



CO₂ hydrates phase behaviour and onset nucleation temperatures in mixtures of H₂O and D₂O: Isotopic effects

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ABSTRACT

In this work, we report the CO₂ hydrate phase equilibria in water (H₂O), heavy water (D₂O), and their binary mixtures following the isochoric pressure search method using a rocking cell apparatus. The phase behaviour was mapped within the temperature and pressure range of 276.32 – 284.80 K and 1.59 – 3.78 MPa, respectively. It was found that there is a difference of ~ 2 K in the equilibrium line of CO₂ hydrates formed in H₂O and in D₂O, respectively. The hydrate dissociation enthalpies obtained using the Clausius-Clapeyron equation indicate almost similar values formed either in D₂O, H₂O or their mixtures. These shifts in this equilibrium temperature were compared with the triphasic equilibrium temperature variation estimation obtained using Molecular Dynamics Simulations and a very good agreement with the experimentally obtained values was observed. Further, a constant cooling method was used to obtain the onset temperature of hydrate nucleation for these systems at 3.6 MPa. It has been found that during the cooling ramps, the nucleation always occurred in the vicinity of the temperature of maximum density (TMD) of the systems where water still retains some structuredness. The nucleation experiments also give information about the metastable zone width (MSZW) of the studied systems. The results reported in this work indicate the magnitude of the isotopic effect on CO₂ hydrate formation and dissociation that may have implications towards the application of hydrate technology for separation and purification processes.

1. Introduction

Gas hydrates (GHs) are crystalline solid materials that resemble ice but are composed of water and gas molecules where the gas molecules got entrapped within the polyhedral cavities formed by the hydrogen bonded water molecules [1]. GHs are metastable crystalline structures that require low temperatures and moderate pressures for their formation [2]. These conditions are often encountered during gas processing thereby the formation of hydrates within the production pipelines is a big flow assurance issue for the oil and gas industry [3]. There are only Van der Waals interactions between the guest (gas) and the host (water). The guest molecule can freely rotate within the three-dimensional hydrogen-bonded cages made up of the hosts [4]. Owing to the possibility of enclathration of a large volume of guest gas, GHs are being

considered as a potential alternative for gas storage, transportation, and many other sustainable applications [5,6]. However, there are some hurdles such as the slow kinetics and stochasticity of nucleation to overcome before scaling up the GH-based technology with the economic viability and energy efficiency [7]. There are primarily three types of hydrate structures viz., sI, sII and sH, which depends on the ratio of the size of gas (host) molecule and of the host cavity. For instance, CH₄ and CO₂ normally form structure I (sI) type of hydrates. CO₂ hydrates are also being considered as an alternative way of carbon capture and sequestration because of their high volumetric storage capacity (167 v/v), hydration number (6.04) and recently demonstrated long term stability in oceanic environment [8–13].

One way to understand the complexities of GHs formation is to study their phase behaviour and the effect of various parameters on their

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formation and dissociation. The hydrate phase behaviour of different gases (guests) in the absence/presence of different additives is well reported [14–16]. The type of water (hosts) also plays a significant role in hydrate formation and dissociation but investigations in this direction are relatively scarce. In a handful of reports the effect on hydrate formation and dissociation behaviour by replacing the host (pure water, seawater, distilled water, or natural water) is investigated [17–20]. However, to the best of our knowledge, the effect of changing the host framework on the hydrate nucleation behaviour is not well explored.

Isotopic effects indicate the difference in the outcome or magnitude of a given property of a material by substituting the isotope of a certain atom within the molecule, for instance, changing the hydrogen (H) atoms of water by deuterium (D) atoms to obtain heavy water. This small difference at the atomic level is generally reflected in the bulk, transport and surface properties [21,22]. Isotopic effects are very interesting because the magnitude of these effects can shed some light on the nature of the intermolecular interactions and structures in liquids and liquid mixtures [23]. Ice crystallization to separate heavy water (D₂O) from water (H₂O) is known for a long time [24] but due to its low separation factor, it is not preferred over other methods [25]. Hydrate-based separation could also be an alternative method. However, there is a need to ascertain the energy and/or economics associated with it. Therefore, in this work, we have used D₂O which is reported to be more structured compared to H₂O [26] as another guest to explore the effect of isotopic substitution on the phase behaviour and nucleation of CO₂ hydrates.

In order to obtain the structural insights of gas hydrates formation by neutron scattering [27–31], X-ray diffraction [32], high-pressure NMR [33], Raman spectroscopy [34], and more recent techniques such as mid-infrared fiber-optic evanescent field sensing [35], deuterated water is used to prepare samples in the majority of these techniques. The physical properties of D₂O and H₂O are not similar and might alter the interaction prevailing in the systems under scrutiny (Table 1). Therefore, it is a prerequisite to have information on the isotopic substitution effect on the behaviour of the system [36].

A survey of the literature indicates that the effect of isotopic substitution or role of water on hydrate formation or dissociation is explored [36–39]. For instance, Jones et al. [37] studied the effect of isotopic substitution on tetrahydrofuran (THF) hydrate dissociation and eutectic temperatures using differential scanning calorimetry at atmospheric pressure. Chun et al. [40] and Kida et al. [41] presented the hydrate phase equilibrium data for CO₂, CH₄, C₂H₆, C₃H₈ and Kr in D₂O to understand the effect of the host substitution. Substitution of hydrogenated water to deuterated one has been shown to shift the hydrate equilibrium towards higher temperatures at a given pressure [40,41]. D₂O was also reported to facilitate the self-preservation effect for methane hydrates above the freezing point of water [42]. More recently, cyclopentane and CO₂ hydrate formation and growth in D₂O were studied with implications towards the tritium separation process [43,44]. However, the effect of isotopic substitution on CO₂ hydrate nucleation temperature in D₂O or mixtures of D₂O + H₂O is not yet explored.

In this work, we have measured the CO₂ hydrate phase equilibria in H₂O, D₂O and in their binary mixtures and compared them with the data

Table 1
Physical properties of H₂O and D₂O.

Property	H ₂ O	D ₂ O
Molar Mass (g.mol ⁻¹)	18.01528	20.0276
Melting Point (K)	273.15	276.97
Boiling Point (K)	373.15	374.55
Temperature of Maximum Density (K)	277.13 [50]	284.36 [51]
Density ^a (g.cm ⁻³)	0.99706 [60]	1.11230 [60]
Viscosity ^a (mPa.s)	0.892 [60]	1.095 [60]
Surface Tension ^a (mN/m)	71.98 ^b	71.87 ^b

^a at 298.15 K; ^bIAPWS.

reported in the literature. A simple correlation was proposed to estimate the hydrate equilibrium temperature with respect to the D₂O fraction. The shift in the three-phase equilibrium temperature of the CO₂ hydrate phase due to the substitution of H₂O by D₂O has also been estimated through Molecular Dynamics, using the direct coexistence technique, providing values compatible with the presented experimental results. Dissociation enthalpies were also calculated from experimental equilibrium data, and the gradual effect of host substitution has been explored and compared to other hydrate formers reported in the literature. Moreover, using a constant ramping method the onset temperature of hydrate nucleation and the metastable zone width (MSZW) of the studied systems were also explored.

2. Experimental

2.1. Materials

Carbon dioxide gas (99.995 %) was purchased from Alphagaz™ (Air Liquide, Portugal). Deuterated water (deuterium oxide, D content of 99.9 %) from Cambridge Isotope Laboratories, Inc., and Milli-Q water were used in all the experiments to prepare the mixtures. The heavy water was handled in dry and inert atmosphere. Mixtures were prepared by weight using an Ohaus balance with ± 0.00001 g precision. The uncertainty in reported mole fractions is ± 0.0001. Three mixtures were prepared corresponding to 75 wt% (75 D), 50 wt% (50 D) and 25 wt% (25 D) of D₂O. The concentrations can also be expressed in terms of mole fractions of D₂O, wherever needed, as 0.7694, 0.5264 and 0.2704, respectively.

2.2. Experimental setup

The CO₂ hydrate phase behaviour and the kinetic experiments in Milli-Q and heavy water were performed in a rocking-rig assembly (PSL Systemtechnik, Germany), which contains 5 stainless steel cells, each with a volume of 40 cm³. A steel ball was placed in each cell for proper mixing. The cells can be filled with liquid phase and mounted on the top of the rocking platform. The platform was immersed in a bath whose temperature can be controlled by a precise thermostat (Huber, Ministat 230) with an uncertainty of ± 0.01 K. The cells can be filled with the gas at a desired pressure using an individual inlet valve for each cell. Each cell is attached with a separate pressure sensor. The software (WinRCS V1.8) provided with the apparatus was used to define the method with desired parameters such as temperature ramp, rocking rate, rocking angle and also to record the P-T-t data. The cells were filled with 15 mL of aqueous phase to be tested, sealed and placed on the rocking axis. Afterwards, the air present in the cells was replaced by flushing the desired gas (CO₂) 2–3 times at 0.5–1.0 MPa pressure. Later, the cells were charged with the CO₂ at desired pressure required for the experiment. A detailed description of the rocking cell apparatus can be found elsewhere [45,46].

2.3. Hydrate phase equilibria

The isochoric pressure search method was used to obtain the hydrate phase equilibrium data. The cells were filled with H₂O, D₂O and their mixtures as per the procedure described earlier. The temperature of the bath was set at 293.15 K and CO₂ was filled in each cell at the desired pressure. The system was left with rocking enabled for a period of 1 h to ensure gas dissolution and stabilization at the desired temperature and pressure. Afterwards, the system was cooled from 293.15 to 274.15 K at a rate of 3.0 K/h, which resulted in the nucleation of gas hydrates. The system was left isothermal at 274.15 K for a period of 12 h for the hydrates to grow. Later, the system was heated from 274.15 to 293.15 K with a very slow heating rate of 0.3 K/h to dissociate the formed hydrates. This heating rate is adequate to obtain good-quality hydrate dissociation points [45]. The cells were rocked at an angle of 45° and a

rate of 10 rocks/min throughout the experiments. Typical P-T loops as described in Fig. 1A were obtained, from where the hydrate dissociation points were calculated at the intersection of cooling and heating curves as described elsewhere [47] and are presented in Table 2.

2.4. Onset of hydrate nucleation temperature

A constant cooling method with continuous cooling and heating cycles throughout the experiment was employed to determine the onset temperatures of hydrate formation (T_{on}) for H₂O, D₂O and their mixtures as depicted in Fig. 1B. The cells were mounted on the rocking axis with 15 mL of aqueous phase. Later, CO₂ was introduced into each cell at an initial pressure of 3.6 MPa. The system was equilibrated at 293.15 K for an hour while rocking. Further, the bath was cooled from 293.15 to 274.15 K with a rate of 0.1 K/min and heated again up to 274.15 K using a similar rate. Throughout the experiments, the cells were rocked at an angle of 45° with a rate of 10 rocks/min. The P-T-t data was collected using the commercial software every 10 s. The pressure-temperature changes over time for a typical constant ramping experiment are depicted in Fig. 1B. From these P-t and corresponding T-t curves onset of nucleation (T_{on}) temperatures can be identified with an abrupt change in pressure as represented in Fig. 1B. After finishing the cooling-heating cycle, the system was allowed to stabilize at the initial P-T conditions for 60 min and the cycles were repeated twice. Each sample was tested in similar conditions at least 4 times and an average value of 12–18 experiments is reported as the average T_{on} in Table 3. More information about this method can be found elsewhere [48,49].

2.5. Temperature of maximum density measurements

The densities of the Milli-Q H₂O, D₂O and their equimolar mixture were measured using an Anton Paar vibrating tube densimeter (DMA 3000). The samples were prepared in an inert environment and injected into the densimeter carefully avoiding bubble formation. The densities were measured in the range of 273.15 K – 287.15 K with a temperature step of 0.10 K. More details about the measurements can be found elsewhere [50,51].

2.6. Molecular Dynamics simulation

A remarkable number of studies have focused on the determination of structural, thermophysical and phase equilibria of hydrates using different Molecular Simulation techniques (see e.g. the exhaustive reviews by English and MacElroy [52] and Barnes and Sum [53], and references therein). In particular, the three-phase equilibrium of different hydrates has been computed using Molecular Dynamics and the direct coexistence technique, providing an insightful estimate of hydrate phase equilibria and stability. Conde and Vega [54] performed a

careful calculation for methane hydrate stability, and the same methodology was later applied by Míguez et al. [55] to estimate triphasic equilibrium for CO₂ hydrate. The direct coexistence method implies simulating a hydrate crystalline phase in direct contact with two fluid phases, one containing water and the other rich in the guest molecule. By performing isothermal-isobaric (NpT) Molecular Dynamics at a given temperature, and close to the triphasic equilibrium curve, depending on the imposed pressure the hydrate in the simulation box will grow or dissociate, and by running different pressure values along the isotherm, the stability limits of the boundary can be determined, thus yielding an estimate of the three-phase equilibrium point for the molecular models used in the calculation, as detailed in the cited references [54,55]. This technique allows comparing the quantitative performance of different molecular models for the hydrate and guest molecules and provides also a detailed atomistic level description of the involved phenomena. In this work, we employed the equivalent approach of simulating our system at a series of temperatures (18 in each series) along isobars (70, 100, 200 and 300 bar) to obtain the respective three phase equilibrium points. The replacement of H₂O by D₂O in the hydrate structure molecules is a quite straightforward step, as only the mass of the lightest H atoms has to be replaced by that of D, while the other characteristic interaction parameters of the force field may be used as provided in the original version. Following the approach used for the previous work describing the stability of CO₂ hydrate [55], the rigid non polarizable TIP4P-Ice model [56] has been used to describe water, while CO₂ was modelled according to TraPPE [57] force field. All the simulations were carried out with Gromacs [58,59] during 10 ns of equilibration and 10 ns of production each point.

3. Results and discussion

Table 1 depicts the difference in various physical properties of water (H₂O) and heavy water (D₂O) due to isotopic substitution. There is a clear difference between various physical properties. The effect of isotopic substitution on the hydrate phase behaviour and nucleation phenomenon was explored in the following section.

To begin, the apparatus and method were first validated by measuring the phase equilibria of CO₂ hydrates in hydrogenated and deuterated water and comparing it with the values reported in the literature. It is clear from Fig. 2 that the values obtained in this work agree very well with the ones reported in the literature [40,61–66]. The scatter in the equilibrium data may be due to several reasons such as different quality of water, purity of CO₂, apparatus, method, and heating rates as depicted in Table S1.

The equilibrium data for CO₂ hydrates formed in H₂O, D₂O and their binary mixtures were obtained from the P-T loops using different initial pressures (Fig. S1) and are presented in Table 2. Several works are available in the literature where CH₄ hydrate equilibria is reported in

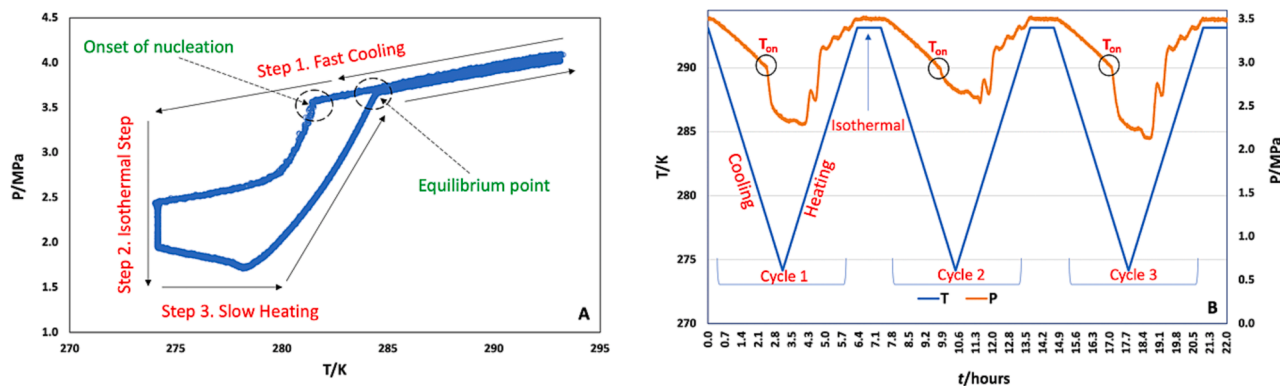


Fig. 1. (A) A typical P-T loop obtained during the isochoric pressure search method to obtain hydrate equilibrium data. (B) The constant cooling method to obtain the onset temperature of hydrate nucleation used in this work.

Table 2

Hydrate vapour liquid equilibrium values of CO₂ hydrates in pure H₂O, pure D₂O and in (H₂O + D₂O) binary mixtures, where nD represents n wt% of D₂O in the mixture.

D ₂ O		75 D		50 D		25 D		H ₂ O	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
284.80	3.73	284.25	3.78	283.57	3.70	282.81	3.61	282.14	3.59
283.04	2.89	282.37	2.93	281.50	2.79	280.95	2.77	280.35	2.81
282.03	2.55	281.36	2.53	280.77	2.53	279.90	2.43	279.33	2.42
280.31	2.04	280.02	2.10	279.28	2.07	278.76	2.07	277.93	2.02
278.71	1.67	278.45	1.73	277.68	1.70	276.58	1.59	276.32	1.66

Expanded uncertainties U(T) = ±0.1 K; U(P) = ±0.05 MPa.

Table 3

Triphasic equilibrium temperature (T₃ / K) of CO₂, H₂O and D₂O hydrates, determined using Molecular Dynamics simulations with the direct coexistence technique.

P / MPa	T ₃ /K (H ₂ O hydrate)	T ₃ /K (D ₂ O hydrate)
3.5	269 ± 1	272 ± 1
7	278 ± 2	282 ± 2
10	277 ± 2	280 ± 2

D₂O [27,41]. However, to the best of our knowledge, only Chun et al. [40] reported the CO₂ hydrate equilibrium measurements in H₂O, D₂O and in 10 %, 50 % and 80 % mixtures of the (H₂O + D₂O). A recent work by Maruyama et al. [44] dealt with a phase equilibrium system (CO₂ and H₂O + cyclopentane + D₂O), but they did not measure the phase equilibrium temperatures of CO₂ hydrates in neat D₂O and H₂O. The equilibrium data of Chun et al. [40] along with the values obtained in this work have been plotted in Fig. 3 for comparison. Both the data sets agree well and follow a consistent trend along with the gradual change in the water fraction of the mixtures.

It can be noticed from Fig. 3 that at a given pressure the CO₂ hydrate equilibrium curve shifts gradually towards higher temperature as the

D₂O fraction increases in the mixture suggesting an isotopic effect on the hydrate equilibria. Fig. 3 also shows that the hydrate equilibrium values obtained in this work in semilogarithmic plots of ln(P) versus 1/T present good linearity. The equilibrium values for CO₂ + D₂O system can be expressed as: ln(P) = -10418(1/T) + 37.88 and the values for CO₂ + H₂O as: ln(P) = -10347(1/T) + 37.94. The overall equilibrium of the (CO₂ + H₂O + D₂O) system can be expressed as a function of the D₂O fraction (nD = wt%) using the following expression:

$$\ln(P) = A + \frac{B}{T} + C \cdot nD$$

Where A, B and C are fitting coefficients with corresponding values as 38.2750623, -10440.945 and -0.0031031, respectively. Using the above expression, the equilibrium values at a given water fraction can be estimated with an accuracy of 0.1 %.

The data was used to calculate the shift in equilibrium temperatures with the change of the host network from H₂O to D₂O. From the linear plots, the shift in the equilibrium temperatures was calculated to be around + 2.3 K, within the range of equilibrium pressure in this work. This value agrees well with the values obtained from the data of Chun et al. for CO₂ hydrates [40]. The magnitude of the ΔT shifts depends on the guest gas as reported for CH₄, C₂H₆, C₃H₈ and Kr hydrates to be +

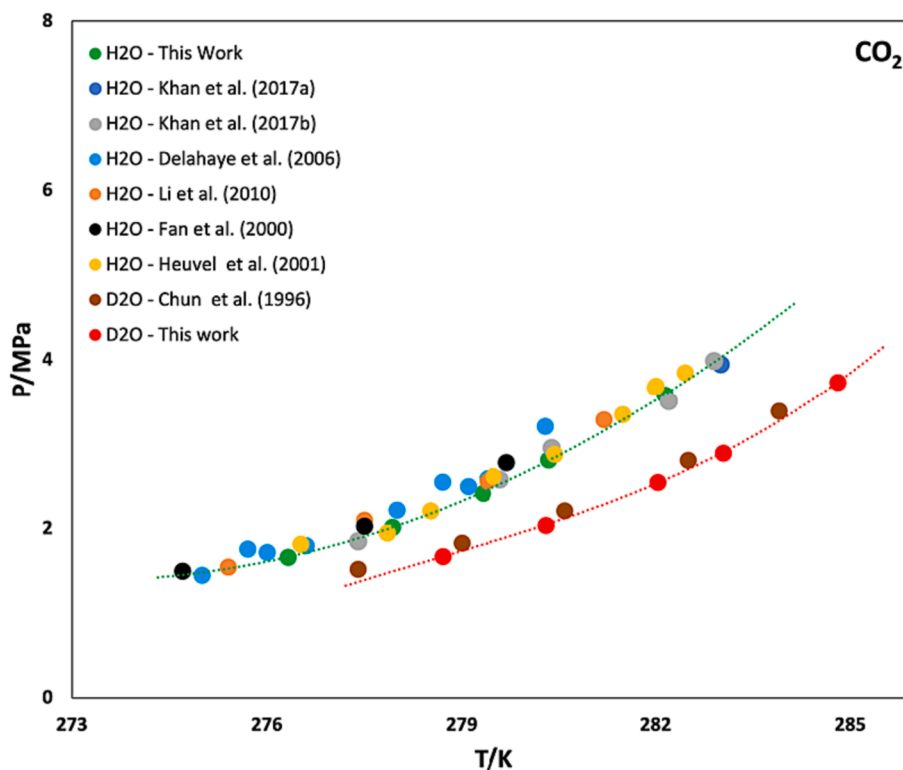


Fig. 2. A comparison of the CO₂ hydrate vapour liquid equilibria in H₂O and D₂O along with the values reported in the literature [40,61–66]. The dotted lines are just a guide to the eye.

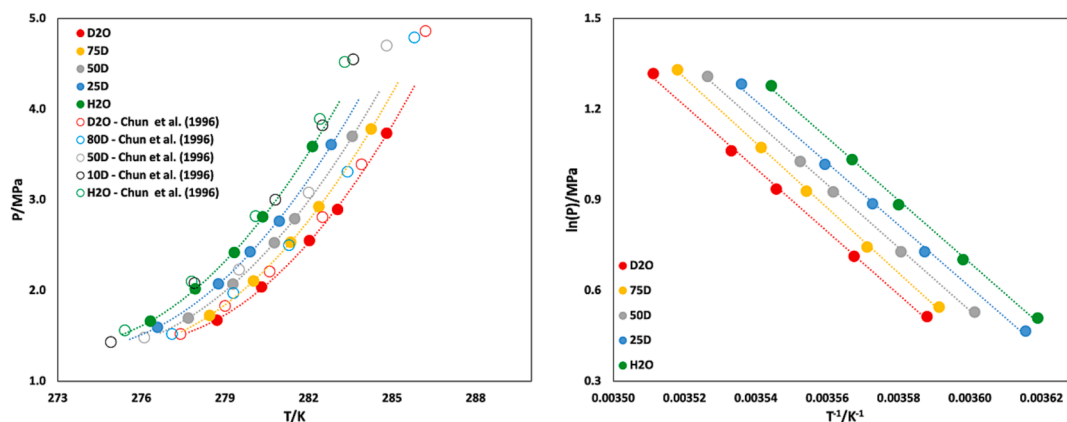


Fig. 3. CO₂ hydrate vapour liquid equilibria in H₂O, D₂O and their binary mixtures obtained in this work along with the dataset of Chun et al. [40]. The dotted lines are just guides to the eye. Hollow points not connected by the dotted lines indicate upper quadruple points (four-phase equilibrium) (left panel). Equilibrium values obtained in this work were translated into a semilogarithmic plot of ln(P) versus 1/T. The slopes of the linear fits were used for the calculation of dissociation enthalpies (right panel).

1.9, +2.1, +2.5 and +2.3 K respectively [41]. A value of +3.5 K and +3.2 K of ΔT for THF and cyclopentane hydrates, respectively (formed at atmospheric pressure) has also been reported [37,43]. It is interesting to note that these shifts are in some cases comparable of using thermodynamic promoter to affect the phase equilibria of CO₂ hydrates [67–69].

This experimental shift in the CO₂ hydrate equilibrium temperature due to the substitution of H₂O by D₂O, which yields a value slightly above 2 K, can be compared with the displacement on the hydrate triphasic equilibrium temperature determined theoretically using Molecular Simulation. Fig. 4 shows the initial setup of the simulation box used for this direct coexistence phase equilibrium calculation. A fully loaded CO₂ sl hydrate structure is placed in contact with two fluid phases, one rich in H₂O or D₂O depending on the case and another rich in the guest molecule. This three-phase equilibrium situation is only stable precisely at the triphasic coexistence temperature T_3 for a given pressure. Thus, if a temperature scan is performed along an isobar at temperatures close to this T_3 equilibrium temperature, the hydrate will crystallize and grow to occupy the whole simulation box or dissociate to yield fluid phases in equilibrium, depending on if the simulation temperature is below or above T_3 , respectively. Each of the two possible scenarios can be identified by monitoring the simulation box's internal energy trend during

the simulation. As plotted in Fig. 5, this magnitude will decrease if the hydrate grows through crystallization but will increase if the hydrate dissociates. This technique allows determining the upper and lower bounds of this triphasic coexistence temperature with remarkable accuracy, as shown precisely in Fig. 5, where the different equilibrium conditions between the H₂O and D₂O hydrates can be clearly stated.

Table 3 summarizes the triphasic equilibrium temperature values calculated using Molecular Dynamics and the direct coexistence technique, at three different pressures, for CO₂ + (H₂O or D₂O) hydrates. In the pressure range studied, the shift in the phase equilibrium line produced by the substitution of H₂O for D₂O is very close to the value obtained experimentally (Fig. S2). It is to be emphasized that the only difference between the H₂O and D₂O molecular models used in these calculations is due to the replacement of the H mass value by that of D, with all the other parameters remaining identical. This provides a useful insight into the possibility of determination of different hydrate properties in cases of isotopic replacement and underlines the transferability of the H₂O molecular model used.

The hydrate dissociation enthalpy is a useful parameter that reflects the interaction between host and guest molecules. Generally, a significant change is indicative of the occurrence of substantial alteration in

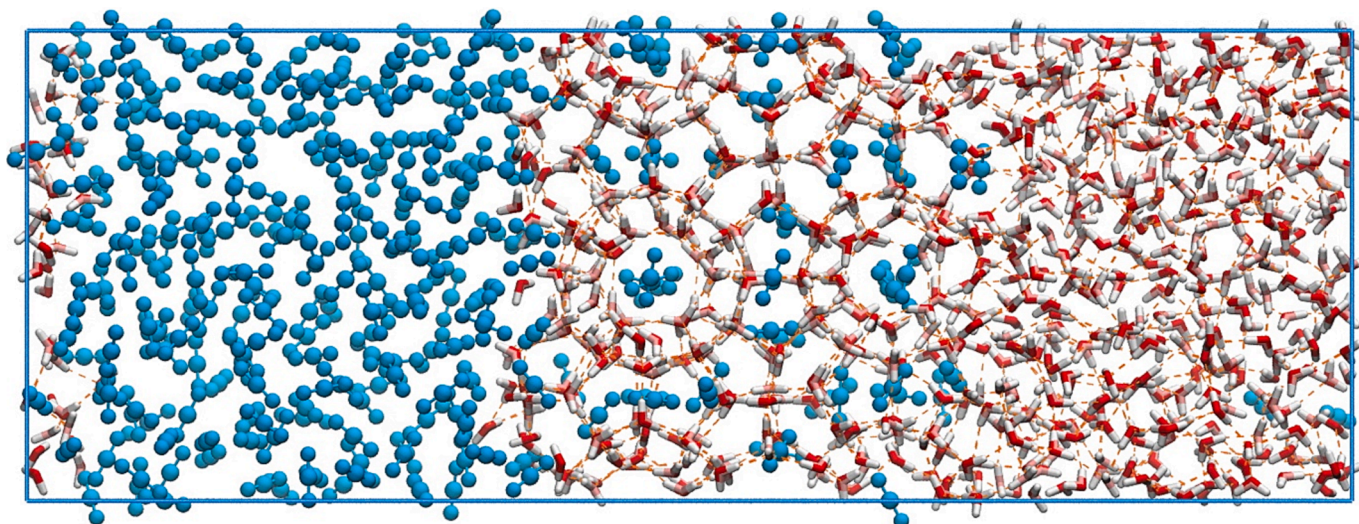


Fig. 4. Initial configuration of the Molecular Dynamics simulation box. Water molecules are represented using rods (red oxygen and white hydrogen) and CO₂ molecules are represented as blue spheres. The three coexisting phases can be clearly identified, corresponding to fluid CO₂ (left), solid CO₂ hydrate (center) and liquid water (right).

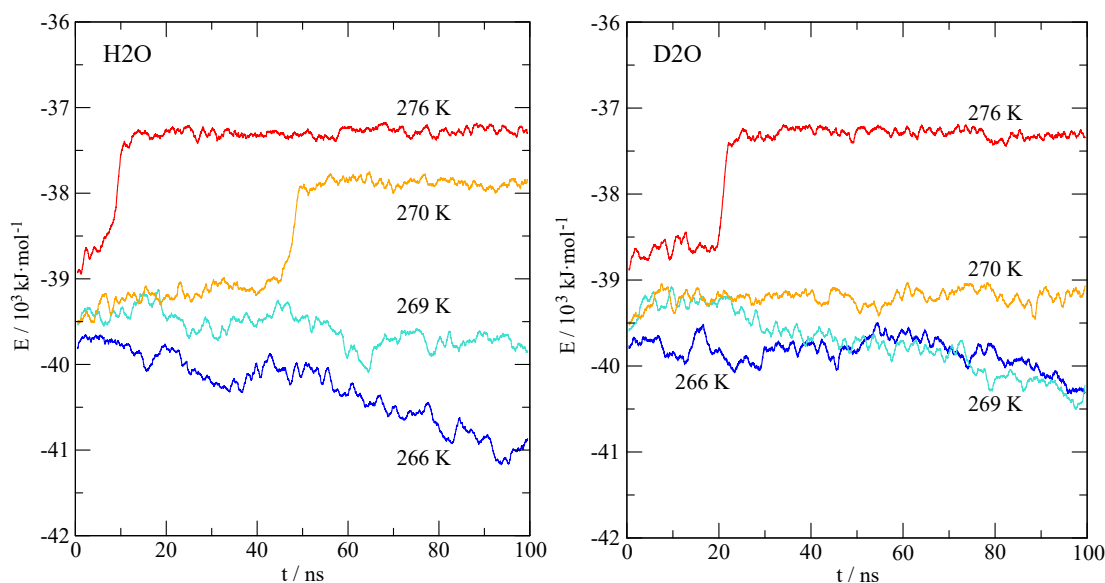


Fig. 5. The internal energy of the sl CO₂ hydrate of H₂O (left) and D₂O (right), as a function of simulation time, at 3.5 MPa and four temperatures: 266 K (blue), 269 K (turquoise), 270 K (orange) and 276 K (red). For the sake of clarity, internal energy fluctuations were smoothed using a running average of 100 frames. (Note that at 270 K, energy grows in H₂O hydrate denoting hydrate structure dissociation, but it is not the case for D₂O illustrating the difference in phase coexistence stability temperature between the hydrate structure composed of light and heavy water).

the hydrate cage structure. The hydrate equilibrium data (Table 2) can be used to calculate the dissociation enthalpies using the Clausius-Clapeyron equation as the data is obtained in the applicable temperature range [70]:

$$\frac{d(\ln P)}{d(1/T)} = \frac{-\Delta H_d}{zR}$$

The left-hand side indicates the slope obtained from the plot presented in Fig. 3; where P, T, ΔH_d , z, and R represent pressure, temperature, dissociation enthalpy, compressibility factor, and gas constant, respectively. The compressibility factor (z) was calculated using the Peng-Robinson equation of state [71]. The values of the calculated dissociation enthalpies for all systems at equilibrium conditions are presented in Table 4.

The values of enthalpies obtained in this work are in good agreement with the ones obtained by the equilibrium data of Chun et al. [40]. Interestingly, no significant change in the dissociation enthalpy values as a function of the mass fraction of H₂O/D₂O has been observed (Table 4), which indicates no change in the hydrate framework. These observations agree with the conclusions made by Kida et al. [41] based on solid-state NMR where no structural changes in the CH₄, C₂H₆, C₃H₈ and Kr hydrate cages were observed on changing the host from H₂O to D₂O.

To gain some further insights into the CO₂ hydrates formation in different hosts (H₂O, D₂O and mixtures), the cooling and heating traces

Table 4

Dissociation enthalpies of CO₂ hydrate in H₂O, D₂O and their binary mixtures calculated using the Clausius-Clapeyron equation at each equilibrium point shown in Table 2.

D ₂ O	75 D	$\Delta H_{diss}/\text{kJ.mol}^{-1}$			H ₂ O
		50 D	25 D		
62.91	62.35	62.82	63.33	63.29	
68.90	68.52	69.30	69.37	68.92	
71.12	71.13	71.07	71.61	71.57	
74.32	73.85	73.97	73.90	74.15	
76.56	76.18	76.29	76.85	76.36	

Expanded uncertainties U(mole fraction) = ± 0.0001 ; U(H) = $\pm 1.5 \text{ kJ.mol}^{-1}$.

obtained from the phase equilibrium loops were plotted in Fig. 6. The plots show some very interesting insights such as i) a clear demarcation of different nucleation time/temperature for H₂O, D₂O and their equimolar mixture in identical conditions, ii) almost similar pressure drop thus identical growth and iii) as the heating step began each system is behaving in a peculiar manner. The H₂O hydrates immediately started to dissociate as the heating began from 274.15 K, whereas D₂O ones started to dissociate around 277.15 K and the hydrates formed from the equimolar mixture started to dissociate around 275.15 K. These temperature values are in close vicinity of the ice melting point of respective waters and the mixture [72]. Therefore, the scenario is a manifestation of the onset of dissociation of hydrate cages as soon as the temperature goes above the respective ice melting points. This peculiar feature also seems responsible for the self-preservation effect in gas hydrates [17,42].

Since hydrate formation is a first-order phase transition and a stochastic phenomenon, statistically significant nucleation data is required to get a deeper understanding of the phenomenon, which can be achieved by specialized apparatuses [73–76]. However, by adopting a constant cooling method, the rocking cell apparatus can be used to explore the hydrate formation and nucleation phenomena. These experiments not only give information about the onset nucleation temperatures but may also indicate the width of the metastable zone (MSZW) of the system. MSZW is defined as the limit of temperature beyond which spontaneous nucleation is likely to occur. Fig. 7 indicates the equilibrium line, nucleation data points obtained from several independent experiments and the MSZW for both D₂O and H₂O systems.

The CO₂ hydrate onset nucleation temperatures in D₂O, H₂O and binary mixtures obtained from the constant cooling method indicate the absence of any memory effect (Fig. S3). Thereby the results are presented in Table 5 as an average of the respective runs along with the standard deviations. Furthermore, plotting the CO₂ hydrate formation and dissociation values obtained from the phase behaviour measurements together with the onset nucleation data gives an idea about the metastable zone width (MSZW) of the studied systems and the effect of isotopic substitution on it (Fig. S4). The MSZWs at an initial pressure of 3.6 MPa are also reported in Table 4. The MSZW value of 4.1 K of D₂O is slightly higher compared to 3.5 K in the case of H₂O.

Plotting the average onset nucleation temperatures as a function of water composition presents a very interesting scenario as depicted in

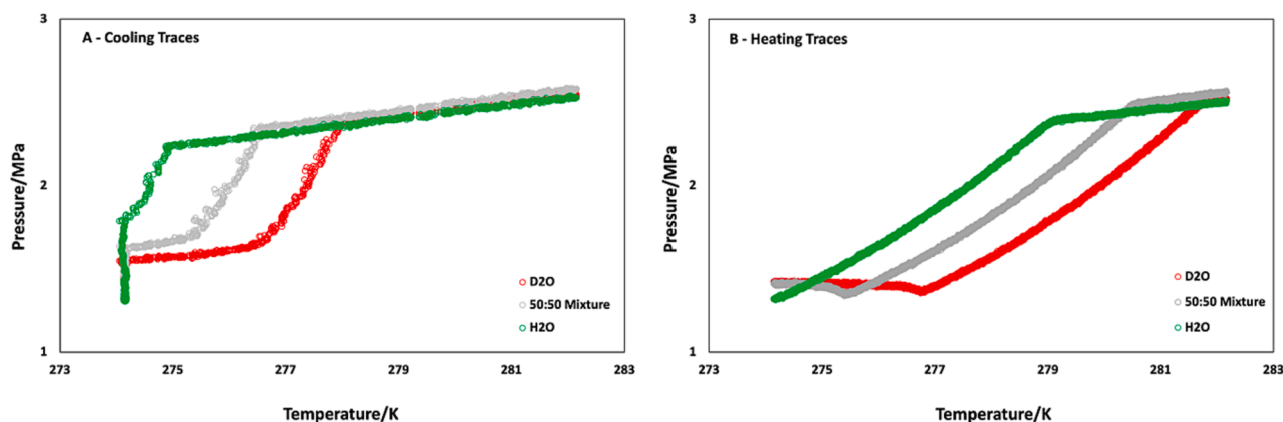


Fig. 6. Cooling and heating traces in an isochoric process indicate CO_2 hydrates formation and dissociation in pure H_2O , pure D_2O and in an equimolar mixture. The cooling rate is 3 K/h whereas the heating rate is 0.3 K/h in all cases.

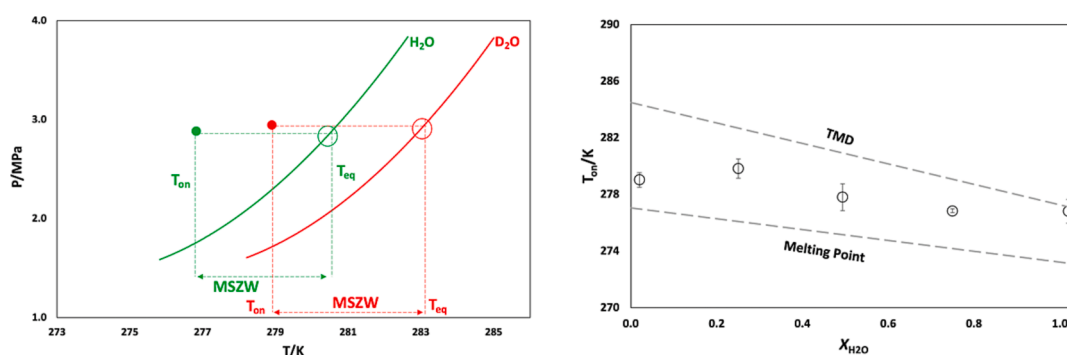


Fig. 7. Metastable zone width (MSZW) of CO_2 hydrates formed by D_2O and H_2O . Solid lines represent the hydrate equilibrium curves obtained in this work, and solid circles are the nucleation points. The difference between the corresponding equilibrium and nucleation temperature represents the MSZW of the system (left panel). The onset temperature of nucleation (T_{on}) for CO_2 hydrates at 3.6 MPa in H_2O , D_2O and binary mixtures as a function of composition. The lower dashed line indicates the “ideal” melting point variation in the mixtures of H_2O and D_2O [72]. The upper dashed line indicates the near-ideal variation of temperature of maximum density (TMD) as a function of mixture composition.

Table 5

Onset nucleation temperature (T_{on}) and metastable zone width (MSZW) of CO_2 hydrates in H_2O , D_2O and in the binary mixtures at 3.6 MPa using a constant cooling method.

$X_{\text{H}_2\text{O}}$	Runs	T_{on}/K	MSZW(ΔT)/K
0.0000	14	279.0 ± 0.5	4.1 ± 0.6
0.2306	18	279.8 ± 0.7	2.4 ± 0.7
0.4736	12	277.8 ± 0.9	3.8 ± 1.1
0.7296	10	276.9 ± 0.1	4.1 ± 0.1
1.0000	14	276.8 ± 0.8	3.5 ± 0.9

Fig. 7. The hydrate nucleation temperature values for pure waters and mixtures are consistently falling within a narrow window above the melting points of the system and in the vicinity of the corresponding temperature of maximum densities (TMDs) (Fig. S5). Similar behaviour of nucleation in the vicinity of TMDs was recently observed for methane hydrates in H_2O and D_2O [77]. Therefore, these results further corroborated the fact that above the melting point around the temperature of maximum density, the enhanced structuredness of water, due to expanded hydrogen bonding provides “templates” for the hydrates to nucleate and grow. This even holds true in the case of complex binary mixtures of H_2O and D_2O . However, the validity of the relation between nucleation and TMD should be further investigated in the presence of additives that are known to shift the TMDs and thereby may alter the nucleation.

4. Conclusions

In this work, the effect of gradual isotopic substitution on CO_2 hydrates formation and dissociation has been explored. The hydrate equilibrium shifted towards + 2.3 K in the case of D_2O compared to H_2O . This experimental determination is closely coincident with estimations obtained using Molecular Dynamics for both hydrates. The hydrate dissociation enthalpies remain unaffected with the gradual change of the host thereby indicating no significant alteration in the cage structure took place. The CO_2 hydrate metastable zone width obtained at 3.6 MPa in the case of H_2O is slightly smaller (3.5 K) compared to D_2O (4.1 K). The onset nucleation temperature as a function of host water composition always falls within a narrow window above the melting point and near the TMD of the system under scrutiny indicating that the open structure of water act as a nucleation site and facilitates the hydrate formation and growth. It would be interesting to test this hypothesis in the presence of additives that might shift the TMD of water in a given direction. These results are useful for the design and development of hydrate based-separation technology as recently proposed for tritium separation.

CRediT authorship contribution statement

Mohammad Tariq: Conceptualization, Methodology, Funding acquisition, Investigation, Writing – review & editing. **Mário R.C. Soromenho:** Investigation. **Manuel M. Piñeiro:** Methodology, Funding acquisition, Investigation, Writing – review & editing. **Martín Pérez-**

Rodríguez: Methodology, Investigation, Writing – review & editing. **Dalip Kumar:** Investigation. **Ana Rodríguez:** Conceptualization, Writing – review & editing. **Francisco J. Deive:** Conceptualization, Writing – review & editing. **José M.S.S. Esperança:** Conceptualization, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2023.123232>.

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