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Heat Stable Salts II

In the first part of this series on Heat Stable Salts (HSSs) we alluded to the fact that HSSs are not amine degradation products, we pointed out several ways to define HSS concentrations, and we listed a set of guidelines for acceptable vs. unacceptable levels of HSSs from a corrosion standpoint. In this Part II we will look at the chemistry of HSSs in amine systems, and how they can affect our ability to measure HSS concentration.

Amine Chemistry and Acid Gases

The simplest way to understand the effect of HSSs on process performance is to begin by looking at how the chemistry of an amine treating system is supposed to work in their absence. Alkanolamines (denoted here as Am) are weak bases that react with water to form hydroxyl ion, OH^-

$$Am + H_2 0 \rightleftharpoons AmH^+ + OH^- \tag{1}$$

 H_2S and CO_2 are often referred to as acid gases because in aqueous solution they give up a hydrogen ion (H^+) :

$$H_2 S \rightleftharpoons H^+ + HS^- \tag{2}$$

$$CO_2 + H_2 O \rightleftharpoons H^+ + HCO_3^- \tag{3}$$

Being weak acids and bases, the equilibria for Reactions (1) - (3) very much favor the molecular forms of the solutes. Dissociation is very limited when the acids or bases are present alone, one without the other.

The other important component is water. Water is both a weak acid and a weak base which makes it a great solvent. It serves as a sink for both hydrogen- and hydroxyl ions.

$$H_2 0 \rightleftharpoons H^+ + 0H^- \tag{4}$$

Note that the reaction products are all ions. When both acids and bases are in solution, we can add Reactions (1) and (2) and use Reaction (4) to eliminate water:

$$Am + H_2S \rightleftharpoons AmH^+ + HS^- + Heat$$
 (5)

Similarly with Reactions (1), (3), and (4):

$$Am + CO_2 + H_2O \rightleftharpoons AmH^+ + HCO_3^- + Heat \qquad (6)$$

Focusing on H_2S , Reaction (5) is reversible and exothermic so heat is generated in the Absorber column as absorption proceeds. The exothermicity is related to the basicity of the amine.

Adding heat to such a system will force the reaction towards conversion of bisulfide to molecular hydrogen sulfide. This is exactly what we want to have happen in the regenerator by the heat furnished by the reboiler. Other reactions occur in this system, too, but they're unnecessary for understanding HSS effects. For example, the reaction with CO_2 is more complex than shown here because for primary and secondar amines bicarbonate attaches to the amino group to form carbamate. Nevertheless, all the reaction products are ionic and the solvent is an ionic soup, not a solution of just molecular species.

Chemistry of Heat Stable Salts

When a HSS dissolves in an amine solution it dissociates into a hydrogen ion and an anion characteristic of the HSS, and it uses the amine as a sink for the hydrogen ion released. This is tantamount to titrating a small portion of the amine (basic) with the HSS (acidic):

$$Am + HX \longrightarrow AmH^+ + X^-$$

where X represents the (monovalent) anion. As the name implies, heat stable salts are resistant to being thermally decomposed; i.e., they are thermally "stable". For this to be the case, they must come from an acid that is stronger than H_2S or CO_2 .

Hydrochloric acid is a good example because it fully dissociates in water into a positively charged hydrogen ion (H^+) and a negatively charged chloride ion (Cl^-) .

$$HCl \rightleftharpoons H^+ + Cl^- \tag{7}$$

More generically, for any relatively strong acid denoted by H_nX where X is the n-valent anion (of a HSS), the dissociation reaction is:

$$H_n X \rightleftharpoons nH^+ + X^{-n} \tag{8}$$

When a strong acid reacts with a weak base such as an amine, it forms a salt that cannot be effectively regenerated with reasonable amounts of heat. This is where the term "heat stable" salt comes from.

$$H_nX + n Am \rightarrow n AmH^+ + X^{-n} + Much Heat$$
 (9)

A consequence of reaction (9) is that the concentration of protonated amine (AmH^+) is increased. The elevated AmH^+ level

drives reaction (5) back towards molecular H_2S , making the amine easier to rid itself of acid gas in the Regenerator. This is especially effective at the lean end of the regenerator. It is referred to as the HSS stripping effect, something we will examine more closely in Part III.

Measuring HSSs

There are two primary methods for measuring HSS in solutions: titration and ion chromatography (IC). Titration is inexpensive and readily available at most plant facilities. In fact, it's often the only method feasible at the plant site. We mentioned that the HSAS measurement has its roots in titrations. An acid titration of the amine solution will produce a titration curve like the one shown in Figure 1. As acid is added, the pH drops slowly at first while there is free amine to buffer the pH. A rapid drop occurs as the free amine is exhausted. The second break occurs when the HSS anions are titrated back to free acid form. Figure 1 is a ProTreat simulated titration curve of a real refinery MDEA sample. The calculated RFB reported as MDEA for Endpoints 1 and 2 are 42.34 wt% and 43.20 wt%, respectively. The bound MDEA or HSAS by titration for this sample is 43.20 – 42.34wt% = 0.86 wt%.



Figure 1: Sample Acid Titration Curve for MDEA Solution — ProTreat® Simulation

IC allows a more detailed breakdown of the individual ions, and it tells us a lot more about the health of the solution. However, the cost of IC limits its use to mainly amine suppliers and reclamation providers, who regularly perform analytical services for many customers and process hundreds of samples. Delays in shipping and processing the samples often preclude sampling more frequently than once per month. Fortunately, most amine systems are large enough that the HSS accumulation rate over this period is tolerable.

For the same sample as is shown in Figure 1, the cation and anion chromatography breakdown is tabulated in Table 1. Lean acid gas loading was undetectable by several methods. Because there was no lean loading and HSS levels were low, the RFB titration results were in good agreement with the IC results. From the IC results using speciation from the ProTreat® simulator, we obtain 0.87%wt bound amine (or HSAS), 42.51%wt free amine, and 43.38%wt total amine as MDEA.

Table 1: IC Results for Refinery Lean MDEA Sample

Component	Concentration	Units
MDEA	42.2	%wt
DEA	1.00	%wt
MEA	118	ppmw
Acetate (CH ₃ COO ⁻)	2189	ppmw
Formate (HCOO ⁻)	553	ppmw
Phosphate (PO ₄ ³⁻)	892	ppmw
Sulfate (SO ₄ =)	90	ppmw
Thiosulate (S ₂ O ₃ =)	97	ppmw

The closeness in agreement between titration and IC analyses for this MDEA sample is not always typical. Pitfalls with titrations are important to understand because they can lead to poor operating choices and costly mistakes. Some of these pitfalls include:

- The acid or base in solution is unknown and has to be assumed. More than one amine or cationic contaminants such as sodium or potassium will titrate equally as amine and be reported as amine because a molecular weight has to be assumed for the base.
- Acid gas loading can titrate and be falsely reported as HSS (and vice versa!) depending upon the titration method and choice of endpoints and pH indicators.
- Colorimetric titrations, in particular, can lead to subjective errors. Some technicians are color blind, and two people will not necessarily see the same shades of color equally.
- Improper matching of a color indicator to the pH range where the endpoint occurs can result in completely erroneous results.

Only one reaction can be distinguished through the titration range, otherwise endpoints and breaks in pH or other indicators (e.g., color, conductivity) become dulled or even lost through interferences. It will pay dividends to give very close attention to the results of titrimetric analyses.

Even measuring HSS levels is an intriguing subject and the effect of HSSs on process performance is even more fascinating (and surprising). In Part III we will use ProTreat® to examine this in detail.

To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. For details visit <u>ogtrt.com/training</u>.

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