Electronic Supplementary Information (8 Pages, 8 Figures, 1 Table)

Molecular dynamics simulation study on the growth of CO_2 hydrate from high-concentration NaCl solutions

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I. Supplementary Figures

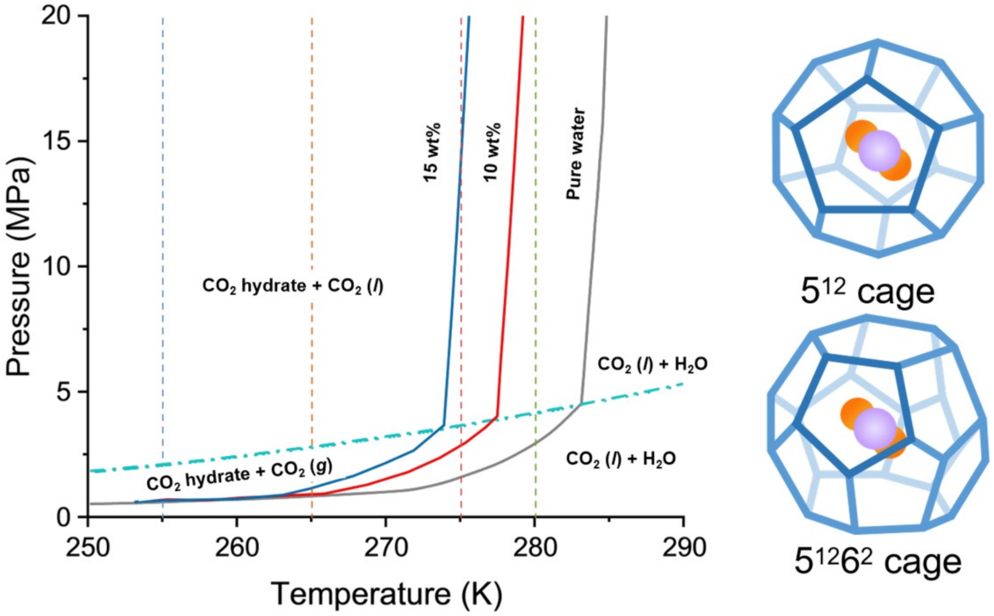

Figure S1. Phase diagram of the CO_2 – water – hydrate system at different NaCl concentrations and the structures of 5^{12} and $5^{12}6^2$ cages. Simulation temperature conditions were plotted within the phase diagram (phase diagram adopted from Reference [1-3]).

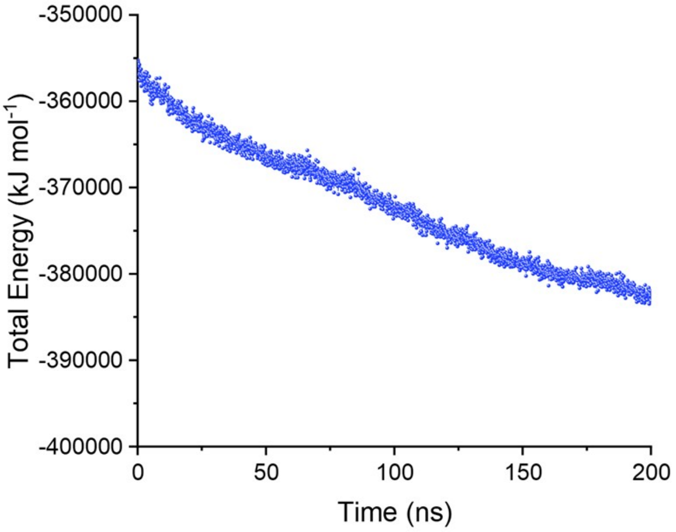

Figure S2. The evolution of system energy with simulation time for a typical simulation case (Case *1*).

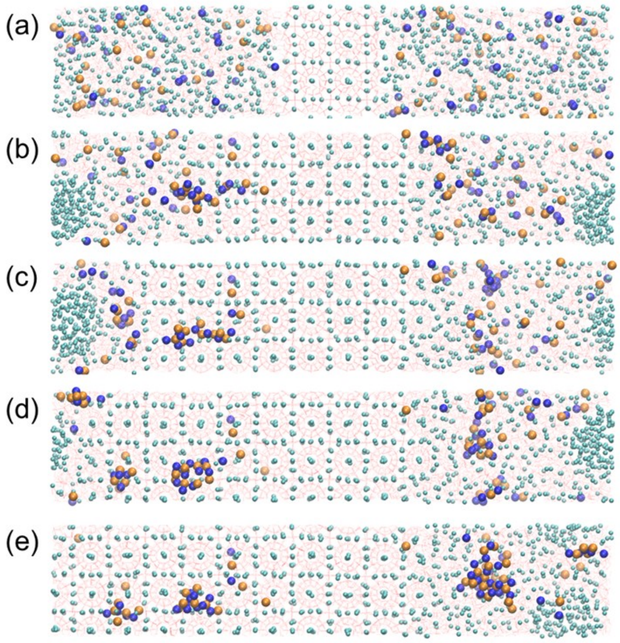

Figure S3. Selected configuration snapshot for simulation Case *2* (*T* = 265 K, *P* = 50 MPa, initial NaCl concentration of 1 mol%) at the simulation time of 0, 50, 100, 150 and 200 ns, respectively. Water molecules are shown as the hydrogen bonds in red colour; only C atoms (cyan spheres) in CO_2 are presented for the ease of identification; Na^+ and Cl^- ions are shown as royal blue and orange spheres, respectively.

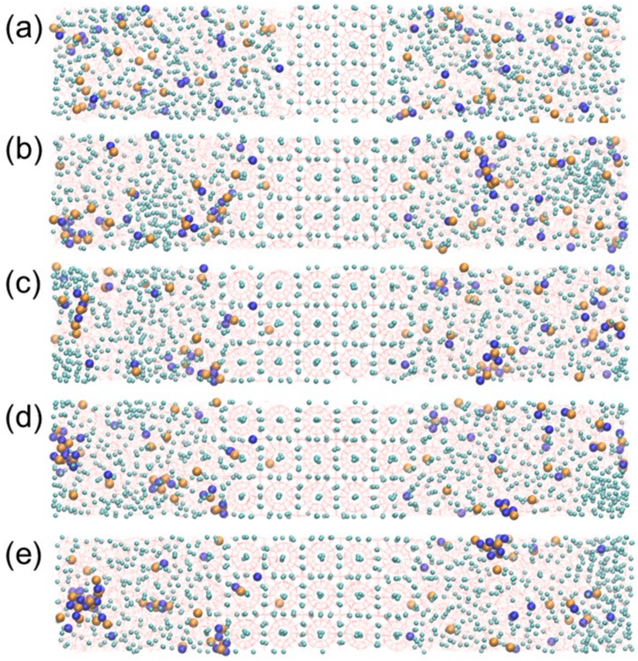

Figure S4. Selected configuration snapshot for simulation Case *3* (*T* = 255 K, *P* = 50 MPa, initial NaCl concentration of 1 mol%) at the simulation time of 0, 50, 100, 150 and 200 ns, respectively. Water molecules are shown as the hydrogen bonds in red colour; only C atoms (cyan spheres) in CO_2 are presented for the ease of identification; Na^+ and Cl^- ions are shown as royal blue and orange spheres, respectively.

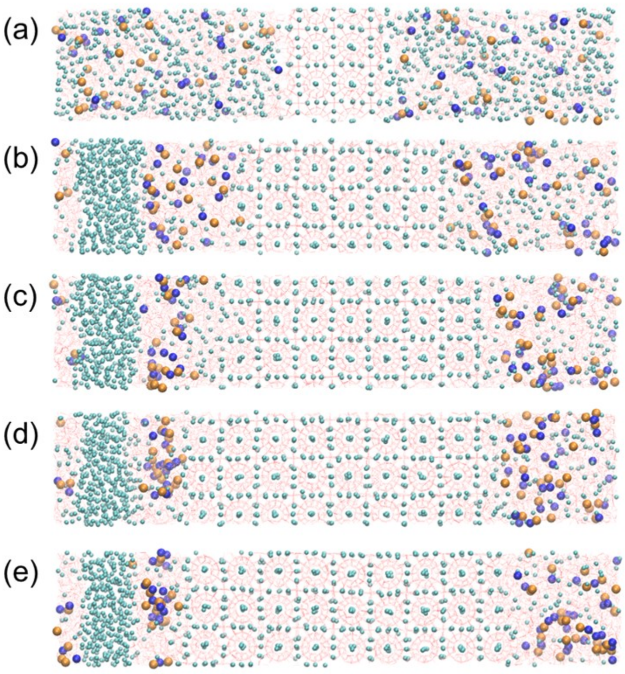

Figure S5. Selected configuration snapshot for simulation Case *4* (*T* = 280 K, *P* = 50 MPa, initial NaCl concentration of 1 mol%) at the simulation time of 0, 50, 100, 150 and 200 ns, respectively. Water molecules are shown as the hydrogen bonds in red colour; only C atoms (cyan spheres) in CO_2 are presented for the ease of identification; Na^+ and Cl^- ions are shown as royal blue and orange spheres, respectively.

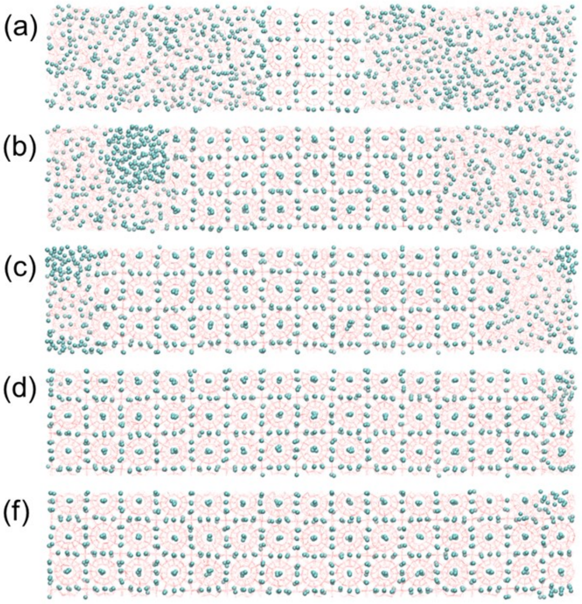

Figure S6. Selected configuration snapshot for simulation Case *7* (*T* = 275 K, *P* = 50 MPa, initial NaCl concentration of 0 mol%) at the simulation time of 0, 25, 50, 75 and 100 ns, respectively. Water molecules are shown as the hydrogen bonds in red colour; only C atoms (cyan spheres) in CO_2 are presented for the ease of identification; Na^+ and Cl^- ions are shown as royal blue and orange spheres, respectively.

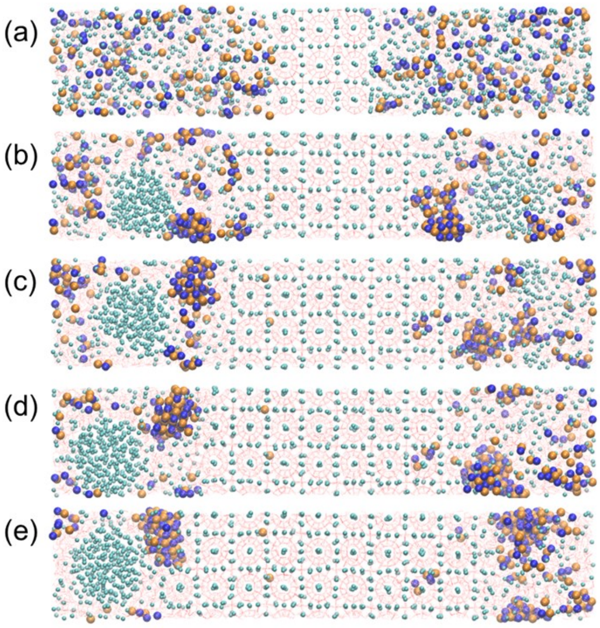

Figure S7. Selected configuration snapshot for simulation Case *5* (*T* = 275 K, *P* = 50 MPa, initial NaCl concentration of 3 mol%) at the simulation time of 0, 50, 100, 150 and 200 ns, respectively. Water molecules are shown as the hydrogen bonds in red colour; only C atoms (cyan spheres) in CO_2 are presented for the ease of identification; Na^+ and Cl^- ions are shown as royal blue and orange spheres, respectively.

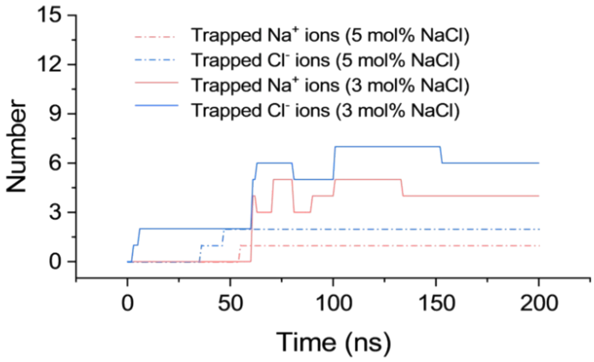

Figure S8. Time-dependent number of trapped Na^+ and Cl^- ions inside the hydrate structure for simulation Cases *5 and 6* (see also Table 1).

II. Simulation Methods

Table S1. Interatomic potentials employed for the simulation cases [a].

Molecule	**Site**	**mass**	**Q/e**	**σ_{lj}/(Angst.)**	**ε_{lj}/(KJ· mol^{-1})**
H_2O	O	15.994	0	3.1668	0.88217
	H	1.008	0.5897	0	0
	M	0	-1.1794	0	0
CO_2	C	12	0.70	2.80	0.22459
	O	15.994	-0.35	3.05	0.65712
Ion	Na^+	22.98977	1.000	3.33045	0.11598
Ion	Cl^-	35.45300	-1.000	4.41724	0.492833

a. $\varepsilon_{O(CO_2)-O(H_2O)} = \chi\sqrt{\varepsilon_{O(CO_2)} * \varepsilon_{O(H_2O)}}$, $\chi = 1.13$.

TIP4P/ICE and TraPPE potential models were employed to describe the interatomic force fields of H_2O and CO_2 molecules, respectively [4-7]. The potential parameters for Na^+ and Cl^- ions were adopted from Reference [6]. All the cross-interaction parameters were calculated according to the Lorentz–Berthelot (LB) combining rules with the exception of the cross-interaction energy parameter between O in H_2O and the O in CO_2 ($\varepsilon_{O(CO_2)-O(H_2O)}$) [4,5,7]. A modification factor, χ, was used to correct the LB cross-interaction energy parameter based on References [4,5,7]. The initial configuration was consisted of a hydrate seed (3×3×3 perfect unit cells, crystallographic information based on References [8-10]) and two adjacent aqueous NaCl solution layers with 2484 H_2O molecules and 414 dissolved CO_2 molecules, respectively. Specific numbers of Na^+ cations and Cl^- anions were added randomly into the aqueous layers to obtain desired NaCl concentrations listed in **Table 1**.

All MD simulations were performed using the GROMACS 2019 open-source code [11], where periodic boundary conditions, an *isothermal-isobaric* ensemble (regulated by the V-rescale thermostat with a time constant of 0.2 ps and the Berendsen with a time constant of 0.5 ps) and the time step of 1 fs were employed [7]. A cutoff distance of 1.4 nm was used to estimate the short-range non-bonded interactions with the long-range corrections applied to energy and pressure. The electrostatic interactions were calculated with particle mesh Ewald (PME) method with a cut-off radius of 1.4 nm [4,5,7]. The cage numbers were analyzed by the GRADE code based on Reference [12]. The radial pair distribution function analysis and visualization of the simulation cases were performed through the VMD software package [13].

References:

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