



The CONTACTOR™

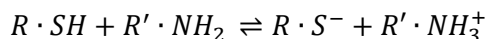
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Factors Affecting Mercaptan Solubility in Aqueous Amines

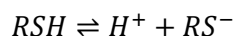
In general, aqueous amines in acid gas service are notoriously poor solvents for mercaptans. The purpose of this issue of The Contactor is to discuss in detail the reasons for their poor performance, and circumstances in which aqueous amines actually can perform usefully as solvents for mercaptans.

Chemistry

Amines work in acid gas removal processes because they are organic bases that act as one of the constituents in an acid-base reaction with dissolved acid gases. Simply put, the acid gases are proton donors while amines are proton acceptors.



The group labeled R can be hydrogen (H₂S), or an organic group such as a methyl, ethyl, propyl or butyl group. These compounds (including H₂S) are called thiols. In water, they all dissociate to some extent:



The extent of dissociation is usually reported as a pKa value which is the negative logarithm of the dissociation constant:

$$pKa = -\log_{10} \frac{[H^+][HS^-]}{[RSH]}$$

This is not to be confused with pH which is the negative logarithm of the hydrogen ion activity; however, they are related through the Henderson-Hasselbalch[†] equation. The higher the pKa value the less a component dissociates and therefore the less acidic it is, and the higher the pH.

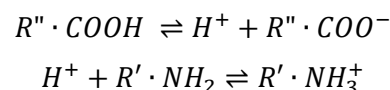
The pKa values of the C₁ through C₄ mercaptans are fairly consistently the same[‡]: about 10.6 at 25°C versus 7.0 for H₂S, also at 25°C. The dissociation constant for H₂S is 4,000 times the value for the mercaptans so at the same total concentration, the hydrogen ion concentration is 4,000 times greater for H₂S, making it far more acidic. This makes it easy to see why even a tiny amount of H₂S dissolved in an aqueous amine renders mercaptans virtually insoluble, at least for practical purposes.

The other aspect of mercaptan chemistry that distinguishes mercaptans from H₂S is their hydrocarbon nature—at one end of a mercaptan molecule lies the -SH group which can dissociate into H⁺ and RS⁻ ions; at the other end is a paraffinic hydrocarbon group giving them increased solubility in more concentrated aqueous (organic) amines and higher solubility in high molecular weight amines than in low. Indeed, the highly hydrocarbon-like nature of certain hybrid solvents such as the Sulfinol® (sulfolane-based) series makes them attractive for mercaptans removal from gases. Only 5–15 wt% of these solvents is water (present to make the amine content reactive with acid gases). The rest is organics with high mercaptan (and aromatics) solubility. For this reason, hybrid solvents are often used for mercaptans removal from liquid hydrocarbons

Heat Stable Salts

Of all the common gas treating amines, MDEA has the best chance of being used effectively for mercaptans removal because it is the amine from which absorbed H₂S and especially CO₂ can most easily be removed. In primary and secondary amines (carbamate formers) it is next to impossible to remove CO₂ to a low enough level to permit much mercaptan absorption. Residual CO₂ loading in lean primary and secondary amines can be almost guaranteed to kill any hope of mercaptans removal—it's just uneconomic to reduce their CO₂ lean loading to values typical of MDEA because the carbamates are too stable.

An amine heat stable salt (AHSS) is the protonated form of the amine generated by partial neutralization of the amine by a weak (usually, but not always, organic) acid. For example, when an organic acid R''·COOH (the heat stable salt, HSS, is R''·COO⁻) enters, or forms in, an amine solvent, perhaps as a result of solvent degradation via a contaminant in the gas, it at least partially dissociates, liberating a hydrogen ion. This in turn neutralizes the amino group of the solvent molecule:



[†] https://chem.libretexts.org/Ancillary_Materials/Reference/Organic_Chemistry_Glossary/Henderson-Hasselbalch_Equation

[‡] Tsionopoulos, C., Coulson, D., and Inman, L., *Ionization Constants of Water Pollutants*, J. Chem. Eng. Data, Vol. 21, No. 2, 1976, pp 190 – 193.

Although the acid itself (R⁺-COOH) may be weak and only partially dissociated, the amine is an almost limitless sink for hydrogen ions so the acid continues to dissociate essentially to completion. Thus, what many might call an expected everyday HSS level of a few hundreds of ppmw in the solvent can virtually kill the solvent's ability to absorb any significant amount of mercaptan. This is because the full concentration of HSSs is at work producing a high background concentration of hydrogen ions, thereby keeping any mercaptans in the non-dissociated molecular (water-insoluble) form.

A formate concentration of 1,000 ppmw in a 40 wt% MDEA solvent is roughly 0.0066 mole formate per mole of MDEA, numerically the same as the equivalent H₂S level. This is a large enough value to affect mercaptan solubility significantly. For example, the calculated results shown in Table 1 are at typical fuel gas treater conditions and indicate that at 40°C and 116 psia, a 40 wt-% MDEA solvent will have double the methyl mercaptan backpressure when it contains 1 wt-% formate vs. none at all.

Table 1 MeSH Equilibrium over 40 wt-% MDEA at Various MeSH Loadings and Formate Levels at 116 psia

Formate in Solvent (ppmw)	MeSH Loading 0.001	MeSH Loading 0.0001	MeSH Loading 0.00001
	MeSH in Vapor (ppmv)		
0	123	11.3	1.12
1,000	187	18.6	1.86
10,000	218	21.8	2.18

Raw fuel gas with a few 100s of ppmv of any mercaptan is not unusual (often much higher values are encountered), and HSS levels can sometimes exceed 5 wt-%. It is apparent from this table that the solvent must be extremely well-stripped of mercaptan and contain very little HSS to achieve one or two parts per million mercaptan in the treated gas. Inattention to HSSs can have a significant negative effect on mercaptans removal by amines.

H₂S loading has the same effect on mercaptan solubility as loading by an equal molar concentration of formate or other monovalent HSS. Therefore, MDEA must be very thoroughly stripped of acid gas and also have a very low HSS level to have any chance of success treating for mercaptans with amines in real acid gas removal applications.

In fact, aqueous amines alone are just not very good solvents for mercaptans in the presence of acid gases. HSSs exacerbate that situation by acting as permanent nonregenerable solvent loading. Another way to view this is to think of acid gases as the equivalent of heat stable salts but ones that can be removed from the solvent by normal thermal regeneration. On the other hand, true HSSs cannot be removed by thermal

solvent regeneration at all because, being ionic salts, they are for all intents and purposes nonvolatile. However, they can be removed by ion exchange and by reverse osmosis technologies.

In summary, solvents having a predominantly organic character (weakly to nonpolar) can be well suited to mercaptans removal. An example is the Sulfinol® family of solvents which use sulfolane admixed with a regular gas-treating amine together with enough water needed to allow the amine-acid gas reactions to proceed. Specifically, the Sulfinol-D, Sulfinol-M and Sulfinol-X solvents use DIPA (di-isopropanol amine), MDEA, and piperazine-promoted MDEA as the amine components. They are examples of Hybrid Solvents because they possess the properties of both physical solvents and chemical ones.

If the solvent does not have a significant concentration of the non-polar component, a high molecular weight amine that is thoroughly stripped of acid gases can work. However, if the mercaptans are to be removed from a gas containing large amounts of acid gases, mercaptans removal will be a struggle, and tend to be a largely unsuccessful lost-cause. One way around this handicap is to treat the gas in a two-step process, *first* for acid gas removal, *then* for removal of the mercaptans.

ProTreat® provides a highly accurate rendering of the effect of HSSs on treating, not just for H₂S and CO₂ removal, but for mercaptans removal as well. It is a valuable and reliable tool for assessing the efficacy of trying to remove mercaptans with amines and trialing the possibility of various approaches to overcoming process limitations.

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 To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. Visit [www.pro-treat.com/seminars](http://www.pro-treat.com/seminars) for details.

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