Thermal Effects of CO_2 Absorption in Aqueous Solutions of 2-Amino-2-methyl-1-propanol

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DOI 10.1002/aic.10523
Published online July 7, 2005 in Wiley InterScience (www.interscience.wiley.com).

In this work, the process of carbon dioxide absorption is analyzed at high partial pressures, in aqueous solutions of 2-amino-2-methyl-1-propanol (AMP), with respect to the thermal effects involved. The experiments were carried out in a stirred tank reactor with a plane and known interfacial area. The variables considered were the AMP concentration and the temperature, within the ranges 0.1–3.0 kmol/m^3 and 288–313 K, respectively. From the results, we deduce that the absorption process of pure carbon dioxide into aqueous solutions of AMP takes place in the instantaneous nonisothermal regime at low concentrations, whereas at high concentrations the regime may be fast. In the experiments at low amine concentrations, we propose an equation, which not only relates the experimental results to the initial amine concentration but at the same time enables the evaluation of the rise in temperature in the gas–liquid interface. From the results at high concentrations, we determined a reaction order of one with respect to the amine and an expression for the kinetic constant valid throughout the entire range of temperatures and concentrations assayed: $k = 4.8 \times 10^{12} \exp(-8186.9/T)$. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 2769–2777, 2005
Keywords: mass transfer, absorption with reaction, carbon dioxide, alkanolamines, 2-amino-2-methyl-1-propanol, temperature effects, kinetic constant

Introduction

In carbon dioxide absorption, it is necessary to differentiate between the use of dissolved alkanolamines in the aqueous medium and organic solvents.[1,2] Currently, in industry, mostly aqueous alkanolamine solutions are used, some of the most common of which are monoethanolamine (MEA), diethanolamine (DEA), 2-di-propanolamine (DIPA), and methyl-diethanolamine (MDEA). There is extensive literature on these amines with respect to their absorption kinetics in an isothermal regime, fundamentally at low partial pressures of CO_2.

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It should be mentioned that in the physical absorption of a highly soluble gas, or during absorption with chemical reactions, the temperature of the liquid phase, especially near the gas–liquid interface, can increase as a result of the heat given off by the dissolution or by the reaction.[3-5] In some systems, these effects are mild with only minor temperature increases at the interface. Nevertheless, in certain gas–liquid systems of industrial interest, high thermal effects have been reported. The best-known systems include: ammonia–water, sulfur trioxide–dodecylbenzene, and hydrogen chloride–ethylene glycol. In addition, thermal effects have been noted in sulfonation reactions, chlorination, and oxidation of hydrocarbons.[4-6]

With respect to CO_2, at partial reduced pressures and in aqueous solutions of alkanolamines, these effects have been considered negligible by practically all research groups work-

ing with these systems. However, it is worth noting that, when absorption occurs under high partial pressures of CO_2, the thermal effects appear to have a certain impact. In fact, there are antecedents such as CO_2 absorption in aqueous solutions of MEA at partial pressures near atmospheric pressure in the work of Clarke.[7] This author, using a laminar-jet apparatus and MEA concentrations from 1.6 to 4.8 kmol/m^3 and working at low pressures (~10.7 kPa) and high CO_2 pressures (~99.9–101.3 kPa), indicated qualitatively that in the latter case the heat of the reaction influenced the absorption rate.

In the present work, we analyze the absorption process of carbon dioxide at high partial pressures in aqueous solutions of 2-amino-2-methyl-1-propanol (AMP) and the thermal effects related to this process.

Experimental

Apparatus

All the experiments were performed using a stirred gas–liquid contactor, operated in batches with respect to the liquid phase and having a smooth and known interfacial area.

Procedure

The use of pure CO_2 enabled the determination of the absorption rate by means of a bubble counter that gave the direct measurement of the CO_2 absorbed.

The variables considered were the AMP concentration within the range of 0.1–3.0 M and temperature within the interval 288–313 K. In all the experiments, the stirring speed in the reactor was 180 rpm, maintaining a smooth interfacial area of 35.26×10^{-4} m^2.

Physical and transport properties

Under these experimental conditions, we measured the viscosity of the amine solutions and their density. The viscosity of the solutions was measured by a capillary viscometer.

The calculation of the initial partial pressure of the CO_2 is given by

$$p_A = P - p_v \tag{1}$$

where P is the total pressure and p_v is the vapor pressure of the water.

To determine the solubility of CO_2 in the liquid phase, we used the relationship of Danckwerts[8]

$$\mathrm{He} = 10^{[5.3+0.035C_{B0}-(1140/T)]} \tag{2}$$

The diffusion coefficient of CO_2 in the aqueous solution was measured using the relationships of Sada et al.[9] and Versteeg and Swaaij[10]

$$\frac{D_{CO_2}}{D_{CO_2,w}} = \frac{D_{N_2O}}{D_{N_2O,w}} \tag{3}$$

where

$$D_{CO_2,w} = 2.35 \times 10^{-6}\exp(-2119/T) \tag{4}$$

$$D_{N_2O,w} = 5.07 \times 10^{-6}\exp(-2371/T) \tag{5}$$

$$D_{N_2O}\mu_B^{\gamma} = D_{N_2O,w}\mu_w^{\gamma} \tag{6}$$

The diffusion coefficients of AMP in aqueous solution were calculated by means of the Wilke–Chang relationship[11]

$$D_{AMP} = 2.70 \times 10^{-15}\frac{T}{\mu_B} \tag{7}$$

Analytical methods

The initial amine concentration was determined by titration with HCl solutions using methyl orange as the indicator. The CO_2 concentration in liquid was determined by standard titration methods. Excess NaOH and the excess $BaCl_2$ solutions were added to the liquid sample and the excess NaOH was titrated with an HCl solution using thymol blue as the indicator.

Results and Discussion

The flow densities (N_A) were calculated assuming that the gas follows ideal behavior, using the following expression

$$N_A = \frac{n'}{A} = \frac{PQ'}{RTA} \tag{8}$$

The value of the volumetric flow coincided with the value of the slope of the straight lines on representing the volume of the CO_2 absorbed against time (t) for each experiment. The determinations were made using the linear regression method of the experimental results.

Initially, to determine the individual transfer coefficients of the liquid phase (k_L), we performed experiments for the physical absorption of CO_2 in water, using the same contactor as in the chemical-absorption experiments. The results obtained during the process of the physical absorption enabled us to calculate the value of k_L for the temperature range used.[12]

In the absorption experiments with pure CO_2 in aqueous AMP solutions, we analyzed the influence of the initial alkanolamine concentration and the operating temperature.

Absorption in AMP solutions

The primary alkanolamine 2-amino-2-methyl-1-propanol [CH_2OH–$C(CH_3)(NH_2)$–CH_3] presents a certain steric impediment with respect to the amino group found in the intermediate position, and therefore, in principle, the reactions of these functional groups (–NH_2 and –OH) with CO_2 have a characteristic reaction ability similar to that reported by different authors for monoethanolamine[13,14] (Eqs. 9 and 10), although such reactions might be expected to take place with lower intensity because the access of the carbon dioxide to these functional groups is somewhat obstructed

$$\text{–}NH_2 + CO_2 \rightarrow \underset{\text{carbamic acid derivative}}{\text{–}NHCOO^-H^+} \tag{9}$$

$$\text{–}OH + CO_2 \rightarrow \underset{\text{carbonic acid derivative}}{\text{–}OCOO^-H^+} \tag{10}$$

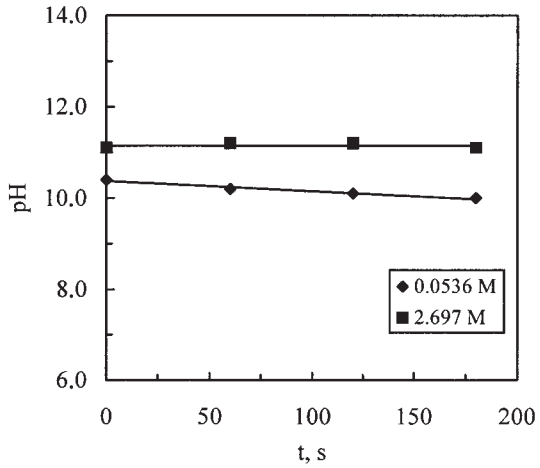

Figure 1. Variation in pH of the AMP solution with time, over the curse of the absorption process at 293 K at corresponding concentrations.

This latter reaction may take place in a basic solution at a pH $\geq$ 11, when the pH is $<$10. Even in a carbonate solution, the formation of the carbonic acid derivative can be considered negligible.[13] The pH measurements taken during the absorption process in all the experiments of AMP solutions and for all temperatures indicate that the pH is generally $<$11, except in the case of high AMP concentrations, where the pH values are $>$11 (Figure 1). Therefore, it might be expected that for carbonation relationship (η, quotient between the moles of carbon dioxide and of amine in solution) of $<$0.5, the reaction of carbamate formation would be similar to the absorption process of other primary alkanolamines such as MEA or MIPA.

According to the information available in the literature, carbamate formation takes place, although its stability is very low[15-17] because of the steric impediment presented by AMP in its tertiary carbon atom, which effect characterizes the absorption process with this alkanolamine.

In this sense, several research groups[15,16,18] hold that the reaction between the CO_2 and the –OH of the AMP group is negligible, given that under the reaction conditions the pH of the solution never exceeds 12, and the only reaction of importance between the carbon dioxide and AMP would be the formation of the bicarbonate ion. In this case, the stoichiometry between CO_2 and AMP is 1:1, as indicated by the reaction

$$CO_2 + RNH_2 + H_2O \leftrightarrows HCO_3^- + RNH_3^+ \qquad (11)$$

although the carbamate formation is a rather unstable intermediate in the mechanism proposed. Before the proof of Eq. 11, these two research groups maintain that the reaction of CO_2 with the amino group of AMP can take place through three reactions:

(1) Formation of carbamate, with a mechanism analogous to that described by Hikita et al.[19] (Eqs. 12 and 13)

$$CO_2 + RNH_2 \rightarrow RNHCOO^- + H^+ \qquad \text{fast} \qquad (12)$$

$$RNH_2 + H^+ \rightarrow R\text{–}NH_3^+ \qquad \text{virtually fast} \qquad (13)$$

(2) Formation of bicarbonate (Eq. 11).

(3) Reversal of carbamate to bicarbonate or formation of the carbonate ion.

Given that the formation of carbamate is inhibited in the CO_2–AMP reaction by steric impediment, and the basic character of AMP is sufficiently small to guarantee that the ion CO_3^{2-} is always displaced toward the formation of the ion HCO_3^-, the main reaction should be Eq. 11. On this basis, the reaction mechanism proposed takes place in two stages

$$CO_2 + RNH_2 \leftrightarrows RNH_2^+COO^- \qquad (14)$$

$$RNH_2^+COO^- + H_2O \leftrightarrows RNH_3^+ + HCO_3^- \qquad (15)$$

where the first step, the formation of zwitterion, constitutes the controlling stage of the process and with it the velocity would be given by the equation

$$-r = k_2[CO_2][RNH_2] \qquad (16)$$

As an example, Figure 2 offers graphic representation of the CO_2 absorbed per unit of surface against time for the experiments conducted at 313 K. A constant operating temperature and partial gas pressure were maintained, varying the initial AMP concentration between 0.056 and 2.83 M.

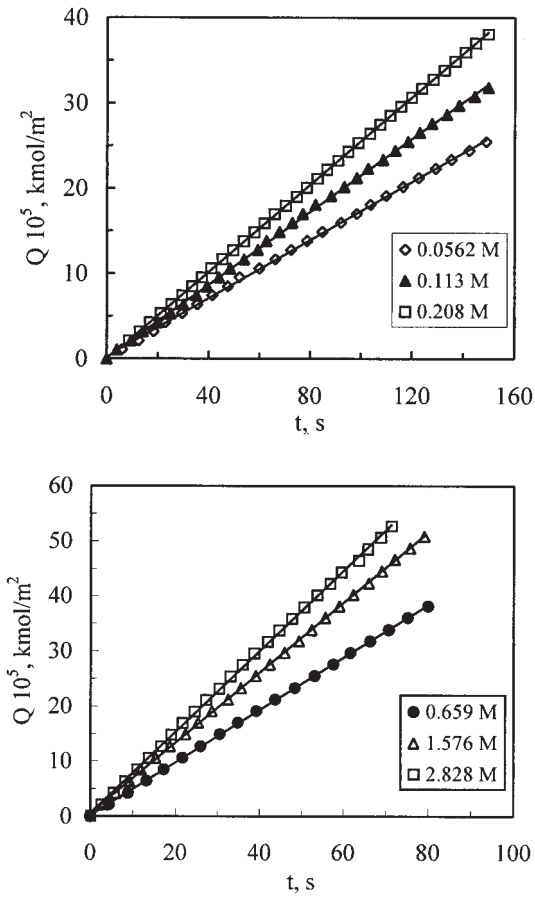

Figure 2. CO_2 absorbed per unit of surface and time in the experiments with AMP at 313 K.

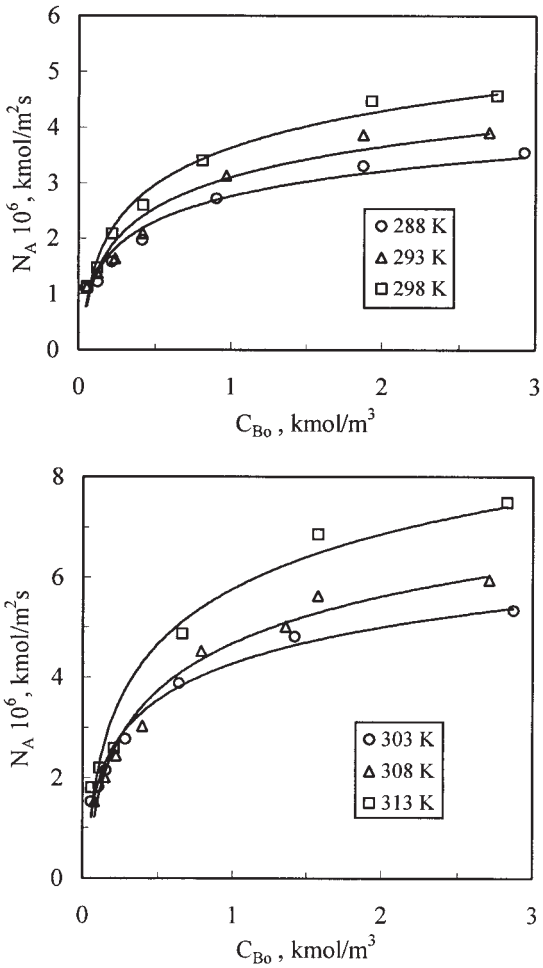

Figure 3. Variation in N_A with the AMP concentration at the temperatures indicated.

Reaction regime

For the determination of the reaction regime, the criteria formulated by Astarita et al.[13] for CO_2 absorption by alkanolamine solutions cannot be used because they require previous knowledge of the kinetic constant of the reaction, and in the absorption process with AMP the literature shows disagreement on the correct value of k. In this sense, Sharma[20] offered a value of 1048 m^3 $kmol^{-1}$ s^{-1} for the constant at 298 K, whereas Bosch et al.[21] determined a value of 400 m^3 $kmol^{-1}$ s^{-1}; meanwhile, Yih and Shen[16] calculated a value of $k = 1270$ m^3 $kmol^{-1}$ s^{-1} for a process carried out at 313 K, and for this same temperature Chakraborty et al.[18] accepted a value of 100 m^3 $kmol^{-1}$ s^{-1}. From these differences, it can be said that the value of the kinetic constant for these processes is not fully established.

In addition, only spotty values for the kinetic constant are available at the two temperatures mentioned. Despite these discrepancies in the kinetic-constant values, the four research groups agree on the overall reaction order of two: one for carbon dioxide and one for AMP.

For the determination of the reaction regime, representations were made of values of flux density, N_A vs. C_{B0}, as shown in Figure 3. No linear relationship existed between the flux density and the amine concentration. It can be seen that there is no linear relationship between the flux density and the amine concentration, at least for values of $C_{B0} > 0.25$ kmol/m^3. This fact could indicate a noninstantaneous reaction regime for all the concentration intervals.

Figure 3 shows a certain linearity between the values of N_A and C_{B0} at low AMP concentrations, which could indicate that for these low concentrations the reaction regime is instantaneous. In addition, it could happen that at high AMP concentrations a fast reaction regime could take place. To test this idea, we would need to accept that the order of the reaction with respect to the carbon dioxide is one, a matter that has been studied and confirmed by different authors and for which there were no discrepancies.[16,18]

If we assume as an initial hypothesis the rapid-reaction regime without a temperature increase with an order m with respect to the CO_2 is one and n with respect to AMP, the molar flux is given by the following equation[22]

$$N_A = \sqrt{\frac{2}{m+1} D_A k_{m,n} C_{A0}^{m+1} C_{B0}^{n}} \tag{17}$$

Assuming the order of reaction with respect to CO_2 in the absorption with aqueous solutions of AMP, then Eq. 17 is reduced to

$$N_A = C_{A0} \sqrt{D_A k_{1,n} C_{B0}^{n}} \tag{18}$$

if we consider that C_A^* is the CO_2 concentration in equilibrium with the gaseous phase. This can be evaluated by Henry's law ($p_A = \mathrm{He} C_A^*$), with the result

$$\log\left[\frac{N_A^2 \mathrm{He}^2}{P_A^2 D_A}\right] = \log k_{1,n} + n \log C_{B0} \tag{19}$$

Representations were made of the first member of Eq. 19 against the log C_{B0}, and in all cases and values of $C_{B0} > 0.25$ kmol/m^3 a linear relationship was determined, thus verifying that equation.

As an example, in Figure 4 the absorption process at temperature $T_B = 313$ K is represented as N_A vs. C_{B0} for the values of the amine concentration < 0.25 kmol/m^3 (see Figure 4a) and $\log[(N_A^2 \mathrm{He}^2)/(D_A p_A^2)]$ vs. log C_{B0}, for the higher concentrations (see Figure 4b). Both representations show quite acceptable linearity, which may indicate that for this temperature and amine concentrations < 0.25 kmol/m^3 the reaction regime is instantaneous and, at higher concentrations, there is a fast-reaction regime.

For the temperatures (T_B) of 288, 293, 298, 303, and 308 K, the behavior was similar, although it should be mentioned that the rapid-reaction regime occurs within a broader interval of lower concentrations. In Figure 5, the flow-density values are compared with the amine concentration for the absorption processes assayed with MEA and AMP at the same temperature T_B.

The different behavior of AMP with respect to MEA is reflected, showing that at lower concentrations the N_A values in AMP were higher than those that resulted when aqueous solutions of MEA were used. These results partially coincide with

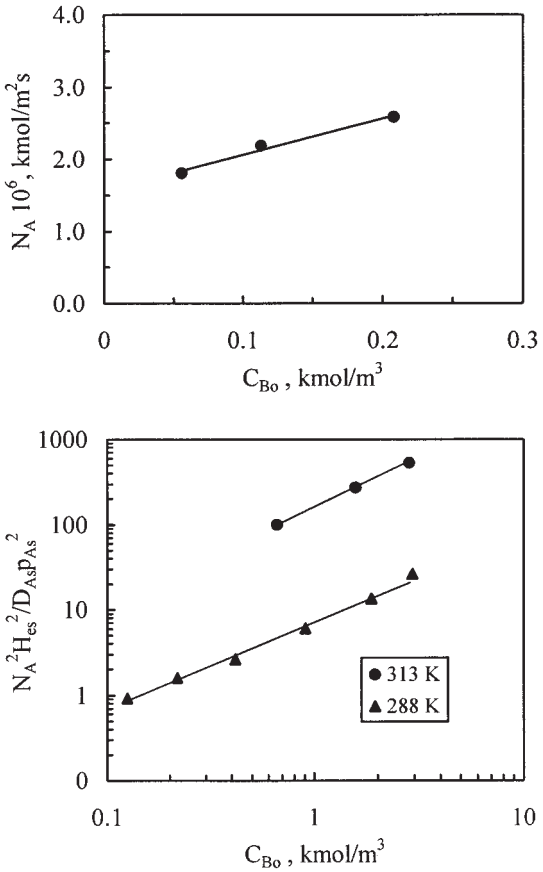

Figure 4. (a) Reaction regime for AMP at 313 K. (C_{B0}: 0.0562, 0.113, 0.208 kmol/m^3). (b) Reaction regime for AMP at 288 K (C_{B0}: 0.125, 0.215, 0.414, 0.902, 1.875, 2.928 kmol/m^3) and 313 K (C_{B0}: 0.659, 1.576, 2.828 kmol/m^3).

those of Sartori et al.[15] and Zioudas and Dadach.[23] These latter authors detected, when using pure CO_2 and a concentration of 0.05 kmol/m^3, that the absorption rate in AMP was 25% higher than when aqueous MEA solutions were used in experiments conducted at 297 K. Similar comparisons to those in Figure 5 resulted for the other temperatures assayed in the absorption processes with AMP.

Rise in temperature

In the experiments of the greatest AMP concentration, control of the temperature in the bulk liquid phase has demonstrated that an appreciable increase of 0.5–1 K should occur. The fact that the reaction took place on a thin film of the gas–liquid interface makes it plausible that the temperature increase was considerable.

In addition, as indicated above, it could be considered, from the criteria of Astarita et al.,[13] that at low AMP concentrations the reaction regime was instantaneous, as observed in the absorption processes carried out at $T_B = 313$ K (see Figure 4a), where there was a linear relationship between N_A vs. C_{B0}, for the first three AMP concentrations.

On the basis of these two observations, it can be assumed that, in the CO_2-absorption processes in AMP solutions and at low amine concentrations, a nonisothermal instantaneous reaction regime may exist. From this, we can determine the rise in temperature at the interface for experiments with AMP concentrations in which the reaction regime is instantaneous. In this sense, temperature in the bulk liquid phase would be T_B, whereas that in the interfacial film would be T_s, with $(T_s - T_B)$ being the increase in surface temperature generated with respect to that preestablished at the beginning of the experiment.

The flow density in a process with a chemical reaction can be expressed in the following way[1,24]

$$N_A = Ek_L C_A^* \tag{20}$$

In addition, because the reaction regime is instantaneous ($E = E_i$), and considering the definition of instantaneous-enhancement factor E_i according to the theory of the film, then

$$N_A = \left[1 + \frac{D_B}{zD_A}\frac{C_{B0}}{C_A^*}\right]k_L C_A^* \tag{21}$$

After assaying the application for our results from the different models proposed for nonisothermal absorption processes, we found the greatest consistency was attained by one modification of Eq. 21—that is, Eq. 22—which enabled us to evaluate the temperature rise in the interface and correlate the experimental results N_A and C_{Bo}

$$N_A = k_L C_{As}^* + \frac{D_B k_L}{zD_{As}} C_{B0} \tag{22}$$

In this equation, it is accepted that the AMP diffuses (D_B) from the bulk liquid phase to the interface at the temperature T_B, and that the individual coefficient of mass transfer (k_L) is also determined at temperature T_B. This contradicts the model of Mann and Moyes,[4] which states that the thickness of the thermal film near the interface is appreciably greater than the thickness of the mass-transfer film. Nevertheless, this equation adjusts well to the results of the present work.

By applying Henry's law, we can determine the concentra-

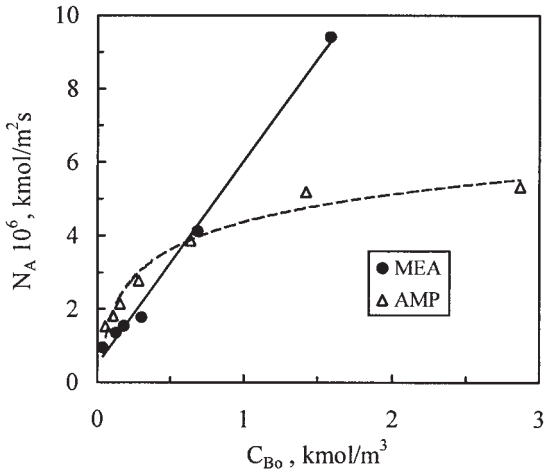

Figure 5. Comparative study of the variation of N_A with the concentration of AMP and MEA at 303 K.

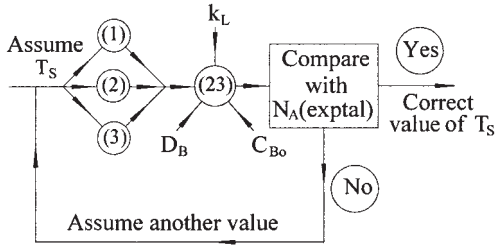

Figure 6. Calculation sequence for the determination of T_s.

tion of carbon dioxide dissolved at the temperature T_s, C^*_{As}, and Eq. 22 can be transformed into the following expression

$$N_A = k_L \frac{p_{As}}{He_s} + \frac{D_B k_L}{D_{As}} C_{B0} \tag{23}$$

where $z = 1$ if we assume the mechanism proposed by Chakraborty et al.[18] shown in Eq. 11. The values of p_{As}, He_s, and D_{As} at temperature T_s can be determined by Eqs. 1, 2, and 3, respectively, and thus by these equations and Eq. 23, we can use an iterative procedure to calculate the value of T_s. Following the calculation sequence reflected in Figure 6, used in previous works,[25] we can calculate the values of the interfacial temperature T_s. Table 1 presents these values.

Kinetics parameters

Once the interfacial temperature T_s is determined in the processes with low amine concentrations, it can be assumed as a beginning hypothesis that in the rest of the experiments of each series the reaction regime is fast (on the basis of Figure 4b) and, in an approximate way, it can be considered that the interfacial temperature is close to the highest value of T_s, calculated in the range of concentrations where the reaction regime was instantaneous. Thus, for example, at a bulk liquid phase temperature $T_B = 313$ K, the first three experiments carried out in the instantaneous reaction regime lead, as shown in Table 1, to the situation in which the highest value of T_s is 338.5 K. From this value, it can be considered in an approximate way that the absorption processes at higher concentrations have the same interfacial temperature, which, accepting that the reaction regime is fast and that the order with respect to the carbon dioxide is one, by Eq. 19, the order with respect to the amine can be deduced, as can the value of the kinetic constant of the reaction k_2. For example, in Figure 4b, for an experimental series at 313 K, the values of $\log[(N_A^2 He_s^2)/(D_{As} p_{As}^2)]$ vs. $\log C_{B0}$ are represented.

Applying the least-squares method, we calculated the slope (n) of 1.14 and an ordinate ($\log k$), which determined a kinetic constant of 161.0 $m^3\ kmol^{-1}\ s^{-1}$. This value is of the same order as that reported by Chakraborty et al.,[18] using pure carbon dioxide and five different reactor configurations. These researchers gave a value of $k = 100\ m^3\ kmol^{-1}\ s^{-1}$ for a temperature (in the bulk liquid phase) of 313 K. In this sense, it should be pointed out that the different research groups that have worked in CO_2 absorption in AMP solutions did not consider thermal effects. The same calculation procedure applied to the experimental series of between 288 and 308 K gave the results listed in Table 2.

In addition, Table 2 indicates the values of the reaction order with respect to AMP (n), the kinetic constant (k), and regression coefficients (r^2) by the application of Eq. 19, as well as the interfacial temperature, which was considered in an approximate way for the experiments in which the reaction regime could be fast.

It was observed that in all the experimental series, the reaction order with respect to the amine was practically one, a result that coincides with that reported by different research groups that have worked with AMP.[16,18,19] In addition, this value of the order with respect to amine ($n = 1$) coincides with the one that is fully accepted in the absorption of carbon dioxide in aqueous solutions of primary alkanolamines.

Once the kinetic constant and the order are determined, one of the criteria of Astarita et al.[13] is applied to confirm that in all the experiments in Table 2 fulfill this equation

$$\frac{C_{B0} He_s}{p_{As}} \gg \frac{1}{k_L} \sqrt{k C_{B0} D_{As}}$$

supporting, to a certain degree, the beginning hypothesis on the rapid-reaction regime. Finally, from the values in Table 2, we seek to fit the value of k and T_s to an Arrhenius-type equation. Thus, in Figure 7, $\ln(k_2)$ vs. $1/T_s$ are represented, in principle, observing an appropriate linearity.

The application of the least-squares method leads to an acceptable fit, enabling the deduction of the following expression

$$\ln k_2 = 29.2 - \frac{8186.9}{T} \tag{24}$$

From this equation, we can deduce the apparent activation energy $(E_a)_{ap}$, giving a value (Table 3) higher than that corresponding to other primary alkanolamines assayed (AP, MIPA, MEA), which are practically of the same order of magnitude, suggesting that the activation energy is higher when the steric impediment of the amine group is greater.

Enhancement factors

After we calculate the temperature in the film of the interface (T_s) and the kinetic constant (k_2), determination of the Hatta number (Ha) is immediate by the following equation

Table 1. Interfacial Temperature in the Experiments with 2-Amino-2-methyl-1-propanol

T_B (K)	C_{B0} (kmol m^{-3})	p_{As} (kPa)	T_s (K)
288	0.0482	93.45	299.5
293	0.0536	89.58	310.0
298	0.0577	87.17	316.0
303	0.0549	90.38	308.0
	0.106	87.51	316.0
	0.154	85.37	320.0
308	0.0768	84.76	321.0
	0.145	80.01	328.0
313	0.0562	88.85	314.0
	0.113	83.31	324.5
	0.208	70.52	338.5

Table 2. Study of the Reaction Regime and Kinetics Parameters in the Absorption with AMP

T_B (K)	C_{B0} (kmol m^{-3})	T_s (K)	p_{As} (kPa)	$\frac{N_A^2 He_s^2}{D_{As} p_{As}^2}$	$\frac{\sqrt{kC_{B0}D_{As}}}{k_L}$	$\frac{C_{B0}He_s}{p_{As}}$	n	k (m^3 kmol^{-1} s^{-1})	r^2
288	0.125	299.5	92.63	0.915	1.75	4.29	1.04	7.4	0.994
	0.215	299.5	92.63	1.60	2.30	7.58			
	0.414	299.5	92.63	2.66	3.10	14.59			
	0.902	299.5	92.94	6.05	4.34	32.95			
	1.875	299.5	92.67	13.46	5.53	74.29			
	2.928	299.5	92.89	26.30	5.76	125.61			
293	0.123	310.0	89.47	1.75	2.19	5.91	1.07	13.4	0.989
	0.239	310.0	90.47	2.53	3.01	11.42			
	0.418	310.0	89.60	4.54	3.92	20.51			
	0.966	310.0	89.33	12.59	5.62	49.67			
	1.876	310.0	89.95	27.48	6.97	103.08			
	2.697	310.0	90.41	41.69	7.31	157.51			
298	0.119	316.0	87.39	2.60	2.77	6.84	1.04	24.0	0.998
	0.218	316.0	86.88	5.46	3.72	12.74			
	0.417	316.0	86.88	9.12	5.04	24.76			
	0.810	316.0	87.67	17.62	6.77	49.24			
	1.930	316.0	87.34	47.42	9.20	128.79			
	2.747	316.0	86.29	73.28	9.74	198.23			
303	0.280	320.0	85.45	11.48	5.47	18.56	0.99	40.7	0.999
	0.638	320.0	85.25	25.47	8.01	43.60			
	1.420	320.0	85.39	60.12	11.08	103.27			
	2.871	320.0	85.85	113.50	13.16	233.33			
308	0.221	328.0	79.64	12.88	6.25	19.06	1.09	65.0	0.983
	0.393	328.0	80.43	20.60	8.22	34.08			
	0.789	328.0	79.98	62.95	11.24	71.09			
	1.358	328.0	80.77	78.70	13.94	126.82			
	1.573	328.0	79.98	109.40	14.66	151.02			
	2.709	328.0	80.77	191.87	16.67	282.17			
313	0.659	338.5	70.75	100.00	16.17	85.17	1.14	161.0	0.999
	1.576	338.5	70.75	270.40	23.03	219.29			
	2.828	338.5	70.42	527.23	26.82	437.14			

$$\mathrm{Ha} = \sqrt{\frac{k_{2s} C_{B0} D_{As}}{k_L^2}} \tag{25}$$

$$E'_{is} = 1 + \frac{D_B}{D_{As}} \frac{C_{B0} He_s}{p_{As}} \tag{26}$$

In addition, using Eqs. 26 and 20, we calculated the enhancement factors, E_{is} and E, at the temperature T_s (Table 4)

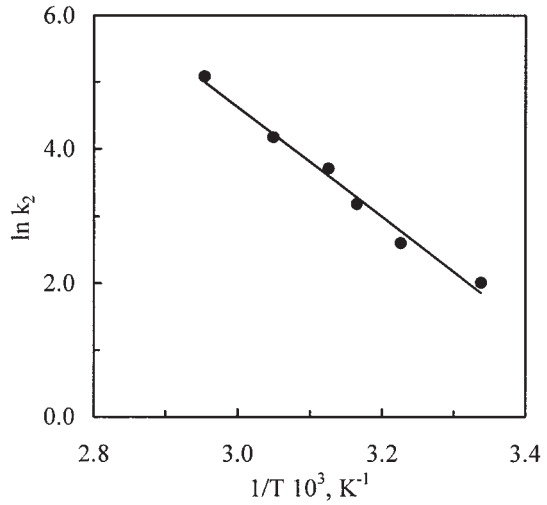

Figure 7. Variation of the kinetic constant with temperature for AMP.

Figure 8 presents the values of the enhancement factor E against the Hatta number in logarithmic coordinates, reflecting that—practically—the points corresponding to the experiments made at medium and high AMP concentrations acceptably fit the bisector of this representation.

It can also be seen that at low concentrations, and fundamentally in the experiments with lower temperatures, there are some points (shaded) that are higher than the bisector, a situation that may have arisen because the experimental conditions under which these assays were made corresponding to carbonations ratios very close to 0.5.

In general, the values calculated for the experiments in which the hypothesis of the fast-reaction regime was used fulfill the expressions

$$E = \mathrm{Ha} \pm 15\%$$

Table 3. Activation Energy

Alkanolamine	$(E_a)_{ap}/R$ (K)	$(E_a)_{ap}$ (kJ/mol)	Reference
MEA	4955.2	41.2	Hikita et al.[14]
MIPA	5033.5	41.8	Hikita et al.[19]
AP	5226.3	43.5	Penny and Ritter[26]
AMP	8186.9	68.1	This investigation

Table 4. Interfacial Temperature, Enhancement Factors, and Hatta Number in the Experiments on AMP

T_B (K)	T_s (K)	E'_{is}	Ha	E	T_B (K)	T_s (K)	E'_{is}	Ha	E
288	299.5	1.57	1.10	1.57	303	308.0	2.04	1.26	2.04
	299.5	2.45	1.75	1.74		316.1	3.13	2.67	3.13
	299.5	3.49	2.30	2.28		320.0	4.21	4.10	4.21
	299.5	5.51	3.10	2.89		320.0	6.70	5.47	5.49
	299.5	9.77	4.34	4.14		320.0	13.23	8.01	7.93
	299.5	16.28	5.53	5.45		320.0	25.07	11.08	11.30
	299.5	22.50	5.76	6.35		320.0	42.81	13.16	12.98
293	310.0	1.81	1.45	1.81	308	320.9	2.88	2.73	2.88
	310.0	2.84	2.19	2.26		328.0	4.85	5.11	4.84
	310.0	4.41	3.01	2.68		328.0	6.79	6.25	5.93
	310.0	6.78	3.92	3.53		328.0	10.93	8.22	7.39
	310.0	12.85	5.62	5.54		328.0	19.83	11.24	12.45
	310.0	20.31	6.97	7.29		328.0	30.62	13.94	13.16
	310.0	26.18	7.31	7.84		328.0	34.75	14.66	15.16
						328.0	53.16	16.67	17.40
298	316.0	2.04	1.94	2.04	313	313.7	2.25	1.42	2.35
	316.0	3.11	2.77	2.64		324.4	4.04	3.45	4.04
	316.0	4.83	3.72	3.80		338.5	7.94	9.43	7.95
	316.0	8.03	5.04	4.82		338.5	21.60	16.17	15.47
	316.0	13.59	6.77	6.45		338.5	45.22	23.03	23.45
	316.0	26.37	9.20	9.31		338.5	73.72	26.82	28.46
	316.0	35.01	9.74	10.26					

$$2 < \mathrm{Ha} < E_i$$

which in a certain way verifies the beginning hypothesis. In agreement with this idea, the equation for the reaction rate of carbon dioxide with AMP can be expressed as follows

$$r = k_2[\mathrm{CO_2}][\mathrm{AMP}] \tag{27}$$

This kinetic equation would be consistent with the mechanism proposed by Chakraborty et al.,[18] who point out that the process takes place in two stages indicated by reactions 14 and 15.

Notation

A = interfacial area, m^2
C_A = concentration of component A (CO_2), kmol/m^3

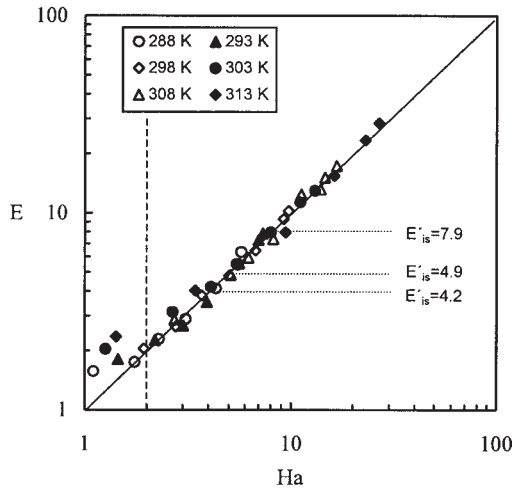

Figure 8. Variation of the acceleration factor (E) with the Hatta number (Ha) in the experiments of AMP at the temperatures indicated.

C_{A0} = initial concentration of component A (CO_2), kmol/m^3
C^*_A = A (CO_2) concentration in equilibrium with the gaseous phase, kmol/m^3
C^*_{As} = A (CO_2) concentration in equilibrium with the gaseous phase at temperature T_s, kmol/m^3
C_{B0} = initial concentration of amine in the aqueous phase, kmol/m^3
D_A (D_{CO_2}) = diffusion coefficient of component A (CO_2) in the aqueous alkanolamine solution, m^2/s
D_{As} = diffusion coefficient of component A (CO_2) in the liquid phase at temperature T_s, m^2/s
D_B (DAMP) = diffusion coefficient of alkanolamine in the liquid phase, m^2/s
$D_{CO_2,w}$ = diffusion coefficient of CO_2 in water, m^2/s
D_{N_2O} = diffusion coefficient of N_2O in the alkanolamine solution, m^2/s
$D_{N_2O,w}$ = diffusion coefficient of N_2O in water, m^2/s
E = enhancement factor, dimensionless
E_i = instantaneous-enhancement factor, dimensionless
E_{is} = modified instantaneous-enhancement factor at the temperature T_s, dimensionless
Ha = Hatta number, dimensionless
He = Henry's law constant, kPa m^3 $kmol^{-1}$
He_s = Henry's law constant at the temperature T_s, kPa m^3 $kmol^{-1}$
k = reaction rate constant
k_L = liquid-phase mass-transfer coefficient, m/s
k_2 = second-order reaction-rate constant, m^3 $kmol^{-1}$ s^{-1}
k_{2s} = second-order reaction-rate constant at the temperature T_s, m^3 $kmol^{-1}$ s^{-1}
n = order of reaction with respect to amine
n' = rate of absorption of CO_2, kmol/s
N_A = rate of absorption per unit interfacial area of component A (CO_2), kmol m^{-2} s^{-1}
p_A = partial pressure of component A (CO_2), kPa
p_{As} = partial pressure of component A (CO_2) at the temperature T_s, kPa
P = total pressure, kPa
p_v = vapor pressure of the water, kPa
Q' = volumetric flow rate of absorbed CO_2, m^3/s
r = reaction rate
r^2 = lineal regression coefficient
R = gas constant, kPa m^3 K^{-1} $kmol^{-1}$
t = time, s
T = temperature, K

T_B = temperature in the bulk liquid, K
T_s = temperature in the interfacial film, K
z = stoichiometric coefficient

Greek letters

γ = constant defined in Eq. 6
η = carbonation ratio, mol CO_2/mol of amine
μ_B = viscosity of the solution amine, Pa·s
μ_w = viscosity of the pure water, Pa·s

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Manuscript received Jun. 10, 2004, and revision received Feb. 2, 2005.