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

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.

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.

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.

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

Probe volume $R=3.3\AA$

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.

Cavity formation energy as a function of salt concentration

Cavity formation energy

$$\mu = -k_B T \ln \left[ P \right]_{n=0}$$
Transferring a CO$_2$ gas molecule into an aqueous solution: first, a cavity forms in the aqueous solution ($\Delta G_{cavity}$), and then a CO$_2$ molecule is inserted into the cavity and interacts with the solvent ($E_{int}$).
\[ \Delta G = \Delta G_{\text{cavity}} + E_{\text{init}} \]

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

This material is based upon work supported as part of the Center for Frontiers of Subsurface Energy Security, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001114.

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

Lennard John potential, \( r_{ij} \) is the distance. \( R_{\text{min},ij} \) and \( \epsilon_{ij} \) 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.