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# Kinetics of Carbon Dioxide Absorption into Aqueous Solution of a Polyamine

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**Abstract:** The absorption of CO<sub>2</sub> into an aqueous solution with 1.45 mol/L 1, 5, 8, 12- tetraazadodecane (APEDA) polyamine has been studied at three temperature (298, 313, 333 K) in a Lewis type absorber with a constant gas- liquid interface area of  $(15.34 \pm 0.05) \times 10^{-4} \text{ m}^2$ . The experimental results have been interpreted using the equations derived from the two film model with the assumption that the absorption occurred in the fast pseudo- first- order kinetic regime. The results confirmed the validity of this assumption for the experimental conditions: the enhancement factor was always greater than 3. The rate constant derived from the experimental data ( $k_{ov}$ , s<sup>-1</sup>) was correlated through the Arrhenius plot ( $\ln k_{ov} = A - B/T$ ), and the optimal values of the constants A and B were obtained by the linear regression. The absorption of CO<sub>2</sub> from flue gas into APEDA solution is a promising process for practical application at least from the kinetic point of view. The rate constant derived from experiments is of the same order of magnitude as that for the absorption into 2-amino- 2- methyl- 1- propanol (AMP) activated with piperazine (PZ) which was found to be the most advanced system among the published data up to now.

**Keywords:** acid gas absorption, Lewis cell absorber, enhancement factor, rate constant

## 1. Introduction

The removal of carbon dioxide from gas streams by selective absorption into aqueous solutions is an important industrial process in both natural gas sweetening and ammonia synthesis gas production. Aqueous hot potassium carbonate promoted by diethanolamine (DEA) is the chemical solvent used in the ammonia plants of Romania. Today, there are seven such ammonia plants in Romania (each of 1000 t NH<sub>3</sub>/ day) where the absorption is operated at 30- 40 bar, 343 K, solution with 25- 30 % K<sub>2</sub>CO<sub>3</sub> and 1-2 % DEA, in packed columns. The carbon dioxide, recovered by the reverse reaction (1) in the stripping column, is then consumed in the reaction (2) with ammonia, to produce urea- the best nitrogen fertilizer [10].



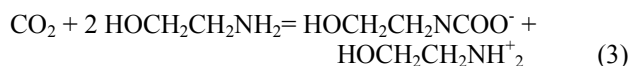
The question is: could be this process applied with the same high performances as in ammonia production to the capture of carbon dioxide from combustion flue gas of the fossil fuel power plants? Unfortunately, the answer is *no*. This is because the flow rates, composition, temperature and pressure of flue gas are different. The CO<sub>2</sub> partial pressure in the flue gas is much lower than in ammonia synthesis gas. It is of maximum 15 kPa. Therefore, more reactive absorbents are needed, like monoethanolamine (MEA) aqueous solution. The absorption of CO<sub>2</sub> into MEA solution is also a well established process [1]. It has been already applied in the only three industrial plants in the

world for CO<sub>2</sub> capture from fossil fuel power plant flue gas [2, 3]. They have the commercial names *Econamine FG*, *Econamine FG Plus*, and *ABB Lummus*, respectively. After the removal of NO<sub>x</sub> and SO<sub>x</sub> the flue gases are cooled at 40°C and transported with a gas blower to overcome the pressure drop caused by the MEA absorber. The MEA solution (30- 40 % MEA) is regenerated in the stripper at elevated temperatures (100- 120°C) and a pressure not much higher than atmospheric. Heat is supplied to the boiler using low- pressure steam which also acts as a stripping gas. Besides the high absorption rate, the MEA process has a number of *drawbacks* that are detailed below.

(1) The first important drawback is the large absorption/stripping enthalpy: 83 kJ/mol CO<sub>2</sub> at 298 K, in a solution 5M of MEA [4]. This is equivalent to 4.0 GJ/t of CO<sub>2</sub> captured. The actual energy requirement in the *Econamine FG* process is of 4.2 GJ/t [2]. The enthalpy of absorption of CO<sub>2</sub> into MEA solution is higher than in both K<sub>2</sub>CO<sub>3</sub> solution (63 kJ/ mol) and in other amine solutions (DEA, AMP, MIPA, PZ, MDEA). Therefore, the energy consumption of MEA capture system could be up to 40% of the power plant output [4] and a proportional more expensive electrical energy which must be payed by consumers. Nevertheless, recently has been found [5] that the absorption enthalpy of CO<sub>2</sub> into a polyamine (TMBPA) is of only 44 kJ/mol. This suggested to the authors of this paper to study the absorption of CO<sub>2</sub> into a similar polyamine: 1, 5, 8, 12- tetraazadodecane (APEDA).

(2) The second major drawback of MEA is the low cyclic absorption capacity. The theoretical value is of 0.5 mol CO<sub>2</sub>/ mol amine, according to the overall reaction (3),

based on the carbamate formation through the zwitterions mechanism:



The practical value is of only 0.35 (from 0.2 of the lean solution to 0.45 of the carbonated solution). Therefore, the MEA process needs about 55 m<sup>3</sup> solution /ton CO<sub>2</sub> captured. The polyamine named TMBPA has a saturation loading of 3 mol CO<sub>2</sub>/ mol amine [5]. A higher cyclic capacity reduces the flow rate of the solution needed. APEDA is expected to have a cyclic absorption capacity of 2 because it includes two primary and two secondary amine groups in the molecule.

(3) The third important disadvantage of MEA is its degradability. The reactions of MEA with NO<sub>x</sub>, SO<sub>x</sub>, CO and O<sub>2</sub> which accompany the CO<sub>2</sub> in flue gases leads to heat- stable salts which must be purged from the recirculated solution [6]. These salts mainly consist of formate (87%), acetate (4.6%), oxalate (0.2%), thiocyanate(6.8%), thiosulphate(1.2%) and sulphate(0.2%). The production of these salts could be from 3.729 to 14.917 kg/ t CO<sub>2</sub> captured [7]. This means that up to 10% of active amine is lost through degradation. It must be noted that the degradation oxidative reactions of MEA begin by the attack at the alcohol function of the alkanol radical [8]. The replacement of MEA with an alkyl amine could avoid or mitigate the degradation reactions.

(4) The presence of heat- stable salts in the absorption solution causes a number of adverse effects: reduction of amine absorption capacity, increase in foaming tendency of the solution, increase in solution viscosity, increase in corrosion, reduced filter runtime due to the solid precipitation in solution. Consequently, the solution must contain at least three types of additives: oxygen scavengers (OS), corrosion inhibitors (CI), and antifoam agents (AA). These special additives make the MEA solution an expensive one. The estimated cost of CO<sub>2</sub> capture by absorption in MEA solution was evaluated at EUR 39.3/ tone of CO<sub>2</sub> avoided [3]. This could increase the cost of electricity production by 82.8 % (from EUR 31.4/MWh to EUR 57.4/ MWh). APEDA is not an alkanolamine and could be not degraded by oxidation with SO<sub>x</sub>, CO and O<sub>2</sub>. In addition, APEDA is frequently used as ingredient for corrosion inhibitors [11].

The objective of this work was to study the kinetics of CO<sub>2</sub> absorption into APEDA aqueous solution. The originality of the present work consists of two things: the solvent, and the apparatus. The solvent was a 1.45 M APEDA aqueous solution, a polyamine which has not yet been used for the CO<sub>2</sub> absorption. The apparatus is described in the next section.

## 2. Experimental

The apparatus (Fig.1) is a Lewis type absorber with a constant gas- liquid interface area of  $(15.34 \pm 0.05) \times 10^{-4}$  m<sup>2</sup>. The total volume available for gas and liquid phases is

$(0.3504 \pm 0.0005) \times 10^{-4}$  m<sup>3</sup>. The temperature is kept constant within 0.05 K by circulating a thermostatic fluid through the double glass jacket. The liquid phase is agitated by a six bladed *Rushton* turbine ( $4.25 \times 10^{-2}$  m diameter). The gas phase is agitated by  $4 \times 10^{-2}$  m diameter propeller. Both agitators are driven magnetically by a variable speed motor. The turbine speed is checked with a stroboscope.

The kinetics of gas absorption is measured by recording the absolute pressure drop through a SEDEME pressure transducer, working in the range  $(0 \text{ to } 200) \times 10^3$  Pa. A microcomputer equipped with a data acquisition card is used to convert the pressure transducer signal directly into pressure P units, using calibration constant previously determined, and records it as function of time.

Water and APEDA are degassed independently and aqueous solutions are prepared under a vacuum. The amounts of water and amines are determined by differential weightings to within  $\pm 10^{-2}$ g.

This uncertainty on weightings leads to uncertainties in concentrations of less than  $\pm 0.05\%$ .

The flask containing the degassed APEDA aqueous solution is connected to the absorption cell by means of a needle introduced through the septum situated at the bottom of the cell. Weighing the flask with the tube and the needle before and after transfer allows the determination of the exact mass of solvent transferred into the cell.

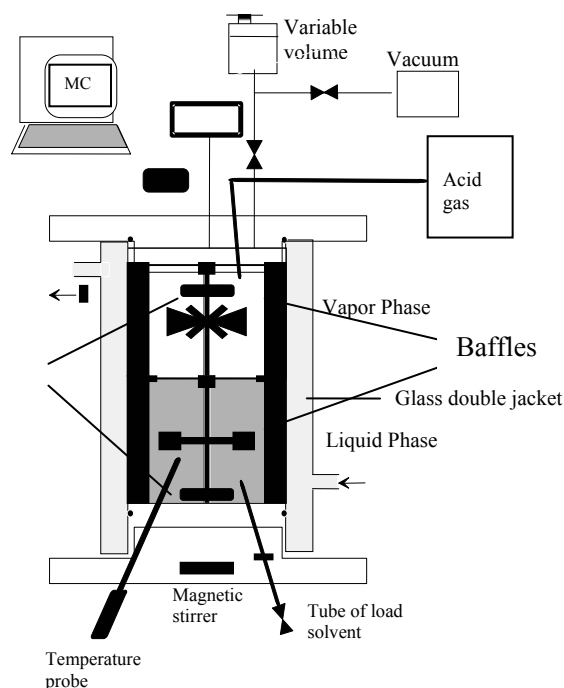


Figure 1. Flow diagram of the absorption equipment

Once the amine aqueous solution is loaded and the temperature equilibrated, the inert gas pressure  $P_i$  corresponding mainly to the solvent vapor pressure plus eventual residual inert gases is measured. The pure CO<sub>2</sub> is introduced over a very short time (about 2 s) in the upper part of the cell, the resulting pressure  $P_0$  is between  $(100-200) \times 10^3$  Pa. Then stirring is started and the pressure drop resulting from absorption is recorded.

The main materials involved have been: water, carbon dioxide, 1, 5, 8, 12- Tetraazadodecane (APEDA). Ordinary twice-distilled water was used. Carbon dioxide, purchased from *Air Liquid*, of 99.995% purity, was used as received. APEDA from *Alfa Aesar* (Store Road, Heysham) material certified 96.5 % was used as received.

Solution densities were measured with an *Anton Paar* (Graz, Austria) vibrating tube densimeter, model DMA 512.

### 3. Results and discussion

The primary experimental results have been interpreted on the basis of the gas- liquid chemical process theory (Siminiceanu, 2004). The rate of the chemical absorption of CO<sub>2</sub> (= i) is of the form (4):

$$-dn_i / A dt = E k_L^0 C_i^e, \text{ mol/m}^2 \text{ s}, \quad (4)$$

The gas phase is assumed ideal ( $P_i V_g = n_i RT$ ), CO<sub>2</sub> is completely consumed by the reaction in the liquid film, and the CO<sub>2</sub> concentration at the interface is replaced by the Henry law ( $C_i^e = P_i^e / H_i$ ). The partial pressure of CO<sub>2</sub> is obtained by subtraction of vapor pressure of the solution ( $P_v$ ) from the total measured pressure ( $P_T$ ):  $P_i = P_T - P_v$ . By integrating (4) under these assumptions, the equation (5) is derived:

$$\ln (P_T - P_v) / (P_T - P_v)_{t_0} = -\beta (t - t_0) \quad (5)$$

where

$$\beta = E k_L^0 A R T / V_g H_i \quad (6)$$

The enhancement factor E can be calculated for each experiment, using the equation (6).

In order to compare our results with those for other solutions at the same temperature, the overall rate constant ( $k_{ov}$ ) of the pseudo- first order reaction has been calculated for the fast reaction regime ( $E = Ha > 3$ ):

$$k_{ov} = (k_L^0 E)^2 / D_i \quad (7)$$

The mass transfer coefficient  $k_L^0$  is calculated with the equation (8) which was established, using the N<sub>2</sub>O analogy, for the absorber also applied in these new kinetic experiments [12]:

$$Sh = 0.352 Re^{0.618} Sc^{0.434} \quad (8)$$

Where the dimensionless Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) numbers have been defined as follows:

$$Sh = k_L^0 D_c / D_i \quad Re = \rho_L N d_{st} / \mu_L; \quad Sc = \mu_L / \rho_L D_i$$

E being calculated with (6), using the experimental values of  $\beta$  from the tables 1 and 2.

The Henry constant ( $H_i^0$ ) and the diffusion coefficient ( $D_i^0$ ) for the system CO<sub>2</sub>- H<sub>2</sub>O have been calculated with the equations (9) and (10), respectively [13]:

$$H_i^0 = 2.8249 \times 10^6 \exp (-2044/T) \quad (9)$$

$$D_i^0 = 2.35 \times 10^{-6} \exp (-2119/T) \quad (10)$$

The presence of the amine in water decreases the gas solubility ("salting out effect"). Taking into account the influence of the ionic strength of the solution on the solubility [10] with an equation of Sechenow type, the  $H_i$  for the solution of 1.45 M APEDA was evaluated with (11):

$$H_i = 1.113 x H_i^0 \quad (11)$$

The diffusivity of CO<sub>2</sub> in the APEDA aqueous solution was evaluated with the equation(12), tested in a previous work [14]:

$$D_i = (D_i^0 / 2.43) (\mu_L / \mu_W)^{0.2} \quad (12)$$

The ratio  $\mu_L / \mu_W$  has been correlated for the APEDA solutions on the basis of experimental data published in a previous paper [15].

The results from the table 2 (first row, for the same loading) can be compared to those obtained for the absorption of CO<sub>2</sub> in a solution of AMP (1.5 M) with different doses of PZ as activator, in a watted wall column absorber at the same temperature and a loading  $a = 0.288 - 0.031$  [16]. The value obtained in this work with APEDA ( $k_{ov} = 17\,255.51 \text{ s}^{-1}$ ) is higher than  $k_{ov}$  for AMP with 0.1 and 0.2 M piperazine, and inferior to that for larger doses of PZ. It must be noted that the solution AMP- PZ- H<sub>2</sub>O gives the grates absorption rate among the new systems studied in the literature in the last decades.

TABLE 1. Experimental and calculated data for the absorption of CO<sub>2</sub> in APEDA (1.45 M) aqueous solution at 298 K

a, molCO <sub>2</sub> /mol APEDA	$\beta$	$H_i$ , Pa.m <sup>3</sup> /mol 2965.85	$D_{CO_2}$ , m <sup>2</sup> /s 2.00E-09	$k_L$ , m/s 1.96E-05	E=Ha	$k_{ov}$ , s <sup>-1</sup>
0.012	0.028				206.04	8 490.91
0.070	0.026				191.32	7 030.98
0.180	0.025				183.96	6 500.34
0.295	0.023				169.24	5 501.79
0.382	0.022				161.88	5 033.48
0.484	0.021				154.52	4 586.39

TABLE 2. Experimental and calculated data for the absorption of CO<sub>2</sub> in APEDA (1.45 M) aqueous solution at 333 K

a, molCO <sub>2</sub> /mol APEDA	$\beta$	$H_i$ , Pa.m <sup>3</sup> /mol 6098.76	$D_{CO_2}$ , m <sup>2</sup> /s 2.23E-09	$k_L$ , m/s 2.49E-05	E=Ha	$k_{ov}$ , s <sup>-1</sup>
0.047	0.041				445.95	55 292.49
0.109	0.041				445.95	55 292.49
0.222	0.040				435.07	52 627.42
0.330	0.033				358.93	35 818.99
0.430	0.029				315.43	27 663.03
0.518	0.026				282.79	22 235.57

TABLE 3. The results for the absorption of CO<sub>2</sub> in 1.5 M solutions of AMP activated with PZ at 313 K [16]

$C_{PZ}^0$ , mol/L	$a \times 10^2$ , mol/mol	$k_L^0 \times 10^3$ , m/s	$D_i \times 10^9$ , m <sup>2</sup> /s	$H_i$ , Pa m <sup>3</sup> /mol	$N_A \times 10^6$ , kmol/m <sup>2</sup> s	$k_{ov}$ , s <sup>-1</sup>
0.1	3.11	3.97	1.72	4 144	3.46	7 530
0.2	2.88	4.05	1.66	4 047	3.88	13 857
0.3	3.10	3.68	1.57	4 095	4.31	20 572
0.4	3.16	3.64	1.42	4 070	4.52	27 819

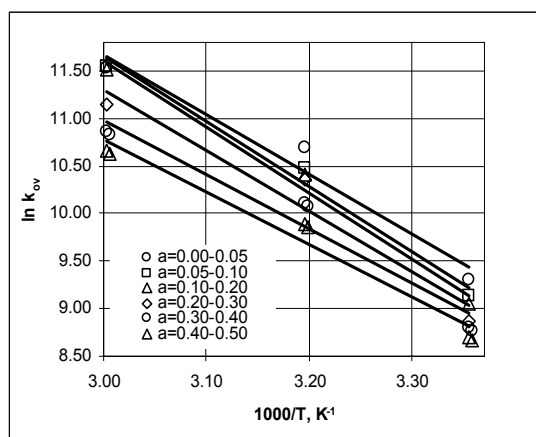


Figure 2. The Arrhenius plots for all experimental loadings

TABLE 4. The kinetic parameters derived from the Arrhenius plot

a molCO <sub>2</sub> /mol APEDA	Ea		A = $\ln k_{ov}^0$	B = Ea/R, K
	cal/mol	kJ/mol		
0.00-0.05	10 553.89	44.11	26.496	5 311.02
0.05-0.10	10 616.18	44.37	26.877	5 342.72
0.10-0.20	10 782.52	45.06	27.272	5 426.27
0.20-0.30	10.552.85	44.11	25.931	5 310.52
0.30-0.40	9 599.42	40.12	24.238	4 830.90
0.40-0.50	8 890.80	37.16	24.671	4 474.08

#### 4. Conclusions

The aqueous monoethanolamine (MEA) is now considered the most convenient among the available absorption technologies for removing carbon dioxide from flue gas streams. Nevertheless, this process has a number of drawbacks, pointed out in the introductory section of this paper, which make it rather expensive. Its application to fossil fuel power plants could increase the cost of electricity production by up to 82.8 % [3]. This paper presents some results of a study aiming to develop a new solvent in order to improve the efficiency of the CO<sub>2</sub> removal from flue gas.

The absorption of CO<sub>2</sub> into an aqueous solution with 1.45 mol/L 1, 5, 8, 12- tetraazadodecane (APEDA) polyamine has been studied at three temperature (298, 313, 333 K) in a Lewis type absorber with a constant gas-liquid interface area of  $(15.34 \pm 0.05) \times 10^{-4} \text{ m}^2$ . The experimental results have been interpreted using the equations derived from the two film model with the assumption that the absorption occurred in the fast pseudo-first-order kinetic regime. The results confirmed the validity of this assumption for the experimental conditions: the enhancement factor was always greater than 3.

According to the results, the rate constant ( $k_{ov}$ ) increased with the temperature, and decreased with the carbonation degree/ loading ( $a = \text{mol CO}_2/\text{mol amine}$ ). For each loading the Arrhenius equation was satisfactorily verified (Fig.2). The activation energy (41.9 kJ/mol) indicated that the process proceeded close to the boundary between the kinetic and the mass transfer regime. The optimal values of the constants A and B from the Arrhenius equation ( $\ln k = A - B/T$ ) were derived by linear regression, for each loading (Table 4). These will be useful for the industrial absorption column modeling and simulation.

The rate constant derived from experiments is of the same order of magnitude as that for the absorption into 2-amino- 2- methyl- 1- propanol (AMP) activated with piperazine (Table 3) which was found to be the most advanced system among the published data up to now (Sun et al., 2005). At  $T = 313 \text{ K}$  and  $a < 0.05$ , for instance,  $k_{ov} = 17\,255 \text{ s}^{-1}$  for APEDA, compared to  $20\,572 \text{ s}^{-1}$  for 1.5M of AMP with 0.3M of PZ under the same conditions.

The preliminary results presented in this paper show that, from the kinetic point of view, the absorption of CO<sub>2</sub> from flue gas into APEDA solution is a promising process for practical application. Other potential advantages of APEDA compared to MEA: higher loadings (smaller solution flow rates), less energy required for regeneration, lower degradability and corrosiveness. It is still to prove the unavoidable existence of some drawbacks, such as, volatility, toxicity and cost.

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