

Thermal stability and corrosion of tertiary amines in aqueous amine and amine-glycol-water solutions for combined acid gas and water removal

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Abstract

Thermal stability and corrosion of seven tertiary amines (20 wt.%) solutions in water and water-glycol [ethylene glycol (MEG)/tri-ethylene glycol (TEG)] loaded with CO₂ in stainless steel reactors has been studied for combined acid gas removal along with hydrate control. The pKa of the tested amines varied from 7.85 to 9.75. Titration and inductivity coupled plasma mass spectrometry (ICP-MS) are used to quantify the remaining alkalinity and metal concentrations in amine solutions respectively. The presence of MEG and TEG profoundly influenced the amine stability. Triethanolamine had the highest thermal stability. Furthermore, the results also show that an increase in pKa generally decreases corrosion. 3-(Diethylamino)-1,2-propanediol (DEA-1,2-PD) has the lowest corrosion in water and water-TEG solutions while 2-(Diethylamino)ethanol (DEEA) has the least corrosion in water-MEG solutions.

Keywords: Thermal stability, corrosion, tertiary amines, glycols

Abbreviations: BDEA, N-Butyldiethanolamine; C₀, Fresh amine concentration; C_i, Amine concentration after certain time; CO₂, Carbon dioxide; Cr, Chromium, DEA-1,2-PD, 3-(Diethylamino)-1,2-propanediol; DEEA, 2-(Diethylamino) ethanol; EDEA, N-Ethyldietanolamine; Fe, Iron; ICP-MS, Inductivity coupled plasma mass spectrometry; k, First order rate constant; MDEA, N-Methyldiethanolamine; MEG, Ethylene glycol; Mo, Molybdenum; Ni, Nickel; r, Reaction rate; R², Correlation coefficient; t, Time; t-BDEA, N-tert-Butyldiethanolamine; TEA, Triethanolamine; TEG, Triethylene glycol.

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1. Introduction

Natural gas is less harmful to the environment than other fossil fuels, and the consumption of natural gas has increased during the past few years. On combustion, natural gas emits less carbon dioxide, nitrous oxide, and sulfur dioxide than other carbon-based fuels [1]. However, raw natural gas typically contains impurities such as hydrogen sulfide (H_2S), carbon dioxide (CO_2), water vapor, and mercury. CO_2 , which is a significant source of global warming, causes corrosion in the presence of water vapor and during sour gas treatment [2, 3]. Furthermore, high CO_2 quantities in the natural gas stream also reduce the heating value [4]. H_2S is a poisonous gas and can cause instant death at concentrations over 500 parts per million (ppm) [5, 6]. Finally, water vapor and methane can form ice-like solids called hydrates in natural gas wells and/or in pipelines. These hydrates can increase the corrosion rate or plug manifolds, the gas transport pipelines and/or various accessories like valves and fittings [7]. Thus, the removal of acid gases and water vapor from raw natural gas is essential. Traditionally, acid gases and water vapors are removed separately increasing the investment and operational costs [8, 9].

Subsea processing is a relatively new concept in oil and gas production. Development of a combined selective regenerative process for acid gas (H_2S/CO_2) removal along with water vapor on the seabed will reduce both the environmental footprint and the operational costs.

Amines are widely used for gas sweetening and CO_2 capture processes while tertiary amines are known to absorb H_2S selectively. Ethylene glycol (MEG) and triethylene glycol (TEG) are generally used for H_2O removal and hydrate control [10]. A potential regenerative absorption process solvent for combined subsea CO_2/H_2S and water removal could be a blend of amine and glycol. This concept has already studied. Hutchinson [11] introduced the idea of combined H_2S and water removal in 1939 by using amine glycol solution. McCartney [12] improved the Hutchinson concept and presented the regeneration process in two stages. Moisture and vaporized amine were absorbed in the glycol absorbent. It followed by the vaporization of the absorbed amine and moisture from the glycol, and

amine recovery by introducing the vapor mixture to an aqueous reflux stream in the amine still. Chapin [13] improved the McCartney [12] process by reducing amine vaporization by entering a side stream in the first stage treated solution to the second stage. MEA is the benchmark amine for the removal of CO₂ from natural gas, the first system used for combined acid gas removal and dehydration consisted of MEA and di- or triethylene glycol. This system is no longer considered competitive due to low amine thermal stability and severe corrosion at a high reboiler temperature [14]. Tertiary amines can be used as an alternative for CO₂ absorption due to their higher theoretical CO₂ loading capacity per mole of amine and low energy requirement during the regeneration process [15]. CO₂ doesn't absorb directly into tertiary amines and water is required to proceed with this reaction. Tertiary amines form an unstable carbamate in the presence of water and it leads to the formation of bicarbonate ions as shown in equation 1 [15-17].



Solvent thermal stability and equipment corrosion are known problems in amine-based gas treatment processes. Amine stability generally decreased by two main types of degradation: thermal degradation and oxidative degradation. Thermal degradation occurs due to high temperature with or without the presence of acid gas while oxidative degradation occurs due to oxygen [18, 19]. Amine stability is reduced due to irreversible side reactions of amine mainly with CO₂ and O₂ but also with NO_x and SO_x. These reactions can create various problems during the gas treatment process such as solvent loss, the formation of dangerous volatile compounds or by-products, an increase in solvent viscosity, foaming, fouling and corrosion [20-24]. Moreover, loss of amine due to its low thermal stability can also reduce the absorption capacity of solvents [25, 26]. Amine stability plays a significant role in solvent management, and the study of corrosion caused by amines is required to decide suitable construction materials for the plants. For subsea purposes, high-quality materials need to be used, since the installations should operate for 5-10 years without any maintenance.

In our previous work, it was concluded that using a tertiary amine such as N-Methyldiethanolamine (MDEA) in an amine-glycol solution instead of MEA decreased corrosion by more than ten times in the amine-MEG solution and three times in the amine-TEG solution while at the same time increasing the thermal stability of the solutions [27]. In the current work, thermal stability and corrosion of seven tertiary amine solutions loaded with CO₂ are investigated by blending the amines with water, Ethylene glycol (MEG) and Triethylene glycol (TEG). These amines are chosen based on our previous in-house work for combined desulfurization and hydrate control for subsea natural gas processing. CO₂ is major sour gas impurity along H₂S in natural gas and have a significant effect on thermal stability of amine solvents in gas sweetening process. Therefore, it is essential to study amine solutions thermal stability and corrosivity in the presence of CO₂ at high temperatures. The work provides insight into the influence of amine alkanol groups [DEEA → N-Ethyldietanolamine (EDEA) → TEA], alkyl chain length [MDEA → EDEA → N-Butyldiethanolamine (BDEA)], increase in hydroxyl group and its length [DEEA → 3-(Diethylamino)-1,2-propanediol (DEA-1,2-PD)] as well as hindrance in the alkyl chain [BDEA → N-tert-Butyldiethanolamine (t-BDEA)] of the tertiary amine on thermal stability and corrosion. The chemical structures of all the tertiary amines used in this study are shown in Figure 1.

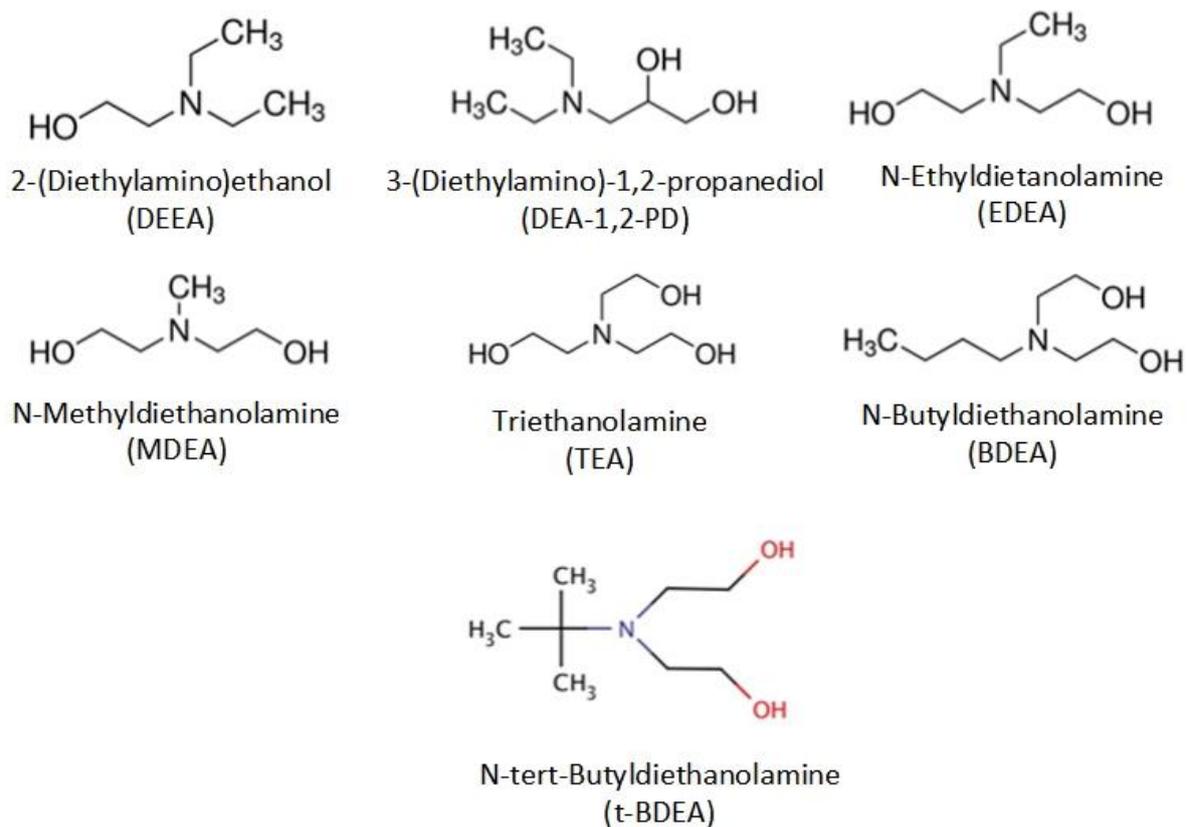


Figure 1: Chemical structure of the amines used in this study

1.1 Literature review

Both stirred cell reactors [28-30], and metal cylinders [26, 27, 31] have been used to study thermal stability. Metal cylinders are convenient in cases where the objective is to test many solutions since multiple cylinders can easily be manufactured and placed in the same heated cabinet. More complex stirred cells could then be used for detailed studies for selected solvents since only one amine at a specific concentration can be tested at one time. Thus, in this work cylinders were used to enable the testing of multiple solvents.

Chakma and Meisen [30] studied 20-50 wt.% MDEA in the stirred cell between 100-230°C, $p\text{CO}_2$ 1.38-4.24 MPa and found maximum thermal stability up to 120°C in the presence of CO_2 while above 120°C MDEA starts to lose its thermal stability rapidly. Lepaumier et al. [29] used the same method as Chakma and Meisen [30] and studied 47.6 wt.% MDEA at 140°C for 15 days with and without CO_2 .

They concluded that MDEA is less stable in the presence of CO₂, and 10% MDEA loss was observed in 15 days when CO₂ was present. Furthermore, Cloosmann and Rochelle [32] studied CO₂ loaded seven molal MDEA (83.4 wt.%) in the temperature range of 120-150°C and they reported amine loss at the rate of 3.0±0.7 millimoles/hr at 150°C. Eide-Haugmo [33] studied the thermal stability of CO₂ loaded 30 wt.% aqueous solutions of several amines, including MDEA, at 135°C in metal cylinders. She reported that 37 wt.% of MDEA was lost after five experimental weeks. Cloosmann and Rochelle [32] data also showed 37.03 wt.% MDEA loss after five weeks similar as Eide-Haugmo [33] but their amine loss after 15 days is 1.58 times more (15.87 wt.%) as compared to Lepaumier et al. [29]. Finally, Gouedard et al. [21] reviewed by-products produced due to MDEA loss in a high-temperature environment and their formation mechanisms. They concluded that the main by-product was diethanolamine (DEA) and most of the other byproducts, like triethanolamine (TEA), can be formed by DEA.

Thermal stability of DEEA was studied by Eide-Haugmo [33] and Gao et al. [28] who used metal cylinders and stirred cell reactor methods respectively. Gao et al. [28] reported that at temperatures >135°C DEEA thermal stability reduced by half with every 15°C increase in temperature. Furthermore, Gao et al. [28] observed 6% amine loss in 35.1 wt.% aqueous DEEA after 300 hr while Eide-Haugmo [33] found 14% amine loss after 840 hr in 30 wt.% aqueous DEEA at 135°C. Moreover, Eide-Haugmo [33] also studied 30 wt.% aqueous TEA at 135°C and observed 10% amine loss after five weeks. There is no thermal stability data available for the other studied tertiary amines in the literature. MEG is thermally stable up to 157°C in the absence of oxygen [34] while TEG remains thermally stable at 210°C without O₂ [35].

Only two sources of literature data for hybrid solvents, blends of amine and organic solvents have found. Al Harooni et al. [36] studied MDEA-MEG-H₂O solution (6.7wt.% MDEA, 74.64 wt.% MEG and 18.66 wt.% H₂O) at 135-200°C for 240 hours. They reported that MEG degradation caused the acids formation, which leads to corrosion and reduction of hydrate inhibition performance. Our

previous work [27] studied the thermal stability of 30 wt.% MDEA solutions at 135°C for seven weeks with the CO₂ loading for aqueous MDEA, MDEA-MEG and MDEA-TEG solutions using metal cylinders. The maximum amine loss was 9% in all solutions. Tertiary amines first degrade into primary or secondary amines, which further makes various by-products. General pathway of tertiary amine degradation in the presence of CO₂ is given by Lepaumier et al. [29] as shown in Figure 2.

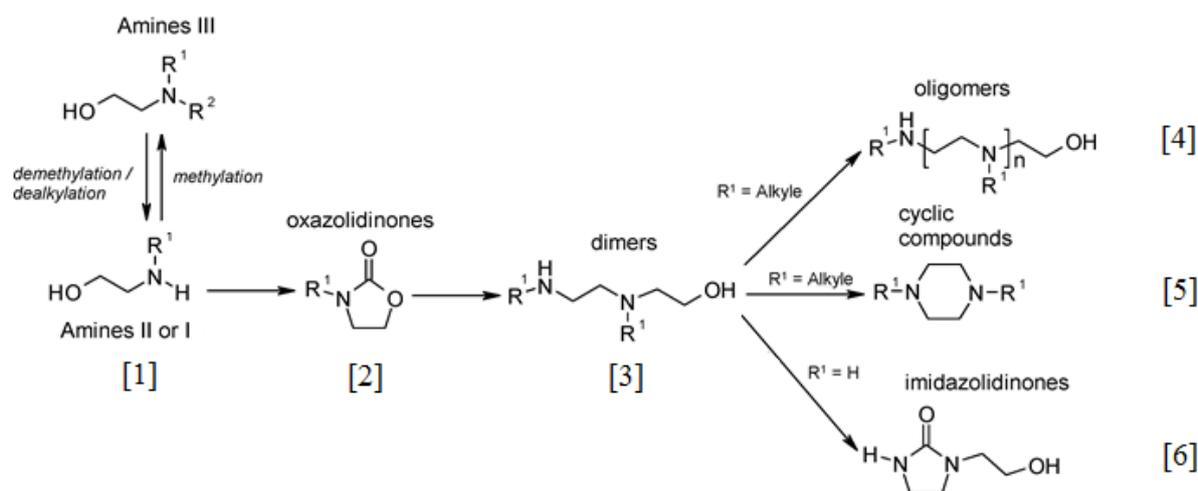


Figure 2: General pathway of thermal degradation for aqueous tertiary ethanolamines in the presence of CO₂ [29].

Corrosion is typically studied using metal coupons in a glass cell [37] or an autoclave type stainless steel corrosion cell [38]. The main disadvantage of these methods is that only one concentration of amine can be tested in one experimental run. Grimstvedt et al. [39] studied thermal stability in metal cylinders, analyzed the solutions for total Fe, Cr, Ni & Mo, and compared the metal concentrations to pilot data. They concluded that there is a correlation between corrosivity at the pilot plant conditions and high metal concentrations in thermal stability experiments. After that, the same approach has used in several studies [27, 31, 33]. Eide-Haugmo [33] found iron concentration in amine solutions in the order TEA>MDEA>DEEA while chromium concentration in order MDEA>TEA>DEEA at 135°C after 5 weeks of experiment in 30 wt.% solutions whereas in our previous study [27] the highest iron concentration was found in MDEA-TEG followed by MDEA-MEG and aqueous MDEA solutions.

Corrosion and thermal stability are connected since by-product due to amine loss can increase corrosion. Other reasons for corrosion are for example heat stable amine salts, water vapor, organic acids, oxygen and acid gas [40-42]. So when looking for solvent blends for combined H₂S removal and water control, it is essential to consider the corrosivity.

2. Materials and Methodology

2.1 Materials

All chemicals used in this study, shown in Table 1, were purchased from Sigma-Aldrich except for DEA-1,2-PD and CO₂ which were purchased from TCI Europe and AGA AB respectively. All chemicals were used without further purification. The 20 wt.% amine solutions were prepared gravimetrically in flasks by using Mettler Toledo scale, model MS6002S/01 (± 0.01 g). In the case of the glycol solutions, a solution of 60 wt.% MEG or TEG and 20 wt.% amine (the remaining 20wt.% was water) was prepared. All the solutions were loaded with CO₂ prior to experiments by using a gas wash bottle in an isolated environment. The gas wash bottle continuously weighed during CO₂ loading and the solutions were loaded until the required amount of CO₂ equivalent to loading 0.4 (mole CO₂/mole amine) was achieved. After the loading process, the solutions were titrated for amine and CO₂ concentrations.

Table 1: Name, abbreviation, CAS, purity, and pKa of all chemicals

Chemical	CAS	Purity	Molecular weight (g/mol)	pKa
2-(Diethylamino)ethanol (DEEA)	100-37-8	$\geq 99.5\%$	117.19	9.75 [43]
3-(Diethylamino)-1,2-propanediol (DEA-1,2-PD)	621-56-7	$>98.0\%$	147.22	9.68 [43]
N-Ethyldietanolamine (EDEA)	139-87-7	$\geq 98.0\%$	133.19	8.86 [15]

N-Methyldiethanolamine (MDEA)	105-59-9	≥ 99.0%	119.16	8.65 [15]
Triethanolamine (TEA)	102-71-6	≥ 99.0%	146.19	7.85 [15]
N-Butyldiethanolamine (BDEA)	102-79-4	≥ 98.6%	161.24	8.90 [44]
N-tert-Butyldiethanolamine (t-BDEA)	2160-93-2	≥ 97.0%	161.24	9.06 [15]
Carbon dioxide (CO ₂)	124-38-9	≥ 99.9%	44.01	6.37 ² , 10.3 ³ [45]
Ethylene glycol (MEG)	107-21-1	≥ 99.5%	62.07	14.44 [46]
Triethylene glycol (TEG)	112-27-6	≥ 99.8%	150.17	14.50 [47]

2.2 Methodology

The experimental setup consisted of multiple reactors and a forced convection oven. The reactors consisted of 316 stainless steel cylindrical tubes, 1.3 inches in diameter and 10 cm length. Swagelok[®] end caps were used to close both ends. A known amount of the pre-loaded solution (approximately 9 g) was added to the reactors by weighing the cylinders on a scale. With this amount of solution, about 1 cm space was obtained between the solution and cap. The reactors were stored in a forced convection oven at 135°C in an upright position [27, 31, 33]. A relatively high temperature (135°C) was used to enhance thermal effects on amine stability, shorten the experimental time and compare with the data already available. The total running time for the experiment was seven weeks. The two reactors with each solution were taken out from the oven for analysis at the same time of day after 1, 3, 5 and 7 weeks. The results presented in the results section are the averages of the two reactors

² During formation of HCO₃⁻ by aqueous CO₂

³ During formation of CO₃²⁻ by HCO₃^{-s}

for non-leaked reactors. New reactors were used for week five experiments while old clean reactors were used for weeks 1, 3 and 7. After removing the samples from the oven, the reactors were cooled down to room temperature before opening in a fume cabinet. All reactors were weighed before and after the experiments for possible leakage detection. A difference of >5% in solutions weight was considered leaked. On average, the difference in weight of the reactors before and after the experiment was <2%.

The solutions in both the reactor and duplicate were titrated with 0.2 M H₂SO₄ to quantify the amine group in the solutions and thus examine the thermal stability of the amines. The average difference between amine group concentrations of the non-leaked solutions duplicates was less than 3% indicating good reproducibility of the data. Cation ionized chromatography was also used to determine the concentration of DEEA & MDEA for the week seven solutions; the difference between total alkalinity and the DEEA or MDEA concentration in these solutions was less than 3%-points. Therefore, only the amine concentration measurements from titration are used to measure remaining amine group (%) from equation 2 and is presented in the results section. CO₂ loadings were measured by using the titration method described in Ma'mun et al. [48] and Monteiro et al. [49]. Inductivity coupled plasma mass spectrometry (ICP-MS) was used for the quantification of Fe, Cr, Ni, and Mo as an indication of relative corrosivity on the stainless steel by the amine solutions [27, 31, 50]. Since the focus is on identifying the effect of TEG and MEG on amine stability, by-products produced due to amine loss were not studied in this work.

$$\textit{Remaining amine group} (\%) = 100 \times \frac{C_t}{C_o} \quad \text{Equation 2}$$

2.2.1 Modeling

A linear regression model [51] can be used to calculate the rate constants of amine loss in all solutions by using equations (3-4). Where equation 4 is obtained by assuming first order reactions towards by-product formation with respect to amine and integrated over time “t”.

$$\frac{dC}{dt} = r = kC \quad \text{Equation 3}$$

$$\ln \frac{C_o}{C_i} = k \cdot t \quad \text{Equation 4}$$

Where C_o is the concentration of the amine group in the fresh solution and C_i is the concentration after the specific period during the experiment. From equation 4, plotting $\ln(C_o/C_i)$ as a function of time gives the first order rate constants (k) as the slope in linear regression and correlation coefficient (R^2) tells the accuracy of the model. Remaining amine group (%) can be predicted by using (C_i/C_o) value from equation 5 in equation 2. First order Rate constants used to predict the remaining amine group (%) are given in Table 2.

$$\frac{C_i}{C_o} = \frac{1}{e^{kt}} \quad \text{Equation 5}$$

3. Results

3.1 Thermal Stability

Thermal stability results are shown in figure 3-5 in the form of total remaining alkalinity as a function of experiment duration (days) for all solutions. Experimental remaining amine group % (total remaining alkalinity) for each solution is given as markers, while predicted values are given as solid lines. Rate constants along experiment duration and correlation coefficients (R^2) for all solutions are given in Table 2.

Table 2: Rate constants (k) for all solutions with linear regression fit (R^2)

Name	Experiment duration (days)	Rate constant (k) $\times 10^{-3}$ [day ⁻¹]	R^2
DEEA.H ₂ O	49	2.063	0.939
DEA-1, 2-PD.H ₂ O	49	3.414	0.985
EDEA.H ₂ O	49	3.598	0.983
MDEA.H ₂ O	49	3.101	0.913
TEA.H ₂ O	35	1.914	0.976
BDEA.H ₂ O	49	4.569	0.974

t-BDEA.H ₂ O	49	14.719	0.936
DEEA.MEG.H ₂ O	49	3.586	0.986
DEA-1, 2-PD.MEG.H ₂ O	49	3.874	0.847
EDEA.MEG.H ₂ O	49	3.615	0.979
MDEA.MEG.H ₂ O	49	3.661	0.948
TEA.MEG.H ₂ O	35	2.140	0.887
BDEA.MEG.H ₂ O	49	2.826	0.983
t-BDEA.MEG.H ₂ O	49	10.041	0.958
DEEA.TEG.H ₂ O	49	2.558	0.980
DEA-1, 2-PD.TEG.H ₂ O	49	2.523	0.965
EDEA.TEG.H ₂ O	49	2.485	0.968
MDEA.TEG.H ₂ O	49	2.721	0.963
TEA.TEG.H ₂ O	35	1.632	0.973
BDEA.TEG.H ₂ O	49	1.523	0.972
t-BDEA.TEG.H ₂ O	49	4.700	0.979

Correlation factor (R^2) values are close to one in all solutions except DEA-1,2-PD.MEG.H₂O solution, showing the good fit of the linear regression model and is apparent from figures 3-5. Rate constants values increase with the addition of MEG in aqueous solutions except for BDEA and t-BDEA solutions and by replacing MEG with TEG rate constant decrease for all solutions except DEEA. When comparing, amine.MEG.H₂O solutions with amine.TEG.H₂O solutions rate constants decrease in all solutions.

The results of all aqueous solutions are shown in Figure 3. The TEA solution reactors found leaked after seven weeks and, therefore the TEA results are only reported up to 5 weeks (35 days) in this work.

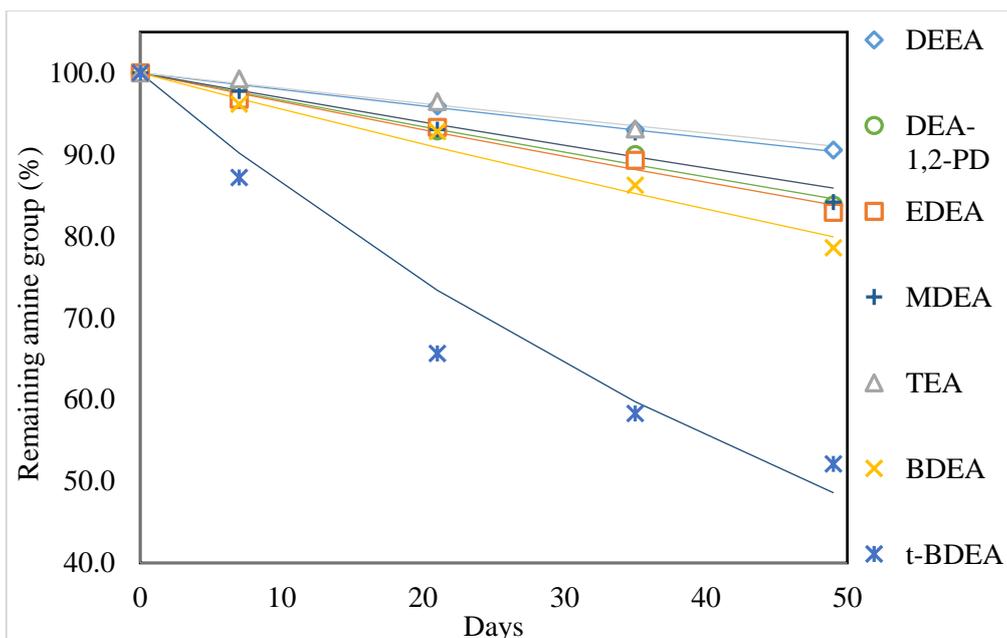


Figure 3: Remaining amine group concentration in amine-H₂O solution with solid line representing predicted values from the model

Up to week 5, the TEA solution showed the highest thermal stability together with DEEA while the t-BDEA solution had the lowest stability since week 1. Except for DEEA and MDEA, the trend of the amine loss curves for all solutions is very smooth. MDEA, BDEA, and DEA-1,2-PD showed slightly lower overall stability than DEEA and TEA, this was followed by BDEA which showed slightly lower stability than other three amines. When considering the amine structure, the number of hydroxyl groups seems irrelevant to the thermal stability. However, the results here indicate that the number and length of carbon chains can be an important parameter affecting thermal stability which was also observed in Eide-Haugmo [33] work on polyamines. t-BDEA is a hindered version of BDEA, but its aqueous solution losses amine's more than 25%-points compared to BDEA.

There is an acceptable agreement between our data and the literature data. Eide-Haugmo [33] found 7%-points higher amine loss in DEEA after five weeks and Gao et al. [28] around 2%-points higher amine loss after 12.5 days compared to our DEEA results, mainly due to higher amine concentrations as well as higher CO₂ loading. Eide-Haugmo's [33] MDEA results showed higher amine loss (37%) values compared to this study. In this work, 7.3% amine loss was observed after five weeks while in

another study, Shoukat et al. [27] found 4% amine loss, which is in line with the findings of this work. The difference in CO₂ loadings can explain the 3.7%-points higher amine loss in this work, compared to Shoukat et al. [27]. Eide-Haugmo's [33] TEA result is 3%-points higher amine loss than this work, and this is most likely due to higher initial amine concentration. As discussed earlier, no literature data for the for other tested amines was found.

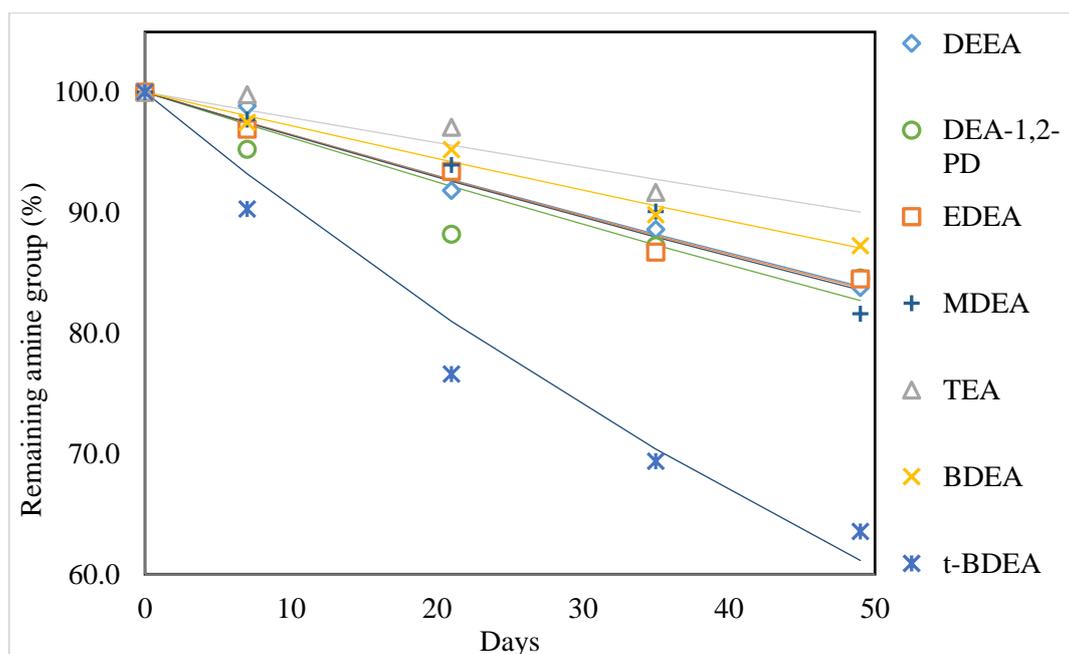


Figure 4: Remaining amine group concentration in amine-H₂O-MEG solution with solid line representing predicted values from the model

The thermal stability in aqueous amine-MEG solutions is presented in Figure 4. In the presence of MEG, TEA showed the highest thermal stability up to week five while, as in aqueous solutions, t-BDEA has the least thermal stability. The EDEA thermal stability was almost equal to DEEA and DEA-1,2-PD at week 7. Contrary to the aqueous solutions, in MEG solutions, BDEA showed higher thermal stability. In this work, 9%-points lower thermal stability was observed in the MDEA.MEG.H₂O solution compared to Shoukat et al. [27] due to the higher CO₂ loading used in this study. A similar trend was also observed in the MDEA.TEG.H₂O solution.

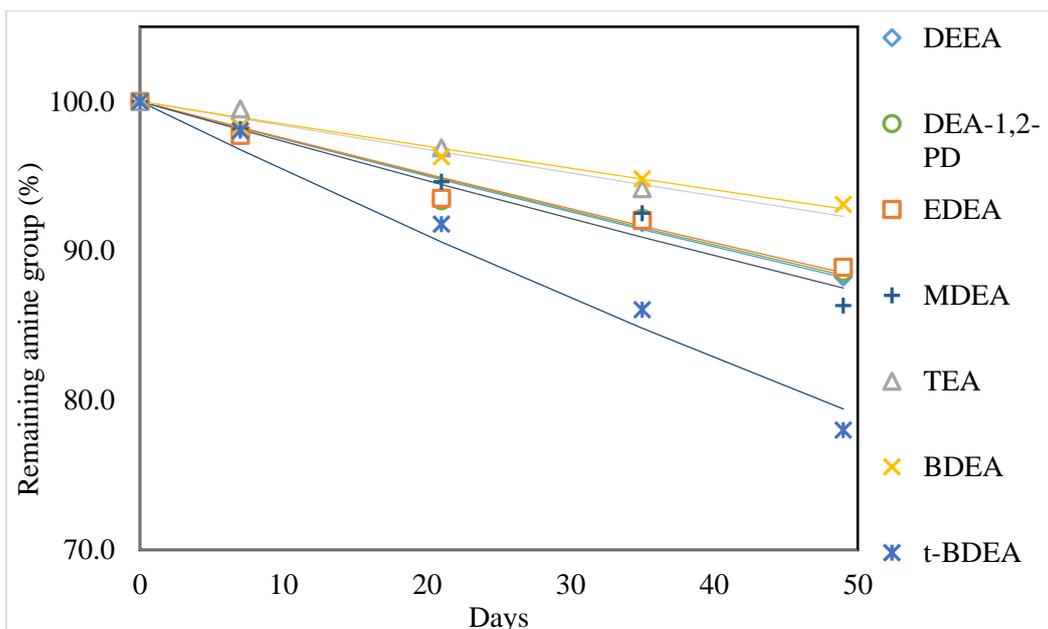


Figure 5: Remaining amine group concentration in amine-H₂O-TEG solution with solid line representing predicted values from the model

The thermal stability of amine-H₂O-TEG solutions is shown in Figure 5. Like the aqueous solutions of amine and amine-H₂O-MEG up to week 5, TEA showed the highest thermal stability and t-BDEA had the lowest thermal stability. BDEA showed the highest thermal stability after week seven the other amines showed similar thermal stability trend as of MEG solutions.

Figure 6 shows the difference between the amine loss of aqueous amine and aqueous amine-MEG solutions. Thermal stability of aqueous amine solutions increased by adding MEG except for MDEA and DEEA aqueous solutions. The addition of MEG in aqueous amine solutions decreased the amine loss in t-BDEA and BDEA aqueous solution. The highest decrease was observed in t-BDEA (11.4%-points) while the maximum increase was observed in DEEA (6.7%-points). Figure 7 presents the difference between the remaining alkalinity of the aqueous amine solution and aqueous amine-TEG solutions. TEG addition increased the amine stability in all solutions except DEEA which was unaffected by the addition of TEG. It seemed that TEG acted as an inhibitor. Finally, as shown in Figure 8 it is clear that by replacing the TEG with MEG in the solutions, the amine stability increased for all the solutions.

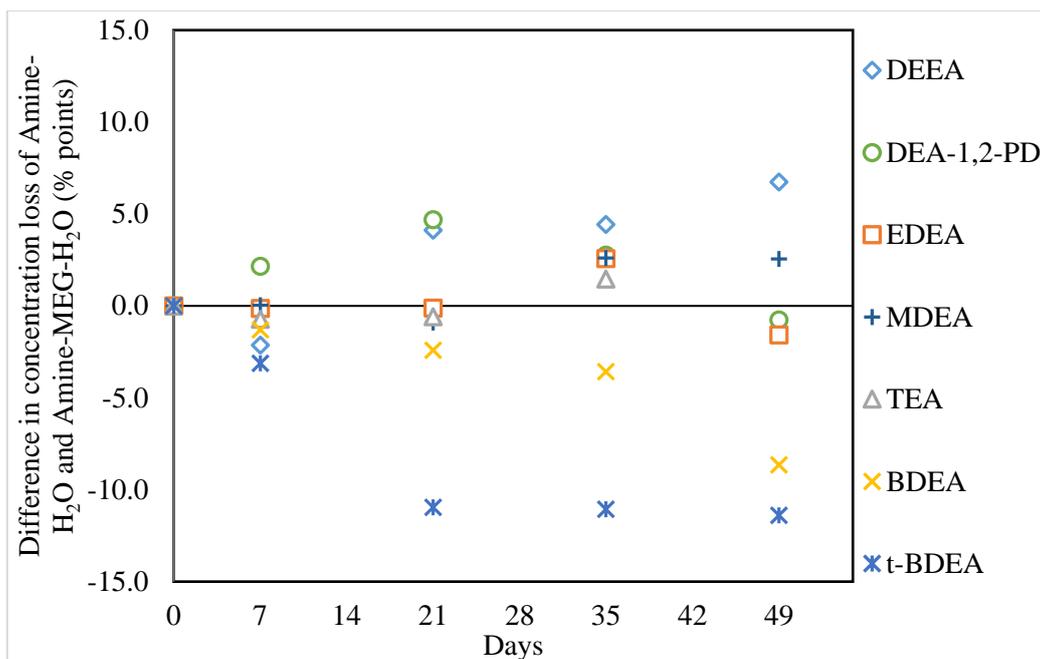


Figure 6: Difference between remaining amine groups (percent points) in amine-H₂O and the amine-MEG-H₂O solution

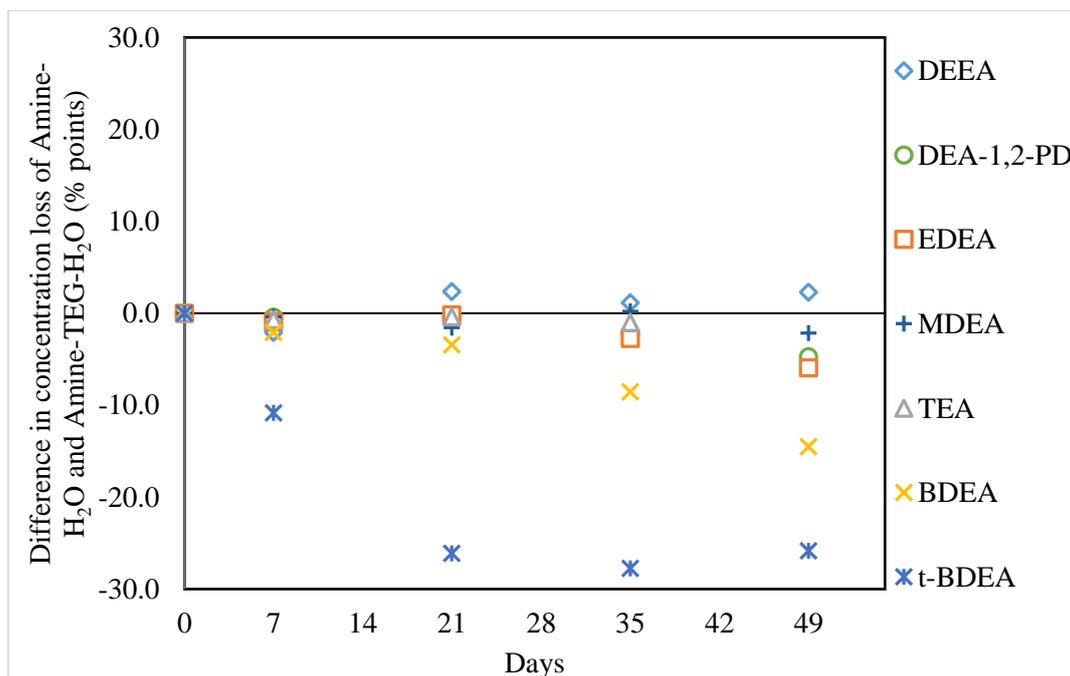


Figure 7: Difference between remaining amine groups (percent points) in amine-H₂O and the amine-TEG-H₂O solution

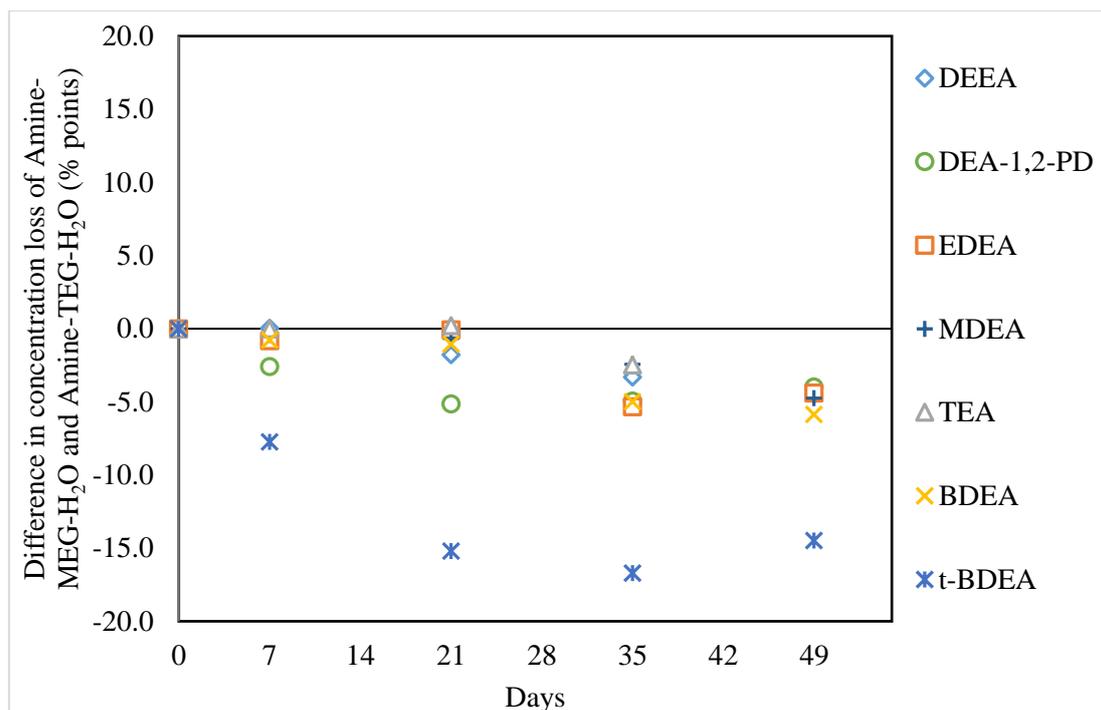


Figure 8: Difference between remaining amine group (percent points) in Amine-MEG-H₂O and Amine-TEG-H₂O solution

3.2 Corrosion

The solutions from week five were analyzed for corrosivity using ICP-MS. Higher metal concentrations in the solutions indicate higher corrosivity. Duplicates of each solution were analyzed, and the average of these results was used. The average difference in the duplicates and the maximum deviation were 0.2 and 0.5 mg/L, respectively.

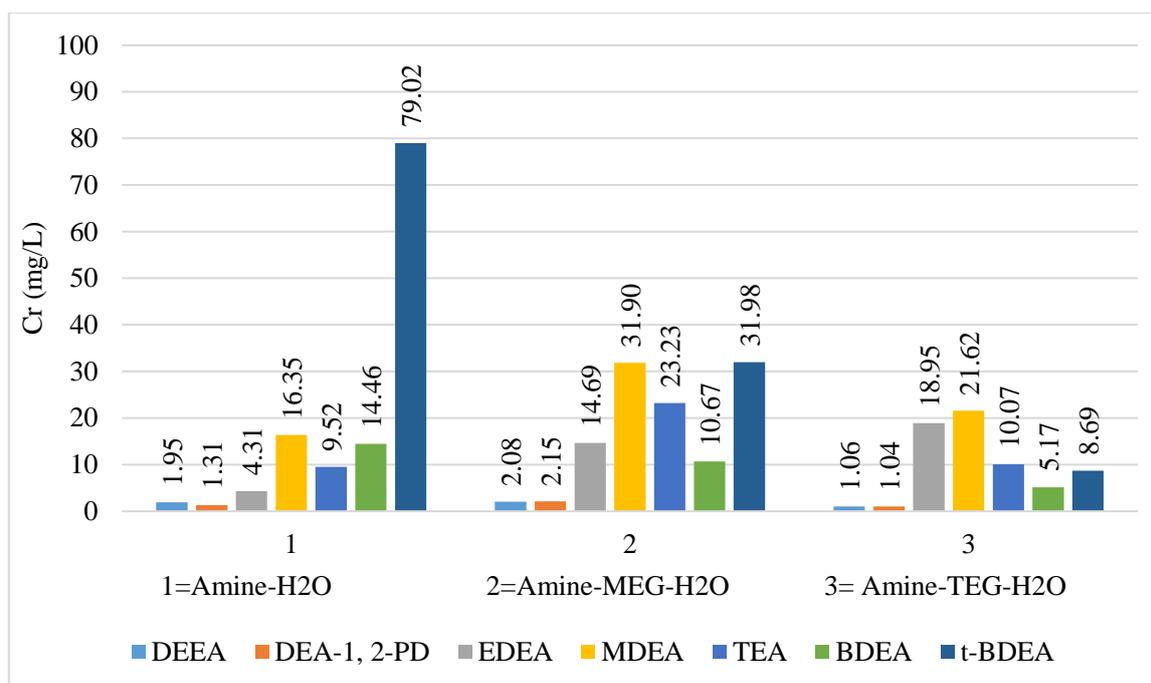


Figure 9: Chromium concentration in all solutions after five weeks

Chromium concentrations in all solutions are shown in Figure 9. The Cr concentration was highest in aqueous t-BDEA solution while small quantities were found in DEEA and DEA-1,2-PD solutions. The addition of MEG increased the chromium concentration in EDEA, MDEA, and TEA solutions, while the addition of TEG decreased the Cr concentrations in all solutions except aqueous EDEA, MDEA. The TEA, DEEA, and DEA-1,2-PD solutions were unaffected. Hydroxyl groups increased the Cr concentration in aqueous amine and aqueous amine-MEG solutions, i.e. (DEEA<EDEA<TEA); however, in aqueous amine-TEG solutions the trend was different. The EDEA solution had the highest corrosion while DEEA the lowest and TEA was in between them. The increase in alkyl chain length decreased the Cr concentration in amine-glycol solutions (MDEA>EDEA>BDEA), but in aqueous amine solutions, MDEA had the highest Cr concentration while EDEA had the lowest (BDEA is in between them). Cr concentration was in the order MDEA>TEA>DEEA for aqueous amine solutions. The same trend has also been observed by Eide-Haugmo [33].

Individual metal concentrations were very low (>2mg/L) in all DEEA and DEA-1,2-PD solutions; therefore, it was difficult to observe the effect of an increase in the hydroxyl group and its length on

corrosion. Hindrance in the alkyl chain increased all metal concentrations significantly in all the solutions, i.e. (BDEA<t-BDEA).

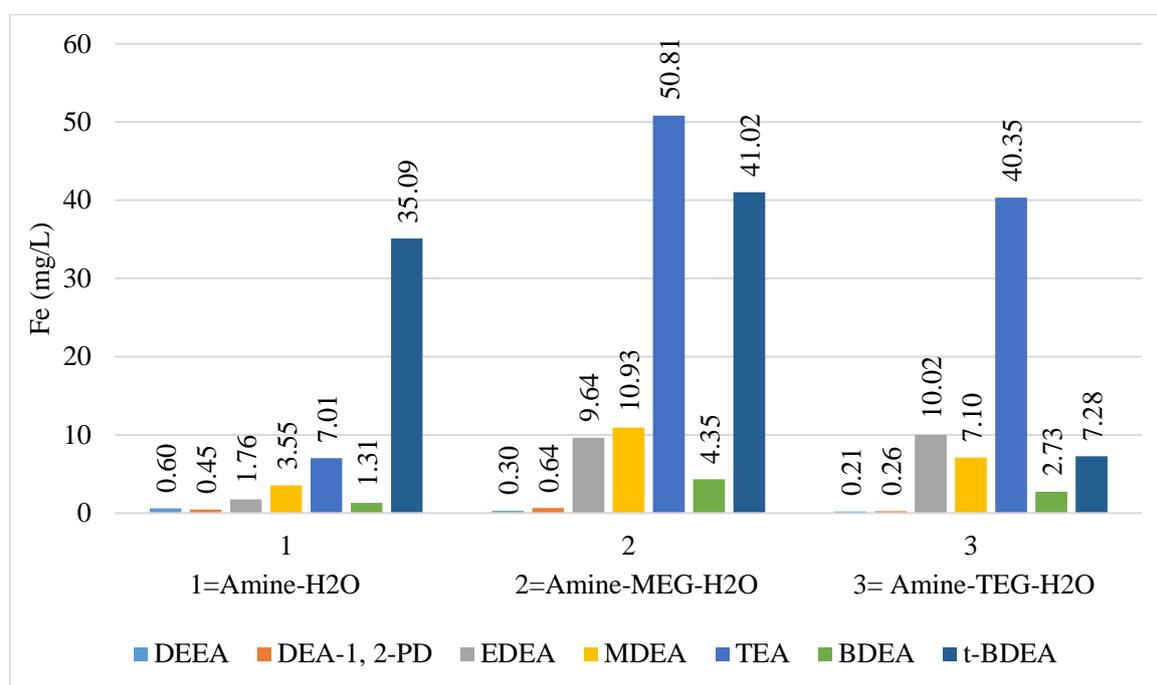


Figure 10: Iron concentration in all solutions after five weeks

Figure 10 presents the iron concentrations in all solutions. The addition of MEG in the solutions increased the Fe concentrations in all solutions (except DEEA and DEA-1,2-PD), while the addition of TEG increased the Fe concentration in BDEA, TEA, MDEA, EDEA solutions (except DEEA, DEA-1,2-PD, and t-BDEA). An increase in amine alkanol groups increased the Fe concentration in all solutions, i.e. (DEEA<EDEA<TEA). An increase in the alkyl chain length increased the Fe concentration in aqueous amine and amine-MEG-H₂O solutions (MDEA>EDEA>BDEA) while in amine-TEG-H₂O solutions the iron concentration followed the order of EDEA>MDEA>BDEA. As mentioned earlier, Eide-Haugmo [33] found iron concentrations in aqueous amine solutions in the order TEA>MDEA>DEEA which is in accordance with this work. Shoukat et al. [27] found iron concentration in the order MDEA.H₂O<MDEA.MEG<MDEA.TEG while in this work the iron concentration was in the order of MDEA.H₂O<MDEA.TEG.H₂O<MDEA.MEG.H₂O. The maximum iron concentration was present in TEA.MEG.H₂O solution (51mg/L), which was still of very low.

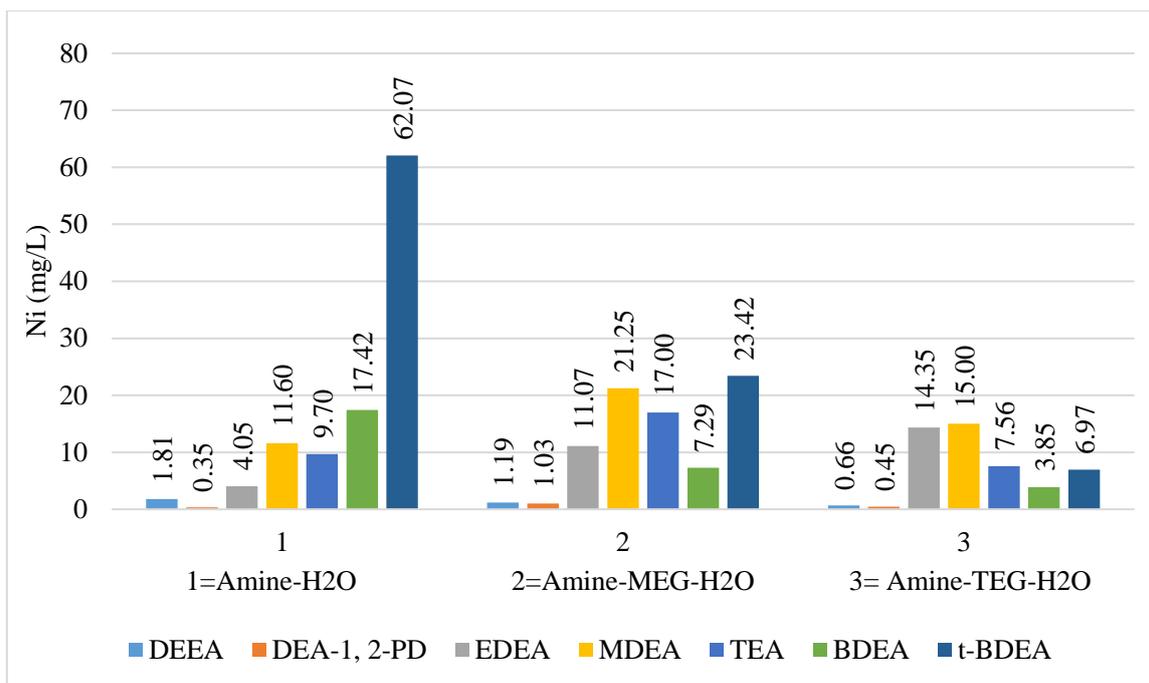


Figure 11: Nickel concentration in all solutions after five weeks

Concentrations of nickel and molybdenum are shown in Figure 11 and Figure 12, respectively. Both metals have shown trends similar to that of chromium, but the magnitude of corrosion caused by molybdenum was less compared to Ni and Cr. The Ni and Cr concentrations showed similar values in all the solutions which might be due to their close quantities in stainless steel composition.

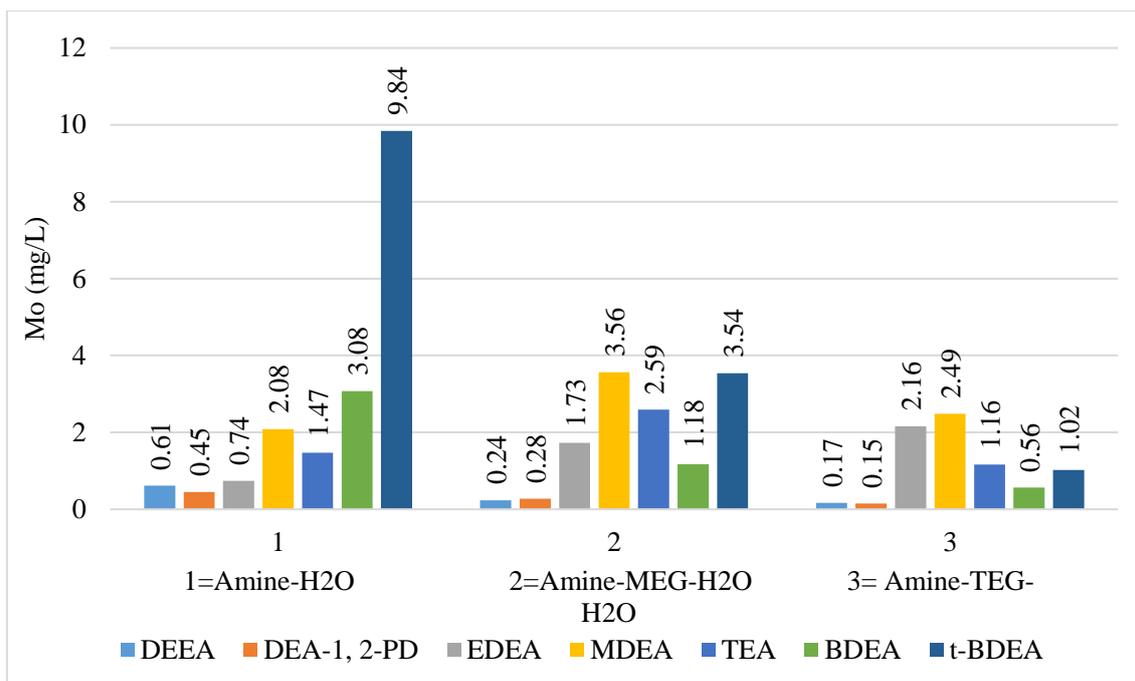


Figure 12: Molybdenum concentration in all solutions after five weeks

DEEA and DEA-1, 2-PD showed the lowest corrosion among all studied amines while t-BDEA was the highest. The effect of MEG and TEG on amines varied, but the addition of glycols significantly reduced the corrosion in t-BDEA and increased the corrosion in EDEA, MDEA, TEA solutions.

3.3 Effect of pKa on thermal stability and corrosion

Figure 13 presents thermal stability (lost amine group) and corrosion (total metal concentration) as a function of pKa for week five solutions in aqueous, MEG and TEG solutions. t-BDEA is a sterically hindered amine and may be due to this it is showing a different type of behavior compared to the other tertiary amines. Therefore, excluding t-BDEA solutions following trends can be observed; In the case of aqueous amine and amine-MEG-H₂O solutions, a slight decrease in thermal stability at lower pKa values but thermal stability becomes better at higher pKa values (≈ 9.60). Thermal stability decreased with increase in pKa in amine-TEG-H₂O solutions where BDEA-TEG-H₂O solution is acting as an outlier. Effect of pKa on corrosion is more observable as compared to its effect on thermal stability. It appeared that corrosion is inversely proportional to pKa.

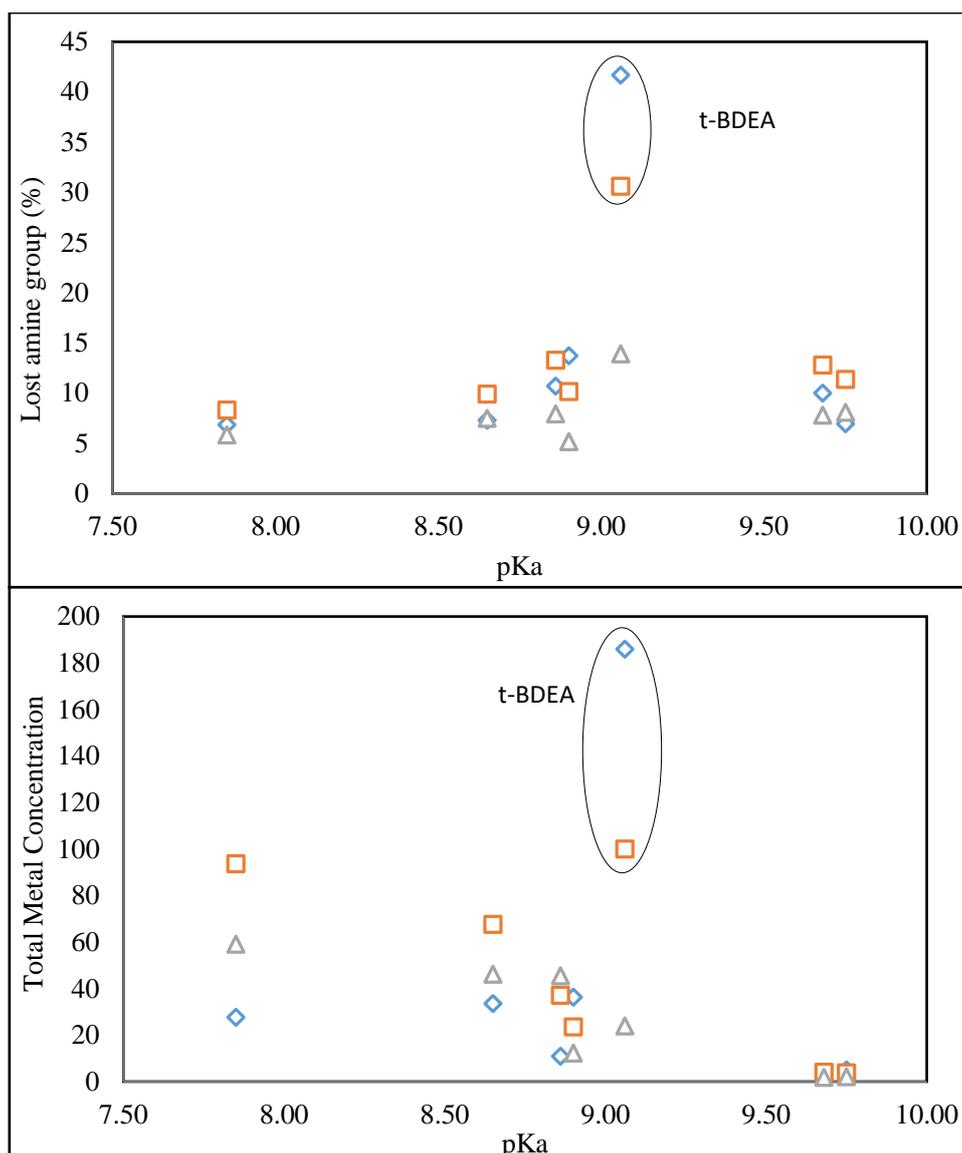


Figure 13: Effect of pKa on thermal stability (upper graph) and corrosion (lower graph) in aqueous amine solutions (\diamond), amine-MEG-H₂O (\square) and amine-TEG-H₂O (Δ) solutions respectively

The effect of the thermal stability on corrosion can be studied by making the total amount of analyzed metals as a function of total amine loss in a solution. In general, no direct correlation was observed between corrosion and amine loss, which contradicts the general statement that thermal stability is linked to corrosion [33, 39]. It might be due to low corrosion rate and high thermal stability of these amines except t-BDEA.

4. Conclusions

In this work, the thermal stability of seven tertiary amines loaded with CO₂ has been studied in water and water-glycol [ethylene glycol (MEG)/tri-ethylene glycol (TEG)] solutions using stainless steel reactors at 135°C for seven weeks. The results show that there is no trend in thermal stability with respect to an increase in the alkanol group. However, the increase in alkyl group length decreases the thermal stability in aqueous amine solutions and vice versa for amine-water-glycol solutions. Hindrance in amine seems to reduce the thermal stability and increase corrosion significantly in all solutions. Linear regression model gives a good fit to data for all solutions. The increase in the pKa seems to decrease the corrosion except for t-BDEA solutions which act like outliers. It appears that at pKa values <9.10 thermal stability is weakly dependent on pKa. Both DEEA and DEA-1,2-PD showed low corrosion and higher thermal stability in amine-water and amine-water-glycol solutions. Additionally, when only considering amine-water-glycol solutions, BDEA showed higher thermal stability and low corrosion.

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Appendices

Appendix A: Amine group concentrations in all solutions

Solvent	Remaining amine group concentration (mole/kg)				
	Week 0	Week 1	Week 3	Week 5	Week 7
DEEA.H ₂ O	1.643	1.590	1.577	1.529	1.488
DEA-1, 2-PD.H ₂ O	1.315	1.281	1.222	1.184	1.102
EDEA.H ₂ O	1.458	1.411	1.361	1.302	1.209
MDEA.H ₂ O	1.604	1.568	1.492	1.487	1.350
TEA.H ₂ O	1.309	1.300	1.264	1.220	
BDEA.H ₂ O	1.206	1.160	1.120	1.041	0.948
t-BDEA.H ₂ O	1.210	1.055	0.794	0.706	0.631
DEEA.MEG.H ₂ O	1.644	1.626	1.510	1.457	1.378
DEA-1, 2-PD.MEG.H ₂ O	1.312	1.250	1.158	1.145	1.110
EDEA.MEG.H ₂ O	1.436	1.392	1.342	1.246	1.214
MDEA.MEG.H ₂ O	1.593	1.557	1.497	1.435	1.300
TEA.MEG.H ₂ O	1.317	1.314	1.279	1.207	
BDEA.MEG.H ₂ O	1.203	1.172	1.145	1.080	1.049
t-BDEA.MEG.H ₂ O	1.204	1.087	0.922	0.835	0.765
DEEA.TEG.H ₂ O	1.628	1.609	1.524	1.496	1.437
DEA-1, 2-PD.TEG.H ₂ O	1.310	1.281	1.223	1.207	1.160
EDEA.TEG.H ₂ O	1.433	1.400	1.340	1.319	1.274
MDEA.TEG.H ₂ O	1.598	1.568	1.512	1.478	1.380
TEA.TEG.H ₂ O	1.304	1.298	1.263	1.228	
BDEA.TEG.H ₂ O	1.196	1.176	1.152	1.134	1.114
t-BDEA.TEG.H ₂ O	1.198	1.175	1.100	1.031	0.935

Appendix B: Linear regression results

Solution	Cr	Fe	Ni	Mo	Total
DEEA.H ₂ O	1.945	0.597	1.812	0.613	4.967
DEA-1, 2-PD.H ₂ O	1.306	0.448	0.350	0.449	2.554
EDEA.H ₂ O	4.307	1.759	4.049	0.737	10.852
MDEA.H ₂ O	16.349	3.550	11.600	2.082	33.580
TEA.H ₂ O	9.524	7.009	9.695	1.471	27.699
BDEA.H ₂ O	14.458	1.315	17.419	3.078	36.269
t-BDEA.H ₂ O	79.022	35.088	62.066	9.841	186.016
DEEA.MEG.H ₂ O	2.079	0.296	1.189	0.235	3.799
DEA-1,2-PD.MEG.H ₂ O	2.149	0.641	1.025	0.277	4.092
EDEA.MEG.H ₂ O	14.691	9.641	11.069	1.727	37.129
MDEA.MEG.H ₂ O	31.897	10.934	21.246	3.563	67.640
TEA.MEG.H ₂ O	23.233	50.815	17.005	2.591	93.644
BDEA.MEG.H ₂ O	10.671	4.347	7.286	1.175	23.479
t-BDEA.MEG.H ₂ O	31.985	41.021	23.424	3.541	99.970
DEEA.TEG.H ₂ O	1.064	0.209	0.657	0.167	2.097
DEA-1, 2-PD.TEG.H ₂ O	1.040	0.256	0.450	0.154	1.899
EDEA.TEG.H ₂ O	18.947	10.023	14.353	2.163	45.486
MDEA.TEG.H ₂ O	21.620	7.097	15.004	2.487	46.207
TEA.TEG.H ₂ O	10.070	40.345	7.561	1.160	59.136
BDEA.TEG.H ₂ O	5.166	2.727	3.855	0.564	12.311
t-BDEA.TEG.H ₂ O	8.689	7.281	6.968	1.024	23.962

Appendix D: Comparison of data with previous studies

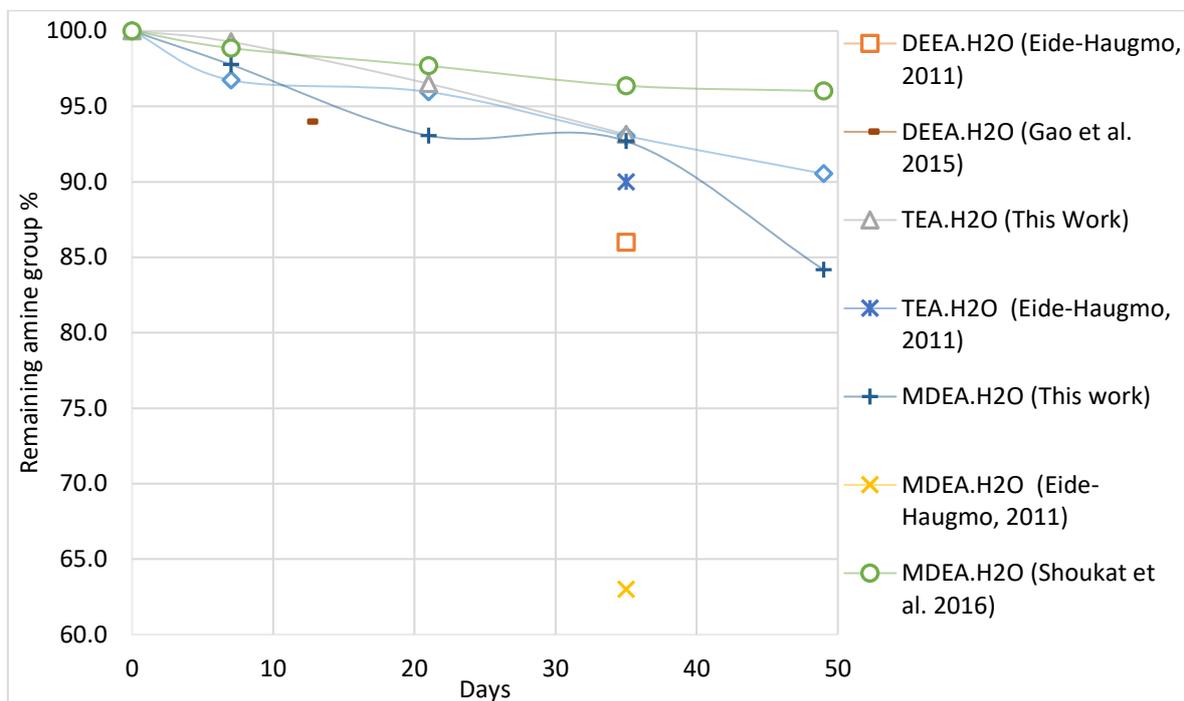


Figure 14: Comparison with the literature on remaining amine group concentration in amine-H₂O solutions. DEEA.H₂O (Eide-Haugmo, 2011) [33], DEEA.H₂O (Gao et al. 2015) [28], TEA.H₂O (Eide-Haugmo, 2011) [33], MDEA.H₂O (Eide-Haugmo, 2011) [33], MDEA.H₂O (Shoukat et al. 2016) [27]

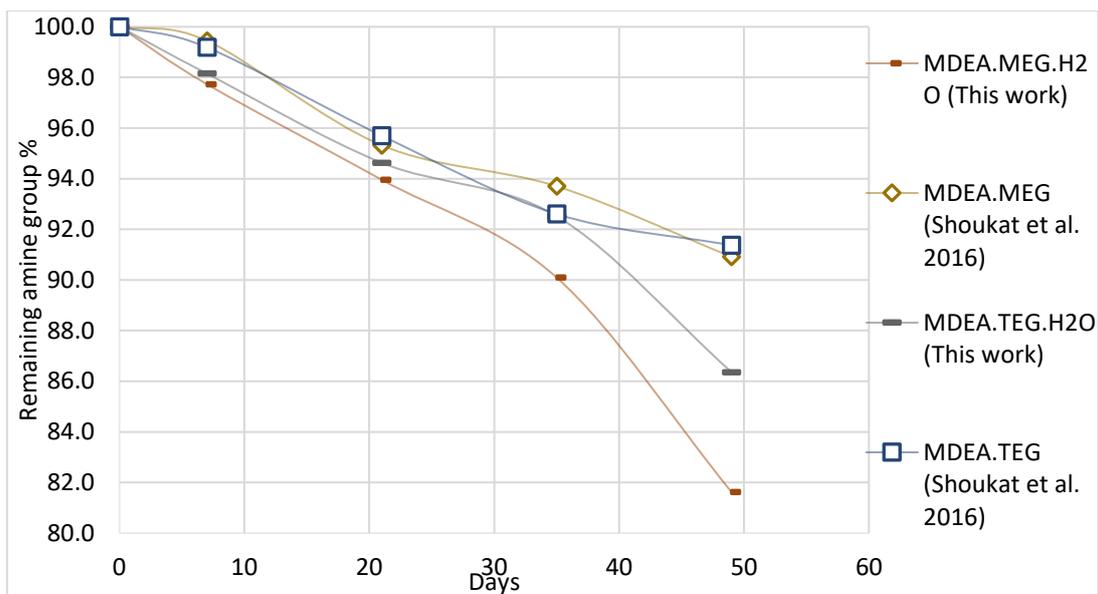


Figure 15: Comparison with the literature on remaining amine group concentration in amine-H₂O-glycols and amine-glycols solutions with MDEA.MEG (Shoukat et al. 2016) [27], MDEA.TEG (Shoukat et al. 2016) [27] solutions

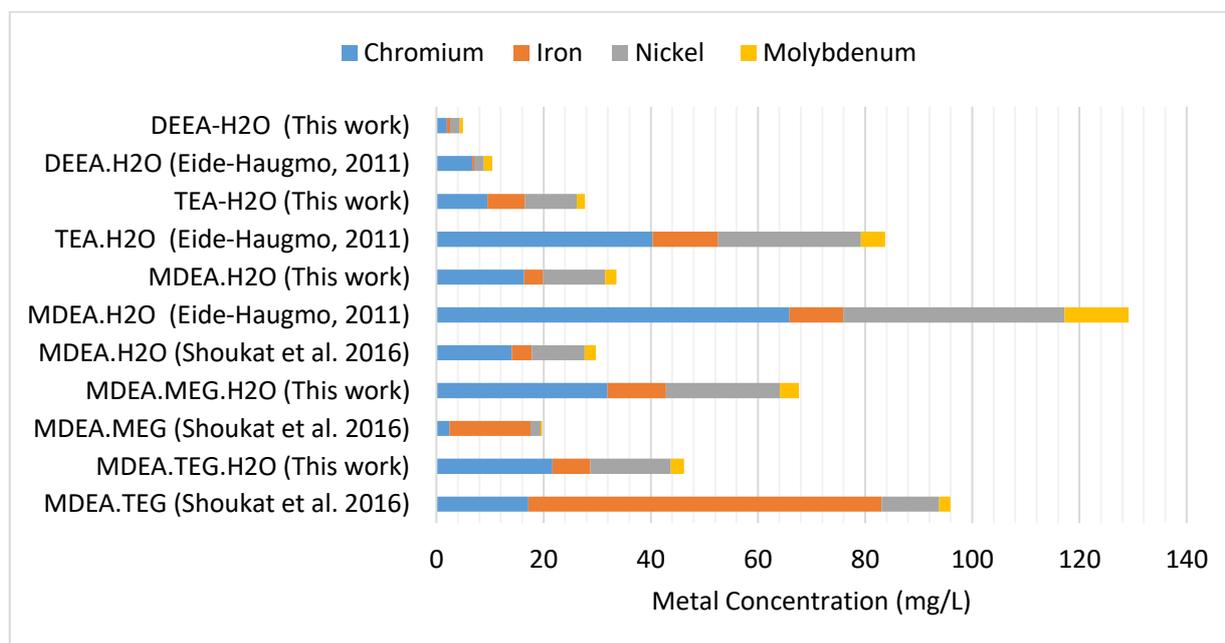


Figure 16: Various metal concentrations in solutions. DEEA.H₂O (Eide-Haugmo, 2011) [33], TEA.H₂O (Eide-Haugmo, 2011) [33], MDEA.H₂O (Eide-Haugmo, 2011) [33], MDEA.H₂O (Shoukat et al. 2016) [27], MDEA.MEG (Shoukat et al. 2016) [27], MDEA.TEG (Shoukat et al. 2016) [27]