Alkanolmonoamines as Activators for the Hot Potash Process for CO₂ Capture

MAMSHAD AHMAD[1,*], ASHA MASOHAN[2] and S.S. SAWHNEY[1]

[1]Department of Chemistry, Uttaranchal College of Science and Technology, Dehradun-248 001, India,
[2]Department of Advanced Gas Separation, Indian Institute of Petroleum, Dehradun-248 005, India

*Corresponding author: E-mail: mamshad_ahmad_786@yahoo.com; mamshad.ahmad.2012@gmail.com

The present study is based on use of activators in the hot potash process. Glycine is commonly used as an activator in the Giammarco Vetrocoke process. This paper presents a systematic study on use of alkanolmonoamines as possible alternate activators. These alkanolmonoamines contain only one amino group that may be unsubstituted/substituted (-NH₂, -NRH or -NR₂) and thus the acidity of these compounds is one that arises from the only amino group that is there in the molecule. Out of these, monoethanolamine, diethanolamine and triethanolamine are previously reported as activators in the literature. This paper reports the experimental studies on such alkanolmonoamines including the new alkanolmonoamine structures also. The proposed amines as activators have shown highly promising results. A 632-700 % increase in rate of absorption, 493 % increase in capacity of absorption of K₂CO₃ and 313-400 % increase in the CO₂ regenerated has been observed for some of these amines. In case of glycine this increase is 134, 214 and 161 %, respectively. A combination of these with diethanolamine increases the rate of absorption considerably. This study is directed towards finding a non-degradable, cheaper, environmentally friendly and more efficient alternative to glycine as activator.

Keywords: Alkanolamines, Activator, Hot potash process, Carbon dioxide, Absorption, Amine activator.

INTRODUCTION

Carbon dioxide plays an important role in the greenhouse effect. It is mostly emitted from the burning of fossil fuels in power plants and utilities. CO_2, being a major greenhouse gas, is known for its impending global danger mainly because of its global warming effect. Although carbon dioxide is emitted by animals and plants in respiration but this amount is very small and can be balanced by the green plants. It is the added amount by the man-made sources in the form of industries that has led to the alarmingly high levels of carbon dioxide in the atmosphere. Unless the CO_2 emissions are checked at the industries, the levels are expected to rise beyond control[1].

Carbon dioxide can be separated from the gas stream, by various processes including adsorption, absorption and membrane separation[2]. Chemical absorption processes are attractive because of their efficiency and lower equipment size and ability to tackle varying stream compositions with respect to CO_2 content. Solvents employed in these processes include amines and inorganic salt solutions. Among amines mostly alkanolamines are used for CO_2 separation. Monoethanolamine (MEA) is a common alkanolamine which is used preferentially in CO_2 separation processes. Monoethanolamine shows greater rate of absorption than other amines. Other amines employed, are

diethanolamine (DEA)[3], triethanolamine (TEA), N-methyl-diethanolamine (MDEA)[3], 2-(methylamino)ethanol (MAE), piperazine *etc.*[4]. Blended amines are also reported for the separation[5]. Amines are good absorbing solvents for CO_2 but these are highly corrosive in nature and get degraded at elevated temperatures during stripping process. As such utility costs are high. But they can be used as activator in little amount with inorganic salt due to their high efficiency for CO_2.

In hot potash process aqueous potassium carbonate solution is used for carbon dioxide separation[6]. The rate of absorption in inorganic salts is slower than amine based solvents because the interaction of carbonic acid (HCO_3^- + H^+) is greater with organic amines. But the advantage is the stability of inorganic solvents at higher temperatures and cost factor. Potassium carbonate is low cost and less corrosive than amines has greater capacity for CO_2 absorption and ease of handling.

However, considering the fact that rate of absorption of carbon dioxide into aqueous potassium carbonate solution is very low[7,8], additives or activators are added to the potassium carbonate solution. These activators are able to enhance the rate of absorption in small quantities. Mostly theses activators are amines. Activators, other than amines, which are reported, are hydration catalyst[9], boric acid[10], *etc.*

30 % (w/v) aqueous K_2CO_3 is taken for absorption in commercial hot potash process and activators are added in 3 % (w/v) concentration. Carbon dioxide is firstly captured by amine in the activated potassium carbonate and is subsequently released for the capture by potassium carbonate. In this process the K_2CO_3 solution is contained in mild hot condition at 40 ºC during the absorption step. Under such condition the absorption of CO_2 increases in K_2CO_3 solution and solubility of resulting $KHCO_3$ is increased.

Various types of amines have been used as activators in the hot K_2CO_3 processes. These include primary, secondary and tertiary amines. Aqueous primary amines show fast reaction rates. The most common amine used is MEA[11]. Diethanolamine and triethanolamine can also be used as activator in combination with potassium carbonate[11-13]. Many of the hindered amines are also reported by Sartori *et al.*[14-16]. These hindered amines include monoprimary diamines, cyclodiamines and di-secondary aliphatic amines, *etc*. Leder and Savage[17] describe a method in which ethylenepolyamines such as ethylenediamine and diethylene triamine, are used in aqueous potassium carbonate for CO_2 capture. 2-Methylaminoethanol, 2-ethylaminoethanol (EAE), morpholine and pyrrolidone are reported as activator by Shrier *et al.*[18].

Ostwald *et al.*[19] have disclosed an activator which is an N-aminoalkyl alkylpiperazine. Extensive work is done by the group of Rochelle in this field of K_2CO_3 with activators. They proposed piperazine as an activator for the hot potash process[20,21]. Kinetic study of piperazine has shown that it may be a good activator due to high rate of absorption[22].

Some other activators have also been reported which are not amine in nature. Ghosh studied boric acid as an activator for hot potash process[10]. Several activators have been tested by Tang *et al.*[23], including piperidine, piperazine, pyrazine, morpholine, imidazole, N-hydroxyethylpiperazine, N-aminoethylpiperazine, 2-amino-2-methyl-1-propanol. They have reported piperidine as a good activator for the hot potash process[23].

The Giammarco Vetrocoke[24] process is a commercial process in which glycine is used as an activator with potassium carbonate. Glycine is an expensive compound and it gets degraded at elevated temperatures because the stripping is done in the process at 120-130 ºC. Therefore to maintain the absorption maxima, there is a need to change the degraded activator glycine along with whole solvent.

This paper presents a study of alkanolmonoamines as activators and their comparison with K_2CO_3 (with/without glycine as activator). For the first time the authors report a systematic work on exploring various alkanolmonoamines as activators for the hot potash process. It will be the key point to screen these and study the effect of chemical structure of alkanolmonoamines as activator on CO_2 recovery process *vis a vis* glycine as activator in an effort to look for an alternative to glycine. The aim of the present study is to look for an efficient and cost-effective replacement for glycine.

Mechanism of CO_2 absorption in K_2CO_3: When carbon dioxide is absorbed in the aqueous solution of potassium carbonate, it first reacts with water to form carbonic acid which is a very weak acid and gets dissociated into protons and bicarbonate ions.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (1)$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (2)$$

This carbonic acid reacts with potassium carbonate to form potassium bicarbonate.

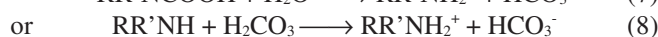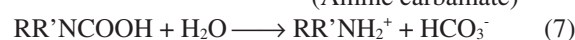$$K_2CO_3 + H_2CO_3 \longrightarrow 2KHCO_3 \qquad (3)$$
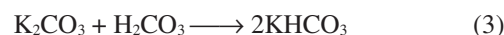
There is another theory which is given for the above absorption process[25]. According to this theory the carbonate ion first reacts with water to generate hydroxyl ions, which then react with CO_2 as follows-

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^- \qquad (4)$$
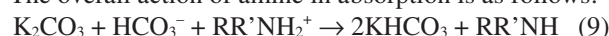$$CO_2 + OH^- \longrightarrow HCO_3^- \qquad (5)$$

Effect of activator on CO_2 absorption in potassium carbonate: When a small amount of amine, is added in K_2CO_3 solution, the absorption rate of carbon dioxide is considerably enhanced according to the following reactions:
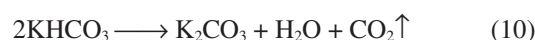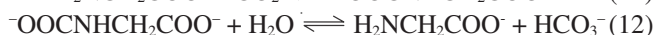
$$CO_2 + RR'NH \longrightarrow RR'NCOOH \qquad (6)$$
$$\text{(Amine carbamate)}$$
$$RR'NCOOH + H_2O \longrightarrow RR'NH_2^+ + HCO_3^- \qquad (7)$$
or $\quad RR'NH + H_2CO_3 \longrightarrow RR'NH_2^+ + HCO_3^- \qquad (8)$

The overall action of amine in absorption is as follows:

$$K_2CO_3 + HCO_3^- + RR'NH_2^+ \rightarrow 2KHCO_3 + RR'NH \quad (9)$$

It is clear that amine acts as an activator. As the amount of CO_2 increases in the potassium carbonate solution, correspondingly the concentration of potassium bicarbonate increases. Thus CO_2 absorbed can be determined by determining the concentration of bicarbonate in the solution[26]. During the regeneration process the reactions get reversed and pure CO_2 comes out from the solution.

$$2KHCO_3 \longrightarrow K_2CO_3 + H_2O + CO_2\uparrow \qquad (10)$$

If glycine is used as an activator the reactions may be written as

$$H_2NCH_2COO^- + CO_2 \rightleftharpoons {}^-OOCNHCH_2COO^- + H^+ (11)$$
$${}^-OOCNHCH_2COO^- + H_2O \rightleftharpoons H_2NCH_2COO^- + HCO_3^- (12)$$

EXPERIMENTAL

The reagents and chemicals which are used in the present study include potassium carbonate (main solvent) and activators which are organic amines. Other supporting chemicals and reagents used are HCl, Na_2CO_3, KOH *etc*. The chemicals used in this method and their manufacturer are given in the Table-1.

A specially designed absorber is taken for laboratory studies. It is a jacketed vessel and is provided a liquid outlet at the bottom and the gas inlet (reaching the bottom of absorber) and outlet at the top of the reactor vessel. Temperature in the absorber is maintained by circulation of water through the jacket by a circulatory bath. The absorber temperature is maintained at 40 ºC during the absorption process. The schematic diagram (Fig. 1) for the experimental set up is given below:

First of all a synthetic mixture of N_2 and CO_2 with required CO_2 composition is made by setting the flow rates of each gas individually. A flow rate of 5.75 s/50 mL for N_2 and 7.69 s/10 mL for CO_2 yields 13 % (v/v) CO_2 in the feed gas. This composition was maintained for all the experiments while screening different activators. The constant composition of the gas mixture is attained by mixing the gases in a specially designed gas mixer for at least 45 min after setting of the flow rates. This gas mixture, termed as feed gas, is analyzed to estimate the

TABLE-1
LIST OF CHEMICALS AND ACTIVATORS
WITH THEIR MANUFACTURER/SUPPLIER

S. No.	Chemical	Make
1	Hydrochloric acid	SDFCL
2	Sodium carbonate	Qualigens
3	Potassium carbonate	Fisher Scientific
4	Potassium Bicarbonate	CDH
5	Potassium hydroxide	Merck
6	Sodium hydroxide	Merck
7	Barium chloride	Rankem
8	Phenolphthalein	Rankem
9	Methyl red	Rankem
10	Bromocresol green	Merck
11	Ethanolamine	Alfa Aesar
12	Diethanolamine	Fisher Scientific
13	Triethanolamine	Fisher Scientific
14	N-Methyldiethanolamine	Merck
15	Diisopropanolamine	Acros
16	2-Amino-2-methyl-1-propanol	Acros
17	Methylaminoethanol	Alfa Aesar
18	Ethylaminoethanol	Merck
19	Dimethylaminoethanol	Merck
20	Tris(hydroxymethyl)aminomethane	Merck
21	Glycine	Merck
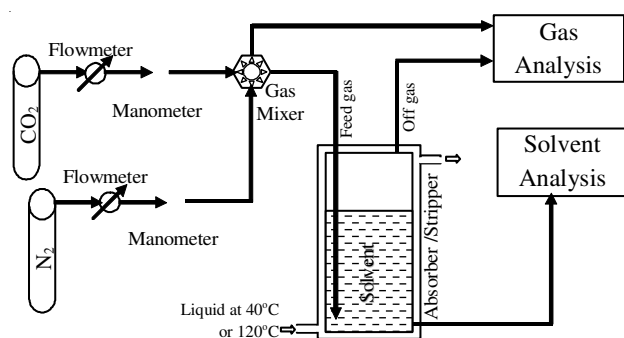
Fig. 1. Schematic diagram of the process in absorption/ regeneration study

composition of mixture experimentally. The feed gas is then passed through the mixture of aqueous solution of 30 % potassium carbonate and 3% activator as solvent. The solvent is taken in the absorber at 40ºC. Solvent samples are collected from the bottom of absorber for estimation of CO_2 content in the solvent at the regular interval of time. When the CO_2 loading attains a constant value, the solvent becomes completely saturated with CO_2 and absorption is completed. All the experiments are done for 210 min for absorption in the present study and thus all the comparisons are done by taking the 210 min as absorption time.

After absorption, regeneration is done at 120 ºC. Temperature is maintained in the absorber by passing oil through the jacket of the absorber by an oil circulatory bath. At this temperature, CO_2 comes out from the absorber. When regeneration is completed, a sample of the lean solvent is taken and analyzed for CO_2 content. The amount of the CO_2 regenerated from the rich solvent is obtained by subtracting the CO_2 content of lean solvent from that of the rich solvent.

A mixture of 30 % (w/v) potassium carbonate solution and 3 % (w/v) activator is taken for all the absorption experiments. The concentration of bicarbonate in the solvent (obtained due to absorption of CO_2 in K_2CO_3) is determined

by the $BaCl_2$ method[26]. This method involves taking 1 mL of sample from the absorption cell and adding to it 10 mL of 1.0 N KOH. All the $KHCO_3$ formed is converted into K_2CO_3 by KOH. This K_2CO_3 is converted into $BaCO_3$ after adding 25 mL of 1 N $BaCl_2$. The remaining amount of the KOH is then titrated with 0.25 N HCl. The calculations yield the amount of the CO_2 in the solvent.

CO_2 in feed gas and off gas stream is analyzed by passing the gas stream through 25 mL of 1.0 N KOH for 15 s. KOH is converted to K_2CO_3 after reaction with CO_2. After absorption 25 mL of 1 N $BaCl_2$ is added to this loaded KOH. $BaCl_2$ converts the K_2CO_3 into $BaCO_3$. The excess un-reacted KOH is then titrated against 0.25 N HCl. The amount of CO_2 can then be calculated in the gas stream. Both gas and liquid samples are analyzed for CO_2 content at regular intervals of time during each experiment.

Another exercise is the determination of pKa values of the amine, tested as activators. The pKa values of the amines are determined pH metrically. First of all a standard solution of H_2SO_4 is prepared. In a titrating flask a desired (same in all the titrations) volume of the amine (base) solution is taken and titrate it against standard H_2SO_4 solution using mixed indicator (bromocresol green + methyl red). Amine solutions are prepared in 1 % (w/v) concentration. After adding a little acid to the amine solution pH value is noted. A pH plot is drawn between the titre readings (volume of H_2SO_4 added). pKa value is then calculated from the graph as pKa of base is considered as the pH value at half neutralization of base against acid. The pH value is highly dependent on the temperature, thus the temperature of the titrating flask is kept at 25 ºC.
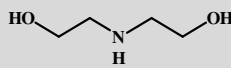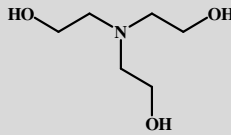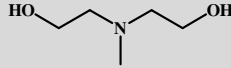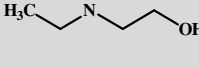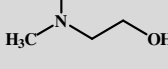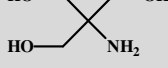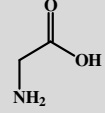
RESULTS AND DISCUSSION
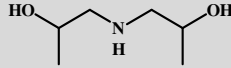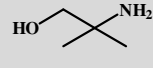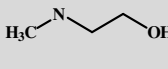
Alkanolamine, when used as dedicated absorption solvents, show high rate of absorption of CO_2, because CO_2 is acidic in nature and amines are organic bases. These alkanolamines also enhance absorption of CO_2 in K_2CO_3 when used as activator in small amounts. This increase in rate of absorption depends on the structure of activator (alkanolamine) added.

Table-2 shows the alkanolmonoamines studied as activators in the present study. It also shows the experimental and literature values of pKa of the alkanolmonoamines, their chemical structural formula and the experimental results of absorption and regeneration results of CO_2 in K_2CO_3 without and with the use of these activators.

Effect of alkanolmonoamine activator on rate of absorption: Effect of different alkanolmonoamines mentioned in Table-1 was studied on rate of absorption of CO_2 in K_2CO_3. Rate of absorption is calculated in the beginning of the absorption because the rate of absorption is higher in the beginning. The amount of CO_2 absorbed in the first 0.5 h gives the rate of absorption. Figs. 2 and 3 show the trend of absorption in K_2CO_3 solvent using different alkanolmonoamines as activators. It can be seen that the alkanmonoamines used as activators increase the absorption capacity and rate of absorption of the K_2CO_3.

It is observed that the rate of CO_2 absorption is lowest when aqueous K_2CO_3 is used as such, without any activator. The primary alkanolamine MEA, one of the most commonly

TABLE-2
pKa, STRUCTURES, RATE OF ABSORPTION, ABSORPTION CAPACITY AND
REGENERATABILITY OF ACTIVATORS (WITH POTASSIUM CARBONATE)

| Amine/K₂CO₃	pKa (experiment alvalues at 25 °C)	pKa (literature values at 25-30 °C)	Structure	Rate of absorption (mmol CO₂/min)	Absorption (mol CO₂/mol solvent)	Regeneration (mol CO₂/mol solvent)
K₂CO₃	10.0	10.239[27]	–	0.1539	0.094970	0.053573
Ethanolamine (MEA)	9.41	9.51[28] 9.44[29]		0.5370	0.219958	0.076507
Diethanolamine (DEA)	8.87	8.95[28] 8.88[29]		0.7850	0.419398	0.241771
Triethanolamine (TEA)	7.80	7.78[28] 7.72[29]		0.3847	0.229294	0.101909
N-Methyldiethnaolamine (MDEA)	8.58	8.63[28] 8.52[29]		0.1564	0.161520	0.060269
Diisopropanolamine (DIPA)	8.82	8.89[28] 8.84[29]		0.5226	0.356909	0.149516
2-Amino-2-methyl-1-propanol (AMP)	9.66	9.7[28] 9.68[29]		0.4304	0.343302	0.066753
2-(Methylamino)ethanol (MAE)	9.82	9.94[31]		1.1276	0.564021	0.268390
2-(Ethylamino)ethanol (EAE)	9.75	9.7[30]		1.2334	0.563065	0.221679
2-(Dimethylamino)ethanol (DMAE)	9.20	8.99[31]		0.3417	0.221454	0.058753
Tris(hydroxymethylamino)methane (THAM)	8.12	8.075[32]		0.1769	0.262891	0.077655
Glycine	–	9.78[33]		0.3612	0.298185	0.140057
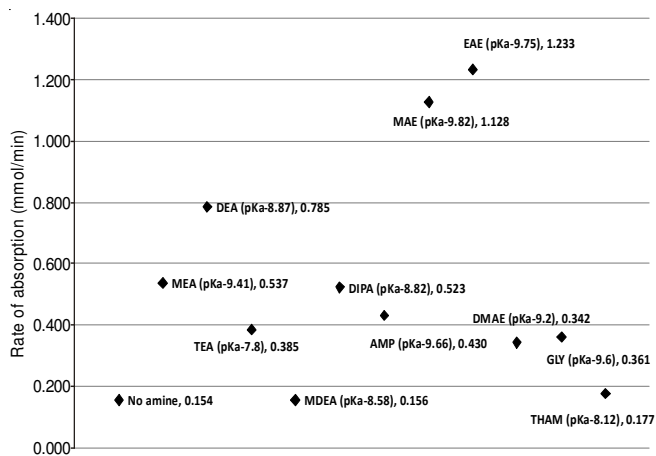
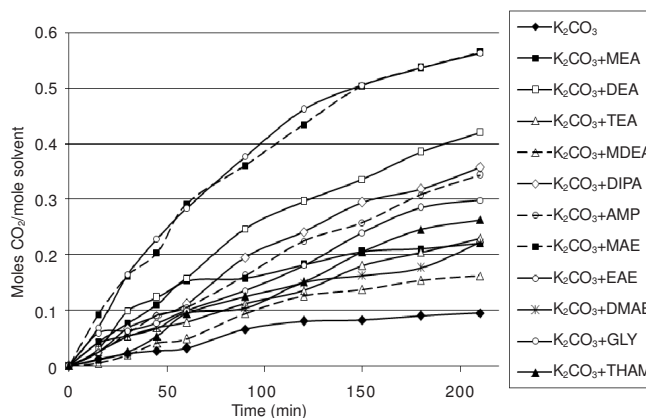Fig. 2. Rate of absorption of CO₂ in aqueous K₂CO₃ with different alkanolmonoamine activators

Fig. 3. Effect of different monoalkanolamine activators on absorption behaviour of CO₂ in K₂CO₃

used amines in the amine treating units in the history of sour gas treating industry, shows a significant increase in the rate of absorption when added as activator in K_2CO_3.

This increasing trend is also observed for DEA, MAE and EAE. One of the most striking observations is a nearly 8-fold increase in the rate of absorption of CO_2 in K_2CO_3 with EAE and nearly 7.3 times increase with MAE. DEA also shows a substantially increased (5.1 times) rate of absorption. Thus the alkanolmonoamines, as activators, that have shown pronounced effect on rate of CO_2 absorption is in the order EAE > MAE > DEA.

Considering the structure of these three molecules, all of these are secondary amines. EAE and MAE have an alkyl group on nitrogen atom while the second group is hydroxyethyl group. For DEA both the substituents are hydroxyethyl groups. As expected, the electron donating effect of alkyl group makes nitrogen more electronegative, thus increasing the affinity of nitrogen (of the amine) for proton, while the second hydroxyethyl group of DEA has slight electron withdrawing effect which decreases the electronegativity of the nitrogen atom and thus its affinity for proton is slightly decreased.

In case of tertiary amines like MDEA and 2-(dimethyl-amino)ethanol (DMAE), the molecules are sterically highly hindered and as such they are far more slow than other amines as activators. However, TEA, another tertiary amine, but with all the substituent groups as hydroxyethyl group is more active than MDEA and DMEA which have one or two alkyl substi-tuents. Surprisingly, glycine (an aminoacid), which is presently being used with DEA in the commercial K_2CO_3-based CO_2 separation processes is much nearly the same in its effect as MDEA/DMEA.

It is thus observed that all the alkanolmonoamines have positive effect on rate of absorption of CO_2 in aqueous K_2CO_3. The present results also suggest EAE and MAE as promising alkanolmonoamine because of their effect as activators which far surpasses the effect of other alkanolmonolamine activators.

Effect of alkanolmonoamine activator on absorption capacity: Selection of a suitable attractive activator also requires positive effect in terms of increased absorption capacity of K_2CO_3 along with rate of absorption. The results on this aspect of the study are shown in Fig. 4.
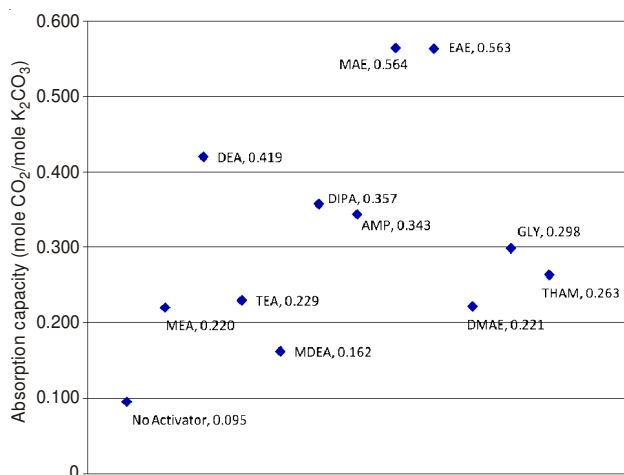

Fig. 4.　Effect of different alkanolmonoamine activators on absorption capacity of aqueous K_2CO_3

It has been practically observed that, similar to their effect on rate of absorption, the alkanolmonoamines also increase the absorption capacity of K_2CO_3 which is highest for MAE and EAE (nearly equal with the range of experimental error) followed by DEA, DIPA, AMP and glycine in decreasing order. Both EAE and MAE show nearly six-fold increase in the absorption capacity while the commercial activator, glycine shows half the increase of EAE and MAE. As seen in Fig. 4, the difference in the effect of each alkanolmonoamine activator on absorption capacity of K_2CO_3 is much more pronounced than on rate of absorption. Again, all the activators studied in this category show an increase in the absorption capacity of K_2CO_3.

Effect of alkanolmonoamine activator on regeneration of CO_2: The third important criterion that defines an activator as attractive is the amount of CO_2 that can be released from the loaded rich solvent (in the absorption step) during regene-ration.

The less is the solvent loading left after regeneration, the more desirable is activator. The results of regeneration are shown in Fig. 5 which shows the amount of CO_2 regenerated *vis a vis* the CO_2 loading of the solvent after the regeneration step.

It is observed that EAE and MAE are again outstanding as regards the CO_2 absorbed and regenerated. A further experimentation on these solvents by running cyclically for a few numbers of cycles would show their performance for continuous operation. For now the data, for the sake of compa-rison, is again encouraging for these two solvents. Another good solvent is DEA, which shows very high CO_2 regener-ation and very low CO_2 loading in the regenerated solvent (Fig. 5).
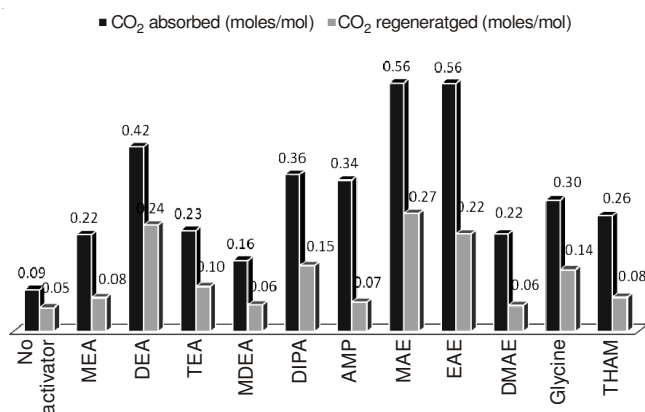

Fig. 5.　Effect of different alkanolmonoamine activators on regeneration of CO_2 and solvent loading after regeneration

Overall effect of alkanolmonoamine activators on performance of K_2CO_3 solvent: The overall results are once again analyzed in terms of percentage increase in rate and capacity of absorption and CO_2 regenerated. This analysis is shown in Fig. 6. It is observed that among the alkanolmonoamines tested in the present studies activators, MAE and EAE, have maximum effect in all three respects, *i.e.*, rate and capacity of absorption as well as amount of CO_2 regenerated as compared to when K_2CO_3 is used without an activator. This is followed
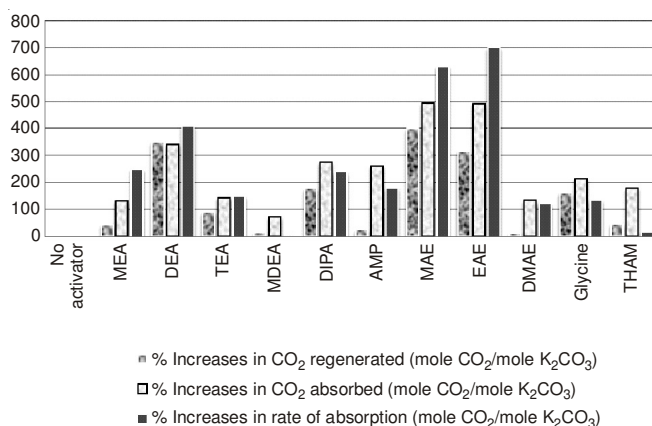
Fig. 6. Overall effect of different alkanolmonoamine activators on absorption/ regeneration behaviour

by DEA with substantial effect. Diisopropanolamine is also better than glycine. Monoethanolamine though, has good rate of absorption, is not good for stripping of CO_2. This behaviour is same as when MEA is used as solvent in amine treating for CO_2 removal.

Conclusion

This is the first systematic study of its kind where the effect of structure of alkanolmonoamines on absorption of CO_2 in K_2CO_3-based solvents has been studied in detail. As discussed, the results have been encouraging. A comparison of results of K_2CO_3 with different alkanolmonoamine activators has been made with K_2CO_3 as such and with glycine as commercial activator. In general, there is a beneficial effect of using an alkanolmonoamine along with DEA as activator in the aqueous K_2CO_3 solvent. 2-(Ethylamino)ethanol and 2-(methylamino)ethanol have been outstanding. Among the remaining amines some are good for absorption, while others are good for amount of CO_2 regenerated. The studies are directed in the lookout for an activator in the K_2CO_3-based process as an alternative to glycine. A higher rate and capacity of absorption and higher CO_2 regeneration can have a great effect on economics of the process both in terms of capital and operating cost.

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