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Short Communication

The effect of urea in the nucleation process of CO_2 clathrate hydrates

Len Herald V. Lim *, Ana Victoria Lloren, Rheo B. Lamorena

Institute of Chemistry, University of the Philippines, Diliman, 1101 Quezon City, Philippines

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ABSTRACT

The role of urea in the promotion and stability of CO_2 clathrate hydrates in the context of nucleation was investigated through isothermal–isobaric molecular dynamics simulations. A comparison of structural and dynamic properties was made for aqueous solutions of CO_2 interstitial to model montmorillonite surfaces in the presence and absence of urea. The results showed that meta-stable amorphous hydrates associated through proximity interact through cross-relaxation of H-bonds. Urea appears to mediate this effect by functioning as a bridge for thermal fluctuations of H-bond networks between nearby CO_2 hydrates. The implications have significant bearing in the modification of solution properties for the enhancement of clathrate hydrate formation in geologic and aquatic sediments through the control and stabilization of nucleation using organic matter.

1. Introduction

The past decade has given testament to the growing interest in using hydrates for “trapping” anthropogenic CO_2 in view of its potential in carbon capture and storage (CCS) — a technology framework aimed at mitigating pollution in the atmosphere without necessarily decreasing dependence to fossil fuel [1,2]. Because CO_2 does not naturally form thermodynamically stable phases in an aqueous solution, the process necessary to trap CO_2 using water (i.e. through the formation of clathrate hydrates) requires a considerable input of work (e.g. in pressurization and cooling). However, cleverly designed enhancement schemes may provide a means of minimizing energy cost for hydrate formation, which become the target of contemporary research incentives. In an aqueous phase, capture from point source (e.g. flue gas) can be aided by employment of water-soluble additives [3], which help in enhancing the kinetics to a degree amenable to laboratory capacity. The concept has recently been revisited by Castellani and co-workers in the formulation of a gas hydrate technology [4]. Although the use of chemical additives is particularly appealing with regard to the rapid production of CO_2 clathrate hydrates, it is not particularly directed to the notion of long-term storage since both pressure and temperature requirements must be met and maintained artificially. On the other hand, such requirements can be naturally satisfied by geologic environments (e.g. deep sea settings). Rochelle and co-workers highlighted the use of hydrates for underground storage of CO_2 [5]. The scheme of marine geologic sequestration is attractive primarily because of the naturally high reservoir capacity, but is challenged by the full understanding of equilibrium conditions necessary for long-term stability and energy costs for transport. For example, Sloan and his co-workers identified possible complications leading to instability of CO_2 hydrate layers in the seafloor [6]. More recently, however, new indications of viability on the notion of marine geologic sequestration have surfaced. Lamorena and Lee in their work on the Ulleung Basin in South Korea [7] identified the possibility of organic matter in deep sea sediments to contribute to the enhancement of hydrate formation. Indeed, gas hydrate formation has been found to be associated with different types of organic matter in other marine settings [8,9], which brings a new dimension in the prospect of long-term storage of CO_2.

The promotion of clathrate hydrate formation through soil organic matter in marine sediments may be no more different than that which can be achieved using THF or SDS [3,10], but that the former may require the presence of a mineral substrate to induce heterogeneous nucleation. The molecular principles underlining clathrate hydrate formation are largely eluded in experimental investigations of promotion, but appear to be more readily interpreted in the case of inhibition [11,12] where organic compounds are thought to compete with guest molecules for water by forming more favorable hydrogen bonds. Nevertheless, it is a meaningful assumption to regard nucleation events (as opposed to growth) as being most susceptible to the presence of organic molecules. The answer to the question of how an organic molecule influences the solution structure necessary for the onset of stable CO_2 hydrates may be the key to finding the connection between promotional and inhibitory characteristics of organic compounds in CO_2 clathrate hydrate forming systems, and may help construct a basis for the qualification of long-term storage of CO_2 in marine settings rich in organic material.

In contrast to a similar study endeavored by Moon and his co-workers on the role of organic additives to the control of clathrate

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* Corresponding author at: Institute of Chemistry, National Science Complex, University of the Philippines, Diliman, Quezon City 1101, Philippines. Tel./fax: +63 920 5427.
E-mail address: lenheraldlim@yahoo.com.ph (L.H.V. Lim).

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hydrate formation and growth [13], the present study aligns to the notion of CO_2 storage in geologic matrices, which now necessitates the incorporation of heterogeneous nucleation. In the same spirit, molecular dynamics simulations are invoked in elucidating microscopic effects in solution, but with the use of reduced models that would allow the exploration of important features without sacrificing too much fidelity to real-world scenarios. This can be achieved by integrating into related computational findings for heterogeneous nucleation [14,15] the concept of influence from an organic molecule chosen on the basis of its hydration properties. Urea offers itself as a simple yet demonstrative candidate in that it is small enough not to impose a large disruption to hydrogen-bonding networks and it has no full qualification as a structure-forming or structure-breaking solute in aqueous media [16–18]. The minimal model of geologic matrices (i.e. interstitial mineral spacings) that is chosen for the study allows for expedient analysis for obtaining an initial impression on the role of organic molecules in incipient CO_2 clathrate hydrate formation, which can be perceived simply from hydration dynamics.

2. Methodology

The montmorillonite model structure with the formula $(K, Na)_{0.533}$ $[Si_4O_8][Al_{1.467}Mg_{0.533}O_2(OH)_2]$, CEC = 143 mmol/100 g taken from the work of Heinz et al. [19], was originally optimized for the Polymer Consistent Force Field (PCFF) [20] and the Consistent Valence Force Field (CVFF) [21]. However, to simplify the assignment of charges and atom-types, the model phyllosilicate was represented instead with the Clay Force Field (ClayFF) introduced by Cygan and his co-workers [22]. The simplicity of the ClayFF in modeling phyllosilicate properties with optimized Lennard–Jones parameters allow for fast equilibration and structure optimizations. The imposition of charge neutrality for the simulations using the ClayFF led to the removal of the Na ions. This was done instead of the introduction of counter-ions (e.g. Cl^-) to let the nucleation events be removed from the effects of electrolytes [23,24] which are still to be fully understood, and to isolate the effects more particular to the presence of urea. The model phyllosilicate, therefore, has the primary role of introducing the solid–liquid interface that would enhance confinement for the hydrates and provide the physical requirements of heterogeneous nucleation. On the other hand, CO_2 and urea were modeled using CVFF parameters with atomic charges modified to ESP point charges obtained from HF/6-31G* ab initio computations. Typically, mixing of force fields introduces complications in generating valid results. However, the successful use of CVFF non-bonded parameters together with those of ClayFF has been demonstrated in other studies [15,25]. In either force field, the SPC/E water model is used. All simulations, including energy minimization, were performed using the DL_POLY package [26].

While the reproduction of the full induction times (i.e. the time to full crystallization) is ideal, much information on the role of organic matter in CO_2 clathrate hydrate formation can already be obtained by simply focusing on periods around nucleation. To understand the underlying dynamics, four simulation systems were prepared. These correspond to different scenarios that would allow for a contextual analysis of nucleation. The assumption is that a promoter or an inhibitor would likely influence clathrate hydrate formation by enhancing or diminishing pertinent hydration patterns in the nucleation process. Two of the model systems were set at clathrate-forming conditions (low temperature, high pressure), while the other two were set at clathrate-destabilizing conditions (relatively high temperature, low pressure). Table 1 summarizes the description for the four simulation systems for different conditions investigated in the present study. The temperature and pressure settings for the clathrate forming simulation systems were initially based on the CO_2 hydrate phase diagram reported by Sloan and other researchers [27]. However, a working pressure of 1 katm was ultimately decided from re-optimization of the montmorillonite structure with interstitial water molecules included. It should be noted, in general, that the temperature and pressure settings, although representative of different areas in the CO_2 hydrate phase diagram, are working values particular to the force fields used.

Table 1
Summary of composition and T–P conditions used in the simulations.

Label	Composition	Temperature (K)	Pressure (katm)
A	CO_2 + water + mineral	262	1
B	CO_2 + water + mineral	302	0.1
C	CO_2 + water + mineral + urea	262	1
D	CO_2 + water + mineral + urea	302	0.1

The study follows a very simple principle for elucidating the process of nucleation. That is, the process of nucleation is analyzed by inspecting the degrees of destabilization of nucleation clusters: simulation systems B and D are run from their clathrate-forming counterparts, A and C, respectively. Equilibration was, therefore, only applied to systems A and C with a total accumulated computation period of approximately 500 ps through a conjugate gradient minimization algorithm in DL_POLY. This produced starting configurations where the simulation cells are relaxed to appropriate lattice parameters (i.e. triclinic). Molecular dynamics simulations under constant temperature and pressure using an anisotropic Berendsen algorithm were then conducted for a total of 3 ns for each system using a 0.001 ps timestep. Long range corrections were handled using the Reaction Field method with a Coulombic cutoff of 10 Å. Non-bonded interactions on the other hand were set with a cut-off of 8 Å. For all of the systems, the number of CO_2 molecules was set to 10 and solvated with 700 water molecules resulting to ca. 3.5% w/w concentration. On the other hand, the number of urea molecules was set to 5. This brings the urea concentration to ca. 2% w/w. The choice of concentrations was made to ensure that the simulation systems were dilute with respect to both CO_2 and urea. This allows an easy isolation of effects coming from CO_2–urea interactions in the analysis, and the proper propagation of water dynamics in the bulk (i.e. high concentrations of either CO_2 or urea may lead to unintended clustered phases). Although the dependence of solution features to variations in the concentration of organic molecule may reveal much richer information, it is largely beyond the scope of the present work. Finally, to achieve more adequate solution volume, each simulation cell was replicated twice in the X and Y directions with the mineral surfaces placed in bounding faces of the simulation cells in the Z-direction forming a slab configuration.

3. Results and discussion

3.1. Structural features

Incipient clathrate hydrate formation may be detected from trajectory by inspecting either structural or dynamic properties. Analysis on structural properties typically buries the information contained in the three-dimensional H-bonded network of hydrate cages through spherical averaging. Therefore, nucleation events were more appropriately indentified using dynamic properties. Nevertheless, the computation of structural properties from simulation trajectories provided a basis for detecting more prominent differences between simulation systems as well as spatial markers over which analysis of dynamic data had been performed.

Of particular merit is the computation of radial distribution functions (RDFs) using atomic centers to approximate molecular centers-of-geometry. Fig. 1 shows the C (carbon dioxide)–O (water) radial distribution functions from each of the simulation systems. Because the RDFs measure the average variation of the number of water molecules at a distance from carbon dioxide, a smooth peak is indicative of lability. In the case of system A (Fig. 1a), this suggests that all CO_2 hydrates lack sufficient stability to form a definite structure (i.e. a well-pronounced