ROLE OF ACID AND HEAT STABLE SALT IN THE DEGRADATION PROCESS OF ALKANOLAMINE DURING SOUR GAS SWEETENING PROCESS

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ABSTRACT

The formation of several acids and heat stable salt in the sour gas absorption process are common phenomenon. Amines are basic in nature, which react easily with the acidic components to form heat stable salts and other degradation products. Heat stable salt and degradation products are problematic in the operation of CO₂, H₂S removal unit, they reduce the solvent capacity to absorb CO₂ and H₂S, cause corrosion, foaming and solvent losses. This paper gives an insight on the degradation of amine solvent due to these acidic components and highlights the latest findings on the formation of heat stable salt. This paper also focused some research work carried out in this area of study.

Keywords: Acid; Degradation; Amine; Alkanolamine; Absorption; Heat stable salt.

NOMENCLATURE

NG  Natural gas
DIPA  Di-isopropanolamine
DEA  Diethanolamine
MDEA  Methylene diethanolamine
MEA  Monoethanolamine
DGP  Degradation products
DGA  Diglycolamine
HSS  Heat stable salts
HSAS  Heat stable amine salts
AMP  Aminomethyl propanol
HEP  Hydroxyethyl piperazine
BHEED  N,N-Bis(hydroxyethyl) ethylenediamine
BHEP  N,N-Bis(hydroxyethyl)-piperazine
HEOD  Hydroxyethyl-oxazolidone
THEED  N,N,N-Tris(hydroxyethyl)- ethylenediamine
BHEI  N,N Bis (hydroxyethyl)- imidazolidone
BHEEU  N,N-Bis(hydroxyethoxy-ethyl)urea
NMR  Nuclear magnetic resonance
GC-MS  Gas chromatography mass spectrometer
HPLC  High performance liquid chromatography
IC  Ion chromatography
FTIR  Fourier transforms infrared resonance spectrometer
HPLC-RID  High performance liquid chromatography-refractive index detector

1. INTRODUCTION

Amines and alkanolamines are widely used in the natural gas refining for the sweetening of sour gas by absorbing the CO₂ and H₂S acidic gases. During the absorption process amine are highly degraded by this acidic oxide as a result amine loses its capacity to absorb these acidic gases. All acidic gases of natural gas composition play an important role to form amine to aldehyde and acids. Oxygen directly oxidized the amine and converted into carbonyl compounds like aldehyde or ketone or acid compound. Aldehydes react with water; in aqueous solution of formaldehyde is hydrated (Singh, 1969). Aldehydes also react readily with primary amines. These reactions would not be significant with tertiary amines. In aqueous solution of monoethanolamine, formaldehyde will be present as an equilibrium mixture primarily in the form of imine with some hydrated aldehyde, carbinolamine, and aminal. Similar reactions can occur with other aldehydes such as hydroxyacetdehyde. The imine formed from primary or secondary amines such as MEA may be subject to similar attack by radical oxidants. The presence of formaldehyde may also facilitate the oxidation of the amine molecule. Other less compounds easily hydrated to aldehydes, such as
acetaldehyde and hydroxyacetaldehyde, react at room temperature with oxygen to produce the corresponding organic acid (Denisov, 1977; Sajus et al., 1980). The oxidation usually takes place by a free radical chain mechanism. An initiator extracts a H from the α carbon to produce a free radical. The radical reacts with O₂ to produce a peroxyacid radical. The peroxyacid radical reacts with aldehyde to propagate the reaction with the production of the aldehyde radical and a peroxyacid. So the prevention of amines loss is the major focus of interest for the chemical engineer. The prevention of amine losing by acid is the one of the condition for successful plant operation. This prevention of amine loss is also the key of economical benefit. Hence, to identify the alkanolamines degradations are important. Amine degradation compounds are quantified by chromatographic methods. Identification of degradation products is performed with several analytical methods like GC/MS, IC and HPLC etc. In some cases, synthesis of molecules is necessary to confirm structure of degradation products. The highest molecular weight compounds are identified with a high resolution mass spectrometry technique (FT-ICR/MS) with electrospray ionization (ESI). In some cases, NMR analyses are useful to determine compound structure. Formic, glycolic, acetic and oxalic acids, nitrite and nitrate are quantified by ion chromatography. The role of these acids and degradation path way was critically reviewed and a brief discussion was given by the following representation.

2. AMINE BASED ABSORPTION AND STRIPPING SYSTEM

For over seventy years the alkanolamine process has been considered the best approach in removing H₂S and CO₂ for the purpose of purification and separation. It is based on the reaction between weak acid (H₂S and/or CO₂) and weak base (alkanolamines) to give a water soluble amine acid gas salt. An amine based sour gas sweetening plant was configured with absorber and regenerator. The temperature range is 40-60°C and 100-120°C at the absorber and the stripper respectively. Mainly amine solvents are used as absorbents for sweetening natural gas and for prolong use of this solvent that is transferred to the stripper by means of regenerating absorbed gases. Figure-1 represents a sweetening process of sour gas.

Sour gas components react with amine solvent during absorption-desorption cycles gradually at higher and lower temperature and some of these reactions (Equs. 1-11) are given in the following to show how DGP is formed (Haws, 2010).

\[
\begin{align*}
\text{H}_2\text{S} + \text{HCl} &\rightarrow \text{H}_2\text{S}\text{Cl}_2 + \text{H}_2 \quad \text{(1)} \\
\text{H}_2\text{S} + \text{HCl} &\rightarrow \text{H}_2\text{S}\text{Cl}_2 + \text{H}_2 \quad \text{(2)} \\
\text{NH}_2 + \text{O}_2 &\rightarrow \text{NH}_3 + \text{O}_2 \quad \text{(3)} \\
\text{MEA} + \text{CO}_2 &\rightarrow \text{HME, MEI, THEED} \quad \text{(4)} \\
\text{MEA} + \text{CO}_2 &\rightarrow \text{HME, MEI, THEED} \quad \text{(5)} \\
\text{DEA} + \text{CO}_2 &\rightarrow \text{DEOD, BHEEP, THEED} \quad \text{(6)} \\
\text{BHEEP} + \text{MEA} &\rightarrow \text{BHEEU} \quad \text{(7)} \\
\text{DIPA} + \text{CO}_2 &\rightarrow \text{HMPO} \quad \text{(11)}
\end{align*}
\]

3. BASIC DEGRADATION CHEMISTRY

Degradation products are contaminants in solution that are derived from the breakdown of the base amine molecule and often caused reversibly and irreversibly to form totally different chemical species. Examples of degradation products are ethylenediamine derivatives (THEED) in the case of (Liu), which can form when CO₂, COS or O₂ are in an amine system. The basic chemistry of degradation of alkanolamine is explained in the open literature and these are given below. In the following chemical reaction it is clear that amines occur due to the protonation and carbamate formation.
reaction brought about by the hydrolysis of water and acids.

\[ H_2O \rightarrow H^+ + OH^- \] .......................... (12)
\[ H_2S + H_2O \rightarrow HS^- + H_2O \] .......................... (13)
\[ CO_2 + H_2O \rightarrow HCO_3^- + H^+ \] .......................... (14)
\[ RNH_2 + H^+ \rightarrow RNH_3^+ \] .......................... (15)
\[ RNH_2 + CO_2 \rightarrow RNHCOO^- + H^+ \] .......................... (16)

The same reaction is also explained in the literature (Dawodu and Meisen, 1994; Dawodu and Axel Meisen, 1994; Choy and Meisen, 1980) for DEA degradation. These reactions are as follows. Hydrogen sulfide emitted hydrogen ion (Eq. 17) in water and carbon dioxide as well as carbonyl sulfide and produces COS and HS⁻ respectively (Eq. 18). This reaction causes additional reactions with DEA molecule.

\[ H_2S \rightarrow H^+ + HS^- \] .......................... (17)
\[ CS_2 + H_2O \rightarrow CO_3^2- + H_2O \] .......................... (18)
\[ CO_2 + H_2O \rightarrow CO_3^2- + H_2S \] .......................... (19)
\[ H_2O + CO_2 \rightarrow H^+ + HCO_3^- \] .......................... (20)

DEA molecule directly reacts with CS₂ and successively produces DEA thio carbamate salt (Eq. 21 & 22). On the other hand it produces carbamate with CO₂ (Eq. 24). DEA carbamate reacts with MEA and DEA and forms BHEED and THEED respectively. These two DGP further form BHEI and BHEP with CO₂ respectively. HEOD is one of the familiar DGP of DEA and this is also from DEA carbamate. Protonated DEA molecule reacts with CO₂ and converts into MEA, ethanol and water. The formation of MEA is better for DEA system because the author assume that it has better absorption capacity. It is also assume that any amine system where higher molecular weight compound break down into lower molecular mass amine like MDEA or DEA to MEA that process will rich at the high absorption rate. Alkanolamines are oxidized and form aldehyde or ketone then formed acid. This acid finally forms HSAS. So to protect the formation of HSAS the intermediate reaction should control at first. However there is insufficient information in this connection in the open literature. Ethanol can easily degrade to aldehyde and then an acid. This acid forms various acetate and ester compounds in amine system. An over view of the reaction pathways of DEA are mentioned below.

\[ DEA + CS_2 \rightarrow DEA_{thio carbamate} \] .......................... (21)
\[ DEA_{thio carbamate} + DEA \rightarrow DEA_{thio carbamate} salt \] .......................... (22)
\[ DEA + H^+ \rightarrow DEA^+ \] .......................... (23)
\[ DEA + CO_2 \rightarrow DEA_{carbamate} \] .......................... (24)
\[ DEA^+ + CO_2 \rightarrow DEA + CO_3^2- \] .......................... (25)
\[ DEA + H^+ +MEA \rightarrow BHEED + CO_2 + H_2O \] .......................... (26)
\[ DEA + H^+ + DEA \rightarrow THEED + CO_2 + H_2O \] .......................... (27)
\[ THEED + CO_2 \rightarrow BHEP + CO_2 + H_2O \] .......................... (28)
\[ DEA + H^+ \rightarrow DEA^+ + H_2O \] .......................... (29)
\[ MEACOOH + MEA \rightarrow MEACOOH + MEA + H_2O \] .......................... (30)
\[ BHEED + CO_2 \rightarrow BHEE + H_2O \] .......................... (31)

4. ACID FORMATION REACTION IN AMINE SYSTEM

The reaction in this scheme was proposed to account for the presence of all the anions observed in this study. This acid formation mechanism could be applied to any alkanolamine. Also, it was noted that although the acid form of acetic, formic, glycolic, glyoxylic, and oxalic acids are shown in the following reaction, each of these anions are almost completely ionized to the amine heat stable salt in basic solutions. The literature (Rooney and Daniels, 1998) cited a oxidation reaction of MEA which are as follows.

5. TYPICAL HSS IN AMINE SYSTEM

Heat stable salt (HSS) formation is another form of active amine loss. The amine and an acid form a salt that cannot be regenerated in the stripper (The Dow Chemical Company, ; Kennard and Allelsen, 1985). Strong acid anions such as formate, acetate, thiosulfate, thiocyanate, and chloride can tie up an amine molecule to form a salt that is not capable of being regenerated by the addition of heat and are thus referred to as Heat Stable Salts. Not only do they tie up the amine and thereby reduce the acid gas carrying capacity, but they are also considered corrosive. However, there is still a considerable amount of
confusion in the industry over the term “Heat Stable Salt”. Many times the term is used in a generic sense to mean “contaminant”, while in fact it is only one type of amine contaminant, and may not even be the most offensive contaminant. New engineers assigned to amine and sulfur plant areas, then often assume that the only contaminants in their amine system are the Heat Stable Salts. This idea can be reinforced when lab analyses show only Heat Stable Salt contaminants, but do not report other types of contaminants such as degradation products.

Table 1 Common HSS species in amine system (Stewart and Lanning, 1994)

<table>
<thead>
<tr>
<th>Name of Ions</th>
<th>Chemical Formula</th>
<th>Origin of HSS anions</th>
<th>Limit, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>NO₃</td>
<td>Inorganic</td>
<td>-</td>
</tr>
<tr>
<td>Nitrite</td>
<td>NO₂</td>
<td>Inorganic</td>
<td>-</td>
</tr>
<tr>
<td>Formate</td>
<td>CHO₂</td>
<td>Organic</td>
<td>500</td>
</tr>
<tr>
<td>Oxalate</td>
<td>C₂H₂O₄</td>
<td>Organic</td>
<td>250</td>
</tr>
<tr>
<td>Acetate</td>
<td>C₂H₄O₂</td>
<td>Organic</td>
<td>1000</td>
</tr>
<tr>
<td>Sulfate</td>
<td>SO₄</td>
<td>Inorganic</td>
<td>500</td>
</tr>
<tr>
<td>Sulfite</td>
<td>SO₃</td>
<td>Inorganic</td>
<td>500</td>
</tr>
<tr>
<td>Phosphate</td>
<td>PO₄</td>
<td>Inorganic</td>
<td>-</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>S₂O₃</td>
<td>Inorganic</td>
<td>10,000</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>CNS</td>
<td>Inorganic</td>
<td>10,000</td>
</tr>
<tr>
<td>Glycolate</td>
<td>C₂H₄O₁</td>
<td>Organic</td>
<td>500</td>
</tr>
<tr>
<td>Malonate</td>
<td>C₂H₄O₂</td>
<td>Organic</td>
<td>500</td>
</tr>
<tr>
<td>Succinate</td>
<td>C₂H₄O₄</td>
<td>Organic</td>
<td>1000</td>
</tr>
<tr>
<td>Chloride</td>
<td>Cl</td>
<td>Inorganic</td>
<td>500</td>
</tr>
</tbody>
</table>

6. AMINE SPECIFIC DEGRADATION PRODUCTS BY ACID

While Heat Stable Salts (HSS) are common to all amine solvents, degradation products are solvent-specific (Meisen, 1996; Cummings et al., 1997; Rooney et al., 1996; Liu, 1995). A description of common degradation products found in various gas treating solvents follows.

6.1 Formamides

N-formyl amines (formamides) are degradation products generally found in gas treating solutions that are based on primary and secondary amines (Koike, 1987). Under certain conditions all primary and secondary amines react with the formic acid in solution (via dehydration) to form n-formyl amines. The data from process solutions containing formate as a HSS anion show that the following equilibrium relationship exists in the solution between the formate HSS and the n-formyl MEA (MEA-F) (HCTT, 1999).

\[
\text{Formic Acid} + \text{MEA} \rightleftharpoons \text{MEA-F} + \text{Water}
\]

Since the above equation represents equilibrium, it is also possible to hydrolyze MEA-F back into MEA and formic acid. The heat and water present in the stripper of the amine unit will generate a new equilibrium if removing one of the above components disturbs the balance of the equation.

6.2 HEED

Hydroxyethylethlenediamine (HEED) is a degradation product of MEA from reactions with CO₂. There is a wealth of literature on the reaction mechanisms and the corrosive nature of HEED (McCullough, 1996). While much of the literature has focused on MEA in CO₂ service only, HEED has been found in many combined systems treating H₂S and CO₂.

6.3 HEEU

Hydroxyethylethyleneurea (HEEU) is a degradation product of MEA that is not that well known since most of the literature has focused on MEA in CO₂ service only, HEED has been found in many combined systems treating H₂S and CO₂.

6.4 Polymers

We generally find polymers when HEED, is present in MEA systems treating H₂S and CO₂. These polymers are formed from the reaction of HEED with MEA molecules to make longer chained ethylenediamines (Holub, 1998). We also find polymers when THEED is present in DEA systems treating H₂S and CO₂ (Holub, 1998).

6.5 BHEEU

N,N bis(hydroxyethoxy-ethyl)urea (BHEEU) is an inert degradation product of DGA which formed in the presence of COS and CO₂ (Kohl and Nielsen, 1997). Formation of BHEEU can be reversed by thermal reclaiming.

6.6 Morpholine

This is an inert degradation product of DGA that, while rare, can occur when the solution is subjected to high temperatures.

6.7 THEED

Tris-hydroxyethyl ethlenediamine (THEED) is a well-known degradation product of DEA from
reactions with CO\textsubscript{2}. There is a wealth of literature on the reaction mechanisms and the corrosive nature of THEED (McCullough, 1996; Kohl and Nielsen, 1997). While much of the literature has focused on DEA in CO\textsubscript{2} service only, THEED has been found in combined systems treating H\textsubscript{2}S and CO\textsubscript{2}.

6.8 Bis-HEP

Bis-hydroxyethyl piperazine (bis-HEP) is a well-known degradation product of DEA from reactions with CO\textsubscript{2}. There is a wealth of literature on the reaction mechanisms of bis-HEP (Kohl and Nielsen, 1997; McCullough, 1996). While much of the literature has focused on DEA in CO\textsubscript{2} service only, bis-HEP has been found in combined systems treating H\textsubscript{2}S and CO\textsubscript{2}.

6.9 MEA

In the presence of certain chemical compounds (oxygen) or intermediates, it is possible to degrade or break down the DEA molecule to simpler amines. Monoethanolamine (MEA) is one of the simpler amines that may be formed from DEA degradation. It is important to monitor the level of MEA in the circulating DEA system due to Amine Stress Corrosion Cracking (ASSC) concerns associated with MEA. MEA will also generally further degrade in the system leading to concerns with the compounds reviewed above.

6.10 Bicine

Bis-(hydroxyethyl) glycine (Bicine) is a degradation product formed in the presence of DEA and unstable chemical intermediates, and is considered corrosive (Cummings, 1997; Howard, 2001).

6.11 DIPA-OX

Hydroxypropylmethyloxazolidone (HPMO or DIPA-OX) is a well-known degradation product of DIPA from reactions with CO\textsubscript{2}. There is a wealth of literature on the reaction mechanism of DIPA-OX (McCullough, 1996; Kohl and Nielsen, 1997; van Grinsven, 1999). The literature also states that DIPA-OX is the endpoint of DIPA degradation in CO\textsubscript{2} service (due to steric hindrance), so polymers of DIPA are not supposed to be formed like they are with MEA and DEA.

6.12 MDEA Fragments

MDEA in Tail Gas Treating units (TGTU), Acid Gas Enrichment units (AGE), and in some main amine systems should be monitored for MDEA fragments. These include MMEA, DEA, Bicine and C\textsuperscript{2+} HSS anions (Critchfield, 1999). It is also important to note that as ethanolamines (from MDEA degradation) accumulate in the solvent, they will generally undergo further degradation to compounds listed in the above sections. The presence of these primary and secondary amines may affect the gas treating selectivity of the amine solution.

6.13 Dimers

The literature states that steric hindrance prevents further degradation of DIPA-OX to diamines (“dimers”). However, we generally do find dimers in Sulfinol-D systems treating H\textsubscript{2}S and CO\textsubscript{2}. These “dimers” are similar to the diamines found in MEA and DEA systems, and are likely formed via the same pathway.

6.14 TIPA

Triisopropanolamine (TIPA) may be found in systems treating H\textsubscript{2}S and CO\textsubscript{2} utilizing Sulfinol-D, when evidence of oxygen degradation is present. Literature shows that when amines degrade they generally form simpler amines, but sometimes these simpler amines react with the base amine molecule (or others) to form a more complex amine (Chakma, 1997).

7. COMMON DEGRADATION PRODUCTS AND THEIR EFFECT

All alkanolamine degradation products are not same in behavior, some of these are acidic and some of these are alkaline based. Depending on the nature of the degradation products these are classified as follows.

7.1 Acidic degradation product

Acidic degradation products are highly corrosive for plant unit, thus metallic unit of the gas sweetening plant is highly interactive by this product. So the acidic degradation products are very harmful among all degradation products. Heat stable salts are the common degradation products of amine stripping system and these are potentially corrosive. All of these amines degraded and formed carboxylic acids. These acids are capable of causing further chemical reaction with
miscellaneous degradation products. By this reaction the concentration of contaminants increases continuously during absorption-desorption cycles and finally shows operational problems.

7.2 Basic degradation product
The alkaline degradation products are less corrosive than acidic or some of these are noncorrosive but both still have a bad impact on plant operation or even the neutral DGP has the same effect too. It increases the viscosity and as a result it highly inhibits the solution flow rate. This lower flow rate should affect the efficiency of the plant (Haws and Jenkins, 2000). To accelerate the plant lower flow rate to satisfactory flow rate, high energy consumption is required. For this reason no degradation products are expected.

7.3 Ionic degradation product
The degradation product which contains charge at the chain end and it may be positive or negative these are defined as ionic degradation products. The literature is cited its effect on the plant performance (Dawodu and Meisen, 1996; Supap et al., 2006; Thitakamol et al., 2009). Ionic degradation products are more prone to affect the plant performance because it is easily react with the components and form miscellaneous reaction products.

7.4 Polymeric degradation product
Many articles reflect a lot of information on polymeric degradation products but there is no specific polymer formation degradation reaction (Dawodu and A. Meisen, 1996; Lepaumier et al., 2009; Lepaumier et al., 2010). Polymeric degradation products identified by GC-MS detection may be neutral or living. Living polymer means it contains a functional group at the chain ends of the molecule which are capable of causing further chemical reaction with acidic oxide or any reactive unit. The literature cited very inadequate information regarding the polymerization reaction mechanism though it has a satisfactory detection report. Wide ranges of research on polymerization reaction are suggested to recover this literature gap. Literature (Wenten, 2010) focused that THEED, Bicine, HSS, HE-Sarcocine, HEED, HEOD, BHEED and THEED are corrosive compounds (Bedella, 2009; Dawodu and A. Meisen, 1996). Actually these are corrosive because all of these are acidic or basic or contain a living functional group or oxazolidone ring at the chain end or in its structure.

7.5 Neutral Degradation product
Neutral degradation products having no active functional group are very harmful for fouling effect. These degradation products are inactive and just move towards the entire solution direction. It also makes the solution more viscous. Neutral degradation products having no movement so there is a great probability to adhering with plant pipelines, as a result that place easily corrode or destroy. Carl and Haws studied the effect of neutral degradation products (Carlson et al., 2001).

7.6 Volatile degradation product
Volatile degradation products are highly harmful to the environment. Generally these gases cause green house effect, world climate change and so on. The effects of the amine were well conducted in the literature (Eide-Haugmo et al., 2009) last year.

The foaming behavior of degradation products was conducted by Thitakamol and Veawab (Thitakamol and Veawab, 2008; Thitakamol et al., 2009). Corrosion behavior of degradation products were conducted by Dawodu and Meisen (Dawodu and A. Meisen, 1996) and also conducted by the following researchers (Franco et al., 2009; Bedella, 2009; Eide-Haugmo et al., 2009). The recent article (Bedella, 2009) pointed out several problems which occurred due to irreversible degradation reaction.
8. CONCLUSIONS

During the sour gas sweetening process a lot of solvent are losses by amine degradation. The degradation products arises various difficulties and as a result the remediation of this problem has become a major focus of interest for the last few decades. HSAS neutralization techniques (vacuum distillation, electrodialysis, ion exchanges) are still being developed to improve plant efficiencies and operation problems. The literature mostly cited the heat stable salt and its minimization. HSAS are basically the reaction products of acid and amine. Amine is the main solvent; on the other hand an acid is the by product, if we control the acid formation in amine system then automatically reduces the HSAS formation. Acids are also can be converted as acid amides by adding some additives. Because amides are contains -CONH₂ functional group this is capable to capture more acidic gases. So we need further research on it to recover the research gap. The author suggested the acid remediation by converting into amides compound. Author also would like to put emphasis for the minimization of the acidic content inside the solution. Knowledge of the reaction mechanism aids the development of procedures to minimize degradation or purify partially degraded solutions. Therefore, the overall representation would help to understand the role of acids and heat stable salt on amine degradation.

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REFERENCES


