

# Absorption of Carbon Dioxide into Aqueous Solutions of Triethanolamine

**Jose L. Sotelo**

Departamento de Ingenieria Quimica  
Universidad Complutense  
28040 Madrid, Spain

**F. Javier Benitez**

**Jesus Beltran-Heredia**

**Concepcion Rodriguez**

Departamento de Ingenieria Quimica  
Universidad de Extremadura  
06071 Badajoz, Spain

In industrial gas treating processes, acid gases such as  $\text{H}_2\text{S}$  and  $\text{CO}_2$  must be removed from sour gas streams. Tertiary amines have been found to be effective solvents for the selective absorption of  $\text{H}_2\text{S}$ . The reaction between  $\text{H}_2\text{S}$  and aqueous amines involves only a proton transfer, and it can be considered as infinitely fast (Danckwerts and Sharma, 1966). The reaction of  $\text{CO}_2$  with an amine, however, has a finite rate and therefore governs the degree of selectivity of the process. This reaction must be studied to model the rates of absorption that are found in industrial absorbers.

The tertiary amines that have been studied most extensively are triethanolamine (TEA) and methyldiethanolamine (MDEA). The reaction between carbon dioxide and TEA has been investigated by Sada et al. (1976), Hikita et al. (1977), Donaldson and Nguyen (1980), Barth et al. (1981) and Blauwhoff et al. (1984). More recently, Sada et al. (1989) have studied the same reaction in nonaqueous solvents.

While for the  $\text{CO}_2$ /MDEA system there is good agreement between the kinetic results reported by several authors at different temperatures, for the  $\text{CO}_2$ /TEA system most of the authors mentioned above only report values for the rate constant at 25°C; further, there are significant discrepancies among the rate constants reported by them for 25°C.

In this work we confirm the mechanism proposed for the reaction between  $\text{CO}_2$  and tertiary amines; we verify the value of the kinetic rate constant at 25°C, and we report new data at

temperatures from 20 to 40°C for the absorption of  $\text{CO}_2$  into aqueous solutions of TEA.

## Theory

While the mechanism for the reaction of  $\text{CO}_2$  with the tertiary amines has been studied by several authors, it is not fully understood. The overall reaction can be written as:

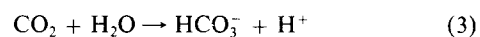


According to Blauwhoff et al. (1984), for the experimental conditions used in this work (pH between 8 and 10), the following reactions can occur in aqueous solutions:

*Bicarbonate formation:*



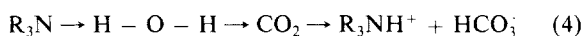
*Carbonic acid formation:*



However, the rates measured for  $\text{CO}_2$  absorption into aqueous tertiary amines are higher than those predicted theoretically by assuming that only reactions 2 and 3 occur in parallel. Donaldson and Nguyen (1980) suggested a base catalysis of the  $\text{CO}_2$  hydration, reaction 3: they deduced that because of hydrogen bonding between the free amine and water, the unprotonated amine acts as a base catalyst, which increases the reactivity of

Correspondence concerning this paper should be addressed to F. J. Benitez.

water towards CO<sub>2</sub>:



This reaction is of first order in both carbon dioxide and unprotonated amine.

In conclusion, the most important reactions which CO<sub>2</sub> undergoes in aqueous solutions of tertiary amines are Eqs. 2 and 4. The overall rate of reaction may be expressed as

$$r = (k_{OH^-}[OH^-] + k_2[R_3N])[CO_2] = k_{ov}[CO_2] \quad (5)$$

where  $k_2$  is the second-order rate constant for reaction 4, and  $[R_3N]$  is the free amine concentration. Reaction 2 has been studied extensively by Pinsent et al. (1956) including the rate constant.

According to the film theory (Levenspiel, 1972; Charpentier, 1981), during the absorption of a gas into a liquid accompanied by an irreversible chemical reaction in the liquid, the gas finds three resistances in series: the gas film, the liquid film, and the liquid bulk. Chemical reaction can occur in both the liquid film and the liquid bulk. Fast reactions occur in the liquid film during the transport of gas. Slow reaction, take place mainly in the liquid bulk, even though a negligible amount reacts in the diffusion film.

The parameter that allows us to ascertain the type of kinetic regime is the Hatta number. For a second-order irreversible reaction, this number is given by:

$$Ha = \sqrt{\frac{D_A k_2 C_B}{k_L^2}} \quad (6)$$

where  $k_2$  is the reaction rate constant,  $D_A$  is the diffusivity of the solute in the liquid, and  $c_B$  is the bulk solute concentration. According to Charpentier (1981), low values of  $Ha$  (viz.

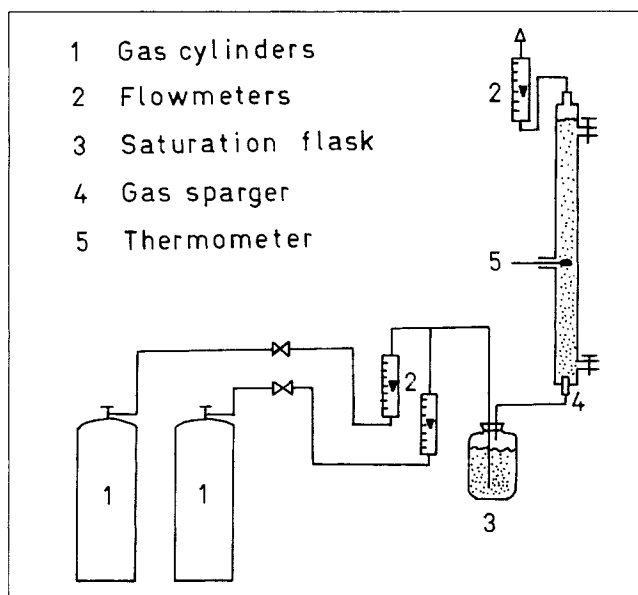


Figure 1. Experimental setup.

Table 1a. Solubility of CO<sub>2</sub> in TEA Solutions

[TEA] mol/m <sup>3</sup>	20°C He (CO <sub>2</sub> -TEA) kPa · m <sup>3</sup> /mol	30°C He (CO <sub>2</sub> -TEA) kPa · m <sup>3</sup> /mol	40°C He (CO <sub>2</sub> -TEA) kPa · m <sup>3</sup> /mol
10	2.62	3.29	4.09
50	2.63	3.31	4.11
100	2.65	3.33	4.14
250	2.71	3.42	4.24
500	2.85	3.59	4.46

between 0.02 and 0.3) indicate that the reaction is slow, while values higher than 3 indicate that the reaction is fast.

For the case of slow reaction, the absorption rate is given by:

$$N_A \cdot a = \frac{P_A}{\frac{1}{k_{Ga}} + \frac{He}{k_L a} + \frac{He}{k_2 C_B (1 - E_G)}} \quad (7)$$

## Experimental Apparatus and Procedure

The bubble column shown in Figure 1 was used for the kinetic studies. The gas sparger used was a single nozzle, located at the bottom of the column. The bubble column operated continuously with respect to the gas and batchwise with respect to the amine solutions. Other details of the apparatus are given by Sotelo et al. (1990).

Pure carbon dioxide, or carbon dioxide mixed with oxygen to adjust the partial pressures, flows initially through a flowmeter. The gas is then saturated at room temperature and introduced to the column through the gas sparger.

The amine solution concentrations ranged from 10 to 500 mol/m<sup>3</sup>. Partial pressures of CO<sub>2</sub> varied from 5 to 101 kPa, and the experiments were carried out at 20, 30 and 40°C. The total gas flow rate was kept constant at 16 L/h at room conditions.

The initial concentration of amine was determined by titration with HCl solutions using methyl-orange as an indicator. The rate of absorption was calculated from inlet and outlet CO<sub>2</sub> flow rates, measured with flowmeters, according to the procedure reported by Haimour et al. (1987).

Values for the solubility and diffusivity of CO<sub>2</sub> in TEA solutions were calculated by means of the CO<sub>2</sub>-N<sub>2</sub>O analogy. This method has been used, among others, by Sada et al. (1977, 1978), Alvarez-Fuster et al. (1980, 1981), Laddha et al. (1981), Haimour and Sandall (1984), and Al-Ghawar et al. (1989) to estimate these parameters for CO<sub>2</sub> in various amine solutions with good results.

Table 1 shows the final values determined for CO<sub>2</sub>-TEA

Table 1b. Diffusion Coefficient for CO<sub>2</sub> in TEA Solutions

[TEA] mol/m <sup>3</sup>	20°C D <sub>A</sub> (CO <sub>2</sub> -TEA) m <sup>2</sup> /s	30°C D <sub>A</sub> (CO <sub>2</sub> -TEA) m <sup>2</sup> /s	40°C D <sub>A</sub> (CO <sub>2</sub> -TEA) m <sup>2</sup> /s
10	1.68 · 10 <sup>-9</sup>	2.14 · 10 <sup>-9</sup>	2.67 · 10 <sup>-9</sup>
50	1.67 · 10 <sup>-9</sup>	2.12 · 10 <sup>-9</sup>	2.65 · 10 <sup>-9</sup>
100	1.66 · 10 <sup>-9</sup>	2.10 · 10 <sup>-9</sup>	2.63 · 10 <sup>-9</sup>
250	1.62 · 10 <sup>-9</sup>	2.05 · 10 <sup>-9</sup>	2.56 · 10 <sup>-9</sup>
500	1.55 · 10 <sup>-9</sup>	1.97 · 10 <sup>-9</sup>	2.46 · 10 <sup>-9</sup>

**Table 2. Values of  $k_L a$ ,  $E_G$  and  $k_{OH}$**

$T$ °C	$k_L a \cdot 10^4$ $s^{-1}$	$E_G \cdot 10^3$	$k_{OH} \cdot 10^{-3}$ $m^3/kmol \cdot s$
20	36.09	17.62	5.68
30	37.41	17.67	12.04
40	39.11	17.70	24.31

solubilities and diffusivities at different temperatures and concentrations.

## Results and Discussion

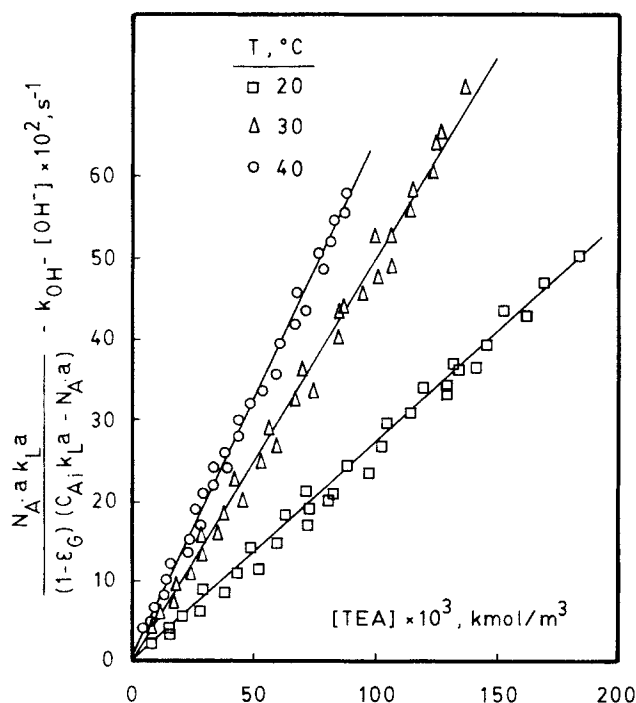
For all the kinetic experiments conducted in the present work, the condition of slow-reaction regime is fulfilled; this point will be proved later. Equation 7 gives the absorption rate of  $CO_2$  under this condition.

As was mentioned earlier, reactions 2 and 4 must be taken into account. Moreover, since  $CO_2$  is sparingly soluble in water, for the absorption of  $CO_2$  into aqueous solutions gas-phase resistance to mass transfer can be considered negligible. Under these assumptions, Eq. 7 becomes:

$$N_A \cdot a = \frac{P_A}{\frac{He}{k_L a} + \frac{He}{(k_2[TEA] + k_{OH}[OH^-])(1 - E_G)}} \quad (8)$$

Assuming that Henry's law can be used, Eq. 8 can be rearranged to give:

$$\frac{(N_A \cdot a)(k_L a)}{(1 - E_G)(C_{Ai} k_L a - N_A \cdot a)} - k_{OH}[OH^-] = k_2[TEA] \quad (9)$$



**Figure 2. Rate constant determination.**

**Table 3. Values for  $k_2$**

$T, ^\circ C$ $k_2, m^3/kmol \cdot s$	20	30	40
	2.72	4.96	6.62

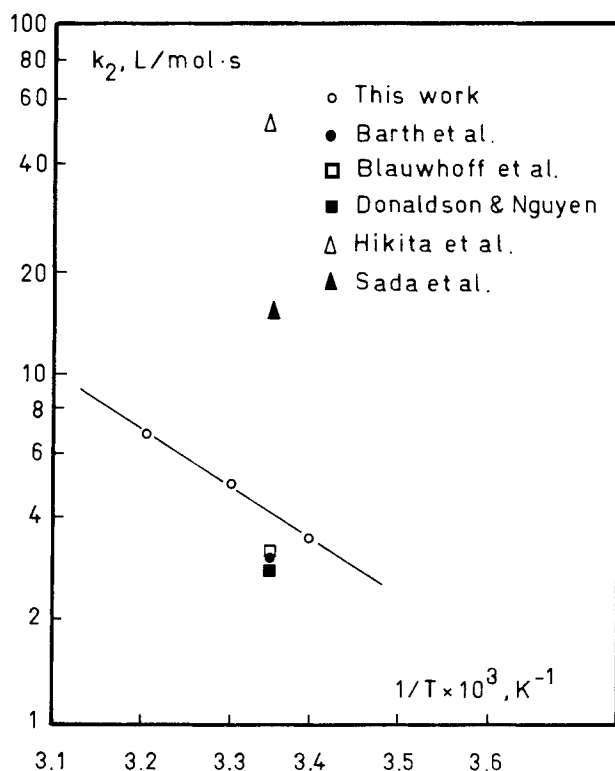
According to this equation, a plot of the lefthand side against the free amine concentration must give a straight line; the slope of this line can be used to determine the second-order rate constant.

Values of hydroxyl ion and unprotonated amine concentrations can be estimated for each experiment using the equilibrium model described by Blauwhoff et al. (1984). The product  $(N_A \cdot a)$  was obtained experimentally from the absorption data. The equilibrium concentration  $c_{Ai}$  was deduced from the Henry's law constants given in Table 1. The constant  $k_{OH^-}$  was obtained from Pinsent et al. (1956). The volumetric mass transfer coefficient  $k_L a$  and the gas holdup  $E_G$  were deduced experimentally in previous work by Sotelo et al. (1990). Table 2 summarizes the values of these parameters corresponding to the temperatures studied here.

Figure 2 shows the results corresponding to experiments at 20, 30 and 40°C. Table 3 gives the second rate constants deduced by a least-squares analysis. As shown in Figure 3, a plot of  $\log k_2$  v.  $T^{-1}$  indicates that the Arrhenius relationship is followed. The data are well correlated by the expression:

$$k_2 = 3.311 \times 10^6 \exp(-4,089/T) \quad (10)$$

Figure 3 also shows the interpolated constant at 25°C and the values reported by other authors. Note the good agreement



**Figure 3. Arrhenius relationship for  $k_2$ .**

among the values  $2.71 \text{ m}^3/\text{kmol} \cdot \text{s}$  by Donaldson and Nguyen (1980),  $2.85 \text{ m}^3/\text{kmol} \cdot \text{s}$  by Barth et al. (1981),  $2.9 \text{ m}^3/\text{kmol} \cdot \text{s}$  by Blauwhoff et al. (1984), and  $3.6 \text{ m}^3/\text{kmol} \cdot \text{s}$  from the present investigation. These values are all significantly lower compared to the  $16.8 \text{ m}^3/\text{kmol} \cdot \text{s}$  reported by Sada et al. (1976) and the  $50.1 \text{ m}^3/\text{kmol} \cdot \text{s}$  reported by Hikita et al. (1977). As Versteeg and van Swaaij (1988) pointed out, these higher values are probably due to small amounts of primary and secondary amine impurities that can have an overruling effect (even at very low concentrations) on the reaction rates that are measured experimentally.

The deduced constants are used to verify the condition of slow kinetic regime. The Hatta number, which for this system is given by

$$Ha = \sqrt{\frac{D_A(k_2[TEA] + k_{OH^-}[OH^-])}{k_L^2}} \quad (11)$$

has been calculated for all the experiments, and it is always found to be between 0.08 and 0.22. The condition of slow regime is therefore satisfied for all the temperatures and amine concentrations studied in this work.

## Notation

- $c_{Ai}$  = interfacial concentration of solute gas,  $\text{kmol}/\text{m}^3$   
 $c_B$  = free amine concentration in liquid bulk,  $\text{kmol}/\text{m}^3$   
 $D_A$  = diffusivity of gas in the liquid phase,  $\text{m}^2/\text{s}$   
 $E_G$  = gas holdup  
 $Ha$  = Hatta number  
 $He$  = Henry's law constant,  $\text{kPa} \cdot \text{m}^3/\text{mol}$   
 $k_2$  = second-order rate constant,  $\text{m}^3/\text{kmol} \cdot \text{s}$   
 $k_{OH^-}$  = second-order rate constant for reaction of  $\text{CO}_2$  with  $\text{OH}^-$ ,  $\text{m}^3/\text{kmol} \cdot \text{s}$   
 $k_{ov}$  = pseudofirst-order overall rate constant,  $\text{s}^{-1}$   
 $k_L$  = liquid mass transfer coefficient,  $\text{m}/\text{s}$   
 $k_L a$  = volumetric mass transfer coefficient in liquid phase,  $\text{s}^{-1}$   
 $k_G a$  = volumetric mass transfer coefficient in gas phase,  $\text{kmol}/\text{m}^3 \cdot \text{s} \cdot \text{kPa}$   
 $N_A \cdot a$  = rate of absorption of solute gas in liquid,  $\text{kmol}/\text{s} \cdot \text{m}^3$   
 $[\text{OH}^-]$  = concentration of  $\text{OH}^-$  ions,  $\text{kmol}/\text{m}^3$   
 $P_A$  = gas partial pressure,  $\text{kPa}$   
 $r$  = rate of reaction of solute gas,  $\text{kmol}/\text{m}^3 \cdot \text{s}$   
 $T$  = temperature absolute,  $\text{K}$   
 $[TEA]$  = concentration of unprotonated amine,  $\text{kmol}/\text{m}^3$

## Literature Cited

- Al-Ghawas, H. A., G. Ruiz-Ibanez, and O. C. Sandall, "Absorption of Carbonyl Sulfide in Aqueous Methyldiethanolamine," *Chem. Eng. Sci.*, **44**, 631 (1989).
- Alvarez-Fuster, C., N. Midoux, A. Laurent, and J. C. Charpentier, "Chemical Kinetics of the Reaction of Carbon Dioxide with Amines in Pseudo  $m$ -nth-Order Conditions in Aqueous and Organic Solutions," *Chem. Eng. Sci.*, **35**, 1717 (1980).
- , "Chemical Kinetics of the Reaction of Carbon Dioxide with Amines in Pseudo  $m$ -nth-Order Conditions in Polar and Viscous Organic Solutions," *Chem. Eng. Sci.*, **36**, 1513 (1981).
- Barth, D., C. Tondre, G. Lappai, and J. J. Delpuech, "Kinetic Study of Carbon Dioxide Reaction with Tertiary Amines in Aqueous Solutions," *J. Phys. Chem.*, **85**, 3660 (1981).
- Blauwhoff, P. M. M., G. F. Versteeg, and W. P. M. Van Swaaij, "A Study on the Reaction Between  $\text{CO}_2$  and Alkanolamines in Aqueous Solutions," *Chem. Eng. Sci.*, **39**, 207 (1984).
- Charpentier, J. C., *Advances in Chemical Engineering*, Vol. 11, p. 3, Academic Press, New York (1981).
- Danckwerts, P. V., and M. M. Sharma, "The Absorption of Carbon Dioxide into Solutions of Alkalis and Amines," *Chem. Engr.*, **10**, CE244 (1966).
- Donaldson, T. L., and Y. N. Nguyen, "Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes," *Ind. Eng. Chem. Fund.*, **19**, 260 (1980).
- Haimour, N. K., and O. C. Sandall, "Absorption of Carbon Dioxide into Aqueous Methyldiethanolamine," *Chem. Eng. Sci.*, **39**, 1971 (1984).
- Haimour, N. K., A. Bidarian, and O. C. Sandall, "Kinetics of the Reaction Between Carbon Dioxide and Methyldiethanolamine," *Chem. Eng. Sci.*, **42**, 1393 (1987).
- Hikita, H., S. Asai, H. Ishikawa, and M. Honda, "The Kinetics of Reactions of Carbon Dioxide with Monoethanolamine, Diethanolamine and Triethanolamine by a Rapid Mixing Method," *Chem. Eng. J.*, **13**, 7 (1977).
- Laddha, S. S., J. M. Diaz, and P. V. Danckwerts, "The  $\text{N}_2\text{O}$  Analogy: The Solubilities of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  in Aqueous Solutions of Organic Compounds," *Chem. Eng. Sci.*, **36**, 228 (1981).
- Levenspiel, O., *Chemical Engineering Reaction*, 2nd ed., p. 411, Wiley, New York (1972).
- Pinsent, B. R. W., L. Pearson, and F. J. W. Roughton, "The Kinetics of Combination of  $\text{CO}_2$  with  $\text{OH}^-$ ," *Trans. Farad. Soc.*, **52**, 1512 (1956).
- Sada, E., H. Kumazawa, and M. A. Butt, "Gas Absorption with Consecutive Chemical Reaction: Absorption of Carbon Dioxide into Aqueous Amine Solutions," *Can. J. Chem. Eng.*, **54**, 421 (1976).
- Sada, E., H. Kumazawa, and M. A. Butt, "Solubilities of Gases in Aqueous Solutions of Amine," *J. Chem. Eng. Data*, **22**, 277 (1977).
- , "Solubility and Diffusivity of Gases in Aqueous Solutions of Amines," *J. Chem. Eng. Data*, **23**, 161 (1978).
- Sada, E., H. Kumazawa, Y. Ikehara, and Z. Q. Han, "Chemical Kinetics of the Reaction of Carbon Dioxide with Triethanolamine in Nonaqueous Solvents," *Chem. Engr.*, **40**, 7 (1989).
- Sotelo, J. L., F. J. Benítez, J. Beltrán-Heredia, and M. C. Rodríguez, "Retención de Gas y Coeficientes de Transferencia de Materia en Columnas de Burbujeo," *An. Quim., Ser. A*, **86**, 188 (1990).
- Versteeg, G. F., and W. P. M. Van Swaaij, "On the Kinetics Between  $\text{CO}_2$  and Alkanolamines both in Aqueous and Non-aqueous Solutions—II. Tertiary Amines," *Chem. Eng. Sci.*, **43**, 587 (1988).

Manuscript received Jan. 30, 1990, and revisions received May 22, 1990.