The validation of the Setschenow Equation for selected petroleum hydrocarbons in hypersaline solutions

A. S. BURANT[1,2], G. V. LOWRY[1,2], J. A. HAKALA[3] AND A. K. KARAMALIDIS[1,2]*

[1]National Energy Technology Laboratory-Regional University Alliance , Pittsburgh, PA 15236, USA (*Correspondance to akaramal@andrew.cmu.edu)
[2]Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA
[3]National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, PA 15236, USA

The widespread implementation of energy related activities such as carbon storage, including enhanced oil recovery, and unconventional oil and gas extraction will require brine management strategies. Some of the organic compounds associated with the formations in those operations are toxic and hazardous, and may potentially threaten the quality of water resources. A risk assessment of these activities will require a fundamental understanding of the solubility of the organic compounds in the saline waters. Organic compounds, in the presence of salts, typically exhibit a decrease in aqueous solubility with increasing salt content; called the salting-out effect. The empirical Setschenow Equation predicts a log-linear decrease in aqueous solubility with increasing salt content.

The Setschenow Equation has been shown to be valid up to seawater concentrations of salts (e.g. up to 1 M NaCl). The Setschenow Equation has not been validated for most classes of petroleum hydrocarbons up to high salt concentrations typical of some oil and gas reservoirs. Representative compounds were chosen from the major classes of petroleum hydrocarbons found in brines to determine if the Setschenow Equation is valid up to 5 M NaCl, 2 M $CaCl_2$, and mixtures of the two electrolytes, which is typical of oil reservoir brines. Setschenow constants of representative compounds were measured with solid-phase microextraction and analysed by gas chromatography coupled with a flame ionization detector. Results show that the Setschenow Equation is valid up to 5 M NaCl for certain compounds, such as thiophene, naphthalene, and dibenzothiophene. However, for some organic compounds a plateau of the Setschenow Equation was observed after 4 M NaCl. This occurred for benzothiophene, phenanthrene, and fluorene. It is hypothesized that this occurs for compounds that exhibit a larger salting-out effect, i.e., have a larger Setschenow constant.