

## **Mercaptans Removal from Gases by Absorption into Amines and Caustic**

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### **ABSTRACT**

Mercaptans can be rather difficult to remove from gases by absorption into treating solvents. This paper uses a mass transfer rate-based model of the absorption process to discuss quantitatively the ease and extent of removal of methyl through n-butyl mercaptans from gases using MDEA and caustic soda of various strengths. Absorption rates indicate unequivocally that there is a direct positive relationship between the molecular weight of the mercaptan and the ease with which it is absorbed into amines; the relationship is inverted when caustic soda is the solvent.

# Mercaptans in Refinery Gas Treating

Sulfur emissions from refinery combustion sources are typically calculated by measuring H<sub>2</sub>S in the hydrocarbon gas before combustion and converting it to an equivalent amount of post-combustion SO<sub>2</sub>. Of course, in reality all sulfur species present in the hydrocarbon fuel contribute to SO<sub>2</sub> emissions. As the regulatory limits on emissions are progressively lowered, knowledge of the behavior of mercaptans in amine systems and caustic systems will become increasingly important for designers and operators who are required to conform to the limits.

## Scope of This Paper

This paper does not reference a particular mercaptan concentration limit for gases, rather it focuses on how process variables affect mercaptan removal.

We consider the absorption of mercaptans into amine solutions and solutions of caustic soda. The reverse process of removing the mercaptans from the solution using thermal or oxidative regeneration processes is beyond the scope of this paper. The amine used for the analyses is MDEA since it is a typical amine used in refineries.

Four mercaptans are included in the study:

- Methyl Mercaptan or Methanethiol, abbreviated MeSH
- Ethyl Mercaptan or Ethanethiol, abbreviated EtSH
- Propyl Mercaptan or Propanethiol, abbreviated PrSH
- Butyl Mercaptan or Butanethiol, abbreviated BuSH

## Relevant Properties of Mercaptans

Mercaptans are both hydrocarbons and acid gases, and they have the properties of both classes of compounds. As we will show, the relative importance of these two aspects governs much of mercaptan behavior.

### *Acidity*

Mercaptans are weak acids relative to the traditional acid gases H<sub>2</sub>S and CO<sub>2</sub>. The C<sub>1</sub> through nC<sub>4</sub> mercaptans have essentially the same acidity, with a pK<sub>a</sub> of 10.6 at 25°C<sup>[1]</sup>. This is considerably less acidic than H<sub>2</sub>S which has a pK<sub>a</sub> of 7.0 at 25°C<sup>[1]</sup> for its first dissociation reaction.

Acidity is important because the relative acidity of dissolved gases has a strong impact on equilibrium behavior between the liquid and vapor phases. This effect is described in Figure 1 which shows an illustration of vapor liquid equilibrium for H<sub>2</sub>S and methyl mercaptan in water. The molecular form of H<sub>2</sub>S reaches equilibrium across the vapor-liquid interface, but some of the aqueous molecular H<sub>2</sub>S dissociates into ionic species to an extent controlled by reaction equilibrium. Methyl mercaptan participates in analogous equilibria. Note that both the H<sub>2</sub>S dissociation reaction and the methyl mercaptan dissociation reaction produce an H<sup>+</sup><sub>aq</sub> ion. H<sub>2</sub>S is a stronger acid, so it dissociates to a greater extent than methyl mercaptan, producing an excess of H<sup>+</sup><sub>aq</sub> ions. The larger concentration of H<sup>+</sup><sub>aq</sub> ions pushes the methyl mercaptan dissociation equilibrium toward the molecular form of methyl mercaptan.

Having a larger fraction of the aqueous methyl mercaptan in molecular form shifts its vapor liquid equilibrium. The net effect is that the stronger acid ( $\text{H}_2\text{S}$ ) generates a significant concentration of the common ion  $\text{H}^+_{\text{aq}}$  and this pushes the weaker acid ( $\text{MeSH}$ ) out of the liquid phase.

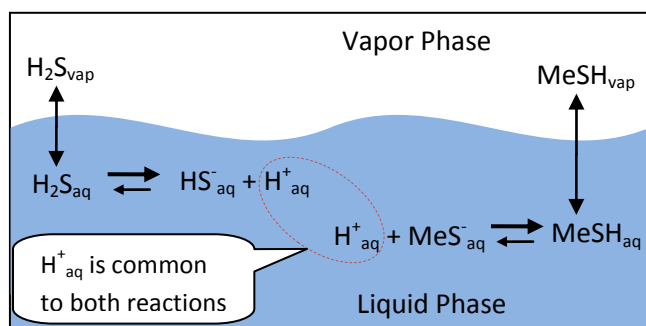


Figure 1 – Simultaneous reactions and VLE with  $\text{H}_2\text{S}$  and  $\text{MeSH}$

## Solubility

The solubility of mercaptans in water is another property of interest. Mercaptans with longer hydrocarbon chains have more hydrocarbon character, making the heavier mercaptans less soluble in water but more soluble in relatively hydrocarbon-like MDEA. Solubility in water will be shown to govern which mercaptan species can be most effectively removed by caustic.

## Interactions between species

The interactions of mercaptans with water, amines, and acid gases significantly affect Vapor Liquid Equilibrium (VLE) behavior. In the ProTreat<sup>®</sup> software, these interactions are quantified through the use of the Deshmukh-Mather activity coefficient model and through binary interaction parameters used in the Peng-Robinson equation of state. Several sources of VLE data were used to regress interaction parameters in the ProTreat<sup>®</sup> model<sup>[2] - [10]</sup>. Two examples of important interactions are: 1) Interactions between caustic and water that influence water's vapor pressure over caustic solutions and 2) Interactions between mercaptans and amines that govern which mercaptan species can be most effectively removed by an amine solution.

## Equilibrium Solubility of Mercaptans

An investigation into the equilibrium behavior of mercaptans in MDEA and caustic soda will reveal the driving forces which impact their behavior in real processes. Factors that determine the equilibrium solubility of a mercaptan in a treating solvent include its solubility in water, non-ideal interactions with solvent molecules, and the reaction equilibrium between all of the species in the solution.

The following cases are based on equilibrium flash calculations performed in the ProTreat<sup>®</sup> simulation software. Various solutions were brought to equilibrium with a typical refinery fuel gas containing 300 ppmv each of the four mercaptans of interest. Table 1 shows the fuel gas composition. Flash calculations were done at 185 psia and 115°F (1.28 MPa and 46°C), conditions that are not atypical for refinery fuel gas systems.

Compound	Mol%
Water	0.77
Hydrogen Sulfide	0.03
Methyl Mercaptan	0.03
Ethyl Mercaptan	0.03
Propyl Mercaptan	0.03
Butyl Mercaptan	0.03
Methane	48.63
Ethylene	4.24
Ethane	18.59
Propene	2.45
Propane	3.94
n-Butane	3.05
Hydrogen	13.66
Nitrogen	4.52

Table 1 - Sour Gas Composition

### ***MDEA solutions***

Mercaptans have a dual chemical nature: part acid and part hydrocarbon. The solubility of mercaptans in MDEA solutions reflects this dual chemical nature. Hydrocarbon-like behavior is exhibited since increasing MDEA strength increases mercaptan solubility, especially for the heavier mercaptans. Acid-like behavior is exhibited by the reduction of mercaptan solubility in the presence of H<sub>2</sub>S.

### **Effect of amine strength**

Fractional removal of H<sub>2</sub>S and mercaptans from a fuel gas stream is plotted against the concentration of MDEA in the treating solution in Figure 2. As expected, H<sub>2</sub>S removal is much deeper than mercaptans at all MDEA concentrations. At solution concentrations less than about 15 wt% MDEA, water solubility (Henry's law) dominates the equilibrium behavior. Consequently, the lower molecular weight mercaptans are removed more effectively than those of higher molecular weight. As solution strength increases above 20 wt% MDEA, the solvent's ability to absorb hydrocarbons increases due to molecular interactions. These interactions, referred to as "salting in", are quantified using activity coefficients or salting-in parameters. In this region of higher amine strength, the higher molecular weight mercaptans are removed more effectively than their low molecular weight counterparts.

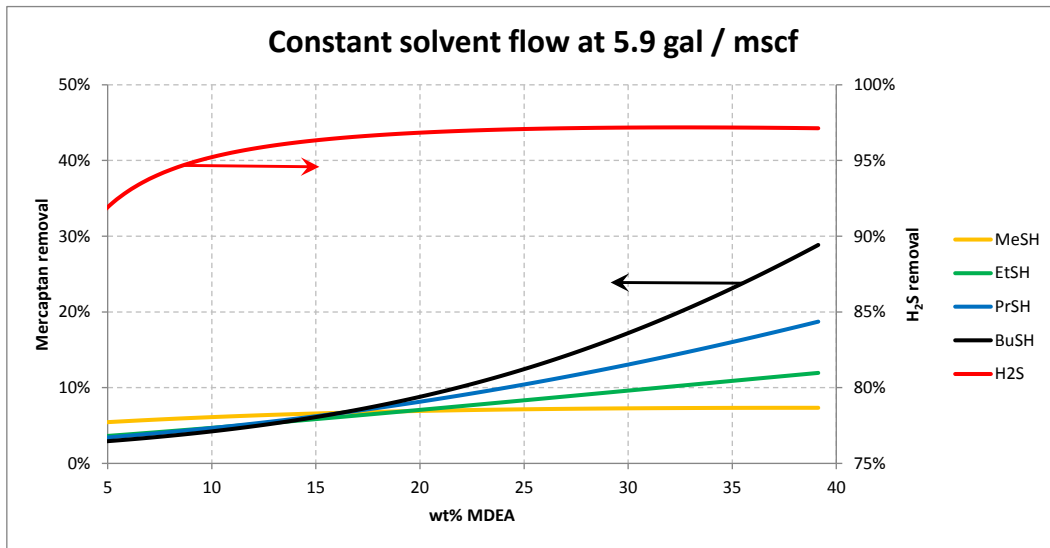


Figure 2 - Mercaptan removal versus MDEA solution strength

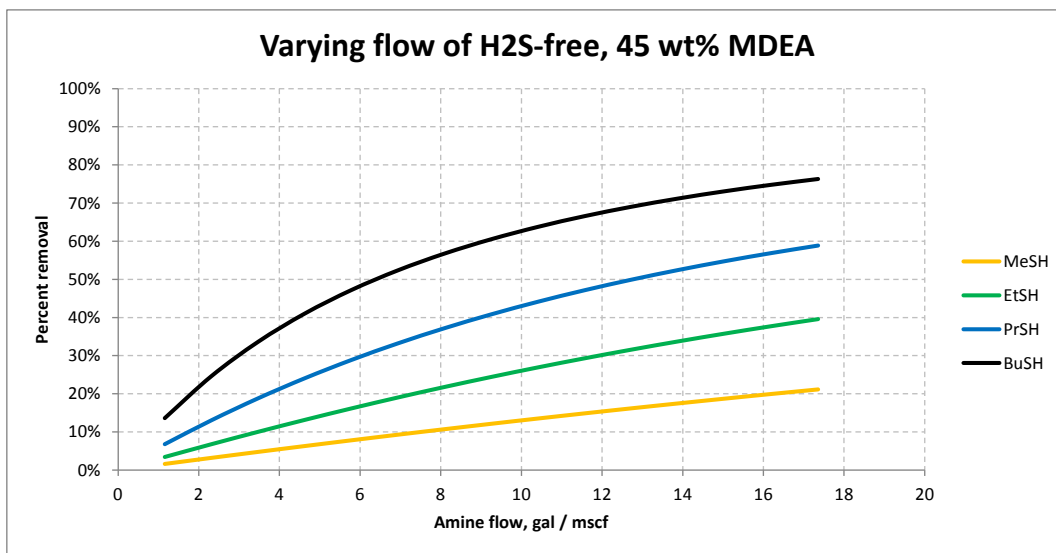


Figure 3 - Mercaptan removal versus MDEA flow rate

### Effect of H<sub>2</sub>S on removal of mercaptans with MDEA

Figure 3 shows the ability of pristine, H<sub>2</sub>S-free, 45 wt% MDEA to remove mercaptans from fuel gas. Some respectable removal rates are possible, especially for heavier mercaptans at higher solvent flow rates. As will be seen later, this is possible only if there is practically no H<sub>2</sub>S in the solvent.

Figure 4 explores how H<sub>2</sub>S affects the ability of a 45 wt% MDEA solution to absorb mercaptans. To prepare the figure, ProTreat's Case Study feature was used to step the concentration of H<sub>2</sub>S in the fuel gas while holding the mercaptan concentrations constant. The ability of an MDEA solution to pick up mercaptans is severely hindered by the presence of only a little H<sub>2</sub>S. This behavior is caused by the much weaker acidity of these mercaptans relative to H<sub>2</sub>S. The conclusion is that an MDEA solution will not be very effective at removing mercaptans from a gas stream, especially if there is any appreciable H<sub>2</sub>S loading. Figure 9 later in the paper will show that, as expected, multi-stage contacting can greatly improve the efficiency of mercaptan removal.

A secondary conclusion is that, while the removal of mercaptans by MDEA solutions is not very effective, it is also *not zero*. Even small amounts of mercaptans absorbed into an amine solvent may contaminate the quality of amine acid gas fed to a downstream unit such as a sulfur plant or affect the quality of flash gas from a rich amine flash drum which is sometimes used as tail gas incinerator fuel.

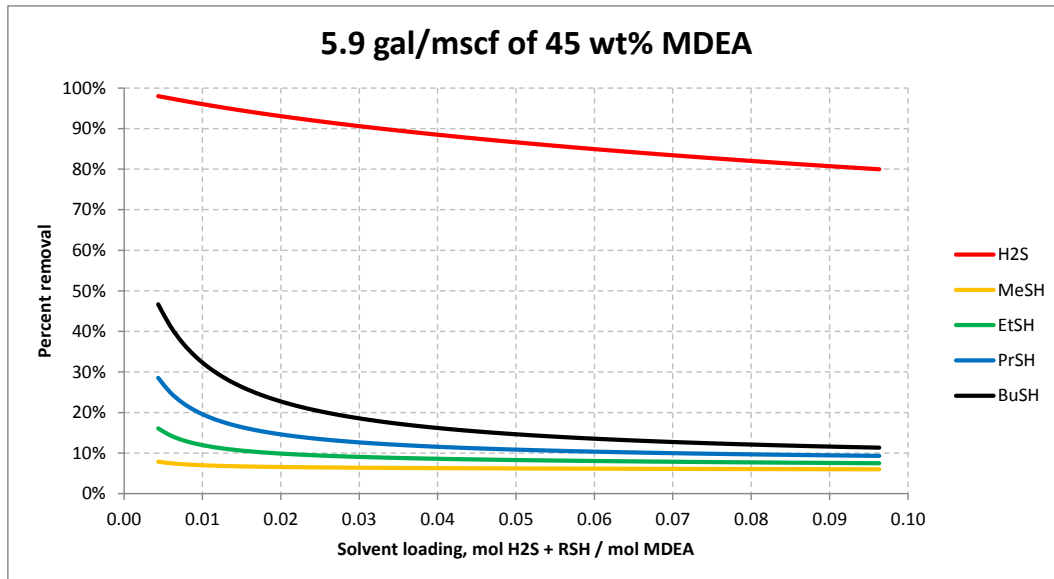


Figure 4 - Mercaptan removal versus solvent loading

### NaOH solutions

Solutions of NaOH are much more effective than solutions of MDEA at absorbing mercaptans. This observation has been leveraged successfully for many decades by UOP and Merichem in the application of the Merox™ and FIBER FILM® contactors. Until now, however, most of the finer process insights have been confidential to the licensors.

As a strong base, fresh NaOH can neutralize dissolved acidic gases, holding them in the liquid phase by keeping them in their dissociated ionic form. Figure 5 shows the effectiveness of even low strength solutions of fresh NaOH in removing essentially all of the H<sub>2</sub>S and mercaptans from a gas stream.

As a fresh solution of NaOH absorbs acidic species, its basicity is spent, and in turn, this reduces the solution's ability to absorb further acidic species. A common industry rule of thumb is that NaOH effectively absorbs mercaptans until the caustic becomes 70% spent. Figure 6 shows how the validity of this rule of thumb depends on which particular mercaptan is being considered. In a single equilibrium stage, a solution of 10 wt% NaOH which is 70% spent will absorb methyl mercaptan from fuel gas at 80% efficiency, but it will absorb butyl mercaptan at only 40% efficiency. Therefore the rule of thumb is applicable for gross approximations, but a more rigorous treatment is needed to accurately quantify the amount of mercaptan slip as a caustic solution becomes more spent. Note that H<sub>2</sub>S absorption efficiency remains close to 100% until the NaOH solution is almost completely spent.

An alternate view of this phenomenon is shown in Figure 7 which shows removal rate of H<sub>2</sub>S and mercaptans against the pH of the caustic solution. Note that as the pH decreases and the basicity of the solution is reduced, the removal effectiveness of the solution falls off at different points for different

mercaptans. The conclusion remains unchanged: higher molecular weight mercaptans are more difficult to remove with a caustic soda solution than their lighter counter parts.

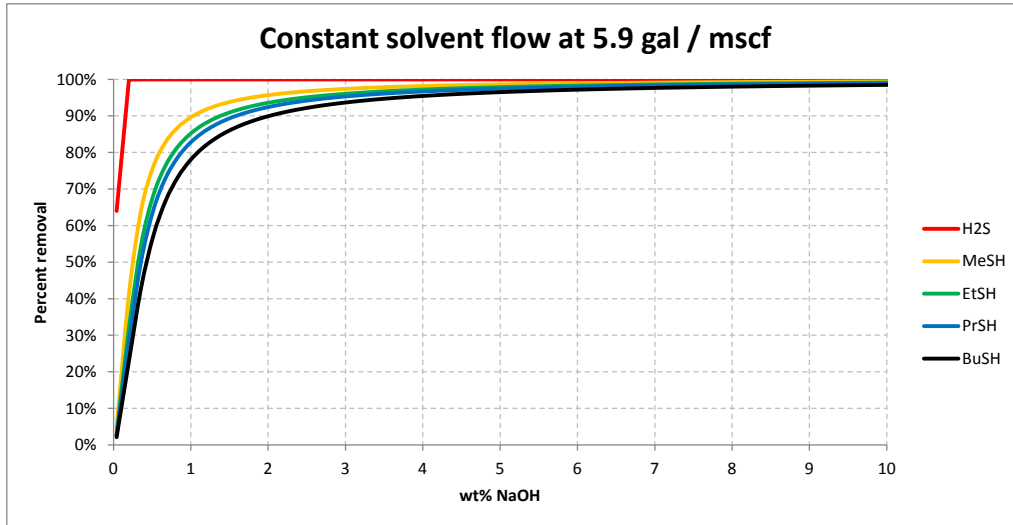


Figure 5 - Mercaptan removal versus fresh NaOH strength

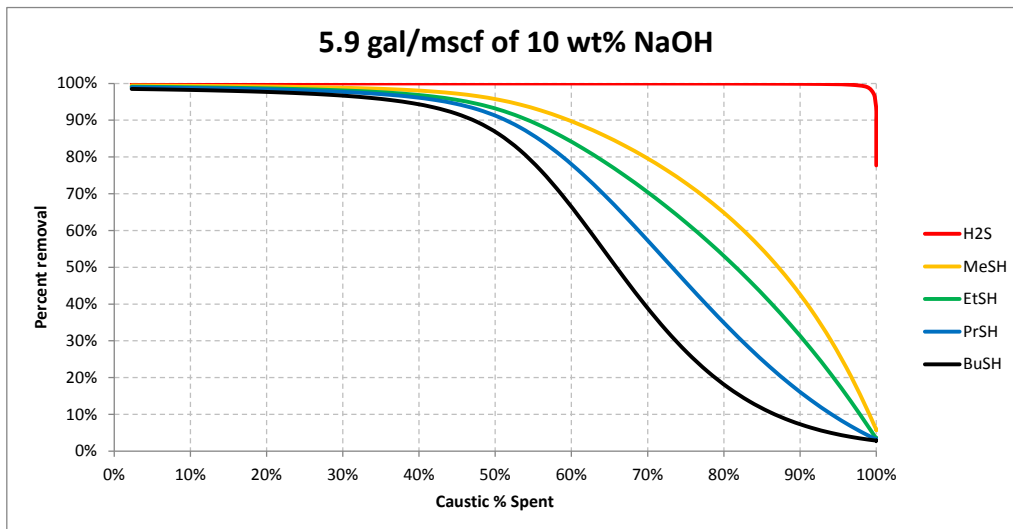


Figure 6 - Mercaptan removal versus caustic loading

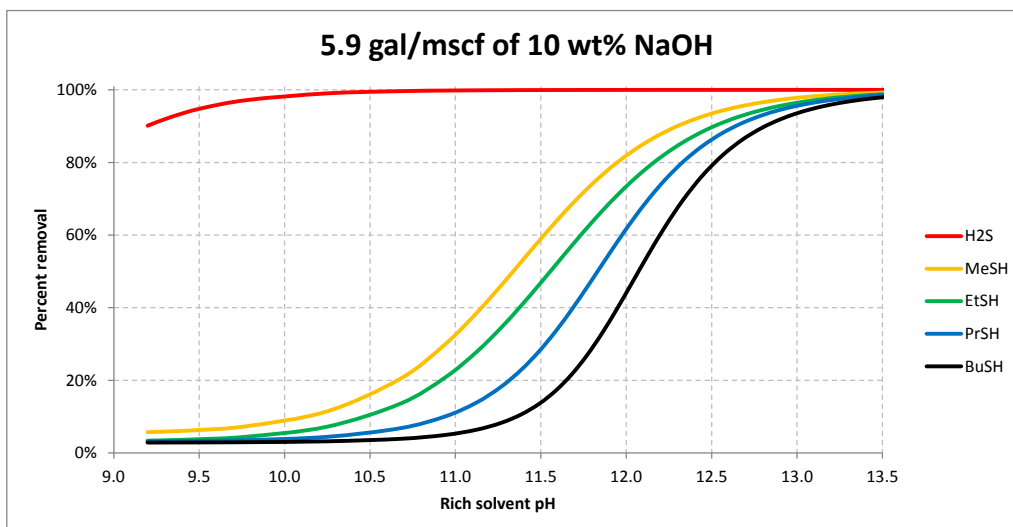


Figure 7 - Mercaptan removal versus caustic pH

## Rate Model

### *MDEA Absorbers*

The same general trends established in our investigation of equilibrium behavior are also observed in absorption towers. Figure 8 is based on a 2.5' diameter absorber with 20 valve trays at 2' spacing which is treating 8.8 MMSCFD of fuel gas with 93 gpm of 45 wt% MDEA. The sour gas contains 300 ppmv of each of the C<sub>1</sub> through nC<sub>4</sub> mercaptans. The lean amine contains no mercaptan but varying amounts of H<sub>2</sub>S. It can be seen that for this particular tower at these conditions, the removal effectiveness of methyl mercaptan is low and insensitive to lean amine H<sub>2</sub>S loading. In contrast, the removal effectiveness of butyl mercaptan is high, although it is also insensitive to lean loading. Removal effectiveness of ethyl mercaptan and propyl mercaptan is intermediate and is strongly affected by lean loading.

Profiles of the vapor phase molar flow rates of each mercaptan are presented in Figure 9 and Figure 10. Figure 9 shows the vapor profiles in the absorber operating with low lean loading: MeSH shows a profile typical of being rich-end pinched, EtSH shows a bulged profile, and both PrSH and BuSH show a profile approaching lean-end pinched. With higher lean loadings that are more typical of a refinery primary amine system treating H<sub>2</sub>S, Figure 10 shows that MeSH, EtSH, and PrSH are all assuming a rich-end pinched profile while BuSH is still maintaining a profile typical of being lean-end pinched (although not nearly as pinched as it was when lean loadings were low). The interaction of the process variables is complex and defies prediction using simplified methods, especially in multi-stage counter-current contact. A mass transfer rate based model is needed to quantify the performance of an amine absorber with respect to mercaptans.

The dual physical/chemical solubility of mercaptans in aqueous solutions requires a VLE model that accounts for both vapor and liquid phase non-idealities as well as chemical reactions. Simple oil-boiling hydrocarbon VLE representation fails miserably to predict the true behavior of these types of systems. Because the mercaptans typically only partially dissociate in the weak base alkanolamine solutions, the system behavior becomes quite non-intuitive. Higher physically soluble butyl mercaptan imparts some aqueous H<sup>+</sup> common ion, which works to some degree to titrate out propyl and lighter mercaptans. Because H<sub>2</sub>S is a stronger acid by several-fold when compared to the mercaptans, only a smidgeon is required to significantly impact the removal of mercaptans as Figure 8 shows.



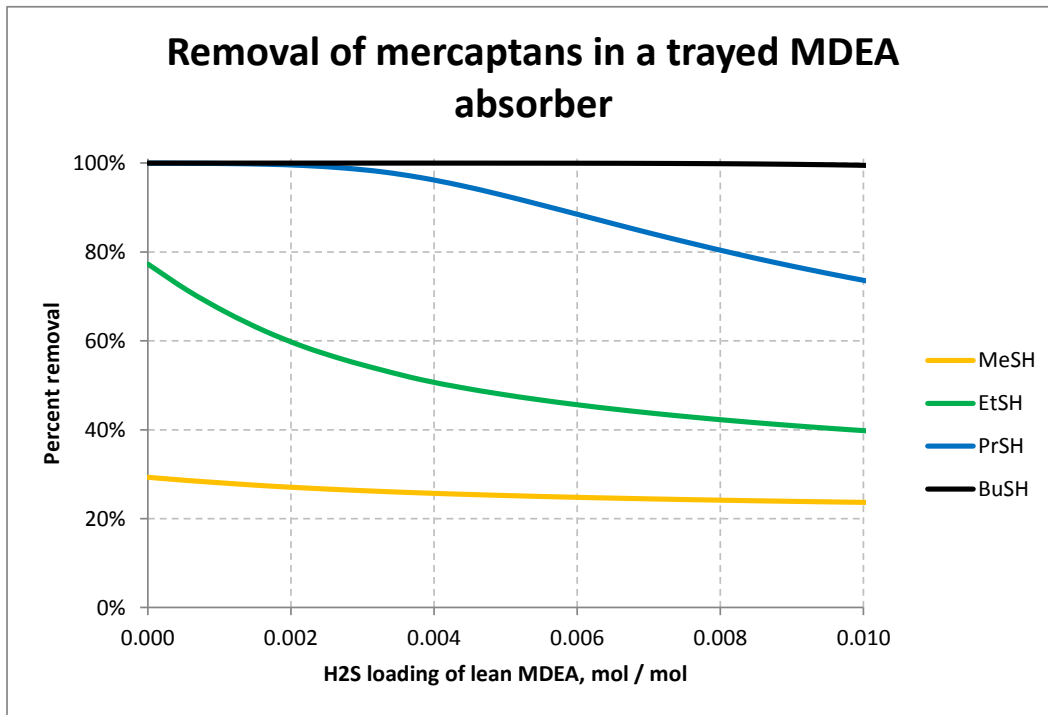


Figure 8 - Mercaptan removal in a trayed MDEA absorber versus lean loading

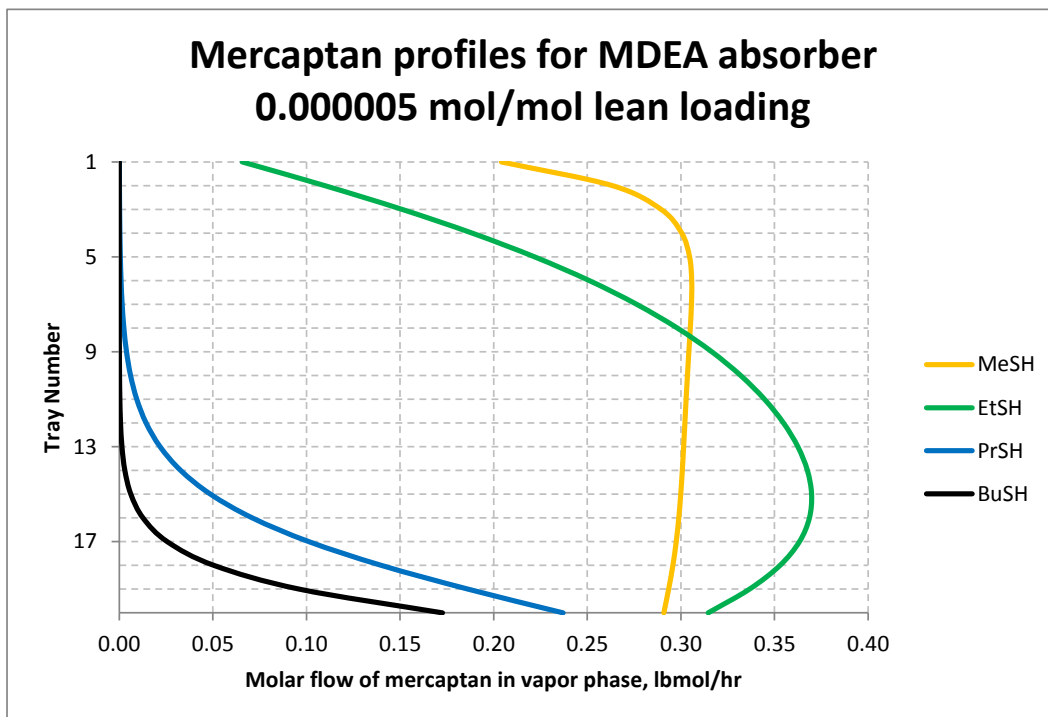


Figure 9 - Vapor phase mercaptan profiles in a trayed MDEA absorber with low lean loading of  $5 \times 10^{-6}$  mol/mol

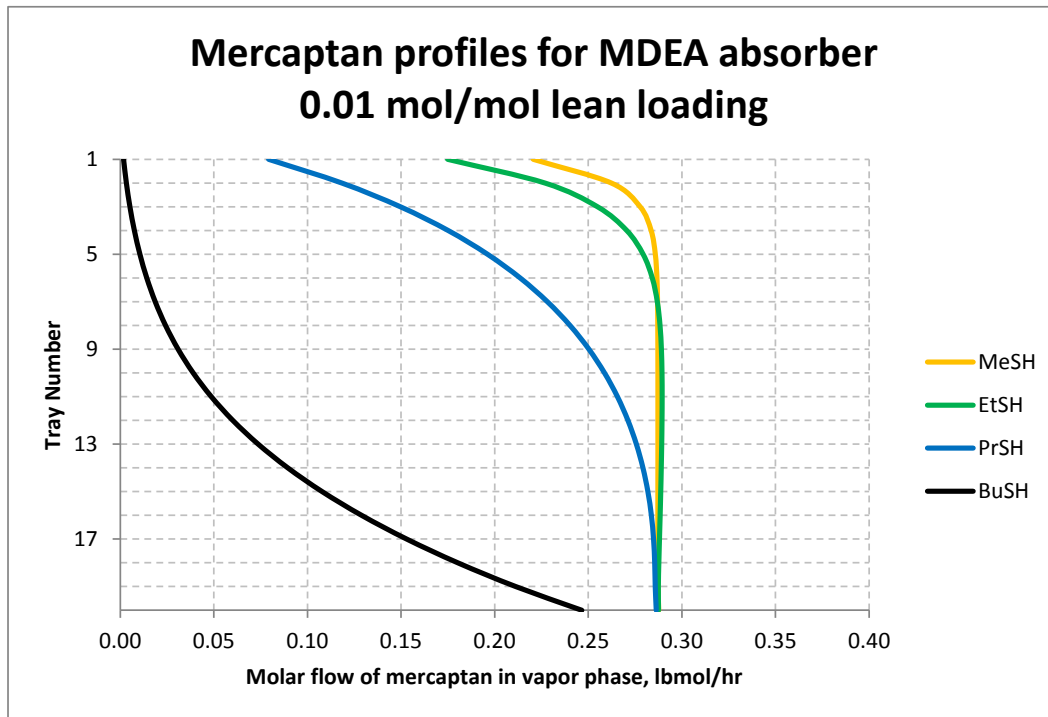


Figure 10- Vapor phase mercaptans profiles in trayed MDEA absorber with high H<sub>2</sub>S lean loading of 0.01 mol/mol

### ***NaOH Absorbers***

Absorbers using NaOH solutions absorb mercaptans differently than MDEA absorbers. Figure 11 shows the performance of a 4.1' diameter absorber with 5 valve trays at 2' spacing which is treating 31 MMSCFD of fuel gas with 128 gpm of 10 wt% NaOH. The sour gas contains 300 ppmv of each mercaptan. To study the impact of spending the caustic, the caustic solution contains varying amounts of H<sub>2</sub>S. It can be seen that the mercaptan removal effectiveness is close to 100% when the caustic is less than 70% spent. For this particular tower, the cut-off point happens to be 70% spent – consistent with the rule of thumb! (Repeating the exercise under different conditions moves the cut-off point significantly, e.g. changing to 20 wt% caustic holding everything else constant moves the cut-off point to 60% spent). As the caustic becomes more spent, the mercaptan removal effectiveness falls off at a different rate for each mercaptan. Figure 12 and Figure 13 show how the vapor phase mercaptan profiles within the absorber evolve as the solvent becomes more spent.

Relative removal rates of the different mercaptans are consistent with the equilibrium study above. Caustic removes lighter mercaptans more effectively than heavier mercaptans due to their greater solubility in water; MDEA removes heavier mercaptans more effectively than lighter mercaptans due to salting-in effects.

A NaOH absorber requires fewer trays than an MDEA absorber. This benefit is counter-balanced by the fact that maintaining fresh NaOH strength and controlling percentage spent is more difficult than regenerating MDEA solutions.

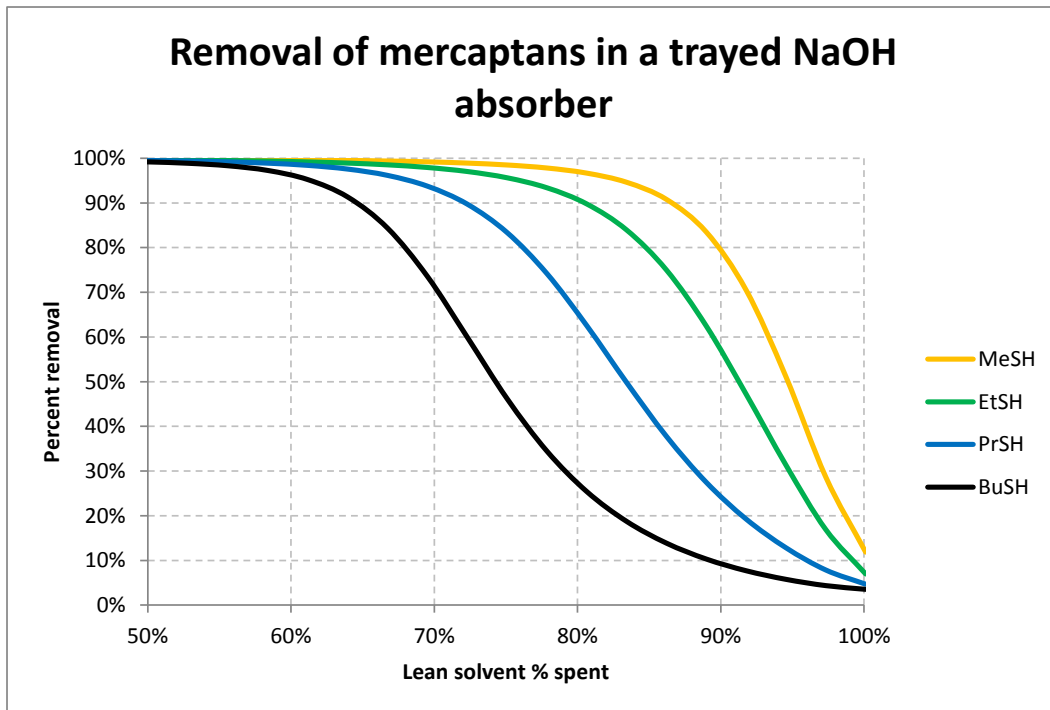


Figure 11 - Mercaptan removal in a trayed NaOH absorber versus solvent % spent

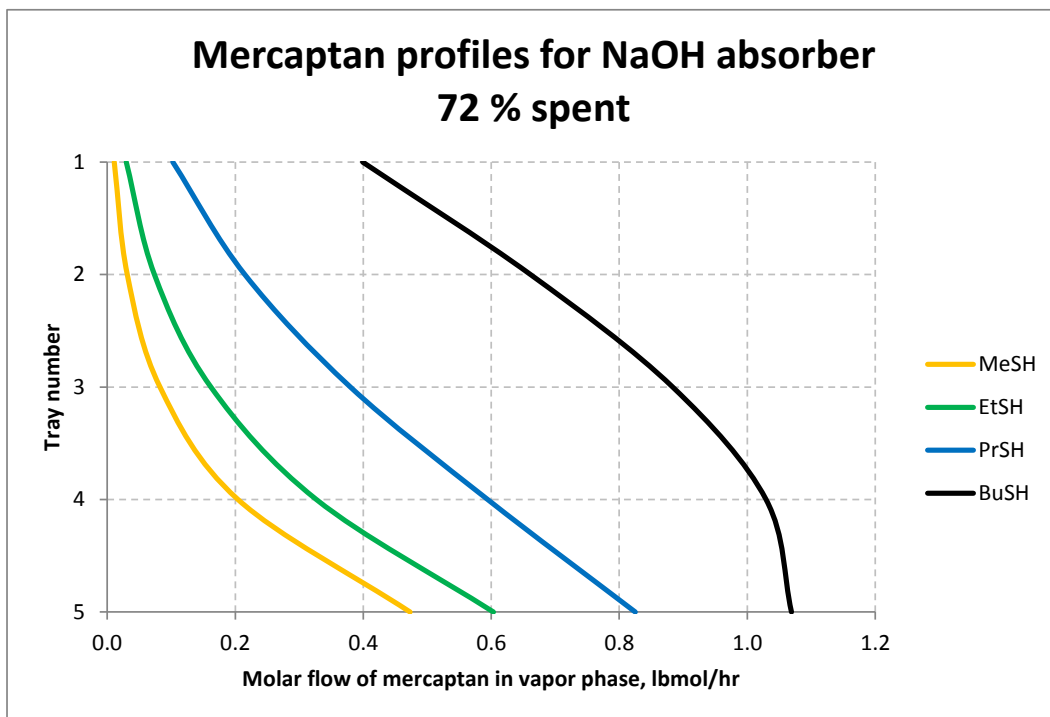


Figure 12 - Vapor phase profiles of mercaptans in trayed absorber using 10 wt% NaOH that is 72% spent with H<sub>2</sub>S

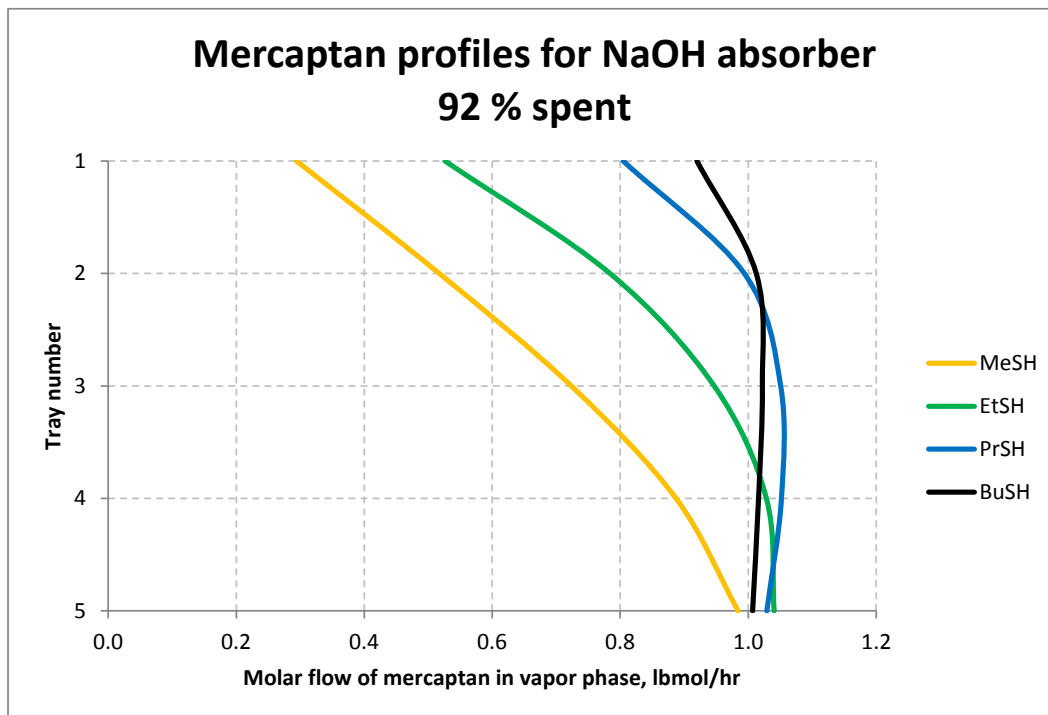


Figure 13 - Vapor phase profiles of mercaptans in trayed absorber using 10 wt% NaOH that is 92% spent with H<sub>2</sub>S

## Conclusions

Through the case studies examined in this paper, we have demonstrated that the ability of MDEA and caustic soda solutions to remove mercaptans is influenced by multiple factors. Caustic soda solutions are more effective at removing lighter mercaptans than heavier mercaptans due to their relative solubilities in water. MDEA solutions are more effective at removing heavier mercaptans than lighter mercaptans due to the attractive salting-in interactions between the hydrocarbon parts of the mercaptan and MDEA molecules. Even though MDEA may not remove enough mercaptan to achieve processing objectives, it does remove enough mercaptan to contribute to emissions and potentially cause performance problems in downstream units. With this knowledge, refinery operators can better plan and predict total sulfur distribution through the sulfur processing systems. Finally, mercaptan behavior in aqueous solutions is governed by multiple interacting factors. Accurately predicting the behavior of mercaptans requires rigorous treatment of solution non-idealities, reaction chemistry, and *mass transfer rate* modeling.

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