Determination of Hydrogen Sulfide and Carbon Dioxide in Amine Solutions in Various Units

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Abstract. This paper presents a comprehensive study of the processes involved in the absorption treatment of natural gas to remove acid gas components using aqueous solutions of diethanolamine (DEA). The work is based on the experimental determination of the content of acid gases, primarily carbon dioxide (CO_2) and hydrogen sulfide (H_2S), in the amine solutions during their absorption and subsequent regeneration. Based on the experimental data, the mass and molar fractions of carbon dioxide and hydrogen sulfide (% W and % mol) in the rich and regenerated diethanolamine were determined, which allows for an assessment of the absorbent regeneration efficiency and the degree of its recovery for reuse. The obtained results are of significant practical importance for optimizing industrial gas treatment units, enhancing the energy efficiency of absorption and regeneration processes, and improving the environmental performance of natural gas systems.

INTRODUCTION

The selection of a process for purifying natural gas from sulfur compounds depends on many factors, the main ones being: the composition and parameters of the raw gas, the required degree of purification and the intended use of the sales gas, its availability, as well as the parameters of energy resources, production waste, etc. An analysis of the accumulated global experience in natural gas purification to date shows that the main processes for treating large gas streams are absorption processes using chemical and physical absorbents and their combinations. The most widely used chemical absorbents are alkanolamines. The use of chemical solvents is based on a chemical reaction between the chemical absorbent and the acid components. The maximum absorption capacity of aqueous solutions of chemical absorbents is limited. Research has shown that among alkanolamines, monoethanolamine and diethanolamine are the most widely used [1-2].

In the modern oil and gas industry, issues of environmental and technological safety are becoming increasingly important. Amine-based processes for removing acid gas components hold a special place among industrial absorption methods, as they ensure a high degree of hydrogen sulfide (H_2S) and carbon dioxide (CO_2) removal. Diethanolamine (DEA) has found the widest application and is used in aqueous solutions of varying concentrations. Due to its physicochemical properties, DEA ensures stable operation of process units and a high level of gas purification. However, during long-term operation, chemical degradation of the absorbent, formation of by-products, and accumulation of heat-stable salts are inevitable, which significantly reduces the efficiency of the entire process [3-5].

Hydrogen sulfide and other sulfur compounds contained in natural gas are toxic components that are extremely hazardous to human health and the environment. Their presence in fuel leads to the formation of sulfur dioxide (SO_2) during combustion, which causes acid rain, corrosion of structures, and has a negative impact on ecosystems. Therefore, the removal of acid impurities from gas is not only an industrial task but also an environmental one [6].

At large gas processing plants, particularly at the facilities of the ShGKhK (Surgut Gas Processing Plant), a 30-33% DEA solution is used. The use of this specific amine is explained by its several advantages: high solubility in water and low solution viscosity; effective binding of H_2S and CO_2 at different pressures and temperatures; and relatively low hydrocarbon absorption, which allows for obtaining high-purity acid gas for further sulfur production. However, along with its benefits, the process also has a number of drawbacks. The most serious among them are amine degradation, the formation of heat-stable salts, and foaming, which leads to excessive consumption of the expensive absorbent and disruption of the technological regime [7,8].

METHODOLOGY

Amine gas treating is widely used in the oil and gas industry today. Aqueous solutions of ethanolamines allow for the removal of hydrogen sulfide, carbon dioxide, and partially mercaptans and other sulfur compounds from natural gas. Depending on the technological objective, different alkanolamines can be used for natural gas purification [9-11].

The need to remove acid gases (H_2S and CO_2) from the natural gas stream is determined by their ability to exhibit corrosiveness in the presence of water, especially at high temperatures, and also by the formation of CO_2 clathrate hydrates in the methane recovery unit. The process of removing H_2S and CO_2 impurities from natural gas is carried out by the method of selective absorption (chemical absorption) of the acid gases by a liquid absorbent [2-3]. As a result, the absorbed substances form chemical compounds with the absorbent and transfer from the gas mixture into the liquid phase.

The following reactions occur in the liquid phase as a result of the interaction of the gaseous substances H_2S and CO_2 with the diethanolamine (DEA) solution:

$$\begin{gathered}(CH_2CH_2OH)_2HN + H_2S \leftrightarrow [(CH_2CH_2OH)_2NH_2]\,HS \leftrightarrow \\ \leftrightarrow [(CH_2CH_2OH)_2NH_2]^+ + HS^- \\ (CH_2CH_2OH)_2HN + CO_2 + H_2O \leftrightarrow [(CH_2CH_2OH)_2NH_2]\,HCO_3 \leftrightarrow \\ \leftrightarrow [(CH_2CH_2OH)_2NH_2]^+ + HCO_3^-\end{gathered} \tag{1}$$

Experimental tests were conducted in the laboratory of the Shurtan Gas Chemical Complex according to the corporate standard Ks 39.2-36:2012. This standard establishes the procedure for determining the amount of carbon dioxide in amine solutions used in process units for purifying natural gas from acid gas components using amines. The standard is applied during natural gas processing and in the work of chemical laboratories analyzing rich and regenerated solutions of diethanolamine or methyldiethanolamine used in the amine section of gas treatment plants' absorbers. It specifies a volumetric method for determining the amount of carbon dioxide in amine solutions.

The essence of the volumetric method for determining the amount of carbon dioxide in an amine solution containing both carbon dioxide and hydrogen sulfide lies in measuring the volume of carbon dioxide released into the gas phase when the amine solution reacts with a solution of copper sulfate in an acidic medium [12,13]. In this process, hydrogen sulfide is converted into copper sulfide, which is insoluble in water.

The main requirements for the measurement conditions pertain to environmental parameters that affect the accuracy of the measurements. These environmental parameters must comply with the standards specified in Table 1.

TABLE 1. Environmental Parameters

Parameter name	Norm
Ambient temperature, °C	
a) when taking samples	-50
b) when conducting analyses indoors	12-37
Relative humidity should not exceed %	78-80
Atmospheric air pressure, kPa	83,0-107,8
Amount of aggressive gases and vapors	within sanitary standards
Temperature of the test solution, °C	12-37

RESULTS

Measurement Procedure. Assemble the laboratory apparatus shown in Figure 1.

The laboratory apparatus consists of a 100 cm³ reaction flask with a two-way tap and a rubber tube, a 0.2 cm³ graduated pipette, a 250 cm³ conical flask sealed tightly with a rubber stopper, and a leveling vessel filled with a saturated sodium chloride solution. A 5-10 cm³ beaker is placed inside the flask [14].

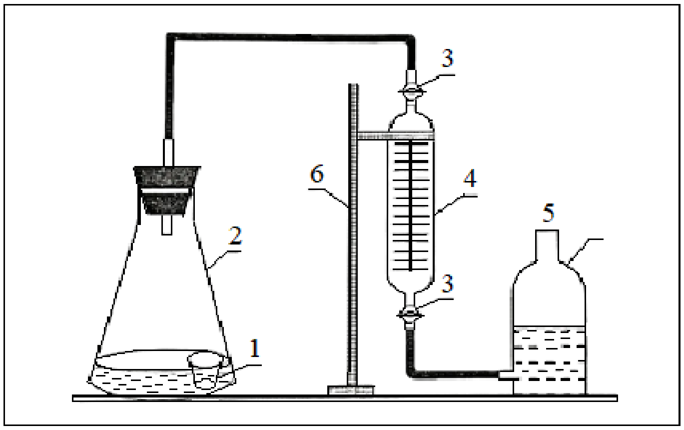

FIGURE 1. Determination of Carbon Dioxide in the Amine Solution.
1 - Beaker for amine solution, 2 - Reaction flask, 3 - Two-way tap, 4 - Gas burette, 5 - Leveling vessel, 6 - Stand.

The measurement method is based on the reaction of the amine solution, containing carbon dioxide and hydrogen sulfide, with a copper sulfate solution in an acidic medium. This reaction causes carbon dioxide to be released into the gas phase, while hydrogen sulfide is converted into water-insoluble copper sulfide.

$$H_2S + CuSO_4 \rightarrow CuS\downarrow + H_2SO_4 \tag{2}$$

5 cm³ of the regenerated amine solution or 2.5 cm³ of the rich amine solution is poured into a beaker (1) and placed inside the reaction flask (2), which contains 10 cm³ of a 10% mass fraction copper sulfate solution and was pre-filled with 20 cm³ of a 20% mass fraction sulfuric acid solution. The flask is tightly sealed, and the pressure in the burette (4) is equalized to atmospheric pressure using the tap (3). The reaction flask (2) is carefully shaken to overturn the beaker and mix the amine solution inside with the acidic solution. The pressure inside the burette is equalized to atmospheric pressure using the leveling vessel (5), and the volume of the released carbon dioxide gas is measured.

After completing the experiment, the results for determining the measured amount of carbon dioxide in the diethanolamine solution were calculated.

Calculation of Results.

a) The amount of carbon dioxide in the amine solution, X_1 (g/dm³), is calculated using the following formula:

$$X_1 = \frac{V_{CO_2} \cdot 1000 \cdot M_r}{22400 \cdot V_{PA}} \tag{3}$$

where:

V_{CO_2} is the volume of carbon dioxide released under normal conditions (pressure 760 mm Hg and temperature 0°C), cm³;

Mr is the mass of one mole of carbon dioxide (44 g);

V_{PA} is the volume of the amine solution taken for analysis, cm³;

22400 is the volume occupied by one gram-molecule of carbon dioxide under normal conditions (pressure 760 mm Hg and temperature 0 °C), cm³;

1000 is the coefficient for converting cm³ to dm³.

b) The mass fraction of carbon dioxide in the amine solution X_2, W %, is calculated using the following formula:

$$X_2 = \frac{v_{CO2}}{10 \cdot \rho} \tag{4}$$

where: v_{CO2} is the amount of carbon dioxide in the amine solution, g/dm³;

ρ is the density of the amine solution, g/cm³;

10 is the conversion factor for expressing the mass fraction as a percentage.

The results of the carbon dioxide content analysis in the diethanolamine solution, expressed in various analytical units, are presented in Table 2.

TABLE 2. Results of the analysis of the amount of carbon dioxide in diethanolamine solutions

№	Concentration of DEA solution, %	Density of DEA solution, g/cm^3	Volume of released carbon dioxide, cm^3	Mass fraction of carbon dioxide, % W	Molar fraction of carbon dioxide, % mol
Saturated solution of DEA					
1	30,27	1,107	81,0	5,749	3,292
2	31,76	1,111	80,5	5,734	3,380
3	30,68	1,109	82,0	5,810	3,383
4	30,96	1,108	78,5	5,571	3,323
5	31,29	1,110	80,5	5,702	3,310
6	30,54	1,109	78,0	5,537	3,230
7	31,35	1,106	81,4	5,806	3,324
8	31,57	1,105	80,0	5,573	3,298
Regenerated DEA solution					
1	32,87	1,048	5,4	0,225	0,107
2	32,76	1,054	5,2	0,216	0,119
3	33,01	1,046	5,8	0,224	0,120
4	32,82	1,050	5,5	0,218	0,097
5	32,96	1,041	5,3	0,195	0,127
6	32,29	1,049	5,0	0,221	0,196
7	32,91	1,053	4,9	0,222	0,100
8	32,79	1,052	6,0	0,201	0,126

This table provides data for both mass fraction (% W) and molar fraction (mol), allowing for a more detailed assessment of the DEA solution's saturation level with the acid gas component [15-17]. This comparison of different units of measurement provides a more comprehensive understanding of the quantitative carbon dioxide content in both the rich and regenerated solutions, and also allows for the correct comparison of the obtained data with the results of other studies and literature sources.

The hydrogen sulfide content in the rich and regenerated diethanolamine solutions used in the absorbers of natural gas treatment plants employing alkanolamines was also determined by potentiometric titration according to the established standard. The experimental tests were conducted following Corporate Standard CSt 39.2-35:2012.

Sampling is performed in special glass (polyethylene) containers, which are washed with synthetic detergents and concentrated technical hydrochloric acid, at designated locations in accordance with the analytical control schedule. After washing with reagents, the containers are thoroughly rinsed with tap water and then flushed with distilled water. Special sample preparation is not required [18]. For analysis, 180–200 ml of the amine solution is needed.

Measurement Procedure. The analysis should always begin with the regenerated diethanolamine solution. Place 160 ml of the sample into a 250 ml graduated cylinder and add 50 ml of 2 N NaOH solution to it. Then, using a Mohr pipette, transfer 10 ml of the prepared sample into a separate cylinder and dilute it with distilled water to a total volume of 50 ml. The dilution factor is 5. Cover the cylinder with a watch glass, mix thoroughly, and let it stand for 4-5 minutes. Next, place 50 ml of the sample into a 100 ml beaker, add 1 ml of 2 N NH_4OH solution, and place the solution into an ORION 900 A potentiometric titrator for determination. This potentiometric titrator performs automatic titration by adding 0.05 ml drops of a 0.03 mol/L $AgNO_3$ solution. Measurements are taken at least three times, and the average value is calculated.

The same measurements are performed with the rich diethanolamine solution. In this case, only 1 ml of the sample (rich diethanolamine solution) is taken and diluted with distilled water to 50 ml [19-20]. The dilution factor in this case is 50.

The addition of NaOH to the diethanolamine solution is necessary because, in addition to hydrogen sulfide, the gas also contains mercaptans and CO_2 ions. NaOH forms complex compounds with these ions. Sometimes, other mechanical additives are also introduced along with the gas. Subsequently, NH_4OH is added dropwise to precipitate $AgNO_3$. On average, the potentiometric titrator consumes 1.40 ml of $AgNO_3$ (0.05 ml).

$$H_2S + AgNO_3 \rightarrow Ag_2S \downarrow + HNO_3 \tag{5}$$

After completing the experiment, the results for determining the measured amount of hydrogen sulfide in the diethanolamine solution were calculated.

CALCULATION OF MEASUREMENT RESULTS

a) The amount of hydrogen sulfide, X_1 (g/dm³), in the diethanolamine solution is calculated using the following formula:

$$X_1 = \frac{V_{H2S} \cdot 50 \cdot 1,31 \cdot M_r}{A_r \cdot 1000} \tag{6}$$

V_{H_2S} – the hydrogen sulfide reading from the potentiometric titrator, g/dm³;
50 – the sample dilution factor;
1.31 – the dilution factor for the NaOH solution;
Mr – the molecular mass of 1 mole of hydrogen sulfide (34 g);
Ar – the relative atomic mass of sulfur (32 g);

TABLE 3. Results of analysis of hydrogen sulfide content in diethanolamine solutions

№	Concentration of DEA solution, %	Density of DEA solution, g/cm³	Hydrogen sulfide content in the titrator, g/cm³	Mass fraction of hydrogen sulfide, % W	Mole fraction of hydrogen sulfide, mol%
Saturated solution of DEA					
1	31,10	1,108	21,6	0,0011	0,0010
2	30,76	1,110	21,9	0,0014	0,0011
3	31,69	1,109	24,4	0,0012	0,0014
4	30,28	1,107	23,0	0,0011	0,0013
5	31,91	1,111	22,8	0,0014	0,0012
6	31,51	1,109	22,7	0,0010	0,0011
7	30,31	1,106	22,1	0,0015	0,0012
8	31,66	1,105	23,2	0,0016	0,0013
9	31,84	1,112	21,9	0,0014	0,0010
10	30,34	1,109	22,5	0,0013	0,0012
Regenerated DEA solution					
1	32,47	1,049	14,5	0,00014	0,00010
2	32,46	1,053	14,7	0,00013	0,00010
3	32,18	1,046	15,2	0,00015	0,00011
4	32,02	1,050	11,4	0,00008	0,00006
5	32,79	1,041	11,6	0,00009	0,00005
6	32,88	1,048	14,3	0,00012	0,00009
7	32,90	1,054	12,8	0,00009	0,00007
8	32,80	1,052	13,9	0,00011	0,00009
9	33,00	1,051	13,5	0,00010	0,00008
10	32,94	1,047	12,9	0,00008	0,00007

1000 – the conversion factor for mg to g (Note: This appears to be a correction. The original text said "мг3" which is likely a typo, and "1000" is the standard factor for converting mg to g or for unit adjustment in such formulas).

b) The mass fraction of hydrogen sulfide X_2, % W, in the diethanolamine solution is calculated using the following formula:

$$X_2 = \frac{v_{H2S} \cdot M_r}{A_r \cdot 1000 \cdot \rho} \qquad (7)$$

where:

v_{H2S} – the hydrogen sulfide content in the amine solution, g/dm³;

Mr – the molecular mass of 1 mole of hydrogen sulfide (34 g);

Ar – the relative atomic mass of sulfur (32 g);

1000 – the conversion factor for mg to g (Note: This corrects the original "мг3" which is likely a typo);

ρ – the density of the diethanolamine solution, g/cm³.

The results of the hydrogen sulfide content analysis in the diethanolamine solution, expressed in various units, are presented in Table 3 below.

DISCUSSION

This study experimentally investigated a two-stage laboratory method for determining hydrogen sulfide (H_2S) in diethanolamine (DEA) solutions. The obtained results demonstrate that the applied methodology provides a sensitive and reproducible analysis, allowing for the accurate determination of hydrogen sulfide even at low concentrations. The chemical basis of the reaction is the facile interaction of hydrogen sulfide with copper(II) sulfate or silver nitrate in the presence of sulfuric acid. During the initial stage of the reaction with copper(II) sulfate, the precipitation of H_2S as a solid CuS phase was observed, which facilitated the release of CO_2 into the gas phase. This process allows for the determination of the amount of CO_2 released from the amine by directly measuring the gas volume. This stage is particularly important when evaluating purified and regenerated amine solutions, as the amount of CO_2 reflects the degree of amine saturation [21].

The quantitative determination of H_2S was carried out based on the reaction with $AgNO_3$ during the potentiometric titration stage. The formation of a stable, water-insoluble Ag_2S precipitate with silver cations enhanced the method's selectivity. The capability of the titrator to add reagents in micro-volumes (0.05 ml) significantly improved the accuracy of the results and reduced the variance of the obtained values. An average $AgNO_3$ solution consumption of 1.40 ml allowed for the identification of substantial differences between the H_2S concentrations in the regenerated and rich DEA solutions. The multiplication factors applied during result processing, particularly the overall dilution factor of 1.31 after NaOH addition, helped to mitigate the influence of additional components in the solution (mercaptans, CO_2 ions, and mechanical additives). The presence of NaOH also created conditions for maintaining H_2S in a stable form, which enhanced the accuracy of the titration process. This approach is particularly important when dealing with mechanical impurities, additional gas components, and degradation products contained in industrial amine solutions. Furthermore, the use of different dilution factors (50 and 5, respectively) for the rich and regenerated solutions improved the accuracy of the results and ensured optimal sensitivity for highly loaded amine samples. Conducting at least three replicate analyses increased the statistical reliability, and the obtained values were evaluated based on the average [22-25].

In general, the applied methodology demonstrated sufficient reliability, high selectivity, and suitability for the industrial quantitative analysis of hydrogen sulfide in DEA solutions. The research results enable the assessment of amine solution loading, monitoring of regeneration efficiency, and early detection of issues related to foaming or the accumulation of mechanical impurities in the gas treatment process. This approach significantly contributes to ensuring the optimal operation of DEA-based absorbers in actual production processes and to enhancing the stability of technological operations.

CONCLUSION

The conducted research involved a detailed study of the physicochemical properties of diethanolamine (DEA), as well as the specifics of its interaction with the main acid-forming components of natural gas—hydrogen sulfide (H_2S) and carbon dioxide (CO_2). The obtained data confirmed that the efficiency of the absorption process directly depends on the ability of the DEA solution to selectively absorb the target components, as well as on the degree of solution regeneration and the stability of its operational characteristics.

The results of laboratory studies showed that the natural gas purified at the Shurtan Gas Chemical Complex belongs to the low-sulfur category. In accordance with the designed process flow scheme, a 30-33% DEA solution is used at the plant for acid gas removal. This concentration provides an optimal balance between absorption capacity, equipment corrosion resistance, and the working solution's stability against foaming. Given that excessive foaming can lead to reduced regeneration efficiency, increased content of mechanical impurities, and disruption of the absorption-regeneration column operation, the research work was aimed at accurately determining the concentrations of acid gases in the working DEA solutions.

The obtained experimental data confirmed a significant difference in the acid gas content between the rich and regenerated DEA solutions. The results showed that the hydrogen sulfide content in the rich diethanolamine solution averaged 5.471% W : 3.218% mol, while in the regenerated DEA solution it averaged 0.223% W : 0.123% mol. The carbon dioxide content in the rich diethanolamine solution averaged 5.471% W : 3.218% mol, while in the regenerated solution it averaged 0.223% W : 0.123% mol.

These differences confirm the high efficiency of the regeneration process, which ensures nearly complete removal of acid gases from the DEA solution. The obtained results demonstrate that the DEA-based absorption system at the Shurtan Gas Chemical Complex operates stably and efficiently within the established technological parameters. Regular monitoring of the H_2S and CO_2 content in the rich and regenerated DEA solutions allows for the timely detection of system deviations, prediction of potential by-product accumulation, control of amine degradation, and prevention of foaming. Furthermore, the conducted measurements provide an important scientific and practical basis for developing inhibitor compositions aimed at reducing foaming in natural gas treatment systems. The obtained data can be used to optimize absorption conditions, enhance regeneration efficiency, and extend the service life of the working DEA solutions.

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