Heat effect on mass transfer in N-methyldiethanolamine aqueous solutions
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Heat effect on mass transfer in N-methyldiethanolamine aqueous solutions

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Abstract

A bubble column was used to study the heat effect on CO_2 absorption in methydiethanolamine solutions and on volumetric mass transfer coefficient. It was found that the temperature varied until 4 ºC between the beginning and the end of the process. Our studies provide an empirical correlation type Boltzmann to estimate the temperature at different amine concentration (0-1M) and gas flow rate (10-25 L/h). An excellent agreement has been shown between predicted and experimental data (r^2>0.994).

Keywords: heat effect, gas-liquid mass transfer coefficient, absorption, CO_2, MDEA, bubble column.

1. Introduction

Many processes in the field of chemical engineering are based on a chemical reaction between a gas and some soluble or insoluble materials present in a liquid. The gas has to be dissolved in the liquid phase such that the chemical reaction can take place. This reaction can occur in isothermal or non-isothermal conditions.

Most past theories of gas absorption accompanied by chemical reaction have assumed isothermal conditions in order to facilitate the treatment of the experimental data. Shah [1] reviewed the literature concerning heat effects in systems involving gas-liquid reactions and concluded that in the majority of the systems involving chemical reactions temperature effects are not very important. There exist, however, a large number of industrially important gas-liquid reactions which are accompanied by large heat effects.

Generally, during the physical absorption of a highly soluble gas, or in the absorption with a chemical reaction, the temperature of the liquid phase, especially near the gas-liquid interface, can rise due to the heat given off by the solution or by the reaction [2,3]. In some systems these effects are minor, but in certain gas-liquid systems of industrial interest high thermal effects have been recorded, such as the removal of carbon dioxide with alkanolamine solutions. When CO_2 is absorbed at reduced partial pressures in aqueous solutions of alkanolamines, these effects have been considered negligible and have disregarded [4-7]. Nevertheless, if the absorption is carried out at high partial pressures of CO_2 the thermal effects appear to be considerable [8,9].

In spite of a significant amount of experimental and theoretical work on the absorption of CO_2 in MDEA solutions [10-12] there is still a lack of quantitative accurate data on the heat effect on the absorption process. The motivation for the present work was in part the small amount of work found in the literature on this particular subject. The present work aims to study the temperature change during the absorption of CO_2 in MDEA aqueous solutions and the heat effect on volumetric mass transfer coefficient.

2. Theory

The methyldiethanolamine (MDEA), CH_3-N-(CH_2-CH_2-OH)$_2$, is a tertiary amine in which the nitrogen is bonded to two ethanol group and a methyl group, but it does not react directly with the CO_2. There are no discrepancies in accepting that the reaction of carbon dioxide with MDEA is a first-order reaction with respect to the CO_2 and to the alkanolamine giving an overall second-order reaction.

Many studies have been performed on the kinetics of the reaction of carbon dioxide and MDEA, operating under different conditions and contactors [13-16], concluding the reaction regime between CO_2 and MDEA solutions is rapid. In this case, the rate of absorption of carbon dioxide per unit volume, R_A, is computed from the following expression:

$$R_A = C_A^* \sqrt{(k_L a)^2 + a^2 \cdot k \cdot C_{Bo} \cdot D_A} \tag{1}$$

where C_A^* is the solubility of CO_2, in kmol·m^{-3}, k_La is the volumetric mass transfer coefficient, expressed in s^{-1}, a is the interfacial area, in m^{-1}, k is the kinetic constant, C_{Bo} is the initial concentration of methyldiethanolamine, in kmol·m^{-3} and D_A is the diffusion coefficient of CO_2 in the aqueous amine solution, in m^2·s^{-1}.

This equation gives, after rearrangement:

$$k_L a = \sqrt{\left(\frac{R_A}{C_A^*}\right)^2 - a^2 \cdot k \cdot C_{Bo} \cdot D_A} \tag{2}$$

With this expression is possible to obtain the volumetric mass transfer coefficient, known the absorption rate, the kinetic constant, the diffusion coefficient, the solubility and the interfacial area. If the absorption process occurs in non-isothermal regime, a rise in temperature would affect the three main temperature dependent properties: the diffusion coefficient (D_A) and the reaction rate constant (k) would increase, while the solubility of the gas (C_A*) would decrease. Therefore, according to equation 5, the volumetric mass transfer coefficient will depend on the temperature.

The second-order rate coefficient for the reaction between carbon dioxide and methyldiethanolamine used was estimated using the Arrhenius relation proposed by Maceiras [17].

3. Experimental

3.1. Experimental set-up

The sketch of the experimental setup is shown in Fig. 1. A bubble column was used in this work for the absorption of CO_2 into aqueous monoethanolamine solutions. Absorption measurements were performed to room temperature, operating in batches with respect to the liquid phase. The bubble column is made of methacrylate, 1.03 m height, and has a square cross-section (side length 6 cm). For the injection and uniform distribution of the gas phase, a gas sparger, i.e., a porous plate of 4 mm in diameter is installed at the centre of the bottom plate. This plate has another orifice for liquid outlet. There are also three orifices at the top plate: liquid inlet, gas outlet and a thermometer.

3.2. Materials and methods

Aqueous methyldiethanolamine (MDEA) solutions of different concentrations were employed as liquid phase, while the gas phase was carbon dioxide with a different gas flow rate for each run. The following amine concentrations were employed: 0.05, 0.1, 0.3 and 1.0 M. Gas flow rates were varied between 10 and 25 L/h. In all experiments the volume of liquid has been constant and equal to 3.6 L.

Each experimental run was started by filling the column with the liquid phase up to 100 cm above the sparger. The carbon dioxide, saturated with water vapour at ambient temperature, was fed to the bottom of the bubble column. The gas flow, before entering the bubble column, was metered by a flow meter and controlled with a flow controller Brooks 0154. The gas flow in the outlet was measured with a soap meter. The gas absorption rate was calculated as the difference between the flow rates gas into and out of the bubble column.

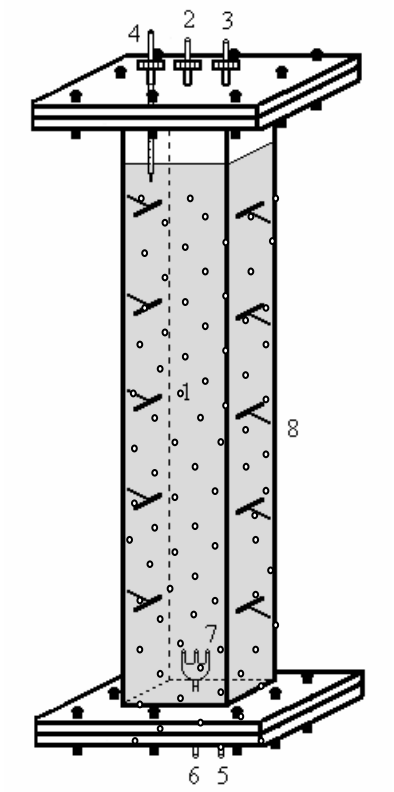

Figure 1. Schematic figure of the bubble column reactor: (1) Bubble column, (2) Liquid inlet, (3) Gas outlet, (4) Thermometer, (5) Liquid outlet, (6) Gas inlet, (7) Gas sparger, (8) Electrodes.

3.3. Physical Properties

The interpretation and correlation of the experimental mass-transfer data require knowledge of the physical properties of the liquid phases as well as the solubilities and diffusivities of the gas in these phases, which depends on temperature.

The densities, ρ, and viscosities, μ, were measured at 20, 25 and 30 ºC using a Anton Paar DSA 5000 densimeter, with a precision of ± 10^{-5} g·cm^{-3}, and a Shott-Gëratte AVS 350 automatic viscometer, with a precision of ± 0.01 s, respectively. The experimental values were correlated simultaneously with the amine concentration and with the temperature obtaining the following expressions:

$$\rho = 10.95 \cdot C_{B_o} + 908.33 \cdot \exp^{\frac{27.7}{T}} \quad (3)$$

$$\ln \mu = 0.49 \cdot C_{B_o} - 18.7 \cdot \exp^{\frac{-291.4}{T}} \quad (4)$$

where T is the temperature expressed in K.

The solubilities and diffusivities of the CO_2 were calculated using the correlation equations found in the literature [18-21].

4. Results and Discussion

The plot of Figs. 2 and 3 shows the dependence of the temperature on operating time for different amine concentration and gas flow rate. It can be observed that the great temperature variation occurs at high amine concentration (Fig. 2) and at low gas flow rate (Fig. 3). The results suggest that the absorption of CO_2 into methyldiethanolamine solutions occurs in non-isothermal conditions, since it was observed during the absorption process that the temperature in the bulk liquid phase could reach for the highest amine concentration an increment of 4 ºC.

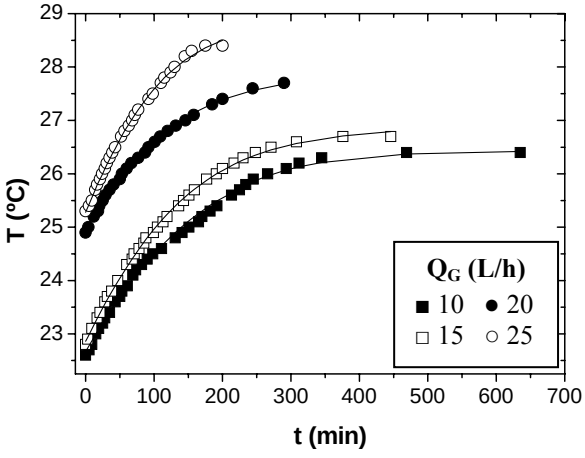

Figure 2. Temperature vs. time for a concentration of 1 M at different gas flow rate: (–) Boltzmann equation.

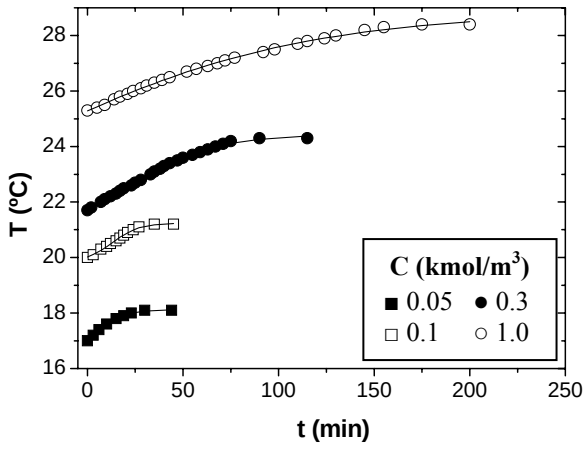

Figure 3. Temperature vs. time at different concentrations and 25 L/h: (–) Boltzmann equation.

The metyldiethanolamine, tertiary amine, is less reactive than primary or secondary amines and, therefore, the temperature increase is lower than monoethanolamine (MEA) or diethanolamine (DEA) [17].

An empirical equation type Boltzmann (Eq. 5) was proposed to adjust the experimental data. This equation reproduces the experimental values reasonably well (Fig. 2-3). The obtained adjustment parameters are reported in Table 1.

$$y = A_2 + \frac{A_1 - A_2}{1 + e^{\frac{x - x_0}{dx}}} \tag{5}$$

Table 1. Adjust parameters of Boltzman equation.

[MDEA] (kmol/m^3)	Q_e (L/h)	A_1 (ºC)	A_2 (ºC)	x_0 (s)	dx (s)	r^2	$\sigma^2 \cdot 10^4$
0.05	10	20.518	22.230	18.486	14.609	0.998	5.400
	15	19.056	21.248	3.559	13.296	0.999	1.330
	20	16.048	18.845	-5.312	10.140	0.999	1.250
	25	15.868	18.132	-0.040	8.444	0.999	3.700
0.10	10	17.737	21.937	-12.836	32.150	0.997	10.000
	15	20.983	23.347	8.651	14.267	0.999	4.000
	20	21.066	22.649	16.049	9.193	0.999	1.480
	25	19.795	21.251	12.695	7.425	0.996	8.200
0.30	10	18.875	24.161	-15.170	75.758	0.997	19.800
	15	20.372	23.415	40.205	34.969	0.999	7.100
	20	21.883	26.275	23.308	29.149	0.998	16.600
	25	20.738	24.436	22.126	22.534	0.998	13.100
1.00	10	19.409	26.436	8.718	98.145	0.994	85.800
	15	14.341	26.865	-78.148	103.620	0.999	16.100
	20	17.803	27.883	-87.354	97.127	0.998	13.600
	25	22.597	28.569	9.588	54.519	0.997	36.400

Now, the heat effect on mass transfer coefficient will be analyzed. Generally, two opposed effects occur when increasing the temperature of the liquid phase near the interphase. On the one hand, the temperature increase produces an increase of the kinetic constant and, therefore, of the speed of absorption; on the other hand, the gas solubility decreases.

Additionally, a change in the temperature affects the k_La value, since this coefficient is influenced by physical properties and kinetic constant which depend on temperature.

In Figs. 4 and 5, the volumetric mass transfer coefficient at constant temperature is compared with the volumetric mass transfer coefficient at variable temperature. The first one was calculated with the mean temperature, while the second one was obtained with the temperature experimental values measured during the absorption process.

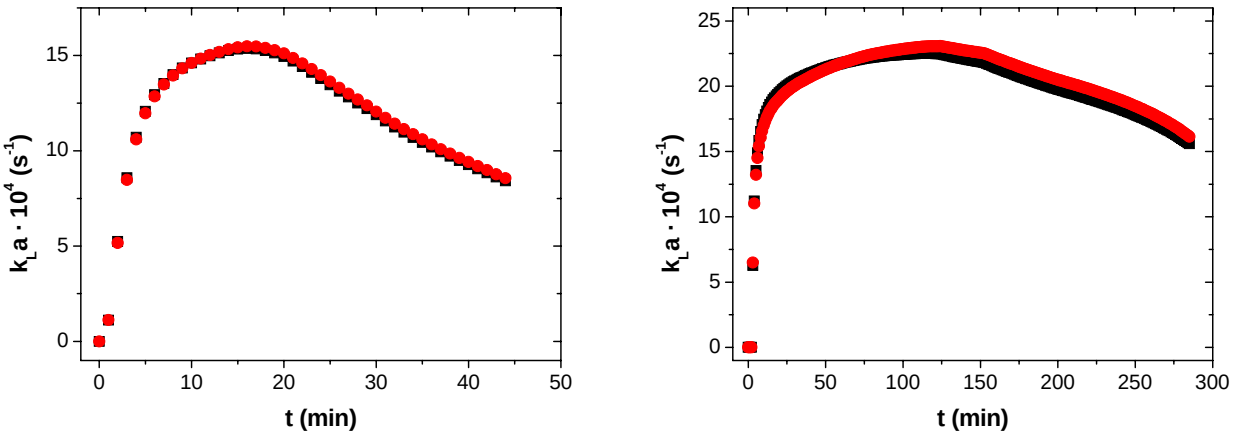

Figure 4. Temperature effect on volumetric mass transfer coefficient for a gas flow rate of 25 L/h and different MDEA concentrations: (a) 0.05 M and (b) 1.0 M; constant temperature (black), variable temperature (red).

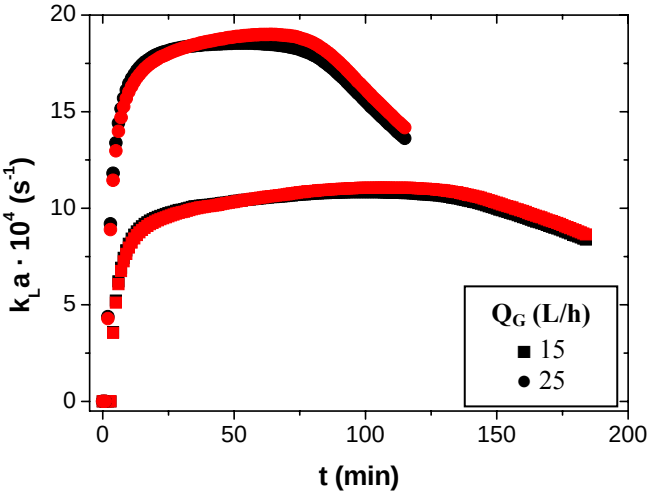

Figure 5. Temperature effect on volumetric mass transfer coefficient for a concentration of 0.3 M at different gas flow rate: constant temperature (black), variable temperature (red).

From the plot of Fig. 4, it could be concluded that the heat effect on mass transfer is higher when the amine concentration increases. It is due to at lower concentrations (0.05 and 0.1 M) the increment of temperature is between 1.0 and 1.6 ºC, while at higher concentrations (0.3 M and 1.0 M) reaches an increment between 3.0 and 4.0 ºC. Because of this, the greater differences in the volumetric mass transfer coefficient will be at the highest concentrations. Fig. 5 shows the change in the $k_L a$ with the gas flow rate, and it is observed that the temperature effect is higher when the gas flow decreases.

Also, it was expected that the volumetric mass transfer coefficient is lower at the beginning of the process because the temperature is lower than the mean temperature whereas the opposite effect occurs after that temperature is equal to mean temperature. In all the cases, the maximum deviation between the volumetric mass transfer coefficients is less than 4.5 %

for MDEA concentrations of 0.3 and 1 M, less than 3 % for 0.1 M and less that 2.0 % for 0.05 M. As a consequence of which if we suppose that the absorption process take place in isothermal regime, the error is higher to increase the amine concentration.

5. Conclusions

From the results obtained in this study, it is possible to conclude that the absorption of CO_2 in aqueous MDEA solutions takes place in a non-isothermal regime, since the temperature varies with time for a certain concentration of amine and gas flow-rate. An empirical equation was proposed to adjust reasonably well the data in the range of amine concentration and gas flow rate studied.

After, the effect of temperature on the volumetric mass transfer coefficient was analyzed. It was observed that the coefficient values increase with the temperature and with the amine concentration; since the greater values of temperature are reached at the highest amine concentration. On the assumption that the absorption of CO_2 into MDEA solutions is isothermal, errors of 4.5 % are made in the range of concentration and gas flow rate studied.

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