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Selecting AQ, MSE or MSE-SRK for your Scaling Calculation

The OLI Software contains three frameworks for predicting activity/fugacity coefficients in electrolyte[1] and hydrocarbon solutions. They are the Aqueous (AQ), the Mixed Solvent Electrolytes (MSE), and the Mixed Solvent Electrolyte-Soave Redlich Kwong (MSE-SRK) frameworks.

Explanation of the three frameworks

The MSE framework is ideal for brines with high glycol or methanol concentrations

The AQ framework is OLI's original activity coefficient model. It was created in the 1970's and is based on a combination of Debye-Hückel, Bromley, Meissner, and Pitzer models. In 2000, OLI published the more comprehensive MSE framework. This theory is based on Debye-Hückel-Pitzer, UNIQUAC, and ion-interaction-virial expansion models. In 2017, OLI published MSE-SRK framework. This theory combines the mixed solvent capabilities of the MSE theory with the industry-accepted SRK model for hydrocarbons (gas and oil).

The AQ framework is designed around water being the primary electrolyte solvent; consistent with how these strong electrolyte theories were developed. The MSE and MSE-SRK frameworks by comparison, are not designed around this assumption, and can therefore model systems in which the solvent is pure H_2SO_4, methanol, glycol, amines; or other that ionize salts.

The AQ framework has a composition limit. The dissolved solute may be no greater than 35 mole % of the electrolyte solution[2]. This is roughly the solubility of NaOH. The MSE and MSE-SRK frameworks by comparison, have no theoretical composition limit. It is possible to calculate the compositional range of an electrolyte phase from pure water to the fused salt (e.g., from 100% H_2O to 100% $ZnCl_2 \cdot nH_2O$).

All three frameworks have similar temperature limits but there are also differences. The theoretical temperature limit for the AQ framework is about 340 °C, but the practical limit is 300 °C. For the two MSE frameworks, the limit is 90% of T_c of the electrolyte solution. Thus, for pure water, that value is 340 °C. For 90% H_2SO_4, the temperature limit is >500 °C.

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[1] The term *electrolyte* is used instead of *aqueous* or *water*, because this phase, commonly presumed to be water, does not, in fact, require water. Both ethanol and glycol for example, dissolve salts and conduct electricity. Both therefore form electrolyte phases.

[2] This 35% limit applies to the dissolved solute in the water phase. It does not apply to the size of hydrocarbon phase, nor the oil-water ratio.

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All three frameworks use the same equation of state (Helgeson-Kirkham-Flowers-Tanger or HKFT)[3] to compute the equilibrium constants in the electrolyte phase. Therefore, they have the same theoretical pressure limits of 5,000 bar. The practical pressure limits however, differ depending on the chemistry selected. OLI suggests a pressure limit of 1000 to 1500 bar for the AQ framework. This is due to the paucity of available high pressure data when this framework's database was developed. The MSE databases were developed more recently and are based on substantially more high pressure data. Therefore, MSE validations exceed 4,000+ bar for some systems.

All three frameworks can be used for most standard oilfield applications

Each framework has separate databases. The AQ database contains approximately 6,000 basic species (solid, vapor, organic, aqueous). The MSE databases contains approximately 3,500 species and the and MSE-SRK database is slightly smaller. The AQ database is no longer in development, and so this number will not increase. The MSE databases undergo regular development and the species number increases with each software release. There is substantial species overlap among the three databases. However, there are some species in the AQ database not found in the MSE databases, and visa-versa.

The compositional advantage of MSE/MSE-SRK databases is because of the systematic approach to their development. OLI thermodynamicists start with binary mixtures, e.g., $NaCl-H_2O$ and $CaCl_2-H_2O$, and expand to ternary and multi-component systems, e.g., $NaCl-CaCl_2-H_2O$, etc. They collect, review, and incorporate peer-reviewed data and build the database using this brick-by-brick approach. The result is an internally consistent and predictive database.

The number of species in the MSE and MSE-SRK databases will eventually exceed the AQ database, and at that point, the AQ framework will be made redundant. Until that time all three frameworks are made available, and advice is provided as to which framework to use for a given system.

Calculation Speed: The AQ calculates the fastest, because of the assumption that a water phase is always present. This same assumption also causes AQ calculations to fail when the brine phase evaporates to dryness. MSE-SRK compute relatively fast, because the there is no assumption that ions dissolve in

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[3] The limit is 5,000 bar when the HKFT equation is used directly. This is always the case in the MSE model but requires the "Use Helgeson Direct" option in the AQ model. Without the latter option, the accuracy of the equilibrium constants in the AQ model gradually declines beyond several hundred bar.

The MSE frameworks has advantages at extreme compositions and conditions

the hydrocarbon or critical fluid phase. The MSE framework is the slowest. OLI software engineers are regularly optimizing algorithms to reduce all runtimes.

Prediction range: The MSE and MSE-SRK frameworks are more predictive than AQ framework in the following systems.

1) Brines containing >10% glycol or methanol

2) High pressure (>1000 bar) wells

3) Brines with high hardness:alkalinity or hardness:sulfate ratios

The MSE/MSE-SRK theory includes a miscible-solvent interaction model, enabling the solvation effects of glycol and methanol to be captured. This effect does not exist in the AQ framework.

The extended pressure prediction of MSE/MSE-SRK is in part, because of experimental data availability. The AQ database was created in a production era where 500 to 1000 bar was considered high pressure. By comparison, the MSE database, which is still being expanded, is being developed with experimental data that exceeds 2,000 bar for some systems.

Existing limitations or technical issues with MSE. At certain pressures and for specific gas compositions, MSE predictions produces phase discontinuities. Systems containing CH_4 and CO_2 show a phase discontinuity as pressures cross about 200 bar. This is the limitation of the MSE theory; specifically, the demands on the theory to allow hydrocarbon phases to dissolve electrolytes.   In some instances, the discontinuity is small and irrelevant, in other cases it is detectable and creates uncertainties. OLI continues to correct this limitation.

MSE-SRK smooths out phase discontinuities and is the preferred option for oil and gas production

Correcting MSE limitations using MSE-SRK. Starting with V9.5.4, OLI added the MSE-SRK framework. This extension smooths out the discontinuity. The compromise is that the dissolved electrolytes in hydrocarbon/critical fluids is no longer computed. **This MSE-SRK framework will be the preferred option for oil and gas production.** A separate white paper is available that describes the MSE-SRK model in detail.

Guidelines for oil and gas production applications

Most oilfield applications can utilize all three frameworks. Oilfield waters are derived from seawater, and in general, have a consistent slate of dissolved species such as Na, K, Ca, Mg, Cl, SO_4, HCO_3, etc. All three framework contain these standard brine species.

Roster of applications for using AQ, MSE, or MSE-SRK

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The table below contains a generalized list of oilfield scaling applications. The adjacent columns indicate which framework is appropriate for that work

Application	AQ	MSE	MSE_SRK
Brine composition to 200,000 mg/l TDS	++	++	++
High density NaCl brines (>200,000 mg/l TDS)	++	++	++
High density NaCl brines containing >1m Ca^{+2} and Mg^{+2}	+	++	++
High density $CaCl_2$, $MgCl_2$, or $ZnCl_2$ brines	+	++	++
Glycol- or methanol-containing brines	-	++	++
Standard temperature wells (<150C)	++	++	++
High temperature wells (>175C)	+	++	++
Moderate pressure wells (<700 bar) for standard scales[4]	++	++	++
High pressure wells (<700 bar) for standard scales	+	++	++
Sulfide scales[5]	+	+	+
Low water cut wells for carbonate and sulfide scales	+	+	+
High gas-water ratio wells where evaporating or condensing conditions exist	++	++	++
Brines with high hardness to alkalinity/sulfate ratios (e.g., 10:1)[6]	+	++	++
Brines with low hardness to alkalinity/sulfate ratios (e.g., 1:10)[7]	++	++	++
Brines with high organic acid concentrations (>2000 mg/l)	+	+	+
High CO_2 gas/cond/oil wells (>10% or >100 bar pp)	++	++	++
High H_2S gas/cond/oil wells (>2% or 20 bar pp)	++	++	++
Dissolving ions in polar hydrocarbons		++	

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[4] Standard scales include: $CaCO_3$, $FeCO_3$, $BaSO_4$, $CaSO_4$, $CaSO_4 \cdot 2H_2O$, $SrSO_4$, and NaCl.

[5] Sulfide scales are FeS, FeS_2, Fe_3S_4, ZnS, PbS, and HgS

[6] Ratios are on molar basis

[7] Ratios are on molar basis

White Paper: Selecting an OLI thermodynamic framework for oil and gas production

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Note that historical MSE isssues have been addressed

Historically, the MSE framework had two issues that have been addressed as of OLI Engine V9.2.7:

1) Erratic convergence patterns in systems with two liquid phases when one phase appeared in small amounts (resulting in a saw-tooth appearance of some surveys, especially as a function of temperature)

2) Serious deficiencies in the predictions of hydrocarbon phase behavior. OLI recommends anyone experiencing these problems to upgrade their OLI software to V9.2.7 or higher.

Occasionally, interaction parameters may be still missing between some components, usually neutral species. While this may happen for both the MSE and AQ frameworks, the resulting prediction errors may be more severe when these interaction parameters are missing in MSE. This is because the liquid phase in MSE does not assume that water will be dominant, and so there is no limit imposed by the existence of water. In the AQ framework, the requirement that water constitutes more than 65% of the phase inherently limits the uncertainty and constrains the solution.

For MSE, it is a good practice to check the interactions matrix in the OLI Studio: Stream Analyzer

Therefore, OLI recommends checking if the interactions are present in the interaction matrix (available in the OLI Studio: Stream Analyzer) and contacting OLI for an assessment of the application if the interactions are missing.

Finally, if the chemistry of interest is covered in both the AQ and the MSE framework, OLI recommends the MSE framework.

For MSE-SRK suitability for your application, please see further documentation to screen whether your chemistry is covered in the MSE-SRK framework.

White Paper: Selecting an OLI thermodynamic framework for oil and gas production