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The selective role of multipolar interaction in the formation of CH_4 and CO_2 clathrate hydrates

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Abstract

The interaction of sodium dodecyl sulfate (SDS) with CH_4 and CO_2 has been analyzed by performing Molecular Dynamics simulations. Results indicate that SDS while promoting the formation of methane clathrate inhibits the formation of the carbon dioxide one. The effect is attributed to the different charge distribution on the gas molecules. The CH_4 molecule is, in fact, characterized by the absence of permanent dipole and quadrupole moments (having only a small octupole moment compatible with a very symmetric charge distribution), while the CO_2 one has a large quadrupole moment. Accordingly, the SDS-CH_4 interaction has almost null electrostatic nature while the SDS-CO_2 one has a remarkable electrostatic nature.

1.Introduction

Several gas phase molecules have a size suited to form hydrates. Among these are methane (CH_4) and carbon dioxide (CO_2). As a matter of fact hydrated gases are, essentially, water clathrates in which the water cage crystallizes in the isometric crystallographic system rather than in the hexagonal one of normal ice. Gas hydrates are icelike solid inclusion compounds in which the gas molecules are trapped within a lattice-like cage of water molecules. Accordingly, clathrates are solid inclusion compounds in which the cage of water molecules (host) is stabilized by the trapped gas molecule (guest). Without the contribution of the trapped gas, the lattice structure of hydrate clathrates would collapse into a conventional ice crystal or liquid water.

An important property of gas hydrates is that they form worldwide (though under particular conditions) a large potential source of fossil fuel. Another important property of gas hydrates is the fact that, because of their metastable nature, they can act as regulators (capture/release) of greenhouse gases. Furthermore, their condensed nature mitigates the temperature and pressure conditions (by consequently improving safety and economic benefits) at which methane can be transported. This makes of extreme importance the investigation of the conditions at which clathrates are produced, stabilized and destabilized.

The mechanisms of formation of gas hydrates involves typically the gas dissolution, the formation of crystallographic nuclei, and their subsequent growth. On the theoretical side, the determination of the mechanism of a clathrate formation requires as a first step an accurate description of the noncovalent interactions between the water molecules as well as between them and the gas. At the same time the fact that gas hydrates grow mainly at the gas-water interface[1] the effect of several surfactants on the formation of clathrates has been investigated in order to understand how they modify the surface tension of water. The particular aim of the present paper is to discuss the different role played by sodium dodecyl sulfate (SDS) in the formation of CH_4 and CO_2 clathrates. To this end the involved inter and intramolecular interactions are examined in section 2 and the related outcomes of Molecular

Dynamics (MD) simulations of water gas mixtures (containing and not containing SDS) are discussed in section 3. Finally, the main conclusions are given in section 4 and 5.

2.The interaction potential energy

As usual, the total interaction is decomposed here in intermolecular and intramolecular components. The main purpose of the decomposition is to provide an accurate description of the nonelectrostatic component of the intermolecular interaction, V_{nel}, that is assumed to be independent of the electrostatic one, V_{el}, which includes only permanent electric charge and/or permanent electric multipole contributions.

V_{nel} includes exchange or size (of repulsive nature), and induction and dispersion (of attractive nature) contributions. In our model, V_{nel} is formulated as a sum of Improved Lennard Jones (ILJ) functions,[2,3] applied to pairs of interaction centers placed on the molecules. The ILJ function is defined as,

$$V_{ILJ}(r) = \varepsilon \left[\frac{m}{\beta + 4\left(\frac{r}{r_0}\right)^2 - m} \left(\frac{r_0}{r}\right)^{\beta + 4\left(\frac{r}{r_0}\right)^2} - \frac{n(r)}{\beta + 4\left(\frac{r}{r_0}\right)^2 - m} \left(\frac{r_0}{r}\right)^m \right] \qquad (1)$$

where ε and r_0, as in the usual LJ potential, represent the depth of the potential well and the intermolecular distance associated with the energy minimum, respectively. However, the ILJ function, contains the additional parameter β (with respect to the LJ potential) which removes most of the inadequacies of the LJ function at both, short and long range.[4]

Based on our previous experience[3,5–7] only one interaction center placed on the O atom of the water molecule (OW) has been considered. Similarly, also only one interaction center, placed on the C atom (CM), has been considered for CH_4. On the contrary, several interaction centers have been considered for both, CO_2 and SDS. In particular, three interaction centers, placed on the C and O atoms, have been considered on the CO_2 molecule. All inter-

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action centers have an assigned value of the polarizability compatible with the value of the whole molecular polarizability. This means that the polarizability associated to OW and CM is equal to that of water and methane, respectively, and that the sum of the polarizabilities associated with the C and O atoms of CO_2 is equal to the whole CO_2 polarizability. As to SDS, two different decompositions of the polarizability have been considered. In fact, the interaction centers placed in the CH_3, CH_2, SO_4 and Na have been considered for CH_4-SDS, while in order to calculate both the CO_2-SDS and the H_2O-SDS interactions the SO_4 group has been further decomposed in one S and four O centers. In both cases, the polarizability values assigned to the different interaction centers are compatible with the SDS polarizability. The formulation of the potential energy function and the corresponding parameters are given in Refs. 8 and 9.

For the V_{el} of water we have considered a three point charge distribution compatible with the dipole moment of the molecule[3,5–7] while a five point charge distribution, compatible with the value of the quadrupole moment, has ben considered for CO_2.[9] For that of SDS, the same charge distribution used to study the formation of SDS micelles in water[10] has been employed. In the CH_4 molecule, the C and H atoms, because of their shared electron pairs, have similar electronegativity. This fact, together with the high symmetry of the molecule and the absence of permanent dipole and quadrupole moments prompted the use of a null effective charge on each atom.[8,11]

The CH_4 and CO_2 molecules have been considered as rigid while the water and SDS molecules have been considered as flexible. The intramolecular potential for water has been described considering harmonic bonds and angles[3,12] while that of the SDS molecule, is formulated as a sum of the covalent bonds, the angles and dihedral interaction terms plus the noncovalent contributions, described as the corresponding intermolecular ones. The parameters for covalent bonds and angles are taken from AMBER Intramolecular Generalized Force Field,[13] while for dihedrals we have adopted the parameters given in Ref. 10

3. The CO_2-water and the CH_4-water systems

The possibility of forming clathrates without the presence of the SDS surfactant molecule has been analyzed by surrounding a different number of gas molecules (1, 5 and 50) by a total of 256 flexible water molecules. MD simulations considering an NpT ensemble of particles have been performed at different conditions of pressure p and temperature T. Cubic boundary conditions have been imposed. A time step of 1 fs has been used and the systems have been equilibrated along 40 ps. Once equilibrated, the trajectories have been run for 10 additional ns. Bearing in mind the results from neutron diffraction experiments[14] indicating that the conversion of ice to clathrate hydrates is a temperature dependent process with a complete conversion of ice into clathrate hydrate occuring at 276.8 K by slowly warming the pressurized sample from 272.2 to 278 K and suggesting that incomplete conversions can be observed in the 230 K $\leq$ T $\leq$276 K temperature range, we have performed MD simulations in a similar range of T. In particular, MD simulations in the 200-300 K have been performed at a pressure of 8 MPa. The propensity of water molecules to cluster around the CO_2 ones is quantified by the pair radial distribution functions between the C atom of CO_2 and the O atom of the water molecules (see Fig. 1). As can be seen from the figure even for a system formed by only 1 molecule of carbon dioxide and 256 molecules of water, the radial distribution functions are different to the ones observed for neat water (see for instance Ref. 3).

The structural organization observed in Fig. 1 is similar to that obtained in an MD simulation of the CO_2 capture by montmorillonite.[15] Moreover, the values of the mean diffusion coefficients of CO_2 obtained at different temperatures are also consistent with the clathrate formation. The coefficient of water is higher than that of CO_2. Then, when slowly increasing T, as a consequence of the the trapping of the carbon dioxide molecule within a water molecule cage, the difference in the diffusion coefficient of water and CO_2 vanishes. However, by further increasing T, due to the destabilization of the trapping cage and to the consequent release of the CO_2 molecule, the diffusion coefficient of CO_2 quickly increases.

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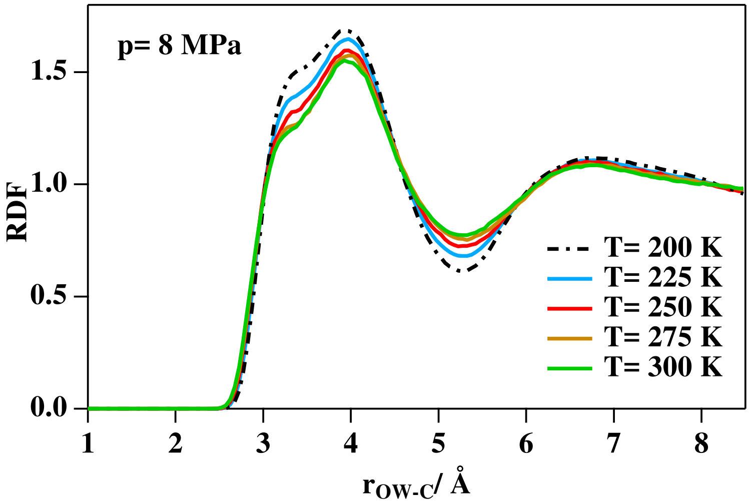

Figure 1: Radial distribution functions, RDF, for OW-C, at 8 MPa of pressure and different temperatures in the 200-300 K temperature range.

Similar results have been obtained by considering more CO_2 molecules.

A different result has been obtained when the formation of methane clathrates has been investigated. In fact, in absence of SDS, the presence of CH_4 molecules seems not to affect the structural order of neat water. In Fig. 2, the OW-C RDFs for the methane-water and carbon dioxide-water systems are represented at the same conditions of pressure and temperature.

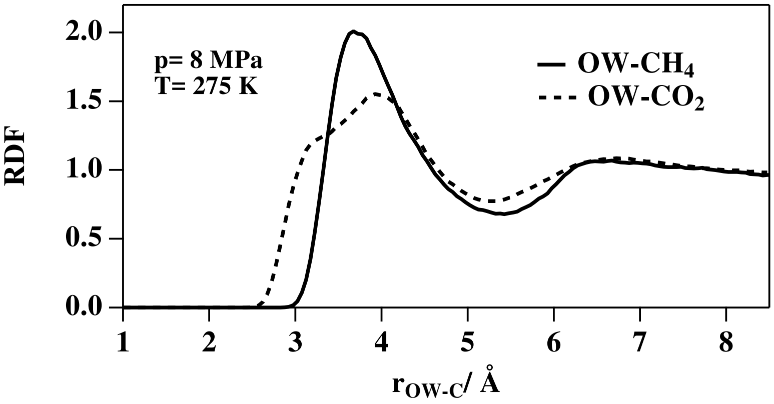

Figure 2: Radial distribution functions, RDF, for OW-C, at 8 MPa of pressure and 275 K for the CO_2-water and CH_4-water systems.

The difference on the RDF functions for the two systems persists independently of the

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number of guest molecules considered and at several p-T conditions. Moreover, the structure of the water molecules around the CH_4 molecule has been investigate along the trajectory, every 100 steps and no clathrate structures have been observed. Moreover, no evidence of the clathrate formation has been observed from the analysis of the mean diffusion coefficients. Such observations suggest that, at the investigated conditions, the formation rate of the methane clathrate is very low.

4. The CO_2-SDS-water and the CH_4-SDS-water systems

In order to analyze how the presence of a surfactant affects the formation of clathrates we have considered the CO_2-SDS-water and the CH_4-SDS-water systems. The equilibrium structures of CO_2-SDS and CH_4-SDS surrounded by water molecules have been taken as initial configurations. MD simulations for both systems have been performed using the same conditions as in the previous section. By analyzing the final configuration of the systems it can be observed that, independently of the p-T conditions, the SDS molecule remain close to the guest molecule for the CO_2-SDS-water system, thus preventing the formation of the cage. Such behavior, due to the CO_2-SDS interaction is reflected in the OW-C RDF for the CO_2-SDS-water system, as can be seen in Fig. 3.

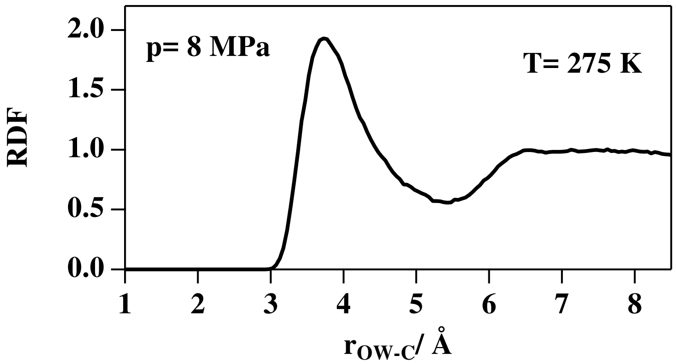

Figure 3: Radial distribution functions, RDF, for OW-C, at 8 MPa of pressure and 275 K for the CO_2-SDS-water system.

On the contrary, the SDS molecule is placed far away of the CH_4 molecule at the end if the trajectory, allowing the formation of the cage around methane. In fact, the analysis of the coordinates reveals that the SDS molecule, interacting with water in presence of CH_4 tends to form a sort of basket, driving water molecules around the guest. The folding of SDS helps the formation of a cage suitable to host a CH_4 molecule, thus producing a catalytic effect. Moreover, as was observed for CO_2 in the previous section, in a range of p-T conditions the mean diffusion coefficients of CH_4 and H_2O are the same. Such behavior has not been observed for CO_2-SDS-water. In spite of the fact that the formation of the methane clathrate can not be observed from the RDF functions, the analysis of the steps along the trajectory allow to detect the incipient formation of clathrate structures, as shown in Fig. 4.

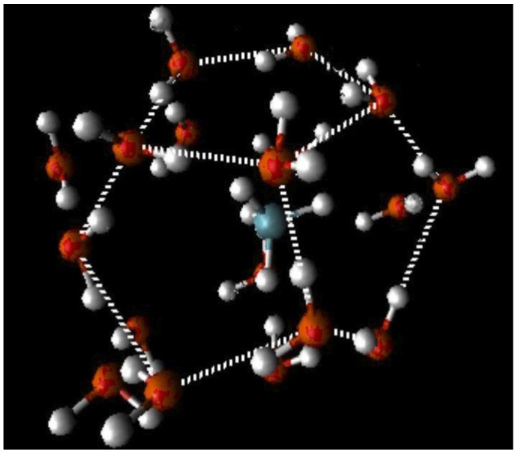

Figure 4: Incipient formation of a methane clathrate cage.

5. Discussion of the results

The obtained results clearly indicate that the SDS surfactant plays a different role when interacting with the CO_2-water and the CH_4-water systems. Such result is not surprising bearing in mind the strong electrostatic contribution in the CO_2-SDS-water system in comparison with the CH_4-SDS-water one. However, to ensure that the results are not due to the different masses of the guests, additional MD calculations were performed by artificially assigning to CO_2 the same molecular mass of CH_4. The simulations indicate that no appreciable effect could be attributed to the heavier mass of CO_2 in comparison with the CH_4. Accordingly, the differences in the formation of clathrate hydrates in the CO_2-SDS-water and the CH_4-SDS-water systems can only be attributed to the different charge distribution in the guest molecules. As it has been already mentioned, the CO_2 molecule is characterized by a high quadrupole moment, while the CH_4 molecule has neither dipole nor quadrupole moments and it is characterized only by a small octupole moment. In the case of the CO_2-SDS-water system, the strong SDS- CO_2 electrostatic contribution disrupts the natural tendency to form the clathrate observed for the CO_2-water system whose interaction is dominated by a quadrupole-dipole moment contribution. On another hand, the CH_4-water system is dominated by a nonelectrostatic contribution, which probably requires long integration times before observing the formation of the clathrate. In this case, the presence of SDS catalyzes the clathrate formation. These observations allow to conclude that the SDS surfactant is adequate to promote the formation of clathrate hydrates only when the guest does not interact strongly with it.

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