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Density Fluctuation in Aqueous Solutions and Molecular Origin of Salting-out Effect for CO_2

(*J. Phys. Chem. B*, 2017, 121, 11485)

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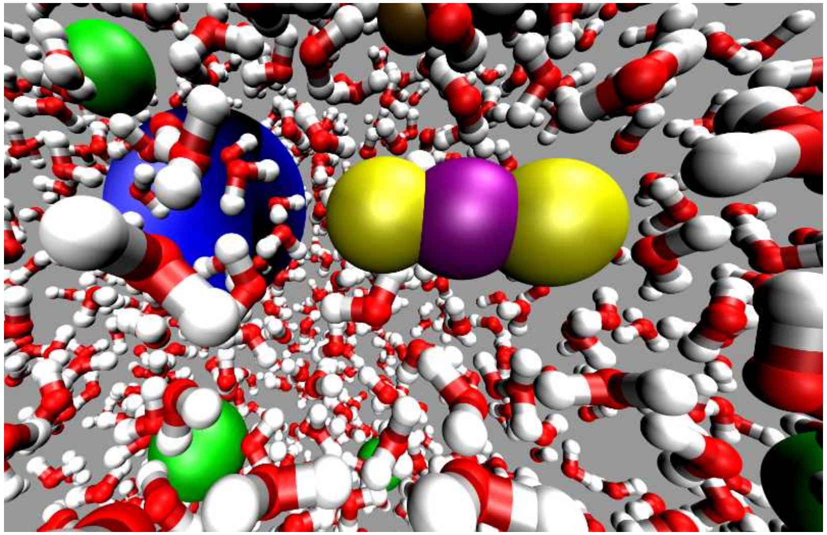

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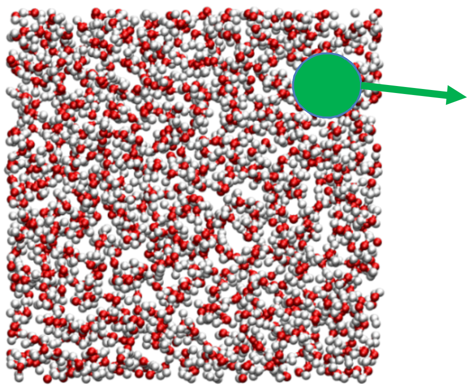
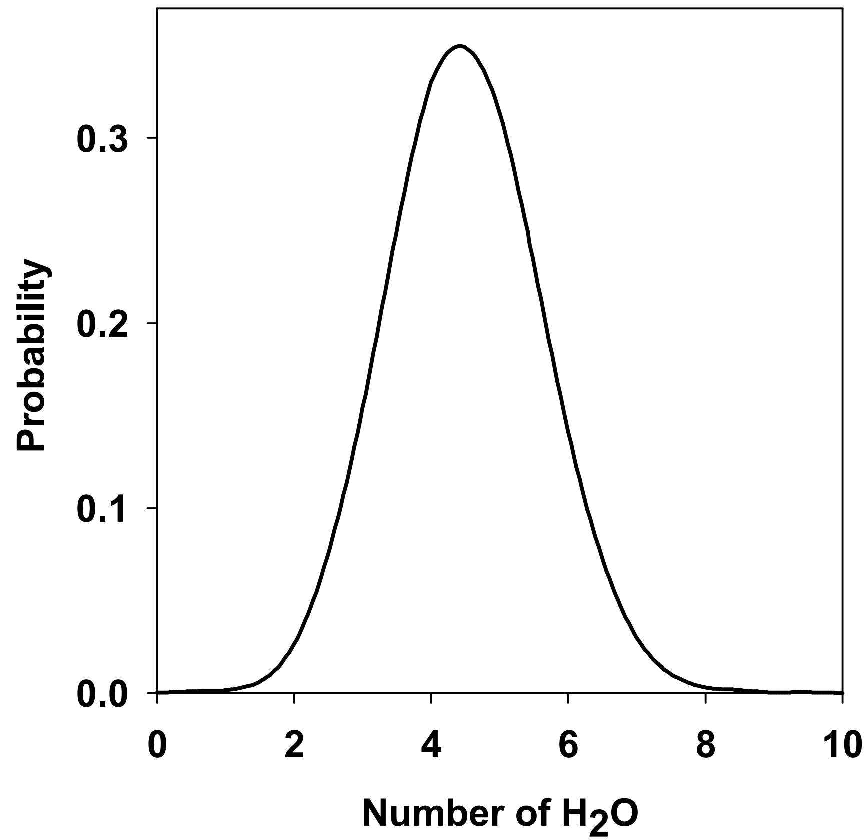
Density Fluctuation in Aqueous Solutions



Probe volume R=3.3Å

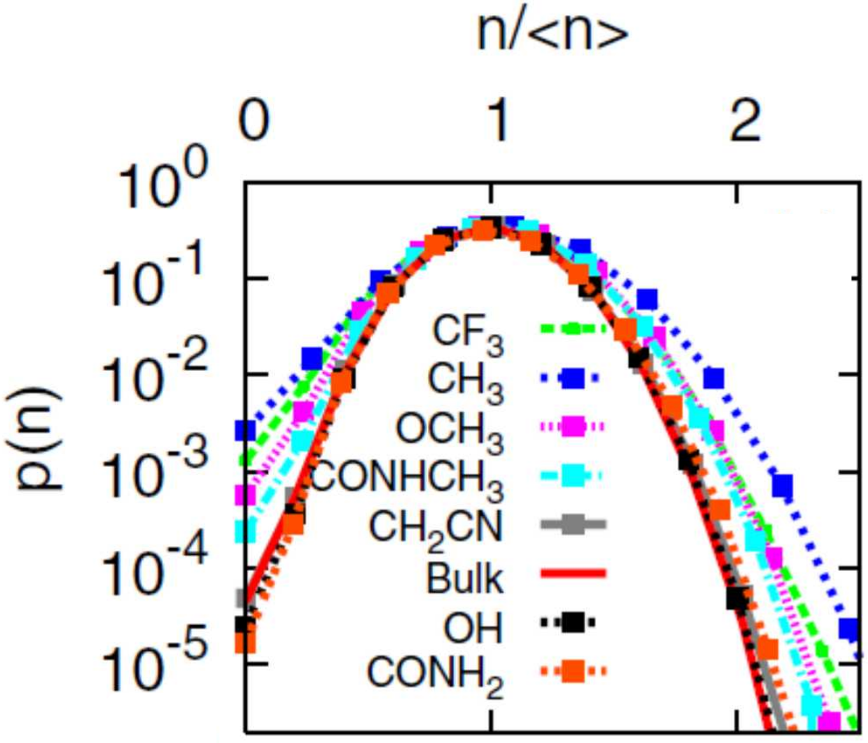
Probability of observing n number of water in the probe volume



Density of water: 1g/ml → 5 water molecules in the probe volume. However, number of water in probe volume fluctuates.

Density Fluctuation in Aqueous Solutions

Density fluctuation serves as an excellent signature of hydrophobicity
(PNAS 2009, 106, 15119)

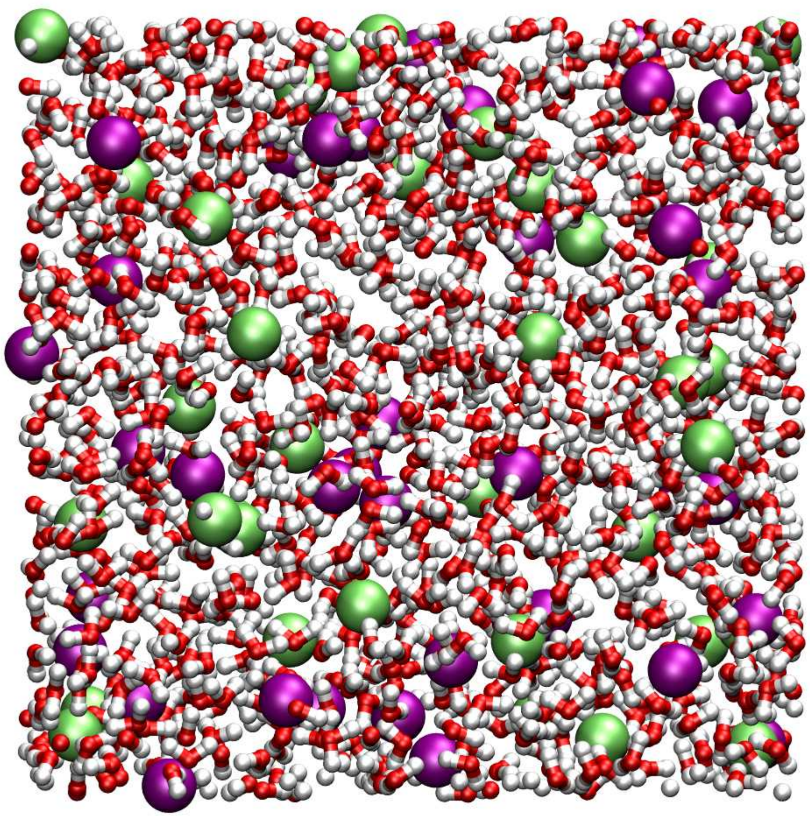


Probability distribution is wider near the hydrophobic surfaces and becomes narrower with increasing hydrophilicity.

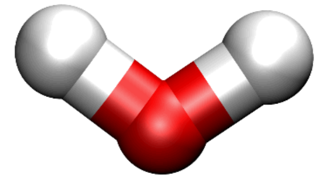
How does the density fluctuation change when adding more ions to water?

Density Fluctuation in NaCl Solution

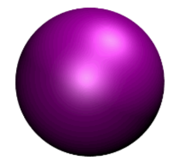
Molecular dynamics simulation



T = 298K, P = 1 atm

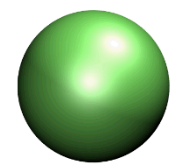


Water (SPC model)



Na^+

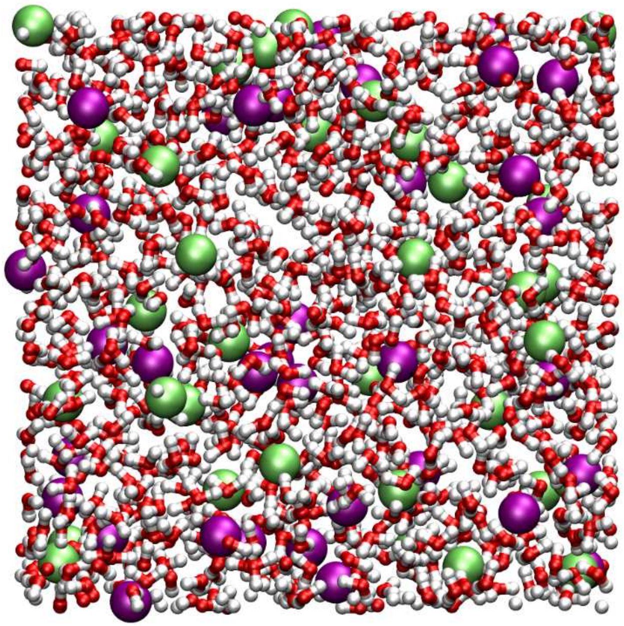
(Dang's model)

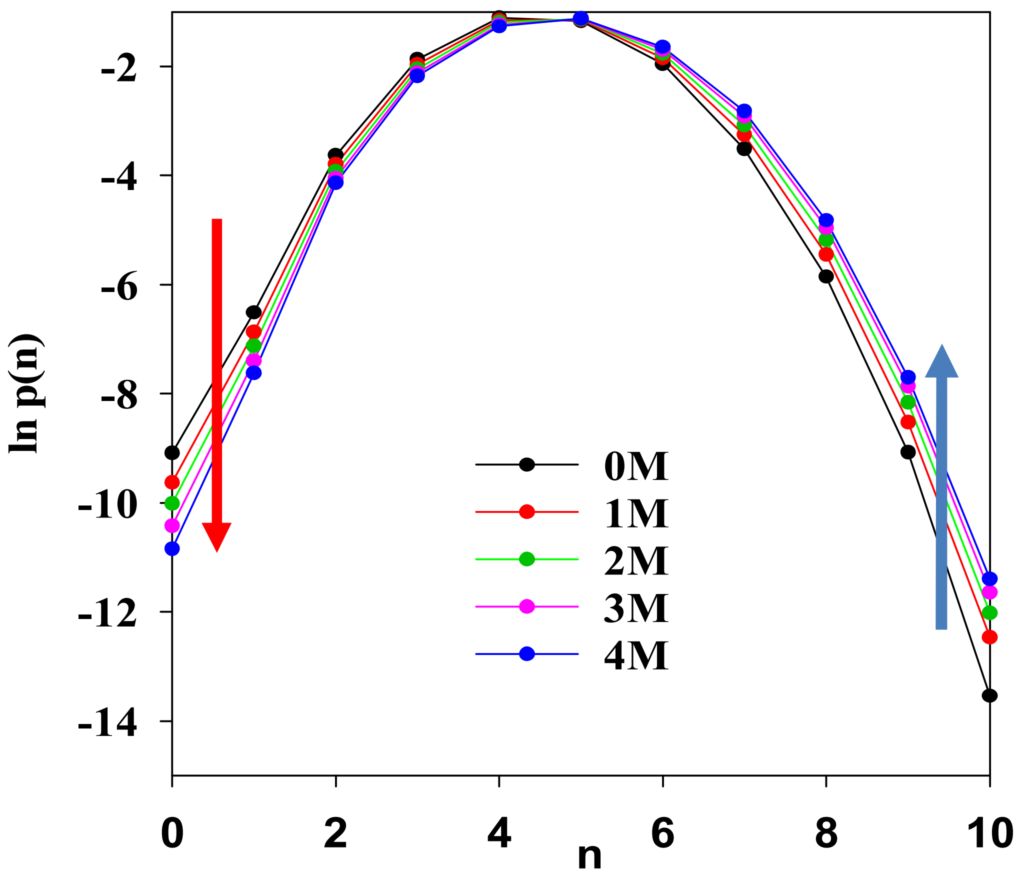


Cl^-

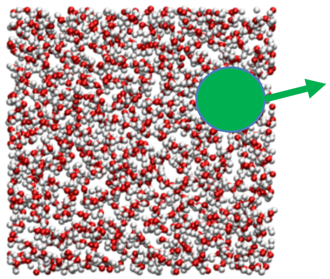
$$\sum_{\text{LJ}} 4\epsilon_{ij}\left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}}\right) + \sum_{\text{elec}} \frac{q_i q_j}{r_{ij}}$$

Density Fluctuation in NaCl Solution

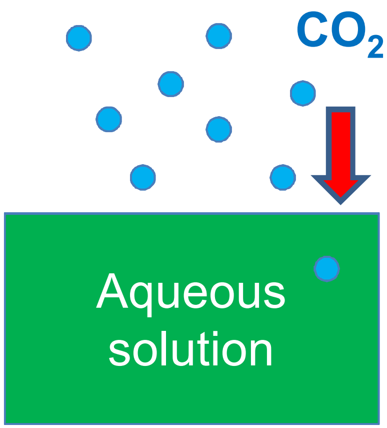


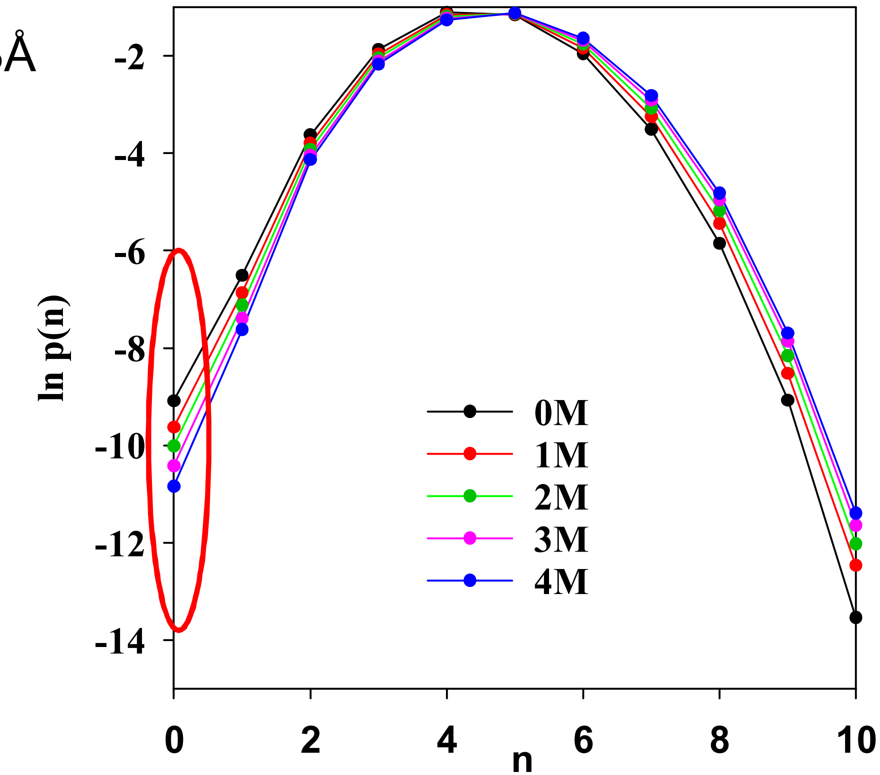


Cavity Formation in NaCl Solution



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





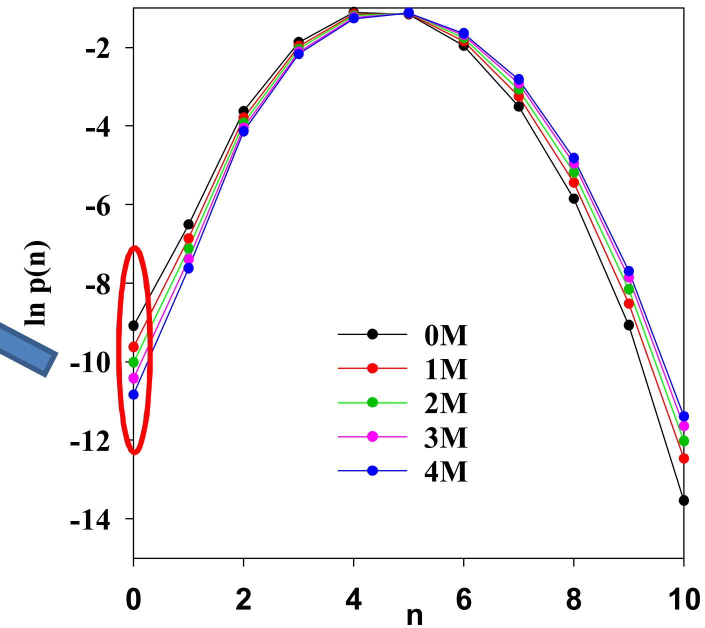
$$\Delta G = \Delta G_{cavity} + E_{int}$$

Transferring a CO_2 gas molecule into an aqueous solution: first, a cavity forms in the aqueous solution (ΔG_{cavity}), and then a CO_2 molecule is inserted into the cavity and interacts with the solvent (E_{int}).

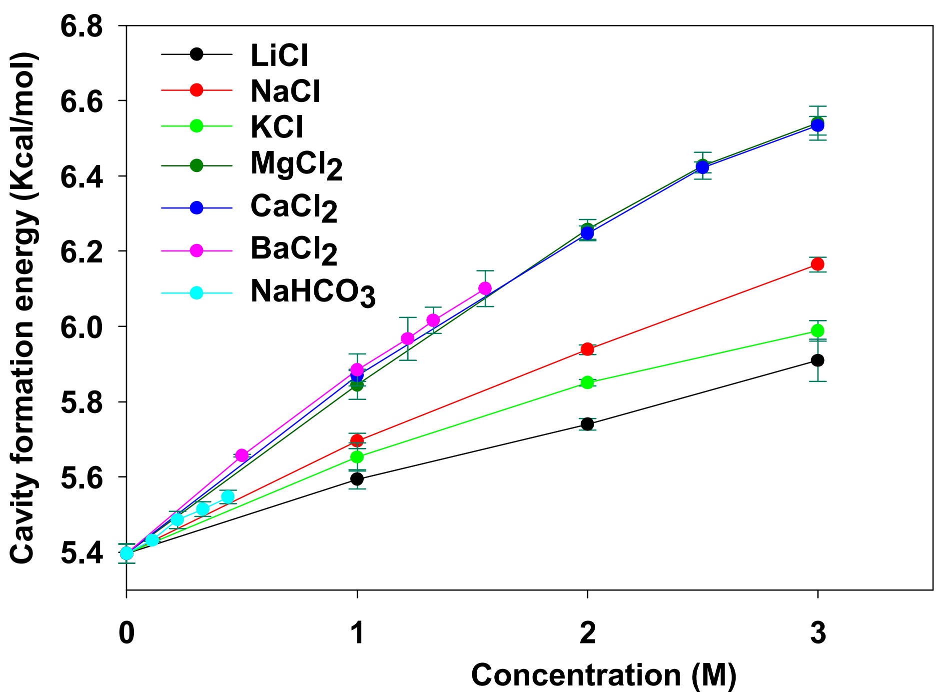
Cavity Formation in NaCl Solution

Cavity formation energy

$$\mu = -k_B T ln[P(n=0)]$$



Cavity formation energy as a function of salt concentration

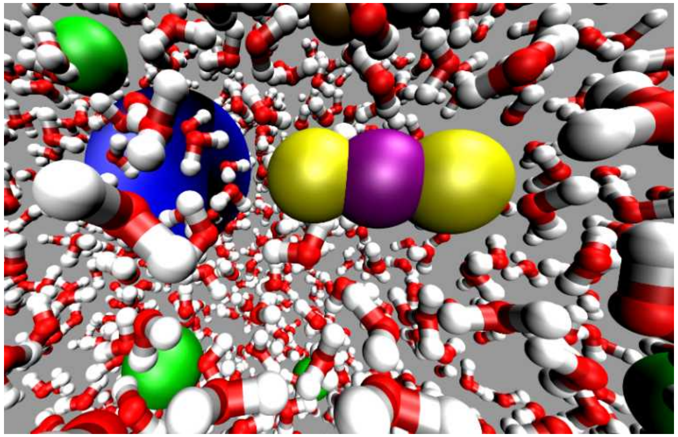


Increase salt concentration
→ increase cavity formation energy

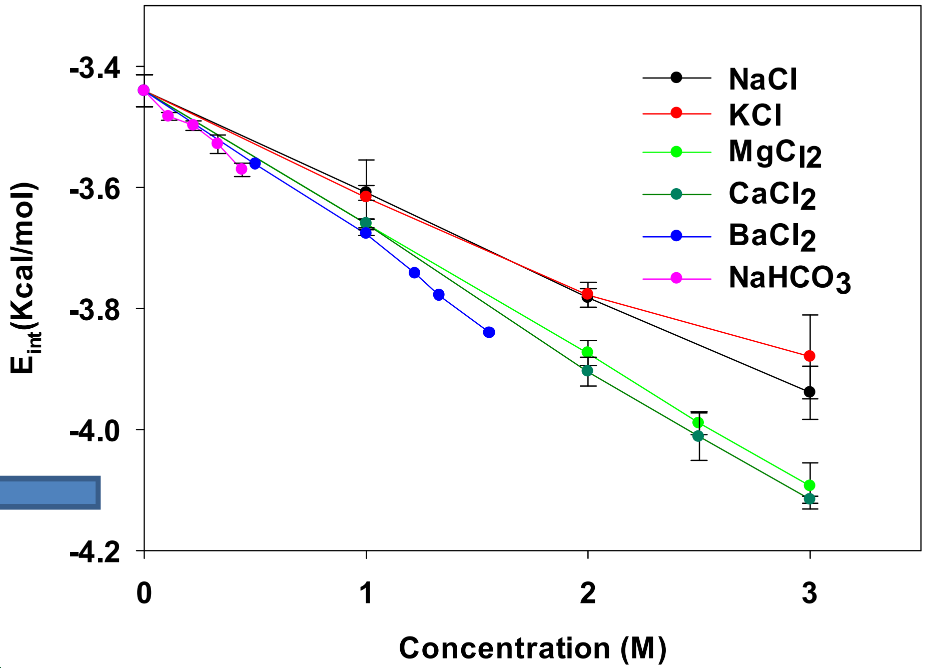
Interaction Energy between CO_2 and Aqueous Solution

$$\Delta G = \Delta G_{cavity} + E_{int}$$

$$E_{int} = \sum_{LJ} 4\epsilon_{ij}\left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}}\right) + \sum_{elec} \frac{q_i q_j}{r_{ij}}$$



Interaction energy between CO_2 and aqueous solutions

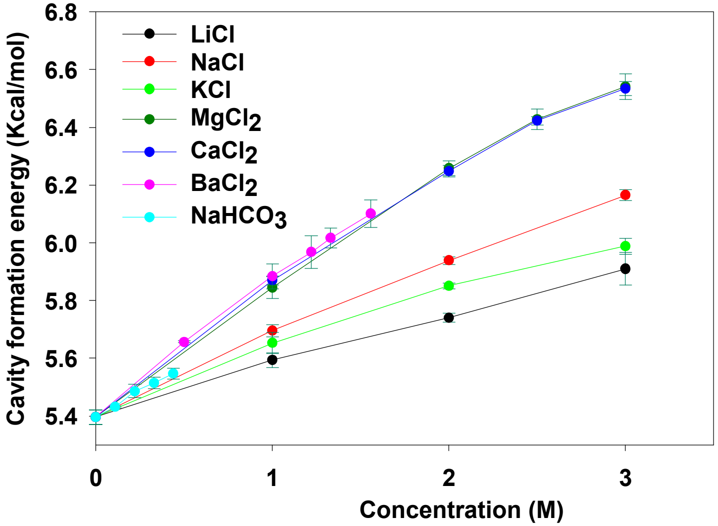


Increase salt concentration favors the interaction between CO_2 and aqueous solution.

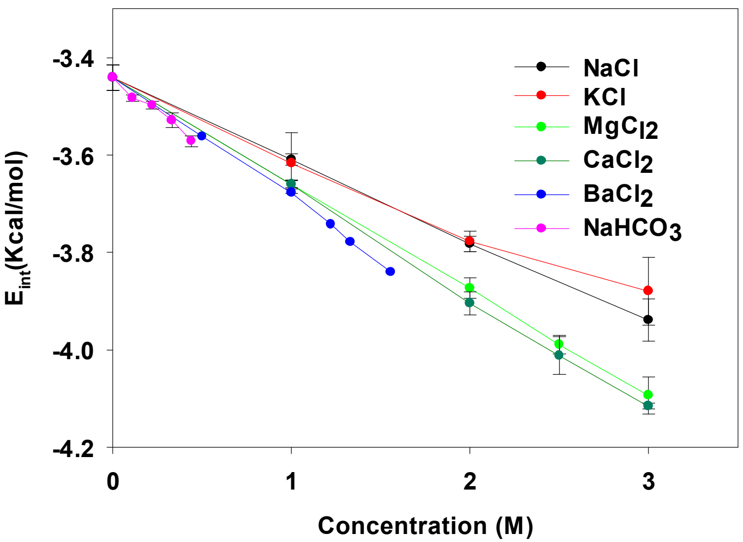
Summary

$$\Delta G = \Delta G_{cavity} + E_{int}$$

Cavity formation energy as a function of salt concentration



Interaction energy between CO_2 and aqueous solutions

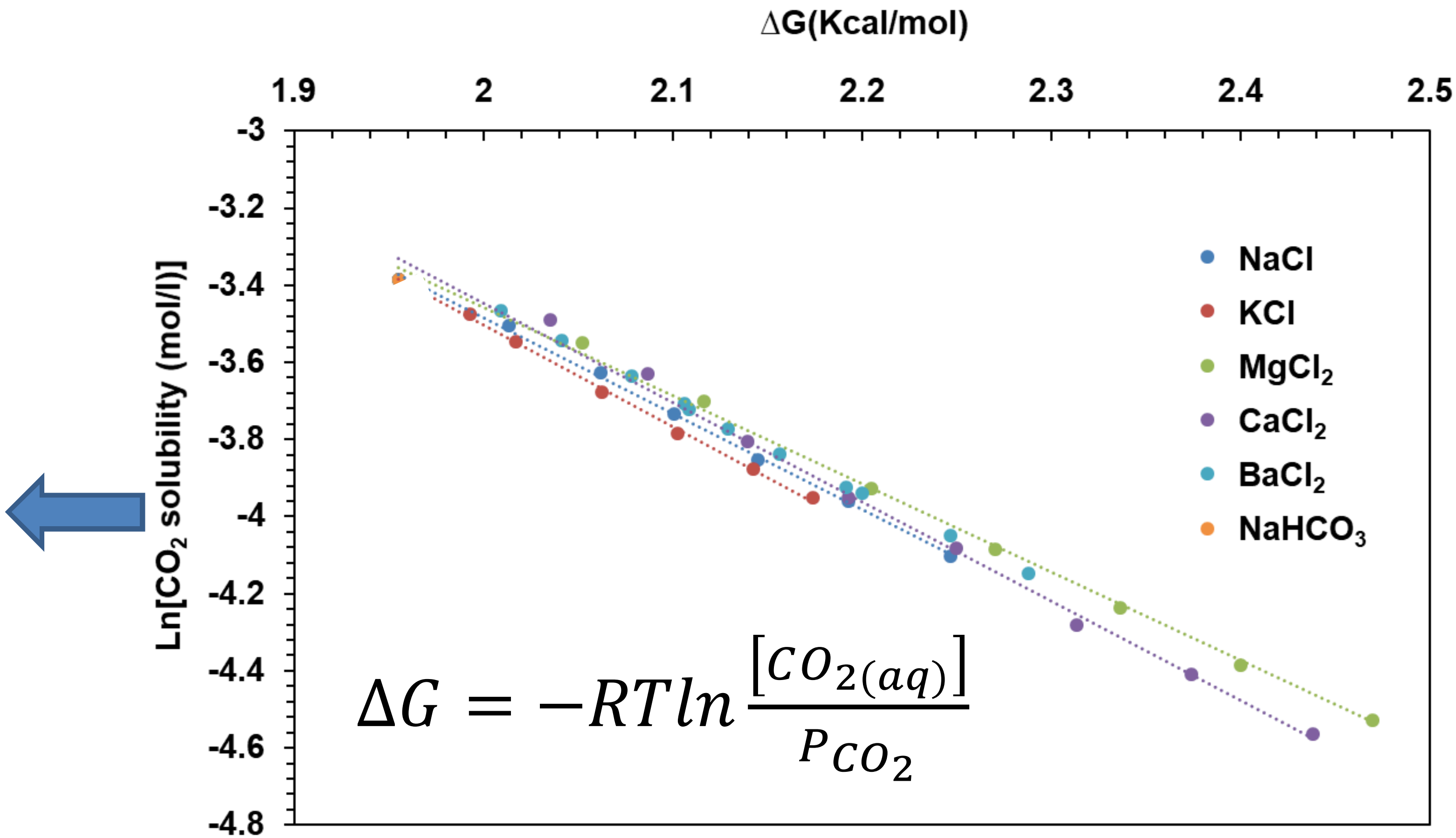


The decrease in the formation of cavities in aqueous solutions with increasing salt concentrations is responsible for the CO2 salting-out effect

Summary

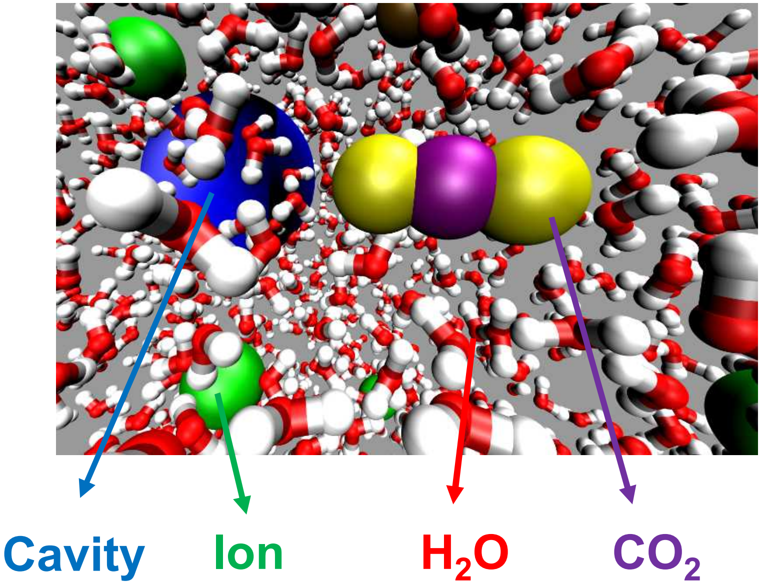
$$\Delta G = \Delta G_{cavity} + E_{int}$$

Literature experimental solubility



$$\Delta G = -RT \ln \frac{[CO_{2(aq)}]}{P_{CO_2}}$$

Density Fluctuation in Aqueous Solutions and Molecular Origin of Salting-out Effect for CO_2



Molecular dynamics simulation system containing CO_2 (pink and yellow), H_2O (red and white), and ions (green). Cavity (blue) formation energy and interaction energy between CO_2 and aqueous solution were estimated to understand salting-out effect of CO_2.

Reference

Ho, Tuan and Ilgen, Anastasia,
J. Phys. Chem. B, 2017, 121, 11485

Scientific Achievement

When increasing salt concentration, the interaction between CO_2 and aqueous solutions favors the solubility of CO_2. However, due to the decreasing number of cavities forming when salt concentration is increased, the solubility of CO_2 decreases. The formation of cavities was found to be the primary control on the dissolution of gas, and is responsible for experimentally observed CO_2 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 CO_2. These scientific achievements are important to understand solubility trapping mechanism in geological carbon storage.

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