The CONTACTOR™

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Gas Treating with Hybrid Solvents

Hybrid solvents are members of a class of extractive agents in which, typically, some of the water and amine content of a conventional amine-based solvent is replaced by a *physical, non-reactive* component. The earliest commercial example is the Sulfinol-D™ solvent as developed and licensed by Shell Catalysts & Technologies over the last 60 years. Here, some of the water and some of the amine (diisopropanolamine, DIPA) are replaced by the purely-physical solvent, sulfolane. Later, Sulfinol-M™, and Sulfinol-X™ were developed for other gas treatment applications. Their purpose is to enhance the removal of trace organic sulphur such as mercaptans, COS, disulfides, etc. while still being effective for CO_2 and H_2S removal with varying degrees of CO_2 slip and/or depth of CO_2 removal. Each mixed solvent brand contains unique components but in varying amounts, which allows the solvent to be nicely tailored to the application.

Sulfolane is a cyclic sulfone with the formula $(CH_2)_4SO_2$ with the following structure:

Sulfolane has *high affinity for certain sulphur-containing compounds and aromatics*, but low affinity for aliphatics. Indeed, it has been used for many years as an extractive agent for the selective removal of aromatics from liquid hydrocarbons.

Solvent suppliers are beginning to develop new hybrid solvents with different added physical-solvent components but with the same intended purpose in gas treating. On the other hand, one could view conventional amine-based solvents, contaminated with glycols for example, as hybrid solvents and to which the same modelling principles apply.

As a gas treating solvent, the amine content is reactive toward CO_2 and H_2S, but water is an essential ingredient because it allows the amine to react with the acid gases (aqueous and non-aqueous amine chemistries are quite different). Water allows the amine to dissociate and form ionic reaction products, thereby giving the solvent high capacity for acid gas. But water and aqueous amines alone are very poor solvents for mercaptans and most other organosulphur compounds commonly found in natural gases. The organic, physical part of the hybrid mixture solubilizes the organosulphur components. Thus, one achieves the best of both worlds— high capacity for both of the acid gases CO_2 and H_2S, as well as for organosulphur components, all in a single solvent.

OGT has used the well-proven mass transfer rate-based technology and electrolyte thermodynamics within the framework of OGT | ProTreat® to develop the ability to simulate a wide range of hybrid solvents containing water, a reactive component such as an amine, and an inert organic constituent, not limited to sulfolane. Development of hybrid solvents began in the early 1960s with Sulfinol-D and much of the fundamental data generated in the ensuing 60 years has been used in the ProTreat simulator. In more recent years numerous academic institutions have published the results of measurements of phase equilibrium and physical and transport properties of acid gases in MDEA- and piperazine-containing solvents with sulfolane, and even a small amount of absorber performance data have been published.

Mass Transfer Rate-Based Simulation

Simulating a separation process with ideal stages requires only accurate vapour-liquid equilibrium. The disadvantage is the lack of any reliable methodology for translating theoretical stages into physical equipment.

Mass transfer rate-based methods are rigorous and reliable, they are based on sound scientific and engineering principles, and they provide simulated performance of extraordinary predictive accuracy and reliability with absolutely no need to make any translation from theoretical stages to real internals [2]. Mass and heat transfer behaviour of tower internals are characteristics of the internals themselves, and they depend on certain properties of the gas and liquid, and of the species being transported. Such properties include density, heat capacity, phase viscosity, diffusion coefficients of species in the gas and liquid phases. Properties depend on the species present and their concentrations and always need mixing rules to go from pure components to mixtures.

Vapor-Liquid Equilibria

OGT | ProTreat® already has a solid electrolytic thermodynamic framework for aqueous amine systems. Hybrid

solvents merely add another inert (nonreactive, physical) liquid component to the solvent. A rigorous thermodynamic model has been implemented to represent the VLE of mixed solvent systems that can simulate any arbitrary combinations of chemical and physical solvents. The interaction parameters in OGT's activity coefficient model have been fine-tuned to accurately represent all the VLE data for acid gases in amine-water-sulfolane mixtures available in the open literature.

Physical and Transport Properties

Critical physical and transport properties have been derived from experimental data available in the open literature. The data were identified and fitted for the binary systems of amine-water and sulfolane-water both with and without simultaneously dissolved gases.

Aqueous Amines vs Hybrid Solvents

To give some appreciation of how equilibrium in a hybrid solvent compares with the corresponding traditional aqueous amine, simulated behavior of four solvent formulations are compared in Figures 1–3, at a fixed temperature. The original sulfolane-free solvent is 40 wt% MDEA in water. Sulfolane solvent is obtained by replacing some of the original aqueous amine with sulfolane, keeping the non-sulfolane part of the solvent at 40 wt% MDEA. Note that the loading of a solute component (CO_2, H_2S, EtSH) is defined to be the moles of solute per mole of *amine* (*not* per mole of total solvent).

Figures 1 and 2 show that in this case the replacement of aqueous amine with sulfolane actually slightly *reduces* the solubility of the acid gases CO_2 and H_2S. The CO_2 partial pressure required to hold a given CO_2 concentration in the solvent is about 25% higher with 25wt% sulfolane, and for H_2S it is about 18% higher (25% and 18% less soluble, respectively). This should have been anticipated because these acid gases are less soluble in sulfolane than in aqueous MDEA. With mercaptans, however, the situation is reversed.

Figure 3 shows that higher sulfolane concentrations require ever lower mercaptan partial pressures to load the solvent to the same extent with EtSH. The solubility of the mercaptan in 25 wt% sulfolane is 60% higher than in the generic 40 wt% aqueous MDEA. That can be a very important improvement to meeting sulfur emissions regulations. For the

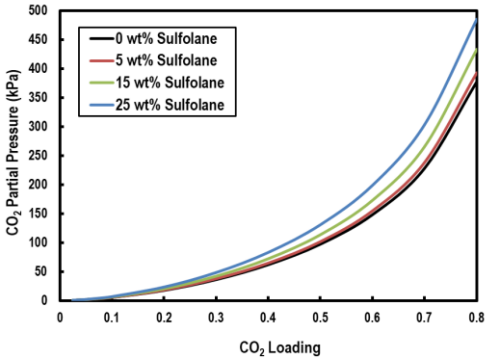

Figure 1 How Sulfolane Affects CO_2 Partial Pressure Over Solvent with Fixed MDEA:H_2O Ratio.

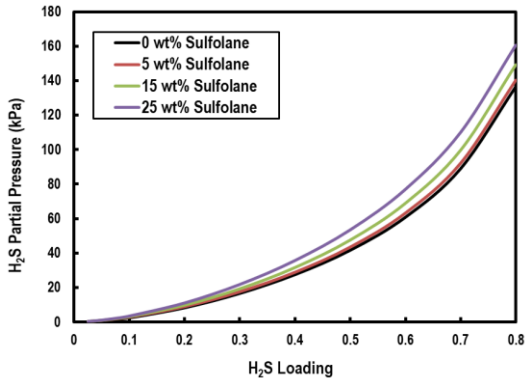

Figure 2 How Sulfolane Affects H_2S Partial Pressure Over Solvent with Fixed MDEA:H_2O Ratio.

conditions of this case, the hybrid solvent has a distinct advantage over its more conventional sister, especially when the raw gas has a high mercaptan concentration.

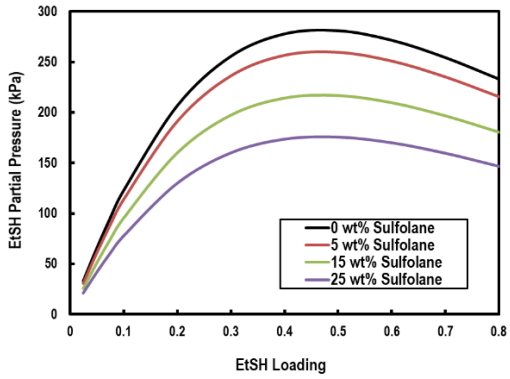

Figure 3 Effect of Sulfolane on EtSH Partial Pressure Over Solvent with Fixed MDEA:H_2O Ratio.

Summary

OGT | ProTreat® now offers a mass transfer rate-based simulation capability for hybrid solvents using a rigorous activity coefficient basis and develops the ternary and quaternary solvent description using mixing rules based on sound thermodynamics. Mass transfer rate calculations use the same proven rate-based model as is used in the ProTreat simulator generally.

References

1. Weiland, R. H.; Dingman, J. C.; *Eliminating Guesswork*, Hydrocarbon Engineering, February, 2001.

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To learn more about this and other aspects of gas treating and sulphur recovery, plan to attend one of our training seminars. Visit www.protreat.com/seminars for details.

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An extended version of this issue of The Contactor™ will appear in the April issue of Hydrocarbon Engineering.