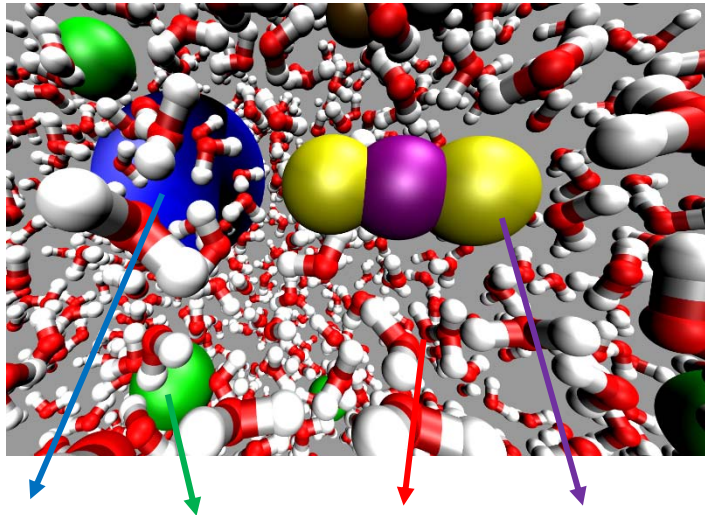


Density Fluctuation in Aqueous Solutions and Molecular Origin of Salting-out Effect for CO₂



Cavity

Ion

H₂O

CO₂

Molecular dynamics simulation system containing CO₂ (pink and yellow), H₂O (red and white), and ions (green). Cavity (blue) formation energy and interaction energy between CO₂ and aqueous solution were estimated to understand salting-out effect of CO₂.

Reference

Ho, Tuan and Ilgen, Anastasia, JPC B, in press

Scientific Achievement

When increasing salt concentration, the interaction between CO₂ and aqueous solutions favors the solubility of CO₂. However, due to the decreasing number of cavities forming when salt concentration is increased, the solubility of CO₂ decreases. The formation of cavities was found to be the primary control on the dissolution of gas, and is responsible for experimentally observed CO₂ salting-out effect

Significance and Impact

Provide a mechanistic understanding of density fluctuation and cavity formation in aqueous solution and molecular origin of salting-out effect for CO₂. These scientific achievements are important to understand solubility trapping mechanism in geological carbon storage.

Research Details

Perform molecular dynamics simulations of LiCl, NaCl, KCl, MgCl₂, CaCl₂, BaCl₂ and NaHCO₃ aqueous solutions at different concentrations to calculate cavity formation energy and interaction energy including van der Waals and electrostatic interactions between CO₂ and aqueous solution.



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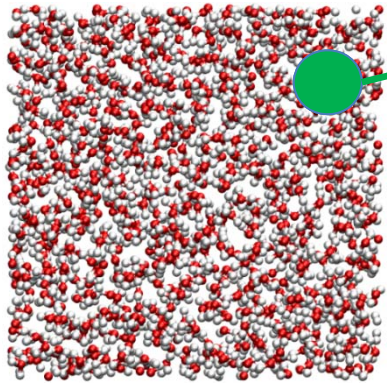


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Results

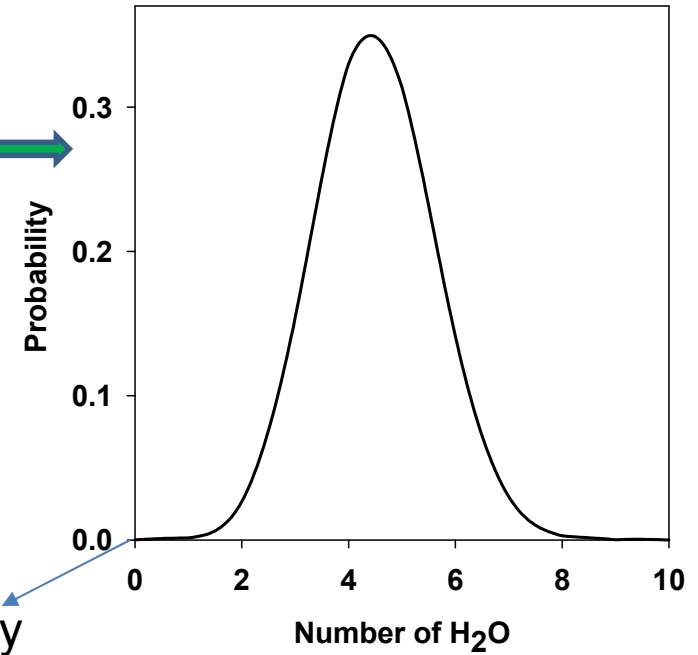


Probe volume $R=3.3\text{\AA}$

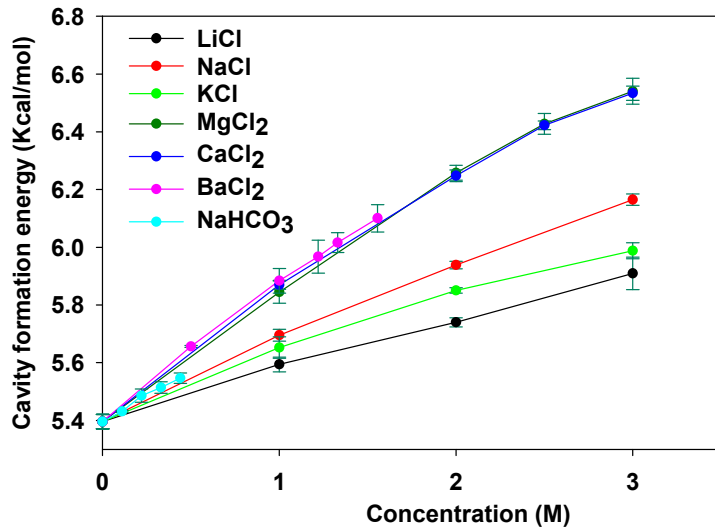
Density of water: $1\text{g/ml} \rightarrow 5$ water molecules in the probe volume. However, number of water in probe volume fluctuates.

When there is no water in the probe volume, it becomes a cavity

Probability of observing n number of water in the probe volume



Cavity formation energy as a function of salt concentration



Non-zero probability

Cavity formation energy

$$\mu = -k_B T \ln [P|_{n=0}]$$



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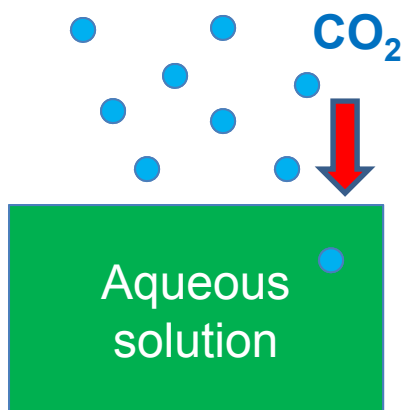


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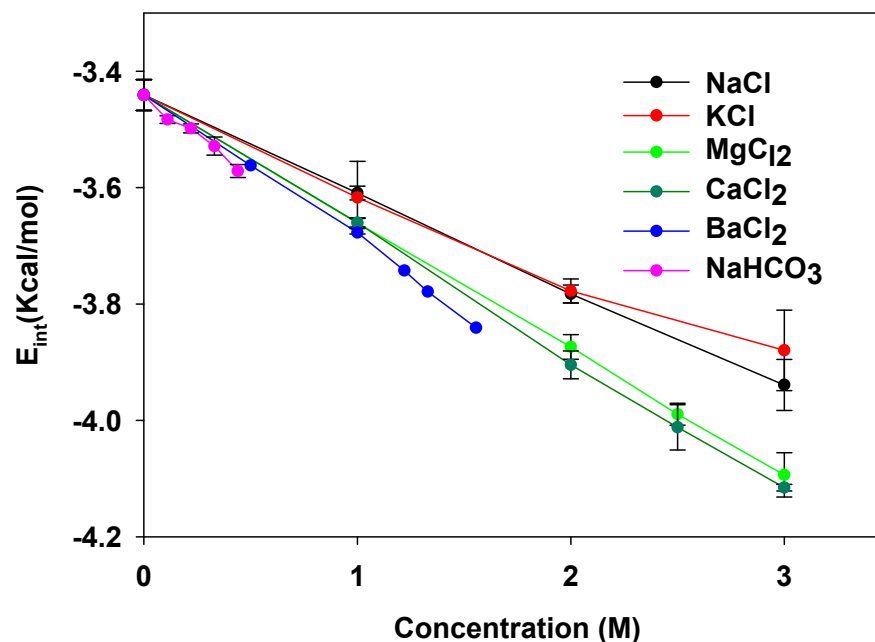
Results

$$\Delta G = \Delta G_{\text{cavity}} + E_{\text{init}}$$

Interaction energy between CO₂ and aqueous solutions



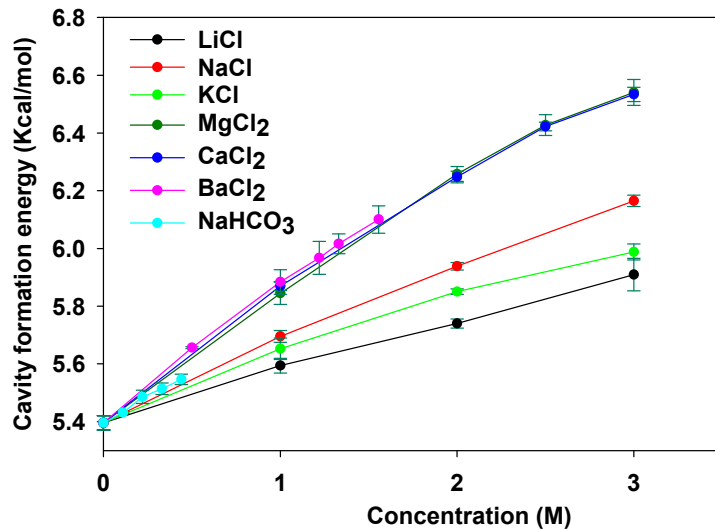
Transferring a CO₂ gas molecule into an aqueous solution: first, a cavity forms in the aqueous solution (ΔG_{cavity}), and then a CO₂ molecule is inserted into the cavity and interacts with the solvent (E_{int}).



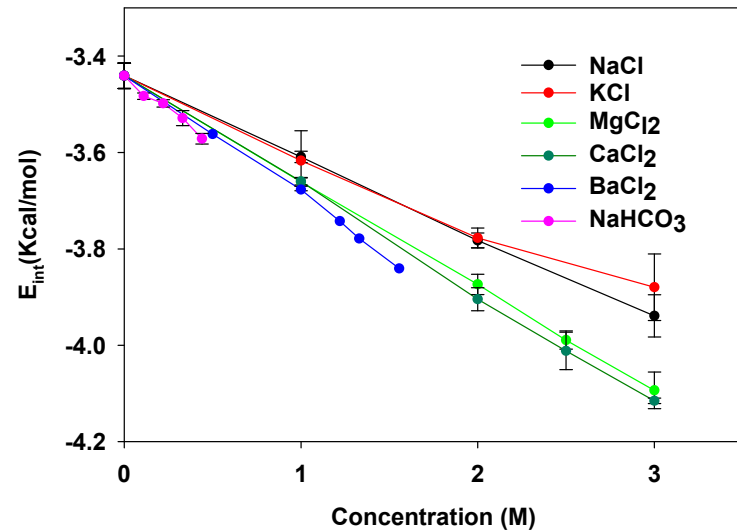
Summary

$$\Delta G = \Delta G_{\text{cavity}} + E_{\text{init}}$$

Cavity formation energy as a function of salt concentration



Interaction energy between CO₂ and aqueous solutions



The decrease in the formation of cavities in aqueous solutions with increasing salt concentrations is responsible for the CO₂ salting-out effect



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$$U_{ij}(r_{ij}) = \epsilon_{ij} \left[\left(\frac{R_{\min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{\min,ij}}{r_{ij}} \right)^6 \right] + \frac{e^2 Q_i Q_j}{r_{ij}}$$

Lennard John potential, r_{ij} is the distance. $R_{\min,ij}$ and ϵ_{ij} are the depth of the potential well and the distance at which the inter-particle potential is zero, respectively

Electrostatic interaction Q_i, Q_j are the charge of atoms

