

# COS and mercaptans removal from gases

Challenges with removing trace sulphur species can be better understood and resolved with a new kinetic model validated by plant data in its ability to predict COS removal

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Gas and liquid hydrocarbon streams from refineries and gas plants must be well cleaned of sulphur compounds such as H<sub>2</sub>S, COS, and mercaptans (RSH), dictated mainly by environmental concerns. LPG can be subtle because although a copper strip test may indicate acceptable sulphur content today, COS slowly reverts to H<sub>2</sub>S and CO<sub>2</sub> in the presence of water, so the same test administered tomorrow may fail.

This contribution offers a new model for COS absorption into alkaline solvents based on mass transfer rates enhanced by reaction kinetics – the first time commercial software has had the ability to simulate this aspect of COS absorption accurately. As part of the reported work, a compilation of plant performance test data on mercaptans removal is also presented. It shows plenty of room for improvement in reliability and accuracy of simulation tools.

Amines are excellent solvents for H<sub>2</sub>S, but, by and large, they are horrible for removing other less acidic, trace sulphur species such as COS and mercaptans. Until now, no simulator has been able to model COS and mercaptans adequately. With mercaptans, the basic problem seems to be insufficient, inaccurate phase-equilibrium data. Almost all the public domain mercaptans solubility data are academic in origin, which may explain why there is so little of it.

Very few academic institutions welcome researchers who handle mercaptans – academia is generally ill equipped to handle them safely and therefore avoids the risk associated with their malodorous and toxic nature. Good-quality data in the range of commercial interest are hard to come by. For COS, one of the main issues has been that simulators have ignored its reactive nature in aqueous amine solutions, treating its chemistry in an over-simplified way as a purely physically dissolved, non-reacting solute. The COS absorption rate is thus wrongly computed because the calculations fail to account for significant absorption rate enhancement that results from the chemical reactions of COS with non-tertiary amines.

## Reactions of COS and mercaptans

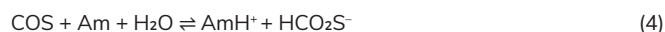
Reaction kinetics of H<sub>2</sub>S and CO<sub>2</sub> in aqueous amines are too well known to benefit from further discussion here. RSH merely dissociates in aqueous media. But to describe the decomposition of COS in water just by the reaction  $\text{COS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$  is deceptively oversimplified. The reaction

mechanisms and kinetics of COS in amines are much more complex than that and can benefit from a brief explanation:



Reaction (1) is a simple dissociation involving a single hydrogen ion and, as such, is known to be essentially instantaneous. Thus, it is always at equilibrium. The limitation with RSH is that it is an extremely weak acid, so even a low level of acidification of the solvent will drive Reaction (1) back towards the formation of molecular RSH, and mercaptans have very low physical solubility in water. Significant acidification can be had even with a modest amount of dissolved CO<sub>2</sub> or H<sub>2</sub>S. In regenerative caustic solutions, the CO<sub>2</sub> and H<sub>2</sub>S spend the caustic from its intended purpose of RSH removal. The significance of these effects is discussed in the next section by looking at the vapour-phase profile of mercaptans in a typical absorber.

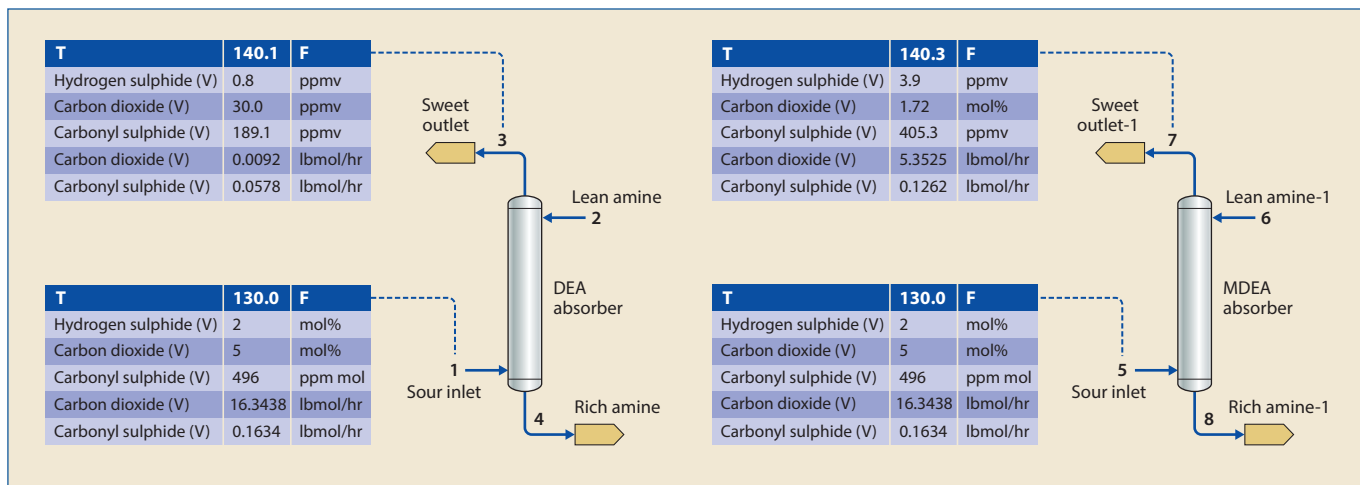
COS reacts in aqueous solutions first to form thiocarbonate Reaction (2), which further hydrolyses to bicarbonate and bisulphide Reaction (3). The combined form of Reactions (2) and (3) along with other speciation reactions of CO<sub>2</sub> and H<sub>2</sub>S is equivalent to the overall simplified hydrolysis of COS to CO<sub>2</sub> and H<sub>2</sub>S already mentioned. Reactions (2) and (3) are very slow unless a base is present in the solution to catalyse them. In the presence of amines, it is postulated that COS reacts by a base-catalysed mechanism according to:



In addition to these reactions, COS forms thiocarbamate with primary and secondary amines via a zwitterion mechanism:



Reaction (6) represents zwitterion formation (AmH<sup>+</sup> in Reaction (6) stands for the primary or secondary amine with at least one mobile hydrogen). Reaction (7) describes the zwitterion's deprotonation to thiocarbamate, AmCOS<sup>-</sup>.



**Figure 1** Absorber case study comparing COS pick-up in MDEA vs DEA

Any base, B, present in solution deprotonates the zwitterion. These reactions are responsible for quite significant COS absorption rates into primary and secondary amines, but they do not occur with tertiary amines. Reaction (4) is known to be equilibrium limited. The rate of the reverse reaction is observed to be practically zero for Reaction (5), thus indicating that, for any amine, COS will completely hydrolyse to CO<sub>2</sub> and H<sub>2</sub>S in the fullness of time.

Thiocarbamate formation is significantly limited by the rate of deprotonation, Reaction (7). In fact, for several amines, the COS absorption rate is almost completely determined by the rate of deprotonation. This is unlike CO<sub>2</sub>, where the zwitterion deprotonation rate has much less influence on the overall conversion. As a result of these factors, the COS-amine reaction rate is much slower than amine-CO<sub>2</sub>. Nevertheless, COS reaction rates are significant enough for a substantial fraction of the COS in a typical feed gas to be removed by primary and secondary amines. However, such is not the case for mercaptans beyond MeSH because they are very weak acids and easily displaced by co-absorbed CO<sub>2</sub> and H<sub>2</sub>S.

Recently, we finished developing a COS absorption model that treats COS as a rigorous mass transfer rate-controlled component and incorporates it along with its reaction kinetics into the OGT ProTreat simulator. The model results were validated against some 20 proprietary sets of field-performance data for various amine systems. They showed the model accurately simulates COS removal in amine absorbers for the first time. What follows is a case study showing:

**Comparison of absorber outlet concentrations as predicted by the Legacy vs Kinetic Model for the absorber models shown in Figure 1**

Model	CO <sub>2</sub>	DEA		MDEA		
		H <sub>2</sub> S	COS	CO <sub>2</sub>	H <sub>2</sub> S	COS
		ppmv		mol%		ppmv
Legacy (equilibrium)	30	0.8	523 <sup>†</sup>	1.7	3.9	508 <sup>†</sup>
Kinetic (reaction rate)	30	0.8	189	1.7	3.9	405

<sup>†</sup> Removal of CO<sub>2</sub> and H<sub>2</sub>S concentrates COS above its 500 ppmv inlet value

**Table 1**

- Mass-transfer and reaction-rate control in the COS removal model
- A comparison between various amines' performance for COS removal in a simple absorber
- Comparison between simulation and actual plant performance in RSH removal
- Summary of literature renditions of VLE in RSH-amine systems.

Because of the role played by reaction kinetics, different types of amines (primary, secondary, tertiary) have quite different COS removal effectiveness. For mercaptans removal, on the other hand, it is mainly the pKa of the amine that determines RSH removal – kinetics plays no role at all. Therefore, it makes sense to treat COS and mercaptans removal in separate ways.

### Case studies

The following case studies elucidate the absorption mechanism of COS and mercaptans in typical absorbers:

#### COS

**Figure 1** shows the simulation of two simple absorbers, one using a 3M solution of DEA and the other using MDEA at the same molar strength and circulation rate. In both cases, the feed gas is 5 mol% CO<sub>2</sub> and 2 mol% H<sub>2</sub>S; 500 ppmv of COS was assigned to the inlet gas. Callouts attached to the gas streams show the gas analyses.

For MDEA and DEA respectively, the CO<sub>2</sub> removal efficiency is about 67% and 99% compared with 23% and 65% for COS. As expected, amines do not remove COS as effectively as CO<sub>2</sub>, although a significant amount of pick-up is seen. In addition, DEA, a secondary amine, reacts much faster with COS by forming thiocarbamate via the zwitterion mechanism. This leads to almost three times greater efficiency than MDEA which, as a tertiary amine, cannot form thiocarbamate.

**Table 1** compares predictions using our new model for COS absorption ('Kinetic' in table) with what has been the only type of simulation commercially available until now ('Legacy' in table). The Legacy and Kinetic Models give identical predictions of CO<sub>2</sub> and H<sub>2</sub>S removal, as one might expect. However, the Legacy Model predicts that

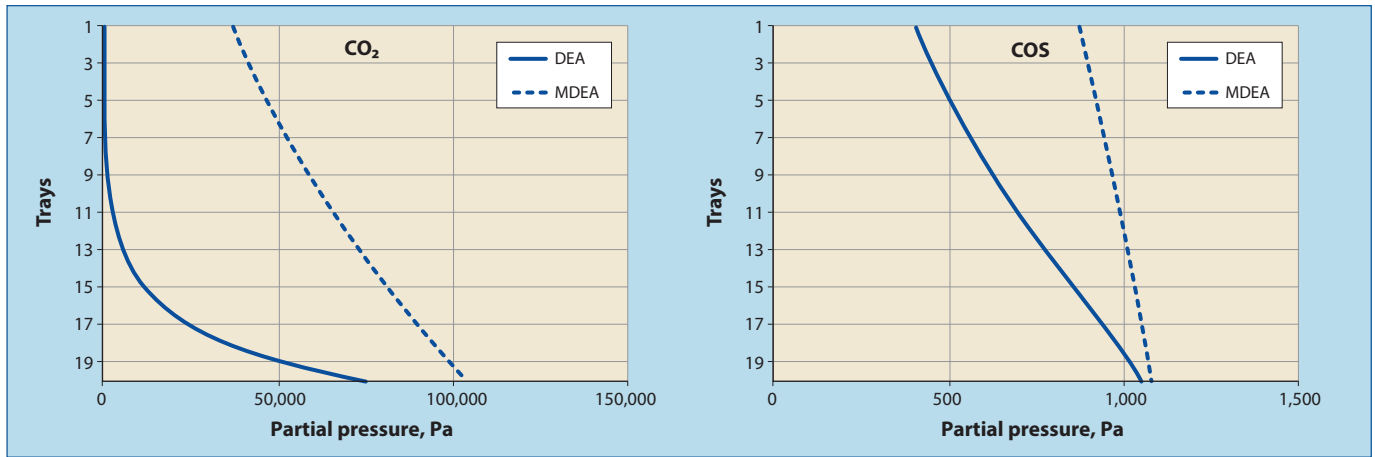


Figure 2 CO<sub>2</sub> and COS partial pressure in absorbers

2% of the COS is removed by DEA and 3.3% by MDEA, whereas the Kinetic Model predicts the removal of 65% and 23% by DEA and MDEA, respectively.

Figure 2 shows how the Kinetic Model predicts that CO<sub>2</sub> and COS approach final outlet values in the DEA absorber. The gentler decrease in COS partial pressure reflects the much slower reaction kinetics of COS compared with CO<sub>2</sub>. In DEA, CO<sub>2</sub> falls rapidly from 5 mol% to a few ppmv, whereas the same 20 trays only take COS from 500 ppmv to 189 ppmv. However, relative to MDEA, both CO<sub>2</sub> and COS decrease rapidly simply because DEA reacts with both. MDEA does not.

COS is severely mass transfer rate limited in a typical amine absorber. It cannot be properly simulated using only its physical (Henry's Law) solubility in the amine, even augmented with salting-in and salting-out corrections. COS reacts with primary and secondary amines at rates that greatly affect its absorption and therefore affect the ability of any absorber to remove it from the inlet gas.

### Mercaptans

The deprotonation of mercaptans into mercaptide ion is known to be instantaneous, leading to huge enhancement factors and hardly any liquid-side resistance to absorption. Therefore, unlike COS, absorption of mercaptans in aqueous amines is almost always VLE limited. However, being a much weaker acid than CO<sub>2</sub> and H<sub>2</sub>S, mercaptans have much lower chemical solubility in the basic amine solutions. So, even any

low to moderate amounts of H<sub>2</sub>S and CO<sub>2</sub> stronger acids dissolved in the solvent severely impair the ability of the solvent to remove the mercaptans from feed gases efficiently.

Figure 3 shows the vapour phase ethyl mercaptan content along with the total acid gas loading of the solvent in a typical absorber that treats a feed containing 10 mol% CO<sub>2</sub>, 2 mol% H<sub>2</sub>S and 100 ppmv of ethyl mercaptan using 30 wt% DEA. The absorption profile of the mercaptan in vapour can be split into two zones. The top part of the absorber is actively removing mercaptans from the gas, but as we go down the column, the vapour phase mercaptan content decreases. This indicates that the absorbed mercaptan in the liquid phase is getting stripped back into the vapour. This reversal in the profile can be attributed to the increased bulk acid gas loading in the liquid. As previously discussed, the bulk acid gases, being stronger than mercaptans, start neutralising the mercaptide ions back into free mercaptans, which get salted out of the vapour. The plot shows that with the increase in the solvent circulation rate, as seen from the increasing L/G ratio, the bulge in the vapour phase mercaptan content moves down the column corresponding to the shift in the loading profile. In all three cases, the critical point of mercaptan removal occurs around a total acid gas loading of only 0.02-0.03 mol/mol of amine.

This case study also shows that, in absorbers that show such a trend, the treating levels of mercaptans can be increased by raising the solvent circulation rate, which

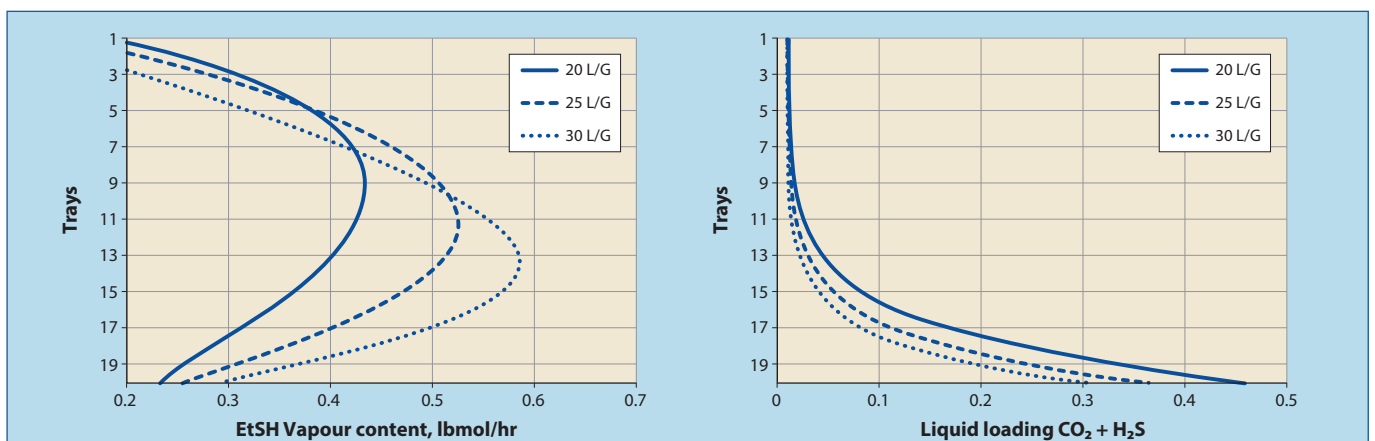
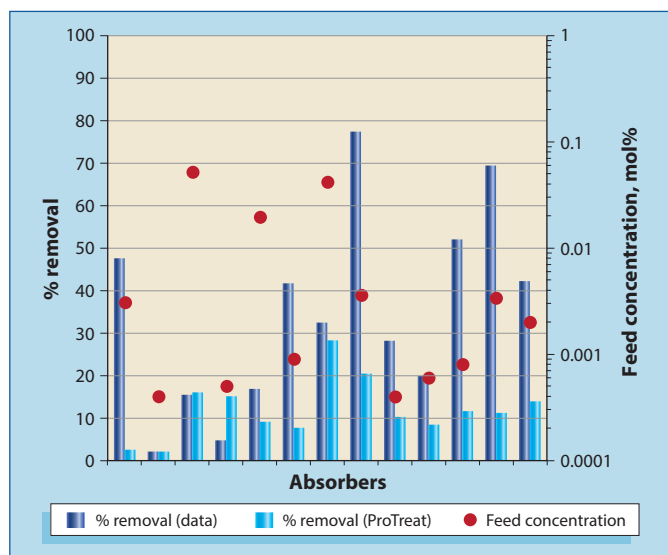


Figure 3 Vapour phase ethyl mercaptan content and liquid phase total acid gas loading in absorber trays. The different curves denote varying liquid to gas ratio in the units of US gal/min of solvent and MMSCFD of feed gas

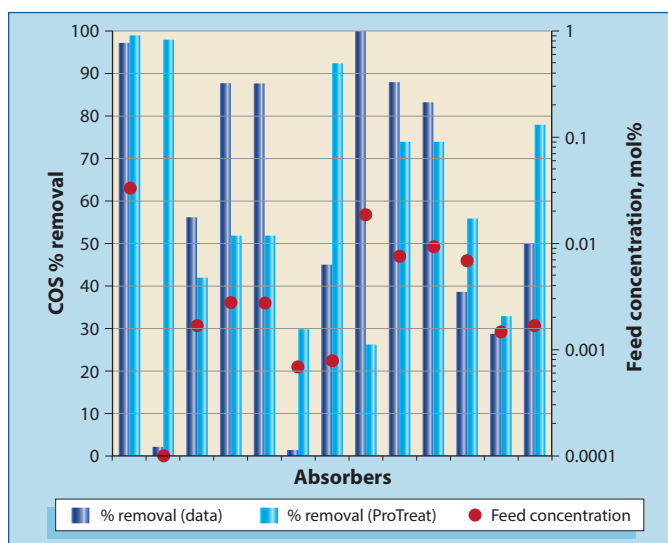


**Figure 4** Removal of COS in MDEA solvent

gives more absorption region for mercaptans in the column. Likewise, a reduction in the lean loading will also aid mercaptans removal by providing more solvent capacity in the active part of the absorption profile. However, contrary to the usual expectation, oversizing the absorber with more trays/packing height would have zero to negative benefits on mercaptans removal. Accurate simulation tools can aid designers and operators to identify opportunities for meeting the treated gas specifications. For simulators to reliably predict the treating of mercaptan, accurate VLE data and models that represent the solubility of mercaptans in amines across a range of temperature and acid gas loading values are required.

### Validation against plant data

**Figure 4** compares the measured (dark blue columns) and simulated (light blue columns) percentages of COS removal by MDEA. **Figure 5** shows the same for MEA and DEA solvents as measured in commercial absorbers. In the case of MEA and DEA, the measured and predicted per cent removals match well with the exceptions where the predictions go either side. For MDEA, however, a few cases suffer from an underprediction by the model. It is important to note that



**Figure 5** Removal of COS in MEA and DEA

most disagreement occurs for absorbers containing feed gas COS ppmv levels in the range of single to low double digits. In these ranges, the calculation of per cent removals will be susceptible to error magnification from uncertainties and inaccuracies of gas chromatographic measurements.

In addition, going back to the COS kinetic mechanism, it is impossible for MDEA to absorb anything like over 40% of the inlet COS. However, 50% and higher removal by DEA, and even more by MEA, is to be expected (and is, in fact, observed). These expectations are supported by the relatively rapid kinetics of deprotonation to thiocarbamate for MEA and DEA and the complete absence of thiocarbamate formation by MDEA; hence slow absorption by MDEA and increasingly rapid absorption by DEA and MEA, in that order. MDEA is likely to suffer from degradation that leads to a significant accumulation of primary and secondary amine contaminants in the solvent, thus aiding and increasing the removal of COS. The original source acknowledges that several of the cases presented in this study lacked a full solvent analysis.

In comparing the predicted mercaptans removal against plant data in MDEA, MEA, and DEA solvents, data collected from absorbers showed H<sub>2</sub>S and CO<sub>2</sub> being simultaneously removed in much larger amounts than the mercaptans. Typical mercaptans concentrations in the feed gas to the absorbers are 100 ppmv, although there are data showing feed concentrations from 3 ppmv to 1,000 ppmv.

Plots generated indicate considerable scatter in the results. Perhaps this should not be too surprising since it is next to impossible even to reproduce removal rates when inlet concentrations are 100 ppmv and lower in many cases, and the mercaptan absorption rate is greatly affected by the absorption of much more acidic H<sub>2</sub>S and CO<sub>2</sub> at several orders-of-magnitude higher concentration. Small changes in acid gas absorption rates can be expected to have a profound effect on the absorption rate of such weak acids as mercaptans. However, there is a more disturbing trend – except for C<sub>1</sub>SH in MEA and DEA, simulation results are almost uniformly biased towards underprediction of mercaptans removal rates.

One piece of data missing from information on mercaptans is an assessment of the pK<sub>a</sub> of each individual mercaptan and its temperature dependence. pK<sub>a</sub> has a direct effect on physical solubility and the dissociation of dissolved mercaptan. This is directly affected by the amine in question as well as the carbamate or bicarbonate ion concentration and the bisulphide and sulphide concentrations.

However, enough data are available only for pK<sub>a</sub> of EtSH, but not for MeSH, PrSH, and BuSH. As shown in **Figure 6**, the pK<sub>a</sub> of these mercaptans are not monotonic with respect to carbon number, making it difficult to make a generic estimation of pK<sub>a</sub> based on carbon number. Only one data point in *Dean's Handbook of Organic Chemistry*<sup>1</sup> is available for pK<sub>a</sub> of MeSH, whereas two data points, one each by Dean<sup>1</sup> and Yabroff<sup>2</sup>, have been reported for PrSH, which are inconsistent with each other. Similarly, only one data point by Yabroff<sup>2</sup> is available for the pK<sub>a</sub> of BuSH. The pK<sub>a</sub> of EtSH was studied thoroughly by Tsonopoulos et al.<sup>3</sup>, covering a wide temperature range of 298 to 423 K. To make an accurate determination of pK<sub>a</sub>, it is important to have consistent experimental data for all mercaptans covering a broad temperature range,

which is currently lacking in the literature studies. One of the main results of this study is emphasis on the very poor quality of mercaptans solubility data and the tremendous scatter in what little data exist. Since the data available in the literature are not measured at isobaric conditions, we have presented these data sets in our study in terms of an Apparent Henry's Law constant for better representation:

$$\text{Apparent Henry's Constant, } H \text{ (in Pa)} = \frac{y_{\text{RSH}} P}{x_{\text{RSH}}}$$

where  $y_{\text{RSH}}$  = vapour phase mole fraction of mercaptan,  $P$  = total system pressure,  $x_{\text{RSH}}$  = liquid phase mole fraction of mercaptan.

Apparent Henry's Constant data for the four mercaptans in aqueous MDEA and DEA solutions are very scattered and do not follow a generic trend as a function of temperature. Another drawback of these experimental data sets is the limited amount of data available at the acid gas loadings of interest. For example, no experimental data are available for MeSH or EtSH in aqueous DEA in the loading range of 0.05 to 0.4. This range is critical for accurate determination of speciation and VLE behaviour, and lack thereof could lead to erroneous estimation of thermodynamic properties.

Simulation accuracy relies directly on the quality of the data underlying the models. The thermodynamic and mass transfer models themselves are quite sound, but the correlational data are weak. The apparent randomness in the plots is a manifestation of data inadequacies highlighted by the fact that each data set is for an absorber in a unique situation involving simultaneous absorption of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  under non-isothermal conditions. There are too many factors at play to ascribe randomness to any one or two of them. Thus, we would encourage the collection of more extensive fundamental mercaptans data, such as accurate  $pK_a$  and VLE data as a function of temperature.

## Conclusion

The fundamentals behind the absorption of COS and mercaptans in aqueous amines were discussed. With this work, a new and accurate kinetic model for predicting the removal of COS has been introduced. Users of Legacy simulators have complained for years that predicted COS removal has been far removed from observations. That deviancy has now been rectified; ProTreat's Kinetic Model predictions conform well. Because of the slow kinetics, COS is expected to be severely mass transfer rate limited, even more so than  $\text{CO}_2$ . The model predictions were validated with a range of plant data. For MDEA systems, the level of COS pick-up will be influenced by the degree of solvent degradation and/or feed contamination with primary or secondary amines, which can vary considerably.

For mercaptans, it was demonstrated that the lack of good-quality public data on solubility is a big roadblock to developing a fundamental model that can predict mercaptans removal with a high level of accuracy and reliability. The authors appeal to the community to make high-quality experimental measurements on the  $pK_a$  and VLE of mercaptans across a range of temperatures and acid gas loading.

ProTreat is a mark of Optimized Gas Treating, Inc.

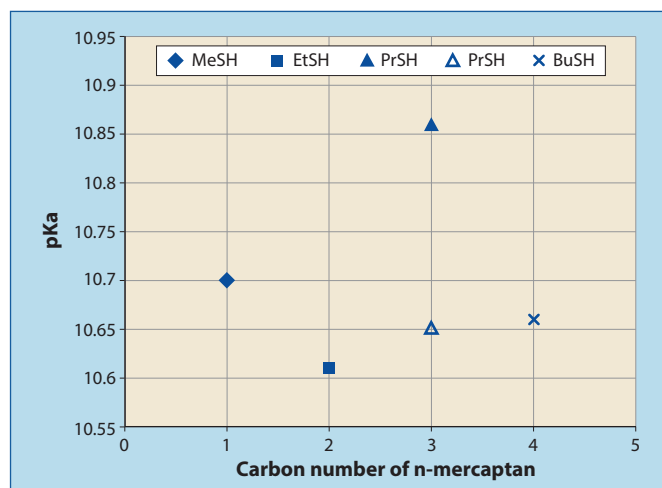


Figure 6  $pK_a$  of mercaptans as a function of carbon number

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