

# 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 (CO<sub>2</sub> 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 CO<sub>2</sub> 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-

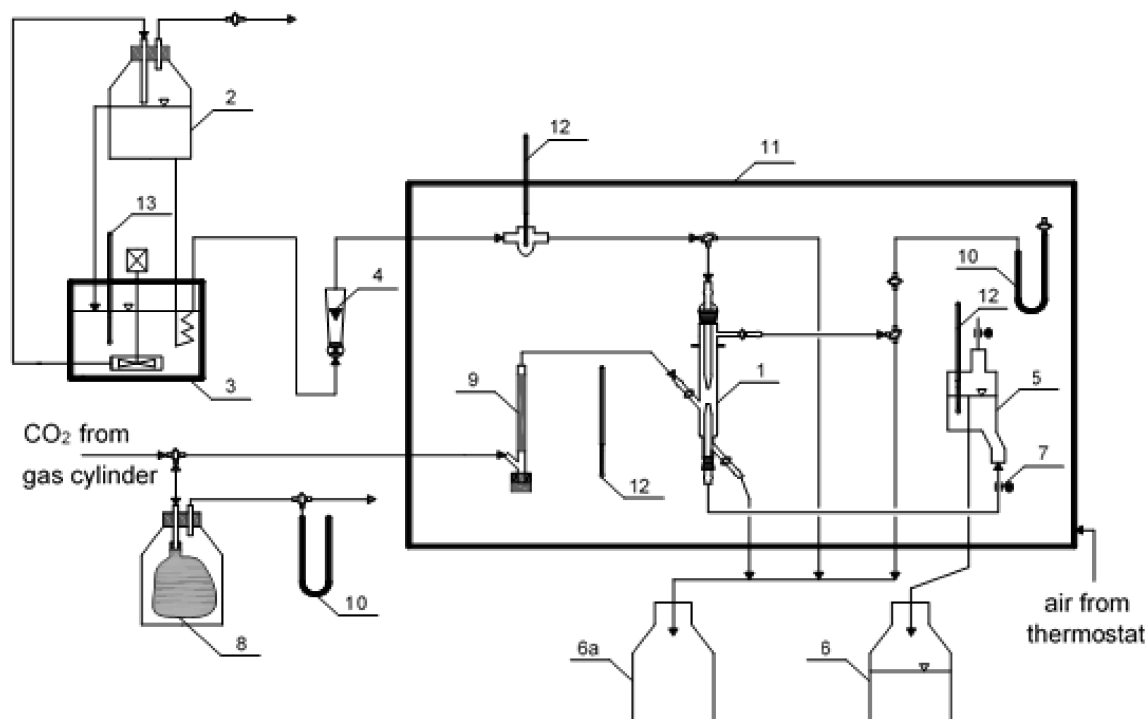


Fig. 1. Scheme of the experimental apparatus; 1 – laminar jet absorber, 2 – liquid tank, 3 – thermostat, 4 – rotameter, 5 – overflow, 6 – receiving tank, 7 – clamp, 8 – balloon with CO<sub>2</sub>, 9 – soap-film meter, 10 – manometer, 11 – perspex chamber, 12, 13 – thermometers

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  $1.03 \cdot 10^{-6} - 1.94 \cdot 10^{-6}$  m<sup>3</sup>/s. Pure CO<sub>2</sub> 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):

$$k_1 = k_{H_2O} + k_{OH^-} [OH^-] + k_{Am} [Am] \quad (3)$$

The methods of calculations of reaction rate constant  $k_{H_2O}$  and product  $k_{OH^-} [OH^-]$  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  $k_{H_2O}$  is in the range of 0.017–0.068 s<sup>-1</sup>, the value of the second term  $k_{OH^-} [OH^-]$  lies in the range of 0.5–3.20 s<sup>-1</sup>), the values of  $k_1$  are practically equal to  $k_{Am} [Am]$ , which allows easy calculation of  $k_{Am}$ .

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

$$k_1 = k_{H_2O} + k_{OH^-} [OH^-] + \sum k_{Am} [Am] \quad (4)$$

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

$$k_1 \cong \sum k_{Am} [Am] = k_{Am_1} [Am_1] + k_{Am_2} [Am_2] \quad (5)$$

## 4. RESULTS AND DISCUSSION

### 4.1. Single amines

On the basis of the conducted kinetic measurements,  $k_1$  and  $k_{Am}$  constants for CO<sub>2</sub> 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  $k_{Am} [Am]$ .

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 <sub>2</sub> – TEPA	304	487	792	603	974	1581	964	1588	2427
CO <sub>2</sub> – Pz	1227	1989	2975	2686	4154	5997	4297	6435	9344
CO <sub>2</sub> – EtPz	888	1553	2788	1778	3060	5396	2873	5391	8601
CO <sub>2</sub> – 2-IAE	243	356	529	491	706	1051	773	1124	1575
CO <sub>2</sub> – GLY	268	371	599	534	747	1189	841	1207	1766
CO <sub>2</sub> – 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 CO<sub>2</sub> – 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.

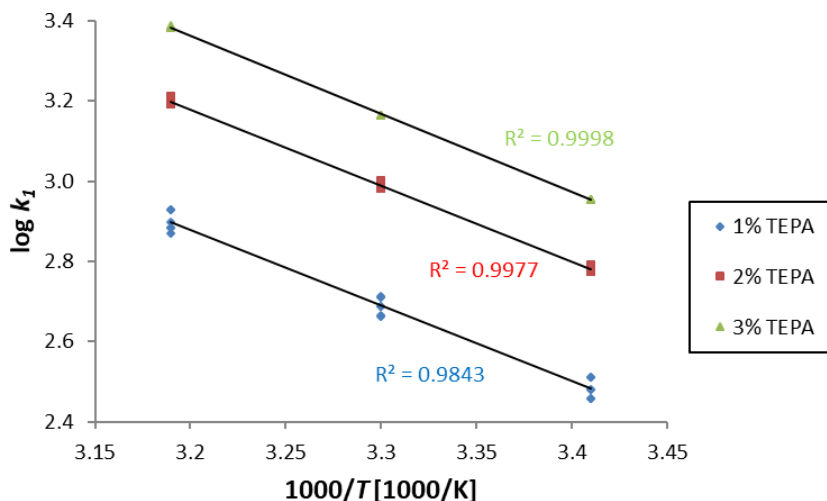


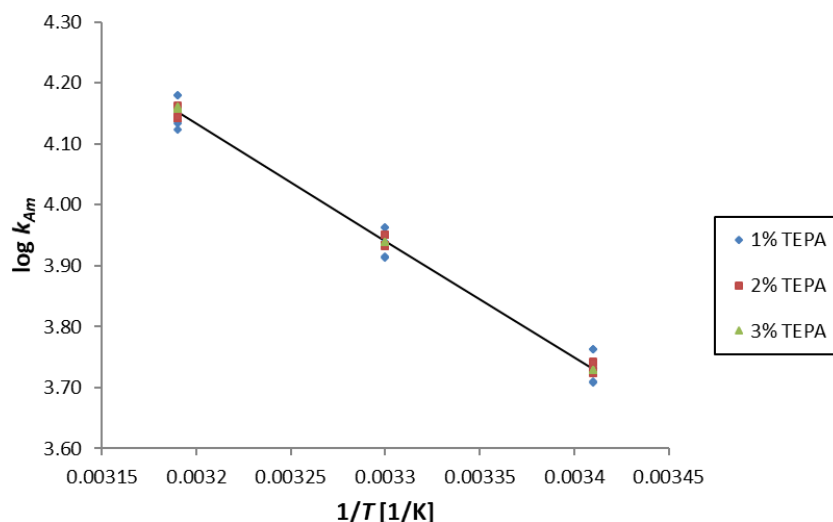
Fig. 2. Arrhenius plot for CO<sub>2</sub> – TEPA system

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 <sup>3</sup> /kmol·s] at 298 K	Arrhenius equation
CO <sub>2</sub> – 2-EAE	4470	$\log k_{Am} = 10.362 - \frac{2000.8}{T}$
CO <sub>2</sub> – Pz	13180	$\log k_{Am} = 9.6818 - \frac{1658.1}{T}$
CO <sub>2</sub> – EtPz	12590	$\log k_{Am} = 11.686 - \frac{2260.3}{T}$
CO <sub>2</sub> – TEPA	6760	$\log k_{Am} = 10.265 - \frac{1916.4}{T}$
CO <sub>2</sub> – 2-IAE	2880	$\log k_{Am} = 8.5366 - \frac{1514.1}{T}$
CO <sub>2</sub> – 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 CO<sub>2</sub> – 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 CO<sub>2</sub> – 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 K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub> 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 CO<sub>2</sub> reaction rate constants in aqueous solutions of amines

$T$ [K]	Activator concentration [kmol/m <sup>3</sup> ]	$k_{Am}$ [m <sup>3</sup> /kmol·s]	Source
1	2	3	4
CO <sub>2</sub> – 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 <sup>*)</sup>	3560	Pohorecki et al., 1988
CO <sub>2</sub> – 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 <sub>2</sub> – EtPz (aqueous amine solutions)			
298	0.02–0.08	7070	Rayer et al., 2011

Table 4 [cont.]

1	2	3	4
CO <sub>2</sub> – GLY (aqueous amine solutions)			
298	1 <sup>*)</sup>	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 <sub>2</sub> – 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 <sup>*)</sup>	4200	Bińczak et al., 2016
CO <sub>2</sub> – 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 <sup>*)</sup>	6610	Bińczak et al., 2016
CO <sub>2</sub> – TETA (aqueous amine solutions)			
298	0.22–0.44	1240	Marc and Bouallou, 2009
298	0.07–0.2 <sup>*)</sup>	8320	Bińczak et al., 2016
*) amine concentration in aqueous K <sub>2</sub> CO <sub>3</sub> /KHCO <sub>3</sub> 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

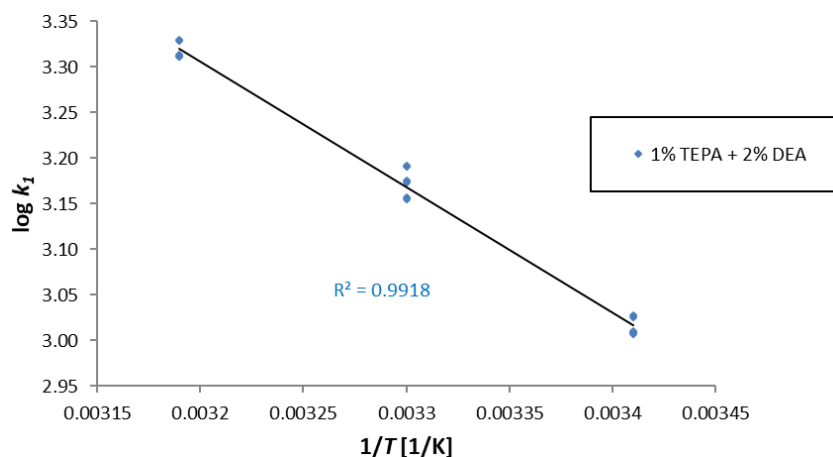


Fig. 4. Arrhenius plot for the mixture of two amines (1% wt. TEPA and 2% wt. DEA)

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.

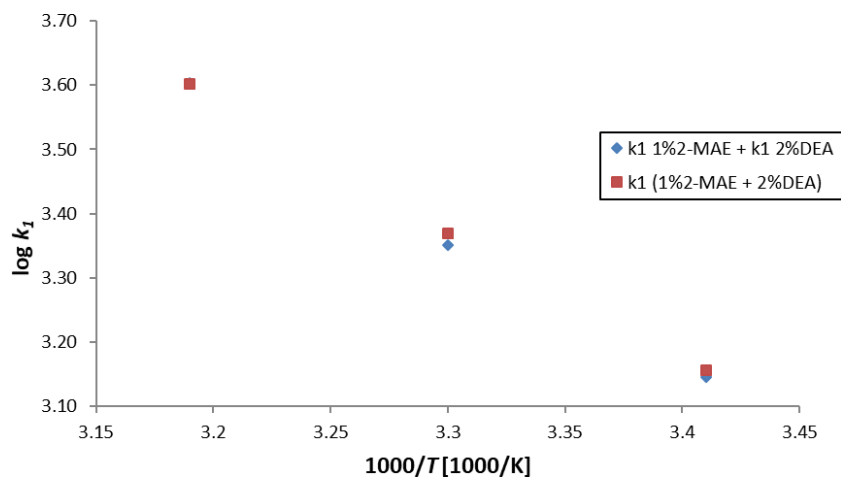


Fig. 5. Comparison of the experimental and calculated  $k_1$  values (1% wt. MAE and 2% wt. DEA)

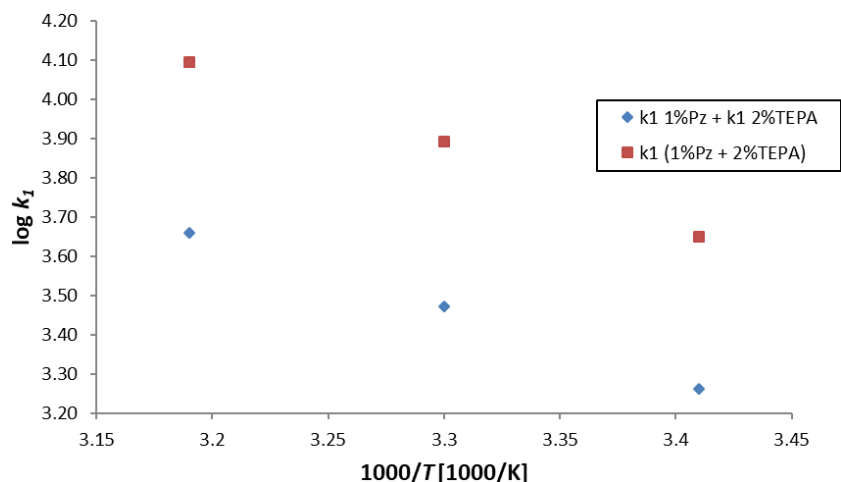


Fig. 6. Comparison of the experimental and calculated  $k_1$  values (1% wt. Pz and 2% wt. TEPA)



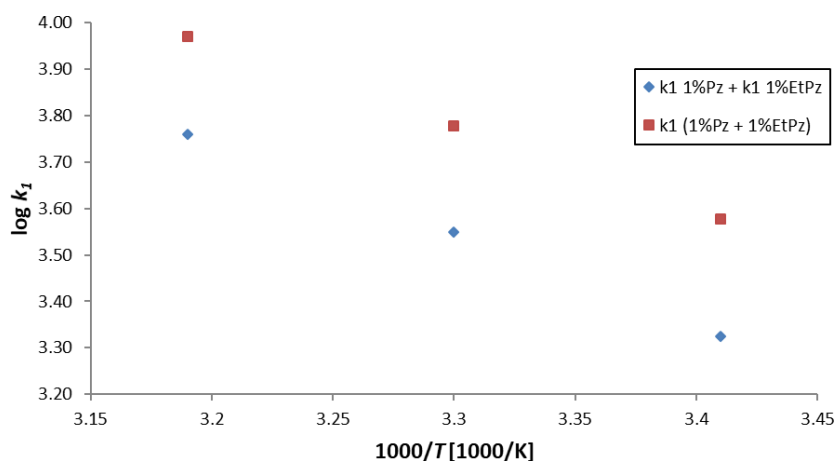


Fig. 7. Comparison of the experimental and calculated  $k_1$  values (1% Pz + 1% EtPz)

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 CO<sub>2</sub> 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 CO<sub>2</sub> 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, m<sup>2</sup>  
 $C_A$  molar concentration of component A, kmol/m<sup>3</sup>  
 $D_A$  diffusivity of the absorbed gas in the liquid phase, m<sup>2</sup>/s  
 $k_1$  pseudo-first order reaction rate constant, 1/s  
 $k_{Am}$  reaction rate constant, m<sup>3</sup>/(kmol·s)

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

### Subscripts

$A$	absorbed gas
$i$	interface
$r$	chemical equilibrium

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