THE IMPACT OF ACID GAS LOADING ON THE HEAT OF ABSORPTION AND VOC AND BTEX SOLUBILITY IN AMINE SWEETENING UNITS

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ABSTRACT

In amine sweetening units, the heat of absorption and VOC and BTEX solubility have been found to vary significantly with acid gas loading as well as with temperature, amine type, and amine concentration. The heat of absorption declines by up to 20% while VOC and BTEX solubility can drop by as much as 40 to 50% with loadings up to 0.5 mol/mol for MDEA solutions. VOC and BTEX solubility are also highly dependent on temperature and amine concentration. As a result, amine sweetening units should be operated at the lowest circulation rate possible as limited by corrosion and treating requirements. For example, over circulation of 100 gpm in amine sweetening units can cost about $250,000/yr in additional reboiler fuel, can greatly increase pick up of VOC and BTEX, and lead to problems with emissions or in downstream sulfur recovery units.

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INTRODUCTION

Even though amine sweetening of gases and liquids has been used for many decades, the process is still being refined and improved to be more efficient. The cost of fuel to operate sweetening units has increased. Environmental limitations on the allowable emission rates have become more stringent for volatile organic compounds (VOC's) consisting of methane through octane and other light organics and aromatic compounds consisting of benzene, toluene, ethylbenzene and xylenes (collectively referred to as "BTEX"). As a result, efficient design and operation of amine sweetening units has become more critical.

This paper considers the impact of acid gas loading on two properties which affect the efficient operation of amine sweetening units: the heats of absorption for H_2S and CO_2, and the solubilities of VOC's and BTEX in amine solutions. Since the heats of absorption and the VOC/BTEX solubility in amine solutions also vary with temperature, amine type, and solution concentration, the impact of those parameters is also investigated. A case study is presented to show how the impact of loading, temperature, amine type, and solution concentration can be used to improve and optimize the design and operation of amine sweetening units.

Essentially all absorbed VOC/BTEX compounds exit the amine unit in the rich amine flash gas and stripper overhead acid gas streams. The VOC's and BTEX are a major source of concern for environmental considerations. The Clean Air Act limits the amount of VOC's to 250 tons per year and BTEX are limited to 25 tons per year and 10 tons per year for any individual aromatic compound. In addition, BTEX compounds are quite difficult to combust completely and tend to burn with a sooty flame which causes a number of problems for sulfur recovery unit operations, such as fouling of catalyst beds.

BACKGROUND

To facilitate the discussion and to clarify a few points, a brief review is helpful.

Heat of Absorption

The process of absorbing CO_2 and H_2S into amine solutions involves two steps: initial physical absorption of the molecular species followed by dissociation of a portion of the molecular species into ionic components. At equilibrium, the degree of dissociation is governed by

$$\frac{\left[HS^-\right]\times\left[H^+\right]}{\left[H_2S\right]} = Keq_{H_2S} = f\ \left(T\ \ only\right)$$

$$\frac{\left[HCO_3^-\right]\times\left[H^+\right]}{\left[CO_2\right]} = Keq_{CO_2} = f\ \left(T\ \ only\right)$$

The equilibrium constant, Keq, is a function of temperature only, while the H^+ ion concentration is a function of the amount and type of the amine and the temperature.

The heat of absorption for either H_2S or CO_2 may be expressed in simplified terms as follows:

$$\text{Heat of absorption} \approx \begin{bmatrix} \textit{Fraction} \\ \textit{physically} \\ \textit{absorbed} \end{bmatrix} \begin{bmatrix} \textit{Heat of} \\ \textit{physical} \\ \textit{absorption} \end{bmatrix} + \begin{bmatrix} \textit{Fraction} \\ \textit{Ionized} \end{bmatrix} \begin{bmatrix} \textit{Heat of} & & \textit{Heat} \\ \textit{physical} & + & \textit{of} \\ \textit{absorption} & & \textit{dissociation} \end{bmatrix}$$

The heat of physical absorption is relatively small compared to the heat of dissociation. At very low acid gas concentrations, the acid gas would be highly ionized and the concentration of the molecular acid gas would be very low. Thus, the heat of absorption would be highest at very low acid gas concentrations and would decrease as the amine loads up (*i.e.* acid gas partial pressure increases) and the fraction of physically absorbed acid gas increases.

Solubility of VOC’s and BTEX

The effect of acid gas loading in amine solutions on the solubility of VOC’s and BTEX is less complicated as compared to the heat of absorption. Since VOC’s and BTEX are organic compounds that are nonpolar or low polarity and do not ionize, their solubility is based only on physical absorption. Water is a polar liquid and organic amines make amine solutions less polar, particularly if there is nothing acidic in the solution such as H_2S and CO_2 which cause the amines to extensively ionize. Thus, as acid gases are added to the amine solution, they not only contribute their ionization, but cause the amine to ionize more completely. Since aromatics have a resonance structure based on the alternating single and double bonds, aromatics have greater attractive forces to polar solvents as compared to saturated hydrocarbons that do not have a resonance structure or double bonds. As a result, BTEX compounds tend to be a great deal more soluble in polar amine solutions than normal paraffins.

Fundamental Data and Process Simulation

To properly quantify the above trends requires the collection of fundamental data on the various systems. GPA has long recognized this need for fundamental data and has been one of the most active organizations in the collection of fundamental data in the gas processing field. GPA has sponsored an extensive study, GPA Project 821 by Oscarson *et al.* [1], to measure the heats of absorption for H_2S and CO_2 in amine solutions as a function of acid gas loading. This is the most complete study of this type that has been undertaken at the present time.

In Project 821, the enthalpy of absorption and partial pressures of carbon dioxide and hydrogen sulfide in DEA, DGA, and MDEA at various temperatures, pressures, concentrations, and loadings were measured. The technique involved mixing varying amounts of acid gas with a fixed flow of clean amine solution, then using a flow calorimeter to measure the cooling required to exit at the same temperature and pressure as the inlet. A series of tables were compiled listing the “enthalpy of solution” calculated as the total energy required to maintain the inlet conditions divided by the total number of moles of acid gas flowing in the system. The “total loading” values were calculated as the total moles of acid gas flowing through the system divided by the total moles of amine flowing through the system. It should be noted that in the high “loading” ranges, above the point defined by Oscarson *et al.* as the “saturation loading point”, not all the acid gas in the system resides in the liquid solution. Indeed, at “loadings” of up to 6 moles acid gas per mole of amine, most of the acid gas in the calorimeter actually remains in the vapor. An example “saturation loading point” is identified in

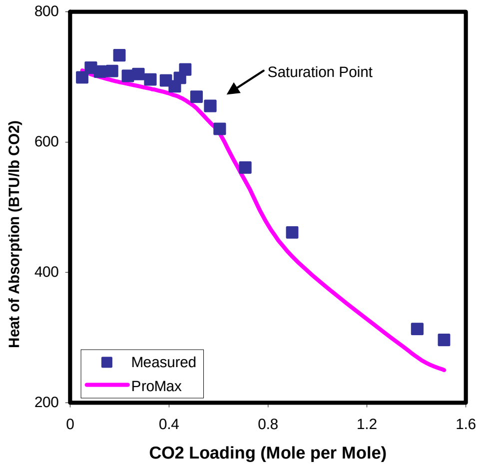

Figure 1 - Heat of Absorption for CO2 in 49.8 wt% DEA at 80 F and 32.6 psia Oscarson *et al.* [1]

Figure 1. Thus, at loadings higher than the “saturation loading point”, Oscarson’s “enthalpy of solutions” drops sharply and must be properly adjusted to reflect the true enthalpy of solution beyond the “saturation loading point”. In the present work, only values up to the “saturation loading point” were considered.

Both fundamental data and plant operating data regarding the solubility of VOC’s and BTEX in amine solutions are limited, especially as a function of acid gas loading. Thorough discussions and reviews of VOC’s and BTEX solubilities in amine solutions with no acid gas loading have been presented by Bullin and Brown [2] and McIntyre *et al.* [3]. The previous studies did not focus on the impact of acid gas loading on the solubility of VOC’s and BTEX in amine solutions due to the lack of fundamental data. The GPA has sponsored Project 971 by Valtz *et al.* [4] and Project 011 by Valtz and Richon [5] to measure the solubilities of BTEX compounds and VOC in amine solutions as a function of acid gas loading, respectively. Another excellent source of hydrocarbon solubility in amine solutions as a function of acid gas loading is that of Carroll *et al.* [6].

These experimental data sets along with other data were used to develop and verify the electrolytic thermodyamic models in the ProMax® process simulation software [7]. ProMax calculates all of the thermodynamic properties such as Gibbs free energy, enthalpy, and entropy, and phase compositions as a function of temperature, pressure, compositions, acid gas loadings, and all process conditions. From these stream enthalpies and compositions the heats of absorption as well as the VOC’s and BTEX solubilities in amine solutions as a function of acid gas loading can be determined.

IMPACT OF ACID GAS LOADING

The impact of acid gas loading on the heat of absorption and VOC/BTEX solubility is examined by comparing the process simulation calculations to the fundamental data and some plant data. A case study demonstrates the benefits of the fundamental data and calculational methods to optimize the design and operation of amine sweetening units.

Heat of Absorption

The data presented by Oscarson *et al.* [1] were used in the development of the calculation procedures for the impact of acid gas loading on the heat of absorption. To compare the calculations to the Oscarson *et al.* [1] data, a ProMax simulation was set up to represent the experimental technique of Oscarson as previously described. Only selected sets of data are presented here to show the trends of the impact of loading combined with amine type and concentration, as well as temperature.

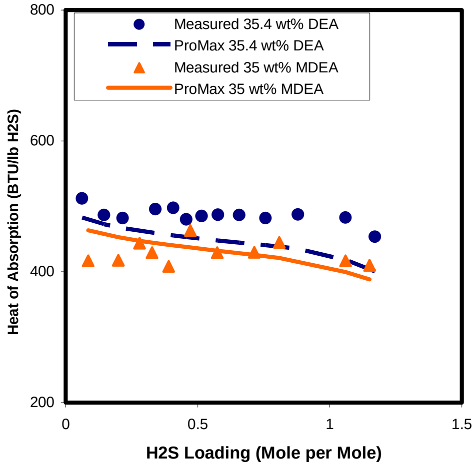

Figure 2 - Heat of Absorption for H2S in Amines at 80 F and 162.6 psia Oscarson *et al.* [1]

An example of the impact of amine type on the heat of absorption as a function of acid gas loading is shown in Figure 2. DEA has higher heat of absorption than MDEA as would be expected since DEA is a stronger base. For H_2S the heat of absorption is about 5 to 10% greater for DEA as compared with MDEA.

When compared on an acid gas loading basis, the heat of absorption decreases as loading increases but does not appear to be a strong function of amine concentration for either H_2S or CO_2 as shown in Figures 3 and 4. The heat of absorption is a function of both loading and temperature as presented in Figure 5 for H_2S and Figure 6 for CO_2. These figures show variations in the heat of absorption up to about 20% with both loading and temperature. Most surprising about these figures is the increase in the heat of absorption as the temperature of the system increases. This fact has not been sufficiently appreciated previously. The increase in heat of absorption of up to 20% from the absorber to the stripper temperature may cause a deficient duty calculation with the reboiler if a constant heat of absorption at the lower value is used. Insignificant variation in the heat of absorption occurs with changes in pressure as shown for H_2S and CO_2 in Figures 7 and 8.

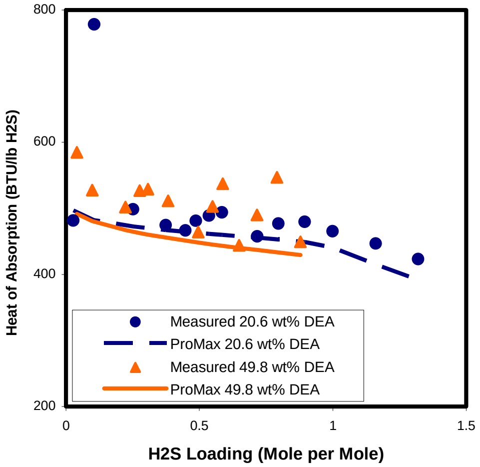

Figure 3 - Heat of Absorption for H2S in DEA at 80 F and 162.6 psia Oscarson *et al.* [1]

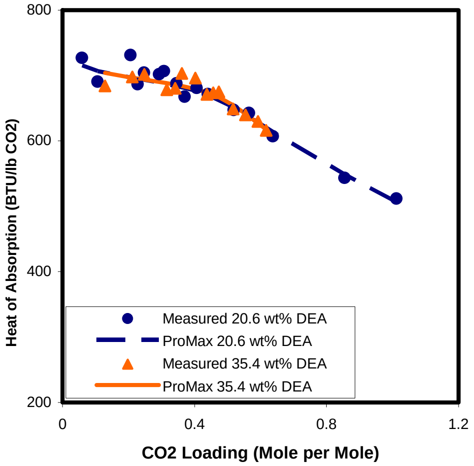

Figure 4 - Heat of Absorption for CO2 in DEA at 80 F and 162.6 psia Oscarson *et al.* [1]

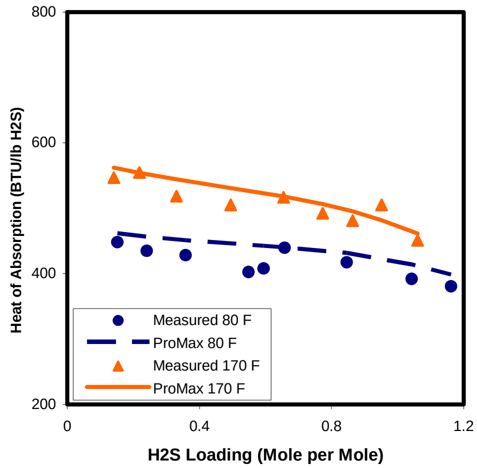

Figure 5 - Heat of Absorption for H2S in 20 wt% MDEA at 162.6 psia Oscarson *et al.* [1]

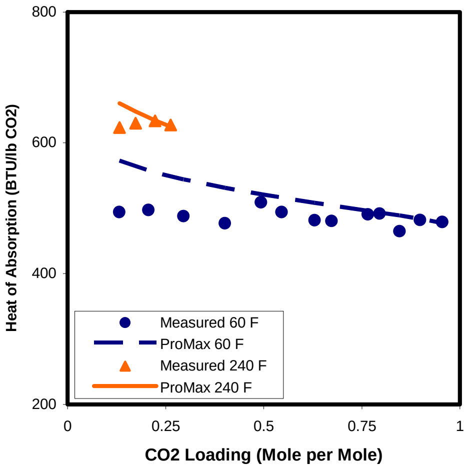

Figure 6 - Heat of Absorption for CO2 in 40 wt% MDEA at 162.6 psia Oscarson *et al.* [1]

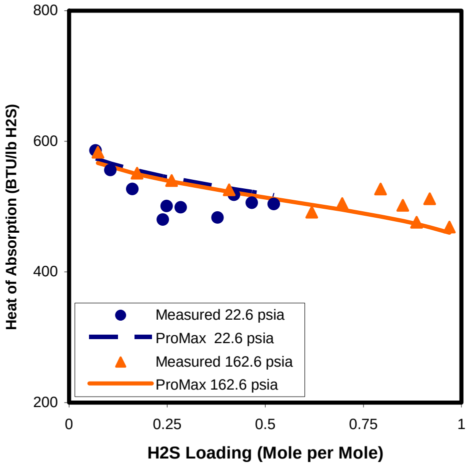

Figure 7 - Heat of Absorption for H2S in 35 wt% MDEA at 170 F Oscarson *et al.* [1]

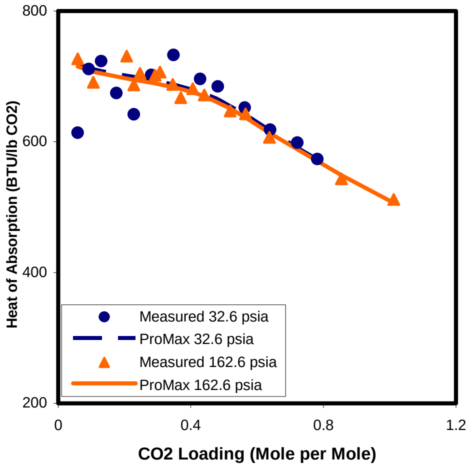

Figure 8 - Heat ofAbsorption for CO2 in 20.6 wt% DEA at 80 F Oscarson *et al.* [1]

The comparisons of the experimental data on the heat of reaction for H_2S and CO_2 in amine solutions shown in Figures 1-8 represent only about 10% of the total number of comparisons of ProMax to the Oscarson *et al.* data. The comparisons demonstrate that the calculational methods used in ProMax for the total enthalpy of amine solutions matches the data for heat of solution closely and properly accounts for the thermodynamic effects including temperature, pressure, concentrations, and acid gas loadings.

In summary, although acid gas loading affects the heat of absorption, the amine type and temperature are equally or more important variables with regard to heat of absorption. Stronger amines and amines that form carbamates have higher heats of absorption as compared with weaker amines and amines that do not form carbamates. Most important is that the heat of absorption increases with temperature by up to 20% from absorber to stripper conditions. Pressure and amine concentration do not significantly affect the heat of absorption.

Benefits of Accurate Heat of Absorption Predictions

Knowledge of the effects of acid gas loading and other parameters on the heat of absorption can be used to more accurately predict and improve calculations in designing and operating amine sweetening facilities. Improved values for the heat of absorption allow more accurate calculations of the temperature profiles as well as exit rich amine temperatures from absorbers. For primary amines such as DGA with more significant temperature bulges, the magnitude and location of the maximum temperature should be more accurately predicted with process simulators that incorporate the more sophisticated thermodynamic models. For example, improved predictions will allow engineers to locate the proper stage for a side cooler in an absorber with an excessive temperature bulge.

Two examples of improved predictions of temperature profiles are shown in Figures 9 and 10 for the Dome North Caroline plant [8]. This paper contains measured absorber temperature profiles for five sets of operating conditions and represents one of the very few sets of published data which includes absorber temperature profiles. The Dome North Caroline plant used 33 wt% MDEA and was designed to slip CO_2. As shown in Figures 9 and 10 for two of the Dome cases, there is a significant improvement in using ProMax's method of calculating the total enthalpy for the amine solution (which includes all of the thermodynamic effects including temperature, pressure, concentrations, and acid gas loading) compared to using an assumed constant value of 475 BTU/lb for CO_2 as suggested by Kohl and Riesenfeld [9] in their fourth edition (which was prior to the Oscarson *et al.* study). In Figures 9 and 10, the arrows near the top and bottom designate the inlet and exit stream temperatures.

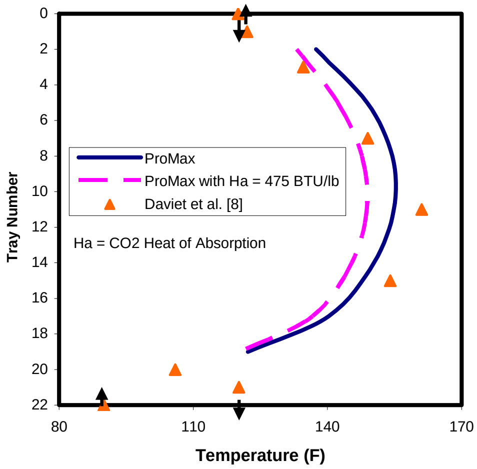

Figure 9 - Dome 5 Temperature Profile from Daviet *et al.* [8]

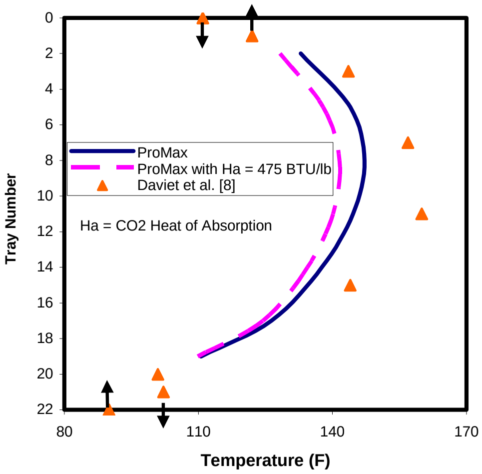

Figure 10 - Dome 3 Temperature Profile from Daviet *et al.* [8]

The amine unit selected for the following case study has previously been reported by Skinner, Reif, Wilson, and Evans [10] as Test Plant A. The unit employs 100 gpm of 32 wt% DEA to remove 7 mol% CO_2 from 9.5 MMSCFD of feed gas at 1000 psi. Simulations by ProMax match this data and suggest that the unit is being operated at approximately 85% of maximum loading at about 0.5 moles acid gas per mole of amine. The amine circulation rate for this unit was varied from 90 to 135 gpm to examine the impact on the heat of absorption as well as the total reboiler duty. As shown in Figure 11, the heat of absorption/desorption did increase on the order of 10% with higher circulation rates (lower

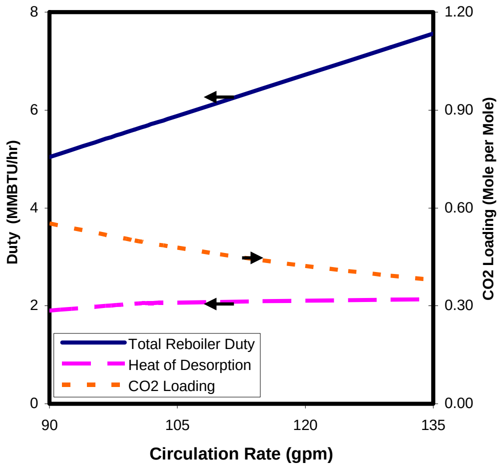

Figure 11 - Effect of Circulation Rate on Reboiler Duty and Rich Loading from ProMax

loadings), however, for this case, the effect was small compared to the increase in total reboiler duty. As can also be seen from Figure 11, the total reboiler duty increased directly proportional to the circulation rate.

Thus, there is an additional impact from increasing circulation rates and, as a result, amine sweetening units should be operated at the lowest circulation rate possible as limited by corrosion considerations and sweet gas requirements. For example, a reduction of 100 gpm in the circulation rate would result in fuel savings of about \$250,000/yr with fuel at \$5/MMBTU. Since these are annual costs, they could justify the use of stainless steel in selected areas to raise loadings and mitigate corrosion problems.

VOC's and BTEX

The data of Valtz *et al.* [4], Valtz and Richon [5] and Carroll *et al.* [6] for the impact of acid gas loading in amine solutions on VOC and BTEX solubility along with numerous other data sets for the solubility of VOC and BTEX in unloaded amine solutions were used in the development of the electrolytic thermodynamic models in ProMax. The previously mentioned data sets include hydrocarbon solubility as a function of acid gas loading in amine solutions.

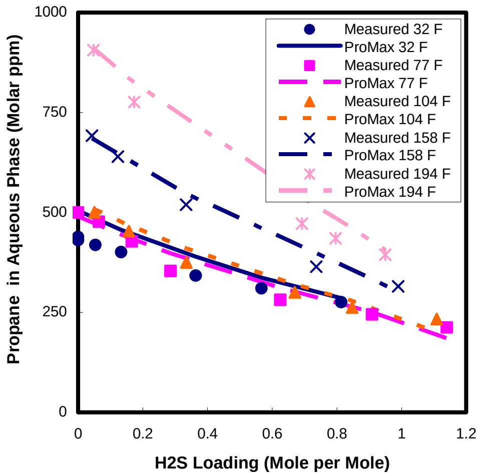

Figure 12 - Vapor-Liquid-Liquid Propane Solubility in 35 wt% MDEA with H2S, Carroll *et al.* [6]

The impact of loading on the solubility of propane in 35 wt% MDEA for a vapor-liquid-liquid equilibrium (VLLE) system from the Carroll *et al.* data is shown in Figure 12. The solubility of propane decreases with loading and increases with temperature for this VLLE system. In an operating plant treating liquids (LLE system), the solubility of both VOC's and BTEX generally increases with temperature while, in gas treating (VLE system), the solubility usually decreases with temperature.

Based on the representation of the data in Valtz *et al.* [4] and Valtz and Richon [5] there are several different techniques to perform the flash calculation for comparison purposes. For a system with five components in equilibrium with two phases, there are five equilibrium expressions relating the fugacities of each component in each of the phases. There are a total of 10 intensive variables that may be set or calculated: the temperature, pressure, the four mole fractions in the liquid phase, and the four mole fractions in the vapor phase. For the generation of Figures 13 through 16 in the present work, the following technique was used. Five parameters were specified: (1) temperature, (2) pressure, (3) the mole fraction of hydrocarbon (cyclohexane, benzene or toluene) in the vapor phase,

(4) the mole fraction of amine in the liquid phase, and (5) the mole fraction of CO_2 in the liquid phase. The following values were calculated: mole fraction of hydrocarbon in the liquid phase, mole fraction of methane in the vapor and liquid phase, and mole fraction of H_2O in the liquid phase. This is not the only way to perform the flash calculations as another approach could be used (*i.e.* specify the temperature and the four mole fractions in the liquid, perform a bubble point flash, and the pressure and the mole fractions in the vapor would be calculated). There are other ways to perform the flash calculation keeping in mind that for this VLE system, five independent intensive variables may be specified.

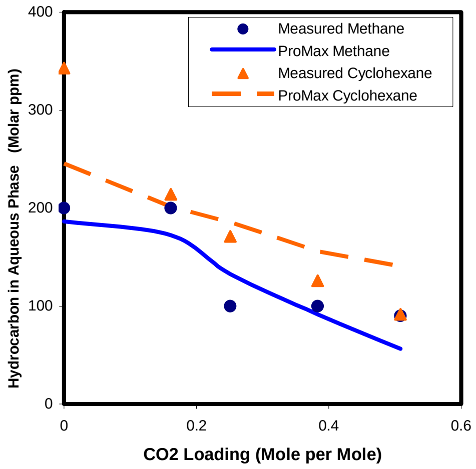

Figure 13 - Cyclohexane Solubility in 50 wt% MDEA 140 F and 73 psia Valtz and Richon [5]

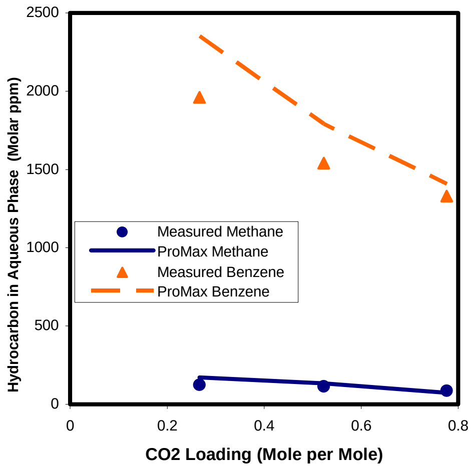

Figure 14 - Benzene Solubility in 50 wt% MDEA 77 F and 73 psia Valtz *et al.* [4]

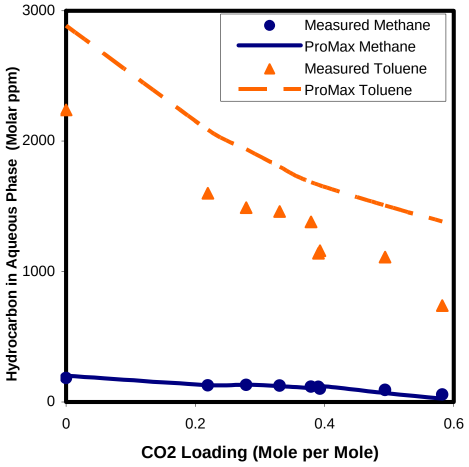

Figure 15 - Toluene Solubility in 50 wt% MDEA at 140 F and 73 psia Valtz *et al.* [4]

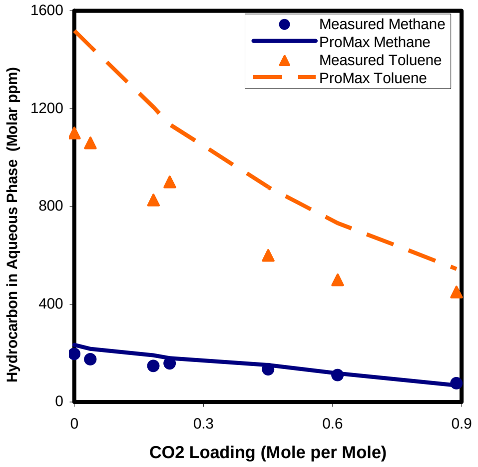

Figure 16 - Toluene Solubility 50 % MDEA at 77 F and 73 psia Valtz *et al.* [4]

For the Valtz *et al.* data, the overall trend of acid gas loading on the solubility of methane, cyclohexane, benzene and toluene in MDEA solutions with the concentration range between 45 to 50 wt% amine is shown in Figures 13-16. Furthermore, the data are for solutions with variations in amine concentration of 2 to 5 wt% MDEA. Since the solubility of VOC's and BTEX tends to rise very sharply in the 40 to 50 wt% MDEA range as shown in Figure 17, small changes in the amine concentrations can result in very large changes in the BTEX solubility. For example at 100°F and 100 psia, a 2 wt% change from 46 to 48 wt% MDEA can result in about a 20 to 25% change in the BTEX solubility. This accounts for most, if not all, of the unusual variations in moving from data point to data point in Figures 13 – 16. Thus, since the MDEA concentrations vary as much as 2 to 5% within any one figure, the results as presented in Figures 13-16 should be interpreted only for general trends for the impact of acid gas loading on the solubility of VOC's and BTEX in amine solutions.

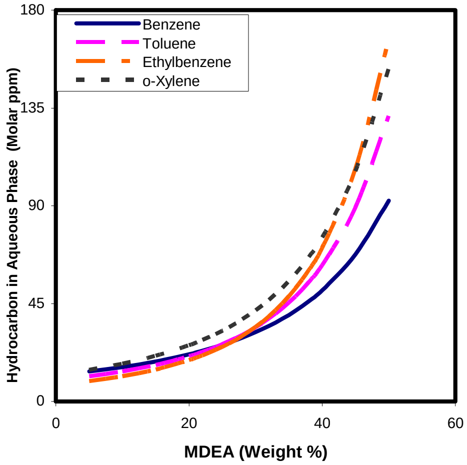

Figure 17 - Effect of MDEA Concentration on Aromatic Hydrocarbon Solubility at 100 F and 100 psia from ProMax

As shown in Figures 12-16, the trends for the impact of acid gas loading calculated by ProMax agree very well with the trends in the data. For the Valtz *et al.* data, some of the ProMax values were high by up to 20 to 25% for individual data points in the 45 to 50 wt% MDEA range. Due to the sharp increases of up to 20 to 25% in solubility of BTEX for a 2 wt% change in MDEA concentration for the 45 to 50 wt% range, significant variations in solubility would be expected.

The relative solubility of various VOC's and BTEX compounds as a function of amine concentration is shown in Figures 17 and 18. These plots were generated from ProMax for an MDEA system at 100°F and 100 psia and with 0.1 mol% in the vapor for each component included in Figures 17 and 18. Comparison of these two figures shows that overall the paraffins are far less soluble than the BTEX compounds. The temperature of the rich amine as it exits the absorber has a strong impact on BTEX solubility as illustrated in Figure 19 for 30 wt% MDEA with no acid gas loading. This plot was also generated from ProMax for a 30 wt% MDEA system at 100°F and 100 psia and with 0.1 mol% of each of the BTEX components. For example, the solubility of toluene can increase from about 22 ppm at 120°F to about 32 ppm at 100°F.

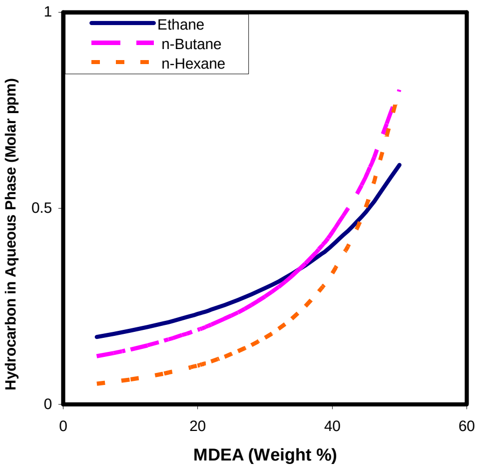

Figure 18 - Effect of MDEA Concentration on Normal Hydrocarbon Solubility at 100 F and 100 psia from ProMax

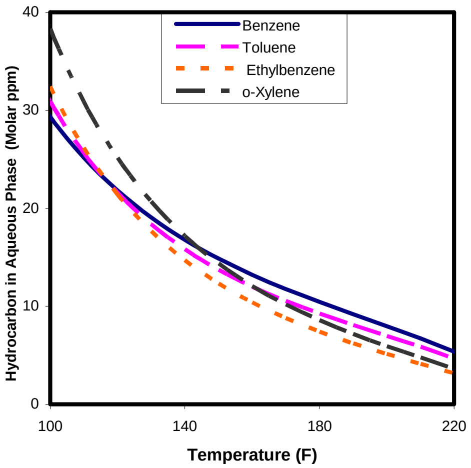

Figure 19 - Effect of Temperature on Aromatic Hydrocarbon Solubility in 30 wt% MDEA at 100 psia from ProMax

As shown in Figure 20, the solubility of BTEX can drop as much as 30 to 40% in going from 0 to 0.5 mol/mol. Although Figure 20 is for CO_2, the impact of H_2S is similar but somewhat lower. The solubility curves for VOC and BTEX in DEA on a wt% basis are very close to the values for MDEA. Thus, as far as VOC and BTEX solubility is concerned, DEA would have a significant advantage over MDEA only in the sense that lower concentrations of DEA are usually used. The common highest concentration limit is about 35 wt% for DEA compared to 45 to 50 wt% for MDEA. For 35 wt% DEA with no loading and at 100°F, 100 psia and 0.1 mol% in the gas, the solubility of any individual BTEX compound would be about 40 ppm compared 90 to 170 ppm for a 50 wt% MDEA solution.

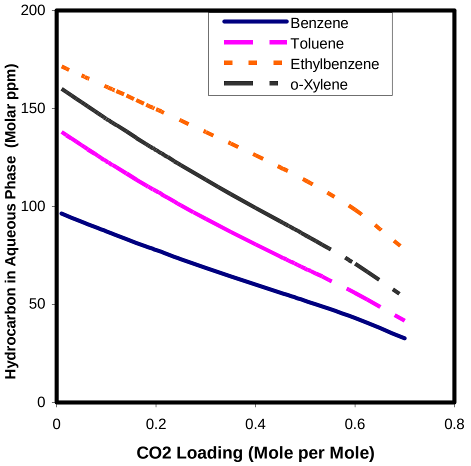

Figure 20 - Effect of CO2 Loading on Aromatic Hydrocarbon Solubility in 50 wt% MDEA at 100 F and 100 psia from ProMax

Comparison of VOC and BTEX Calculations to Plant Data

In 1997, Skinner *et al.* [10] reported data for the emissions from regenerator vents including several hydrocarbons and BTEX compounds for six operating amine units. For Cases B & F, the inlet CO_2 was not reported and was assumed to be 3.5 and 6.3 mol%, respectively. The solvent was DEA for Cases A-F except Case B which was MEA. The measured values are compared to the calculated values in Table I. Overall, the model matches the data reasonably well but tends to consistently over predict xylene.

Table I - Comparison of Reported and Calculated VOC and BTEX Emissions from Amine Units[a]
(Tons per Year)

Species	**Case A**			**Case B**		**Case C**		
	Meas. Canister	**Meas.** Amine	**ProMax**	**Meas.** Amine	**ProMax**	**Meas.** Canister	**Meas.** Amine	**ProMax**
Ethane	5.8	NM[b]	**2.04**	NM	**8.32**	12.0	NM	**2.20**
n-Hexane	0.16	0.42	**0.01**	0.096	**0.01**	0.06	0.014	**0.00**
Benzene	5.8	5.6	**6.11**	5.5	**8.37**	7.5	7.1	**8.70**
Toluene	2.5	2.4	**3.21**	2.5	**2.38**	3.5	3.2	**4.44**
Et-benzene	0.06	ND[c]	**0.13**	0.19	**0.13**	0.06	0.08	**0.11**
Xylene	0.51	0.42	**0.95**	0.41	**0.19**	0.5	0.66	**1.16**

Species	**Case D**				**Case E**			**Case F**			
	Meas. Canister	**Meas.** Amine	**Meas.** GC	**ProMax**	**Meas.** Canister	**Meas.** GC	**ProMax**	**Meas.** Canister	**Meas.** Amine	**Meas.** GC	**ProMax**
Ethane	8.68	NM	CO[d]	**14.48**	2.21	CO	**2.27**	4.86	NM	NR[e]	**7.99**
n-Hexane	ND	1.35	ND	**0.08**	0.06	0.10	**0.01**	ND	1.1	0.12	**0.03**
Benzene	53.9	44.1	38.9	**51.02**	9.8	8.2	**8.50**	59.8	56.3	42.2	**59.77**
Toluene	29.3	23.7	22.4	**33.24**	5.7	5.3	**5.85**	47.0	45.7	34.8	**54.65**
Et-benzene	0.78	0.66	0.58	**1.86**	0.18	0.2	**0.33**	1.1	1.3	0.94	**1.34**
Xylene	6.2	6.4	4.7	**20.12**	1.5	1.5	**3.75**	9.9	14.4	10.3	**25.47**

	Eunice Gas Plant					
Species	**Absorber OH**		**BTEX Stripper OH**		**Acid Gas**	
	Meas.	**ProMax**	**Meas.**	**ProMax**	**Meas.**	**ProMax**
Benzene	1153	**1100**	37.7	**38.42**	25.4	**29.49**
Toluene	514	**525**	22.8	**17.14**	19.3	**7.4**
Et-benzene	20.2	**19.6**	2.2	**0.65**	2.6	**0.2**
Xylene	60.5	**65.8**	4.4	**2.55**	4.8	**3.08**

a - Cases A-F from Skinner *et al.*[10] and Eunice Gas Plant from Azodi *et al.*[11]
b – NM = Not Measured
c – ND = Not Detected
d – CO = Coeluted with Methane
e – NR = Not Reported

The data comparisons to the Eunice gas plant using 53.5 wt% DGA (Azodi, *et al.* [11]) are also included in Table I. In this case, the overheads from the BTEX stripper were included along with the acid gas stream. The calculated values agree quite well with the data from both the BTEX stripper and acid gas stream. Interestingly, the calculated values for xylene agree reasonably well also but both calculated values were below the data.

Benefit of Accurate Predictions of Impact of Acid Gas Loading on VOC and BTEX Solubility

As stated previously, the essential question is: what are the benefits of the above in designing and operating amine sweetening units. The case study analyzed in the previous section and described by Skinner *et al.* [10] used 32 wt% DEA and included 200 ppm benzene and 350 ppm total BTEX in the feed gas. This case is also used to examine the impact of acid gas loading on the solubility of VOC's and BTEX. The acid gas loading decreases as the circulation rate increases and for this case ranged from 0.55 mol/mol at 90 gpm to 0.38 mol/mol at 135 gpm.

As shown in Figure 21, the benzene and BTEX emissions increase quite dramatically. The benzene increases from about 5 tons/yr at 90 gpm to about 9.9 tons/yr at 135 gpm while the total BTEX increases from about 8.4 tons/yr to about 17.3 tons/yr. Thus, for this case, the BTEX absorption is about doubled with a 50% increase in circulation rate. This large increase in BTEX pickup is due to the compound effect of a 50% increase in solution circulation rate which includes: (1) a direct 50% increase in BTEX pickup due to increased circulation, (2) an increase of about 15% due to a decrease in acid gas loading from 0.55 to 0.38 mol/mol, and (3) an increase of about 10% due to the decrease in rich amine temperature from 162 to 151°F.

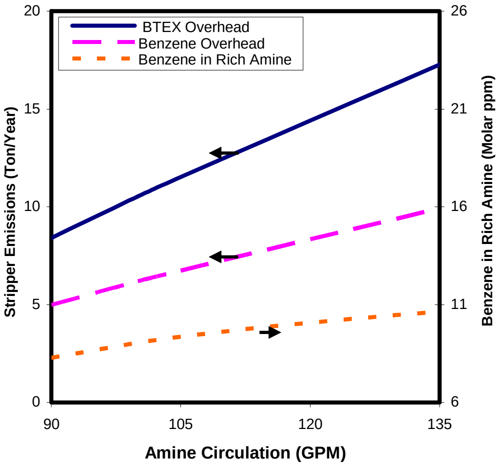

Figure 21 - BTEX Overhead From Acid Gas Stripper from ProMax

SUMMARY AND CONCLUSIONS

Both heat of absorption and VOC and BTEX solubility have been found to vary significantly with acid gas loading as well as with temperature, amine type, and amine concentration in amine sweetening units. The heat of absorption was found to vary by about 20% with loading as well as with temperature. These variations can result in significant changes in the column temperature profiles and rich amine temperature for many cases which, in turn, can affect the column performance as well as VOC and BTEX solubility.

Acid gas loadings in the range of 0.5 to 0.6 mol/mol can decrease the VOC and BTEX solubility in MDEA solutions by as much as 50 to 60% compared to lean amines. In addition, the BTEX solubility in MDEA solutions can decrease by as much as 50% by going from 100 to 140°F rich amine temperature. BTEX solubility increases very sharply with amine concentration in the 40 to 50 wt% MDEA range. MEA and DEA solutions absorb less BTEX and VOC's since these solvents are usually used in lower concentrations: ≤ 20 wt% for MEA and ≤ 35 wt% for DEA.

Amine sweetening units should be operated at the lowest circulation rate possible as limited by corrosion and treating requirements. For example, over circulation of 100 gpm in amine sweetening units will cost about $250,000/yr in additional reboiler fuel at $5/MMBTU for fuel and can cause large increases in VOC and BTEX absorption. If the acid gas is being fed to a sulfur recovery unit, over circulation can lead to increased acid gas volume from over scrubbing and to increased bed fouling and plugging from dramatically increased VOC and BTEX.

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