CHEMICAL ENGINEERING TRANSACTIONS

VOL. 52, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Peng-Yen Liew, Jun-Yow Yong, Jiří Jaromír Klemeš, Hon Loong Lam

ISBN 978-88-95608-42-6; **ISSN** 2283-9216

DOI: 10.3303/CET1652100

A New CO_2 Absorption Data for Aqueous Solutions of N-methyldiethanolamine + Hexylamine

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The aim of this work is to develop a new chemical solvent for CO_2 capture and compare its performance with a reference based solvent MDEA (MethylDiEthanolAmine). A mixture of MDEA and Hexylamine activator (HA) is designed to improve the performance of the process and allow a substantial gain in terms of energy regeneration and reducing the cost of capture. New CO_2 absorption data is obtained using a Lewis cell gas-liquid interface at 298, 313 and 333 K with mass concentrations MDEA 37 wt%+ HA 3 wt%, MDEA 35 wt%+ HA 5 wt% and MDEA 33 wt%+ HA 7 wt%, to assess the CO_2 absorption flux and the absorption capacity of the new solvent. Our results show that for the mixture of MDEA 37 wt%+ HA 3 wt%, the kinetics reaction is fast with reduced activation energy compared to that of MDEA 40 wt%.

1. Introduction

Carbon dioxide is non-flammable and non-toxic gas, however, its concentration in the atmosphere has increased because of human activities (power generation, oil and gas ...). This increase has caused an imbalance in the ecosystem, so, it is necessary to minimize CO_2 emissions and especially those for the most polluting industries with fixed sources of emissions. There are different techniques for capturing CO_2 (Kanniche et al., 2010), the chemical absorption method is the most used one for CO_2 capture using a chemical solvent usually amine-based. There are two main features to be taken into account. The first is the kinetics of the CO_2 absorption reaction: primary amines like MEA (MonoEthanolAmine) are more reactive than secondary amines like DEA (DiEthanolAmine) which are more reactive than tertiary amines like MDEA (MethylDiEthanolamine). The CO_2 absorption rate will affect the design of the absorption column and thus the investment cost of the capture process. Secondly, the CO_2 solubility in the solvent: a reactive amine with CO_2 will have a very good solubility of CO_2 but will be less easily generable. Selecting more easily generable amine is tempting but this comes at the expense of the reaction rate and the solubility of CO_2. The size of the installation will be greater and thus more costly.

The chemical absorption methods are therefore too expensive to be used for CO_2 capture. This study aims to develop a new chemical solvent to reduce the amount of energy required for regeneration, while maintaining a sufficient absorption flow to limit the size of the columns. Experimental measurements characterizing the reaction kinetics as well as CO_2 solubility measurements were performed in a new solvent consisting of a mixture of MethylDiEthanolAmine (MDEA) activated by Hexylamine (HA) at temperatures of 298, 313 and 333 K and CO_2 partial pressures below 1 MPa.

Hexylamine is a primary amine, its solubility in water varies depending on the mass fraction and the temperature (Zhang et al., 2012), it has a very fast kinetics with CO_2, the more lipophilic nature makes Hexylamine very interesting for CO_2 capture (minimizing energy regeneration), this is why we have chosen to activate the MDEA by Hexylamine.

Please cite this article as: Mehassouel A., Derriche R., Bouallou C., 2016, A new co2 absorption data for aqueous solutions of n-methyldiethanolamine + hexylamine, Chemical Engineering Transactions, 52, 595-600 DOI:10.3303/CET1652100

2. Experimental Procedure

The apparatus used is a Lewis cell (Figure 1) consisting of a jacket Pyrex glass which allows the circulation of a fluid temperature regulator (Molina and Bouallou, 2013). The cell can withstand a maximum pressure of 3 bars and a temperature of 423 K. The inside diameter is 63 × 10^{-3} m. The effective cell volume is 369.7 × 10^{-6} m^3. The ends of the cell are fitted two metal flanges and are sealed by two seals. The upper flange has a DRUCK pressure (thermostatically controlled at 373 K to avoid condensation problems), that allows monitoring changes in pressure over time in the gas phase and makes the gas injection for kinetic measurements through the valve. The lower flange has a platinum probe to measure the temperature of the liquid phase at any time and a charging valve for the solution. The agitation of the gas phase is accomplished by a four-blade impeller 40 × 10^{-3} m in diameter. It is driven by a magnetic stirrer located inside the cell and set in motion by a magnetic stirrer located outside the cell. Magnetic stirring for the liquid phase is assured by a Rushton turbine with six blades 42.5 × 10^{-3} m in diameter. The stirring speed in the liquid phase is measured by a photo tachymeter reflection. Four Teflon baffles are located inside the cell to avoid the formation of vortexes and to hold in place a central ring to stabilize and then to fix the interfacial area. The acquisition allows the pressure to determine the absorption flows.

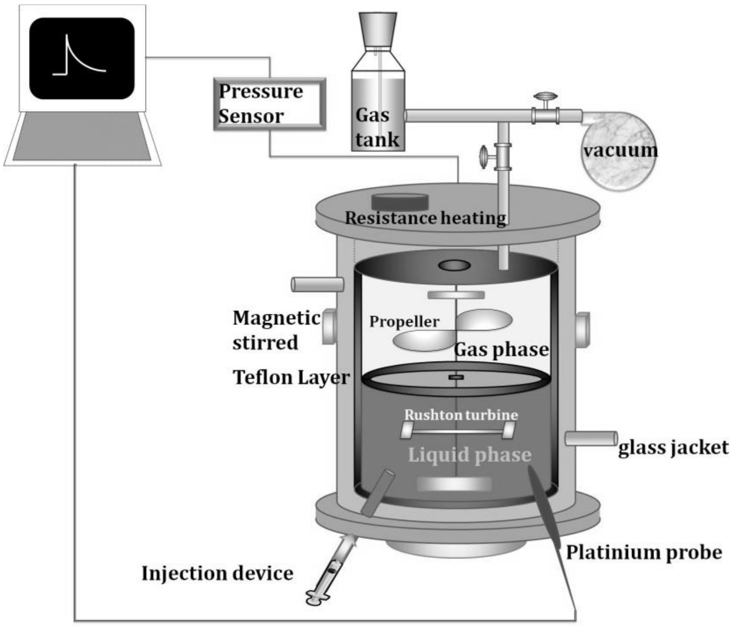

Figure1: Experimental apparatus

3. Result and discussion

The absorption measurements were made at three different temperatures 298, 313 and 333 K, for the three solvents (MDEA 37 wt% + HA 3 wt%), (MDEA 35 wt%+ HA 5 wt%) and (MDEA 33 wt% + HA 7 wt%).
On the basis of mass balance of the CO_2 in the gas phase of the reactor we can to determine the absorption flux.

$$\varphi_{CO_2}.A_i = \frac{d(n_{CO_2})}{dt} = -\frac{V_g}{RT}.\frac{d(P_{CO_2})}{dt} \tag{1}$$

A_i is the gas liquid interfacial area (m^2) and Vg the volume of the gaseous phase (m^3)
The influence of the absorption kinetics of the chemical reaction between the CO_2 and the reagent solutions is expressed by the enhancement factor E according to the following relationship

$$\frac{dP_{CO2}}{dt} = \frac{RT}{V_G}.k_L AEC_{CO2i} \tag{2}$$

k_L is the liquid side mass transfer coefficient; R is the ideal gas constant 8.3143 J.K^{-1}.mol^{-1}, T is the absolute temperature, V_G is the volume of gas.

The gas is considered ideal and the CO_2 concentration in the liquid is negligible to its concentration at the interface C_{CO2i} .
At the interface the vapor liquid equilibrium is reached, the partial pressure P_{CO2} is connected to its concentration in the gas phase according to Henry's law:

$$P_{CO2} = H.C_{CO2i} \tag{3}$$

Where H is the Henry's law constant, P_{CO2} is obtained by

$$P_{CO2} = P - P_{sol} \tag{4}$$

The concentration of CO_2 resulting from absorption does not change much the composition of the solution
So , k_l, *H*, and *E* remain constant with time, and integration of Eq(1) yields:

$$Ln\left(\frac{P - P_{sol}}{P_0 - P_{sol}}\right) = -bt \tag{5}$$

Where P is the total pressure in the apparatus and P_{sol} is the solvent pressure before introducing CO_2 and

$$b = \frac{RT}{V_G..H}.k_L.E.A \tag{6}$$

The k_L coefficient is calculated using the correlation obtained by (Amararene and Bouallou, 2004), from physical measurements of N_2O absorption into aqueous solutions of MDEA. And that involves the Reynolds number $Re = \frac{\rho\ N\ d_{Ag}^2}{\mu}$, Schmidt $Sc = \frac{\mu}{\rho\ D_i}$ and Sherwood $Sh = \frac{k_L\ d_{cell}}{D_i}$.

$$Sh = 0.352 \times Re^{0.618} \times Sc^{0.434} \tag{7}$$

This correlation is valid for a Reynolds number ranging from 215 to 5,666, a Schmidt number varying from 46 until 21,710 and a Sherwood number included in the range 378 – 985. µ = dynamic viscosity (Pa s) d_{cell} = inner diameter of the Lewis cell (m) D = diffusivity ($m^2\ s^{-1}$) d_{Ag} = diameter of the Rushton turbine (m) ρ= solvent density (kg m^{-3}).
The enhancement factor E is obtained from b by using Eq(6), the density and viscosity of the solutions are measured for different temperatures.
The diffusion coefficient and the Henry constant are obtained by applying the correlation of (Al-Ghawas et al.,1989), N = 100 rpm, is the stirring speed of the liquid phase, it is maintained constant during the experiment.
It is possible to determine the reaction system through the test of Hatta, noted Ha. This criterion is used to differentiate the mass transfer phenomena unique to a chemical reaction between the liquid within, the interface and the boundary layers. For an order of 1-1 reaction with rate constant k, the criterion of Hatta is calculated using Eq(8)

$$Ha = \frac{1}{k_L}\sqrt{kD_{co_2}C_{reactif\ ,0}} \tag{8}$$

Dimensionless number that allows us to locate the place of the reaction:
Ha <0.3: in the liquid phase
0.3 <Ha <3: both in the liquid phase and in the film diffusion
Ha> 3 in the film diffusion
In several literatures, kinetics of CO_2 absorption by an aqueous mixture of MDEA is second order, the reaction of CO_2 with MDEA is expressed by

$$r_{CO2-MDEA} = k_{CO_2-MDEA} C_{CO_2} C_{MDEA} \tag{9}$$

$k_{CO2-MDEA}$: is the second order constant kinetics reaction ($m^3.s^{-1}.mol^{-1}$)

Therefore, for the absorption of CO_2 into ($HA+MDEA+H_2O$), the overall CO_2 reaction k_{ov} (s^{-1}), is expressed as follows:

$$r_{ov} = r_{CO_2-HA} + r_{CO_2-MDEA} \tag{10}$$

$$r_{ov} = k_{CO_2-HA} C_{CO_2} C_{HA} + k_{CO_2-MDEA} C_{CO_2} C_{MDEA} \tag{11}$$

$$r_{ov} = k_{ov} C_{CO_2} \tag{12}$$

$$E = \frac{1}{k_L}(K_{OV} D_{CO2})^{1/2} \tag{13}$$

The instantaneous enhancement factor, noted E_i, is also determined according to Eq (14)

$$E_i = 1 + \frac{D_{reactif} * C_{reactif}}{D_{CO2} * C_{CO_2}} \tag{14}$$

The calculation of different parameters of CO_2 absorption by the different amine mixtures at different temperatures are summarized in Table1.

Table 1: Calculation of different absorption parameters

Solvant (wt %)	T (K)	$V_G.10^6$ (m^3)	$b.10^3$ s^{-1}	$D_{amine}10^9$ $m^2.s^{-1}$	$D_{CO2}10^9$ $m^2.s^{-1}$	H_{CO2} $Pa.m^3.mol^{-1}$	k_L10^{-5} $m.s^{-1}$	E	Ei
MDEA 40	298.15	196.24	0.4	0.148	0.50	3,663.72	0.772	9.80	19.81
MDEA 37	298.15	192.27	0.3	0.14	0.48	3,670.58	0.74	7.46	14.20
+HA 3	313.15	184.01	0 .6	0.24	0.80	4,625.24	1.12	11.38	26.20
	333.15	188.69	0.78	0.46	1.45	6,024.47	1.77	11.76	25.13
MDEA 35	298.15	208.41	9	0.14	0.5	3,677.41	0.76	236.92	25.11
+HA 5	313.15	207.55	9.5	0.25	0.82	4,629.39	1.14	200.32	32.31
	333.15	203.92	9.2	0.46	1.45	6,020.08	1.78	148.87	19.87
MDEA 33	298.15	185.48	5.9	0.14	0.48	3,578.97	0.74	138.31	22.18
+HA 7	313.15	197.85	5.42	0.24	0.8	4,633.51	1.25	99.56	17.52
	333.15	184.72	4.6	0.46	1.46	5,884.63	1.19	66.03	23.11

According to the results we note that Ha >3 for all examined mixtures, which means that the reaction takes place in the film diffusion, the condition of the reaction of pseudo first order (Ei/2 >Ha >3) is satisfied for the mixture MDEA 40 wt% and the mixture MDEA 37 wt% + HA 3 wt% at 298.15, 313.15 and 333.15 K.

The calculation of the activation energy for the reaction of CO_2 with aqueous mixture MDEA 37 wt% + HA 3 wt% is carried out by applying the Arrhenius law.

$$\ln(k) = \ln(A) - \frac{Ea}{RT} \tag{15}$$

The calculated activation energy (Ea) is 22. 25 $kJ.mol^{-1}$, On the other hand, the overall rate law is

$$k = 26.78*10^2 * \exp(\frac{-2678.5}{T}) \tag{16}$$

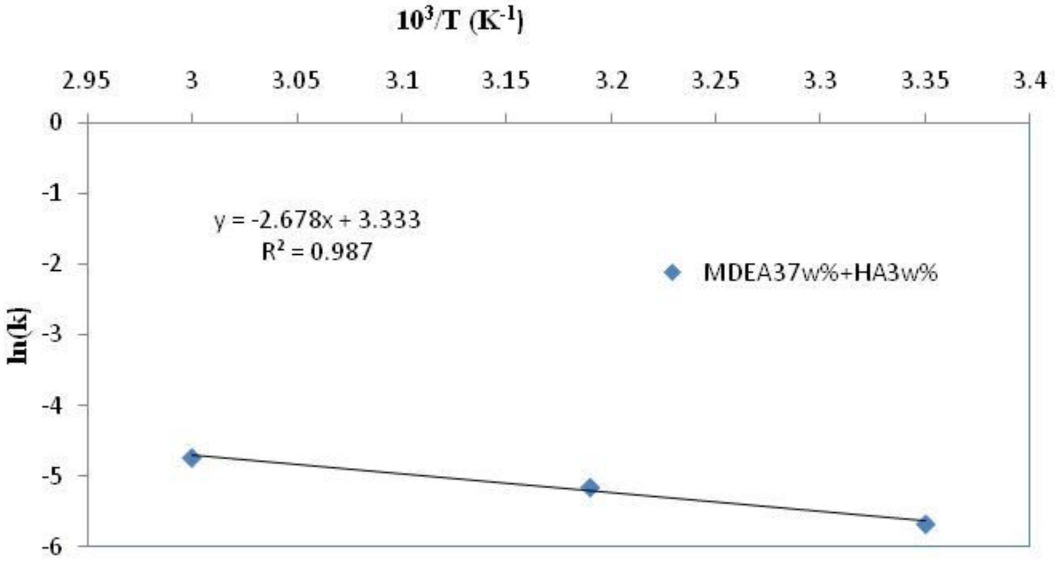

Figure 2: Arrhenius law for the CO2 absorption in aqueous (MDEA 37 wt% + HA 3 wt%) solution

The Comparison of the activation energy and the kinetic constant with the literature is given in the table 2.

Table 2: Comparison of the activation energy and the kinetic constant with the literature

References	Temperature K	Solvent	Concentration wt %	k ($m^3.mol^{-1}s^{-1}$) at 298.15K	Ea ($kJ.mol^{-1}$)
Amann and Bouallou , 2009	298 -333	MDEA+TETA	(40 + 3)	1.5	20.30
Our result	298	MDEA	40	3.38×10^{-3}	
Cadours and Bouallou, 1998	296 - 343	MDEA	(10 - 50)	5.05×10^{-3}	44.30
Pani et al.,1997	296 -343	MDEA	(0- 50)	4.55×10^{-3}	44.30
Gonzalez-Garza et al., 2009	278 - 303	MEA	30	1.53	37.73
Sema et al., 2013	298 - 318	DEAB	(14.5-29)	0.43	62.55
Our result	298 - 333	MDEA+HA	(37+3)	3.44×10^{-3}	22.25

We note that adding a small amount of Hexylamine activates the absorption reaction, activation energy decreases from 44.30 kJ. mol^{-1} for MDEA (10- 50) wt% to 22.25 kJ. mol^{-1} for the studied solvent, we note also that the activation energy of the solvent studied is the same order compared to solvent mixture of MDEA with TriethyleneTetraAmine (TETA) with mass concentration (40 + 3) wt %, latter is more reactive than our solvent, because TETA has four amino group in its structure , we can also confirm that the 4-diethylamino-2-butanol (DEAB), which is a tertiary amine is more reactive than our solvent and the MEA is the most reactive solvent.
The absorption rate of the mixture MDEA 37 wt% + HA 3 wt%, is better compared to MDEA 40 wt% and compared to other solvents, MDEA 35 wt% + HA 5 wt% and MDEA 33 wt% + HA 7 wt% at 298.15 K.

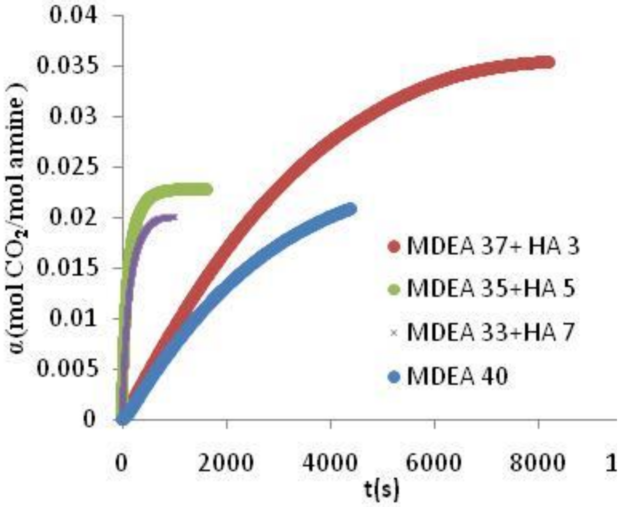

Figure 3: CO_2 loaded versus time for different solvents at 298.15 K

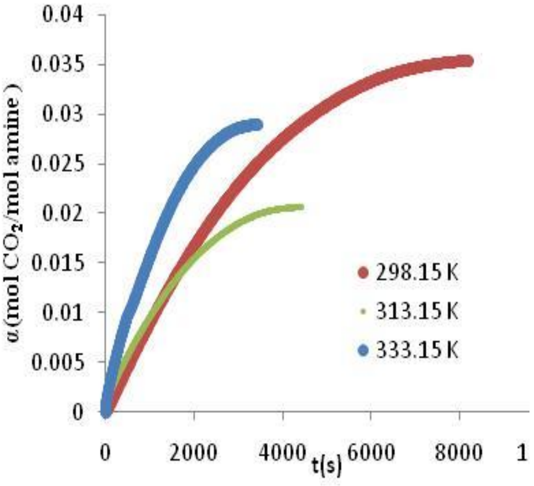

Figure 4: CO_2 loaded versus time for different temperatures and MDEA 37+HA 3 solvent

4. Conclusions

New CO_2 absorption data with different solvent are obtained. The kinetic results are in agreement with a pseudo first order regime of absorption according to film theory for the mixture of MDEA 37 wt% + HA 3 wt%. The activation energy decreased from 43.3 kJ.mol^{-1} for MDEA 40 w% to 22.25 kJ.mol^{-1} for the new formulated solvent leading to an energy saving during the regeneration step. The addition of small amount of HA leads to a high increase in the CO_2 absorption rates and improve the performance of the process allowing a substantial gain in terms of energy regeneration and reducing the cost of CO_2 capture.

References

Amararene F., Bouallou C., 2004, Kinetics of carbonyl sulfide (COS) absorption with aqueous solutions of diethanolamine and methyldiethanolamine, Ind. Eng. Chem. Res., 43(19), 6136-6141.

Al-Ghawas H.A., Hagewiesche D.P., Ruiz-Ibanez G., Sandall O.C., 1989, physicochemical properties important for carbon dioxide absorption in aqueous methyldiethanolamine, J. Chem. Eng. Data 34,385 - 391.

Amann J.M.G., Bouallou C., 2009, Kinetics of the Absorption of CO_2 in Aqueous Solution of N-Methyldiethanolamine +Triethylene Tetramine , Ind. Eng.Chem.Res., 48, 3761-3770.

Cadours, R., Bouallou C., 1998, Rigorous Simulation of Gas Absorption into Aqueous Solutions, Ind. Eng. Chem. Res., 37, 1063-1070.

Gonzalez-Garza, D., Rivera-Tinoco, R., Bouallou, C., 2009, Comparison of ammonia, monoethanolamine, diethanolamine and methyldiethanolamine solvents to reduce CO_2 greenhouse gas emissions, Chemical Engineering Transactions, 18, 279-284, DOI: 10.3303/CET0918044.

Kanniche M., Gros-Bonnivard R., Jaud Ph., Valle-Marcos J., Amann J.M., Bouallou C., 2010, Pre-Combustion, post-combustion and oxy-combustion in thermal power plant for CO_2 capture, Applied Thermal Engineering, 30, 53–62.

Pani F., Gaunand A., Cadours R., Bouallou C., Richon D., 1997, Kinetics of absorption of CO_2 in concentrated aqueous methyldiethanolamine solution in the range 296 K to 343 K, J. Chem. Eng. Data, 42, 353-359.

Sema T., Naami A., Liang Z., Idem R., Ibrahim H., Tontiwachwuthikul P., 2013, 1D absorption kinetics modeling of CO_2–DEAB–H_2O system , International Journal of Greenhouse Gas Control 12, 390–398.

Molina C.T., Bouallou C., 2013, Kinetics study and simulation of CO_2 absorption into mixed aqueous solutions of methyldiethanolamine and diethanolamine, Chemical Engineering Transactions, 35, 319-324, DOI: 10.3303/CET1335053.

Zhang J., Qiao Y., Agar D.W., 2012, Intensification of low temperature thermomorphic biphasic amine solvent regeneration for CO_2 capture, Chemical Engineering Research and Design 90, 743–749.