Contaminated Solvents — DEA and MMEA in MDEA

The secondary amines methylmonoethanolamine (MMEA) and diethanolamine (DEA) are fragments of the decomposition of *N*-methyldiethanolamine (MDEA). They can also appear as byproducts of MDEA synthesis. A detailed and intriguing discussion of MDEA degradation in TGTUs can be found in Critchfield and Jenkins (1999). Whenever there are organic acid heat stable salts (HSSs), there is almost always MMEA and often DEA as well. Indeed, as a percentage of the original amine, the total concentration of secondary amine fragments is roughly *twice* that of the total organic acids present. There is usually more DEA than MMEA, (roughly a 2:1 ratio) in a TGTU amine sample.

MMEA as a contaminant at a concentration of 1 wt% is not rare, nor is DEA at 2 wt%. But the presence of MMEA is potentially much more deleterious to tail gas treating, i.e., affecting CO_2 slip, than DEA because the rate constant for the reaction of MMEA with CO_2 is surpassed only by piperazine. MMEA reacts 10 times faster than DEA and about 30 to 40% faster than even MEA at absorption conditions. Thus, MDEA solvent containing 1 wt% total secondary amine with a DEA to MMEA ratio of 2 to 1 reacts at roughly four times the rate of the same solvent containing only 1 wt% of DEA alone. There is potential then for MMEA-contaminated MDEA solvent to suffer a significant loss of its ability to slip carbon dioxide because of the highly reactive nature of the MMEA contaminant.

As borne out by the case study to follow, the impact of MMEA on such applications as TGTUs (and also AGE units) which require high selectivity for hydrogen sulphide can be quite severe (Keller, 2012). In contrast, as a contaminant, DEA has only a relatively modest effect on selectivity.

Fortunately, MMEA is a rather volatile amine. Although it seems to form rapidly during an SO_2 breakthrough event, over time it is removed from the solvent by being stripped into the gas being treated. However, its removal rate is not high enough to prevent it from having a severely deleterious effect on process performance over the long term Thus, unless SO_2 breakthrough is a very common and frequent event, the MMEA level is naturally kept in check, although performance will suffer during, and for some time following, an SO_2 breakthrough. Any anionic heat stable salt can potentially cause this effect.

Effect on VLE

Generally when VLE data from several sources are collected together, one sees a wide disparity between the data of various researchers. The disparity is usually greatest at the lowest values of solvent lean loading, which is exactly where the final treated gas composition is determined and highest accuracy is needed. Furthermore, with older, more vintage data, there is often no indication of purity, and even when purity is quoted, there is no indication of what the impurities might be. How significant is this effect likely to be? Perhaps a couple of examples will help answer this.

DEA and MMEA are common contaminants. Figures 1 and 2 show the effect on the equilibrium CO_2 partial pressure of 1, 2, and 3 wt% DEA and MMEA contamination of a 45 wt% total amine solvent, mostly MDEA.
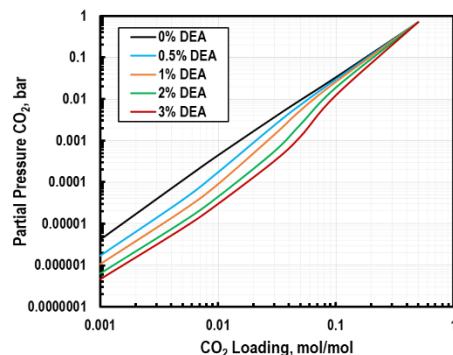

Figure 1   Effect of DEA Contamination on VLE in 45 wt% MDEA as a function of CO_2 Loading

Although both contaminants greatly reduce equilibrium CO_2 partial pressures, the effect of *DEA* is more severe. In fact, 45 wt% total amine with 1 wt% DEA has a CO_2 partial pressure

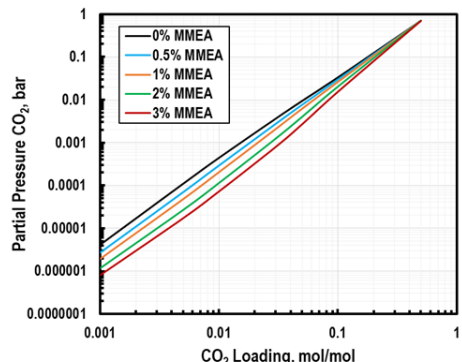**Figure 2   Effect of MMEA Contamination on VLE in 45 wt% MDEA as a function of CO_2 Loading**

four times lower than 45 wt% MDEA alone when the CO_2 loading is 0.001 mol/mol. When the loading is 0.01 the difference is a factor of five. With 3 wt% DEA the CO_2 partial pressure is lowered by factors of 10 and 15 at these same loading values. But MMEA contamination lowers CO_2 partial pressures by only half as much.

Note: these contaminants' effect on *equilibrium* has nothing whatsoever to do with their *rates of reaction* with CO_2. MMEA reacts five and a half times faster than DEA but lowers equilibrium CO_2 partial pressures by only half as much.

Case Study

This example refinery tail-gas treating unit contains 20 feet of 2-in Pall Rings and handles 28 MMscfd of gas with 1.70% H_2S and 3.48% CO_2 in a stream of mostly nitrogen. The solvent is nominally 37 wt% MDEA. Ion chromatography shows the solvent contains the following heat stable salt contaminants: 0.33 wt% thiosulfate, 0.15 wt% formate, and 0.15 wt% sodium ion. In addition, another peak eluted on the IC, but it was unidentified and was *assumed* to be DEA with a concentration of 1.0 wt%. The entire TGTU was modeled using the ProTreat® mass transfer rate-based simulator.

Table 1 shows simulated treating for the virgin solvent, solvent with the known HSS slate, and the same solvent with 1.0 wt% and 2.0 wt% DEA. When the unidentified peak is assumed to be 1.0% DEA, the H_2S leak increases because of a factor of nearly 9 times higher CO_2 loading in the lean amine—CO_2 reacts with DEA and is harder to strip out. The H_2S back-pressure is increased over the lean solvent. But none of these results agreed with measured unit performance. The CO_2 slip through this TGTU was consistently measured by the plant at 83%, and the H_2S leak was considerably higher than predicted by these three cases. When the assumed 1 wt% DEA is replaced, however, with the more likely 2:1 mix of DEA and MMEA, the simulated CO_2 slip falls to 83.6%, almost perfectly

predicting the measurement. The additional CO_2 absorption causes the H_2S leak to rise to just over 200 ppm—unfortunately there are no comparison H_2S data.

The effect of doubling the total concentration of the secondary amine degradation products shows an even lower CO_2 slip, but the change from doubling the MMEA content isn't nearly as great as from having a first small amount of MMEA.

As shown by ProTreat® mass transfer rate-based simulation, the presence of even a seemingly quite small concentration of MMEA, a known product of MDEA degradation and a coproduct of MDEA manufacture, can have a surprisingly large and detrimental effect on the CO_2 being slipped through a TGTU.

References

Critchfield, J. E., Jenkins, J. L., *Evidence of MDEA Degradation in Tail Gas Treating Plants*, PTQ, Spring, 1999.

Keller, A. L., *The Aftermath of SO_2 Breakthrough and Ways to Prevent and Mitigate It*, Brimstone Sulfur Symposium, Vail, Colorado, September 10–14, 2012.

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Table 1   Effect of DEA/MMEA on Performance

Case	H₂S Leak (ppmv)	CO₂ Slip (%)
Virgin Solvent	73	93.4
w/ HSSs	61	93.9
1 wt% Secondary Amines		
w/ HSSs + 1 wt% DEA	89	93.4
w/ HSSs + 0.67 wt% DEA + 0.33 wt% MMEA	208	**83.6**
2 wt% Secondary Amines		
w/ HSSs + 2.00 wt% DEA	128	91.9
w/ HSSs + 1.33 wt% DEA + 0.67 wt% MMEA	219	76.5