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Effect of temperature on carbon dioxide absorption in monoethanolamine solutions

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Abstract

The effect of temperature on volumetric mass transfer coefficient was studied during the absorption process of carbon dioxide in monoethanolamine aqueous solutions, using a square bubble column. Our studies provide an empirical correlation type Boltzmann to estimate the temperature operated, at different amine concentrations and gas flow rates. An excellent agreement has been shown between predicted and experimental data ($r^2 > 0.991$).

Keywords: Temperature effects; Mass transfer; Absorption; Carbon dioxide; Monoethanolamine; Bubble column

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1. Introduction

A lot of 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].

The heat transfer rate in gas–liquid flow of bubble columns is generally 100 times larger than in single phase flow [10], which favours highly exothermic and endothermic reactions. In literature, numerous studies have been devoted to understanding the heat transfer in bubble columns using simple systems, like air–water [10–13] in absence of chemical reaction. The present work, however, shows a different approach. Our aim is to examine the effect of the temperature on the absorption process and analyse the mass transfer coefficient behaviour when the temperature changes.

2. Theory

Monoethanolamine (MEA) solution is an important solvent in the CO_2 removal process because it reacts quickly with carbon dioxide for its primary amine characteristics. The reactions between CO_2 and MEA solution have been described in the literature by two mechanisms; namely the zwitterion mechanism introduced by Danckwerts [14] and the termolecular mechanism introduced by Crooks and Donnellan [15]. The zwitterion mechanism consists of the formation of a complex called a

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Nomenclature

a	interfacial area (m^{-1})
A_1	parameter defined in Eq. (16) (°C)
A_2	parameter defined in Eq. (16) (°C)
C_A^*	solubility of CO_2 (kmol/m^3)
C_{B_o}	initial concentration of monoethanolamine (kmol/m^3)
dx	parameter defined in Eq. (16) (s)
D	diffusion coefficient (m^2/s)
D_A	diffusion coefficient of CO_2 in the aqueous monoethanolamine solution (m^2/s)
D_B	diffusion coefficient of monoethanolamine in the aqueous solution (m^2/s)
He	Henry's law constant (atm m^3/kmol)
k_La	volumetric mass transfer coefficient (m/s)
M	molecular weight of water (kg/kmol)
p_A	partial pressure of the CO_2 (atm)
R_A	absorption rate per unit volume (kmol/(L s))
T	temperature (K)
V_A	molar volume of alkanolamine (m^3/kmol)
x_0	parameter defined in Eq. (16) (s)
z	stoichiometric coefficient

Greek letters

γ	constant defined in Eq. (13)
φ	"association" parameter for the solvent water
μ	viscosity (Pa s)
ρ	density (kg/m^3)

zwitterion, followed by the deprotonation of the zwitterion by a base [5,14,16–19].

Ten reactions may occur when CO_2 absorbs into and reacts with aqueous MEA. Although the zwiterion formation (Eq. (1)) and carbamate formation by deprotonation of the zwitterion (Eqs. (2)–(4)) are the most important

$$CO_2 + RNH_2 \rightarrow RNH_2{}^{+}COO^{-} \tag{1}$$

$$RNH_2{}^{+}COO^{-} + RNH_2 \rightarrow RNH_3{}^{+} + RNHCOO^{-} \tag{2}$$

$$RNH_2{}^{+}COO^{-} + H_2O \rightarrow H_3O^{+} + RNHCOO^{-} \tag{3}$$

$$RNH_2{}^{+}COO^{-} + OH^{-} \rightarrow H_2O + RNHCOO^{-} \tag{4}$$

The second reaction may take place in basic solution at a $pH \geq 11$; when the pH is less than 10, even in a carbonate solution, the formation of the zwiterion can be considered negligible [16]. The measurements indicate that, in our experiments, the pH values were less than 11 from the beginning of the absorption process and decreased gradually over the process. On the basis of the results obtained, the main reaction can be considered the formation of the zwiterion (Eq. (1)).

On the other hand, the reaction regime between CO_2 and MEA solutions is instantaneous [5,8]. In this case, the rate of absorption of carbon dioxide per unit volume is computed from the following expression:

$$R_A = k_La \times C_A^* \left(1 + \frac{D_B}{z \times D_A} \times \frac{C_{Bo}}{C_A^*}\right) \tag{5}$$

This expression allows to obtain the volumetric mass transfer coefficient, known the absorption rate, the diffusion coefficients and the solubility. If the absorption process occurs in non-isothermal regime, a rise in temperature would affect the two main temperature dependent properties: the diffusion coefficients (D_A and D_B) would increase, while the solubility of the gas (C_A^*) would decrease. Therefore, according to Eq. (5), the volumetric mass transfer coefficient will depend on the temperature.

3. Experimental

3.1. Experimental set-up

A bubble column experimental setup (Fig. 1) 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, 1, 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, 2, a gas sparger, i.e., a porous plate of 4 mm in diameter is installed at the centre of the bottom plate, 3. This plate has another two orifices for liquid outlet, 4, and for a thermometer, 5. There are also three orifices at the top plate: liquid inlet, 6, gas outlet, 7, and another thermometer, 8.

3.2. Materials and methods

Aqueous monoethanolamine (MEA) 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 experiment run was started by filling the column with appropriate liquid phase up to 100 cm above the sparger. The carbon dioxide, 9, saturated with water at ambient temperature, 10, was fed to the bottom of the bubble column. The gas flow, before entering the bubble column, was metered by a flow meter, 11, and controlled with a flow controller Brooks 0154, 12. The gas flow in the outlet was measured with a soap meter, 13. The pressure was measured with a digital manometer Testo 512, 14. The gas absorption rate was calculated as the difference between the flow rates gas into and out of the bubble column. The temperature was measured each 1 min until the end of the absorption process.

3.3. Physical properties

The interpretation and correlation of the experimental mass transfer data require knowledge of the physical properties of the

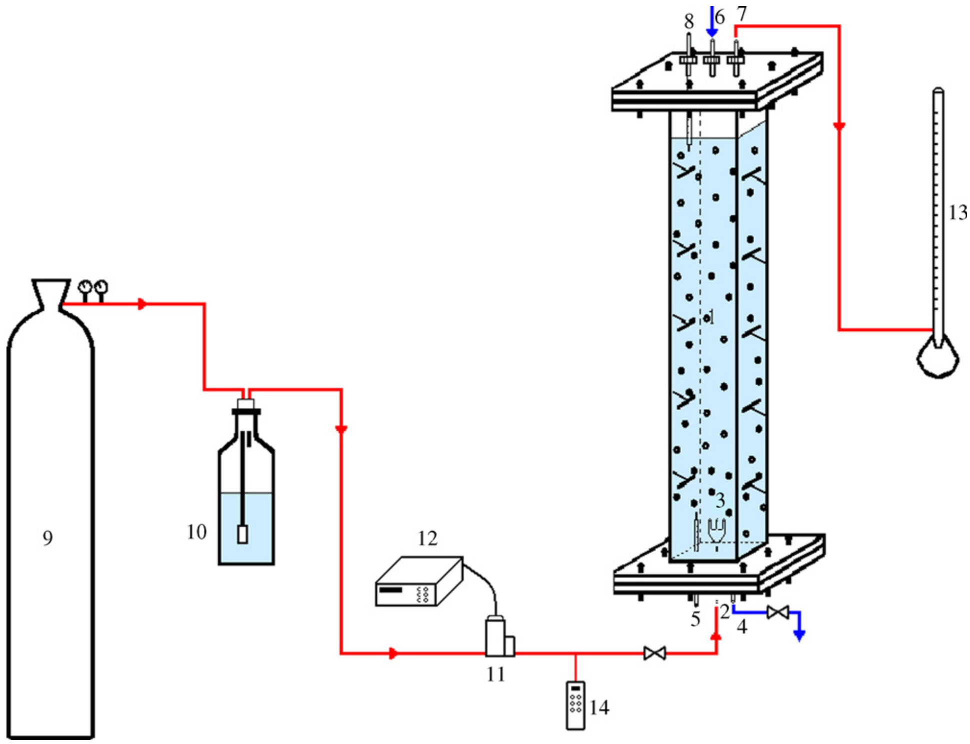

Fig. 1. Schematic figure of the bubble column reactor: (1) bubble column; (2) gas inlet; (3) gas sparger; (4) liquid outlet; (5) thermometer; (6) liquid inlet; (7) gas outlet; (8) thermometer; (9) pressurized CO_2 source; (10) humidifier; (11) flow meter; (12) flow controller; and (13) soap meter.

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 °C using a Anton Paar DSA 5000 densimeter, with a precision of $\pm 10^{-5}$ g/cm^3, and a Shott-Gëratte AVS 350 automatic viscometer, with a precision of ±0.01 s, respectively (Table 1). The experimental values were correlated simultaneously with the amine concentration and temperature obtaining the following expressions with $r^2 > 0.999$ in both cases:

$$\rho = 2.45C_{B_o} + 919.13\exp^{24.23/T} \tag{6}$$

$$\ln \mu = 0.16C_{B_o} - 19.1\exp^{-298.3/T} \tag{7}$$

The solubilities and diffusivities of the CO_2 were calculated using the correlation equations found in the literature. The solubility of CO_2 in the liquid phase was calculated using the Henry's law:

$$p_A = \mathrm{He} \times C_A^* \tag{8}$$

The Henry's law constant was determined with the equation proposed by Danckwerts [20] (Table 2):

$$\mathrm{He} = 10^{(5.3 - 0.035C_{B_o} - 1140/T)} \tag{9}$$

The diffusion coefficient of carbon dioxide into the aqueous monoethanolamine solutions was calculated using the correlation presented by Sada et al. [21]:

$$\frac{D_{CO_2}}{D_{CO_2,w}} = \frac{D_{N_2O}}{D_{N_2O,w}} \tag{10}$$

Table 1
Experimental values of density and viscosity in the range of temperature and concentration

[MEA] (kmol/m^3)	$\rho \times 10^{-3}$ (kg/m^3)			$\mu \times 10^3$ (Pa s)		
	20	25	30	20	25	30
0.0000	0.99820	0.99709	0.99567	1.0022	0.8904	0.7965
0.0149	0.99826	0.99713	0.99571	1.0101	0.8971	0.8033
0.0540	0.99831	0.99724	0.99576	1.0102	0.8973	0.8034
0.1000	0.99843	0.99732	0.99593	1.0178	0.9037	0.8090
0.3000	0.99894	0.99778	0.99632	1.0536	0.9343	0.8354
0.9800	1.00045	0.99932	0.99775	1.1883	1.0495	0.9345
3.0016	1.00612	1.00442	1.00253	1.6377	1.4332	1.2646

Table 2
Values of Henry constant obtained with Eq. (9)

T (°C)	[MEA] (kmol/m^3)	He (atm m^3/kmol)
20	0.05	25.7611
	0.1	25.8652
	0.3	26.2854
	1.0	27.8109
25	0.05	29.9396
	0.1	30.0605
	0.3	30.5490
	1.0	32.3219
30	0.05	34.6237
	0.1	34.7635
	0.3	35.3284
	1.0	37.3787

The diffusion coefficient of CO_2 into water was obtained with the equation proposed by Versteeg et al. [22]:

$$D_{CO_2,w} = 2.35 \times 10^{-6}\, e^{-2119/T} \tag{11}$$

On the other hand, the diffusion coefficient of N_2O into water was calculated with the following expression proposed by Versteeg and van Swaaij [23]:

$$D_{N_2O,w} = 5.07 \times 10^{-6}\, e^{-2371/T} \tag{12}$$

Whereas the diffusion coefficient of N_2O into aqueous monoethanolamine was obtained using the Store–Einstein equation [23]:

$$D_{N_2O}\mu^{\gamma} = D_{N_2O,w}\mu_w^{\gamma} \tag{13}$$

Sada et al. [21] evaluated the value of γ from the diffusion coefficient of N_2O in different alkanolamine solutions, obtaining a value of 0.51 for MEA solutions.

As regards the diffusion coefficient of MEA in water, its value was calculated with the equation proposed by Wilke and Chang [24] (Eq. (14)), obtaining the Eq. (15):

$$D_{A,B} = \frac{(117.3 \times 10^{-18})(\varphi M)^{0.5}T}{\mu V_A^{0.6}} \tag{14}$$

$$D_B = 3.586 \times 10^{-15}\frac{T}{\mu} \tag{15}$$

The diffusivities of CO_2 and MEA in aqueous monoethanolamine solutions obtained were compared with the available experimental diffusivity data [25–27] and both of them are in very good agreement (maximum deviation <1% and 10%, respectively).

4. Results and discussion

The results suggest that the absorption of carbon dioxide into MEA solutions occurs in non-isothermal conditions, since it was observed that the temperature in the bulk liquid phase, during the absorption process, could reach for the highest amine concentration an increment of 6.5 °C. Figs. 2 and 3 show the temperature measured at the top of the column for different concentrations and gas flow rates. It can be observed that the great temperature variation occurs at high amine concentration (Fig. 2). And also, the sharp of temperature profiles changes with the amine concentration (Fig. 3). The temperature data at the bottom of the column are not presented because they are practically constant.

The experimental data were adjusted reasonability well using the Boltzmann equation (Eq. (16)). The obtained adjustment parameters are reported in Table 3.

$$y = A_2 + \frac{A_1 - A_2}{1 + e^{(x-x_0)/dx}} \tag{16}$$

Therefore, it is possible to affirm that the absorption process takes place in a non-isothermal regime. The heat generation is owing to the processes are exothermic, and when increasing the temperature of the liquid phase near the interphase, two opposed effects occur. On the one hand, the increase of temperature also produces an increase of the kinetic constant and, therefore, of the speed of absorption; on the other hand, the solubility of the gas decreases with the increase of the temperature.

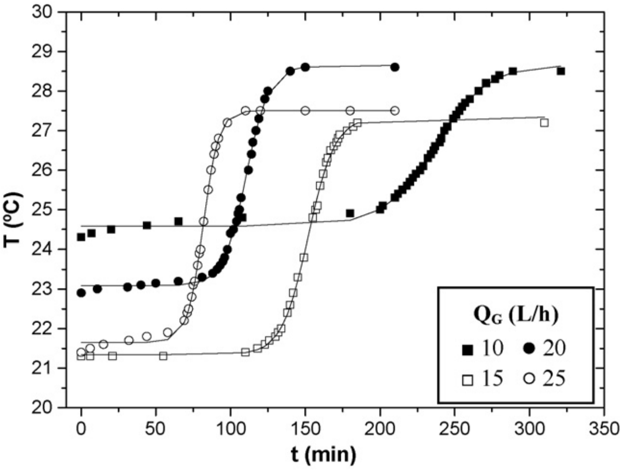

Fig. 2. Temperature vs. time for a concentration of 1 M at different gas flow rate: (–) Boltzmann equation.

Moreover, the temperature variation during the absorption process affects the volumetric mass transfer coefficient, since its value is influenced by physico-chemical properties which depend on temperature. The values of k_La were calculated with the Eq. (5) where the solubilities and diffusivities are necessary. These properties were calculated with Eqs. (9)–(15) at each time in two different ways: with constant temperature (mean temperature of the process) and with variable temperature (temperature experimental values measured during the process).

In Figs. 4 and 5, the volumetric mass transfer coefficient at constant temperature is compared with the volumetric mass transfer coefficient at variable temperature. It was observed that the temperature effect is higher when the amine concentration increases (Fig. 4). It is due to at lower concentrations (0.05 and 0.1 M) the increment of temperature is between 0.3 and 1.5 °C,

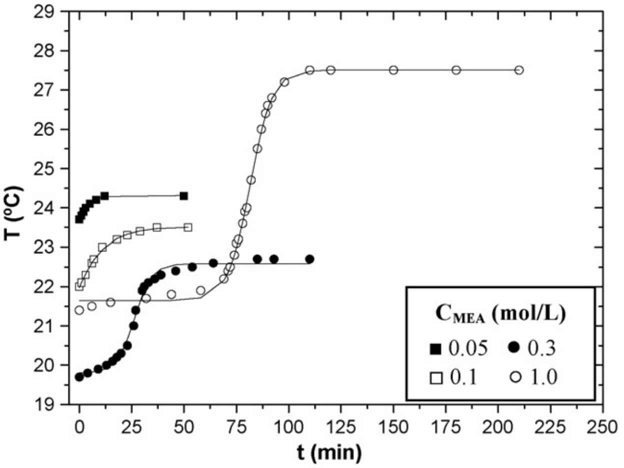

Fig. 3. Temperature vs. time at different concentrations and a gas flow rate of 25 L/h: (–) Boltzmann equation.

Table 3
Adjust parameters of Boltzman equation

[MEA] (kmol/m^3)	Q_e (L/h)	A_1 (°C)	A_2 (°C)	x_0 (s)	dx (s)	r^2	$\sigma^2 \times 10^5$
0.05	10	20.628	22.697	1.112	15.290	0.997	103.00
	15	23.799	24.100	8.994	1.446	1.000	0.00002
	20	23.889	24.401	4.327	3.423	0.999	3.48
	25	22.392	24.309	−2.748	3.620	0.997	31.00
0.10	10	20.831	24.374	−9.224	18.429	0.996	109.00
	15	22.542	23.603	15.180	8.773	0.999	2.72
	20	20.383	22.708	0.659	8.683	0.999	4.17
	25	9.706	23.515	−21.468	10.329	0.998	107.00
0.30	10	20.101	22.886	63.574	14.172	0.993	821.00
	15	21.631	24.218	46.821	5.502	0.999	122.00
	20	20.800	23.574	33.036	4.628	0.999	209.00
	25	19.807	22.586	26.378	4.247	0.991	1360.00
1.00	10	24.581	28.667	237.265	17.437	0.996	766.00
	15	21.341	27.304	151.867	8.821	0.999	612.00
	20	23.087	28.647	110.500	7.689	0.999	646.00
	25	21.646	27.513	81.514	5.353	0.999	884.00

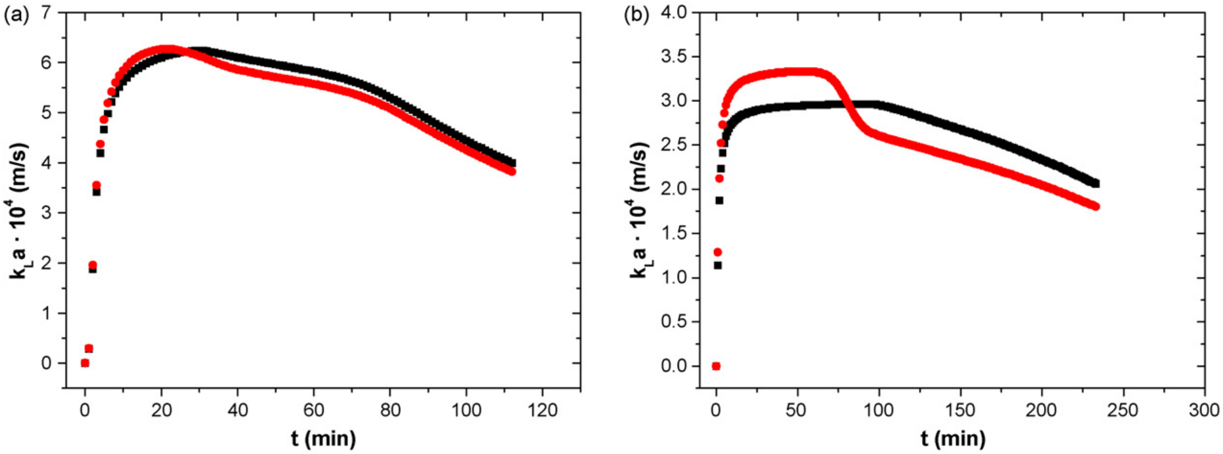

Fig. 4. Temperature effect on volumetric mass transfer coefficient for a gas flow rate of 25 L/h and different MEA concentrations: (a) 0.3 M; and (b) 1.0 M; constant temperature (black), variable temperature (red).

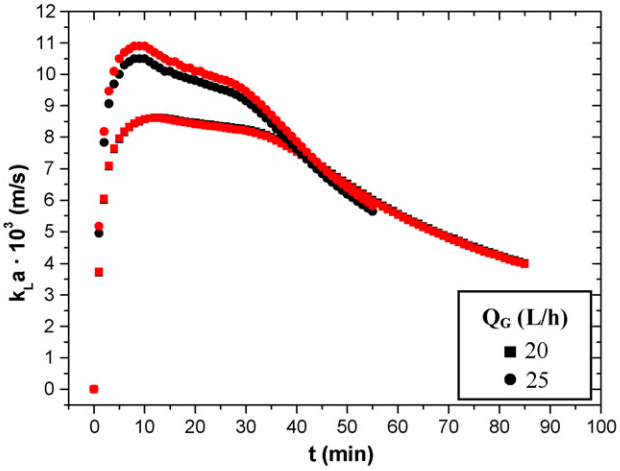

Fig. 5. Temperature effect on volumetric mass transfer coefficient for a concentration of 0.1 M at different gas flow rate: constant temperature (black), variable temperature (red).

while at the concentrations of 0.3 M it is of 3.1 °C and at 1.0 M reaches an increment of 6.1 °C. Therefore, the greater differences in the volumetric mass transfer coefficient will be at the highest concentrations. Also, the volumetric mass transfer coefficient is higher when the temperature is higher than the mean temperature while that it is lower when the temperature is lower that the mean.

5. Conclusions

The absorption process of CO_2 in aqueous solutions of MEA takes place in a non-isothermal instantaneous regime, since the temperature varies with the time for a certain concentration of amine and gas flow rate.

We have analyzed the effect of temperature on the volumetric mass transfer coefficient and this coefficient increases with the temperature and with the amine concentration; since the greater values of temperature are reached at the highest amine concentration.

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