



The CONTACTOR™

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Vaporization Losses from Mixed Solvents

A mixed solvent is one containing two or more amines. Over time one can expect the basic composition of the solvent to change, albeit slowly, because the amine constituents each have a different pure component vapor pressure. In addition, different amines have different non-ideal interactions with water, different reaction equilibria with water and CO₂, etc. For all of these are reasons they will volatilize at different rates leading to a slowly changing mixture formulation.

Case Study

Among the most commonly used mixed solvents are piperazine-MDEA blends. Applications are in deep CO₂ removal such as LNG production and synthesis gas purification in ammonia, methanol, and hydrogen manufacture. This blend pair is of interest for this study because piperazine and MDEA present very different pure component vapor pressures and have disparate reaction equilibrium constants for the CO₂-amine reactions.

There are three locations where solvent losses through vaporization pertain: (1) the top of absorbers where volatilized solvent can leave with the treated gas, (2) flash gas emitted by the rich solvent in a flash drum, and (3) the acid gas stream coming from the regenerator. The first case is most important because the solvent will usually have a very low lean CO₂ loading; the second case is less important because of the higher solvent loading; the third case is moot because regenerators usually have a reflux wash section on top.

Effect of Solvent Acid Gas Loading

When it comes to amines in gas treating, only the unreacted molecular form of the amine is volatile. Ionic forms such as protonated amine and amine carbamate are non-volatile and therefore cannot be lost by vaporization (although they can certainly be lost via entrainment). Thus, if the solvent has appreciable acid gas content it must be computationally speciated (ionic makeup characterized) to make a realistic appraisal of the potential for the deterioration of the solvent formulation that would result from differential vaporization.

Solvents with Low Loading

The ProTreat® simulator uses an activity coefficient model to calculate solvent thermodynamic properties. The vapor pressure of a component (*i*) is

$$p_i = p_i^* x_i \gamma_i (PF)_i \varphi_{i,Sat}^* / \varphi_{i,vap}$$

where p_i^* is pure component vapor pressure, x_i , γ_i , PF_i are liquid-phase mole fraction, activity coefficient and Poynting Factor, respectively, and the φ are fugacity coefficients. Table 1 shows the pure-component vapor pressure of piperazine ratioed to MDEA.

Table 1 Pure Comp Vapor Pressure Ratios

Temperature, °F	75	100	125	150
Ratio Pip/MDEA	514	304	194	131

At a constant total amine concentration of 9.0 mol% and for the three MDEA to piperazine molar ratios of 8.4/0.6; 7.8/1.2; 6.7/2.3 (wt% ratios of 37/1.9; 35/3.9; 30/7.5) the vapor pressure ratio was calculated at fixed temperatures of 75, 100, 125 and 150°F. These formulations correspond roughly to a 38–39 wt% total amine with 2, 4, and 7.5 wt% piperazine promotor, and they cover a range similar to solvents in commercial use. Figure 1 shows the results. In Figures 1, 2, and 3, ratios greater than 1 indicate that piperazine is more volatile than MDEA. Values less than 1 indicate the opposite.

Piperazine vapor pressure is highest relative to MDEA at the lowest temperature. Generally this occurs at the top of the absorber where vaporization losses actually occur. Furthermore, this is also where the loading is lowest which, as discussed later, worsens piperazine vaporization loss. In other words, vaporization losses will be highest, and piperazine will be lost most rapidly relative to MDEA, at the top of an absorber. Fortunately piperazine is used at only relatively low concentrations so solvent formulation creep resulting from differential vaporization is slower. Figure 2 shows vapor pressure ratios for the same solvents at 0.05 CO₂ loading. This value is fairly representative of lean loadings found in LNG and synthesis gas purification.

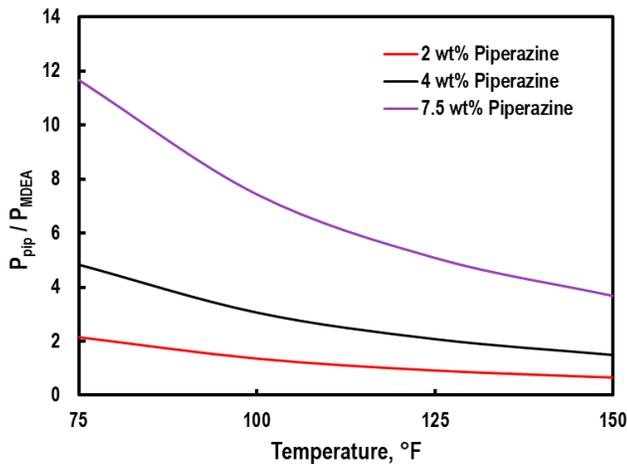


Figure 1 Vapor Pressure Ratio for 37 wt% Piperazine Promoted MDEA vs. Temperature; unloaded solvent

Even such light loading of a 2 wt% piperazine solvent keeps the piperazine vapor pressure below that of MDEA. But at higher piperazine concentrations, a solvent with typical lean loading will still lose piperazine several times faster than MDEA.

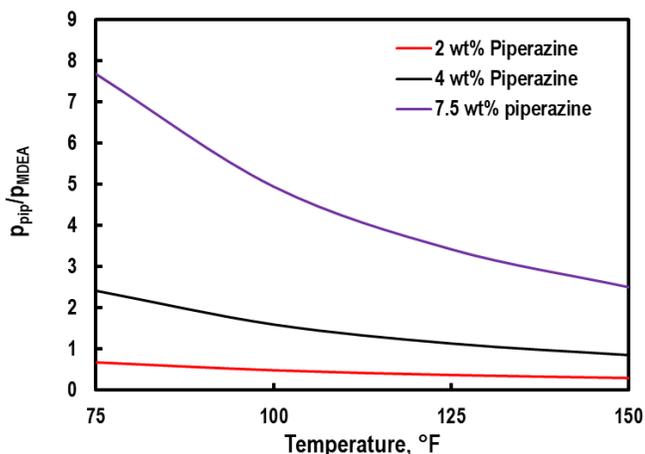


Figure 2 Vapor Pressure Ratio for 37 wt% Piperazine Promoted MDEA vs. Temperature. CO₂ Loading = 0.05

Solvents with High Loading

When the calculations are repeated for the same conditions but with the solvent CO₂ loaded to 0.4 mol/mol, typical of a loaded solvent, the results in Figure 3 are obtained. A highly loaded solvent leaves piperazine relatively nonvolatile for all piperazine promoted MDEA-based solvents of commercial interest. The reason for this is the way CO₂ distributes between various piperazine and bicarbonate/carbonate species. High concentrations of carbonate and bicarbonate can exist because MDEA acts as

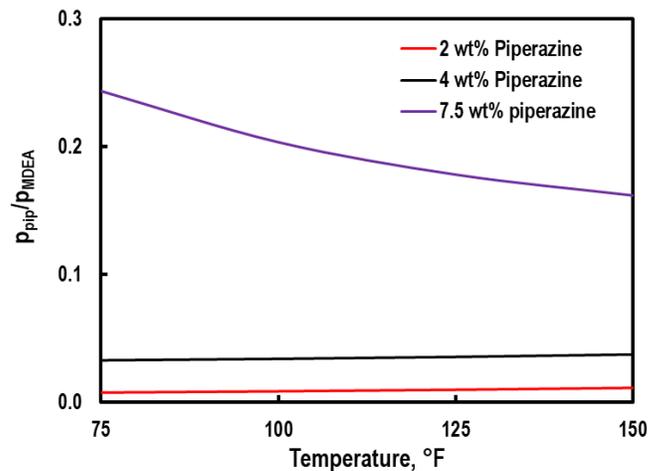


Figure 3 Vapor Pressure Ratio for 37 wt% Piperazine Promoted MDEA vs. Temperature. CO₂ Loading = 0.4

a receptacle for the hydrogen ions release by their formation. In a speciated solvent containing 37 wt% amine with 4 wt% piperazine at 100°F, roughly half the MDEA is in each of the free and protonated forms. With piperazine, less than one percent of the piperazine is in the free (volatile) form. The rest is bound with CO₂ as mono- and dicarbamate and protonated monocarbamate. Of the total CO₂ in solution, about half is bound to piperazine and rest is in the bicarbonate form, with 1/10th as much in carbonate.

The main escape route for amine, and particularly piperazine, is in the treated gas and it is precisely here that amine volatilities are at their greatest. There is nothing one can do to escape this fact. But there is a remedy: a relatively low cost solution is to provide one or two water wash trays at the very top of the absorber in a pump around with wash water bleed and feed. And this is a great place to introduce makeup water back into the amine system. Pro-Treat® thermodynamics accurately predicts amine vaporization losses. Incidentally, the acid gas stream from the regenerator overhead system is not a significant escape route because the high acid gas concentrations there fully saturate the amine, rendering it completely nonvolatile.

The learnings here are equally valid for other blends. *Over time, do not expect blends to stay constant.*

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

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