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Measurement and Calculation for CO_2 Solubility and Kinetic Rate in Aqueous Solutions of Two Tertiary Amines

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Abstract

Absorbing CO_2 with amine solutions is one of the most promising methods of CCS and has been widely applied. In order to improve efficiency and reduce costs, new solvents need to be selected. In this work, two amine solvents, N,N-dimethylethanolamine(DMEA) and Triethylene diamine (TEDA), have been characterized, with the use of gas-liquid reactor for CO_2 solubility and kinetic rate measurements. Solubility of CO_2 has been measured for amine concentrations of 1.0, 2.5 and 4.0 mol/L at temperatures of 313.2K, 343.2K, 373.2K, and 393.2K while partial pressure of CO_2 varies from 1 to 300kPa. The e-NRTL model has been used for these amine-water-CO_2 systems in order to calculate CO_2 solubility. Meanwhile the thermo-regulated constant interfacial area Lewis-type cell was also operated to obtain absorption kinetic data for CO_2 absorption in 0.5M and 1.0M amine solutions.

Keywords: Absorption, Carbon dioxide, solubility, kinetics.

1. Introduction

Rapid and significant reduction of emissions of greenhouse gases is recognized as necessary to limit the potential impacts of global warming. CO_2 is the main contributor to the greenhouse effect. Post-combustion capture and storage of the CO_2 emitted by fossil fuels power plants is a promising technology to achieve the reduction targets. The most mature technology to capture CO_2 is reversible chemical absorption of CO_2 in an aqueous amine solution. This technology can be readily deployed on existing power plants as retrofit and could be the best technology for future plants built.

The absorption of CO_2 in amine-based solvent is a standard purification step in the gas industry since the 1950s. These methods are also used to separate hydrogen from the CO_2 in the steam reforming or ammonia production units. The application of these processes to capture CO_2 from power plants flue gas

presents a number of challenges. Indeed, adaptation of these processes to the power raises four specific issues:

- the large quantity of CO_2 to be captured induces significant loss of efficiency on power plants, approximately 11%-pt. The energy consumption of the process must be reduced,
- the partial pressure of CO_2 in the flue gas is significantly lower. The solvent must have a high affinity with CO_2 and therefore, generally, a high heat of desorption,
- the amount of gas to be treated is much more important: one or two orders of magnitude. This involves designing very large equipment,
- the gas to be treated contains many impurities such as ash, oxygen, SO_X and NO_X. Solvents loss of activity and degradation in the presence of these impurities must be limited.

To meet these challenges, most studies focused on the discovery of new solvent emphasize the fact that the capture processes are based on proven technologies and little performance improvement could be expected on the process. Solvents improvements are, therefore, the only solution to tackle these issues. A more nuanced approach shows that even if the process can be improved, new solvents are needed to reduce the energy penalty below 6%-pt.

Many criteria must be considered when developing new solvents and selecting new molecules that constitute them. The liquid / gas equilibrium thermodynamic behavior is the most important parameter of the process: it determines the flow of solvent, through solvent cyclic capacity, and reboiler duty, through solvent heat capacity and CO_2 absorption heat of reaction. Absorption kinetic is also critical to keep the size of the absorber low and reduce the cost of the process. Research continues to propose and characterize novel amines for CO_2 capture such as EDA, AEEA or MAPA. However, most promising research efforts focus on the formulation of a solvent consisting of water, an amine with low heat of regeneration (i.e. the base) and an amine with high absorption kinetics (i.e. the activator or promoter) in order to find an optimal compromise between heat of regeneration and absorption kinetics. Bases are usually tertiary or hindered amines, the most common being MDEA and AMP. Activators are primary or secondary amines, the most common being MEA and PZ.

This work focuses on the characterization of two promising tertiary amines that could act as bases: N, N-dimethyl ethanolamine (DMEA) and Triethylene diamine (TEDA). CO_2 solubility has been measured at partial pressures from 1 to 300kPa, for solvent concentrations of 1.0, 2.5 and 4.0M, and temperatures of 313.2K, 343.2K, 373.2K and 393.2K. This thermodynamic data has been completed with absorption kinetic rate measurements for 0.5M and 1.0M amine concentrations and temperatures ranging from 308K to 343K. Electrolyte-NRTL interaction parameters and kinetics parameters have also been regressed in order to allow a future preliminary evaluation of these solvents performances for CO_2 capture through process modelling.

2. Measurement and calculation of CO_2 solubility

2.1. Experimental Section

2.1.1. Materials

Chemically pure DMEA and TEDA have been purchased from *Sinopharm Chemical Reagent Co., Ltd*, with a mass fraction purity > 98% and used without any further purification. Carbon dioxide and nitrogen gases had a mass fraction purity of 99.9%. Aqueous solutions were prepared with deionized water. DMEA is liquid at room temperature and has pungent odor. It is soluble in water and exothermic while dissolving. TEDA is solid at room temperature and is usually hydrated in these conditions. It is odourless

and has limited solubility at room temperature (460g/l at 298.15K, which is about 2.8M). Heating was applied in order to prepare TEDA solutions.

2.1.2. Apparatus

The solubility measurements have been carried out in a cell reactor shown in Figure 1. The reactor (model KCFDU2-2, Tianzhouhaitai Co.) consists in an electrically heated stainless steel cylindrical tank of volume 430 ± 2 cm^3 fitted with a magnetic stirrer in the upper part. A calibrated thermometer (PT100, Kunlunhaian Co.) has been inserted into the cell to measure the temperature with an uncertainty of $\pm$ 0.1 K. An oil bath was used to control the cell. A calibrated pressure transducer (model JYB-KDHAG, Kunlunhaian Co.) has been used to measure t the cylinder pressure and gas container pressure with an uncertainty of $\pm$ 0.5 kPa.
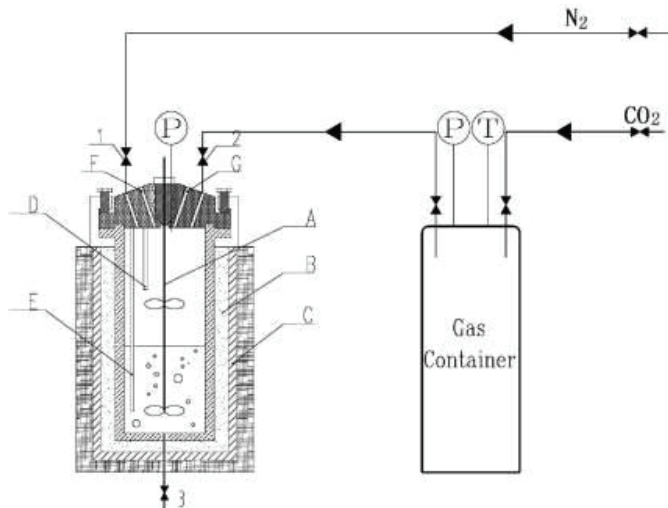

Fig. 1. Schematic diagram of the experimental equipment: 1, N$_2$ inlet valve; 2, CO$_2$ inlet valve; 3, liquid outlet valve; A, magnetic stirrer; B, oil bath; C, heating jacket; D, gas thermo detector; E, liquid thermo detector; F, gas outlet valve; G, liquid inlet valve.

2.1.3. Procedure

Initially, the cell has been completely emptied then purged with nitrogen gas in order to remove the remaining air, and a 100 cm^3 volume of the desired concentration amine solution has been injected. The temperature has been adjusted to the desired value. Absorption has been carried out during 10 h while stirring at 80 rpm then vapor-liquid equilibrium is assumed to be achieved.

The CO$_2$ quantity added to the reactor, n_{CO_2}, was calculated by the Peng-Robinson cubic equation of state.

At equilibrium, the equilibrium pressure P_1, has been measured. The CO$_2$ partial pressure in the vapor phase has been determined by assuming that the phase obeyed Dalton's law and is therefore expressed as the difference between the total equilibrium pressure and the CO$_2$-free, aqueous amine solution:

$$P_{CO_2} = P_1 - P_0 \tag{1}$$

where P_0 is the initial pressure. The amount of CO$_2$, $n_{CO_2}^g$, remaining in the gas phase has been calculated by the Peng-Robinson cubic equation of state[6] with the known pressure, P_{CO_2}, and the temperature and volume of the gas phase (calculated with the known volume of the liquid phase and the reactor).

The amount of CO_2 absorbed in the liquid phase has been calculated as follows:

$$n^l_{CO_2} = n_{CO_2} - n^g_{CO_2}$$
(2)

From the amount of dissolved CO_2 in the solution and the amount of amine in the cell, the CO_2 loading in the liquid phase is defined as

$$\alpha_{CO_2} = n^l_{CO_2} / n_{amine}$$
(3)

where n_{amine} is the mole number of amine in the liquid phase.

The uncertainty of α is determined from the uncertainty in temperature, pressure, and volume, which are respectively ± 0.1 %, ± 0.5% (when pressure differences are larger than 100kPa before and after the CO_2 is injected into the gas container), and ± 0.5 %, respectively, to give the estimated uncertainty in α of ± 2 %.

For CO_2 partial pressure, the estimated uncertainty is ± 0.5kPa. When the CO_2 partial pressure is lower than 10kPa, the relative uncertainty for CO_2 partial pressure might be higher than 10%.

Before the CO_2 injection into the reactor, only nitrogen and water vapor are present in the gas phase. The partial pressure of water corresponds to its saturated vapor pressure at the reactor temperature. From the saturated vapor pressure of water at the desired temperature, P^{sat}_{water} and the mole fraction of water in the liquid phase, x_{water}, the partial pressure of water in the gas phase is calculated:

$$P^g_{water} = x_{water} P^{sat}_{water}$$
(4)

The partial pressure of nitrogen can therefore be determined:

$$P^g_{N_2} = P_0 - P^g_{water}$$
(5)

The loading of CO_2 in the amine solution can then be calculated by the method mentioned above. CO2 solubility data is presented in Figures 2 and 3 for DMEA from 40°C to 120°C. CO2 solubility data is presented in Figure 4 for TEDA from 40°C to 120°C.

2.2. Thermodynamic Model

In order to represent the thermodynamic behavior of DMEA and TEDA, the e-NRTL model has been regressed from the experimental solubility data. The range of concentration and temperature covered by experiments are wide enough for a suitable regression of thermodynamic model parameters.

2.2.1. Mechanisms of CO_2 absorption

In tertiary amine systems, the following reactions occur in liquid phase.
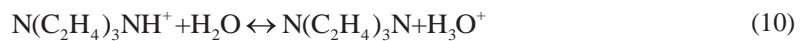Hydrolysis reaction of ternary amine [7]:

$$R_3NH^+ + H_2O \leftrightarrow R_3N + H_3O^+$$
(6)
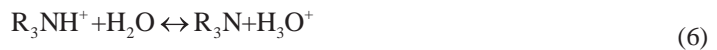
Dissociation of carbon dioxide and bicarbonate:

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$
(7)

$$HCO_3^- + H_2O \leftrightarrow CO_3^= + H_3O^+$$
(8)

Dissociation of water:

$$2H_2O \leftrightarrow H_3O^+ + OH^-$$
(9)

TEDA is a tertiary amine with two amino groups. TThe hydrolysis reaction is therefore divided into two steps:

$$N(C_2H_4)_3NH^+ + H_2O \leftrightarrow N(C_2H_4)_3N + H_3O^+$$
(10)

$$[N(C_2H_4)_3N]H_2^{2+} + H_2O \leftrightarrow N(C_2H_4)_3NH^+ + H_3O^+ \tag{11}$$
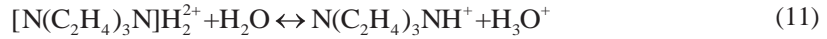
In this work, only the first reaction is used because of low loading less than 1.0.

2.2.2. Thermodynamic Model

Based on the measured CO_2 solubility data, the thermodynamic model has been regressed for both amines. The following equations are used to calculate vapor-liquid equilibrium.

For CO_2:

$$f_i = x_i \gamma_i^* H_i \tag{12}$$

in which, f is the fugacity in vapor phase, H_i is the infinite dilution Henry's constant of CO_2, x_i is the CO_2 mole fraction in liquid phase, and γ_i^* is the asymmetrical CO_2 activity coefficient.

And for H_2O and amine:

$$f_i = x_i \gamma_i P_i^0 \tag{13}$$

in which γ_i is the activity coefficient of water or amines, P_i^0 is the saturated pressure of water or amines.

The electrolyte-NRTL model [8]-[10] is used in order to calculate activity coefficients of all components. The excess Gibbs energy is calculated by summation of three terms: an electrolytic Pitzer-Debye-Hückel contribution to consider long-range ionic interactions, a local NRTL contribution for short-range interactions and a Born correction to consider the change of reference from infinite dilution in water to infinite dilution in a mixed solvent:

$$\frac{g_{ex}^*}{RT} = \frac{g_{ex,PDH}^*}{RT} + \frac{g_{ex,Born}^*}{RT} + \frac{g_{ex,NRTL}^*}{RT} \tag{14}$$

Activity coefficients for each compound are then calculated by derivation of the excess Gibbs energy with respect to the molar composition:

$$\ln \gamma_i = \left[\frac{\partial(n_t g_{ex}^* / RT)}{\partial n_i} \right]_{T,P,n_{j \neq i}} \tag{15}$$

The local NRTL term requires interaction parameters for each pair of compounds present in the liquid mixture. Such parameters must be regressed from experimental data. These binary parameters are temperature dependent and assumed to fit the following relation:

$$\tau = a + b/T \tag{16}$$

In this work, the Data Regression System (DRS) of Aspen Plus® software has been used to regress the a and b coefficients for each pair of molecules.

In addition, the equilibrium constant for reaction the hydrolysis reaction (6) is regressed simultaneously, assuming the following relation:

$$lnK = a + b/T \tag{17}$$

2.3. Results for CO₂ solubility

The regressed parameters obtained are respectively reported in Table 1 and Table 2 for DMEA and TEDA; the corresponding CO_2 solubility calculations are presented with experimental results in Figures 2 and 3 for DMEA and Figure 4 for TEDA.

Tab. 1. Electrolytic-NRTL and reaction constant parameters for DMEA-H_2O-CO_2 system

i	j	a	b
H_2O	$(DMEAH^+,HCO_3^-)$	-0.49156	1651.5
$(DMEAH^+HCO_3^-)$	H_2O	-1.8082	-145.44
DMEA	$(DMEAH^+,HCO_3^-)$	8.9025	5000.0
$(DMEAH^+,HCO_3^-)$	DMEA	28.347	181.81
CO_2	$(DMEAH^+,HCO_3^-)$	20.580	-2715.7
$(DMEAH^+,HCO_3^-)$	CO_2	-15.367	6773.2
H_2O	DMEA	13.879	-5201.2
DMEA	H_2O	-7.4375	2640.5
CO_2	DMEA	-19.365	4347.5
DMEA	CO_2	16.541	-2032.7
Equilibrium constant for reaction Eq.(6)		-4.1864	-6683.1

Tab. 2. Electrolytic-NRTL and reaction constant parameters for TEDA-H_2O-CO_2 system

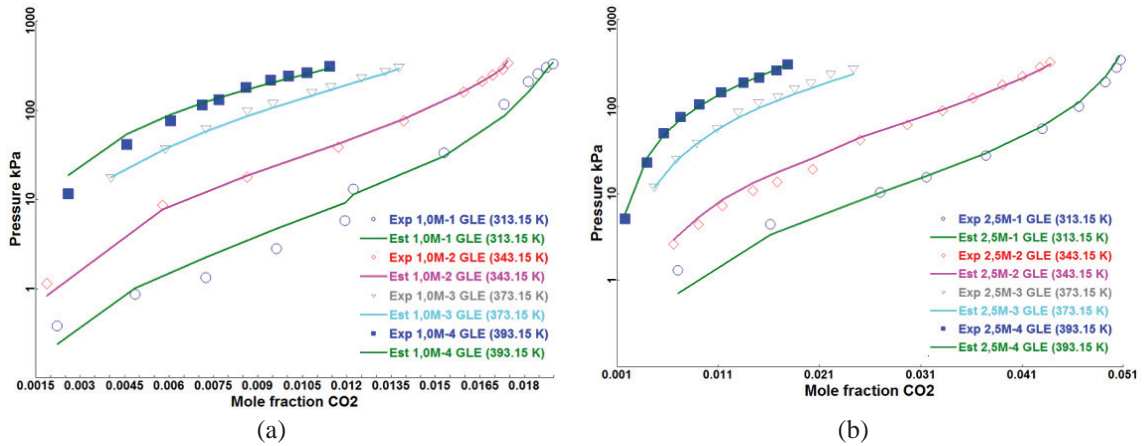| i	j	a	b
H_2O	$(TEDAH^+,HCO_3^-)$	-2.6934	3954.9
$(TEDAH^+,HCO_3^-)$	H_2O	-0.1922	-1475.3
TEDA	$(TEDAH^+,HCO_3^-)$	499.07	-6031.9
$(TEDAH^+,HCO_3^-)$	TEDA	474.58	-1023.7
CO_2	$(TEDAH^+,HCO_3^-)$	0.083682	-313.34
$(TEDAH^+,HCO_3^-)$	CO_2	-8.9477	4252.78
H_2O	TEDA	12.018	-3544.3
TEDA	H_2O	-11.853	3653.5
CO_2	DMEA	-18.128	3662.6
DMEA	CO_2	31.147	963.62
Equilibrium constant for reaction Eq.(6)		-19.967	-572.60

Fig. 2. Experimental and simulated CO_2 solubility in aqueous 1M (a) and 2.5M (b) DMEA solution from 40°C to 120°C
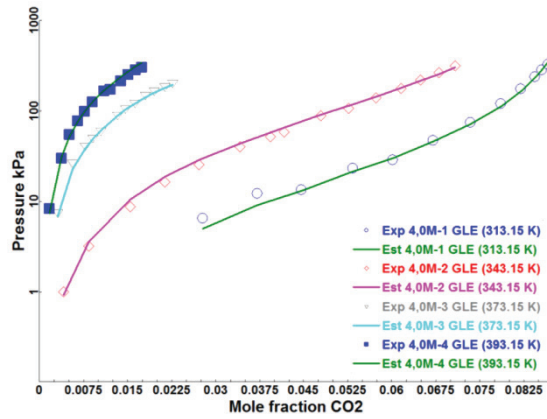
Fig. 3. Experimental and simulated CO_2 solubility in aqueous 4M DMEA solution from 40°C to 120°C
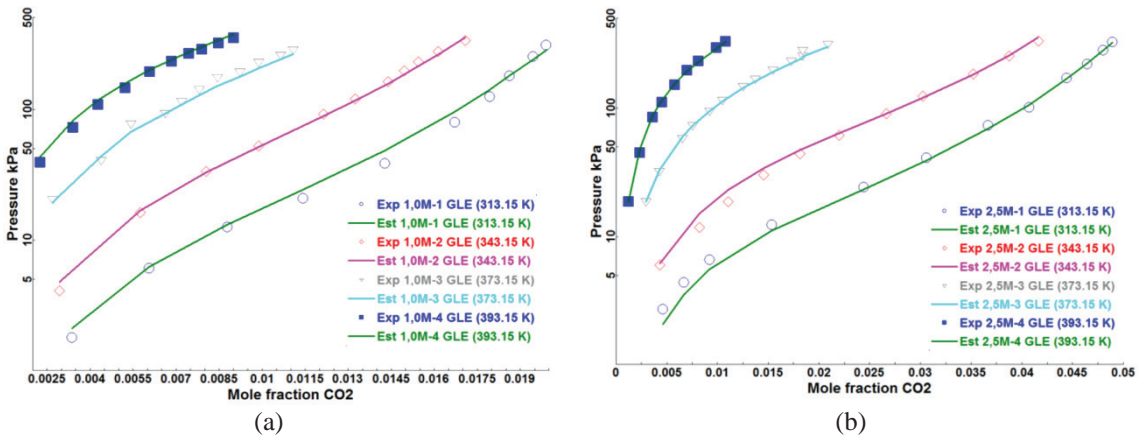

Fig. 4. Experimental and simulated CO_2 solubility in aqueous 1M (a) and 2.5M (b) TEDA solution from 40°C to 120°C

From the vapor-liquid equilibria curve, the rich loading ratio can be estimated. For coal-fired power plant, the flue gas enters the absorber with a CO_2 partial pressure around 15 kPa and a temperature around 40°C. Using the curve, the rich loading ratio could be estimated by reporting the 15 kPa isobar line on the 40°C isotherm. For DMEA, the rich loading ratio is estimated to 0.6 mol_{CO2}/mol_{DMEA} and for TEDA to 0.3 mol_{CO2}/mol_{TEDA}. In comparison with a classic tertiary amine, methyldiethanolamine (MDEA), whose rich loading is around 0.5 mol_{CO2}/mol_{MDEA}, DMEA seems to be a better solvent than TEDA since CO_2 solubility is higher. However, further calculations are mandatory in order to determine the optimal lean loading ratio, the cyclic capacity and heat of regeneration. To do so, process simulation with a simple absorption/desorption loop or the short-cut method proposed by Notz et al. [11] could be used.

3. Measurement and Calculation of reaction kinetics

3.1. Experimental section

The kinetics of CO_2 absorption in aqueous solutions of N,N-dimethylethanolamine (DMEA) and Triethylene diamine (TEDA) have been measured for temperatures between 308K and 343K. A thermo-regulated constant interfacial area Lewis-type cell as shown in Figure 1 has been operated by recording the pressure decrease during batch absorption.

3.2. Methodology

Experimental operations are summarized by the following steps: a. Clean and empty the equilibrium room completely at ambient pressure; b. Purge the cell with nitrogen; c. Inject the amine solution through liquid input valve; d. Adjust the temperature to the desired value; e. Inject CO_2 up to around 200kPa, and keep stirring at 100 rpm, and record pressures within about 1 hour.

3.3. Kinetic Calculation Procedure

The kinetic determination has been performed using the calculation procedure detailed by Pani et al. [12]. The procedure is based on the integration of gas CO_2 mass balance, leading to a linear relation with respect to time:

$$ln\frac{P - P_I}{P_0 - P_I} = -bt \tag{18}$$

where P is the total pressure, P_I the partial pressure of inert, P_0 the initial total pressure, t the time and the slope b is defined as:

$$b = \frac{RT}{V_G H_{CO_2}} k_L A E \tag{19}$$

with V_G the gas volume, H_{CO2} the Henry's constant, R the ideal gas constant, T the temperature, k_L the liquid mass transfer coefficient, A the interface area and E the enhancement factor.

The procedure consists in the regression of the slope b from experimental data at different temperature and concentrations. From the slope, an estimation of the enhancement factor is deducted for each temperature and concentration, knowing the different terms by measurements (T, V_G, A) and correlations (H_{CO2}, k_L). Assuming a first order reaction with respect to the amine, generally the case for tertiary amines, an expression of the kinetic constant is then obtained from the Arrhenius plot:

$$r = k_2 C_{CO_2} C_{Amine} \tag{20}$$

3.4. Kinetic Measurement Results

In order to validate the kinetic determination method, kinetic data for CO_2 absorption in aqueous MDEA solution has been measured and compared with literature data reported in Pani et al. [12] in Figure 5.
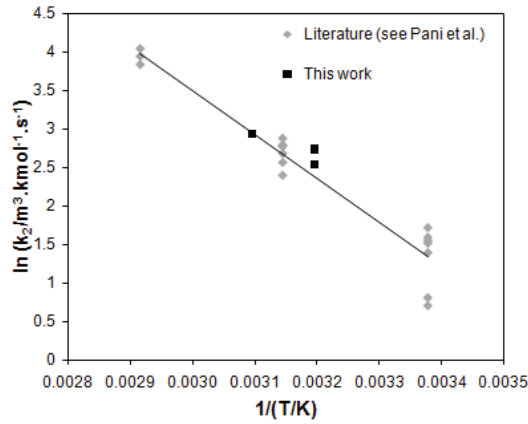
Fig. 5. Kinetic results of 1.0M MDEA compared with literature data

Then kinetic measurements for CO_2 absorption in aqueous DMEA solution of 1.0M and 0.5M have been carried out, as well as absorption in aqueous TEDA solution of 1.0M and 0.5M; the results are shown in Figure 6.

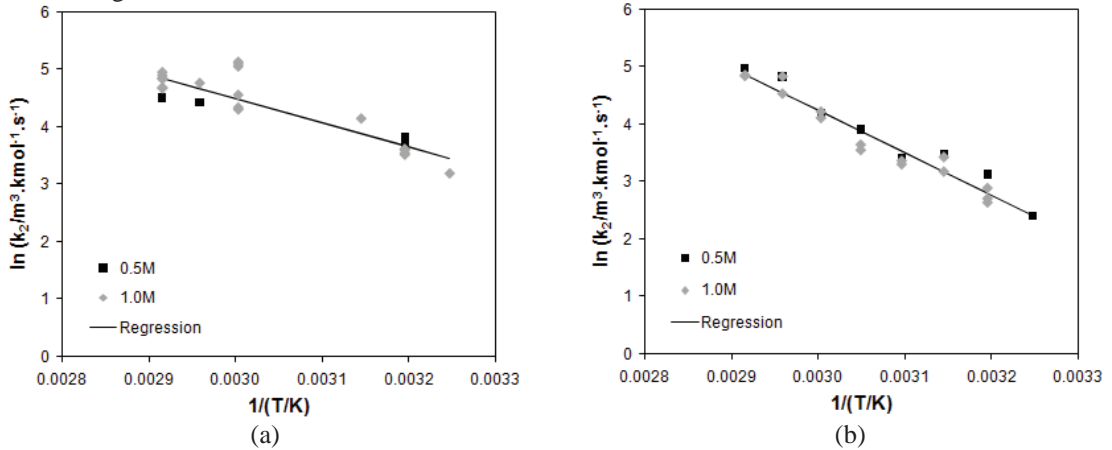(a)   (b)

Fig. 6. Kinetic experimental and regression results for (a) 1.0 and 0.5M DMEA; (b) 1.0 and 0.5M TEDA

The difference between 0.5 and 1.0M Arrhenius plots for DMEA suggest that the assumption of first order reaction with respect to DMEA may not be satisfactory but it gives a good estimation of the kinetic order of magnitude. The regressed kinetic constants of CO_2 with DMEA are correlated in the range of 313 to 343K and 0.5 to 1.0M DMEA with 5.8% as the relative root mean square average error:

$$\ln(k_2 \ /m^3 . kmol^{-1} . s^{-1}) = 17.20 - \frac{4231.1}{T/K} \qquad (21)$$

The regressed kinetic constants of CO_2 with TEDA are correlated in the range of 308 to 343K and 0.5 to 1.0M TEDA with 5.1% as the relative root mean square average error:

$$\ln(k_2 \ /m^3 . kmol^{-1} . s^{-1}) = 26.54 - \frac{7429.5}{T/K} \qquad (22)$$

These kinetic results show that reaction rates of CO_2 with DMEA and TEDA are very slow, as usual with tertiary alkanolamines. The reaction constant is in the order of magnitude of 15 $m^3.kmol^{-1}.s^{-1}$ for MDEA at 40°C and respectively of 40 and 17 $m^3.kmol^{-1}.s^{-1}$ for DMEA and TEDA. If these amines are used as the main composition in the solvent for CO_2 capture, a kinetic activator component should be used to accelerate their absorption rate for CO_2.

4. Conclusions

CO_2 solubility and reaction kinetics were measured for CO_2 absorption in aqueous solutions of DMEA and TEDA. The measurement methods using the Lewis-type stirred reactor are established and tested with available data. CO_2 solubility is calculated with the Electrolyte-NRTL model in Aspen with satisfactory results. The kinetic data are correlated with the corresponding Arrhenius Law. All these measurements and calculations can be used for further research work on mixed solvents and on process simulation for CO_2 capture.

Acknowledgements

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