Determination of the concentration of diethanolamine by titrimetric

Gulrukh Eshdavlatova [1,a)], Arzikul Panjiev[1], Eldor Nurkulov[1], Chinnigul Bobilova[1], Farrux Eshdavlatov[2]

[1] *Karshi State Technical University, Karshi, Uzbekistan*
[2] *Karshi Turan University, Karshi, Uzbekistan*

[a)] *Corresponding author: eshdavlatovagulrux@gmail.com*

Abstract. This article presents the results of laboratory experiments on determining the concentration of a diethanolamine (DEA) solution. The determination of the active component content in the solution was performed by acid-base titration using a 0.501 N HCl solution. The amount of DEA was calculated based on the volume of titrant consumed up to the equivalence point, ensuring the accuracy and reproducibility of the obtained analytical data. The conducted studies demonstrated a clear relationship between the concentration of the DEA solution and its physicochemical properties – pH, viscosity, absorption capacity, and foaming tendency. It was established that changes in solution concentration directly affect the efficiency of gas purification processes, technological stability, and the formation of mechanical impurities and degradation products.

INTRODUCTION

Currently, a significant portion of extracted gas contains acidic components such as H_2S and CO_2. The concentration of these substances in gases from different fields constantly varies in fractions. Hydrogen sulfide is a toxic substance, and its maximum allowable content in gas supplied to pipelines is regulated. Hydrogen sulfide, like carbon dioxide, forms acids in the presence of water, which cause chemical and electrochemical corrosion of metals. Under certain conditions, hydrogen sulfide induces sulfide stress cracking of metals. A high concentration of carbon dioxide in gas reduces its commercial value and promotes corrosion. These factors have driven the development and industrial implementation of numerous methods for removing acidic components from natural gases. Our republic is very rich in natural resources, one of which is natural gas. As mentioned above, natural gas contains components such as H_2S and CO_2, as well as mercaptans, thiols, and alkyl sulfides, which must be removed at the initial stage of gas processing [1].

In the modern conditions of the oil and gas industry, environmental and technological safety issues are becoming increasingly important. Amine-based gas purification processes for removing acidic 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 the form of 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 the long-term operation of the absorbent, its chemical degradation, the formation of by-products, and the accumulation of heat-stable salts inevitably occur, which significantly reduces the efficiency of the entire process [2].

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

On large gas processing plants, particularly at facilities like the Shurtan Gas Chemical Complex (ShGChC), a 30–33% diethanolamine (DEA) solution is used. The choice 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 varying pressures and temperatures; and relatively low hydrocarbon absorption, which enables the production of high-purity acid gas for subsequent sulfur production. However, along with its benefits, the process also has a number of drawbacks. Among these, the most significant are amine degradation, the formation of heat-stable salts, and foaming, which leads to excessive consumption of the costly absorbent and disrupts the stability of the process regime [3].

METHODOLOGY

Analysis of global practices shows that one of the best methods for removing acidic components, particularly hydrogen sulfide, from natural gas is the absorption method using amine solutions. For the purification of natural gas from acidic components (H_2S and CO_2), amine absorbers (monoethanolamine, diethanolamine, methyldiethanolamine) are primarily used. In the process of natural gas treatment, it is crucial to remove impurities and separate it into target fractions. Gas separation units are widely employed for this purpose. The design of such units distinguishes two technologically important zones: the amine treatment zone and the dehydration and gas fractionation zone. In the amine treatment zone, the main contaminating components of natural gas – carbon dioxide (CO_2) and hydrogen sulfide (H_2S) – are separated using an absorption method with a diethanolamine (DEA) solution. The absorption process is based on the chemical-physical properties of the gas, resulting in the effective removal of acidic natural impurities.

In the dehydration and gas fractionation zone, the gas is dried and separated. First, moisture is completely removed from the gas using zeolitic adsorbents. Then, the dried gas is separated into fractions by rectification. During rectification, various hydrocarbon fractions are separated from the natural gas—methane, ethane, propane, butane, as well as C5+ hydrocarbons. The obtained products are used as valuable feedstock in various industries. Specifically: methane is the main commercial product supplied to consumers via main gas pipelines and used as fuel at gas processing complexes. Ethane is a valuable feedstock for pyrolysis in the petrochemical industry, as it is used to produce ethylene and other important organic substances. Propane and butane are supplied to consumers as commercial products and are widely used as domestic and industrial fuel. C5+ hydrocarbon fractions are valuable products, serving as feedstock in various organic synthesis processes and as components of motor fuels.

Therefore, the gas separation unit not only purifies natural gas but also produces high-quality products from its fractions. These processes are carried out with strict adherence to material balance, meaning the quantity of each component in the gas is accounted for in both the input and output streams. This approach is a key factor in enhancing the efficiency of technological processes, ensuring product quality, and maintaining production volumes.

The necessity of removing acidic gases — hydrogen sulfide (H_2S) and carbon dioxide (CO_2) — from the natural gas stream is driven by several factors. Firstly, these gases exhibit high corrosive activity in the presence of water, especially at elevated temperatures. Secondly, during the separation of the methane-rich fraction of natural gas, carbon dioxide clathrate hydrates can form, which may adversely affect process stability and equipment efficiency. Therefore, the effective removal of these components from natural gas is of particular technological importance.

Diethanolamine (DEA) solutions are widely used in gas absorbers for removing acidic gases (CO_2, H_2S). The functional properties, reaction kinetics, and process efficiency with DEA directly depend on its concentration. The DEA molecule has two hydroxyl groups and one amino group, and exhibits high hydrophilicity in solution, enabling it to participate in reversible reactions with CO_2. As the DEA solution concentration increases, its physicochemical properties change significantly. In industrial processes, DEA solutions are typically used in the range of 30–32%. In low-concentration solutions, gas absorption capacity decreases due to an insufficient number of active amino groups. Solutions with moderate concentration are optimal, as they operate stably in the absorber. In high-concentration solutions (≥30%), DEA increases heat absorption, chemical activity, and viscosity, which significantly affects the hydrodynamic properties of the system [4-5].

The concentration of DEA also significantly affects the foaming process. As the concentration increases, the surface tension of the solution decreases, its viscosity rises, and gas bubbles within the solution become more stable. Consequently, both the foam height and its stability increase. Mechanical impurities in the solution also play an important role in this process: they adsorb onto the surface of the bubbles and extend the foam's collapse time [6]. Therefore, in high-concentration DEA solutions, foaming is further intensified and can adversely affect the stability of the technological process.

The concentration of DEA is most often determined by the titrimetric method. This method is based on the basic properties of the amine and allows for the determination of its total amount by titration with standard acid solutions. The refractometric method is also used for rapid control, as the refractive index changes directly proportionally to the DEA concentration.

The DEA concentration is one of the primary factors influencing the physicochemical stability of the solution, gas absorption efficiency, and the foaming process. Maintaining an optimal concentration value is crucial for the reliable operation of the technological process and preventing foam formation. Therefore, DEA concentration is considered a key parameter in the development of antifoam formulations.

The concentration of diethanolamine (DEA) solutions is a decisive factor for the stability and efficiency of technological processes. As the concentration increases, the physicochemical properties of the solution change significantly. In particular, the viscosity of the solution rises and the surface tension decreases, which directly affects the mass transfer process in the gas-liquid system. Increased viscosity reduces the liquid flow rate, slows down the rise of gas bubbles, and creates favorable conditions for foam stability. Reduced surface tension, in turn, promotes bubble formation and prevents their rapid coalescence and rupture. However, concentrations above 30% lead to increased heat release in the solution, heightened reaction activity, and an increase in the number of fine colloidal particles. Such particles remain in the solution for a long time and, by adsorbing onto the surface of bubbles, slow down foam breakdown. Therefore, high-concentration DEA solutions are often prone to significant foaming.

Another important aspect of DEA concentration is its influence on thermal and chemical stability. As the concentration of DEA increases, it becomes more sensitive to temperature, which can lead to the formation of various degradation products, organic acids, and oxidized amines in the solution. These substances reduce the overall stability of the solution, increase its corrosivity, and generate additional mechanical impurities, which further enhance foaming. Therefore, maintaining the quality of high-concentration DEA solutions requires additional control during the regeneration process [7-8].

Hanges in concentration also directly affect the kinetics of DEA absorption of CO_2 and H_2S gases. In low-concentration solutions, gas absorption occurs slowly due to the lack of amino groups. Absorption is most efficient at medium concentrations, while at high concentrations, efficiency may decrease due to intensified foaming during gas-liquid contact. Additionally, at high concentrations, the formation of carbamate with CO_2 increases, leading to the formation of additional stable colloidal phases in the solution [9-10]. Overall, DEA concentration is a key parameter determining the physicochemical stability of the solution, the kinetics of the gas absorption process, regeneration efficiency, and, particularly, the degree of foaming. Therefore, when testing formulations designed to prevent foaming, such as antifoam inhibitors, strict control of DEA concentration is required. Determining the optimal concentration range is of significant scientific and practical importance for ensuring the efficient operation of the technological system and preventing foaming.

RESULTS

This experiment allows for the determination of the exact concentration of diethanolamine in an aqueous solution, as well as for assessing the accuracy and reproducibility of the titrimetric method under laboratory conditions. The results were recorded under the experimental conditions, and the errors and measurement accuracy were analyzed. The analysis begins with purified DEA. It should be noted that DEA can cause issues with respiration, circulation, the central nervous system, liver, and other organs. It is rapidly absorbed through the skin. Therefore, when handling it, it is necessary to use skin and eye protection and to exercise caution.

Analysis Methodology. Before starting the analysis, samples are collected in one take. The analysis is conducted in a dry, clean 100 ml volumetric flask. First, the volumetric flask is weighed on an analytical balance (OHAUS AP-310). Then, 1 ml of the sample is taken using a 2 ml pipette and quickly weighed on the balance. Since DEA is a volatile substance, its evaporation could mislead the precise calculation of the experiment. The grams of the measured sample are recorded. It weighs slightly more in grams. Afterwards, the measured sample is placed in the flask and diluted to 100 ml with distilled water, creating the necessary conditions for convenient titration of the solution. Five to six drops of Groak's indicator (a 1:1 mixture of methyl red and methylene blue) are added to the flask, which is then placed on a magnetic stirrer. Titration is then performed using a standard 0.501 N HCl solution. After adding the indicator to the solution, it is titrated until the color changes from green to light purple. Titration is stopped upon reaching the equivalence point. The amount of titrant used from the burette is then calculated.

The same experiment was conducted with saturated DEA. The concentration of saturated DEA is higher than that of regenerated DEA, as the solution is saturated with acid gases.

Based on the titration results, the DEA concentration is calculated using the following formula:

$$W_{\%} = \frac{N \cdot A \cdot K}{M} \tag{1}$$

where:

N - is the normality of the HCl solution, equal to 0.501 N;

A - is the volume of the HCl solution used for titration, ml;

K - is the correction factor for the 0.501 N HCl solution, equal to 10.5;

M - is the mass of the sample, measured on a balance.

The obtained experimental data for determining the amount of diethanolamine based on titration results are presented in Table 1. The table shows that the average titrant consumption during the experiments was 5.4 ml. Based on the calculations, it was determined that the concentration of the DEA solution was approximately 30%. This result corresponds to the concentration of technical-grade solutions used at the Shurtan Gas Chemical Complex. The density and pH value of the solution (pH = 10.4–11.0) were determined, establishing a direct correlation between them and the concentration. As the amount of DEA increases, the alkalinity of the solution also increases.

The average DEA concentration is 30.18%, which meets the industry standard. This analysis confirms the stability of the solution and its suitability for use in practical purification processes [11-12].

DISCUSSION

The conducted experiments to determine the concentration of diethanolamine (DEA) using the acid-base titration method allowed for a comprehensive evaluation not only of the analysis accuracy but also of the specific behavior of regenerated and saturated DEA solutions under laboratory conditions. The use of a 0.501 N hydrochloric acid solution as a titrant demonstrated high reproducibility of the results and confirmed the suitability of this approach for the regular monitoring of process solutions used in the purification of natural and industrial gases from acidic components [13].

One important aspect of the experiment is the comparison of the properties of purified (regenerated) and saturated DEA. Saturated DEA solutions, containing a significant amount of absorbed acidic gases (primarily H_2S and CO_2), demonstrated a considerably higher titrant consumption, indicating an increase in the number of acid-active sites in the solution. This is explained by the fact that the interaction of DEA with acidic gases leads to the formation of carbamates, bicarbonates, and ionic forms, which alter the acid-base balance of the solution and increase its titratable acidity. Thus, the titration results allow not only for determining the concentration of free amine but also for indirectly assessing the degree of solution loading with acidic gases.

Table 1. Results of determination of DEA concentration by titration method

Type of DEA	Normality of HCl	Volume of HCl used for titration, ml	Correction factor	The mass of the sample measured on a scale.	Density of DEA, g/cm3	DEA concentration, %
1706 Regenerated DEA	0,501	6,22	10,5	1,0680	1,051	30,64
	0,501	6,01	10,5	1,0014	1,053	31,57
	0,501	6,05	10,5	1,0185	1,054	31,25
	0,501	6,32	10,5	1,0680	1,050	31,13
	0,501	6,34	10,5	1,0507	1,052	31,76
	0,501	4,12	10,5	0,6833	1,050	31,56
1705 Rich in DEA	0,501	6,46	10,5	1,0178	1,108	33,84
	0,501	6,35	10,5	1,0088	1,105	33,11
	0,501	6,54	10,5	1,0577	1,110	33,60
	0,501	6,36	10,5	1,0120	1,110	33,06
	0,501	6,68	10,5	1,0361	1,108	33,90
	0,501	6,32	10,5	0,9925	1,109	33,50

The obtained average titrant consumption value of 5.4 ml for purified DEA confirms the stability of the used methodology. The solution concentration of approximately 30% fully complies with the regulatory requirements for working DEA solutions at gas processing plants, including the facilities at the Shurtan Gas Chemical Complex. The pH values (10.4–11.0) determined during the experiment also align with literature data, indicating that an increase in diethanolamine concentration leads to higher solution alkalinity. This fact confirms the correctness of the analysis and demonstrates a direct relationship between DEA concentration, its absorption capacity, and its chemical properties.

It should be noted that the accuracy of the results significantly depends on proper sample preparation, as DEA is a volatile and hygroscopic substance. Its tendency to evaporate can lead to a reduction in sample mass, potentially causing errors in calculations. Therefore, particular attention was paid to prompt sample weighing and strict adherence to safety protocols. It is important to emphasize that diethanolamine possesses pronounced toxic properties, capable of adversely affecting the respiratory and central nervous systems, liver, and skin. This necessitates the use of protective equipment (gloves, goggles, lab coats) and compliance with safety rules for handling volatile amines.

The experiment also demonstrated the high effectiveness of the chosen indicator (a mixture of methyl red and methylene blue), which provides a clear and easily interpretable color change upon reaching the equivalence point. The use of a magnetic stirrer ensured solution homogeneity and improved the accuracy of detecting the color change moment. Collectively, all these factors contributed to a high degree of reproducibility and reliability of the results.

The obtained data demonstrate that the titrimetric method is a reliable tool for monitoring the quality of DEA solutions, which are widely used in amine-based gas purification units. It allows for the timely detection of deviations in concentration from standard values, which is crucial for preventing increased equipment corrosion, a reduction in the solution's absorption capacity, and excessive reagent consumption. Therefore, the conducted work holds significant practical value and can be used as methodological material for laboratory analysis and for process control at gas processing plants [14].

The conducted analysis also allows for a comparison of the solution's regeneration degree. The difference between the regenerated and saturated solutions indicates how completely regeneration has been carried out in the absorption-desorption column. In cases of insufficient regeneration, an increase in the solution's acid number, a change in pH, and a higher consumption of titrant during laboratory titration are observed. These deviations are reflected in operational indicators: the solution's ability to absorb acidic components deteriorates, the likelihood of foaming increases, and the corrosive impact on metal surfaces intensifies.

Foaming should be considered a key operational parameter of DEA solutions. As noted in laboratory observations, saturated solutions are prone to increased foaming, which can lead to potential flooding of the gas-liquid layer and disruption of absorber operation. Therefore, titration data characterizing the solution's loading degree can serve as an indirect indicator of foaming tendency. The higher the concentration of absorbed gases in the solution, the greater the likelihood of unstable foam formation, especially in the presence of surface-active impurities, DEA degradation products, and thermal and mechanical influences [15].

An important result of the conducted experiment is the establishment of a correlation between DEA concentration and solution density. The data show that an increase in the content of the free amine component leads to an increase in density, while saturated solutions exhibit a somewhat different dynamic due to the presence of carbamate and bicarbonate forms. This confirms that density can serve as a rapid method for preliminary assessment of the amine solution's condition before more precise titrimetric or chromatographic measurements.

The analysis also revealed that the use of Groak's indicator ensures optimal visualization of the equivalence point. The clear color change helps significantly reduce subjective errors, which often arise during the titration of polybasic amine-containing solutions. Therefore, the choice of indicator is a critically important component of the analytical methodology, especially in conditions requiring high reproducibility and minimization of operator error. It is essential to emphasize that safety measures for handling diethanolamine were considered during the experiment. Due to its high volatility and toxicity, strict control of experimental conditions is required: the use of gloves, protective goggles, work under a fume hood, and minimization of skin contact. Adherence to these rules is not only important for occupational hygiene but also affects the accuracy of the analysis, as the loss of sample mass due to evaporation can distort the actual concentration.

The obtained results hold significant importance for industrial gas purification processes. Monitoring DEA concentration is part of the regulated control procedures at gas treatment facilities like the Shurtan Gas Chemical Complex. Systematic analysis allows for the timely adjustment of the solution composition, prevents deviations from the technological regime, avoids excessive reagent consumption, and reduces operational costs.Thus, the conducted research not only confirms the accuracy of the titrimetric method but also highlights its practical significance for the gas purification industry [16]. The totality of the obtained data leads to the conclusion that the method can be used as a primary laboratory tool for monitoring the quality of DEA solutions, ensuring the stable operation of absorption-regeneration systems and enhancing the efficiency of natural gas purification.

CONCLUSION

The conducted research confirms that the titration method using a 0.501 N HCl solution is a highly accurate, reproducible, and reliable analytical approach for determining the concentration of diethanolamine in working solutions. The obtained average concentration value of 30% indicates proper reagent preparation and corresponds to the optimal technological parameters required for the effective removal of acidic gases from natural and industrial gases. The analysis data hold significant practical value, as they enable not only the operational monitoring of the diethanolamine solution quality but also ensure the stability of the gas purification process. Accurate concentration determination is a key factor in preventing excessive reagent consumption, reducing the corrosive activity of the medium, and maintaining a high level of solution absorption capacity.Thus, the obtained results confirm that the application of the titrimetric method is a rational tool for the regular monitoring of the working solution's condition, enhancing the efficiency, reliability, and cost-effectiveness of the entire gas purification process.

REFERENCES

1. Lohse, D., Zhang, X. Bubble dynamics and collapse. Reviews of Modern Physics, 2020, 92:
research is conducted. E3S Web of Conferences 539, 01022 (2024). https:// 041002.
2. Shahouni, R., et al. Foaming mitigation strategies in amine plants. Journal of Natural
3. H.D.Ismoilova, G.E.Eshdavlatova. Analysis of soil composition in experimental areas where scientific doi.org/10.1051/e3sconf/202453901022. RSE-III-2024.
4. Kumar A., Hartland, S. Contamination effects on amine solvents. Chemical Engineering Journal, 1988, 38(1): 1–8
5. Hamid, S., et al. Block copolymers as antifoams. Polymer, 2018, 149: 46–58.
6. Maddox R.N., Campbell J.M. Fluid Sweeting Sulfur Recoveri. A part of the Campbell Petroleum Series.
7. Rakhimov, O., Rakhimova, D., Mirzaev, O., Azizov, S. Analysis of developmental education models in the ecological education system in Uzbekistan. *E3S Web of Conferences*, 2023, 458, 06020
DOI 10.1051/e3sconf/202345806020
8. G.E.Eshdavlatova, A.Kh.Panjiyev. Studying the Rheological Properties of Thickening Compositions for Fabric Padding Based on Mixed Fibers. AIP Conf. Proc. 3243, 020024 (2024) https://doi.org/10.1063/5.0247308
9. G.Eshdavlatova, Kh.Ismailova, O.Rakhimov. Application of Strengthening Compositions in Floral Printing on Mixed Fiber. *AIP Conf. Proc.* 3243, 020022 (2024) https://doi.org/10.1063/5.0247303
10. Chen, Q., Rochelle, G.T. Foaming of monoethanolamine and amine blends. Energy Procedia, 2011, 4: 531–536.
11. H.Ismoilova, O.Rakhimov, N.Turabaeva, G.Eshdavlatova. Irrigation regime of fine fiber cotton in the karshin steppe. Conference Committee. Indexed in leading databases – Scopus, Web of Science, and Inspec. Scopus & Web of Science indexed.
12. Chen, X., et al.Foam formation due to heat-stable salts (HSS). Fuel Processing Technology, 2017, 159: 31–39.
13. Rakhimov, O.D., Ehsev S., Latipov S., Rakhimov J.Positive and Negative Aspects of Digitalization of Higher Education in Uzbekistan. *AIP Conference Proceedings*, 2022, 2432, 03006 DOI 10.1063/5.0089690
14. Qiu, G., Rochelle, G.T. Oxidative degradation of amines. Industrial & Engineering Chemistry Research, 2012, 51(45): 14626–14636.
15. Davis, J. Amine foaming due to degradation products. Energy Procedia, 2013, 37: 2275–2284.
16. Chen, X., et al. Foam formation due to heat-stable salts (HSS). Fuel Processing Technology, 2017,159: 31–39.