

Partitioning of hydrophobic and hydrophilic organic compounds in high salinity waters of unconventional oil and gas play

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Unconventional oil and gas extraction, including shale gas and enhanced oil recovery (EOR), results in the production of large quantities of highly saline water. The injection of CO₂, fracking fluids, and other extraction techniques will result in geochemical changes that could lead to the migration of brines and/or CO₂ into overlying aquifers. There are still unknown questions about the fate and transport of many petroleum and synthetic hydrocarbons found in these produced waters, especially in regards to how the presence of high concentrations of salts affects the solubility and partitioning behavior of these organic compounds.

The Setschenow Equation is typically used to predict a log-linear increase in aqueous activity coefficient (i.e. the salting-out effect) with increasing salt concentration, related by the Setschenow constant, which is salt specific. This equation has not been validated at high salt concentrations for a variety of different classes of organic compounds. We will present work on aqueous solubility measurements of both hydrophobic (polycyclic aromatic hydrocarbons and thiophenes) and hydrophilic compounds (phenolic compounds, nitrogen heterocyclics, and carboxylic acids) in high salt environments, including up to 5 M NaCl, 2 M CaCl₂, and mixtures of these salts. These measurements are made using solid phase microextraction, and analyzed by gas chromatography coupled with a flame ionization detector. The measured data will be compared to estimates from Setschenow constants measured at low salt concentrations, and to available linear free energy relationships which are used to predict NaCl Setschenow constants. Deviations from predicted behaviors are discussed.

In addition to comparing predicted NaCl Setschenow constants to experimental NaCl Setschenow constants, we developed new linear free energy relationships for the prediction of both CaCl₂ and KCl Setschenow constants. These models are presented and discussed.