Effect of Trace Amine Contaminants on CO₂ Solubility in MDEA

Methyldiethanolamine (MDEA) is a solvent used extensively in gas treating when a very low residual H_2S level is wanted in the treated gas but with minimal CO_2 removal. High selectivity is possible using MDEA because this amine reacts hardly at all with CO_2 so it does not enhance CO_2 absorption rates through chemical reaction. Nevertheless, MDEA still has high capacity for CO_2 because of its high alkalinity.

The presence of amine contaminants can greatly diminish selectivity. In particular, primary and secondary amines (reactive towards CO_2) can enter an MDEA system either through MDEA degradation, or by using products of inferior quality. Even small amounts of contaminants such as DEA and MMEA can greatly affect selectivity and reduce system performance. The effect of DEA and MMEA on treating performance in MDEA systems has already been discussed in recent issues of The Contactor (TGTUs and AGE Units). This issue deals with the effect of contamination on vapor-liquid equilibrium (VLE).

Purity of Virgin Solvent

In the process of manufacturing MDEA, primary and secondary amines, in particular MMEA (monomethylethanolamine) and DEA (diethanolamine) can be coproduced. Unlike MDEA, these amines are quite reactive towards CO_2. MMEA has about twice the reactivity of caustic soda while DEA has about 25% of caustic's reactivity; thus, even small amounts of either contaminant, but especially MMEA, can greatly affect selectivity. Figures 1 – 4 show gas chromatograms of four MDEA samples provided by four different manufacturers. The main peak (elution time of about 8 minutes) is MDEA. Other peaks are contaminants.
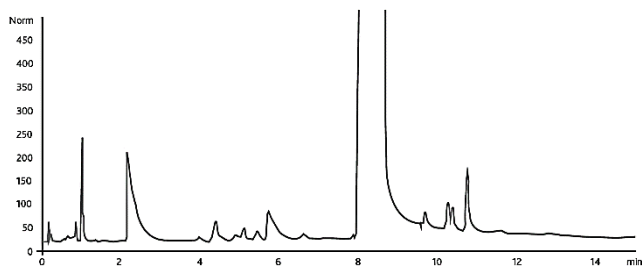

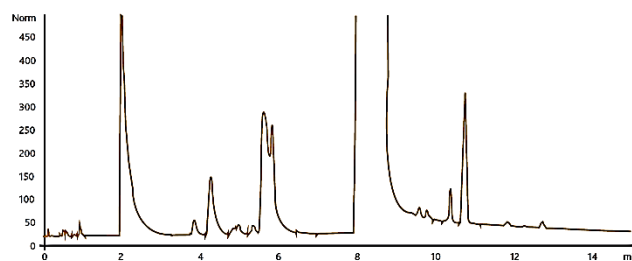**Figure 1   Chromatogram of MDEA from Supplier #1**

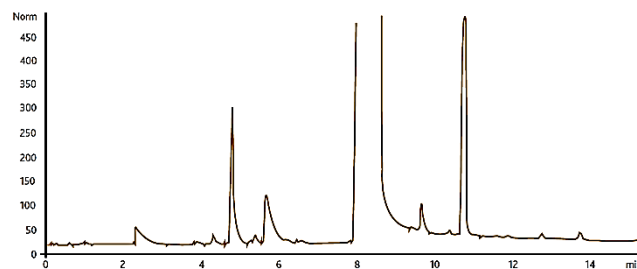**Figure 2   Chromatogram of MDEA from Supplier #2**

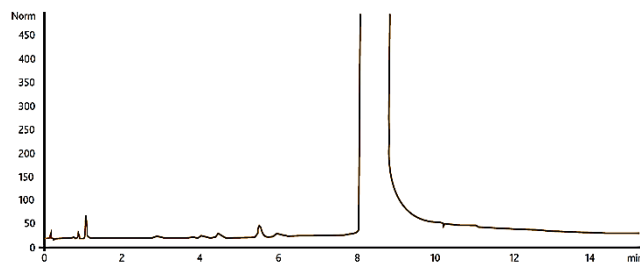**Figure 3   Chromatogram of MDEA from Supplier #3**

Figure 4   Chromatogram of MDEA from Supplier #4

It is evident that commercial MDEA varies widely in quality — all MDEA sources are not equal. The main contaminants of concern in gas treating are DEA and MMEA. DEA reacts rather more slowly with CO_2 than MMEA does (reaction rate constants at 25°C are 1,300 and 7,100 $L \cdot mol^{-1} \cdot s^{-1}$, respectively) and kinetics certainly plays a huge role in determinng the selectivity of a solvent. However, from a fundamentals viewpoint, contamination of an amine solvent by

other reactive materials is also bound to have some effect on vapor-liquid equilibrium measurements, especially for CO_2.

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. 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 a common contaminants. Figures 5 and 6 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. The temperature is 40°C.
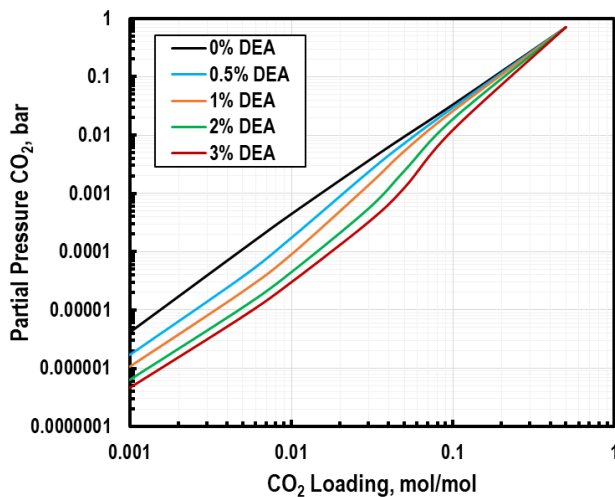

Figure 5   Effect of DEA Contamination on VLE in 45 wt% MDEA as a function of CO_2 Loading; 40°C
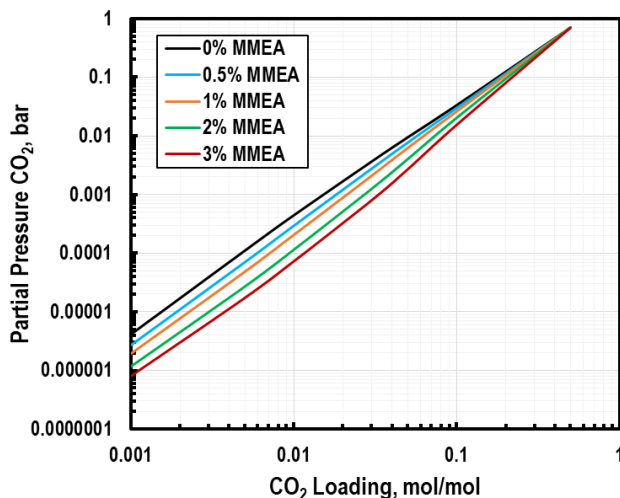

Figure 6   Effect of MMEA Contamination on VLE in 45 wt% MDEA as a function of CO_2 Loading; 40°C

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 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 that 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 reduces equilibrium CO_2 partial pressures by only half as much.

Effect on Simulation

So what does all this have to do with the simulation of MDEA-based amine treating? There are several effects:

- All column simulations (especially the ideal stage approach) rely heavily on accurate VLE models. When estabilishing ProTreat® VLE model parameters by regression to data, we reject data that lie more than a **factor of three** from the mean of the fit. That's a large variability. And more data aren't always better data — just more of the same? Undoubtedly contamination of unpurified solvents is one highly significant reason for the wide variability shown among much literature data.

- Simulation is almost always set in a commerciaal environment. Often the solvents in the plant have been in use for long periods of time, they've been thermally or chemically degraded, the amine system has been abused by poor or nonexistent maintenance, or filters have become plugged, are bypassed, or never existed. Simulations assume clean solvents with the compositions as specified, but real solvents can contain numerous contaminants. If the solvent in the system being simulated has not been analysed chemically (ion chromatography, GC, etc.) one can hardly expect the simulator to produce results in *extremely* close agreement with plant measured data. Often it's not the simlator that's wrong; it's the data it's been fed. But a rate-based ProTreat® simulation using accurate input data will almost always agree with plant measurement.

Reactive contaminants in amine based solvents can affect simulation by altering acid-gas equilibrium. But contaminants in the real solvent can alter the very nature of the solvent in ways known only through detailed solvent analysis.

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