Study of Various Aqueous and Non-Aqueous Amine Blends for Hydrogen Sulfide Removal from Natural Gas

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Abstract: Various novel amine solutions both in aqueous and non-aqueous [monoethylene glycol (MEG)/triethylene glycol(TEG)] forms have been studied for hydrogen sulfide (H2S) absorption. The study was conducted in a custom build experimental setup at temperatures relevant to subsea operation conditions and atmospheric pressure. Liquid phase absorbed H2S, and amine concentrations were measured analytically to calculate H2S loading (mole of H2S/mole of amine). Maximum achieved H2S loadings as the function of pKa, gas partial pressure, temperature and amine concentration are presented. Effects of solvent type on absorbed H2S have also been discussed. Several new solvents showed higher H2S loading as compared to aqueous N-Methyldiethanolamine (MDEA) solution which is the current industrial benchmark compound for selective H2S removal in natural gas sweetening process.

Keywords: H2S absorption; amine solutions; glycols; desulfurization; aqueous and non-aqueous solutions

1. Introduction

Natural gas is considered one of the cleanest forms of fossil fuel. Its usage in industrial processes and human activities is increasing worldwide, providing 23.4% of total world energy requirement in 2017 [1]. Natural gas is half of the price of crude oil and produces 29% less carbon dioxide than oil per unit of energy output [2]. Methane is a major energy providing component in natural gas. However, it also contains other hydrocarbons and a variety of impurities like acid gasses (CO2 and H2S) and water. Besides reducing the gas energy value, the impurities can cause operational problems such as corrosion in the pipeline and other equipment [3]. Mercury, mercaptans and other sulfur components are also often found in natural gas and must be removed. Sulfur components can produce SO2 during combustion which ultimately leads to acid rain. Therefore, it is necessary to remove acid gases, water vapors, and other impurities before the usage of natural gas.

H2S is an extremely poisonous component, and it can cause instant death when concentrations are over 500 parts per million volume (ppmv) [4,5]. H2S exposure limits by the Norwegian Labour Inspection Authority are 5 ppmv for an eight-hour time-weighted average (TWA) and 10 ppmv for 15 min short-term exposure limit (STEL) [6]. The most commonly used method for H2S removal is liquid scavenging. These processes usually employ non-regenerative chemicals such as triazine or aldehydes, and because of costs and operational issues (e.g., chemicals disposal), scavengers are not used for gases with high H2S concentrations. Alkanolamines, in particularly N-Methyldiethanolamine (MDEA), are generally used for regenerative H2S removal processes [7].

Natural gas is commonly saturated with water increasing the chances of solid gas hydrates formation with methane at high pressure and low temperatures potentially causing plugging in
gas transport pipelines. One common way to avoid hydrate formation and to achieve problem-free continuous gas transportation operations is to add hydrates inhibitors like monoethylene glycol (MEG) or triethylene glycol (TEG) in gas pipelines [8].

A system which could selectively remove H\textsubscript{2}S and control hydrate simultaneously would not only reduce equipment footprint but also help to reduce the installation and operational costs for both subsea and platform operations. This type of system was initially proposed by Hutchinson [9]. The idea of combined H\textsubscript{2}S and water removal was presented in 1939 by using amine glycol solution as a solvent. 2-ethanolamine (MEA) and diethylene glycol (DEG) solution in water solution was the tested solvent for the concept. McCartney [10,11] and Chapin [12] built upon Hutchinson concept and presented the idea of both absorption and regeneration process in two-stages. They discussed various arrangements to get higher efficiency and lower energy requirement. Later on, this process development discontinued due to lower selectivity of H\textsubscript{2}S compared to CO\textsubscript{2}, higher amine degradation and corrosion rate of MEA [7]. However, tertiary amine systems could be very interesting for this type of operations as they are known for their high selectivity to H\textsubscript{2}S. Tertiary amine systems, like a blend of methyl diethanolamine (MDEA) with glycols (MEG/TEG), have, additionally, higher amine stability and reduce corrosion rates [7,13,14].

In the literature, there is limited data available for the tertiary amine-glycols blends and most of the data is available for aqueous Triethanolamine (TEA), diisopropanolamine (DIPA), and MDEA. TEA was the first commercially used alkanolamine for gas treating process [7]. It is now being replaced with other amines like monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), methyl diethanolamine (MDEA), 2-amino-2-methyl-1-L-propanol (AMP), ethyl diethanolamine (EDEA) and 2-(2-aminoethoxy) ethanol (DGA) due to its low capacity and high circulation rate [15]. MDEA based system offered advantages like selective hydrogen sulfide removal over carbon dioxide, low vapor pressure, higher thermal stability, less corrosion, lower heat of reactions and specific heat [7,13]. Equations (1)–(6) show the mechanism and overall reactions of H\textsubscript{2}S with aqueous secondary and tertiary amines. These reactions are instantaneous and involve a proton transfer.

Ionization of water: \[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \]  

Ionization of dissolved H\textsubscript{2}S: \[ \text{H}_2\text{S} \leftrightarrow \text{H}^+ + \text{HS}^- \]  

Protonation of secondary amine: \[ \text{RR}^+\text{NH} + \text{H}^+ \leftrightarrow \text{RR}^+\text{R''NH}_2^+ \]  

Protonation of tertiary amine: \[ \text{RR}^+\text{R''N} + \text{H}^+ \leftrightarrow \text{RR}^+\text{R''NH}^+ \]  

Overall reaction for secondary amine: \[ \text{RR}^+\text{NH} + \text{H}_2\text{S} \leftrightarrow \text{RR}^+\text{R''NH}_2^+ + \text{HS}^- \]  

Overall reaction for tertiary amine: \[ \text{RR}^+\text{R''N} + \text{H}_2\text{S} \leftrightarrow \text{RR}^+\text{R''NH}^+ + \text{HS}^- \]

The solubility of H\textsubscript{2}S in aqueous solutions of MDEA from 11.9 wt.% to 51 wt.% in the temperature range from 10 °C to 120 °C and H\textsubscript{2}S partial pressure from 0.141 kPa–6900 kPa were studied by various authors [16–27]. All the previous studies of aqueous MDEA showed similar trends like increasing the partial pressure of H\textsubscript{2}S (pH\textsubscript{2}S) increases H\textsubscript{2}S loading at given concentration and temperature, while the increase in amine concentration at a given temperature and pH\textsubscript{2}S decreases H\textsubscript{2}S loading. Surplus to MDEA data, TEA from 0.09–6.32 kPa H\textsubscript{2}S and DIPA at a pressure range of 19–1554 kPa has been reported [28,29].

Xu et al. [24] also studied H\textsubscript{2}S absorption in 30 wt.% MDEA in MEG and MEG-H\textsubscript{2}O solutions over a range of partial pressures of H\textsubscript{2}S from 0.34 to 38.8 kPa and found that increasing the water content in solution increases the H\textsubscript{2}S loading at a given temperature (40 °C). Also, the increase in temperature decreases the H\textsubscript{2}S loading for a given concentration (30 wt.% MDEA—65 wt.% MEG—5 wt.% H\textsubscript{2}O). Most of the previous studies were conducted using static cell apparatus and higher liquid phase H\textsubscript{2}S loading can be obtained by using total gas pressure (>101.3 kPa) with higher amine
concentration. Therefore, very few H$_2$S absorption studies are available for low amine concentrations at low temperatures and low acid gas inlet partial pressure range in literature.

The objective of this study is to identify blends where the solute (amine) can give higher H$_2$S removal capacity as compared to MDEA in the presence of glycol. The overall goal for this process is to absorb H$_2$S and water simultaneously at the subsea level in two-steps. In the first step, absorption can take place at the subsea level, potentially using a co-current contactor for absorption and flash drum to separate the natural gas from solvent at subsea levels. In the second step, loaded solution can be sent to a platform for regeneration and natural gas will be transported directly from subsea allowing a system where the natural gas will not enter the platform at all. The current work focuses on the identification of amine-glycol blends with high H$_2$S absorption capacity. The amines for this work were chosen systematically so that insight into the influence of its structure, like amine alkanol groups, alkyl chain length, and a hydroxyl group, can be obtained. In total twelve amines were studied, one secondary sterically hindered amine (diisopropylamine), one tertiary sterically hindered amine (N-tert-butyldiethanolamine), and ten tertiary amines. The list of amines along their chemical structure used in the study is given in Figure 1.

Figure 1. List of amines with chemical structures.
2. Material and Methodology

2.1. Materials

2-Dimethylaminoethanol (DMAE), 2-(Diethylamino) ethanol (DEEA), 2-(Dibutylamino) ethanol (DBAE), Diisopropylamine (DIPA), 3-Dimethylamino-1-propanol (3DEA-1P), N-Methyldiethanolamine (MDEA), Triethanolamine (TEA), Ethylene glycol (MEG), and Triethylene glycol (TEG) were bought from Sigma-Aldrich (Oslo, Norway), while 3-(Diethylamino)-1,2-propanediol (DEA-1,2-PD), 2-[2-(Diethylamino) ethoxy] ethanol (DEAE-EO), 6-Dimethylamino-1-Hexanol (DMAH), N-tert-Butyldiethanolamine (t-BDEA), and 3-Diethylamino-1-propanol (3DEA-1P) were bought from TCI Europe (Zwijndrecht, Belgium) in available maximum commercial purity. Additionally, premixed 1500 ppmv (0.15 vol.%) Hydrogen Sulphide (H$_2$S) in Nitrogen (N$_2$), 10,000 ppmv (1 vol.%) Hydrogen Sulphide (H$_2$S) in Nitrogen (N$_2$) and pure Nitrogen (N$_2$) (99.998 vol.%) were purchased from AGA Norway, Oslo. All chemicals were used without further purifications. Chemicals with their abbreviation, CAS number, purity, molecular weight, and pKa are given in Table 1 except hydrogen sulfide and deionized water.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CAS</th>
<th>Purity (wt.%)</th>
<th>Molecular Weight (g/mol)</th>
<th>pKa</th>
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<tr>
<td>2-Dimethylaminoethanol (DMAE)</td>
<td>108-01-0</td>
<td>≥ 99.5</td>
<td>89.14</td>
<td>9.49 [30]</td>
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<td>2-(Diethylamino)ethanol (DEEA)</td>
<td>100-37-8</td>
<td>≥ 99.5</td>
<td>117.19</td>
<td>9.75 [31]</td>
</tr>
<tr>
<td>2-(Dibutylamino)ethanol (DBAE)</td>
<td>102-81-8</td>
<td>≥ 99.0</td>
<td>173.30</td>
<td>9.04 [32]</td>
</tr>
<tr>
<td>2-[2-(Diethylamino)ethoxy] ethanol (DEAE-EO)</td>
<td>140-82-9</td>
<td>&gt;98.0</td>
<td>161.25</td>
<td>10.15 [31]</td>
</tr>
<tr>
<td>6-Dimethylamino-1-Hexanol (DMAH)</td>
<td>1862-07-3</td>
<td>&gt;97.0</td>
<td>145.24</td>
<td>10.01 [31]</td>
</tr>
<tr>
<td>Diisopropylamine (DIPA)</td>
<td>108-18-9</td>
<td>≥ 99.0</td>
<td>101.19</td>
<td>8.84 [33]</td>
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<tr>
<td>3-(Diethylamino)-1,2-propanediol (DEA-1,2-PD)</td>
<td>621-56-7</td>
<td>&gt;98.0</td>
<td>147.22</td>
<td>9.68 [31]</td>
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<tr>
<td>3-Dimethylamino-1-propanol (3DMA-1P)</td>
<td>3179-63-3</td>
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<td>103.16</td>
<td>9.54 [30]</td>
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<td>3-Diethylamino-1-propanol (3DEA-1P)</td>
<td>622-93-5</td>
<td>≥ 95.0</td>
<td>131.22</td>
<td>10.29 [30]</td>
</tr>
<tr>
<td>N-Methyldiethanolamine (MDEA)</td>
<td>105-59-9</td>
<td>≥ 99.0</td>
<td>119.16</td>
<td>8.65 [30]</td>
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<tr>
<td>Triethanolamine (TEA)</td>
<td>102-71-6</td>
<td>≥ 99.0</td>
<td>146.19</td>
<td>7.85 [30]</td>
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<tr>
<td>N-tert-Butyldiethanolamine (t-BDEA)</td>
<td>2160-93-2</td>
<td>≥ 97.0</td>
<td>161.24</td>
<td>9.06 [30]</td>
</tr>
<tr>
<td>Ethylene glycol (MEG)</td>
<td>107-21-1</td>
<td>≥ 99.5</td>
<td>62.07</td>
<td>14.44 [34]</td>
</tr>
<tr>
<td>Triethylene glycol (TEG)</td>
<td>112-27-6</td>
<td>≥ 99.8</td>
<td>150.17</td>
<td>14.50 [35]</td>
</tr>
</tbody>
</table>

All amine solutions were prepared by weighing the required amount of the amines using the Mettler Toledo MS6002S Scale, with an uncertainty of ±10$^{-5}$ kg. Aqueous solutions were made with deionized water produced by ICW-3000 Millipore water purification system, while for non-aqueous solutions MEG/TEG was used as a solvent. All amines were miscible in DI water, MEG and TEG except DBAE which made visible two phases with DI water but less visible two phases with MEG and TEG. DBAE solutions appeared homogeneous while stirring.

2.2. Methodology and Equipment

A custom-built apparatus, as shown in Figure 2, was used to screen amine solutions for hydrogen sulfide absorption study. The apparatus is designed to operate at atmospheric pressure and temperatures up to 80 °C and is similar to apparatus previously used for CO$_2$ absorption and desorption studies by Ma’mun et al. and Hartono et al. [31]. The apparatus consisted of the water-jacketed reactor with volume of ~200 cm$^3$ (NTNU, Trondheim, Norway) with a magnetic stirrer, Alicat MCS series Mass flow controllers (Tucson, AZ, USA), thermocouple (Omega Engineering Limited, Nærum, Denmark), Hubo® water bath (Huber Kältemaschinenbau AG, Offenburg,
Germany), and sodium hydroxide (NaOH) vessel for caustic wash. LabVIEW (National Instruments Norway, Drammen, Norway) was used to control and record gases flowrates and both reactor and water bath temperatures. The apparatus and H$_2$S gas bottles were installed in a closed fume cabinet equipped with an H$_2$S sensor, alarm and fail-safe system; which shut down the whole apparatus automatically in case of any H$_2$S leakage (limit >10 ppmv) or electrical failure. Personal protective equipment and personal H$_2$S sensor were used during experiments.

Figure 2. Schematic flow diagram of the screening apparatus.

Since the overall goal is to develop a solvent system that could be used at the subsea level, where the total gas pressure is high and H$_2$S content is from 50 ppm and up, higher partial pressure of H$_2$S up to 1 vol.% was used to achieve similar H$_2$S quantity during these experiments at atmospheric pressure.

At the start of each experiment 150 g of the solution was filled in the reactor and cooled/heated to the required experiment temperature after purging it with nitrogen to remove any air present. Pre-mixed H$_2$S and N$_2$ were used to achieve the required inlet hydrogen sulfide partial pressure (pH$_2$S) with the help of MFCs. The reactor was continuously stirred with a magnetic stirrer at isothermal and isobaric condition during the whole experiment. Hubor® water bath was used to maintain the temperature constant. A thermocouple was placed in the liquid phase and used for continuous monitoring of reactor temperature. The exit gas from the reactor was sent to a series of three 10 wt.% NaOH solution vessels in order to remove residual H$_2$S present in it. All experiments were run for 120 min to give sample time to reach close to equilibrium between acid gas and amine solution. To ensure that 120 min is enough, experiments with 20 wt.% MDEA were performed until 240 min at 5 °C with sampling after every 15 min. The data showed that H$_2$S stopped absorbing after 45 min. This is in line with Lemoine et al. [20] and confirms that 120 min is enough time to reach close to equilibrium. Also, several parallel experiments for both aqueous and non-aqueous solutions of various
amines were run and repeatability the data were confirmed. Different solutions were tested at different temperatures (5 °C, 25 °C and 40 °C) and inlet H$_2$S partial pressures (0.03 kPa, 0.5 kPa, 0.75 kPa and 1 kPa). For inlet pH$_2$S = 0.5 kPa to 1 kPa, 10,000 ppm H$_2$S gas mixture at total flow rate of 200 mL/min and for inlet pH$_2$S = 0.03 kPa, 1500 ppm H$_2$S gas mixture at total flow rate of 1000 mL/min were used. The uncertainty of the inlet partial pressure of H$_2$S was estimated to be 2% including both the uncertainty of the ready H$_2$S gas mixture and the pre-calibrated mass flow controllers.

After the experiment, liquid samples were stored at <4 °C in the fridge and later on delivered to the analytical lab (St. Olav’s Hospital Laboratory, Trondheim, Norway) for total sulfur analysis with inductivity coupled plasma mass spectrometry (ICP-MS). The samples were transported in ice box along with ice to keep sample temperature <5 °C. To ensure no amine loss during the experiments, amine concentration was determined by with Mettler Toledo G20 compact titrator [36] using a liquid sample of 0.2 mL that was diluted with 50 mL deionized water and titrated with 0.1 mol/L H$_2$SO$_4$. Each liquid sample was analyzed twice for total sulfur and amine concentration. The standard deviations between the duplicates of each solution were <2.5% for total sulfur and <1.5% for amine concentration. The differences in the amine concentration were less than 2% found in initial and final amine concentrations for all the solutions indicating that there was no significant amine loss during the experiments. The hydrogen sulfide loadings calculated by Equation (7), given in this work are based on the analyzed values for H$_2$S and amine in the liquid phase.

\[
\alpha_{H2S} = \frac{\text{mole of } H2S}{\text{mole of amine}} \tag{7}
\]

3. Results

This screening apparatus was validated with a benchmarking 30 wt.% aqueous monoethanolamine (MEA) for CO$_2$ absorption before using it for H$_2$S absorption. Inlet CO$_2$ partial pressure was 10 kPa and absorption was done at 40 °C until 95% CO$_2$ absorption. Rich loading was found 0.54 mol CO$_2$/mol MEA after titration which was in good agreement with Hartono et al. [31] with an average deviation of 1.9%. 23.8 wt.% aqueous MDEA has been mostly used to study H$_2$S absorption. Therefore, the same amine concentration was used to verify the screening equipment and experimental parameters at 40 °C and pH$_2$S = 1 kPa. The liquid phase of H$_2$S loading was measure 0.14 (mol/mol) with the deviation of 4.6% from Jou et al. [16]. The experimental data are shown in with experimental uncertainties at the end is shown in Table 2.

Table 2. Experimental data.

<table>
<thead>
<tr>
<th>Amine</th>
<th>Initial Amine (wt.%)</th>
<th>Solvent</th>
<th>H$_2$S Loading (α)</th>
<th>Inlet pH$_2$S (kPa)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEA</td>
<td>20% Water</td>
<td>0.015</td>
<td>0.03</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>DEEA</td>
<td>20% Water</td>
<td>0.008</td>
<td>0.03</td>
<td>5</td>
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<tr>
<td>DBEA</td>
<td>20% Water</td>
<td>0.011</td>
<td>0.03</td>
<td>5</td>
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<tr>
<td>DIPA</td>
<td>20% Water</td>
<td>0.012</td>
<td>0.03</td>
<td>5</td>
<td></td>
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<tr>
<td>TEA</td>
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<td>0.013</td>
<td>0.03</td>
<td>5</td>
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<td>t-BDEA</td>
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<td>0.009</td>
<td>0.03</td>
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<tr>
<td>MDEA</td>
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<td>MDEA</td>
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<td>0.5</td>
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<td>0.5</td>
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<td>0.5</td>
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Table 2. Cont.

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<th>Amine</th>
<th>Initial Amine (wt.%)</th>
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<th>H₂S Loading (α)</th>
<th>Inlet pH₂S (kPa)</th>
<th>Temperature (°C)</th>
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<td>40</td>
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<tr>
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<tr>
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<td>0.165</td>
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<tr>
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<tr>
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</tr>
<tr>
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<tr>
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<td>MEG</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>DMAE</td>
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<td>MEG</td>
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<td>0.049</td>
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</table>

\[ u(p_{H_2S}) = \pm 2\%; u(T) = \pm 0.1 \degree C; u(C_{Amine}) = \pm 1.5\%; u(C_{H_2S}) = \pm 2.5\% \]

3.1. Effect of pKa

Effect of pKa on H₂S loading in 20 wt.% aqueous amine solutions at T = 5 °C ± 0.1 °C and pH₂S = 1 kPa is shown in Figure 3. In the reaction between H₂S and aqueous amine solution, H₂S acts as weak acid whereas aqueous amine acts as a strong base, therefore, an increase in pKa increases the hydration of H₂S subsequently increasing the H₂S loading. This is also evident in tertiary amines aqueous solutions with DEEA, t-BDEA, and DBAE acting like outliers. DEEA shows lower absorption capacity than its closest pKa tertiary amine (DEA-1,2-PD), which can be due to short molecular chain of DEEA. t-BDEA. Sterically hindered amine shows the highest loading of all amines whereas DBAE shows the lowest loading, and it makes two phases with almost all the H₂S absorbed in the upper phase, i.e., amine (solute). If the amount of H₂S absorbed only in the amine phase (solute) is used to calculate H₂S loading in DBAE aqueous solutions, these solutions also start to follow the trend. The amount of H₂S absorbed in DBAE amine phase is ≈4.6 ± 0.2 times of absorbed H₂S in the whole solution both in aqueous and non-aqueous solutions.
Aqueous solutions of amines highlighted in the circle in Figure 3 presented higher H$_2$S loading as compared to MDEA and can be potential amines for further studies. t-BDEA showed the highest H$_2$S loading, but in-house data show it also degraded a lot in the presence of CO$_2$ and caused higher corrosion rates leading to damages in steel pipelines and equipment as compared to MDEA [37].

When looking into the amine structure, the results show that an increase in alkyl group decreases the H$_2$S loading in an amino-ethanol group, i.e., DMAE > DEAE (DEEA) > DBAE. It can be due to reduction in activity of nitrogen group due to increase in chain length of alkyl group in ethanol amine, a similar trend was previously observed in carbon dioxide capture studies [38,39]. Structure wise it would have been interesting to test 2-Dipropylaminoethanol (DPAE). Unfortunately, we were unable to purchase the chemical since it is commercially unavailable in Norway as it is being used in the weapon industry. A reverse trend was seen in an amino-propanol group where an increase in the alkyl group increases the H$_2$S loading, i.e., 3DMA-1P < 3DEA-1P. Hydroxyl group attracts electrons therefore, addition of more hydroxyl group reduces the activity of nitrogen atom of amine resulting in decreased H$_2$S loading in aqueous amine solutions, i.e., DMAE > MDEA > TEA and 3DEA-1P > 3DEA-1,2-PD. Also, an increase in the length of chain for hydroxyl group from -N- decreases the H$_2$S loading as seen when comparing DEAE-EO and DMAH (DEAE-EO shows higher capacity). Moreover, by adding the ethoxy group in DEEA, (DEAE-EO) increases the H$_2$S loading significantly.

Effects of pKa on H$_2$S loading in 20 wt.% amine solutions in MEG and TEG at T = 5 °C ± 0.1 °C; pH$_2$S = 1 kPa; amine concentration = 20 wt.% (unloaded); DBAE solutions make two phases.

Effects of pKa on H$_2$S loading in aqueous amine solutions; T = 5 °C ± 0.1 °C; pH$_2$S = 1 kPa; amine concentration = 20 wt.% (unloaded); DBAE solutions make two phases.

Figure 3. Effect of pKa on H$_2$S loading in aqueous amine solutions; T = 5 °C ± 0.1 °C; pH$_2$S = 1 kPa; amine concentration = 20 wt.% (unloaded); DBAE solutions make two phases.
trend seen in aqueous solutions. However, adding an ethoxy group in DEEA has a similar effect in all three solutions.

Figure 4. Effect of pKa on H$_2$S loading in amine-MEG solutions; T = 5 °C ± 0.1 °C; pH$_2$S = 1 kPa; amine concentration = 20 wt.% (unloaded); DBAE solutions makes two phases.

Figure 5. Effect of pKa on H$_2$S loading in amine-TEG solutions; T = 5 °C ± 0.1 °C; pH$_2$S = 1 kPa; amine concentration = 20 wt.% (unloaded); DBAE solutions makes two phases.

3.2. Effect of Solvent

Each aqueous amine solution gives more H$_2$S absorption capacity than its non-aqueous counterpart when compared on weight bases and having same system temperature, inlet partial pressure of gas and residence time of gas in the reactor as shown in Figure 6. Change of solvent from water to ethylene glycol or tri-ethylene glycol has a similar effect on all the amine solutions.
Replacing the solvent from water to monoethylene glycol decreases the H$_2$S loading significantly, the maximum decrease was observed in DEEA solutions while minimum has observed DBAE solutions. H$_2$S absorption decreased more rapidly when TEG has used as a solvent compared to MEG or H$_2$O solutions in respective amines. Furthermore, MEG shows more reactivity than TEG due to the autoprotolyses. However, the H$_2$S absorption capacity in TEG solutions is expected to increase significantly if water is present even at relatively low amounts [40].

![Graph showing the effect of solvent on absorbed H$_2$S](image)

**Figure 6.** Effect of solvent on absorbed H$_2$S; T = 5 °C ± 0.1 °C; pH$_2$S = 1 kPa; mine concentration = 20 wt.% (unloaded); DBAE solutions make two phases.

### 3.3. Effect of H$_2$S Partial Pressure

Hydrogen sulfide loading as the function of inlet H$_2$S partial pressure (pH$_2$S) at T = 5 °C ± 0.1 °C for 20 wt.% amine solutions is shown in Figure 7. The rise in inlet H$_2$S partial pressure (pH$_2$S) increases the H$_2$S loading at given temperature and amine concentration for both aqueous and non-aqueous solutions except DEAE-EO by providing more reaction sites for reaction between H$_2$S and amine solutions. The same trend was seen in previous studies. However, in aqueous DEAE-EO solution, H$_2$S loading starts to decrease with increases in pH$_2$S from 0.5 kPa to 1.0 kPa for an unknown reason. It is not possible to explain the behavior with the current data.
3.4. Effect of Temperature

The effect of temperature on H$_2$S loading on various 20 wt.% amine solutions at pH$_{2S}$ = 1 kPa is shown in Figure 8. As the screening temperature increases from 5 °C to 40 °C, H$_2$S loading decreases for all solutions except DEAE-EO and DEEA. The decrease in loading is as expected since the final loading in the experiments is almost in equilibrium with the gas phase [16,20]. For DEEA, the loading difference between 5 °C and 40 °C is 0.01 mol H$_2$S/mol DEEA indicating that loading capacity is not as dependent on temperature as for some of the other amines. In the case of DEAE-EO, the changes are larger: The loading difference between 5 °C and 40 °C is 1.8% which is within our analytical uncertainty. However, the reason for the increase in loading seen at 25 °C, is unknown. We believe this is due to uncertainties in the analysis of H$_2$S and amine concentrations in the liquid samples.

Figure 7. Effect of inlet H$_2$S partial pressure on H$_2$S loading; T = 5 °C ± 0.1 °C; amine concentration = 20 wt.% (unloaded); DBAE solutions makes two phases.

Figure 8. Effect of temperature on H$_2$S loading; pH$_{2S}$ = 1 kPa; amine concentration = 20 wt.% (unloaded); DBAE solutions makes two phases.
3.5. Effect of Amine Concentration

Figure 9 shows the effect of amine concentration on hydrogen sulfide loading in aqueous solutions at 5 °C and inlet H₂S partial pressure of 1 kPa. The increase in amine concentration from 20 wt.% to 50 wt.% at given temperature and pressure decreases the H₂S absorption (mole/mol) subsequently decreasing H₂S loading. The trends are similar to those reported for MDEA as seen in the figure. In case of MDEA, the absorption capacity decreases by 40–50% when the MDEA concentration increases from 2.5 mol/kg to 4.2 mol/kg and it is similar to the reduction seen for DBEA. For 3DEA-1P and DEAE-EO a higher reduction in the absorption capacity is seen. Overall, the results indicate that increase in amine concentration changes the vapor-liquid equilibria behavior of the system [16,27,41,42].

![Graph showing effect of amine concentration on H₂S loading](image_url)

**Figure 9.** Effect of amine concentration on H₂S loading; T = 5 °C ± 0.1 °C; pH₂S = 1 kPa for all amines except MDEA; DBAE solutions makes two phases.; MDEA is at T = 40 °C and MDEAᵃ pH₂S = 0.3 kPa [27]; MDEAᵇ pH₂S = 0.5 kPa [27], MDEAᶜ pH₂S = 1 kPa [16].

The data at 50 wt% allows us to compare the absorption capacity of 3DEA-1P, DEAE-EO and DBEA in aqueous and MEG solutions with similar mole fraction (mole amine/mole solution). The mole fraction of 3DEA-1P in 3DEA-1P.MEG solution (0.13) is similar to that of aqueous 50 wt% DEA-1P (0.15). Likewise, DEAE-EO and DBEA have similar mole fraction for 50 wt% aqueous solutions and 20 wt.% MEG solutions. For these three amines, the absorption capacity is 60–80% higher in the presence of MEG as compared to water (Figure 10). Further studies will be required to explain the performance differences between water and MEG based solvents.
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**Conflicts of Interest:** The authors declare no conflict of interest.

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