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Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

KINETICS OF CARBON DIOXIDE ABSORPTION INTO NEW AMINE SOLUTIONS

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ABSTRACT. The absorption of CO_2 into activated carbonate buffer solutions is the main process applied in the existing ammonia plants. The major draw back of this process is the high endothermicity of the regeneration step. Therefore, new chemical solvents must be introduced having not only high absorption rate and capacity but also low heat of regeneration. The objective of this work was to study the kinetics of CO_2 absorption into aqueous solutions of ethylenediamine (EDA). A thermo regulated constant interfacial area gas-liquid reactor has been used to measure the carbon dioxide absorption rates into this aqueous amine solution (3% mol) in the temperature range 298 – 333 K. The experimental results have been interpreted using the equations derived from the two film model. The enhancement factor was always greater then 3. The pseudo-first order rate constant derived from the experimental data was of the same order of magnitude as for absorption into mixtures of MEA and MDEA.

Keywords: *carbon capture, ethylenediamine (EDA), Lewis absorber, rate constant, enhancement factor.*

INTRODUCTION

Currently, fossil fuels fired power plants account for 80% of total energy production world wide and are the largest point sources of carbon dioxide emissions, accounting for roughly 40% of total carbon dioxide emissions [1]. A single such power station of 500 MW has emissions of 8,000 tones CO_2/ day.

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In Romania, the largest coal power station (in Turceni) had a generation capacity of 2,640 MW. For such giant flue gas flow rate sources, the chemical absorption is the best method to remove carbon dioxide [2, 3, 4]. The absorbent contains a substance which rapidly reacts with the dissolved carbon dioxide in the liquid phase. This reaction enhances/accelerates the overall mass transfer process. The substance is usually an alkali such potassium carbonate, sodium hydroxide, ammonia, amines. There is an important industrial experience with activated potassium carbonate solutions (Benfield, Carsol) used in ammonia plants to remove carbon dioxide from synthesis gas. A recent paper presents interesting results regarding the enhancement of the absorption using *arginine* as activator [6].Chemical solvents such as alkanolamines are also commonly used to enhance carbon dioxide absorption rates and capacity and to improve selectivity. A wide variety of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), di- isopropanolamine (DIPA), N- methyldietanolamine (MDEA) have been already used industrially [2, 3]. A recent advancement in gas treating is the absorption into blended amines. Blends of primary (MEA) and tertiary (MDEA) amines have been suggested for CO_2 removal [3]. Aqueous ammonia seems to be a practical solution for post- combustion carbon capture [4]. Which chemical solvent is the best? To answer this question, at least ten characteristics must be taken into account. A good chemical solvent for carbon dioxide capture has to meet the following requirements:

(1) High solubility x (small Henry constant H, in: $p = H \cdot x$);
(2) High selectivity for CO_2;
(3) Low energy for solvent regeneration/ enthalpy of absorption;
(4) High cyclic absorption capacity (mol CO_2 / mol solvent);
(5) High absorption rate;
(6) Thermal and chemical stability;
(7) Low vapor pressure;
(8) Low corrosivity;
(9) Low toxicity for humans and environment;
(10) Availability and low cost.

Our group published several papers on the characteristics of new solvents [6, 7, 8, 9, 10, 11] as well as on the absorption modeling and intensification [12, 13, 14, 15, 16, 17, 18, 19]. More recent papers published by other groups are concentrated on the optimization of the absorption into MEA solution [21]

The originality of the present work consists of two things: the system, and the apparatus. The system is a solvent which contains a primary amine (EDA). The results with EDA will be compared with TETA, with primary and secondary amine groups in the same molecule. Then TETA will be compared to the primary amine (EDA) and to the mixture EDA/TETA in aqueous solution.

RESULTS AND DISCUSSION

Table 1 gives the experimental results of the absorption of CO_2 into EDA solution (3 % mol) at three temperatures. R_C in the table is the loading ratio (moles of gas absorbed by one mole of amine).

Table 1. Experimental results for the absorption of CO_2 into EDA aqueous solutions (3%mol).

T/K	R_C, mol/mol	$(P_T)_{to}$, bar	P^e_i, bar	β, s^{-1}	Normal flux m/s
298.15	0.000	0.0687	0.0347	3.87E-02	6.30E-03
298.15	0.011	0.0673	0.0349	3.88E-02	6.32E-03
298.15	0.071	0.0672	0.0377	3.53E-02	5.77E-03
298.15	0.167	0.0649	0.0377	3.23E-02	5.30E-03
298.15	0.283	0.0677	0.0371	2.85E-02	4.69E-03
298.15	0.381	0.0693	0.0371	2.57E-02	4.25E-03
298.15	0.446	0.1294	0.0957	1.94E-02	3.21E-03
298.15	0.460	0.1219	0.0959	1.83E-02	3.04E-03
313.15	0.020	0.1038	0.0776	4.77E-02	1.05E-02
313.15	0.091	0.1039	0.0815	4.05E-02	8.97E-03
313.15	0.204	0.1054	0.0809	3.42E-02	7.61E-03
313.15	0.306	0.1088	0.0804	3.38E-02	7.55E-03
313.15	0.393	0.1110	0.0800	3.02E-02	6.77E-03
313.15	0.478	0.1677	0.1422	2.20E-02	4.95E-03
333.15	0.038	0.2237	0.1991	4.74E-02	1.44E-02
333.15	0.109	0.2311	0.2014	3.88E-02	1.18E-02
333.15	0.217	0.2309	0.2009	3.31E-02	1.02E-02
333.15	0.231	0.2269	0.2007	3.16E-02	9.68E-03
333.15	0.326	0.2306	0.2004	3.05E-02	9.38E-03
333.15	0.408	0.2366	0.2076	3.07E-02	9.48E-03
333.15	0.487	0.3026	0.2748	2.41E-02	7.49E-03

The rate of the chemical absorption of CO_2 (= i) is of the form [2]:

$$-\frac{dn_i}{A \cdot dt} = E \cdot k_L \cdot c_i^e \quad \left[\frac{mol}{m^2 s}\right] \tag{1}$$

The gas phase is assumed ideal ($P_i \cdot V_g = n_i \cdot R \cdot T$). CO_2 is completely consumed by the reaction in the liquid film, and the CO_2 concentration at the interface is replaced by the Henry law ($c_i^e = P_i^e / H_i$).

The partial pressure of CO_2 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 (1) under these assumptions, the equation (2) is derived:

$$\ln \frac{(P_T - P_v)_t}{(P_T - P_v)_{t_0}} = -\beta(t - t_0) \tag{2}$$

where:

$$\beta = \frac{E \cdot k_L \cdot A \cdot R \cdot T}{V_g \cdot H_i} \tag{3}$$

The enhancement factor E can be calculated for each experiment, using the equation (3).

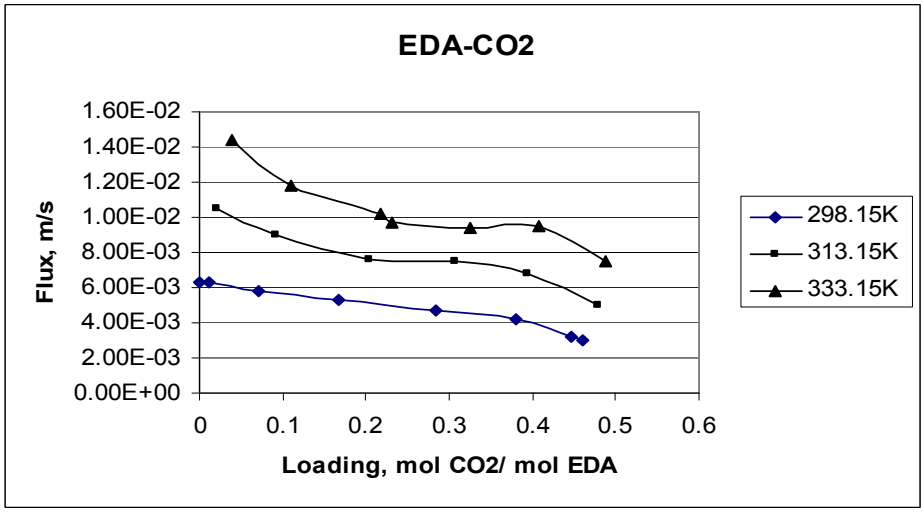

Figure 1. Experimental normal flux versus cell loading.

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)*:

$$k_{ov} = \frac{(k_L \cdot E)^2}{D_i} \tag{4}$$

E being calculated with the equation (3) using the experimental values of β from the tables 1. The results at 313.15 K are presented in the table 2.

Table 2.

The enhancement factor and the rate constant at 313.15 K for the EDA solution.
(k_L = 5x 10^{-4} m/s ; D_i = 1.6x 10^{-9} m^2/s ; Vg = 1.91875x 10^{-4} m^3 ; A= 15.34x 10^{-4} m^2)

R_C	β x 10^2, s^{-1}	E	k_{ov}, s^{-1}
0.020	4.77	11.51	20,700
0.091	4.05	9.77	14,900
0.204	3.42	8.25	10,600
0.306	3.38	8.15	10,400
0.393	3.02	7.29	8,300

Liao and *Li* [20} have obtained at the same temperature a k_{ov} of 195.4 s^{-1} for the absorption of CO_2 in a solution MEA- MDEA- H_2O with 0.1 mol/L MEA and 1.0 mol/L MDEA, and of 1703 s^{-1} by increasing the MEA concentration from 0.1 to 0.5 mol/L. Our values are superior of an order of magnitude for EDA solutions in other identical conditions. The results a promising taking into account that the system investigated by *Liao* and *Li* is considered the most effective from those studied till now.

CONCLUSIONS

Kinetics of CO_2 absorption into a new amine aqueous solution (EDA-H_2O have been investigated at three temperatures (25^{o}C, 40^o C, and 60^o C) on a laboratory Lewis type absorber with constant gas-liquid interface area. The enhancement factor and the pseudo-first order rate constant have been calculated on the basis of experimental data. The fast reaction regime was fulfilled at loadings less then 0.4 for all investigated systems. The rate constants were of the same order of magnitude as those obtained by *Liao* and *Li* [20] with some mixtures of MEA and MDEA. The investigation must be continued with EDA/TETA mixtures. Some properties of the solutions must be determined and correlated in order to improve the mathematical model.

EXPERIMENTAL SECTION

Experimental apparatus

The apparatus has been described in a previous paper [6]. It is a Lewis type absorber with a constant gas-liquid interface area of (15.34 ± 0.05) x 10^{-4} m^2. The total volume available for gas and liquid phases is (0.3504±0.0005) *10^{-4} m^3. 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 (4.25x 10^{-2} m diameter). The gas phase is agitated by 4x10^{-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 to 200) x10^3 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.

Experimental procedure

Water and EDA are degassed independently and aqueous solutions are prepared under a vacuum. The amounts of water and amine are determined by differential weightings to within ±10^{-2} g. This uncertainty on weightings leads to uncertainties in concentrations of less then ± 0.05%.

The flask containing the degassed EDA 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.

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_2 is introduced over a very short time (about 2 seconds) in the upper part of the cell, the resulting pressure P_0 is between (100-200) x10^3 Pa. Then stirring is started and the pressure drop resulting from absorption is recorded.

MATERIALS

The main materials involved have been: water, carbon dioxide, ethylenediamine (EDA). Ordinary twice-distilled water was used. Carbon dioxide, purchased from *Air Liquid*, of 99.995% purity, was used as received. EDA from *Aldrich* Chem.Co. (Milwaukee WI, USA), material of state purity 99%, used as received.

NOTATION

A, area of the gas- liquid interface, m^2;
C_i, molar concentration, kmol/m^3;
D_i, diffusion coefficient of i in solution, m^2/s;
E, enhancement factor of absorption by the chemical reaction;
H_i, Henry constant, bar. m^3/ kmol;

Ha, Hatta number;
k_L, liquid side mass transfer coefficient, m/s;
k_{ov}, pseudo- first order reaction rate constant, s^{-1} ;
n_i , number of moles of i;
P, total pressure, bar;
P_v, vapor pressure of the solution, bar;
R, gas constant (0.082 bar m^3/ kmol K);
T, temperature, K;
t, time, s;
V_g, gas phase volume, m^3;
β, the slope in the equation (3), s^{-1}.

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