

INVESTIGATION OF NEW POTENTIAL AMINE ACTIVATORS FOR CARBON DIOXIDE ABSORPTION IN CARBONATE SOLUTIONS

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Dedicated to Professor Andrzej Burghardt on the occasion of his 90th birthday

Results of an extensive research program, aimed at finding new, more efficient activators of carbon dioxide absorption into aqueous carbonate/bicarbonate solutions are presented. Both single amines (2-ethyl-aminoethanol, 2-isopropyl aminoethanol, piperazine, tetraethylenepentamine, N-ethyl-piperazine and glycine) and amine mixtures have been investigated. Absorption rate measurements were conducted in a laminar-jet absorber. Reaction rate constants for the particular activators were determined. Mixtures of aliphatic amines with cyclic amines, as well as mixtures of cyclic amines with cyclic amines were found to exhibit synergetic effect. Such amine mixtures might be used as new promoters for CO₂ absorption in carbonate solutions in the modified Benfield process.

Keywords: carbon dioxide, absorption, potassium carbonates, amine activators, laminar jet

1. INTRODUCTION

The absorption processes used to remove CO₂ from synthesis gases are very important for the industry. They employ both physical (e.g. methanol, propylene carbonate, 2-methyl-2-pyrrolidone) and chemical (alkanolamine aqueous solutions and sodium/potassium carbonate aqueous solutions containing amine activators) solvents. The main criteria of solvent selection are absorption capacity, reaction kinetics, volatility, stability, corrosion resistance as well as energy consumption in the solvent regeneration process.

The majority of ammonia plants have adopted the method developed by Benson and Field (so called Benfield process), which employs aqueous potassium carbonate solution with the addition of diethanolamine (DEA) as an activator. The absorption process is conducted at temperature of 80–100 °C and pressure of 25–30 bars, whereas the regeneration of the solution (CO₂ desorption) proceeds at 110–125 °C and pressure of 1.2–1.8 bars. The modernization changes introduced in the Benfield process since its first application in the 1950s, concerned both the technology and modifications of the amine promoter.

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Finding of a new, more efficient amine promoter has been the subject of numerous research papers (Behr et al., 2011; Bińczak et al., 2016; Cullinane and Rochelle, 2004; Kim et al., 2012; Pohorecki et al., 1988; Rakimpour and Kashkooli, 2004; Shen et al., 2013; Thee et al., 2012; Tseng et al., 1988; Yih and Sun, 1987).

This was also the aim of an extensive research program, carried out in our laboratory. The program consisted of three parts:

- a screening step aimed to determine the kinetics of the reaction of carbon dioxide with six amines at ambient conditions;
- similar investigation carried out using amine mixtures;
- comparative measurements of selected amine mixtures carried out at industrial conditions.

The present paper reports the results of the first two parts of the program.

2. MEASUREMENTS

The measurements of the CO₂ absorption rate were carried out using a laminar jet absorber. This technique was chosen because of its simplicity and exactness – it allows precise determination of the absorption rate, interfacial area and liquid mass transfer coefficient, which enables an exact calculation of the reaction rate constants and comparison with the literature data.

However, this technique involves temperatures and carbonate solution concentrations lower than those employed industrially, therefore results had to be further checked in industrial conditions.

The experimental apparatus is shown in Fig. 1. A detailed description of the apparatus and the measuring technique can be found elsewhere (Pohorecki and Moniuk, 1988; Pohorecki and Mozeński, 1998). The ex-

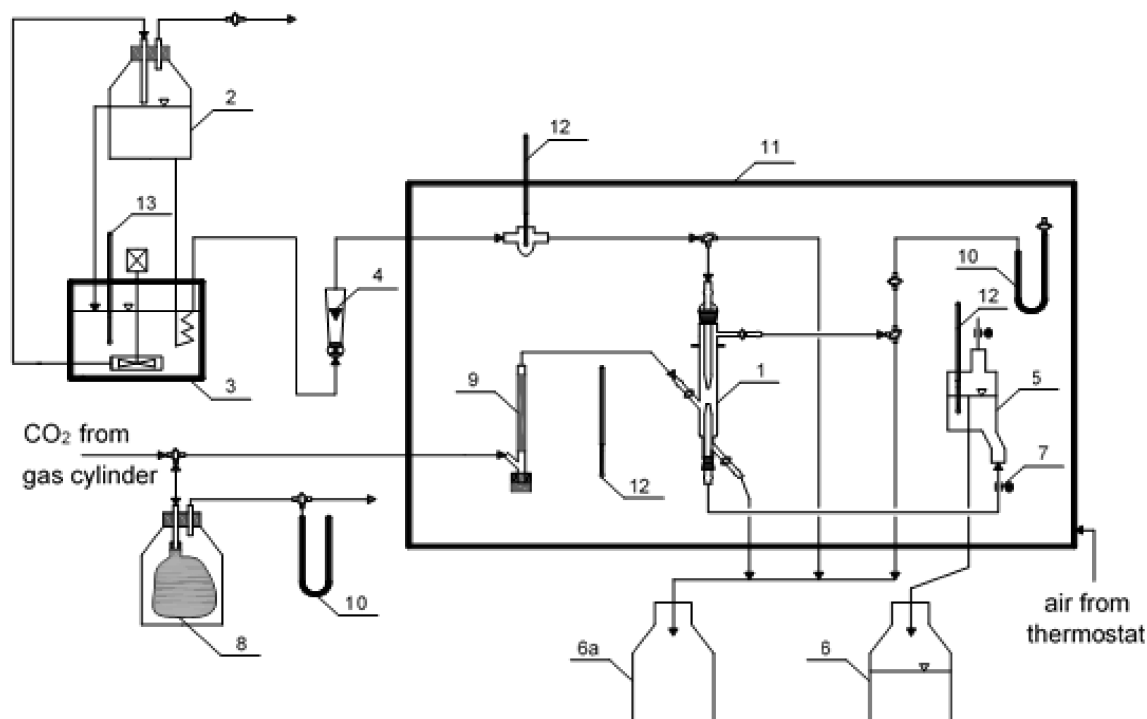


Fig. 1. Scheme of the experimental apparatus; 1 – laminar jet absorber, 2 – liquid tank, 3 – thermostat, 4 – rotameter, 5 – overflow, 6 – receiving tank, 7 – clamp, 8 – balloon with CO₂, 9 – soap-film meter, 10 – manometer, 11 – perspex chamber, 12, 13 – thermometers

periments were carried out at normal pressure in the temperature range of 20–40 °C. Each measurement was repeated at least three times, with average error amounting to 3%. The concentration of aqueous carbonate solution was 8 wt.% and carbonization ratio was 0.4. The dimensions of the laminar jet of liquid were as follows: diameter $8.48 \cdot 10^{-4} - 1.53 \cdot 10^{-3}$ m and length 0.036–0.044 m. The range of the liquid flow rate was $1.03 \cdot 10^{-6} - 1.94 \cdot 10^{-6}$ m³/s. Pure CO₂ was used as the gas phase, so the gas-side mass transfer resistance could be neglected.

As activators the following amine compounds were used: 2-ethylaminoethanol (2-EAE), piperazine (Pz), N-ethyl-piperazine (EtPz), tetraethylenepentamine (TEPA), 2-isopropylaminoethanol (2-IAE) and glycine (GLY). All chemicals used were analytical grade. The amine mixtures used in the measurements are presented in Table 1, where DEA means diethanolamine; 2-MAE – 2 methylaminoethanol; TETA – triethylenetetramine (other activators – as above).

Table 1. Amine mixtures used as activators in the potassium carbonate solutions

| Amine mixtures | concentration of activators (% wt) |
|---|------------------------------------|
| Mixtures of the aliphatic amines | 1% TETA + 2% DEA |
| | 1% TEPA + 2% DEA |
| | 1% 2-EAE + 2% DEA |
| | 1% 2-MAE + 2% DEA |
| Mixtures of the aliphatic and cyclic amines | 1% Pz + 2% DEA |
| | 1% Pz + 2% DEA |
| | 1% Pz + 2% 2-EAE |
| | 1% Pz + 2% TEPA |
| | 1% Pz + 1% DEA + 1% 2-MAE |
| | 1% EtPz + 2% 2-MAE |
| Mixtures of the cyclic amines | 1% EtPz + 2% TETA |
| | 1% Pz + 1% EtPz |

In the experiments the amount of the gas absorbed was measured using a soap-film meter 9 and the amount of the liquid supplied to the jet nozzle was measured by a rotameter 4.

3. METHOD OF CALCULATION

The chemistry of the process investigated has been described in detail in our earlier paper (Bińczak et al., 2016).

In the absorption process with a reversible chemical reaction, the absorption rate R can be expressed as:

$$R = N_A a = k_L^* (C_{Ai} - C_{Ar}) a \quad (1)$$

Making use of the experimental values of the absorption rate R , the values of the mass transfer coefficient with chemical reaction, k_L^* were calculated from Eq. (1). A detailed description of the method of calculations has been given in our earlier paper (Bińczak et al., 2016).

For a fast, pseudo-first order chemical reaction, the coefficient of mass transfer with chemical reaction is equal

$$k_L^* = \sqrt{D_A k_1} \quad (2)$$

The reaction rate constant k_1 can be expressed as in Eq. (3):

$$k_1 = k_{\text{H}_2\text{O}} + k_{\text{OH}^-} [\text{OH}^-] + k_{\text{Am}} [\text{Am}] \quad (3)$$

The methods of calculations of reaction rate constant $k_{\text{H}_2\text{O}}$ and product $k_{\text{OH}^-} [\text{OH}^-]$ are presented in our earlier work (Bińczak et al., 2016).

As the first two terms on the right hand side of Eq. (3) are very small compared to the third term (the value of the first term $k_{\text{H}_2\text{O}}$ is in the range of 0.017–0.068 s⁻¹, the value of the second term $k_{\text{OH}^-} [\text{OH}^-]$ lies in the range of 0.5–3.20 s⁻¹), the values of k_1 are practically equal to $k_{\text{Am}} [\text{Am}]$, which allows easy calculation of k_{Am} .

For a mixture of amines reacting in parallel Eq. (3) becomes

$$k_1 = k_{\text{H}_2\text{O}} + k_{\text{OH}^-} [\text{OH}^-] + \sum k_{\text{Am}} [\text{Am}] \quad (4)$$

and for the same reasons as above, for two amines we have

$$k_1 \cong \sum k_{\text{Am}} [\text{Am}] = k_{\text{Am}_1} [\text{Am}_1] + k_{\text{Am}_2} [\text{Am}_2] \quad (5)$$

4. RESULTS AND DISCUSSION

4.1. Single amines

On the basis of the conducted kinetic measurements, k_1 and k_{Am} constants for CO₂ reaction in aqueous potassium carbonate – bicarbonate solutions containing an addition of the investigated amine activators, have been determined. In Table 2 are presented average values of the pseudo-first order k_1 reaction rate constants in the temperature range of 20, 30 and 40 °C for the activators studied. As mentioned earlier, the first two terms on the right-hand side of Eq. (3) are very small, these values are practically equal to $k_{\text{Am}} [\text{Am}]$.

Table 2. Average values of k_1 constants for different concentrations of the activators investigated at 20, 30, 40 °C

| Studied system | k_1 [1/s] | | | | | | | | |
|-------------------------|---------------------------------|------|------|------|------|------|------|------|------|
| | Activator concentration [% w/w] | | | | | | | | |
| | 1 | | | 2 | | | 3 | | |
| | Temperature [°C] | | | | | | | | |
| | 20 | 30 | 40 | 20 | 30 | 40 | 20 | 30 | 40 |
| CO ₂ – TEPA | 304 | 487 | 792 | 603 | 974 | 1581 | 964 | 1588 | 2427 |
| CO ₂ – Pz | 1227 | 1989 | 2975 | 2686 | 4154 | 5997 | 4297 | 6435 | 9344 |
| CO ₂ – EtPz | 888 | 1553 | 2788 | 1778 | 3060 | 5396 | 2873 | 5391 | 8601 |
| CO ₂ – 2-IAE | 243 | 356 | 529 | 491 | 706 | 1051 | 773 | 1124 | 1575 |
| CO ₂ – GLY | 268 | 371 | 599 | 534 | 747 | 1189 | 841 | 1207 | 1766 |
| CO ₂ – 2-EAE | 434 | 683 | 1137 | 797 | 1371 | 2337 | 1281 | 2048 | 3481 |

Figure 2 illustrates the Arrhenius plots for the first order reaction rate constant k_1 (in form of $\log k_1 = f\left(\frac{1}{T}\right)$), obtained for the CO₂ – TEPA system (the R^2 symbol in Figure 2 is the determination coefficient). As shown in Table 2 and Fig. 2, the pseudo-first order k_1 rate constants depend on the studied amine activator concentrations, as expected.

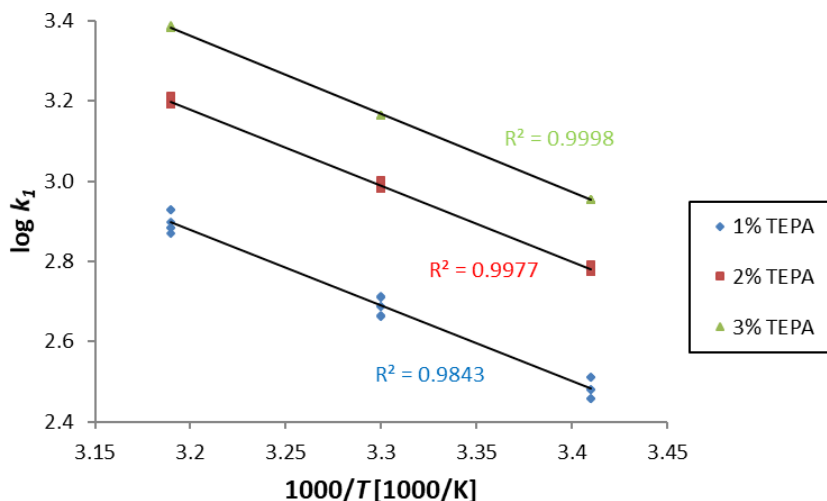


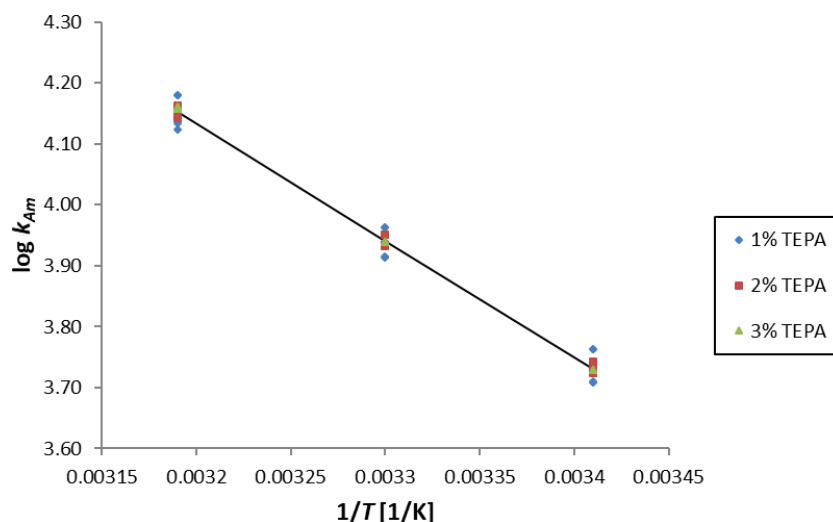
Fig. 2. Arrhenius plot for CO₂ – TEPA system

In Table 3, Arrhenius type equations for k_{Am} reaction rate constants are presented. The values of k_{Am} at 298 K for each of the investigated systems are presented in the same table.

Table 3. Values of k_{Am} at 298 K for investigated systems

| Investigated system | k_{Am} [m ³ /kmol·s] at 298 K | Arrhenius equation |
|-------------------------|--|---|
| CO ₂ – 2-EAE | 4470 | $\log k_{Am} = 10.362 - \frac{2000.8}{T}$ |
| CO ₂ – Pz | 13180 | $\log k_{Am} = 9.6818 - \frac{1658.1}{T}$ |
| CO ₂ – EtPz | 12590 | $\log k_{Am} = 11.686 - \frac{2260.3}{T}$ |
| CO ₂ – TEPA | 6760 | $\log k_{Am} = 10.265 - \frac{1916.4}{T}$ |
| CO ₂ – 2-IAE | 2880 | $\log k_{Am} = 8.5366 - \frac{1514.1}{T}$ |
| CO ₂ – GLY | 2240 | $\log k_{Am} = 8.243 - \frac{1571.5}{T}$ |

Figure 3 shows the $\log k_{Am} = f\left(\frac{1}{T}\right)$ relation for the CO₂ – TEPA system. As expected, the values of the second order reaction rate constant k_{Am} for the system mentioned above, do not, in practice, depend on concentration of the amine compound. Similar correlations have been obtained for other investigated amine activators.

Fig. 3. Arrhenius plot for the CO₂ – TEPA system

As can be seen from the results presented, the optimal activators, which exhibit the greatest values of the k_1 and k_{Am} constants for the K₂CO₃/KHCO₃ solution are: piperazine, ethyl-piperazine, tetraethylenepentamine and 2-ethyl-aminoethanol.

It is difficult to compare k_{Am} constant values, determined for the activators studied, to the literature data due to substantial differences in the results presented by various authors (Table 4). The comparison of the values presented in Tables 3 and 4 shows that k_{Am} constant values determined in the present paper, lie in the range of the quoted literature data.

Table 4. Literature values of CO₂ reaction rate constants in aqueous solutions of amines

| T [K] | Activator concentration [kmol/m ³] | k_{Am} [m ³ /kmol·s] | Source |
|---|--|-----------------------------------|-----------------------------|
| 1 | 2 | 3 | 4 |
| CO ₂ – 2-EAE (aqueous amine solutions) | | | |
| 303 | 0.02–0.08 | 3750 | Rayer et al., 2011 |
| 298 | 1 | 14450 | Sharma, 1965 |
| 298 | 0.9–2.5 | 4170 | Mimura et al., 1998 |
| 298 | 0.05–0.2 ^{*)} | 3560 | Pohorecki et al., 1988 |
| CO ₂ – Pz (aqueous amine solutions) | | | |
| 298 | 0.2–0.6 | 53700 | Bischnoi and Rochelle, 2010 |
| 298 | 0.02–0.1 | 16700 | Rayer et al., 2011 |
| 298 | 0.01–0.05 | 27178 | Ume et al., 2013 |
| 298 | 0.45–1.5 | 24300 | Conway et al., 2013 |
| 303 | 0.025–0.1 | 25800 | Bindwall et al., 2011 |
| 298 | 0.6–1.5 | 70000 | Derks et al., 2006 |
| 303 | 0.1–0.4 | 66450 | Bougie et al., 2009 |
| 298 | 0.23–0.92 | 21270 | Sun et al., 2005 |
| CO ₂ – EtPz (aqueous amine solutions) | | | |
| 298 | 0.02–0.08 | 7070 | Rayer et al., 2011 |

Table 4 [cont.]

| 1 | 2 | 3 | 4 |
|--|------------------------|-------|-----------------------------|
| CO ₂ – GLY (aqueous amine solutions) | | | |
| 298 | 1 ^{*)} | 14690 | Thee et al., 2012 |
| 298 | 0.06 | 7990 | Penny and Ritter, 1983 |
| 291 | 0.05–02 | 5930 | Jensen et al., 1952 |
| 283 | 0.2 | 1650 | Caplow, 1968 |
| CO ₂ – DEA (aqueous amine solutions) | | | |
| 298 | 1 | 1240 | Sharma, 1965 |
| 298 | 0–1.922 | 1340 | Sada et al., 1976 |
| 298 | 0–0.88 | 1400 | Donaldson and Nguyen, 1980 |
| 298 | 0–4 | 655 | Blanc and Demarais, 1981 |
| 298 | 0.021 | 110 | Barth et al., 1986 |
| 298 | 0–2.88 | 1410 | Laddha and Danckwerts, 1981 |
| 298 | 0–2.38 | 7300 | Blauwhoff et al., 1983 |
| 298 | 0–4.358 | 3240 | Versteg and Oyevaar, 1989 |
| 291 | 0–0.3 | 5900 | Jensen et al., 1954 |
| 298 | 0.1–0.4 ^{*)} | 4200 | Bińczak et al., 2016 |
| CO ₂ – 2-MAE (aqueous amine solutions) | | | |
| 298 | 1 | 31620 | Sharma, 1965 |
| 298 | 0.9–2.5 | 7940 | Mimura et al., 1998 |
| 298 | 0.36 | 28100 | Leder, 1971 |
| 298 | 0.1–0.4 ^{*)} | 6610 | Bińczak et al., 2016 |
| CO ₂ – TETA (aqueous amine solutions) | | | |
| 298 | 0.22–0.44 | 1240 | Marc and Bouallou, 2009 |
| 298 | 0.07–0.2 ^{*)} | 8320 | Bińczak et al., 2016 |
| *) amine concentration in aqueous K ₂ CO ₃ /KHCO ₃ solution | | | |

No papers presenting k_{Am} values for TEPA, 2-IAE and CHA have been found in the literature, although the above-mentioned amine compounds have become the subject of research papers on carbon dioxide absorption (Cwalina and Kubicki, 1977; Singh et al., 2009; Yamada et al., 2013).

4.2. Amine mixtures

An exemplary Arrhenius plot for the mixture of 1% wt. TEPA and 2% wt. DEA is shown in Fig. 4 (the R^2 symbol is the determination coefficient).

Similar plots have been obtained for all the mixtures under investigation. In the next step a comparison was made of the k_1 constants determined for single amines and those obtained for the amine mixtures (of course considering the concentration of the amines in question).

The comparison revealed an interesting phenomenon: while the k_1 values determined for mixtures of the aliphatic amines were practically equal to the sum of values obtained for single amines (Fig. 5 shows an example of such comparison), similar comparison performed for mixtures of aliphatic and cyclic amines

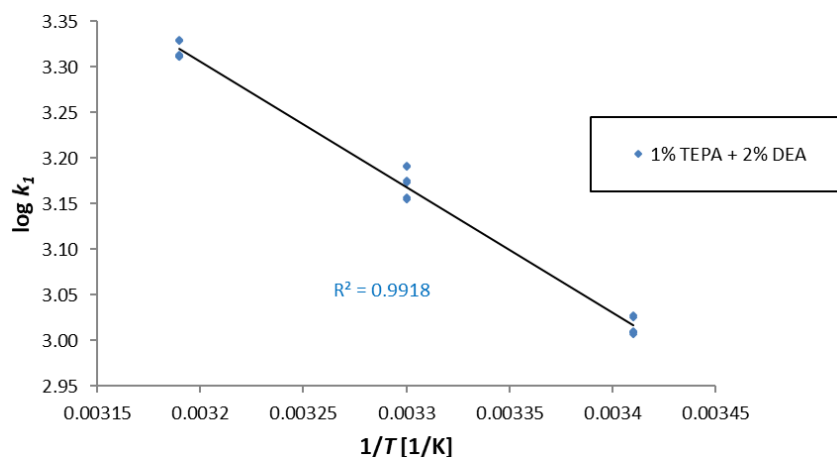


Fig. 4. Arrhenius plot for the mixture of two amines (1% wt. TEPA and 2% wt. DEA)

gave significant differences of the compared values. The values obtained experimentally for such mixtures were significantly higher than those calculated from the data for single amines. This is illustrated by Fig. 6. A similar synergetic effect is exhibited by two cyclic amine mixtures (Fig. 7). A comparison of the experimental values for all the mixtures investigated with those calculated from the values for single amines is shown in Table 5.

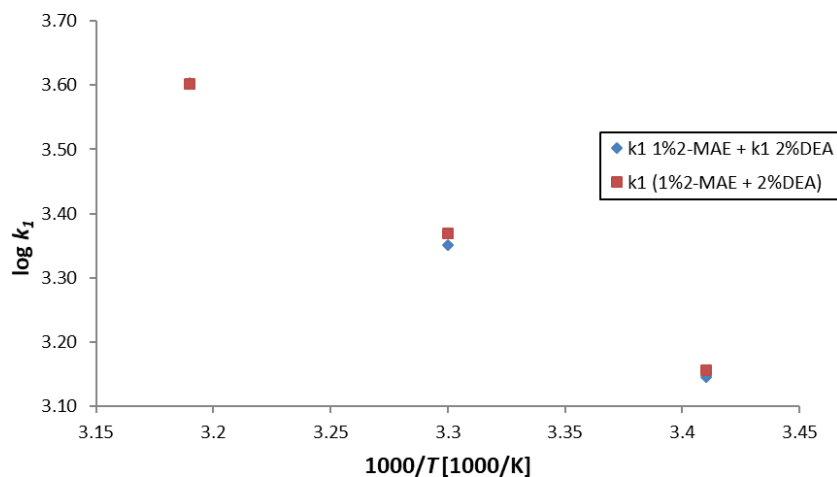


Fig. 5. Comparison of the experimental and calculated k_1 values (1% wt. MAE and 2% wt. DEA)

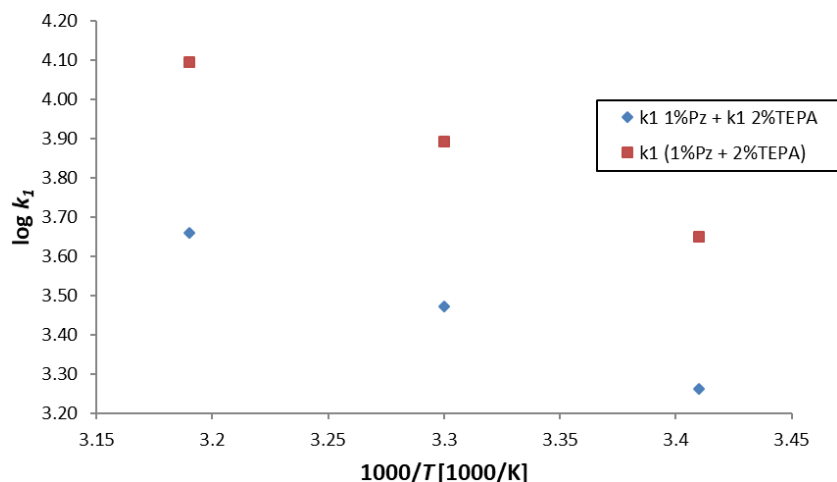


Fig. 6. Comparison of the experimental and calculated k_1 values (1% wt. Pz and 2% wt. TEPA)

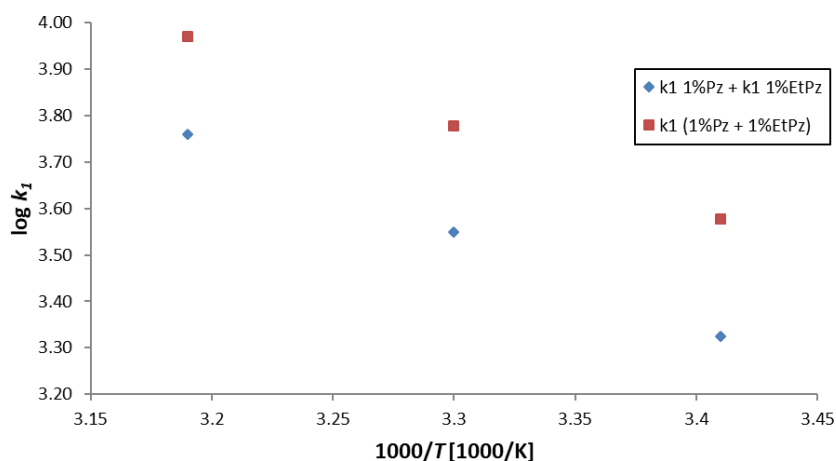


Fig. 7. Comparison of the experimental and calculated k_1 values (1% Pz + 1% EtPz)

Table 5. Comparison of the experimental and calculated k_1 values for all investigated mixtures

| Amine mixtures | k_1 [s^{-1}] | k_1 [s^{-1}] | | |
|--------------------------|---|-----------------------------|------|-------|
| | | Temperature [$^{\circ}C$] | | |
| | | 20 | 30 | 40 |
| 1% TETA + 2% DEA | $k_{11\% \text{ TETA}} + k_{12\% \text{ DEA}}$ | 1207 | 1720 | 2416 |
| | $k_{1(1\% \text{ TETA}+2\% \text{ DEA})}$ | 1278 | 1764 | 2444 |
| 1% TEPA + 2% DEA | $k_{11\% \text{ TEPA}} + k_{12\% \text{ DEA}}$ | 1034 | 1481 | 2044 |
| | $k_{1(1\% \text{ TEPA}+2\% \text{ DEA})}$ | 1035 | 1492 | 2079 |
| 1% 2-EAE + 2% DEA | $k_{11\% \text{ 2-EAE}} + k_{12\% \text{ DEA}}$ | 1164 | 1677 | 2389 |
| | $k_{1(1\% \text{ 2-EAE}+2\% \text{ DEA})}$ | 1206 | 1716 | 2376 |
| 1% 2-MAE + 2% DEA | $k_{11\% \text{ 2-MAE}} + k_{12\% \text{ DEA}}$ | 1398 | 2242 | 4010 |
| | $k_{1(1\% \text{ 2-MAE}+2\% \text{ DEA})}$ | 1430 | 2341 | 4004 |
| 1% Pz + 2% DEA | $k_{11\% \text{ Pz}} + k_{12\% \text{ DEA}}$ | 1957 | 2983 | 4227 |
| | $k_{1(1\% \text{ Pz}+2\% \text{ DEA})}$ | 3329 | 5168 | 7834 |
| 1% Pz + 2% 2-EAE | $k_{11\% \text{ Pz}} + k_{12\% \text{ 2-EAE}}$ | 2024 | 3360 | 5312 |
| | $k_{1(1\% \text{ Pz}+2\% \text{ 2-EAE})}$ | 4432 | 7809 | 13895 |
| 1% Pz + 2% TEPA | $k_{11\% \text{ Pz}} + k_{12\% \text{ TEPA}}$ | 1830 | 2963 | 4556 |
| | $k_{1(1\% \text{ Pz}+2\% \text{ TEPA})}$ | 4451 | 7792 | 12438 |
| 1% Pz + 1% DAE + 1%2-MAE | $k_{11\% \text{ Pz}} + k_{11\% \text{ DEA}} + k_{11\% \text{ 2-MAE}}$ | 2274 | 3735 | 6364 |
| | $k_{1(1\% \text{ Pz}+1\% \text{ DEA}+1\% \text{ 2-MAE})}$ | 4104 | 7111 | 11155 |
| 1% EtPz + 2% 2-MAE | $k_{11\% \text{ EtPz}} + k_{12\% \text{ 2-MAE}}$ | 2239 | 4057 | 8307 |
| | $k_{1(1\% \text{ EtPz}+2\% \text{ 2-MAE})}$ | 2745 | 5131 | 10182 |
| 1% EtPz + 2% TETA | $k_{11\% \text{ EtPz}} + k_{12\% \text{ TETA}}$ | 1875 | 3006 | 5129 |
| | $k_{1(1\% \text{ EtPz}+2\% \text{ TETA})}$ | 3799 | 5990 | 10197 |
| 1% Pz + 1% EtPz | $k_{11\% \text{ Pz}} + k_{11\% \text{ EtPz}}$ | 2115 | 3542 | 5763 |
| | $k_{1(1\% \text{ Pz}+1\% \text{ EtPz})}$ | 3787 | 6008 | 9328 |

The degree of the synergetic effect is summarized in Table 6. As it follows from this table the degree of this effect expressed by the ratio $\frac{k_1(i+j)}{k_{1i} + k_{1j}}$ may reach even up to 2.7 for the studied mixtures of aliphatic and cyclic amines and temperatures.

Table 6. The degree of the synergetic effect

| Amine mixtures | $\frac{k_1(i+j)}{k_{1i}+k_{1j}}$ | | |
|------------------------------------|----------------------------------|------|------|
| | Temperature [°C] | | |
| | 20 | 30 | 40 |
| 1%wt. Pz + 2%wt. DEA | 1.70 | 1.73 | 1.85 |
| 1%wt. Pz + 2%wt. 2-EAE | 2.19 | 2.32 | 2.62 |
| 1%wt. Pz + 2%wt. TEPA | 2.43 | 2.63 | 2.73 |
| 1%wt. Pz + 1%wt. DEA + 1%wt. 2-MAE | 1.80 | 1.90 | 1.75 |
| 1%wt. EtPz + 2%wt. 2-MAE | 1.23 | 1.26 | 1.23 |
| 1%wt. EtPz + 2%wt. TETA | 2.03 | 1.99 | 1.99 |
| 1%wt. Pz + 1%wt. EtPz | 1.79 | 1.70 | 1.62 |

5. CONCLUSIONS

Mixtures of aliphatic amines with cyclic amines, as well as mixtures of cyclic amines with cyclic amines, as opposed to mixtures of aliphatic amines with aliphatic amines, exhibit higher values of the kinetic constants for the reaction with CO₂ in carbonate solutions than the values calculated from the data obtained for single amines. The degree of this synergetic effect is shown in Table 6.

A similar phenomenon has been observed by Dubois and Thomas (2010). The reason of such synergetic effect is not clear, but obviously its existence suggests a reaction mechanism more complicated than simple parallel reactions.

This synergetic effect could be used to select new activators for CO₂ absorption into aqueous carbonate solutions.

However, the laminar jet measurements have been performed at ambient conditions and using carbonate solutions of much lower concentration than that used in industry. To exploit this synergetic effect in industrial practice, one has to confirm its existence in industrial conditions. The next stage of our research program was devoted to such confirmation. The results obtained shall be reported in a later paper.

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SYMBOLS

- A_m amine
 a interfacial area, m²
 C_A molar concentration of component A, kmol/m³
 D_A diffusivity of the absorbed gas in the liquid phase, m²/s
 k_1 pseudo-first order reaction rate constant, 1/s
 k_{Am} reaction rate constant, m³/(kmol·s)

| | |
|---------|---|
| k_L^* | liquid-film mass transfer coefficient with chemical reaction, m/s |
| N_A | molar flux of the absorbed components, kmol/m ² ·s |
| R | rate of absorption, kmol/s |
| [] | molar concentration, kmol/m ³ |

Subscripts

| | |
|-----|----------------------|
| A | absorbed gas |
| i | interface |
| r | chemical equilibrium |

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