Yasuoka K. Water proton configurations in structures I, II, and H clathrate hydrate unit cells. *J Chem Phys* 2013;138:124504.
- [10] Sinehbaghizadeh S, Saptorio A, Naeiji P, Tiong ANT, Mohammadi AH. Insights into the synergistic effects of metal particles (Ag, Cu, and Fe) and urea on CO<sub>2</sub> clathrate hydrate growth using molecular dynamics simulations. *Chem Eng Sci* 2022;264:118194.
- [11] Cadogan SP, Maitland GC, Trusler JPM. Diffusion Coefficients of CO<sub>2</sub> and N<sub>2</sub> in Water at Temperatures between 298.15 K and 423.15 K at Pressures up to 45 MPa. *J Chem Eng Data* 2014;59:519–25.
- [12] Lu W, Guo H, Chou IM, Burruss RC, Li L. Determination of diffusion coefficients of carbon dioxide in water between 268 and 473K in a high-pressure capillary optical cell with in situ Raman spectroscopic measurements. *Geochim Cosmochim Acta* 2013;115:183–204.