Identification and simulation model of mixed solutions of diethanolamine (DEA) and methyl diethanolamine (MDEA) for removal of acid gases

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Abstract. Acid gases are often found in industrial and crude natural gas and represent technological problems to the environment and bad effect to the human health. The high-energy demand and processing restrictions make the amine absorption operation sensitive to any change in conditions. The mixture of diethanolamine (DEA) and methyl diethanolamine (MDEA) was developed as the removal of acid gases. The physical properties and the characteristics of the mixture were examined using FTIR, TGA and SEM-EDS and were described in this work. The HYSYS program were conducted in this work to reasonably predict removal amounts of acid gases from natural gas using the mixture diethanolamine (DEA) and methyl diethanolamine (MDEA) mixture as absorbents based on the plant specifications data from PT Pertamina (Persero)’s refinery unit. The correlations between the characteristics of the mixture and simulation model were revealed. The model predictions were in excellent agreement with the experimental data and the results were useful to represent the acid gas absorption process using alkanolamine solutions.

1. Introduction
Acid gases (e.g. H₂S and CO₂) are undesirable gases that are often found in industrial and crude natural gas and are severe challenges in energy, processing and chemical industries [1]. They may also carry other impurities of short-chain hydrocarbons (C1—C4), benzene, toluene and xylene (BTX), N₂, NH₃, CS₂ and COS that show negative impacts to the environment by greenhouse gas emissions and the human health due to their highly toxic combustion by products [2]. In the petroleum industry, sulfur compounds generate corrosion problems on the refinery units and catalyst poisoning employed to upgrade the fuel quality [3,4]. Therefore, a study on the practical and economical clean up of acid gas becomes essential.

There are many methodologies to decontaminate acid gases from natural gas. Alkanolamine or amine solutions such as monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA) have been reported as valuable methods to absorb carbon dioxide and hydrogen sulfide from natural gas due to their reusability as absorbents and capability to hold acid gases in a large amount [5,6]. Two functional groups in these amines play significant roles i.e. the amino group supplies alkalinity required to increase the absorption rate of the acidic gasses; the hydroxyl group decreases the vapor pressure of the acid gases in the aqueous solution in order to improve their solubility [4,7,8].
Mixed amine systems commonly contain a tertiary amine that reacts spontaneously with H$_2$S by proton transfer yet relatively slowly with CO$_2$ compared to a primary or secondary amine [9–11]. Therefore, modifying CO$_2$ removal in a selective H$_2$S absorptions system by varying the composition of amines is a beneficial feature. A blend of a secondary amine of diethanolamine (DEA) and tertiary amine of methyldiethanolamine (MDEA) is the most commonly employed constituents in the gas processing experiments [3].

Despite their advantages, it should be noticed that very few of the experimental data of the mixture of amines as a capture of acid gases were reported. The objective of the present work was to evaluate the properties of diethanolamine (DEA) and methyldiethanolamine (MDEA) mixture and to investigate their ability to capture acid gases in the simulation model by using the HYSYS program. The accurate information of diethanolamine (DEA) and methyldiethanolamine (MDEA) mixture’s properties is essential before any modeling activity.

2. Materials & methods

2.1 Materials

Aqueous amines mixtures for density and kinematic viscosity analysis were prepared with double-distilled water. The solutes of DEA and DEA were Merck reagents with a purity of > 98%. All solutions were formulated by mass employing a Matrix ESJ210-4B analytical balance with a precision of 0.0001 g.

2.2 Instrumentation

The density of amines solutions was evaluated using an Anton Paar DSA 4500 density meter at a temperature of 20 °C, while the kinematic viscosity of amines solutions was measured based on the transit time of the liquid meniscus through a glass capillary provided by Schott equipped by an electronic stopwatch for calculating efflux times. The viscometer was immersed in a thermostatic bath at 20 °C. Scanning electron micrograph (SEM) images were obtained using a Sigma Zeiss microscope with an attached camera. An elemental analysis of the corrosion effect of the amines solution was evaluated using energy-dispersive X-ray spectroscopy (EDX) spectra recorded on Amatek. Fourier transform infrared spectroscopy (FTIR) spectra were analyzed in the wavenumber of 4000-400 cm$^{-1}$ region, on a Shimadzu infrared spectrophotometer. The thermal stability of the mixture observed during heating at a constant rate of 20 °C/min were performed by thermogravimetric analyzer (TA Instrument).

2.3 Simulated process as acid gas absorbents using HYSYS program

The purification process of acid gases by amines solutions was simulated by using the HYSYS program based on the plant specifications data from PT Pertamina (Persero)’s refinery unit. Various acid gas streams were mixed, compressed and cooled to the final condition of pressure of 5.917 barA and temperature of 40 °C then went into the LP Contactor. The LP contactor is a 16-trayed column where the mixed acid gas was contacted by an amine solvent which enters from the top of column. The treated gas would be sent to other unit for further treatment, while rich amine solutions were sent to amine solvent regeneration to remove dissolved H$_2$S and CO$_2$. Before going into the regenerator, rich amine solutions were flashed down to 2.386 barA in the flash drum. The regenerator is a trayed column with 32 trays. The heated rich amine solutions were fed to the regenerator on tray 28 (tray 1 is the bottom tray in the column). A horizontal thermosiphon regenerator reboiler provided the stripping vapor rising up the column which stripped the H$_2$S and CO$_2$ from the rich amine solutions. The hot lean amine solvent from bottom regenerator was pumped to the lean amine surge tank. Prior to reaching the surge tank, the lean amine solutions were cooled to 40 °C and filtered. The lean amine from surge tank then pumped to the LP Contactor to absorb H$_2$S and CO$_2$ from another mixed acid gas. Detailed simulation process is shown in table 1.
Table 1. Simulation data parameter.

| Parameter                              | MDEA Solutions | DEA+MDEA Solutions |
|----------------------------------------|----------------|-------------------|
| Lean amine concentration, % wt         | 30             | 30                |
| (30% MDEA + 0% DEA)                    | (21% MDEA + 9% DEA) |
| Rich amine concentration, % wt         | 29.16          | 29.14             |
| (29.16% MDEA + 0% DEA)                | (20.4% MDEA + 8.74% DEA) |
| Circulation rate, kg/h                 | 81,250         | Same              |
| Acid gas flow, kg/h                    | 24,090         | Same              |
| H₂S inlet, % vol                       | 10.61          | Same              |
| CO₂ inlet, % vol                       | 0.34           | Same              |

3. Result and discussion

3.1. Density and viscosity of amines solutions
The density and kinematic viscosity data for aqueous MDEA and mixture of DEA+MDEA solutions are presented in Table 2. The data shows that density of mixture DEA+MDEA of 1.0287 g/mL was lower than MDEA solutions. The mixture of DEA+MDEA also showed a lower kinematic viscosity of 4.800 mPa·s than the solutions containing only MDEA of 3.677 mPa·s. Hence, the density and viscosity of aqueous amines measured in this work were affected by the addition of DEA and were in a good agreement with the study reported by Alvarez et al. (2006) [12]. It should be noticed that the transport properties of the fluids such as phase density, surface tension, viscosity and diffusion coefficients might affect the mass transfer coefficients and the interfacial contact area between fluids and gases [13].

Table 2. The experimental data of density and kinematic viscosity of amines solutions.

| No. | Solutions | Density (g/mL) | Kinematic viscosity (mPa·s) |
|-----|-----------|----------------|-----------------------------|
| 1   | MDEA      | 1.0349         | 4.800                       |
| 2   | DEA+MDEA  | 1.0287         | 3.677                       |

3.2. Characterization of the amines solutions
An experimental evidence of the functional group in a mixture of DEA+MDEA solutions was obtained through the FT-IR spectrum (figure 1). The spectrum represented the common characteristic stretching vibrations of O–H at approximately 3365 cm⁻¹. The associated with C–H stretching vibration bands were shown at 2941 cm⁻¹. The band at 1447 cm⁻¹ was caused by the C–O stretching vibration of the primary alcoholic groups in DEA and MDEA.

The thermal stability of amines solutions was investigated by recording the weight change during heating at a constant rate of 20 °C/min using a thermo-gravimetric analysis (figure 2a–b). Figure 2a shows the thermal decomposition of MDEA solutions that started at 30.41 °C and finished at 226.02 °C, while significant loss of its weight occurred at a temperature of 190.65 °C. However, mixture of DEA+MDEA solutions exhibited a more excellent stability compared to the solutions containing only MDEA. The thermal decomposition of the mixture started at temperature of 30.41 °C and finished at 229.25 °C with the major loss occurred at a temperature of 207.95 °C. By comparing peaks between MDEA solutions and mixture DEA+MDEA solutions, it can be noticed that they differ in chemical constituents which promote in stabilizing the matter. Addition of DEA into the solutions might improve the thermal stability of absorbents to capture acid gases.
Figure 1. The FT-IR spectra of amines solutions.

Figure 2. Plots for thermal decomposition as weight percent loss (W %) vs temperature (T/°C) of: (a) MDEA and (b) mixture DEA+MDEA.

3.3 Corrosion effect of amines solutions
It has been reported that amine solutions might induce corrosion to the refinery equipment due to acidic and basic compounds that produce by thermal and chemical degradation [14], while some studies observed the activity of MDEA as corrosion inhibitors [8,9,15]. Table 3 describes the corrosion rate of carbon steel as materials in a 4 h settling time in amines solutions at a maximum temperature of heating mantel (110–120 °C). The DEA+MDEA mixture showed a slower corrosion rate of carbon steel of 0.0269 mm/y compared to MDEA solutions (0.0737mm/y). These data were well agreement with the morphology and the surface structure of the carbon steel used as experimental materials and monitored by a scanning electron microscope (the images are shown in figure 4). The SEM images revealed and confirmed the difference of the morphology of the carbon steel after treatment with amines solutions in a 4 h settling time. The surface of the carbon steel altered to be rougher and inconsistent after treatment with the MDEA solutions compared to that with the DEA+MDEA mixture. The elemental analysis using energy-dispersive X-ray spectroscopy (EDX) revealed that the carbon steel after treatment with solutions containing only MDEA had more elements than the other one. These findings were also in an excellent agreement with our experimental data of thermal stability evaluated by a thermo-gravimetric analysis in which addition of DEA may improve the thermal stability of solutions to absorb acid gases.
Table 3. The experimental data of the corrosion effects of the amines solutions.

| Solutions | Materials       | Settling time (h) | Corrosion rate (mm/y) |
|-----------|-----------------|-------------------|-----------------------|
| MDEA      | Carbon steel    | 4                 | 0.0737                |
| DEA+MDEA  | Carbon steel    | 4                 | 0.0269                |

Figure 3. SEM-EDS images of carbon steel: (a) before treatment, (b) after treatment with MDEA solutions, and (c) after treatment with DEA+MDEA solutions.

3.4 Simulation as acid gases absorbents
The purification process of acid gases by amines solutions was simulated using the HYSYS program based on the plant specification data from PT Pertamina (Persero)’s refinery unit. The simulation results indicated that both solutions were powerful absorbents to reduce H$_2$S and CO$_2$ contents (table 4). The content of H$_2$S decreased extensively after treatment with DEA+MDEA solutions compared to MDEA solutions. By comparing the two amines solutions, the mixture of DEA+MDEA was not only sensitive to capture H$_2$S but also CO$_2$. The final content of CO$_2$ after treatment with DEA+MDEA solutions was 2.5 times lower than treatment with solutions containing MDEA only. These results confirmed the simulated process revealed by Naji and Abd (2019) [5]. They also reported that the plant using the DEA solutions required a lower energy than the plants using MDEA as solvents due to their lower vapor pressure. On our energy performance simulated data, the mixture of DEA+MDEA showed a lower reboiler energy of 9.95 Gcal/h compared to MDEA solutions (12.13 Gcal/h). The data also revealed that energy consumption using mixture of DEA+MDEA was more effective than that using MDEA at the regeneration system.

Table 4. The simulated data of amines solutions as an acid gases absorbent.

| Acid gas | Initial content (% vol) | Final content of acid gases after treatment with different amines solutions (% vol) |
|----------|-------------------------|----------------------------------------------------------------------------------|
|          |                         | MDEA                              | DEA+MDEA                                          |
| H$_2$S   | 10.61                   | 0.00179                           | 0.00032                                           |
| CO$_2$   | 0.3395                  | 0.2175                            | 0.0855                                            |
| Reboiler energy (Gcal/h) | 12.13                  | 9.95                               |                                                   |
4. Conclusions
We have demonstrated the identification and lower corrosion rate of carbon steel after treatment with the mixture of diethanolamine (DEA) and methyl diethanolamine (MDEA) in removing acid gases such as H2S and CO2. The analysis of physical properties and characteristics of the mixture using FTIR, TGA and SEM-EDS confirmed the remarkable activity in absorbing acid gases and excellent stability simulated by using HYSYS program based on the plant specification data from PT Pertamina (Persero)’s refinery unit. The model predictions were in excellent agreement with the experimental data and the results were useful to represent acid gas absorption process using alkanolamine solutions.

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