

Investigating the Effectiveness of Amine Blends with Deep Eutectic Solvents for CO₂ Capture

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Abstract

Natural gas, predominantly methane, contains a considerable amount of acid gases, notably CO₂. This gas poses problems such as corrosion to equipment, greenhouse gas effect, and low heating value. The use of amines for CO₂ removal from natural gas cannot be over-emphasized. The major amines employed are the primary (monoethanolamine, MEA), secondary (diethanolamine, DEA), and tertiary (triethanolamine, TEA; metyldiethanolamine, MDEA) amines. Each of these amines has desirable properties that complement one another. Combining two or more amines tends to improve its ability to absorb CO₂. In this study, MEA, DEA, and MDEA were mixed in different proportions and modified with deep eutectic solvents (DES) to evaluate the CO₂ absorption capacities of the composite samples at temperatures of 26°C, 40°C, and 70°C and pressures of 43.5psi, 72.5psi, and 108.8psi; this was compared with the CO₂ absorbed by the DES-unmodified samples. The results showed that the samples modified with DES increased CO₂ absorption capacity by an average of 19.5%. The highest CO₂ absorption capacity of 1.91mmol/g was noticed for the MEA/DEA/TEA/DES blend, and the least absorption capacity of 0.92mmol/g was seen for the DEA/TEA blend at a temperature of 70°C. This absorption capacity of 1.91mmol/g was attributed to the fact that CO₂ has a reasonable reaction rate with MEA and a high loading capacity with TEA and DES, which accounts for the retention of the gases after absorption. Cost analysis was carried out to determine the most performing blend economically. It was further observed that the blends modified with DES had a 2.1% increase in cost but absorbed 16.7% more CO₂ than the control amine blends.

Keywords: Amine blends; Deep eutectic solvent; Absorption; CO₂ capture.

1. Introduction

Natural Gas (NG) is gas gotten from natural underground reservoirs. It is considered the cleanest form of fossil fuel and comprises a large volume of methane and some other heavier hydrocarbons. These hydrocarbons include ethane, propane, normal butane, and isobutane. It also contains non-hydrocarbons such as acid gases (carbon dioxide and hydrogen sulphide) and nitrogen. The use of NG in industries and domestically is increasing globally and accounting for 23.4% of total energy requirements in 2018 [1]. However, as clean as it may appear, NG cannot be used without purification to remove acid gases associated with it upon production. These gases include carbon dioxide (CO₂), hydrogen sulphide (H₂S), and traces of water vapors, mercury and mercaptans. Specifications required for natural gas have limits on sulphur content (generally, sulphur content should be 5 to 20g/100 SCF (116-460mg/m³) [2].

The availability of CO₂ and H₂S in NG poses a significant risk to the gas, rendering it unmarketable. Acid gases, therefore, must be removed to make the gas as clean and purified as possible to avoid the problems of corrosion, plugging, freezing, and environmental health hazards. The presence of CO₂ in NG lowers the gas's British Thermal Value (BTU) value and forms carbonic acid, which is corrosive. The gas remains unsellable when the concentration is higher than 2-3% [3]. The presence of H₂S majorly causes corrosion to equipment; CO₂ is the primary cause of Greenhouse Gas (GHG), which is responsible for climate change. According to the

Emission Database for Global Atmospheric Research [4], CO₂ emission related to fossil CO₂ was 37.1 billion tons in 2017, representing about 43% more than two decades ago [5].

Chemical solvents (amines) have been mainly used for acid gas removal in the gas treatment industry in a process known as absorption. In absorption technology, different amine solvents are employed for CO₂ capture. The solvents include primary, secondary, and tertiary amines. Of note are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyldiethanolamine (MDEA) [6]. The absorption technology is the most widely used for CO₂ removal from NG [7]. This is mainly due to the advantages, which include:

- i. Rapid reaction rate (MEA and DEA);
- ii. High retention capacity (TEA and MDEA)
- iii. Low molecular weight and high absorbing capacity (TEA and MDEA)
- iv. Low cost of solvents (MEA and DEA);
- v. Thermal stability

The main objective in the design and use of amines in the gas sweetening process is that the sweetened gas meets the specification standards set by the contractual agreement or with the Liquefied Natural Gas (LNG) specification with respect to CO₂ and H₂S content. The other important objective is to select amines or amine blends that will optimize equipment size and reduce operating costs. As described in chemistry, amines are compounds made up of basic nitrogen atoms. The nitrogen atom comprises valence electrons that are not shared with another atom (lone pair). They are obtained from ammonia, where substituents like an aryl or alkyl group have replaced one or some hydrogen atoms. These may be called arylamines or alkylamines, respectively. Amines have been categorized based on the number of hydrogen atoms replaced. We have the following types of amines in cases where the hydrogen groups are alkyl groups. They include primary amines, e.g., monoethanolamine; secondary amines, e.g., diethanolamine; and tertiary amines, e.g., triethanolamine [8-9]. The MEA, DEA, MDEA, and TEA properties can be found elsewhere [10].

Deep Eutectic Solvents are liquid low transition temperature mixtures formed by hydrogen bonding of multiple starting materials that exhibit higher melting temperatures. These temperatures (eutectic temperature) are usually lower than any constituents' temperatures [11]. 12°C is the melting point of DES, indicating that it is in liquid form at room temperature [12]. They are mainly composed of Hydrogen Bond Acceptors (HBAs)/quaternary ammonium salts and metal Hydrogen Bond Donors (HBDs)/halides. Quaternary ammonium salts are positively charged polyatomic ions of the structure NR⁺. Some of the characteristics of DES, which are helpful for CO₂ absorption, include low cost of production, biodegradability, good viscous nature, and low melting point. Other properties and characteristics of DES can be found in the open literature [13-14]. This study employs a type III DES mixture.

2. Reviews

Available literature shows that while the removal of sour gases from NG has been successful with each available amine, it has been achieved better by blending the different amines. In their work on acid gas removal from NG with N-methyldiethanolamine (MDEA), Saeed *et al.* [6] employed the MDEA process to purify NG. Besides the high operating capital, cost, and stripping energy, CO₂ removal was poor. They used a blend of MDEA and DEA to achieve better absorption efficiency and cost-effectiveness than MDEA alone. In a comparative study on the effect of acid gas cleaning by MDEA and MDEA+piperazine, Naveed and Muddasar [15] observed, among other things, that while MDEA has its cleaning effect, a blend of MDEA and 1% mass of piperazine increased the rate of absorption of CO₂ from natural gas.

Usman *et al.* [2], in their study on various aqueous and non-aqueous amine blends for hydrogen sulphide removal from NG, compared MDEA and monoethylene glycol/triethylene glycol in the absorption of H₂S. They concluded that using MEG and TEG blends showed higher loading than MDEA. Adewale *et al.* [16], in their study on the absorption of CO₂ by amine blends solution, showed that single amines agree with recent pieces of literature on the gas sweetening process. Still, blends of Piperazine with the three major amines show that CO₂ removal was bettered by almost 20% compared with single amine cleaning.

Working on CO₂ absorption into biphasic amine solvent with solvent loss reduction, Jiafei *et al.* [17] studied CO₂ absorption into some lipophilic amines (N, N-dimethylcyclohexylamine

(DMC) and dipropylamine (DPA)). The results showed increased CO₂ capture with the blended amines than the single ones. Erik *et al.* [18] compared the absorption capacity of MEA and blended amine solvent. They observed that MEA and blended amine solvent exhibited good CO₂ balance (less than 10% deviation). Both solvents had increased CO₂ removal, but the CO₂ removal was slightly higher in the blended amine solvent. Their work concluded that a significant reduction (5-34%) in heat duty could be obtained using blended amine solvents against the MEA alone.

Studies on amine blends with DES for CO₂ capture are limited in the literature, despite the available evidence that DES can absorb acid gases effectively. Therefore, this study seeks to investigate the effectiveness of amine blends with DES in capturing CO₂. A baseline cost analysis was also performed to examine the cost-effectiveness of the process.

3. Materials and methods

MEA, DEA, and TEA were purchased from Sigma-Aldrich through Bristol Scientific, Lagos State, Nigeria, with 99% purity. Choline chloride and glycerol were purchased from the local market in Lagos town, Port Harcourt, Rivers State, Nigeria. The CO₂ capture apparatus by Aimikhe and Eyankware [19] was used for the investigation. Details of the experimental procedure can be found in the open literature.

3.1. Preparation of deep eutectic solvents

The solution of DES was prepared using choline chloride and glycerol in a ratio of 1:2. 90g Choline chloride was measured in a vacuum chamber to reduce the possible moisture absorption from the atmosphere. Choline chloride is hygroscopic and hence placed in a beaker. 180g of glycerol was also measured under the same conditions and added to the choline chloride. The solution was stirred for three hours at 80°C on a magnetic stirrer to ensure that the solution was adequately mixed and a homogenous solution was obtained. The resultant homogenous solution was used to make MEA, DEA, and TEA blends.

3.2. Preparation and blending of amine solvents with DES

The chosen blend ratios were based on the reactivity and CO₂ holding capacity of the different amine solvents. Generally, MEA has a faster reaction rate than DEA and TEA. The amine solvent's reaction rate with CO₂ decreases from the primary amines to the secondary and tertiary amines. Also, the CO₂ absorption capacity decreases from the tertiary amines to the secondary and primary amines. The idea is to get a blend balance of amine CO₂ reaction and absorption rates.

To obtain a given blend, various measurements of the samples were taken and placed in a beaker on the weighing balance. The beaker was properly sealed (a precautionary measure to avoid atmospheric CO₂ intake, which may alter the final result) with paper and adhesive tapes, placed on the magnetic stirrer, and stirred for one hour to obtain a homogenous mixture. The resultant amine blend was labeled and used for the experimental process. The experiment was repeated for other corresponding amine blends. The various combinations obtained in this study are shown in Table 1.

Table 1. Various combinations of amine and DES blends

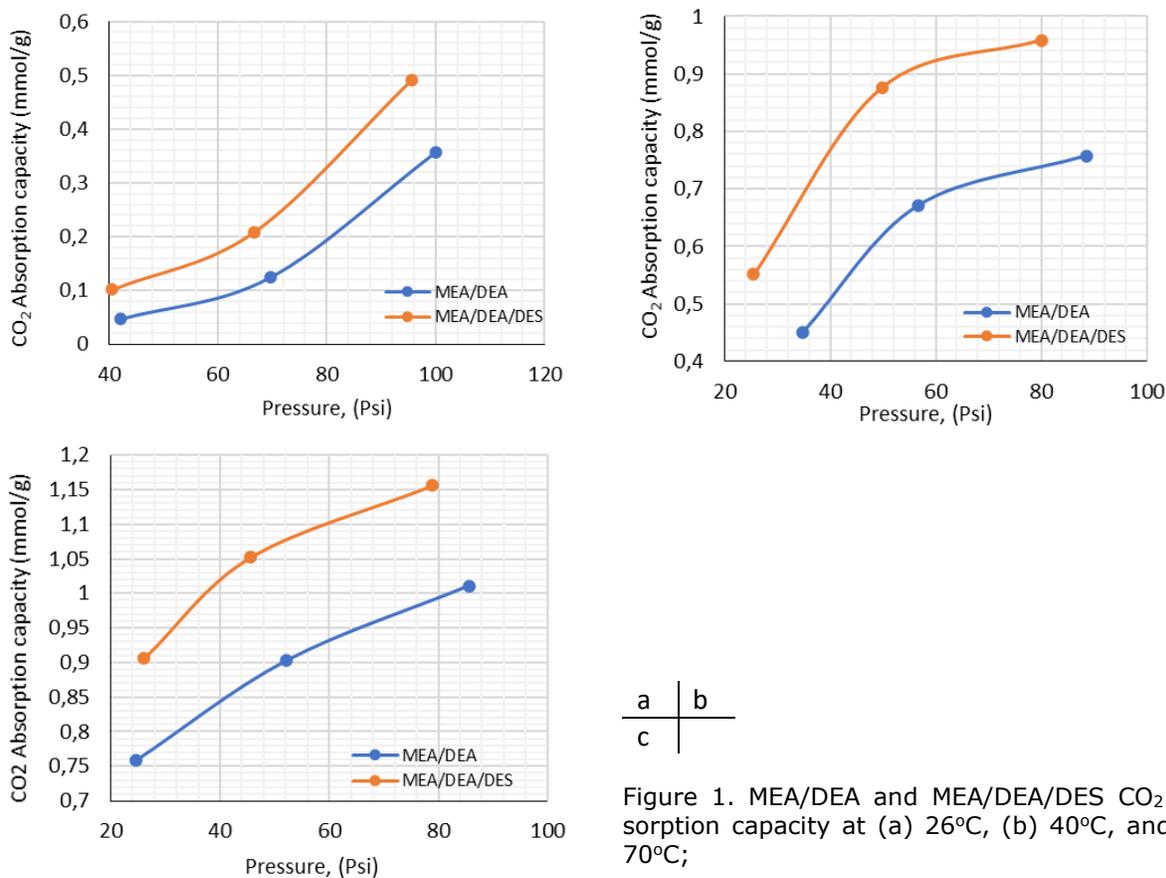
The main blend	The control blend
100g of 20%MEA/20%DEA/60%DES.	100g of 50%MEA/50%DEA
100g of 20%MEA/20%TEA/60%DES.	100g of 50%MEA/50%TEA
100g of 20%DEA/20%TEA/60%DES.	100g of 50%DEA/50%TEA
100g of 20%MEA/20%DEA/30%TEA/30%DES.	100g of 30%MEA/30%DEA/40%TEA

4. Results and discussion

4.1. Absorption results

From Figure 1, the MEA/DEA CO₂ absorption capacity was 0.0465mmol/g at a temperature of 26°C and an equilibrium pressure of 42.1psi, respectively. This absorption rate increased to 0.1016mmol/g when DES was introduced to the blend. An increase in equilibrium pressure

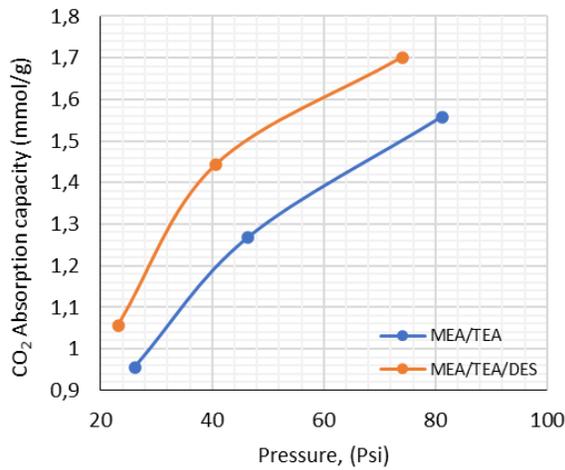
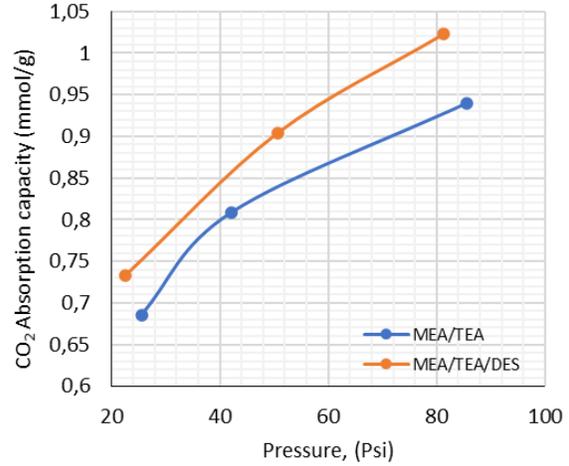
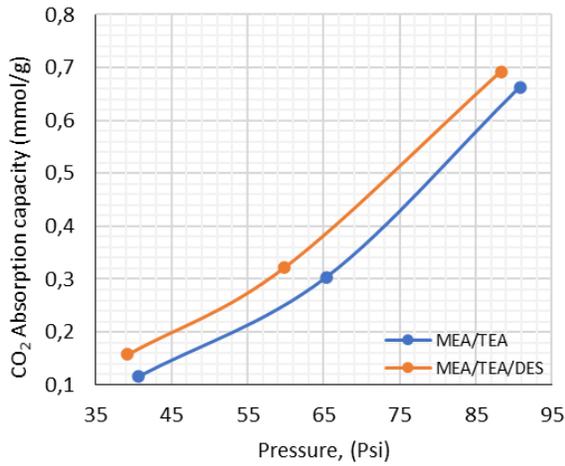
increased the CO₂ absorption capacity in MEA/DEA and MEA/DEA/DES. The results showed that an increase in equilibrium pressure from 69.6 to 100.1 psi increased MEA/DEA CO₂ absorption capacity to 0.1238 and 0.3575mmol/g, respectively. Also, an increase in equilibrium pressure from 66.7 to 95.7 psi for the MEA/DEA/DES blend increased the CO₂ absorption capacity to 0.2085 and 0.4914 mmol/g of CO₂, respectively. Overall, an increase in pressure at ambient temperature (26°C) improved the absorption rate of CO₂ by the amine blends. This is true because the system's pressure forces more molecules of CO₂ into the pores of the blended amine and DES-modified amine blends. The DES-modified amine blend tends to absorb more CO₂ because of its high loading capacity, as seen in its high viscosity. The primary, MEA, and secondary DEA amines facilitate the reaction rate, while the tertiary amine, TEA, and DES, store the CO₂.



a	b
c	

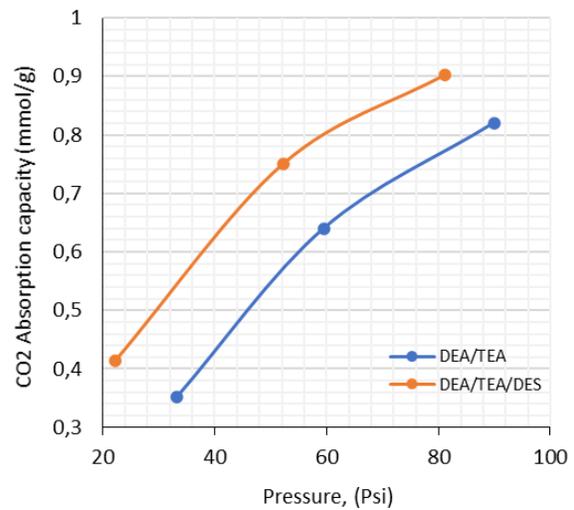
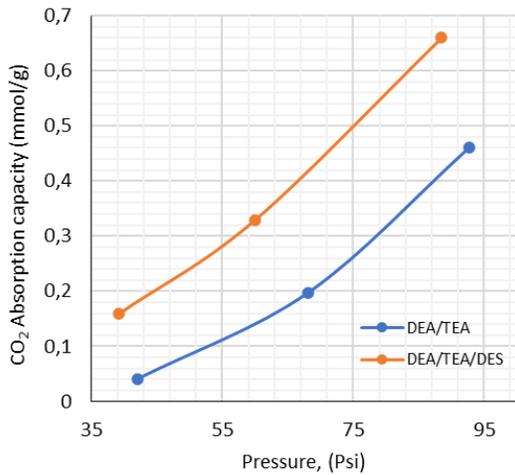
Figure 1. MEA/DEA and MEA/DEA/DES CO₂ absorption capacity at (a) 26°C, (b) 40°C, and (c) 70°C;

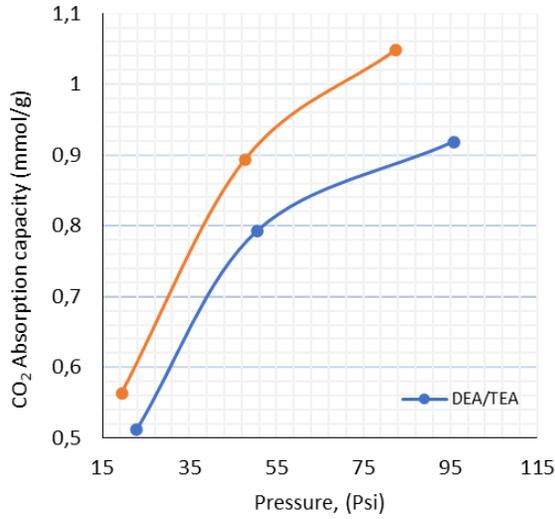
An increase in temperature to 40°C enhanced the CO₂ absorption capacity of both amine blends at equilibrium pressures of 88.5 psi and 80 psi to 0.7571 and 0.9587mmol/g, respectively. A further increase in temperature to 70°C at equilibrium pressures of 85.6 and 78.9 psi for MEA/DEA and MEA/DEA/DES, respectively, increased the CO₂ absorption rate to 1.0108 and 1.1563mmol/g. The increased absorption is connected to the thinning of the solvents by heat, allowing more contact surface for more reaction. In addition, an increase in temperature increases the agitation of the amine blends, thereby creating more movement of molecules and more surface movement in a state of entropy. Similar trends were observed in all the other sample blends shown in Figures 2 - 4. These results agree with Lars's [20] findings in his study on the influence of heat on CO₂ removal. The results also revealed that CO₂ absorption increases initially and then plateaus at higher temperatures and pressures as temperature and pressure increase.



a	b
c	

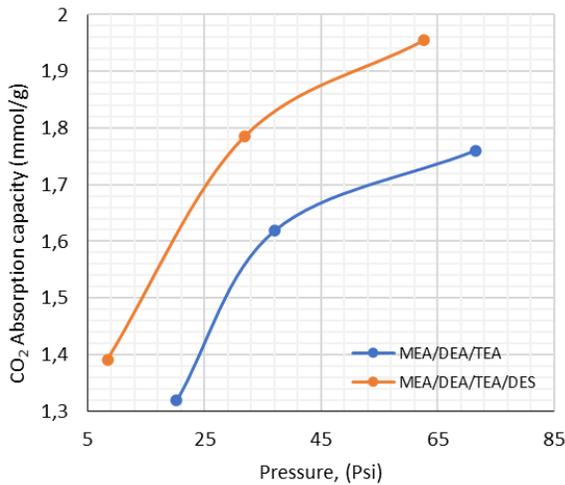
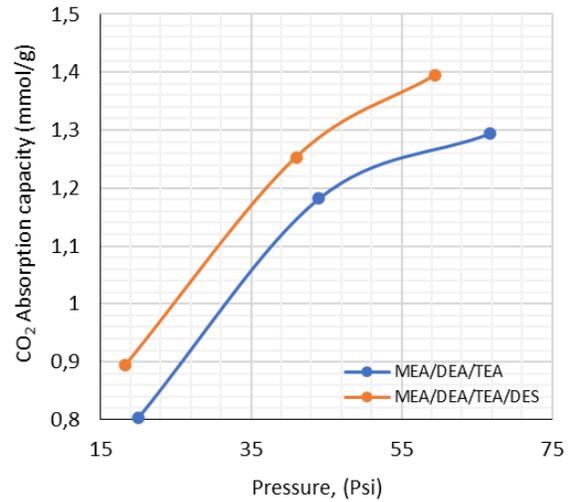
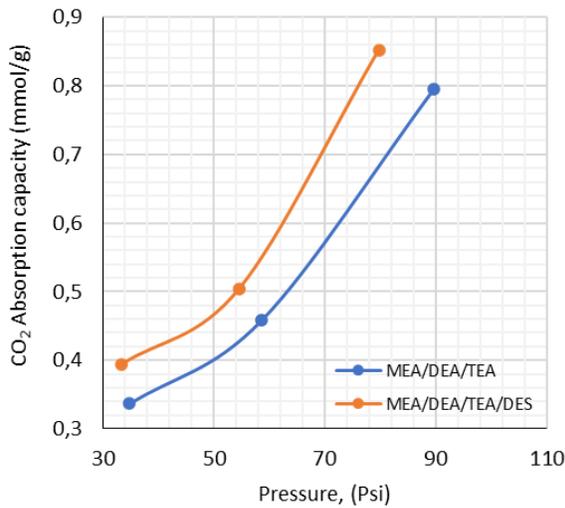
Figure 2. MEA/TEA and MEA/TEA/DES CO₂ absorption capacity at (a) 26°C, (b) 40°C, and (c) 70°C





a	b
c	

Figure 3. DEA/TEA and DEA/TEA/DES CO₂ absorption capacity at (a) 26°C, (b) 40°C, and (c) 70°C



a	b
c	

Figure 4. MEA/DEA/TEA and MEA/DEA/TEA/DES CO₂ absorption capacity at (a) 26°C, (b) 40°C, and (c) 70°C

This is because a fast reactant, as seen in MEA, and a high retention solvent, as seen in TEA and DES, were blended, thereby incorporating two desirable qualities of fast reaction rate

and good loading capacity. This result agrees with the works of Jiafei *et al.* [17] and Erik *et al.* [18]. It could be said that an increase in pressure and temperature directly influences the ability of the absorbents to attract CO₂, and the absorbent's viscosity directly impacts the absorbents' ability to hold CO₂.

Figure 5 compares the CO₂ absorption capacity of all the amine blends and DES-modified amine blends at 26°C, 40°C, and 70°C. At 26°C, the results showed that MEA/DEA had the least absorption capacity of all eight combinations. This is because MEA/DEA has a fast reaction rate but little retention ability.

Adding DES to the blend increased its CO₂ retention capacity by 24%. Also, the CO₂ retention capacity of the blend MEA/TEA increased by 21%, DEA/TEA by 12%, and MEA/DEA/TEA by 21% when DES was added. Similar results were obtained for temperatures of 40°C and 70°C. The highest absorption rate was recorded on the MEA/DEA/TEA /DES sample and its corresponding control, MEA/DEA/TEA.

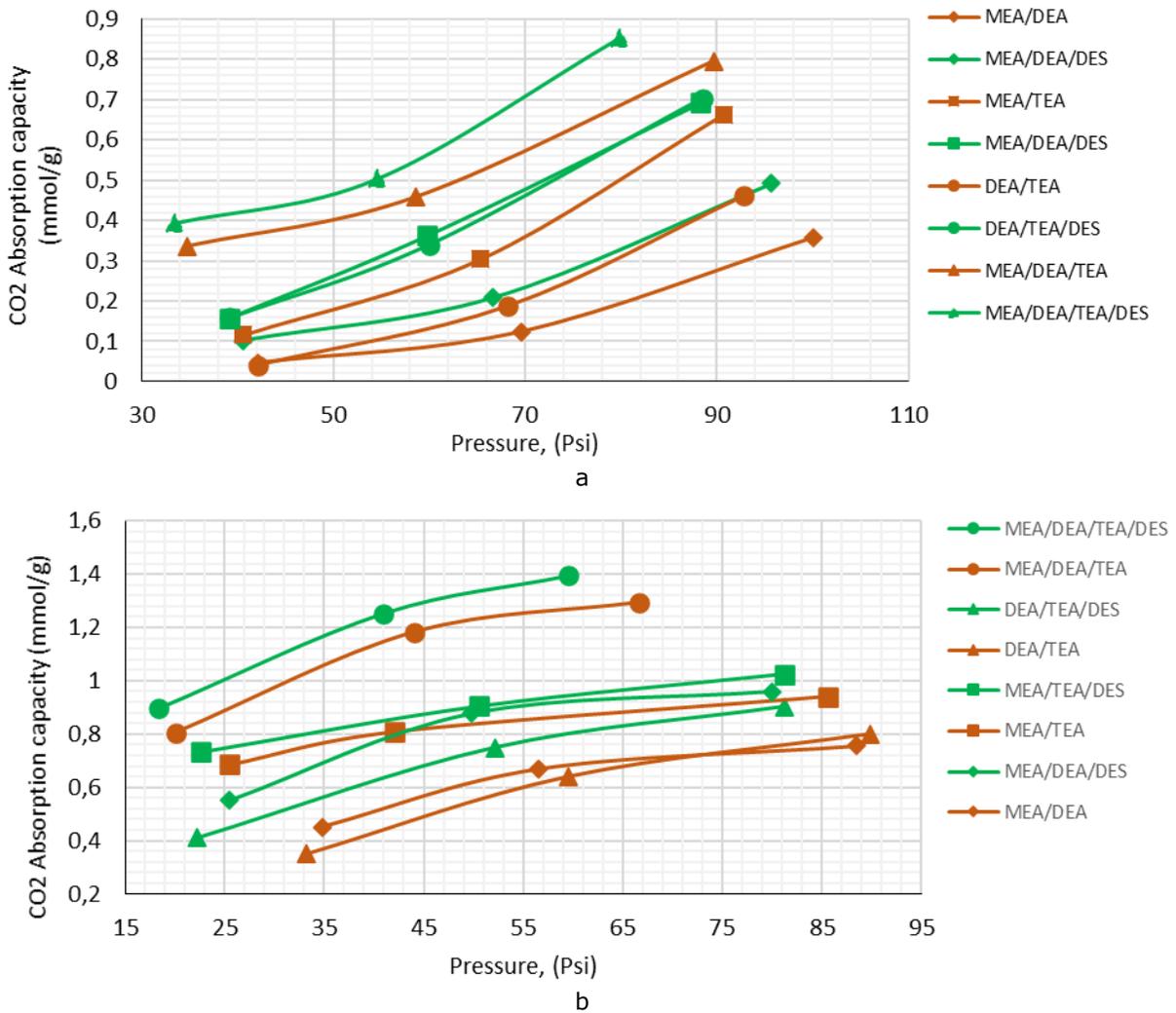


Figure 5. CO₂ absorption capacity of all amine blends at (a) 26°C, (b) 40°C

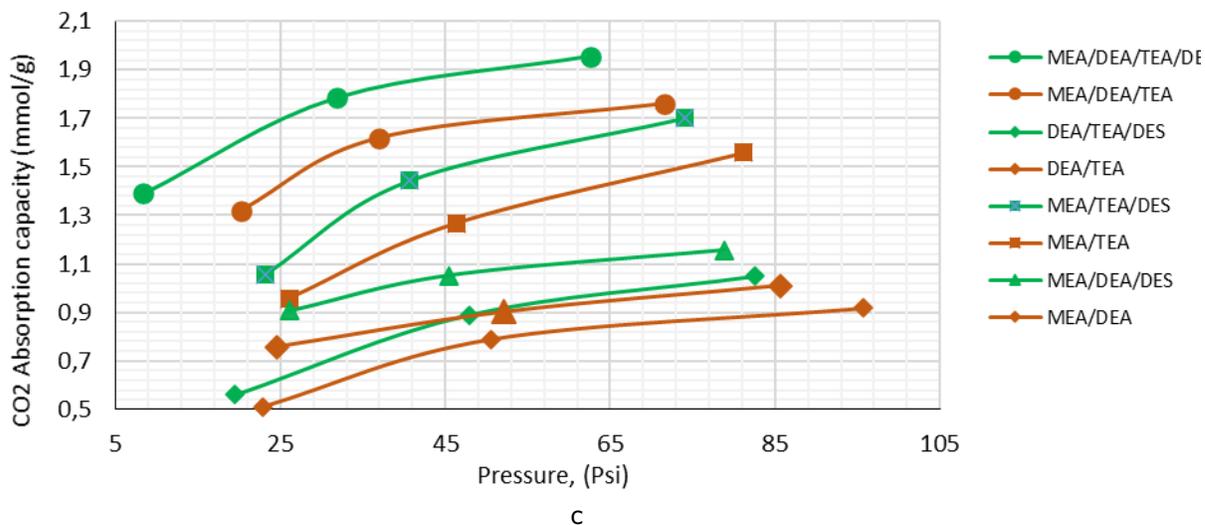


Figure 5. CO₂ absorption capacity of all amine blends (c) 70°C

4.2. Cost analysis

The cost of procuring the materials and analysis of each mixture of amine blend is discussed in this section. Tables 2 to 4 show the costs.

Table 2. Material costs

Solvent name	Cost of materials (\$)	Cost per gram (\$)
Choline chloride (1kg)	126	0.013
Glycerol (1kg)	20	0.020
TEA (500g)	27	0.054
DEA (500g)	26	0.052
MEA (500g)	26	0.052

Table 3. Cost of producing DES (Ratio 2:1; 180g glycerol and 90g choline chloride)

Solvent name	Cost of materials (\$)
Glycerol (180g)	3.60
Choline chloride (90g)	1.17
DES (270g)	16.00
Cost of 1 gram of DES	0.06

Table 4. Cost of producing optimum and control blends

Optimum Blends	Cost (\$)
20%MEA/20%DEA/60%DES	5.31
20%MEA/20%TEA/60%DES	5.28
20%DEA/20%TEA/60%DES	5.28
20%MEA/20%DEA/30%TEA/30%DES	5.17
Control Blends	
50%MEA/50%DEA	5.13
50%MEA/50%TEA	5.05
50%DEA/50%TEA	5.05
30%MEA/30%DEA/40%TEA	5.06

Figure 6 highlights the cost of producing the optimum and control amine blends. The result showed that the cost of producing each optimum amine blend was 2.1% higher than the control amine blends. However, even though more expensive, the optimum amine blend yields a better result as it absorbs 16.7% more CO₂ than the control. This desirable quality saves costs more, especially on a larger scale.

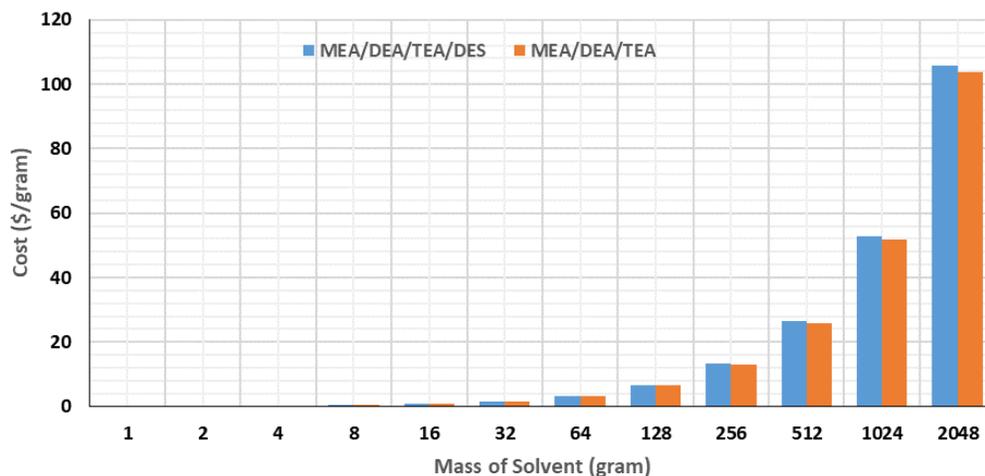


Figure 6. Cost of solvent used for the experiment

5. Conclusion

The experimental work focused on finding the absorption capacity of amine blends modified with Deep Eutectic Solvents at different temperatures and pressures for CO₂ capture. The conclusion derived from this study are highlighted as follows:

1. CO₂ absorption was higher for an amine blend containing DES
2. Absorption increased initially with pressure and temperatures at 26°C but gradually began to plateau as temperatures increased to 70°C
3. Blending primary, secondary, and tertiary amines of MEA, DEA, and TEA with DES will improve CO₂ absorption capacity by 21%.
4. The baseline economics of adding DES to amine blends is relatively cost-effective.

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