

A HYBRID APPROACH



**Prashanth Chandran, Nathan Hatcher,
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present a new technology that offers reliable,
predictive simulation of hybrid solvents.

Hybrid solvents are members of a class of extractive agents for acid gas removal whereby some of the water and amine content of a conventional amine-based solvent is typically 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 on, Sulfinol-M™ and Sulfinol-X™ were developed for other gas treatment applications. Their purpose is to enhance the removal of trace organic sulfur such as mercaptans, carbonyl sulfide (COS), disulfides, etc., while also remaining effective for carbon dioxide (CO₂) and hydrogen sulfide (H₂S) removal with varying degrees of CO₂ slip and/or depth of CO₂ removal. Each mixed solvent brand contains unique components in varying amounts, which allows the solvent to be tailored to the application.

Sulfolane is a cyclic sulfone with the formula $(\text{CH}_2)_4\text{SO}_2$. It has a high affinity for sulfur-containing compounds and for aromatics, but a 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, to which the same modelling principles apply.

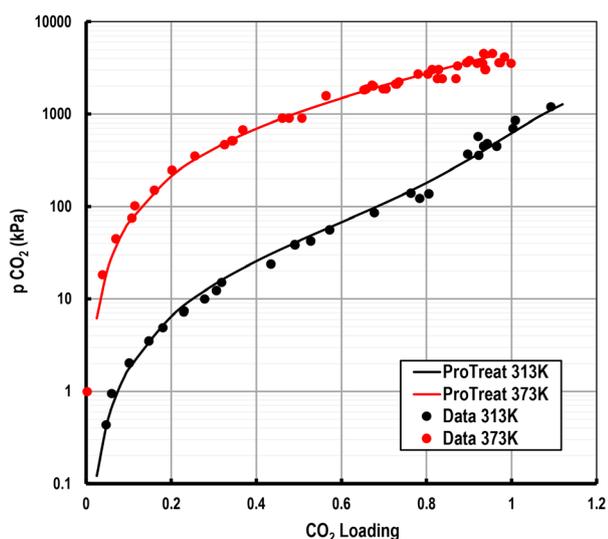


Figure 1. Comparison of model with measured data² for CO_2 partial pressure over MDEA-water-sulfolane solvents.

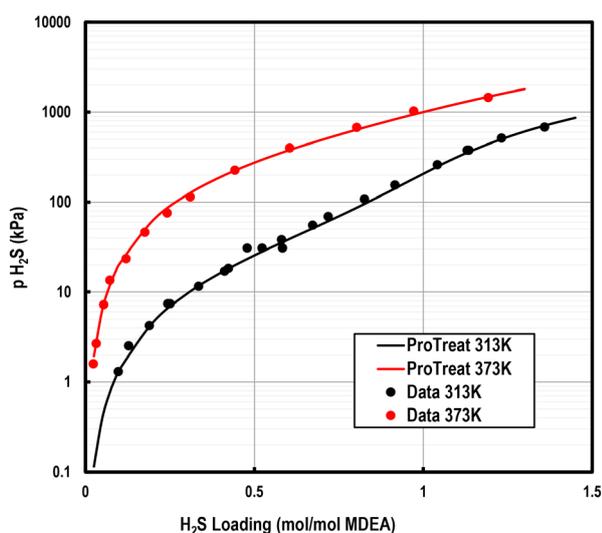


Figure 2. Comparison of model with measured data² for H_2S partial pressure over MDEA-water-sulfolane solvents.

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 providing the solvent with a high capacity to hold a substantial amount of acid gas. However, water and aqueous amines alone are very poor solvents for mercaptans and most other organosulfur compounds that are commonly found in natural gases. The organic, physical part of the hybrid mixture solubilises the organosulfur components. As a result, the best of both possible worlds is achieved: high capacity for both of the acid gases (CO_2 and H_2S), as well as the organosulfur components, all in a single solvent.

Optimized Gas Treating Inc. (OGT) has used the well-proven mass transfer rate-based technology and electrolyte thermodynamics embedded within the framework of OGT | ProTreat[®] to develop a new ability to simulate a wide range of hybrid solvents containing water, a reactive component such as an amine, and an inert organic constituent. Much of the fundamental data generated since the development of the first hybrid solvents in the early 1960s has been used in the ProTreat simulator. In more recent times, numerous academic institutions have published the results of measurements of phase equilibrium and physical and transport properties of acid gases in methyl diethanolamine (MDEA) and piperazine-containing solvents with sulfolane, and even a small amount of absorber performance data.

This article restricts attention to sulfolane as the physical solvent component, and only tangentially touches on the glycols as physical additives that yield mixtures with hybrid solvent characteristics. Reference to other physical components is purposely avoided because they are proprietary to the solvent suppliers developing them.

Mass transfer rate-based simulation

Simulating a separation process with ideal stages only requires accurate vapour-liquid equilibrium data. Physical and transport properties are only needed for tower sizing calculations. The advantage is simplicity; the disadvantage is a calculated result that is extremely hard to translate into the reality of a separation using real trays and packings. There is no reliable method to translate theoretical stages into the physical equipment in gas treating.

When the simulation is mass transfer rate-based, the physical, mass transfer, and hydraulic characteristics of the tower internals are merged with reaction kinetics and phase equilibrium thermodynamics. Rates of mass transfer between the phases are calculated together in a way that parallels how heat exchanger calculations have been carried out for at least a century. The methods are rigorous and reliable; are based on sound scientific and engineering principles; and provide simulated performance that is accurate and reliable, with no need to make any translation from theoretical stages to real internals.¹

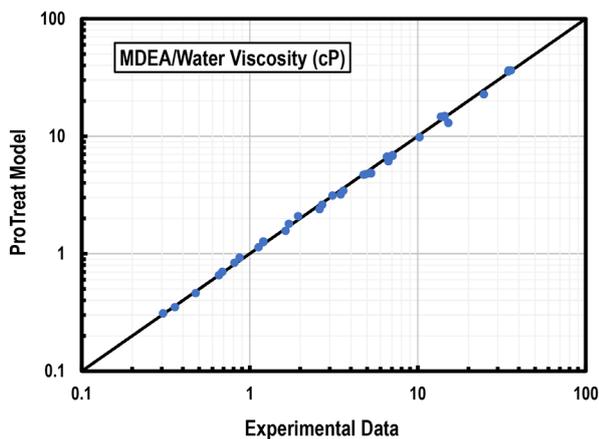


Figure 3. Parity plot showing comparison between measured^{3,4} and calculated viscosity of MDEA-water solvents.

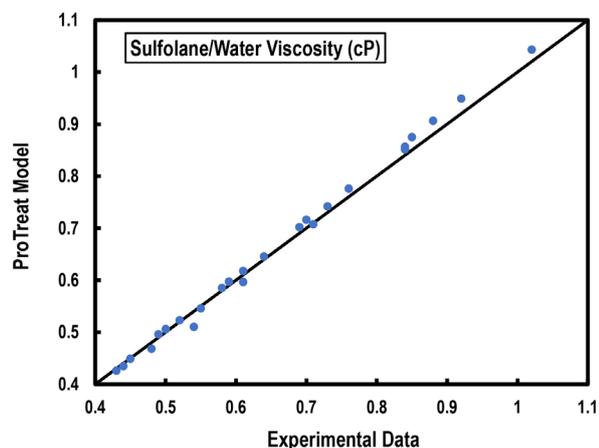


Figure 4. Parity plot showing comparison between measured^{3,4} and calculated viscosity of sulfolane-water solvents.

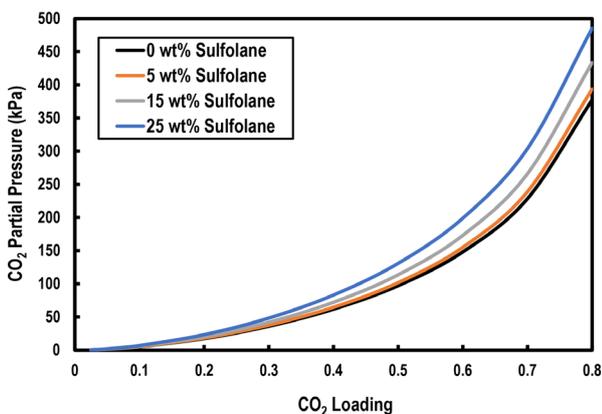


Figure 5. How sulfolane content affects CO₂ partial pressure over solvent with fixed MDEA-to-water ratio.

Mass and heat transfer behaviour of the tower internals are characteristics of the internals themselves, but they also depend on certain properties of the gas and liquid phases, and on the species that are transported between phases. Such properties include density, heat capacity, viscosity, and diffusion coefficients of species in the gas and liquid phases. Properties depend on the concentrations of the species present, and usually require mixing rules to go from pure components to mixtures.

Vapour-liquid equilibria

OGT | ProTreat already has a solid electrolytic thermodynamic framework for aqueous amine systems. Hybrid solvents merely add another inert (non-reactive, physical) liquid component to the solvent. A rigorous thermodynamic model has been implemented to represent the vapour-liquid equilibrium (VLE) of mixed solvent systems that can simulate any arbitrary combinations of chemical and physical solvents. The interaction parameters have been fine-tuned to accurately represent all of the VLE data for acid gases in amine-water-sulfolane mixtures available in the open literature. As an example, Figures 1 and 2 show typical plots comparing the VLE of CO₂ and H₂S, respectively, in MDEA-water-sulfolane mixtures calculated by the ProTreat model with experimental data.²

Similar plots for DIPA-water-sulfolane and for MDEA-piperazine-water-sulfolane show just as close reproducibility between model and data, underscoring that ProTreat accurately represents acid-gas phase equilibrium in these systems over five orders of magnitude in partial pressure. The data spans a wide range of temperatures, from absorber to regenerator conditions, and corresponds to a number of different solvent formulations and a range of acid gas loadings.

This kind of information is all that is required in order to carry out ideal stage calculations; however, mass transfer rate-based models need information on transport properties, as these play a vital role in determining mass transfer rates. This is because they significantly influence the mass (and heat) transfer coefficients that are active within the process. Tower performance is determined by mass transfer rates, so the transport properties are intimately connected to successful mass transfer rate-based simulation.

Physical and transport properties

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

Such data on binary solvent systems formed the fundamental basis for the ProTreat model. However, to arrive at ternary solvent properties, the simulator uses well-established mixing rules to account for the nonidealities that result from mixing diverse chemicals to form mixed solvent systems. Properties that were fitted include: density, viscosity, surface tension, thermal

conductivity, diffusivity, etc., in addition to critical and fundamental properties of the molecules in the mixed solvents.

As an example, Figures 3 and 4 show the viscosity model predictions compared with experimental data for the binary systems of MDEA-water and sulfolane-water, respectively.^{3,4} Solvent viscosity is a particularly important property because it greatly affects the liquid-side mass transfer coefficient, and CO₂ absorption is generally liquid-side controlled. Properties of the binary solvents are combined using mixing rules to arrive at the corresponding properties of the ternary (or quaternary) solvents.

Aqueous amines vs hybrid solvents

To provide some appreciation of how equilibrium in a hybrid solvent compares with its corresponding traditional aqueous amine, four solvent formulations are compared in Figures 5 – 7, all at the same temperature. The original sulfolane-free solvent is 40 wt% MDEA in water. An X wt% sulfolane solvent is obtained by replacing X% of the original sulfolane-free solvent with an equal weight of sulfolane. Thus, the ratio of MDEA to

water remains constant from case to case, i.e. the non-sulfolane part of the solvent is always 40 wt% MDEA. Note that the loading of a solute component (CO₂, H₂S, ethanethiol [EtSH]) in the solvent is defined as the moles of solute per mole of amine (not per mole of total solvent).

Figures 5 and 6 show that in this case, the replacement of aqueous amine with sulfolane actually slightly reduces the solubility of the acid gases CO₂ and H₂S. The CO₂ partial pressure required to hold a given CO₂ concentration in the solvent is approximately 25% higher with 25 wt% sulfolane, and for H₂S 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 story is reversed.

Figure 7 shows that higher sulfolane concentrations require lower and lower EtSH partial pressures in order 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. For the conditions of this case, the hybrid solvent has a distinct advantage over its more conventional sister when the raw gas has a high mercaptan concentration.

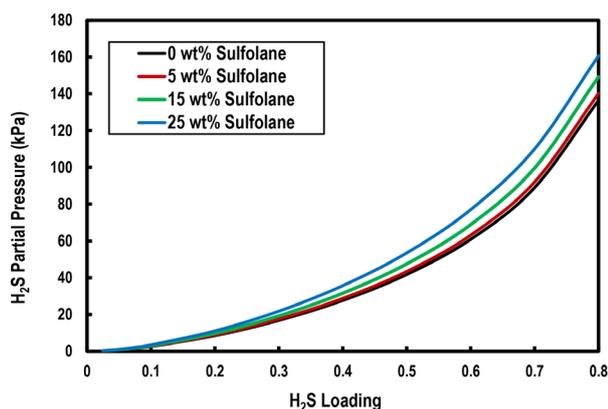


Figure 6. How sulfolane content affects H₂S partial pressure over solvent with fixed MDEA-to-water ratio.

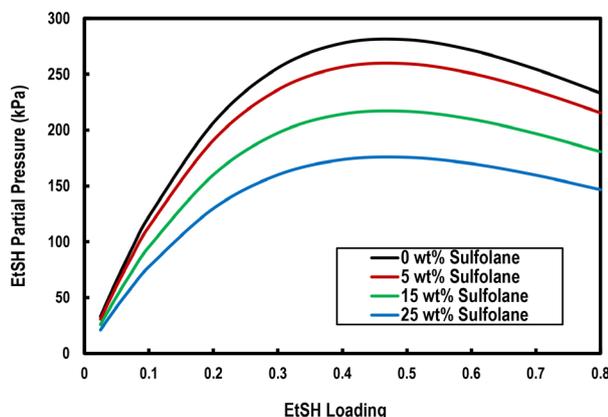


Figure 7. The effect of sulfolane on EtSH partial pressure over solvent with fixed MDEA-to-water ratio.

Conclusion

OGT | ProTreat offers a mass transfer rate-based simulation capability for hybrid solvents. The thermodynamic model uses 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 and well-accepted rate model as is generally used in the ProTreat simulator. The result is the highly-reliable, predictive simulation of hybrid solvents. The non-reactive hybridising component is not limited to sulfolane, and can be applied to new hybrid solvents, as well as those currently under development.

In the example of an MDEA-water-sulfolane solvent that has been expanded upon in this article, the phase equilibrium behaviour of CO₂ and H₂S are shown to not be greatly affected by the inclusion of sulfolane, although the solubility of these components is slightly reduced by the presence of sulfolane. Ethyl mercaptan, on the other hand, shows that sulfolane considerably increases the solubility of EtSH. 

References

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