

The CONTACTOR™

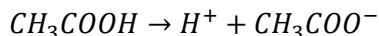
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How Stripping Promoters Work (or, Why the Details of an Ion Chromatogram Matter)

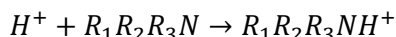
A *heat stable amine salt* (HSAS) is the protonated form (a cation) of the amine that cannot be heat regenerated back to its molecular form. This is because it is associated with one or more anions such as formate, thiosulfate, sulfate, phosphate, etc. Because they are anions, these components are all completely nonvolatile. Thus, no matter how hard the solvent is boiled, the heat stable salts remain dissolved in the solution, along with enough protonated amine to maintain electrical neutrality. An acid with a sufficiently low pKa will not volatilize from an alkaline medium such as an aqueous amine because the acid is simply too strong.

Each of these *anions* is called a *heat stable salt* (HSS) and they all elute on an ion chromatogram to reveal the detailed solvent composition. But are all anions (HSSs) equal — do they all have the same effect on the solvent, and do they affect all solvents equally in terms of treating performance?

All HSSs have a conjugate acid form. For example, acetate is the anion that's formed when acetic acid dissociates in water:



The hydrogen ion reacts with an amine molecule:



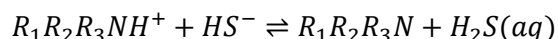
It forms the protonated amine. If the anion is multivalent (e.g., phosphate which is trivalent) there will be as many hydrogen ions liberated per molecule as the valence of the HSS anion formed. Note however, that one cannot simply assume complete dissociation of the conjugate acids. The extent of their dissociation is determined by their pKa values. In summary then, the particular HSS *does* matter, not just because its valence matters, but also because each acid's temperature

dependent dissociation constant depends on the specific anionic HSS.

Not all HSSs are organic, although the majority of them are because their source is reactions of molecules peculiar to oil refining. However, it has been known since the 1980s that adding a *mineral* acid to an amine system may result in better stripping of acid gases from the solvent in the regenerator. Mineral acids and organic acids are all acids and they all bind amine by generating the amine's protonated form. But only mineral acids have been *purposely* added to treating solvents. Phosphoric acid is the most widely used stripping promoter, but it is important to note that *all HSSs act as stripping promoters!* Thus, *over-reclaiming* solvents can lead to treating problems and such as failure to remove H₂S adequately because the solvent lean loading is no longer as low as it was before reclaiming.

For many years now, solvent suppliers have added a heat stable salt (usually the anion associated with a mineral acid such as phosphoric or sulfuric, i.e., phosphate or sulfate ion) to promote solvent regeneration in certain applications. When applied correctly, the technology quite effectively reduces solvent lean loadings. This can permit treating to much lower H₂S levels (e.g., in tail gas treating) to be done routinely. The key to knowing whether the method is being applied correctly is understanding how it works.

Under stripping conditions, bisulfide ion forms hydrogen sulfide by recombining with the hydrogen ion recovered from the protonated amine:



Whether equilibrium is driven to the right or left depends on such things as temperature, pressure and solution composition. In particular, if the

protonated amine concentration ($R_1R_2R_3NH^+$ or AmH^+) can be increased in some way, this will drive the equilibrium reaction away from HS^- towards formation of free H_2S . Herein lies one of the key elements of stripping promoters. The concentration of AmH^+ can be easily raised by adding a small amount of a mineral acid such as phosphoric or sulfuric to the solvent. This artificial raising of the AmH^+ concentration drives H_2S formation and allows stripping to much lower H_2S residual loading. Incidentally, instead of adding a little mineral acid, the same effect is achieved by leaving a little of the naturally-occurring HSSs in the solvent when it is reclaimed. After all, formate, acetate, thiocyanate and so on are also acids and they force a charge-balanced equivalent concentration of AmH^+ (the HSAS) to remain in solution.

It is worth noting, too, that the same technology will result in much lower CO_2 lean loadings for tertiary amines. However, in normal applications of this technology, CO_2 removal to ppm levels is never sought—the objective is always to get the H_2S in the treated gas as low as possible. If the amine is primary or secondary (or even if it is tertiary but contains more than a very small amount of a secondary or tertiary amine) the presence of reactive amine in a system containing CO_2 will nullify any possible gains from using partial acid neutralization of the solvent. CO_2 absorption into a reactive amine forms carbamate and AmH^+ in equal amounts. Thus, the protonated amine level will already be fairly high even when the solvent is well stripped, and adding a few 1,000s of ppmw of a mineral acid won't increase the protonation enough to have any benefit.

It seems not to be generally recognized that if an amine system is being used only for H_2S removal, i.e., it contains no CO_2 , partial neutralization with acid can in principle be effective in springing H_2S from solution regardless of whether the amine is primary, secondary, or tertiary. But if CO_2 gets into a carbamate-forming system, it will be almost impossible to strip it to a low enough level to permit the effective use of a stripping promoter.

Correct application of stripping promoters means using them only with a tertiary amine, unless CO_2 is completely absent from the process. But there are two other factors that must also be considered:

- Using a stripping promoter raises equilibrium H_2S partial pressures in the

absorber, as well as in the regenerator. Thus, depending on how the absorber is operated (e.g., lean-end, rich-end, bulge pinched) a stripping promoter can actually lead to worse overall system performance.

- If treated gas quality does not depend directly on solvent lean loading, then there is little point in sending a more thoroughly stripped solvent to the absorber. Thus, the absorber must be operated lean-end pinched for a stripping promoter to work.

The fact that the stripping promoter raises equilibrium H_2S partial pressures under both absorption and stripping conditions means that some care must be taken to use a promoter only where higher backpressures in the absorber do not completely negate the benefit of lower solvent loading.

Assessing the effect of a mineral acid additive on the performance of an amine unit can be done very reliably using the ProTreat® simulator. There are no assumptions made about complete dissociation of phosphoric acid into three hydrogen ions and a single phosphate anion. Instead, the dissociation into $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} are all accounted for according to well-established chemical reaction equilibrium theory. Furthermore, different HSSs have different effects, and they are treated that way—as different HSSs.

ProTreat mass transfer rate-based simulation can also be used to figure out just how much solvent reclaiming should and can actually be done before a serious negative impact on treating plant performance begins to be felt. The specific ionic makeup of the solvent is important because the individual HSSs cannot be replaced collectively by some equivalent concentration of phosphoric acid—the real chemical species make a difference. Finally, squeaky clean is not always the best answer, and many tail gas units, for example, have failed to meet their previous performance levels following too vigorous solvent cleaning.

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

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