

# Absorption of Carbon Dioxide at High Partial Pressures in 1-Amino-2-propanol Aqueous Solution. Considerations of Thermal Effects

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In the present work, the process of carbon dioxide absorption is analyzed at high partial pressures, in aqueous solutions of 1-amino-2-propanol (monoisopropanolamine (MIPA)), in relation to the thermal effects involved. All experiments were made in a stirred-tank reactor with a plane unbroken gas–liquid interface. The variables considered were the MIPA concentration within the range 0.1–2.0 M and the temperature within the interval 288–308 K. From the results, we deduce that the absorption process takes place in the nonisothermal instantaneous regime and propose an equation which not only relates the experimental results of flow density with the initial concentration of amine but at the same time enables the evaluation of the rise in temperature in the gas–liquid interface.

## Introduction

The absorption of carbon dioxide by alkanolamine solutions has important industrial application, for which the study of the reaction kinetics between CO<sub>2</sub> and these amines bears considerable relevance. The chemistry of CO<sub>2</sub> reactions in amine solutions is complex and not fully understood (Astarita *et al.*, 1983).

In general, the comparison of the kinetic data available for the reactions between CO<sub>2</sub> and alkanolamines is complicated by the different experimental techniques used and by the presence in the liquid phase of traces of contaminants of the amine, which can considerably alter the rate of the reaction (Blauwhoff *et al.*, 1983).

In principle, it is necessary to differentiate alkanolamines dissolved in an aqueous medium from those dissolved in organic solvents. Currently industry uses primarily aqueous alkanolamine solutions. Among the most common alkanolamines are monoethanolamine (MEA), diethanolamine, di-2-propanolamine, and methyl-diethanolamine. There is ample information in the literature concerning the absorption in an isothermal regime and fundamentally at low partial CO<sub>2</sub> pressures. Nevertheless, in the preparation of pure hydrogen, ammonium, and synthetic natural gas, it is necessary to separate a mixture with high partial CO<sub>2</sub> pressures (Astarita *et al.*, 1983).

In relation to this, it should be indicated that the physical absorption of a highly soluble gas, or during absorption with a chemical reaction, the temperature of the liquid phase, especially near the gas–liquid interface, can increase due to the heat given off by the dissolution and/or by the reaction (Danckwerts, 1953; Mann and Moyes, 1977; Al-Ubaidi and Selim, 1992). In some systems, these effects are mild with only minor temperature increases in the interface. Nevertheless, in certain gas–liquid systems of industrial interest, high thermal effects have been recorded. 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 liquid

hydrocarbons (Mann and Moyes, 1977; Chatterjee and Altwicker, 1987).

In relation to CO<sub>2</sub> absorption, at partial reduced pressures and in aqueous solutions of alkanolamines, these effects have been considered negligible by practically all research groups working with these systems. However, it should be pointed out that when the absorption occurs under high partial pressures of CO<sub>2</sub>, the thermal effects appear to have a certain degree of impact. In fact, there are antecedents such as CO<sub>2</sub> absorption in aqueous solutions of MEA at partial pressures near atmospheric pressure in the work of Clarke (1964). This author, using a laminar jet apparatus and MEA concentrations within the range of 1.6–4.8 M and working at low pressures (around 80 mmHg) and high CO<sub>2</sub> pressures (around 750–760 mmHg), 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 CO<sub>2</sub> at high partial pressures in aqueous solutions of monoisopropanolamine (MIPA) and the thermal effects related to this process.

## Materials and Methods

**Experimental Device.** 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<sub>2</sub> enabled the periodic determination of the absorption rate, by means of a bubble counter that enabled the direct measurement of the CO<sub>2</sub> absorbed.

The variables considered were the MIPA concentration within the range of 0.1–2.0 M and temperature within the interval 288–308 K. In all experiments, the stirring speed in the reactor was 180 rpm, maintaining a smooth interfacial area of 35.26 cm<sup>2</sup>.

**Physical and Transport Properties.** Under these experimental conditions, we measured the viscosity and density of the amine solutions. The former parameter was measured by using a capillary viscometer.

The calculation of the initial partial pressure of the CO<sub>2</sub> is given by

$$p_A = P - p_v \quad (1)$$

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The total pressure,  $P$ , was measured in a previously calibrated barometer placed close to the experimental installation. The values of the vapor pressure of the water,  $p_v$ , were correlated with the temperature by an Antoine-type expression (Felder and Rousseau, 1986).

To determine the solubility of the  $\text{CO}_2$  in the liquid phase, we used the relationship of Danckwerts and Sharma (1966):

$$He = 10^{(5.3-1140/T)} \quad (2)$$

where  $He$  is Henry's law coefficient ( $\text{atm}\cdot\text{m}^3\cdot\text{kmol}^{-1}$ ) and  $T$  the temperature (K).

The diffusion coefficients of the  $\text{CO}_2$  in the aqueous solution was measured for the relationships of Sada *et al.* (1978) and Versteeg and Swaaij (1988):

$$D_A = \left[ \frac{D_{\text{N}_2\text{O,am}}}{D_{\text{N}_2\text{O,w}}} \right] D_{\text{CO}_2,\text{w}} \quad (3)$$

where

$$D_{\text{CO}_2,\text{w}} = 2.35 \times 10^{-6} e^{(-2119/T)} \quad (4)$$

$$D_{\text{N}_2\text{O,w}} = 5.07 \times 10^{-6} e^{(-2371/T)} \quad (5)$$

$$D_{\text{N}_2\text{O,am}} = D_{\text{N}_2\text{O,w}} \left[ \frac{\mu_w}{\mu_{\text{am}}} \right]^\gamma \quad (6)$$

The diffusion coefficients of MIPA in the aqueous solution were determined by means of the relationship of Wilke and Chang (1955):

$$D_B = 3.06 \times 10^{-15} \frac{T}{\mu} \quad (7)$$

where  $T$  is the temperature (K) and  $\mu$  the viscosity ( $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ ).

**Analytical Methods.** The initial amine concentration was determined by titration with HCl solutions using methyl orange as the indicator. The  $\text{CO}_2$  concentration in liquid was determined by standard titration methods. Excess NaOH and the excess  $\text{BaCl}_2$  solutions were added to the liquid sample, and the excess NaOH was titrated with HCl solution using thymol blue as an indicator.

## Results and Discussion

In all cases, the flow densities,  $N_A$ , were calculated assuming that the gas follows ideal behavior and using the following expression:

$$N_A = \frac{n'}{A} = \frac{PQ}{RTA} \quad (8)$$

$n'$  being the molar flow ( $\text{kmol}\cdot\text{s}^{-1}$ ),  $A$  the interfacial area ( $\text{m}^2$ ),  $P$  the total pressure (kPa),  $Q$  the volumetric flow of the  $\text{CO}_2$  absorbed ( $\text{m}^3\cdot\text{s}^{-1}$ ), and  $R$  the constant of the gases ( $\text{kPa}\cdot\text{m}^3\cdot\text{K}^{-1}\cdot\text{kmol}^{-1}$ ).

The value of the volumetric flow coincided with the value of the slope of the straight lines on representing the volume of the  $\text{CO}_2$  absorbed against time ( $t$ ) for each experiment; determinations were made using the linear regression method of the experimental results.

Experimental temperatures of the reactor system were practically equal to room temperature. At the beginning of each experiment, the maximum difference

between the exterior temperature and that of the interior of the reactor (in the bulk liquid phase) was  $\pm 1^\circ\text{C}$ .

Initially, with the aim of determining the individual transfer coefficients of the liquid phase,  $k_L$ , we performed experiments of the physical absorption of  $\text{CO}_2$  in water, using the same contactor as in the chemical absorption experiments.

The results obtained during the process of the physical absorption enabled the calculation of the  $k_L$  values for the temperature range used. In general,  $k_L$  was related, by the modified Sherwood number ( $Sh'$ ), to the numbers of Schmidt ( $Sc$ ) and Reynolds ( $Re$ ) in the following form:

$$(Sh') = \alpha (Sc)^{\tau_1} (Re)^{\tau_2} \quad (9)$$

The nonlinear regression method, applied to the results obtained for  $k_L$ , and in the form indicated in eq 9, enabled us to obtain the values for the parameters  $\tau_1$  and  $\tau_2$ , resulting in the expression

$$(Sh') = 11.4 (Sc)^{1/3} (Re)^{-1/2} \quad (10)$$

with the value of the sum-of-squares residuals  $1.35 \times 10^{-3}$ .

In the absorption experiments with pure  $\text{CO}_2$  in aqueous MIPA solutions, we analyzed the influence of the initial alkanolamine concentration and the operating temperature.

## Absorption in MIPA Solutions

Monoisopropanolamine,  $\text{CH}_3\text{--CHOH--CH}_2\text{--NH}_2$ , as a primary alkanolamine, in relation to its functional groups ( $\text{--NH}_2$  and  $\text{--OH}$ ) with  $\text{CO}_2$ , showed a behavior similar to that reported by other authors (Astarita *et al.*, 1964; Blauwhoff *et al.*, 1983) indicated for monoethanolamine:

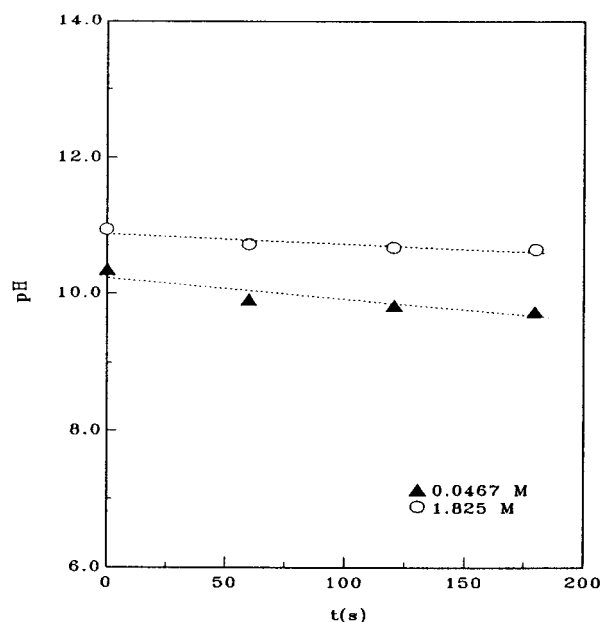


This latter reaction may take place in a basic solution at a  $\text{pH} \geq 11$ ; when the  $\text{pH}$  is less than 10, even in a carbonate solution, the formation of the carbonic acid derivative can be considered negligible (Astarita *et al.*, 1964).

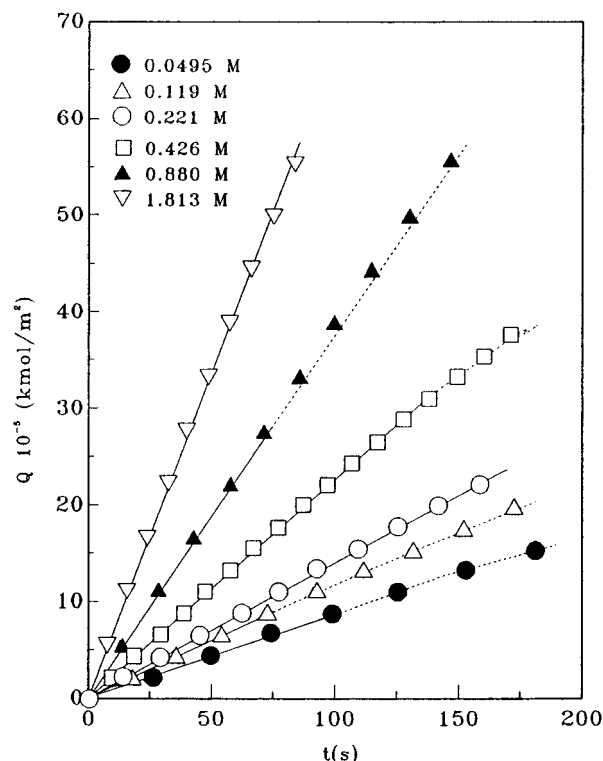
The  $\text{pH}$  measurements taken indicate that in general the  $\text{pH}$  has values of less than 11 from the beginning of the absorption process and diminishes gradually over the process. In the case of low MIPA concentrations, the  $\text{pH}$  is initially around 10; Figure 1 provides a graphic representation indicating the change in  $\text{pH}$  at 293 K, showing that when operating at high concentrations, we acquire somewhat higher  $\text{pH}$  values, but invariably close to 10. On the basis of the results obtained, the main reaction can be considered the formation of a carbamic acid derivative (reaction 11).

For an example, Figure 2 offers graphic representations of  $\text{CO}_2$  absorbed per unit of surface area against time for the experiments conducted at 298 K. A constant operating temperature and partial gas pressure were maintained, varying the initial monoisopropanolamine concentration between 0.05 and 1.8 M.

In all cases, the volumetric flow rate of absorbed  $\text{CO}_2$  increased significantly with increased initial concentra-



**Figure 1.** Variation of pH of the MIPA solution with time, over the absorption process at 293 K at corresponding concentrations.



**Figure 2.** CO<sub>2</sub> absorbed per unit of surface area and time in the experiments with MIPA at 298 K.

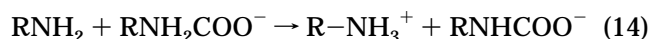
tions, as clearly shown in the rising slopes of the straight lines. Thus, there was an appreciable curvature for times greater than those considered in the  $N_A$  calculation, fundamentally in the experiments performed at low  $C_{B0}$ . Table 1 lists the values of  $N_A$  corresponding to each of the initial MIPA concentrations assayed; flow density increased noticeably with concentration, and more so as  $C_{B0}$  became greater.

In addition, in almost all the experiments carried out with aqueous MIPA solutions, the carbonation relationship ( $\eta$ , quotient between the moles of carbon dioxide and of amine in solution) was less than 0.5, which, in agreement with Astarita *et al.* (1964), indicates that the carbamate was the product of the reaction, and the

**Table 1.** Flow Densities in the Absorption of CO<sub>2</sub> in Monoisopropanolamine Solutions

$T$ (K)	run	$p_A$ (kPa)	$C_{B0}$ (kmol/m <sup>3</sup> )	$N_A \times 10^6$ (kmol/m <sup>2</sup> ·s)
288	I1-T1	94.81	0.0508	1.000
	I2-T1	93.86	0.140	1.211
	I3-T1	92.51	0.214	1.532
	I4-T1	92.00	0.401	2.074
	I5-T1	90.76	0.856	3.222
	I6-T1	90.31	1.814	4.575
293	I1-T2	94.53	0.0467	1.212
	I2-T2	93.02	0.125	1.354
	I3-T2	92.45	0.165	1.496
	I4-T2	91.48	0.379	2.246
	I5-T2	90.14	0.863	3.561
	I6-T2	90.26	1.825	5.696
298	I1-T3	92.62	0.0495	0.889
	I2-T3	92.51	0.119	1.224
	I3-T3	93.12	0.221	1.440
	I4-T3	91.90	0.426	2.283
	I5-T3	90.99	0.880	3.737
	I6-T3	86.66	1.813	6.680
303	I1-T4	91.27	0.0617	0.874
	I2-T4	91.67	0.135	1.326
	I3-T4	91.14	0.204	1.650
	I4-T4	91.33	0.387	2.205
	I5-T4	87.99	0.819	4.058
	I6-T4	89.20	1.753	7.648
308	I1-T5	90.52	0.0725	1.019
	I2-T5	89.89	0.133	1.309
	I3-T5	90.29	0.221	1.650
	I4-T5	87.96	0.385	2.389
	I5-T5	86.97	0.820	4.208
	I6-T5	86.73	1.800	8.526

mechanism would be the one indicated by reactions 13 and 14, analogous to that described for primary and secondary alkanolamines by Danckwerts (1979):



The results of  $\eta$  obtained for MIPA ( $\eta < 0.5$ ) indicate that the reaction occurs by means of a second-order mechanism and that three possible regimes should be considered, which, according to Astarita *et al.* (1964), can take place:

(a) If  $C_{B0}/2C_{A0} \ll 1$ , the absorption rate can be given by

$$N_A = k_L C_{A0} \quad (15)$$

(b) If  $1 \ll C_{B0}/2C_{A0} \ll (kC_{B0}\theta)^{1/2}$ :

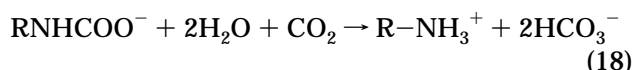
$$N_A = k_L \frac{C_{B0}}{2} \quad (16)$$

(c) If  $(kC_{B0}\theta)^{1/2} \ll C_{B0}/2C_{A0}$ :

$$N_A = C_{A0} \sqrt{D_A k C_{B0}} \quad (17)$$

Case (a) corresponds to the hydrodynamic regime or of physical absorption, (b) corresponds to the instantaneous-reaction regime, and (c) corresponds to the fast-reaction regime.

When  $\eta > 0.5$  (this occurred only in three of the experiments) and  $C_{B0} \leq 0.05$  kmol/m<sup>3</sup>, in addition to reactions 13 and 14, the following reaction would occur:



and the kinetics would correspond to a pseudo-first-order reaction.

### Reaction Regime

In accord with the values of initial amine concentrations, the quotient  $C_{\text{B}0}/2C_{\text{A}0}$  is much greater than 1 and consequently the expression (15) cannot be applied to correlate the experimental values obtained for the  $\text{CO}_2$  absorption by aqueous MIPA solutions.

In addition, if we assume as a starting hypothesis a fast-reaction regime of order " $m$ " with respect to  $\text{CO}_2$ , and " $n$ " with respect to MIPA, then the flow density is given by the following expression (Charpentier, 1981):

$$N_{\text{A}} = \sqrt{\frac{2}{m+1}} D_{\text{A}} k_{m,n} C_{\text{A}0}^{m+1} C_{\text{B}0}^n \quad (19)$$

It has been amply demonstrated that the reaction order with respect to  $\text{CO}_2$  in absorption with aqueous primary-amine solutions is 1. If we accept this fact for the case of MIPA, then eq 19 is reduced to

$$N_{\text{A}} = C_{\text{A}0} \sqrt{D_{\text{A}} k_{1,n} C_{\text{B}0}^n} \quad (20)$$

This equation, which matches that of Astarita *et al.* (1964) when  $n = 1$  (eq 17), can easily be linearized in the following form:

$$\log \left[ \frac{N_{\text{A}}^2}{C_{\text{A}0}^2 D_{\text{A}}} \right] = \log k_{1,n} + n \log C_{\text{B}0} \quad (21)$$

Given that  $C_{\text{A}0}$  coincides with the  $\text{CO}_2$  concentration in equilibrium with the gaseous phase ( $C_{\text{A}}^*$ ) and this can be evaluated by Henry's law ( $p_{\text{A}} = \text{He} C_{\text{A}}^*$ ), the result is that

$$\log \left[ \frac{N_{\text{A}}^2 \text{He}^2}{p_{\text{A}}^2 D_{\text{A}}} \right] = \log k_{1,n} + n \log C_{\text{B}0} \quad (22)$$

From the experimental results, representations were made of the first member of eq 22 against the  $\log C_{\text{B}0}$ . For example, Figure 3 presents one of these representations for one of the experiments. Initially, the fits are not precise, the slope " $n$ " (order of reaction with respect to MIPA) is greater than 1.5 and close to 2. This finding is in complete disagreement with the literature, which affirms that the reaction order is 1 with respect to MIPA, and also, from the ordinate at the origin ( $\log k_{1,n}$ ), should attain a constant kinetic similar to those found in the literature, which, in the range of temperatures in the present study, fluctuates from 3000 to 9000  $\text{m}^3/\text{kmol}\cdot\text{s}$  (Hikita *et al.*, 1977). Nevertheless, we obtained  $k$  values of 2 orders of magnitude lower. In principle, our results rule out the idea of a fast-reaction regime.

In addition, a representation of the density values of flow  $N_{\text{A}}$  against  $C_{\text{B}0}$  lead to a straight line for each of the temperatures assayed—including even those experiments in which the carbonation relationship was greater than 0.5 (Figure 4). This fact could indicate an instantaneous-reaction regime. Nevertheless, in the case of the experiments conducted at greater concentrations and at temperatures of 288 and 293 K, no linear relationship was appreciated between  $N_{\text{A}}$  and  $C_{\text{B}0}$ ,

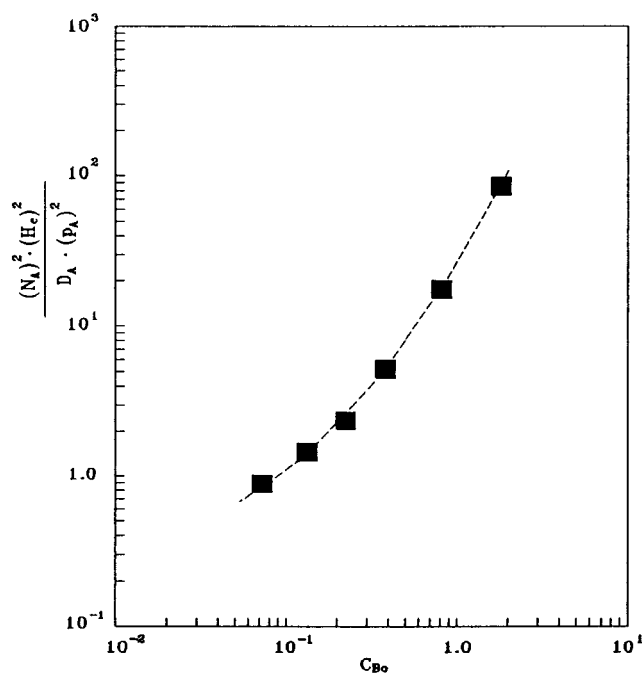


Figure 3. Determination of the reaction regime.

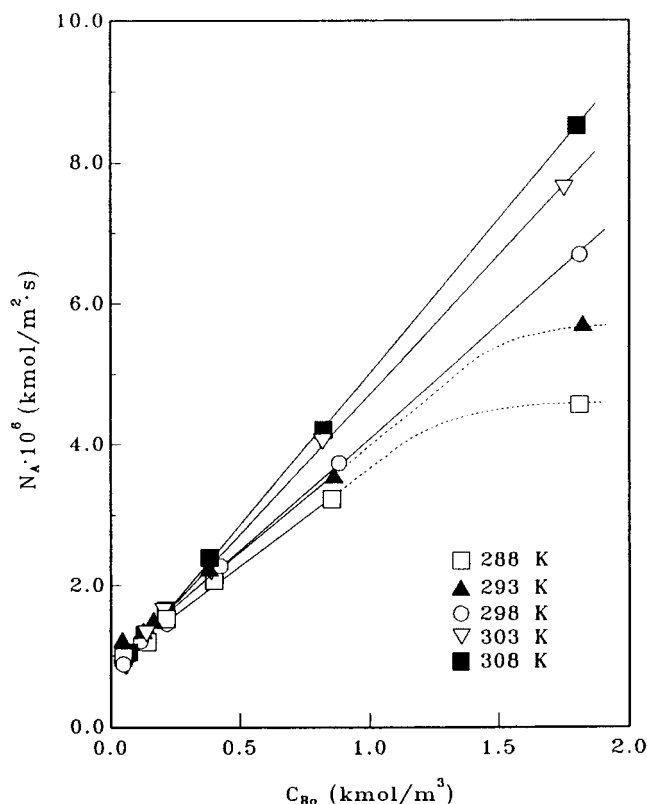


Figure 4. Variation of  $N_{\text{A}}$  with the concentration of MIPA at the temperatures indicated.

suggesting that in these the process of absorption cannot be considered to have occurred in the instantaneous-reaction regime, which requires  $Ha \gg E_i$ . Rather, it must be considered that, as  $C_{\text{B}0}$  increases,  $E_i$  increases more than does  $Ha$ , and on decreasing  $T$ ,  $Ha$  decreases more than does  $E_i$ . Consequently, at the high  $C_{\text{B}0}$  concentrations and low temperatures, the deviations occur toward the intermediate regime between instantaneous and fast.

### Influence of MIPA Concentration and Partial Pressure of CO<sub>2</sub>

After establishing the reaction regime, we sought to correlate the flow-density values with the MIPA concentrations in the bulk liquid phase. In general, the flow density in a process with chemical reaction can be expressed in the following form:

$$N_A = Ek_L C_A^* \quad (23)$$

In addition, since the reaction regime is instantaneous ( $E = E_i$ ), and considering the definition of  $E_i$  (instantaneous-enhancement factor) according to the theory of the film, it would result that

$$N_A = \left[ 1 + \frac{D_B}{zD_A} \frac{C_{B0}}{C_A^*} \right] k_L C_A^* \quad (24)$$

In relation to eq 24, we should indicate that according to the stoichiometry of the reaction that takes place,  $z = 2$ . In addition, we see that this equation is reduced to expression (16) in the cases in which it can be considered that  $D_A \approx D_B$  and  $C_{B0}/2C_A^* \gg 1$ .

In this sense, although the data of  $N_A$  vs  $C_{B0}$  (Figure 4) give rise to a linear relationship, this relationship has an ordinate at the origin with a certain value which cannot be ignored. That is, in principle, the adjustment to eq 16 is not appropriate. Furthermore, we find that the slope obtained does not coincide with the value of  $k_L/2$  for the working temperature that had been obtained in physical absorption.

**Rise in Temperature.** Over the absorption process, and fundamentally at the end of it, we detected that the temperature in the bulk liquid phase, in the experiments of the greatest MIPA concentration, could reach an increase of 1 K. 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. It should be borne in mind that this increased temperature was caused by the release of heat from the solution and reaction of the process.

On the basis of the above discussion, we propose the hypothesis that the absorption process occurs in the nonisothermal instantaneous regime. In this sense, temperature in the bulk liquid would be  $T_B$ , while 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 pre-established at the beginning of the experiment.

After assaying the application of our results from the different models proposed for the nonisothermal absorption processes, we found the greatest consistency was attained by one modification of eq 24, with the aim of correlating the experimental results  $N_A$  and  $C_{B0}$ , which in turn enabled us to evaluate the temperature rise in the interface. This modification gives the following expression:

$$N_A = k_L C_{As}^* + \frac{D_B k_L}{2D_{As}} C_{B0} \quad (25)$$

In this equation, it is accepted that the monoisopropanolamine 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 determined also at the temperature  $T_B$ ; this contradicts the model of Mann and Moyes (1977), which states that the thickness of the thermal film near the interface is

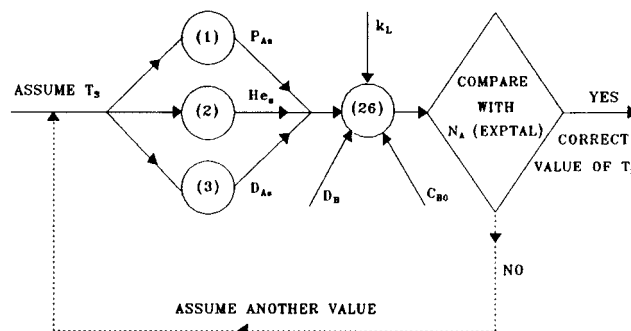


Figure 5. Calculation sequence for the determination of  $T_s$ .

Table 2. Interfacial Temperature, Enhancement Factors, and Module of Hatta in the Experiments on MIPA

run	$p_{As}$ (kPa)	$T_s$ (K)	$E_{is}$	$Ha$	$E$
I1-T1	93.75	297.7	1.33	26.17	1.33
I2-T1	91.88	303.5	1.95	54.19	1.94
I3-T1	90.70	302.7	2.44	64.68	2.44
I4-T1	89.81	306.1	3.67	99.55	3.67
I5-T1	89.40	310.1	6.39	162.75	6.39
I1-T2	93.60	298.1	1.35	21.02	1.35
I2-T2	90.75	306.8	2.00	48.01	1.99
I3-T2	89.72	308.4	2.33	58.37	2.33
I4-T2	87.72	313.3	4.09	104.51	4.08
I5-T2	85.46	319.7	7.87	191.18	7.86
I1-T3	88.21	314.0	1.49	36.12	1.49
I2-T3	87.20	316.1	2.19	60.09	2.19
I3-T3	83.20	324.7	3.36	109.53	3.36
I4-T3	82.41	325.3	5.46	153.00	5.45
I5-T3	80.15	328.4	9.93	236.44	9.91
I6-T3	81.61	326.6	16.67	295.65	16.62
I1-T4	85.02	320.7	1.74	49.16	1.74
I2-T4	85.46	320.2	2.58	71.11	2.58
I3-T4	84.44	322.0	3.41	92.54	3.40
I4-T4	79.04	330.0	5.93	164.91	5.92
I5-T4	79.36	329.3	10.67	226.89	10.65
I6-T4	81.12	326.9	18.59	285.19	18.52
I1-T5	84.45	322.2	1.98	52.40	1.98
I2-T5	82.07	325.8	2.87	79.72	2.87
I3-T5	78.42	330.9	4.29	121.53	4.29
I4-T5	76.23	333.6	6.81	173.06	6.81
I5-T5	73.43	336.1	13.19	265.00	13.16
I6-T5	78.19	331.5	22.54	315.11	22.44

appreciably greater than the thickness of the mass-transfer film. Nevertheless, this equation adjusts well to the results obtained in the present work.

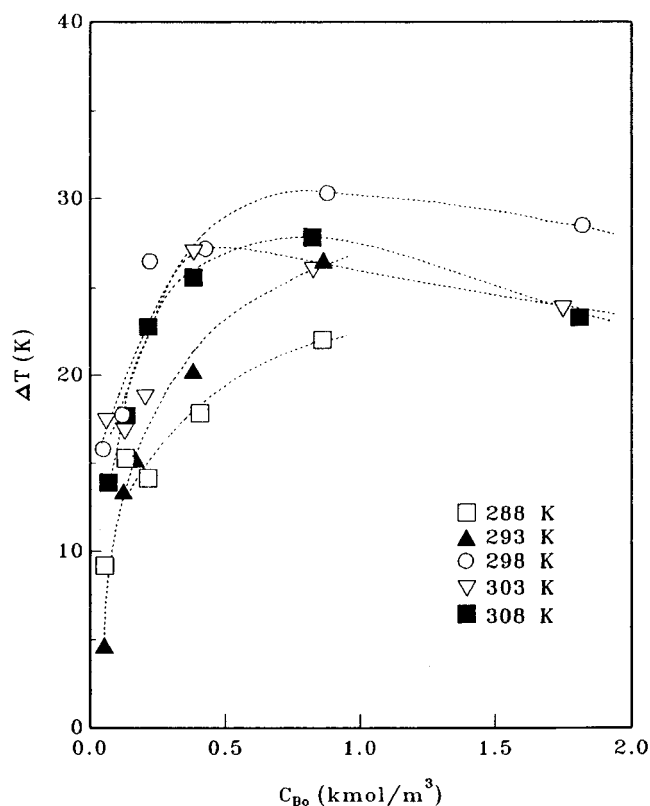
By applying Henry's law, we can determine the concentration of carbon dioxide dissolved at the temperature  $T_s(C_{As}^*)$ , eq 25 being capable of transformation into the following expression:

$$N_A = k_L \frac{p_{As}}{H_{e_s}} + \frac{D_B k_L}{2D_{As}} C_{B0} \quad (26)$$

In the above expression, the values of  $p_{As}$ ,  $H_{e_s}$ , and  $D_{As}$  at temperature  $T_s$  can be determined by eqs 1–3, respectively, so that by these equations and expression (26), using an iterative procedure, we can calculate the value of  $T_s$ . The sequence of the calculation is reflected in Figure 5.

Table 2 presents the interfacial temperature determined for the experiments conducted for the different MIPA concentration and at temperatures,  $T_B$ , of 288, 293, 298, 303, and 308 K.

Figure 6 provides a graphic representation of the temperature increases recorded,  $T_s - T_B$ , against the concentrations of alkanolamine for each series of tem-



**Figure 6.** Variation in the increase of interfacial temperature with the concentration in the experiments of MIPA at the  $T_B$  values considered.

peratures. At low concentrations, we find an appreciable rise in  $\Delta T$ , though at  $C_{B0}$ , at higher concentrations this rise remains constant, possibly due to an elimination of the heat produced by convection transport toward the gaseous phase in addition to transfer toward the liquid phase.

On the other hand, it should be pointed out that the determination of the temperature  $T_s$  also made it possible, after evaluating  $C_{As}^*$  and  $D_{As}$ , using eq 26, to reproduce acceptably the experimental values  $N_A$  vs  $C_{B0}$ , as shown in Figure 4, where the model is represented in an unbroken line.

**Enhancement Factors.** After we calculate the temperature in the film of the interface,  $T_s$ , and consider that the kinetic constant of the  $\text{CO}_2$  reaction with MIPA was well-established and can be determined along a wide range of temperatures by the expression of Hikita *et al.* (1977):

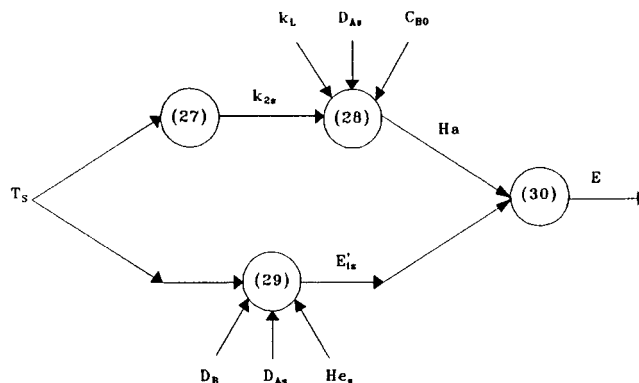
$$\log k_2 = 10.96 - \frac{2186}{T} \quad (27)$$

the determination of the number of Hatta,  $Ha$ , is immediate by the following equation:

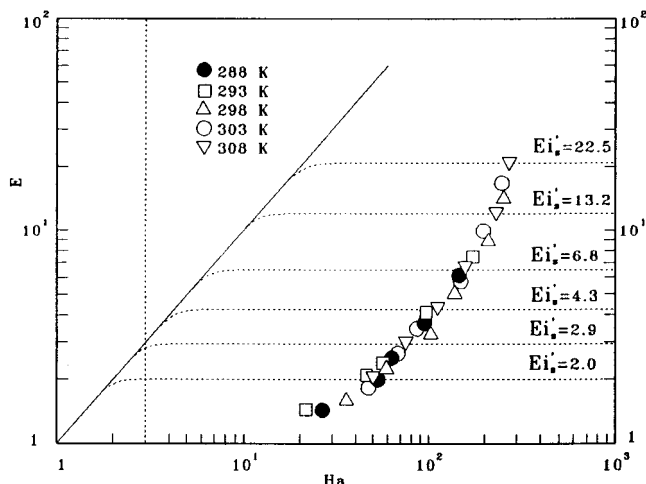
$$Ha = \sqrt{\frac{k_{2s} C_{B0} D_{As}}{k_L^2}} \quad (28)$$

In addition, accepting the hypothesis described in the previous section, we can evaluate the instantaneous-enhancement factor at the temperature  $T_s$ ,  $E'_{is}$ ,

$$E'_{is} = 1 + \frac{D_B}{2D_{As}} \frac{C_{B0} He_s}{p_{As}} \quad (29)$$



**Figure 7.** Calculation sequence for the determination of  $E$  and  $Ha$ .



**Figure 8.** Variation of the acceleration factor ( $E$ ) with the module of Hatta ( $Ha$ ) in the experiments of MIPA at the temperatures indicated.

With the  $E'_{is}$  and  $Ha$  values, and using the expression of Decoursey (1974) to facilitate the calculation as much as possible, we finally determine the enhancement factor,  $E$ :

$$E = \sqrt{\frac{Ha^4}{4(E'_{is} - 1)^2} + \frac{E'_{is} Ha^2}{E'_{is} - 1} + 1} - \frac{Ha^2}{2(E'_{is} - 1)} \quad (30)$$

A summary of the calculation sequence for determining the number of Hatta and the enhancement factors appears in the diagram of Figure 7, and the values are given in Table 2. We find in each experiment, from the five series, that

$$E \approx E'_{is}$$

$$Ha > 10E'_{is}$$

These results confirm that the reaction regime is instantaneous. This fact is demonstrated also on representing  $E$  against  $Ha$  (Figure 8) on logarithm coordinates, showing that all the points adjust acceptably to the same curve.

## Nomenclature

$A$  = interfacial area,  $\text{m}^2$

$C_{A0}$  = initial concentration of  $\text{CO}_2$  in the aqueous phase,  $\text{kmol}/\text{m}^3$

$C_A^*$  =  $\text{CO}_2$  concentration in equilibrium with the gaseous phase,  $\text{kmol/m}^3$   
 $C_{B0}$  = initial concentration of amine in the aqueous phase,  $\text{kmol/m}^3$   
 $D_A$  = diffusion coefficient of component A ( $\text{CO}_2$ ) in the aqueous alkanolamine solution,  $\text{m}^2/\text{s}$   
 $D_{As}$  = diffusion coefficient of  $\text{CO}_2$  in the liquid phase at the temperature  $T_s$ ,  $\text{m}^2/\text{s}$   
 $D_B$  = diffusion coefficient of alkanolamine in the liquid phase,  $\text{m}^2/\text{s}$   
 $D_{\text{CO}_2, \text{w}}$  = diffusion coefficient of  $\text{CO}_2$  in water,  $\text{m}^2/\text{s}$   
 $D_{\text{N}_2\text{O}, \text{am}}$  = diffusion coefficient of  $\text{N}_2\text{O}$  in the amine solution,  $\text{m}^2/\text{s}$   
 $D_{\text{N}_2\text{O}, \text{w}}$  = diffusion coefficient of  $\text{N}_2\text{O}$  in water,  $\text{m}^2/\text{s}$   
 $E$  = enhancement factor, dimensionless  
 $E_i$  = instantaneous-enhancement factor, dimensionless  
 $E_{is}$  = modified instantaneous-enhancement factor at the temperature  $T_s$ , dimensionless  
 $g$  = gravity acceleration,  $\text{m/s}^2$   
 $Ha$  = Hatta number, dimensionless  
 $He$  = Henry's law constant,  $\text{atm}\cdot\text{m}^3/\text{kmol}$   
 $He_s$  = Henry's law constant at the temperature  $T_s$ ,  $\text{kPa}\cdot\text{m}^3/\text{kmol}$   
 $k$  = reaction rate constant,  $\text{m}^3/(\text{kmol}\cdot\text{s})$   
 $k_2$  = second-order reaction-rate constant,  $\text{m}^3/(\text{kmol}\cdot\text{s})$   
 $k_{2s}$  = second-order reaction-rate constant at the temperature  $T_s$ ,  $\text{m}^3/(\text{kmol}\cdot\text{s})$   
 $k_L$  = liquid-phase mass-transfer coefficient,  $\text{m/s}$   
 $m$  = order of reaction with respect to  $\text{CO}_2$   
 $N_A$  = rate of absorption per unit interfacial area,  $\text{kmol}/(\text{m}^2\cdot\text{s})$   
 $n$  = order of reaction with respect to amine  
 $n'$  = rate of absorption of  $\text{CO}_2$ ,  $\text{kmol/s}$   
 $P$  = total pressure,  $\text{kPa}$   
 $p_A$  = partial pressure of the  $\text{CO}_2$ ,  $\text{kPa}$   
 $p_{As}$  = partial pressure of the  $\text{CO}_2$  at the temperature  $T_s$ ,  $\text{kPa}$   
 $p_v$  = vapor pressure of the water,  $\text{kPa}$   
 $Q$  =  $\text{CO}_2$  absorbed per unit interfacial area,  $\text{kmol/m}^2$   
 $Q'$  = volumetric flow rate of absorbed  $\text{CO}_2$ ,  $\text{m}^3/\text{s}$   
 $R$  = gas constant,  $\text{kPa}\cdot\text{m}^3/(\text{kmol}\cdot\text{K})$   
 $Re$  = liquid-phase Reynolds number,  $\omega\phi^2\rho/\mu$   
 $Sc$  = Schmidt number for the liquid phase,  $\mu/(\rho\cdot D_A)$   
 $Sh'$  = modified Sherwood number for the liquid phase,  $(k_L/D_A)(\mu^2/(g\rho^2))^{1/3}$   
 $T$  = temperature,  $\text{K}$   
 $T_B$  = temperature in the bulk liquid,  $\text{K}$   
 $T_s$  = temperature in the interfacial film,  $\text{K}$   
 $t$  = time,  $\text{s}$   
 $z$  = stoichiometric coefficient

#### Greek Letters

$\gamma$  = constant defined in eq 6  
 $\eta$  = carbonation ratio, mol of  $\text{CO}_2$ /mol of amine  
 $\theta$  = average life of surface elements,  $\text{s}$   
 $\mu$  = liquid-phase viscosity,  $\text{Pa}\cdot\text{s}$   
 $\mu_{\text{am}}$  = viscosity of the solution amine,  $\text{Pa}\cdot\text{s}$   
 $\mu_{\text{w}}$  = viscosity of the pure water,  $\text{Pa}\cdot\text{s}$

$\rho$  = liquid-phase density,  $\text{kg/m}^3$   
 $\tau_1, \tau_2$  = constants defined in eq 9  
 $\phi$  = contactor diameter,  $\text{m}$   
 $\omega$  = speed of liquid impeller,  $\text{rpm}$

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