The thermal properties of binary structure sl clathrate hydrate from molecular dynamics simulation

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1. Introduction

Clathrate hydrates are non-stoichiometric crystalline inclusion compounds which the host in the crystalline structure contains cavities, holes or channels that guest atoms or molecules with appropriate size are trapped. The structure of clathrate hydrate is formed by the size of the guest molecules which according to this, the clathrate hydrates have three known common structures; structure I (sI), structure II (sII) and structure H (sH) and five cavities, pentagonal dodecahedron (512), tetrakaidecahedron (51266), hexakaidecahedron (51266), irregular dodecahedron (45566) and icosahedron (51266) [1].

The knowledge of the structural and thermodynamic properties of clathrate hydrates such as thermal expansion, isothermal compressibility coefficient and heat capacity are important for increasing our understanding of intermolecular interactions between guest–host and guest–guest molecules and knowledge of these properties is needed to understand the details of the spectroscopic studies. The research results have been shown most of the properties of clathrate hydrate such as Raman and infrared spectra [2,3] are similar to those of ice Ih due to the similar hydrogen bonded but clathrate hydrates by molecular dynamics simulations. The obtained values of lattice parameters for the guest species are compatible with the experimental values. These clathrate hydrates are simulated with TIP4P/ice four-site water potential. Herein, isobaric thermal expansivity and isothermal compressibility are calculated at a temperature range of 50–250 K and a wide pressure range. These structural properties have been compared for guests which they are isoelectronic and have similar masses but with different size and polarity. We use molecular dynamics simulations to relate microscopic guest properties, like guest–host hydrogen bonding to macroscopic sl clathrate hydrate properties. The temperature dependence of thermodynamic properties such as constant-volume and constant-pressure heat capacity is presented in the atmospheric pressure for these guest species.

Clathrate hydrates depend on the complicated nature of the hydrate lattice and guest type [5–7].

Tse et al. have compared the thermal expansivity of different guests in clathrate hydrate with ice Ih and have reported the thermal expansivity is much larger than that of ice Ih especially below 200 K due to the presence of guest molecules in clathrate hydrate and guest–host interactions between them [8–12]. The guest molecules size and shape, the rotational motions of guests, water cage occupancy percentage and guest–host hydrogen bonding capability affect the lattice parameter and thermal expansivity. Many experimental research [13–15] and theoretical studies have been carried out in order to investigate effect of type and size guest and number of the guest molecules in the cages on the lattice parameter and thermal expansivity clathrate hydrate. The lattice parameters and thermal expansivity have been shown for four Structure I (C2H6, CO2, 47% C2H6 + 53% CO2, and 85% CH4 + 15% CO2) and seven Structure II (C2H6, 60% CH4 + 40% C3H8, 30% C2H6 + 70% C3H8, 18% CO2 + 82% C3H8, 87.6% CH4 + 12.4% i-C4H10, 95% CH4 + 5% C6H10O, and a natural gas mixture) by experimental measurement [13]. Hester et al reported that there is a general correlation between in the thermal expansivities for a given hydrate structure. The thermal expansion for clathrate hydrates of Ar, Kr and C3H8 of cubic sII, Xe and CH4 hydrates of cubic sI and also for empty lattices of sI and sII calculated within framework of lattice dynamics approach in quasiharmonic approximation [16]. The MD simulation performed for measurement the lattice parameter and thermal expansivity of the binary THF and H2 sII clathrate hydrate [17], the CH4 and CO2 sI
clathrate hydrate with using TIP4P/2005 and TIP4P/ice water models [18,19] and large molecule guest substance (LMGS) like NH in sH clathrate hydrate [20] to investigation effect the size of guest molecules and guest molecule occupancies on the thermal expansion. These studies show clathrate hydrate formed by guest molecules with large van der Waals radius lead to expanding of the host lattice and also the thermal expansion coefficients for these molecules are less than hydrate including small guest molecule. The larger the size of the guest molecules, the vibrational anharmonicity and thermal expansivity decrease. However, the effect of hydrogen bonding of the guest molecules and cage water molecules are not fully investigated on the lattice parameter and thermal expansivity. The isothermal compressibility is one of the guest-dependent structural properties. The powder neutron diffraction be used for determining structural properties of N₂, O₂, and air clathrate hydrate such as isothermal compressibility that have specified significant differences in the compressibilities of N₂ and O₂ clathrate hydrates [21]. The unit cell parameters and isotherm compressibilities for O₂-clathrate and N₂-clathrate that N₂ and O₂ molecules have almost identical size appear to be determined not only by the size and shape of the guest molecules but also by the strength of molecular interaction. The unit cell volume and isotherm compressibility for The O₂-clathrate are larger than N₂-clathrate that due to the O₂-clathrate has stronger guest–host interaction. The temperature dependence of polyhedral cage volumes of trimethylene oxide (TMO) sI and sII clathrate hydrates are calculated from atomic positions determined from neutron powder–diffraction data. This study reveals the guest–host interaction in certain cases, and differences between the dodecahedral cages (small cages) of sI and sII containing TMO molecule [22]. Molecular dynamics simulations have been performed on sI methane hydrate for considering the effect of the amount of methane contained in the hydrate. These MD simulations determine that the presence of methane increases slightly the value of the unit cell and decreases slightly the compressibility of the structure [23]. However, studies of thermal expansivity, and isothermal compressibility of the guest species that are different in the ability to form guest–host hydrogen bonding with water lattice by the MD simulation method are fewer. Alavi et al. determined the effect of the guest species (cyclic ethers) like THF, 1,3-dioxolane, THP, and p-dioxane in sII clathrate on the structure, thermal expansivity, and isothermal compressibility [24] but this effect has not been studied for three-member and four-member heterocyclic ethers and small molecules with carbonyl functional groups in sI clathrate hydrate.

The heat capacity of clathrate hydrate is the most important property. The heat capacity of sIethylene oxide clathrate hydrate [25], the pure and KOH-doped argon and tetrahydrofuran clathrate hydrates [26,27] and structure I hydrate of trimethylene oxide have been measured by experimental methods [28]. However, measuring the heat capacity of clathrate hydrate by calorimetric method is also rather difficult. We recently studied the probability of guest–host hydrogen bonding formation trimethylene oxide (TMO), ethylene oxide (EO) and formaldehyde (FA) as polar guests compared with non-polar guest molecules with similar structure cyclobutane (CB), cyclopropane (CP) and ethane (Et), respectively for TMO, EO, and FA using MD simulations with the SPC/E and TIP4P/ice force field [29]. The guest–water hydrogen bonding probability increases with temperature in all of guests and at each temperature, the TMO molecules have the largest probability of hydrogen bonding with cage waters. In this paper, we show that the guest–host interaction plays an important role in the determination of the macroscopic properties of gas hydrates at high temperature.

Herein, in order to study the effect of the size and nature of guest molecules on the structural properties of clathrate hydrate, we plot lattice parameter versus temperature and pressure for guest species such as TMO, EO, FA, CB, CP and Et in large cages and CH₄ help gas in small cages by molecular dynamics simulation on a wide range of pressure and temperature. Using these plots, we calculate thermal expansivity and isothermal compressibility of the clathrate phase for the guest molecules. The heat capacities at constant volume (Cᵥ) and constant pressure (Cₚ) are estimated respectively from MD simulations in NVT and NPT ensembles at 50–250 K.

2. Computational details

In the molecular dynamics simulations, the initial coordinates of the water oxygen atoms in the sI clathrate hydrate cubic unit cell (a = 12.09 Å) are taken from X-ray crystallography [30] and the initial positions of the water hydrogen atoms about the oxygen atoms were assigned to be consistent with the ice rules. In the simulations, 3 × 3 × 3 replica of the sI clathrate hydrate unit cell with 46 water molecules is used. The initial guest molecule structures were determined by quantum chemical structural optimisation at DFT level using (B3LYP parameterisation) with the 6-311+G(d,p) basis set using the Gaussian 09 suite of programs [31]. The intermolecular van der Waals potentials between atoms i and j on different molecules are modelled as a sum of Lennard–Jones (LJ) and electrostatic point charge interactions:

\[ V(r_{ij}) = \sum_{i,j} 4\epsilon_{ij} \left[ \left( \frac{r_{ij}}{\sigma_{ij}} \right)^{12} - 2 \left( \frac{r_{ij}}{\sigma_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}, \]

where \( \sigma_{ij} \) and \( \epsilon_{ij} \) are the distance and energy parameters of the ij pair of atoms separated by a distance of \( r_{ij} \) and \( q_i \) and \( q_j \) are the electrostatic point charges on the atoms. For potentials between unlike atoms, standard combination rules, \( \epsilon_{ij} = (\epsilon_i\epsilon_j)^{1/2} \) and \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \), are used. Partial electrostatic charges on the atoms of the structurally optimised guest molecules were calculated using the ‘charges from electrostatic potential grid’ (CHELPG) method [32]. The values for the parameters \( \sigma_{ii}, \epsilon_{ii} \) and \( q_i \) for selected atom types used in the simulations are given in Table S1 of the Supporting Information (SI).

The large cage guest molecules (TMO, EO, FA, CB, CP) were modelled with the general AMBER force field (GAFF) [33] and the Murad–Gubbins potential [34] and the OPLS force field [35] were chosen for methane and ethane molecules, respectively. The water molecules in the clathrate were modelled using the TIP4P/ice four-charge model [36].

The molecular dynamics simulations on periodic simulation cells were performed using the DL_POLY software program version 2.18 [37] with pressure and temperature regulated...
using the modified Nosé–Hoover thermostat-barostat algorithm [38–40] and thermostat and barostat relaxation times of 0.1 and 1.0 ps, respectively. A cutoff of 15 Å is applied to the short-range Lennard-Jones interactions and the electrostatic interactions are evaluated through the Ewald sum method. In all MD simulations a Verlet leap-frog algorithm with a time step of 1 fs was used for the integration of the equations of motion. At the desired temperature, the NPT or NVT simulations with 270,000 steps is used. The first 70,000 steps are used for equilibration and not included in the averaging. During the equilibration stage, the calculated clathrate hydrate structures and energies were seen to converge. To get good statistics in these calculations, at every temperature, at least five NPT or NVT simulations are performed using different starting configurations for the guest molecules and the average results of all simulations have been used. In this way it was ensured that an ensemble average is taken, which provides sufficient accuracy.

3. Results and discussion

3.1. Thermal expansivity

In our work, we considered the cell vector length dependence on temperature for TMO, EO, FA, CB, CP and Et as guest molecules with using TIP4P/ice water model from temperatures 50–250 K at ambient pressure and 120 bar that have shown in Figure 1. Experimental lattice parameters for TMO, EO and Et hydrates as a function of temperature at atmospheric pressure have been compared with the experimental values. The lattice parameter obtained for Et is in better agreement with the experimental results. The TIP4P/ice model exhibits larger value of the lattice parameters for TMO and EO hydrate than experimental values.

The slopes of the lattice parameters as a function of temperature appear similar. The slope of these figures is related to thermal expansivity ($\alpha$) where this property was obtained according to the following definition, where $n$ is the number of moles in a system and $a$ is lattice parameters, Å:

$$\alpha = \frac{1}{a} \left( \frac{\partial a}{\partial T} \right)_{n, P}. \quad (2)$$

The temperature dependence of $\alpha$ is assumed to be:

$$\alpha = a_1 + a_2(T - T_0) + a_3(T - T_0)^2. \quad (3)$$

By separation of variables and integration we obtain Equation (4):

$$\ln \left( \frac{a}{a_0} \right) = a_1(T - T_0) + \frac{a_2}{2}(T - T_0)^2 + \frac{a_3}{3}(T - T_0)^3. \quad (4)$$

Expansion coefficients of Equation (3) ($a_1$, $a_2$, $a_3$) obtained by fitting the curve of $\ln(a/a_0)$ against $(T-T_0)$. The $\ln(a/a_0)$ against

![Figure 1.](image-url)
As shown in Figure S1, the correlation between data and fitted line of the form of Equation (4) is very good for all of guest molecules. The coefficients \( a_1, a_2, a_3 \) for all of guest species in clathrate hydrate at atmosphere pressure and 120 bar are given in Tables S2 and S3 of the SI, respectively. The thermal expansion of different guest molecules for both pressure have been calculated using the expansion coefficients given in Tables S2 and S3 and Equation (3) and the results are shown in Figure 2.

We have showed in our previous work that the TMO, EO and FA guest molecules form guest–host hydrogen bonds (see Figure S2 of SI) in contrast with non-polar guests with analogous structures, CB, CP and Et, respectively. The guest–host hydrogen bonding probability increases with temperature and so the guest–host hydrogen bonding between the TMO molecule and water is stronger than the other guest molecules. Figure 2(a) indicates that in the low temperature region (100–150 K) the effect of guest molecules size on the value of the thermal expansivity of the mixed hydrates overcomes the effect guest–host hydrogen bonding. Therefore, at high temperatures, the larger value of thermal expansion for TMO, EO and FA compared to CB, CP and Et can be attributed to guest–host hydrogen bonding with water lattice. Figure 2(a) also shows dependence of the sI hydrates thermal expansion on temperature at atmospheric pressure using the experimental data of Hester et al. [13] For comparison, the calculated isobaric thermal expansion for methane sI hydrate using TIP4P/ice water model at atmospheric pressure by Costandy et al. [19] are presented in Figure 2. We observe that the obtained values of thermal expansion in this work are closer to the experimental result.

### 3.2. Isothermal compressibility

The pressure dependence of the unit cell volume for different sI clathrates in the range of pressure 0.01–5 kbar at 150 and 250 K are shown in Figure 3. As seen from Figure 3, with an increase in the size of guest molecules, the unit cell volume of hydrate increases because the large molecule stretches lattice hydrate and has larger unit cell volume. The guest molecules at low temperature (150 K) have less effect on the unit cell volume than high temperature (250 K) because the guest–host interaction at low temperature is weak. The unit cell volume of different sI clathrate hydrate was used to determine the isothermal compressibilities (\( \beta \)) which is defined as:

\[
\beta = -\frac{1}{V} \frac{\partial V}{\partial P} \left| _{n,T} \right.
\]

where \( V \) represents unit cell volume, Å\(^3\). We suppose, \( \beta \) is as a function of pressure that have shown in Equation (6):

\[
\beta = -b_0 - b_1(P - P_0) - b_2(P - P_0)^2.
\]

By separation of variables and integration, Equation (7) is obtained:

\[
\ln \left( \frac{V}{V_0} \right) = b_0(P - P_0) + \frac{b_1}{2}(P - P_0)^2 + \frac{b_2}{3}(P - P_0)^3,
\]

where \( V_0 \) is lattice volume at a reference pressure \( (P_0) \). Expansion coefficients of Equation (6) \( (b_0, b_1, b_2) \) determined by fitting the curve of \( \ln (V/V_0) \) versus \( (P-P_0) \) to cubic equation.
The \( \ln \left( \frac{V}{V_0} \right) \) against \( (P-P_0) \) for variety guest species in sl clathrate hydrate has been shown at 150 and 250 K in Figure S3 of SI.

As shown in Fig. S3, the correlation fits of the data on the base Equation (7) is very good for all of the guest molecules. The expansion coefficients for TMO, EO, FA, CB, CP and Et clathrate hydrate at 150 and 250 K can be seen in Table S4 and S5 of SI, respectively. The isothermal compressibility values for different guest molecules have been calculated by expansion coefficient given in Tables S4 and S5 and Equation (6). These values for both of temperatures are shown at Figure 4.

Figure 4 demonstrates that \( \beta \) is different for variety type of guest molecules at lower pressures and is almost similar at higher pressure. Figure 4(a) shows that the size and geometry of the guest molecules in the large cages at low pressures have a greater effect on the compressibility than at high pressures. The TMO guest molecule is tethered to the water by strong hydrogen bonds which have short average life times at high temperatures with the hydrogen bonds forming and breaking at short time intervals. Therefore, with increasing temperature the vibrational anharmonicity due to the formation and breaking hydrogen bonds increases and the compressibility for this molecule is larger than CB clathrate at 250 K.

In Figure 4(b), the values of the isothermal compressibility are compared with experimental and other MD simulation results. The experimental isothermal compressibility of ethane sl hydrate between 0 and 2 MPa at room temperature. The isothermal compressibility of fully occupied methane sl hydrate was calculated using the MD simulations at 250 K with TIP4P/2005 water model by Docherty et al. [23] and at 271.15 with TIP4P/2005 water model by Ning et al. [18] and also 250 K with TIP4P/ice by Costandy et al. [19]. In Figure 4(b), we find that our isothermal compressibility results for ethane hydrate are similar to those of Docherty et al. on slope.

3.3. Heat capacity at constant volume and pressure

The heat capacity by using molecular dynamics simulation, Parallel-tempering isothermal-isobaric Monte Carlo simulations for Xe hydrate [42], Kr(H2O)20 cluster [43] and experimental methods for Xe-6.17H2O and Kr-5.993H2O [44], EO and THF hydrate [45], methane and ethane hydrates [46,47] have been calculated. Using the experimental method, the heat capacity per unit volume have been measured for structure II clathrate hydrates of 1,3-dioxolane (DO) and cyclobutanone (CB), and compared the results with similar previous measurements for tetrahydrofuran (THF).

In this work, molecular dynamics (MD) simulation was performed to evaluate the specific heat capacities for various guests in the sl clathrate hydrate. By MD simulations in NVT and NPT ensembles, the heat capacities at constant-volume \( (C_V) \) and at constant-pressure \( (C_P) \) for binary clathrate hydrate are estimated between 50–250 K and 1 bar respectively. In order to calculate \( C_P \) and \( C_V \), we have obtained the fourth degree polynomial fit of \( E_{\text{NPT}} \) and \( E_{\text{NVT}} \) as a function of temperature (see S4 and S5 Figs. in SI), respectively and we have used from 8 and 9 equations and differentiate the fitted function to obtain heat capacity. The \( E_{\text{NPT}} \) and \( E_{\text{NVT}} \) are enthalpy of
system and total internal energy of system, respectively.

\[ C_P = \left( \frac{\partial E_{\text{NPT}}}{\partial T} \right)_P, \quad (8) \]

\[ C_V = \left( \frac{\partial E_{\text{NT}}}{\partial T} \right)_V. \quad (9) \]

The constant-pressure heat capacity of EO, TMO, FA, CB, CP and Et guest molecules in sI clathrate hydrate as a function of temperature at 1 bar can be fitted to Equation (10) as follows:

\[ C_P = a + bT + cT^2 + dT^3. \quad (10) \]

The value of fit parameters \(a\), \(b\), \(c\) and \(d\) are given in Table 1.

The calculated \(C_P\) of guest molecules in sI clathrate hydrate is plotted in J kg\(^{-1}\) K\(^{-1}\) in Figure 5. For different guest molecules in clathrate hydrate with increasing temperature, the constant-pressure heat capacities increase slightly. The calculated \(C_P\) of EO and Et hydrate are plotted in Figure 5 compared to publish experimental results of \(C_P\) for EO-6.86H\(_2\)O sI hydrates [25], EO-6.89H\(_2\)O sI hydrates [45] and Et-7.67H\(_2\)O sI hydrates [47]. Although there is different between heat capacities calculated and experimental data especially at low temperatures but the trend of \(C_P\) for both plots (experimental and this work) increases with increasing temperature. The cages in the gas hydrates in the lab and in nature may not be fully occupied by guest molecules and the hydrate samples may have impurity that these empty cages and impurity may also affect the experimental value of the heat capacity. The cage occupancy depends upon the temperature, pressure, guest concentration and the guest and cage types. The results of heat capacities of methane and CO\(_2\) hydrates obtained

![Figure 4](image4.png)

**Figure 4.** (Colour online) Pressure dependence of the isothermal compressibility of various hydrates at (a) 150 K and (b) 250 K. The green pluses represent the calculated isothermal compressibility from the bulk modulus experimental data of methane hydrate at 253.15 K provided by Helgerud et al. [41]. Experimental data for the isothermal compressibility of ethane sI hydrate at room temperature are from Manakov et al. [15] (orange circles). The MD simulation data for methane hydrate isothermal compressibility as a function of pressure at 250 K using the TIP4P/2005 water model by Docherty et al. [23] (violet stars), at 271.15 using the TIP4P/2005 water model by Ning et al. [18] (cyan multiplication sign) and 250 K using the TIP4P/ice water model by Costandy et al. [19] (yellow triangle right).

![Figure 5](image5.png)

**Figure 5.** (Colour online) Temperature dependence of specific constant-pressure heat capacity of guest molecules in sI clathrate hydrates at 1 bar and different temperatures. Experimental data for the heat capacity of EO-6.86H\(_2\)O hydrate are by Yamamuro et al. [18] (green pluses), EO-6.89H\(_2\)O hydrate by Leaist at al. [45] (red multiplication sign), Et-7.67H\(_2\)O hydrate by Handa at al. [47] (blue triangles right) and Et hydrate by Nakagawa at al. [46] (magenta star).
The obtained isochoric heat capacity using the fluctuation formula and reaction field method for 3×3×3 systems of methane hydrate at 265 K and 1 bar is equal to 2.24 kJ kg⁻¹ K⁻¹.

The calculated \( C_V \) of guest molecules in sl clathrate hydrate is plotted in J kg⁻¹ K⁻¹ in Figure 6. As expected, the constant-pressure heat capacity of variety guest molecules is larger than corresponding to the constant-volume heat capacity. The results for the constant-volume heat capacity of methane sl hydrate are presented using MD simulation by English [48] and the results are also in good agreement with experimental reports at low temperatures.

We have obtained the following fourth-order polynomial fit of volume-constant heat capacity of EO, TMO, FA, CB, CP and Et guest molecules in sl clathrate hydrate as a function of temperature at 1 bar which the value of fit parameters are given in Table 2.

\[
C_V = a + bT + cT^2 + dT^3. \tag{11}
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this paper which may be due to the difficulty of compressing clathrate hydrate and the presence of gases within their cavities.

Acknowledgements

The authors would like to thank Saman Alavi for discussions on clathrate hydrate compounds. H. M. and H. G. thank the University of Yazd for computational support.

Disclosure statement

No potential conflict of interest was reported by the authors.

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