All Heat Stable Salts Are Equal, Or Are They?

Most heat stable salts (HSSs) are organic acids. They include the anions formate, acetate, propionate, glycolate, oxalate, sulfate, thiosulfate, sulfite, and thiocyanate, among others. One can also treat sodium ion, potassium ion, and chloride ion as HSSs in that they alter the ionic charge balance of the solution. One particular HSS, phosphoric acid, is often purposely added to MDEA as a stripping promoter, usually with a concentration of 5,000 ppmw or less.

If a process simulator accounts for HSSs at all, it usually uses hand calculation to lump all HSSs together into the milli-equivalents of a single pseudo-component such as phosphate ion. The simulator then calculates how the new ionic species PO_4^{-3} changes the solution speciation and, therefore, the equilibrium partial pressures of acid gases over the solvent. The reason phosphoric acid is used as the equivalent chemical is because it is also the most commonly used additive to promote stripping. This is thought to allow two birds to be killed with one stone. However, phosphoric acid is rarely in the fully dissociated form, PO_4^{-3}, and the weak acids that are the HSSs are not fully dissociated either. This makes the hand calculation of equivalence very rough at best and plain wrong in the worst case. The ProTreat® simulator recognizes that ion chromatography reports the concentration of a whole host of HSSs; it allows you to enter the ionic analysis just as the laboratory presents it, and it accounts properly for the incomplete dissociation of species as influenced by solution pH.

The test for the notion that all HSSs are equal is most easily made in an example. The regenerator shown in Figure 1 has 20 valve trays and is reboiled with 1.25 lb of 50 psig steam per standard gallon of rich solvent feed. The rich feed is 50 wt% MDEA and has H₂S and CO₂ loadings of 0.1 and 0.3 mol/mol, respectively. It enters on the stripper top tray at 200°F and the column top

pressure is 12 psig. Simulations were done for three cases: (A) clean MDEA solvent, (B) MDEA containing 1,500 ppmw of thiosulfate with 1,000 ppmw of formate, and (C) MDEA with 1,571 ppmw phosphoric acid. This phosphoric acid level has the same molar *charge* concentration as the thiosulfate-formate mixture (assuming H_3PO_4 is fully dissociated into phosphate ion, PO_4^{-3}).
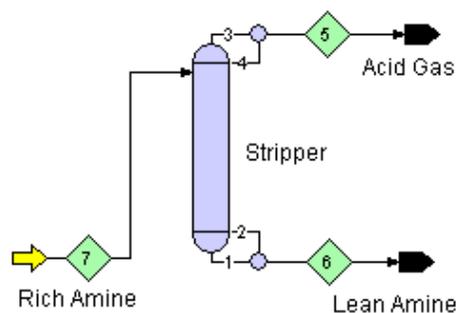

Figure 1   Case Study Regenerator

The important output parameters from the stripper simulations are the regenerated solvent lean loadings because in a lean-end pinched absorber, solvent lean loadings control the residual hydrogen sulfide level in the treated gas. Table 1 compares CO_2 and H_2S lean loadings for these three cases.

Table 1   Lean Loadings for the Study Cases

	Case A	Case B	Case C
H₂S	0.00398	0.001045	0.001771
CO₂	0.0001114	0.0000464	0.0000611

Case A with 50 wt% pristine MDEA (no contaminants) is not stripped nearly as well as Cases B and C where there are significant levels of contamination, whether by organic HSSs or the charge equivalent of phosphoric acid in the form of phosphate, PO_4^{-3}. All the ionic contaminants act as

stripping promoters. However, when the pseudo equivalent of trivalent phosphate is used, the degree of stripping is not quite as good. If it were legitimate to translate the effect of all HSSs into their phosphate ion equivalent, the lean loadings in Cases B and C would be identical, but they are not. The various HSSs, and especially phosphoric acid, do not fully dissociate, and this fact makes the translation almost impossible to make.

Although the numerical differences between Cases B and C do not appear large, an interesting question is how these loadings and contaminant levels would translate into the treated gas H_2S concentrations in a lean-end pinched absorber such as a tail gas treater. When an absorber is lean-end pinched with respect to hydrogen sulfide, almost all the absorption of H_2S takes place in the lower part of the column and the H_2S leak in the treated gas from the column is determined by the lean solvent loading (of both acid gases because both affect the vapor pressure of hydrogen sulfide). In other words, the H_2S in the treated gas is essentially in equilibrium with the lean solvent (the CO_2 content of the treated gas, however, is not).

Table 2a shows the hydrogen sulfide concentration in equilibrium with the three lean solvents shown earlier in Table 1. Contaminated solvent strips better than clean MDEA because the contamination generates an additional level of permanently protonated amine. The additional $MDEA \cdot H^+$ drives the reactions in the regenerator towards further production of more free acid gas. In turn, the free acid gas desorbs from the solution:

$$HS^- + \boldsymbol{MDEA \cdot H^+} \rightarrow H_2S \uparrow + MDEA$$
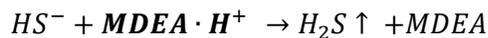
In clean MDEA, there is no *additional* protonated amine so the vapor pressure of hydrogen sulfide corresponds only to the clean solution.

Table 2a H_2S in Equilibrium with Lean Solvent

Case	H$_2$S in Gas (ppmv)
A	66
B	43
C	65

If solutions B and C really held identical charge concentrations of HSS anions the hydrogen sulfide vapor pressure in the two cases would be virtually identical. The fact that they are not is just testimony to the incomplete dissociation of H_3PO_4 and the invalidity of such a simple, direct translation. Incidentally, specifying the H_3PO_4 level and assuming full dissociation gives wrong results.

It is instructive to look at higher HSS concentrations because when phosphoric acid is used as a stripping promoter, it turns out to have an optimal concentration (at least in 50 wt% MDEA) of around 5,000 ppmw. Suppose the solution was actually 2,500 ppmw thiocyanate and 2,000 ppmw formate (Case D). These are not unusually high concentrations in refinery amine systems. With the assumption of complete dissociation of these HSSs and H_3PO_4, the charge equivalent phosphoric acid concentration (Case E) is 2,860 ppmw (a little more one half of the optimal value). Table 2b shows the equilibrium vapor pressures of H_2S in these cases.

Table 2b H_2S in Equilibrium with Lean Solvent

Case	H$_2$S in Gas (ppmv)
A	66
D	16
E	39

The H_2S vapor pressures (in ppmv) were calculated using ProTreat® with allowance for partial dissociation of these HSSs. Table 2b shows that the effect of organic heat stable salts on treating in a tail gas unit, for example, cannot be accurately determined by simple translation into equivalent phosphoric acid because the H_3PO_4 dissociates not only into PO_4^{-3}, but also into $HPO_4^=$ and $H_2PO_4^-$. Assuming complete dissociation of H_3PO_4 will also give an incorrect, optimistic, treated gas H_2S leak from the TGTU. Perhaps of equal importance is the fact that if one too religiously removes HSSs from a tail gas treating solvent, the TGTU may completely fail to meet treated gas specifications—it needed the stripping promoters.

This is yet another example of the importance of getting the physical chemistry right. ProTreat® is based not just on a mass transfer rate model, but on anally-retentive correctness of the fundamental chemistry that is embedded in the simulator. This is witnessed by the fact that not only vapor-liquid phase equilibrium, but enthalpy, entropy, and heat capacity calculations use a single common thermodynamic model in which is also embedded the correct prediction of heats of absorption. In answer to the title question: **All heat stable salts are not equal**.

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