

## AMINE ACTIVATORS OF CO<sub>2</sub> ABSORPTION IN INDUSTRIAL CONDITIONS

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Twenty-eight two-, three-, four-, and five-component amine mixtures have been evaluated as possible activators of CO<sub>2</sub> absorption into aqueous carbonate/bicarbonate solutions. Measurements were performed using a pressure autoclave with a sparger at conditions close to industrial ones. On the basis of these results, a formula for a new, more efficient amine activator named INS13 was developed. The activator was tested both in a pilot plant and on an industrial scale in an ammonia plant producing 300 tons/day of ammonia. Activator INS13 was applied in a number of ammonia plants in Poland and abroad.

**Keywords:** carbon dioxide, absorption, potassium carbonates, amine mixtures

### 1. INTRODUCTION

This paper is the third (and the last) of series of papers describing the results of a research program devoted to the investigation of new potential amine activators of carbon dioxide absorption in carbonate/bicarbonate solutions. In the former two papers (Bińczak et al., 2016; 2018) a detailed description of the chemistry involved as well as methods of calculating results and a review of the relevant literature were given. In the first of the two papers the reaction kinetics of carbon dioxide with single amines was investigated for six aliphatic and cyclic amines. In the second paper two- and three- component amine mixtures were examined.

Measurements were performed using the laminar jet technique, at normal pressure and in the temperature range of 20–40 °C. We found an interesting synergetic effect for mixtures containing cyclic amines, which might be promising for industrial purposes. However, in industrial context (e.g. in the Benfield process) conditions are different from those in the laboratory – both temperature and pressure are significantly higher. Whereas the difference in pressure is not expected to influence the reaction kinetics, any difference in temperature ranges may be of importance. As our ultimate aim was to find a new, more effective amine activator applicable in industrial conditions, it was necessary to check the absorption kinetics in conditions closer to those applied in industry. To this end we executed an investigation program using a different technique, which allowed to extend the temperature range up to 110 °C.

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## 2. MEASUREMENTS

The experimental set up is shown in Fig. 1. The main part of it was a 1 dm<sup>3</sup> autoclave, equipped with a gas sparger and a 6-blade stirrer. The gas mixture was supplied from two gas cylinders. The outlet gas, after drying, was directed to an analyser. At the beginning of the experiment, a mixture of gases (CO<sub>2</sub> and N<sub>2</sub>) was supplied through a three-way valve (10) to the CO<sub>2</sub> analyser (12). During the main part of the experiment the experimental conditions (pressure, temperature and stirrer speed) were kept constant, and the mixture of gases was supplied through the three – way valve to the gas sparger (8) below the stirrer (9). CO<sub>2</sub> concentration at the gas outlet from the reactor was measured by a CO<sub>2</sub> analyser (12). A detailed description of the apparatus and the measurements technique can be found in the paper (Moniuk et al., 2012).

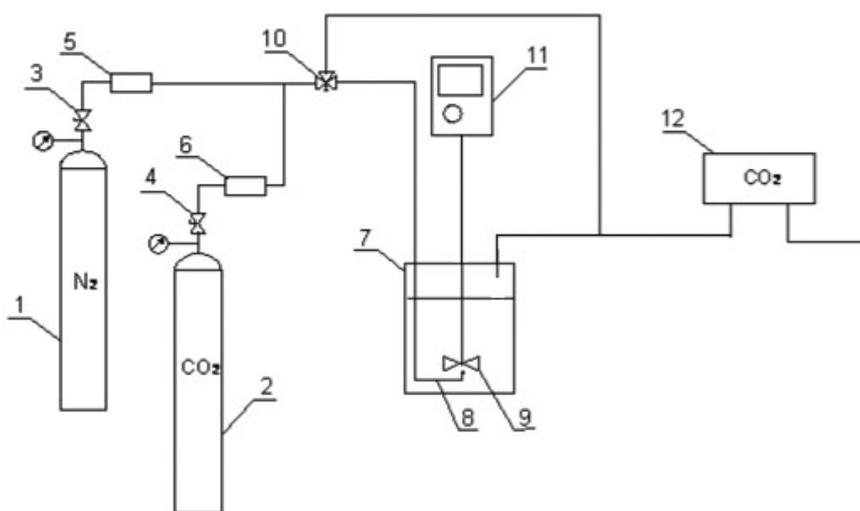


Fig. 1. Scheme of the experimental apparatus; 1, 2 – gas cylinders; 3, 4 – pressure reducing valves; 5, 6 – gas flow meters; 7 – stirred reactor; 8 – sparger; 9 – stirrer; 10 – three-way valve; 11 – temperature, pressure and stirrer speed regulators; 12 – CO<sub>2</sub> analyser

The experimental conditions were as follows:

- pressure: 4 bar,
- temperature: 30–110 °C,
- CO<sub>2</sub> flow rate:  $8.33 \cdot 10^{-3}$  dm<sup>3</sup>/s,
- N<sub>2</sub> flow rate:  $12.5 \cdot 10^{-3}$  dm<sup>3</sup>/s,
- stirrer speed: 600 rpm,
- concentration of carbonate solutions with respect to the K<sub>2</sub>CO<sub>3</sub>: 8 and 30 wt.%,
- carbonization ratio: 0.4.

## 3. METHOD OF CALCULATION

The absorption model and the chemistry involved were described in detail in our previous paper (Bińczak et al., 2016). The values of the interfacial area and physical mass transfer coefficient in the liquid phase for the experimental conditions were determined in our earlier papers (Moniuk et al., 1997a; 1997b). The first of these papers reports measurements of the gas-liquid interfacial area, obtained for a similar vessel and in comparable conditions, using both chemical and photographic methods. The interfacial area per unit liquid

volume changed in the range of 50–140 m<sup>2</sup>/m<sup>3</sup>, depending on the process conditions. The second paper describes measurements of the liquid side mass transfer coefficient, performed with a dynamic method, for both absorption and desorption processes. Depending on the process conditions, the  $k_L a$  coefficient values were in the range of 0.014–0.13 s<sup>-1</sup>.

It was verified that the criteria for fast, pseudo-first order reaction regime were satisfied. It was also verified that the gas side mass transfer resistance was negligible (Moniuk et al., 2013), which means that the interfacial concentration of CO<sub>2</sub> on the liquid side,  $c_{Ai}$ , was practically equal to the equilibrium value with the gas phase

$$p_{Ao} \cong p_{Ai} = \frac{c_{Ai}}{H} \quad (1)$$

The equilibrium partial pressure of CO<sub>2</sub> is described by the relation (Bińczak et al., 2016)

$$p_{Ar} = \frac{c_{Ai}}{H} = \frac{4\alpha^2}{K_p(1-\alpha)} \left\{ [\text{CO}_3^{2-}] + \frac{1}{2} [\text{HCO}_3^-] \right\} \quad (2)$$

where

$$\alpha = \frac{[\text{HCO}_3^-]}{2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]} \quad (3)$$

$$K_p = \frac{K_1}{K_2} H \quad (4)$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (5)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (6)$$

The values of  $K_p$  for potassium carbonate solutions at higher temperatures can be calculated from the relation given by Pohorecki and Kucharski (1983):

$$K_p = (16.1 + 1.8I) \exp\left(\frac{3663}{T} - 10.372\right) \quad (7)$$

Using the above described relations one can determine the liquid side coefficient of mass transfer with chemical reaction,  $k_L^*$

$$G\Delta Y = k_L^* (c_{Ai} - c_{Ar}) \cdot a \cdot V_R \quad (8)$$

For a fast, pseudo-first order chemical reaction (relevant criteria were presented in our earlier work (Bińczak et al., 2016)) the mass transfer coefficient with a chemical reaction is equal:

$$k_L^* = \sqrt{D_A \cdot k_1} \quad (9)$$

The reaction rate constant  $k_1$  is

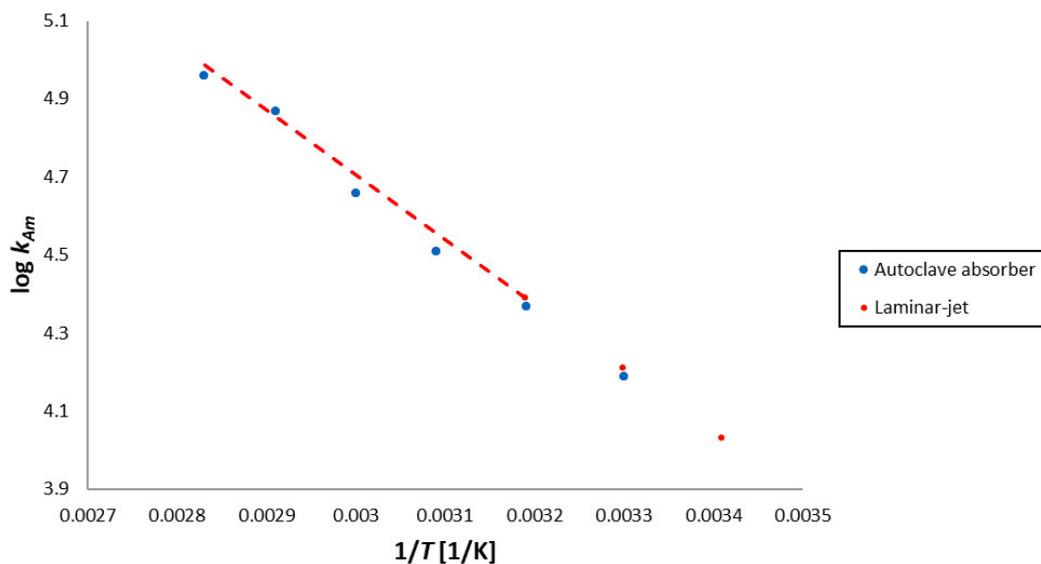
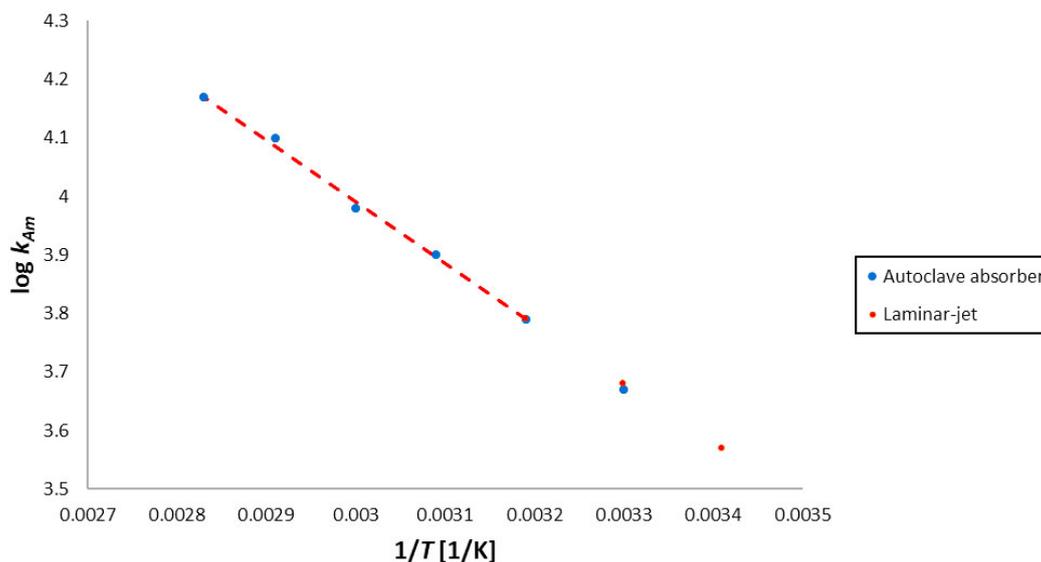
$$k_1 = k_{\text{H}_2\text{O}} + k_{\text{OH}^-} [\text{OH}^-] + \sum k_{\text{Am}} [\text{Am}] \quad (10)$$

The enhancement factor  $E$  is

$$E = \frac{k_L^*}{k_L} \quad (11)$$

## 4. RESULTS

The first task was to check the compatibility of the present experimental technique with the laminar jet technique used in previous papers (Bińczak et al., 2018). To this end, measurements of the absorption rate of CO<sub>2</sub> into carbonate solutions activated by two single amines, diethanolamine and piperazine, were performed and the second order reaction rate constant,  $k_{Am}$  was determined. Total concentration of carbonate solutions 8 wt.%; carbonation ratio: 0.4; Pz = 0.1 wt.%; DEA = 0.3 wt.%. Results are shown in Figs. 2 and 3. As can be seen, the results obtained in the autoclave absorber agree very well with those obtained using the laminar jet technique.

Fig. 2. Arrhenius plot for CO<sub>2</sub> – Pz systemFig. 3. Arrhenius plot for CO<sub>2</sub> – DEA system

The main experimental program involved measurements of the absorption rate for two-, three-, four-, and five component amine mixtures. As the objective was to find the most effective amine mixtures, results were presented as the ratio of the enhancement factor obtained with the amine mixture investigated to the enhancement factor obtained for DEA in the same conditions. Results are shown in Tables 1–4.

Table 1. Values of the  $E/E_{DEA}$  for two-component amine mixtures

Amine mixture [%wt.]	$E/E_{DEA}$				
	Temperature [°C]				
	70	80	90	100	110
1% DEA + 2% Pz	1.43	1.38	1.35	1.32	1.31
1% DEA + 2% EtPz	1.19	1.2	1.2	1.21	1.22
1.5% Pz + 1.5% TEPA	1.19	1.26	1.32	1.35	1.4
1.5% Pz + 1.5% EtPz	1.25	1.3	1.35	1.38	1.41
1.5% Pz + 1.5% TETA	1.35	1.35	1.36	1.36	1.36
1.5% Pz + 1.5% 2-MAE	1.21	1.26	1.3	1.33	1.35
1.5% Pz + 1.5% 2-EAE	1.26	1.28	1.3	1.33	1.34
1.5% TETA + 1.5% EtPz	1.12	1.13	1.25	1.34	1.41
1.5% 2-EAE + 1.5% EtPz	1.27	1.25	1.24	1.24	1.23
1.5% 2-MAE + 1.5% EtPz	1.21	1.22	1.23	1.24	1.25
1.5% TEPA + 1.5% EtPz	1.19	1.24	1.27	1.3	1.32

Table 2. Values of the  $E/E_{DEA}$  for three-component amine mixtures

Amine mixture [%wt.]	$E/E_{DEA}$				
	Temperature [°C]				
	70	80	90	100	110
1% DEA + 1% Pz + 1% TETA	1.2	1.2	1.22	1.23	1.24
1% DEA + 1% Pz + 1% EtPz	1.13	1.17	1.21	1.24	1.25
1% DEA + 1% Pz + 1% 2-MAE	1.3	1.28	1.28	1.26	1.26
1% DEA + 1.5% Pz + 0.5% 2-EAE	1.19	1.21	1.26	1.27	1.28
1% DEA + 1% Pz + 1% 2-EAE	1.08	1.2	1.29	1.35	1.4
1% DEA + 1.5% Pz + 0.5% 2-MAE	1.21	1.21	1.25	1.27	1.28
1% DEA + 1.5% Pz + 0.5% TETA	1.18	1.22	1.27	1.29	1.31

On the basis of these results, a formula for a new, more efficient amine activator was developed. The activator was proposed for industrial use under the name of INS13. Before application in full industrial scale, it was first tested in a pilot plant consisting of two packed columns (carbon dioxide absorber and solvent regenerator-desorber) (Bińczak, 2015). The basic dimensions of these columns are shown in Table 5. Białecki rings 1/2'' were used as the packing.

In Table 6 a summary of the results obtained for the absorber column using two activators (DEA – Benfield process, INS13 – new activator) are presented. As can be seen, the new activator INS13 ensures a considerable decrease of CO<sub>2</sub> concentration in the outlet gas phase.

Table 3. Values of the  $E/E_{DEA}$  for four-component amine mixtures

Amine mixture [%wt.]	$E/E_{DEA}$				
	Temperature [°C]				
	70	80	90	100	110
1% DEA + 1% Pz + 0.5% 2-MAE + 0.5% 2-EAE	1.4	1.32	1.27	1.24	1.22
1% DEA + 1% Pz + 0.5% 2-EAE + 0.5% TETA	1.37	1.31	1.27	1.24	1.22
1% DEA + 1% Pz + 0.5% 2-MAE + 0.5% TETA	1.58	1.44	1.36	1.29	1.23
0.5% DEA + 2% Pz + 0.25% 2-MAE + 0.25% 2-EAE	1.33	1.32	1.32	1.32	1.32
0.5% DEA + 1.5% Pz + 0.5% 2-EAE + 0.5% TETA	1.28	1.31	1.34	1.35	1.37
0.5% DEA + 1.5% Pz + 0.5% 2-EAE + 0.5% 2-MAE	1.18	1.25	1.3	1.34	1.38
0.25% DEA + 1.5% Pz + 0.75% 2-EAE + 0.5% 2-MAE	1.2	1.24	1.28	1.3	1.31
0.25% DEA + 1.5% Pz + 0.5% 2-EAE + 0.75% 2-MAE	1.08	1.2	1.29	1.36	1.42

Table 4. Values of the  $E/E_{DEA}$  for five-component amine mixtures

Amine mixture [%wt.]	$E/E_{DEA}$				
	Temperature [°C]				
	70	80	90	100	110
0.5% DEA + 1.5% Pz + 0.5% 2-EAE + 0.25% 2-MAE + 0.25% TETA	1.33	1.34	1.36	1.37	1.38
0.5% DEA + 1.5% Pz + 0.5% 2-MAE + 0.25% 2-EAE + 0.25% TETA	1.37	1.38	1.4	1.41	1.41

Table 5. Basic dimensions of the pilot plant packing columns

Apparatus	Apparatus height [m]	Packing height [m]	Apparatus diameter [mm]
Absorber	5.2	3.4	80
Desorber	4.16	2.4	107.1

Table 6. Summary of the results obtained in the pilot plant

Aktywator	Gas inlet					Liquid inlet				Gas outlet
	$V_{air}$ [kg/h]	$V_{CO_2}$ [kg/h]	$T$ [°C]	$y_{CO_2}$ [%mol]	$P$ [bar]	$V_L$ [m <sup>3</sup> /h]	$T$ [°C]	$K_2CO_3$ [%wt.]	$KHCO_3$ [%wt.]	$y_{CO_2}$ [%mol]
3% DEA	7.5	7.5	121	39.73	9	0.125	89	20.26	9.16	2.84
3% INS-13	7.5	7.5	99	39.73	9	0.125	86	24.76	9.12	0.72

In the next step INS13 activator was tested in the industrial scale in an ammonia plant producing 300 tons/day of ammonia. The use of a new activator resulted in a decrease of CO<sub>2</sub> concentrations in the gas outlet from the absorption column by about 1000 p.p.m. without any negative influence on the solvent regeneration in the desorption column.

An important factor in the selection of a new activator is its corrosivity. To check the corrosivity during the industrial test (50 days), the concentration of Fe<sup>2+</sup> ions in the solution was determined using the spectrophotometric method. Results are given in Table 7.

Table 7. Fe<sup>2+</sup> concentration in potassium carbonate – bicarbonate solution with INS13 as activator during the industrial test

Days	Fe <sup>2+</sup> [mg/kg]
0	35.64
1	35.22
3	43.29
10	40.00
15	31.23
18	35.62
22	39.53
27	36.17
32	34.15
44	37.00
47	37.35
50	39.24

As can be seen, the new INS13 activator practically did not influence the concentration of Fe<sup>2+</sup> in the solution (corrosivity of INS13 activator was not higher than that of DEA activator). During the industrial test, the concentration of INS13 activator in the solution was also determined using the gas chromatography method. Results had shown that the new activator was more stable than DEA.

After checking the performance of the new activator both in absorption and desorption processes, as well as its stability and corrosiveness, both in pilot plant and in the industrial scale (in an ammonia plant producing 300 t/day of ammonia) the new INS13 activator was commercially applied in industry. In 2015–2016 the new INS13 activator was used in five ammonia industrial plants in Poland and abroad.

## 5. CONCLUSIONS

- Comparative measurements of the performance of 28 amine mixtures used as CO<sub>2</sub> absorption activators were performed using a 1dm<sup>3</sup> autoclave with a sparger, in conditions close to industrial ones.
- All mixtures containing cyclic amines (i.e. mixtures of cyclic and aliphatic or cyclic and cyclic amines) exhibited the synergetic effect described in our previous paper (Bińczak et al., 2018).
- A new activator, named INS13, was checked for its effectiveness, stability, corrosiveness and energetic requirements during solvent regeneration, and applied in a number of ammonia plants in Poland and abroad.

## SYMBOLS

<i>Am</i>	amine
<i>a</i>	specific interfacial area, m <sup>2</sup> /m <sup>3</sup>
<i>c<sub>A</sub></i>	molar concentration of component A, kmol/m <sup>3</sup>
<i>D<sub>A</sub></i>	diffusivity of the absorbed gas in the liquid phase, m <sup>3</sup> /s
<i>E</i>	enhancement factor

$G$	molar flow of nitrogen, kmol/m <sup>3</sup>
$H$	Henry's constant, kmol/(m <sup>3</sup> ·bar)
$I$	ionic strength of solution, kmol/m <sup>3</sup>
$K_1$	equilibrium constant, kmol/m <sup>3</sup>
$K_2$	equilibrium constant, kmol/m <sup>3</sup>
$K_P$	equilibrium coefficient defined by Eq. (4), kmol/(m <sup>3</sup> ·bar)
$k_L$	liquid-film mass transfer coefficient, m/s
$k_L^*$	liquid-film mass transfer coefficient with chemical reaction, m/s
$k_1$	pseudo-first order reaction rate constant, 1/s
$k_{Am}$	reaction rate constant, m <sup>3</sup> /kmol·s
$k_{H_2O}$	reaction rate constant, 1/s
$k_{OH^-}$	reaction rate constant, m <sup>3</sup> /kmol·s
$p$	pressure, bar
$p_A$	partial pressure of component A, bar
$T$	temperature, K; °C
$V$	mass flow rate, kg/h
$V_L$	volumetric flow rate, m <sup>3</sup> /h
$V_R$	liquid volume, m <sup>3</sup>
$Y$	mole ratio CO <sub>2</sub> to N <sub>2</sub> , kmol/kmol
$y$	mole fraction, %mol
[ ]	molar concentration, kmol/m <sup>3</sup>

*Greek symbols*

$\alpha$	carbonization ratio defined by Eq. (3)
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*Subscripts*

$i$	interface
$o$	bulk of the gas phase
$r$	chemical equilibrium

*Amines*

DEA	diethanolamine
2-EAE	2-methylaminoethanol
EtPz	N-ethylpiperazine
Pz	piperazine
TETA	thriethylenetetramine
TEPA	tetraethylenepentamine

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