Distribution of Complex Chemicals in Oil-Water Systems - DTU Orbit (13/10/2019)

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The deepwater energy sector represents one of the major growth areas of the oil and gas industry today. In order to meet the challenges of hydrate formation, corrosion, scaling and foaming the oil and gas industry uses many chemicals and their use has increased significantly over the years. In order to inhibit gas hydrate formation in subsea pipelines monoethylene glycol (MEG) and methanol are injected in large amounts. It is important to know the distribution of these chemicals in oil and water systems for economical operation of a production facility and to evaluate their impact on marine life. Furthermore distribution of chemicals is important information for downstream processing of oil and gas. The purpose of this project is the experimental measurement and the thermodynamic modeling of distribution of these complex chemicals in oil-water systems.

Traditionally distribution of chemicals in oil-water system is calculated using octanol-water partition coefficients. But experiments carried out by Statoil R & D have shown that octanol-water partition coefficients \( K_{\text{ow}} \) do not always mimic oil-water partition coefficients \( K_{\text{oil-water}} \) and therefore calculations may not be always correct. In the first phase of this project experimental data on \( K_{\text{ow}} \), \( K_{\text{oil-water}} \) and \( K_{\text{hw}} \) (hexane-water partition coefficients) are collected and investigations were carried out to develop correlations so that \( K_{\text{oil-water}} \) can be predicted using \( K_{\text{ow}} \) and \( K_{\text{hw}} \). However, due to scarcity of experimental data and limited information about the molecular structure of production chemicals the correlation could only be obtained for few families like alcohols, glycols and alkanolamines with varying degree of reliability.

In order to develop a thermodynamic model for the distribution of chemicals in oil-water systems experimental data are required but such data with natural gas-condensate/oil systems are very rare in the literature. In this project experimental work has been carried at Statoil R & D and an experimental method has been established and tested for such measurements. The mutual solubility of two North Sea condensates, MEG and water has been measured in the temperature range of 275-326 K at atmospheric pressure. The detailed composition of condensates is measured by GC analysis and 85 components are identified up to n-nonane and hundreds of ill-defined components in decane plus fraction.

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When methanol and MEG are used as gas hydrate inhibitors, the most significant disadvantage, especially for methanol, is their loss in hydrocarbon phase(s). The successful estimation of inhibitor loss would enable the inhibitors injection optimization as a function of the system parameters such as temperature and water cut. In this project the distribution of water and inhibitors (methanol, MEG) in various phases is modeled using the CPA EoS. The hydrocarbon phase consists of mixture-1 (methane, ethane, n-butane) or mixture-2 (methane, ethane, propane, n-butane, n-heptane, toluene and n-decane). CPA can satisfactorily predict water content in the gas phase of the multicomponent systems containing mixture-1 over a range of temperature and pressure. Similarly the methanol content in gas phase of mixture-1 + water + methanol systems is predicted satisfactorily with accuracy in the range of experimental uncertainty. For VLE of mixture-2 + water, mixture-2 + MEG + water and mixture-2 + methanol + water systems, the organic phase compositions are satisfactorily predicted whereas modeling results are relatively less satisfactory for vapor phase compositions partially due to uncertainties in the experimental data.

In addition to the multicomponent systems described above, the VLE of the binary system of methane-methanol is also investigated using CPA with satisfactory calculations of methane content of liquid phase using a single temperature independent kij over a range of temperature and pressure. The methanol content in the gas phase is satisfactorily correlated at higher temperatures and lower pressures using the same kij but deviations from experimental data are observed at lower temperatures and higher pressures. In order to extend CPA to reservoir fluids it is of interest to investigate the LLE of binary systems of hydrocarbons and water. In this work CPA is also applied to alkane + water and alkylbenzene + water systems to obtain binary interaction parameters and cross-association volumes respectively. Finally, CPA has been extended to reservoir-fluid + MEG and reservoir-fluid + MEG + water systems. The reservoir fluid consists of three condensates and two oils from the gas fields in the North Sea. The mutual solubility of condensates and MEG is satisfactorily correlated using a single, average and temperature independent kij for all MEG-HC pairs. Similarly the mutual solubility of condensate/oil, MEG and water is predicted satisfactorily using the same average kij for MEG-HC pairs and water-HC kij from a generalized correlation as a function of carbon number. The experimental trends in mutual solubility as a function of temperature and MEG content in polar phase are predicted satisfactorily which are correct in order of magnitude according to the industrial requirements.

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Organisations: Department of Chemical and Biochemical Engineering, CERE – Center for Energy Ressources Engineering
Contributors: Riaz, M.
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