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Methods for Thermal Stability of ALKANOLAMINE Salts (Review)

Anvarova Iroda Anvarovna, Khayitov Jonibek Kurbanovich

Assistant Karshi Institute of Engineering and Economics, Republic of Uzbekistan,Karshi
AssociateProfessor Karshi Institute of Engineering and Economics, Republic of Uzbekistan,Karshi

ABSTRACT: This research paper studies and analyzes the mechanisms of decomposition of amine solutions used in the process of cleaning natural gases from H_2S and CO_2 under the influence of various environments. It is known that during the decomposition of alkanolamines, various organic aldehydes and acids are formed. As a result, under the influence of these acids, various thermally stable salts are formed in the composition of alkanolamines. During gas cleaning, an increase in the content of thermally stable salts in the amine solution reduces the efficiency of the process. Therefore, there are several technologies for separating these thermally stable salts: alkalization of amine solutions with a strong base, thermal regeneration, ion exchange and electrodialysis. Many scientific studies were analyzed to study the advantages and disadvantages of the above cleaning methods.

KEYWORDS: TSS-thermally stable salts, oligomeric destruction, electrodialysis, bipolar ion, sorption, alkanolammonium carbamate, degradation, cyclization, expansion gases, MEA-monoethanolamine, reboiler device, thermal destruction.

I.INTRODUCTION

Natural gas contains acidic components - hydrogen sulfide and carbon dioxide, and the content of these acidic components in natural gas extracted from different fields can vary and can be up to 10 percent. Hydrogen sulfide and carbon dioxide are toxic substances; therefore, they are purified based on regulatory requirements before delivery to consumers. [1]

The chemical structure of alkanolamines includes two polar functional groups connected by a chain of ethylene groups. The amino group chemically interacts with the CO_2 molecule, and the hydroxy group -OH provides sufficiently strong intermolecular bonds and a low saturated vapor pressure. Currently, the interaction of CO_2 with aqueous solutions of primary [monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), diglycolamine (DGA), cyclic diamine piperazine (PDA)] and secondary alkanolamines [diethanolamine (DEA), diisopropanolamine (DIPA)] proceeds by two different mechanisms: [2]

1. The “bipolar-ion” mechanism, first proposed by Caplow [3] and Danckwerts [4];
2. The “three-molecular” mechanism, proposed by Crooks and Donnellan [5].

According to the three-molecular mechanism, the release of CO_2 occurs as a result of chemical reactions in the following:

$$CO_2+R_1R_2NH \rightleftharpoons R_1R_2NCOOH, (1)$$

$$R_1R_2NCOOH + R_1R_2NH \rightleftharpoons R_1R_2NCOO^- R_1R_2H_2N^+, (2)$$

$$CO_2 + R_1R_2NH \rightleftharpoons R_1R_2NH^+ - COO^-, (3)$$

$$R_1R_2NH^+ - COO^- + B \rightleftharpoons R_1R_2NCOO^- + BH^+. (4)$$

Here: R_1 — CH_2CH_2OH, R_2 — H (monethanolamine diethanolamine.

The formation stage of alkanolammonium carbamate R_1R_2NCOO- $R_1R_2H_2N$+ is followed by an intermediate stage of formation of a bipolar – ion (2) , which is then deprotonated by the base “B” (4). In addition to ethanolamine molecules, water molecules and hydroxide ions can also act as the base “B”.

One of the main problems of separating hydrogen sulfide and carbon dioxide from gases using aqueous solutions of alkanolamines is the destruction of the absorbent and its loss of sorption properties under process conditions due to side chemical reactions. In the analysis of the literature, a division of these phenomena into thermal and thermochemical

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(thermooxidative) degradation has been developed [6-7]. First of all, it consists in the cyclization of amine anions to form oxazolidone, which, when reacted with alkanolamine, forms amine dimers and forms trimers.

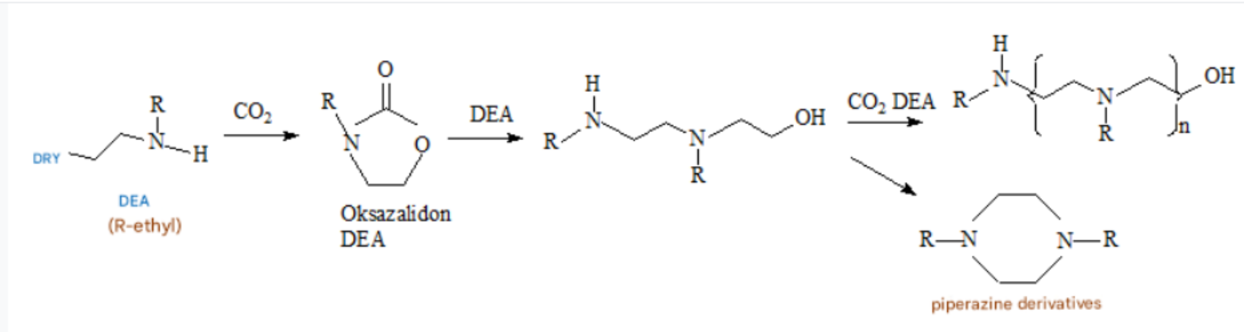

Figure 1. Scheme of thermochemical degradation reactions of diethanolamine

The increase in the amount of thermally stable salts remains in the amine solution in the system during the production process and leads to a significant decrease in the sorption process. It should be noted that all alkanolamines used to remove H_2S and CO_2 from expander gases form carboxylic acids and TSS [8]. The scheme of the MEA degradation reactions to form carboxylic acids is shown in Figure 2.

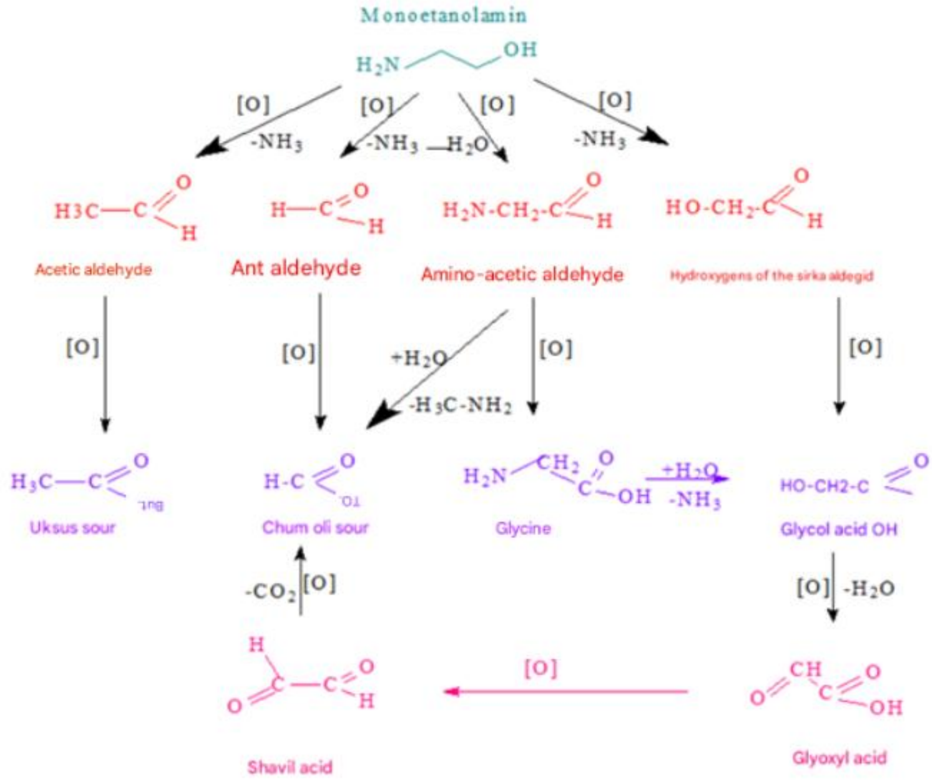

Figure 2. Stages of thermal destruction of monoethanolamine

II. METHODOLOGY

Currently, there are a number of technological solutions for the separation of TSSs from alkanolamine absorbents in the industry. These methods were developed in the 70-90s for the cleaning of absorbents used in natural gas processing. Currently, these methods can be adapted to systems for restoring the sorbent properties of alkanolamines when cleaning expander gases from H_2S and CO_2 gases and for cleaning them from thermally stable salts. One of the simplest methods for cleaning alkanolamine solutions from TSSs is to alkalize amine solutions with a strong base. The addition of alkali

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increases the pH of the system, the OH- ion dissociates the proton from the alkanolammonium cation, and the metal cation binds the TSS anion. Hydroxides, carbonates, and hydrogen carbonates of alkaline metals are used as bases.

$R_1R_2R_3HN^+HCOO^- + NaOH \rightleftharpoons R_1R_2R_3N + NCOONa + H_2O$

$R_1R_2R_3HN^+HCOO^- + Na_2CO_3 \rightleftharpoons R_1R_2R_3N + NCOONa + NaHCO_3$

$R_1R_2R_3HN^+HCOO^- + NaHCO_3 \rightleftharpoons R_1R_2R_3N + NCOONa + H_2O + CO_2$

here: R_1= $-CH_2CH_2$, R_2, R_3 = $-H$, $-CH_3$, $-CH_2CH_2OH$.

Thermal regeneration (distillation)

Thermal regeneration is a thermal process that accelerates the regeneration of spent alkanolamine solutions. According to the regeneration scheme, the amine solution is fed from the bottom of the desorber to a steam-heated reboiler, and a 1-5% solution from the reboiler cube is fed to a second reboiler heated by high-pressure steam. This device is equipped with a droplet catcher and a filter. An alkaline solution is added to this reboiler, allowing the removal of residues from the bottom.

The temperatures of the thermal regeneration process depend on the type of alkanolamines, which differ in their resistance to thermal destruction. MEA and DEA are thermally stable at temperatures up to 150 and 175°C, respectively, while tertiary MDEA does not decompose at temperatures up to 182°C[9]. However, the boiling points of secondary and tertiary alkanolamines at atmospheric pressure reduce their thermal destruction temperatures, so vacuum distillation must be used in this case.

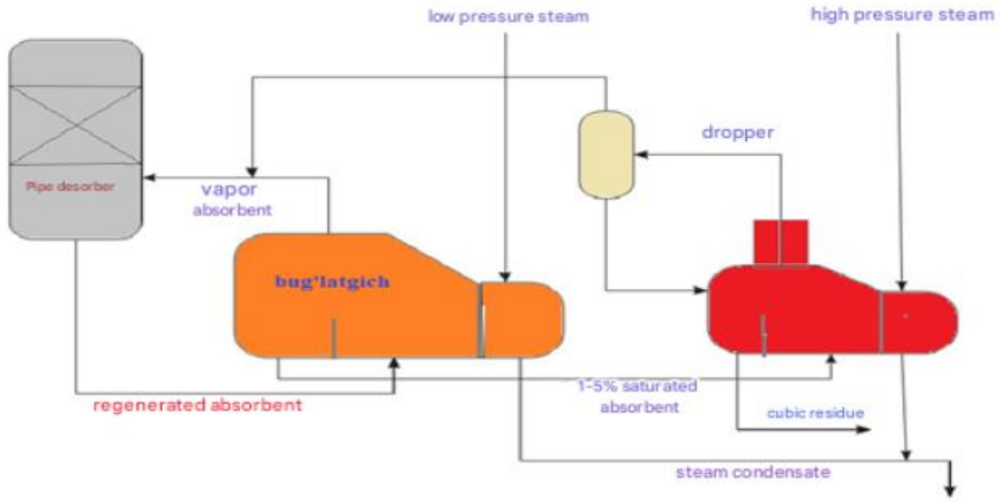

Figure 3. Schematic of the thermal regeneration process.

Ion exchange method

The ion exchange process is based on the interaction of the components of the alkanolamine solution and the solid (strong base ion exchange resin containing hydroxide ions) phases. In this process, the alkanolamine solution is passed through a bed of ion exchange resin pre-treated with a strong base (NaOH or KOH). In this case, the TSS anions from the solution are exchanged for the hydroxide ions of the resin, and the sorption properties of the solution are restored. The typical ion exchange process consists of two stages, which are represented by the following reactions (for example, tertiary alkanolammonium formate): The first stage is the working cycle, during which TSS salts are removed from the absorbent medium:

$R_1R_2R_3HN{+}HCOO^- + [R]{+}OH^- \rightleftharpoons R_1R_2R_3N + [R]{+}HCOO^- + H_2O;$

The second stage is the ion exchange resin regeneration cycle:

$[R]{+}HCOO^- + Na^+OH^- \rightleftharpoons [R]^+OH^- + Na^+HCOO^-$

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here: R_1 = $–CH_2CH_2OH$, R_2, R_3 = –H, $–CH_3$, $–CH_2CH_2OH$, $[R]^+$ - ion coating with a fixed charge.

The regeneration stage consists of treating the ion exchange resin with a strong base to replace the anions of TSSs with hydroxide ions by washing the resin with demineralized water. In this case, the simple salts formed in the form of solutions are sent for disposal.

Electrodialysis method

Electrodialysis is the process of transferring ions through ion-exchange membranes under the influence of an electric potential gradient in special devices - electrodialyzers. In a typical electrodialyzer, two types of membranes are used: anion-selective anion-permeable membranes are replaced by cation-selective cation-permeable membranes, forming a membrane package located between two electrodes (anode and cathode).

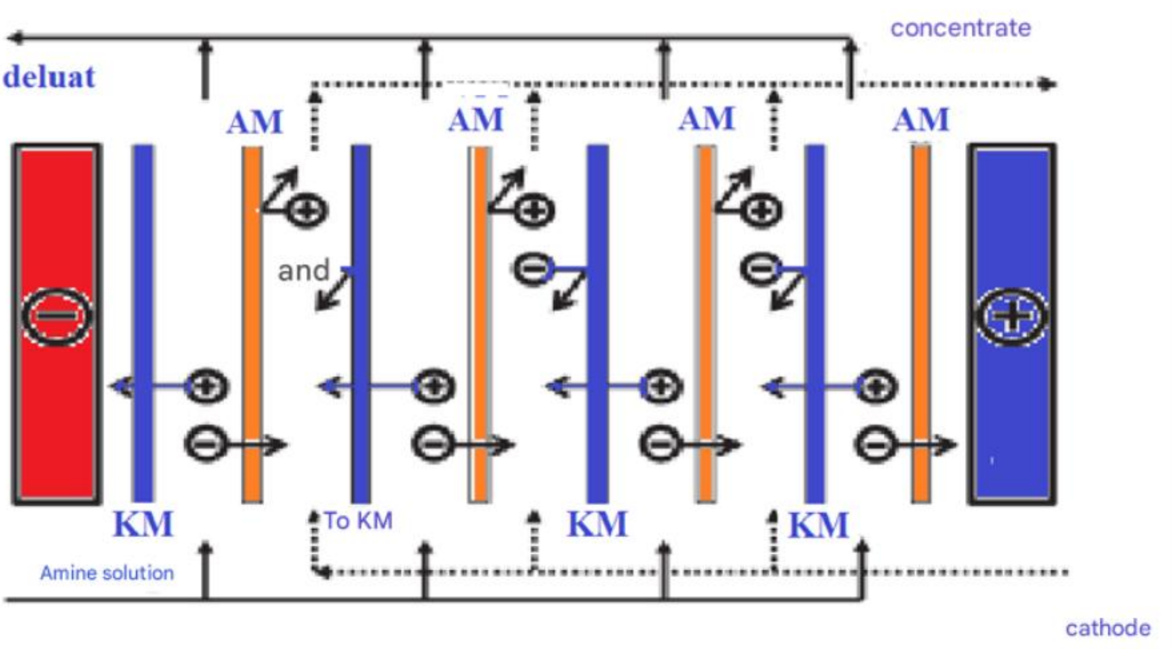

Figure 4. The principle of electrodialysis.

AM-anion exchange membrane, KM-cation exchange membrane

The installation of membranes and the use of special gaskets allows the creation of concentration and desalination chambers. The electric current generated by creating an external electric potential gradient transfers cation from the desalination chamber through a cation exchange membrane to the concentrated acidic solution chamber on the cathode side. At the same time, the removed cations are retained in this chamber by an anion exchange membrane on the cathode side. At the same time, TSS anions enter the acidic solution chamber on the anode side through the anion exchange membrane in the opposite direction and are retained by the cation exchange membrane on the cathode side. The solution (diluate) purified from ions leaves the apparatus.

Advantages and disadvantages of methods for separating heat-resistant salts A comparison of the characteristics of methods for purifying alkanolamines from TSS, their advantages and disadvantages are presented in the table.

Features	Thermal regeneration to make (distill)	Ion exchange method	Electrodialysis method
The process creators and license right	CCR technology , Gazprom VNIIGAZ LLC	Eco -Tec, MPR services	UCARSEP, Electrostep
Waste types	Toxic , anhydrous	Juicy	Harmless , watery
Waste amount	Low (general) 5-15% of the amount)	High (40-50% overall amount)	Average in quantity

Necessary chemical reagents	Stoichiometric amount sodium hydroxide NaOH	Smolani regeneration for NaOH, H_2SO_4	Stoichiometric amount of NaOH ratio or his/her lack
Elementary to the solution to be placed requirements	Elementary solution basics with alkalization	Solution cooling (up to 40-60°C)	Solution basis with alkalization and cooling (up to 40-60°C)
Recovery rate of amines	>85%	99%	98%
Energy consumption for the process	High	Less	Medium
Advantages	TSSs high at the level concentration; alkaloamines all degradation products separation	TSS low alkali with solutions again work for effectively-purified amine -containing of salts very low concentration achieved; low energy expense	Ions own inside received solutions for effective; chemical reagents less consumption to make ; membrane to technology typical was compactness and modularity
Disadvantages	High energy expense and price ; additional thermal to decompose ; to waste alkanolamine big waste disposal toxicity	Process big in size H_2S , CO_2 substances catch processes expensive falls ; ion interchangeable resin poisoning , pollution and thermal degradation ; their update for reagents big expense	Relatively large amounts of waste; limited membrane lifetime due to high pH values of amine absorbents; membrane fouling and thermal degradation

As can be seen from the data presented in the table, the main advantages of thermal regeneration (distillation) of amines are the ability to purify the decomposition products of alkanolamines not only from TSS, but also from high-boiling degradation products, as well as the formation of high-concentration waste.

The ion exchange method, compared with thermal regeneration (distillation), allows for the separation of high TSS with relatively low energy consumption (up to 1%) due to the absence of phase transitions in the system, with low loss of alkanolamine (more than 90% is recovered).

The electrodialysis method, compared with ion exchange, consumes more energy, the amount of waste of this method is higher than thermal distillation. Some limitations of this method include the high cost of developing and manufacturing new selective ion exchange membranes that are resistant to high pH values of alkanolamine absorbers [10], since many existing membranes change their properties when exposed to an alkaline environment at high temperatures. [11]

III.CONCLUSION

The most common method is the purification of natural gas from hydrogen sulfide and carbon dioxide using aqueous solutions of various alkanolamines (primarily monoethanolamine) using various technological processes. However, this process has some drawbacks, as a result of the interaction of alkanolamine with oxygen or acidic components of the gas, thermochemical or thermooxidative destruction of the carbonized amine occurs at high temperatures (110-140°C) of the regeneration stage with the formation of thermally stable salts. The most common methods for purifying thermally stable salts and other destruction products are purification by alkalization or distillation of the absorbent, or, as the most expensive option, its complete replacement.

Alternative methods for separating TSS are ion exchange on ion exchangers and electrodialysis of the solution. The distillation method allows purifying alkanolamine not only from TSSs, but also from uncharged oligomeric destruction products with a high boiling point. However, it requires energy and produces large amounts of toxic waste. Ion exchange and electrodialysis consume less energy, the equipment for their implementation is simpler, and the waste is harmless and small. However, these methods do not allow the separation of uncharged products of the decomposition of alkanolamines. Thus, each technology has its own advantages and disadvantages.

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