

# GAS-LIQUID MASS TRANSFER WITH PARALLEL REVERSIBLE REACTIONS—III. ABSORPTION OF CO<sub>2</sub> INTO SOLUTIONS OF BLENDS OF AMINES

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**Abstract**—A numerical method developed by Versteeg *et al.* (1989, *Chem. Engng Sci.* **44**, 2295–2310; 1990, *Chem. Engng Sci.* **45**, in press) is applied to the absorption of CO<sub>2</sub> into solutions of blends of amines. The experimental results of Critchfield and Rochelle (1987) are evaluated with the numerical model. It is shown that a rigorous numerical solution of the differential equations describing the mass transfer gives more insight into the actual process than analytical approximations based on a reduction of the number of reactions by neglecting or lumping reactions.

## 1. INTRODUCTION

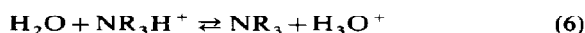
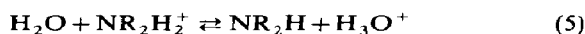
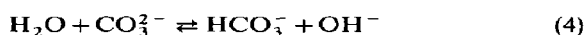
In Part I (Bosch *et al.*, 1989a) the available solutions to models of absorption with multiple parallel reversible reactions were discussed. It was concluded that only numerical solutions are generally applicable. The numerical method developed by Versteeg *et al.* (1989a) was applied to the absorption of CO<sub>2</sub> into aqueous sterically hindered amine solutions. In Part II (Bosch *et al.*, 1989b) the absorption of CO<sub>2</sub> into mixtures of carbonate and amines was discussed.

In this part the absorption of CO<sub>2</sub> into aqueous solutions of mixtures of amines will be the subject. The work of Phukan (1985) and Chakravarty *et al.* (1985), and the publications of Versteeg *et al.* (1990) and Critchfield and Rochelle (1987) will be discussed.

Blending of amines is considered to be attractive because in this way the high capacity of tertiary amines can be combined with the high absorption rates of primary or secondary amines. Blends are also more flexible than singular amines because the relative concentration of the amines can be varied.

## 2. REACTION MODEL FOR ABSORPTION OF CO<sub>2</sub> INTO AQUEOUS SOLUTIONS OF AMINE BLENDS

Usually blends of a primary or secondary amine and a tertiary amine are used. The relevant reactions are



The protonation reactions (4)–(7) are instantaneous with respect to mass transfer and are therefore considered to be at equilibrium:

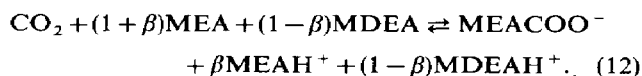
$$K_p = \frac{[\text{NR}_2\text{H}][\text{H}_3\text{O}^+]}{[\text{NR}_2\text{H}_2^+]} \quad (8)$$

$$K'_p = \frac{[\text{NR}_3][\text{H}_3\text{O}^+]}{[\text{NR}_3\text{H}^+]} \quad (9)$$

$$K_{c2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} \quad (10)$$

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+]. \quad (11)$$

As in Parts I (Bosch *et al.*, 1989a) and II (Bosch *et al.*, 1989b) the stoichiometry of the reactions of CO<sub>2</sub> with the amines is not important because of the instantaneous equilibration of the protonation reactions. In fact methyldiethanolamine (MDEA) deprotonates part of the zwitterion formed, giving rise to the overall reaction eq. (12). The influence of the tertiary amine on the primary- or secondary-amine reaction rate through the deprotonation of the zwitterion has to be taken into account, just as for CO<sub>3</sub><sup>2-</sup> in Part II (Bosch *et al.*, 1989b).



## 3. REVIEW OF LITERATURE

### 3.1. General

Blends of amines have recently become a topic in research on gas treating processes. Although there has been much speculation about the use of blends of amines not many experimental results are available in the literature. Contributions to this subject were presented by Chakravarty *et al.* (1985), Phukan (1985), Chakravarty (1985), Critchfield and Rochelle (1987, 1988), Critchfield (1988) and Rangwala *et al.* (1988). Research in a related field was done by Donaldson and Lapinas (1980) who studied the transportation of

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CO<sub>2</sub> through a membrane with two carriers, e.g. monoethanolamine (MEA) and triethanolamine.

An influence of the blending of amines on the absorption rate was indicated by Blauwhoff *et al.* (1984). They ascribed differences in rate constants for slowly reacting amines from various literature sources to the presence of small amounts of faster reacting contaminants. A detailed study on this subject is presented by Versteeg *et al.* (1990). Versteeg and van Swaaij (1988) simulated the effect of contaminants on the absorption rate in order to verify whether this could be neglected for the conditions of their experiments. Critchfield and Rochelle (1988) and Rangwala *et al.* (1988) presented experimental data on the influence of the addition of various primary and secondary amines on the absorption rates of CO<sub>2</sub> into tertiary amine solutions.

### 3.2. Absorption of CO<sub>2</sub> into MEA–MDEA blends

Chakravarty *et al.* (1985) studied absorption of CO<sub>2</sub> and H<sub>2</sub>S into MEA–MDEA blends theoretically. These blends are attractive because they combine the high capacity of MDEA solutions with the high reaction rates of MEA solutions. An additional advantage of blends is that by varying the composition the selectivity towards H<sub>2</sub>S can be controlled. The authors derived an equilibrium model (Chakravarty, 1985) to calculate the CO<sub>2</sub> and H<sub>2</sub>S equilibrium concentrations above loaded amine blends and also developed an approximate analytical solution for the differential equations of the film model (Phukan, 1985). The approximate solution was tested by comparing it with a numerical solution method. The equilibrium and rate models were combined to simulate the absorption of CO<sub>2</sub> and H<sub>2</sub>S into MEA–MDEA mixtures with varying liquid loadings. The results showed that large savings could be achieved in industrial gas cleaners by using blends of amines instead of single amines.

Critchfield and Rochelle (1987) studied the MDEA–MEA system experimentally by means of the absorption of CO<sub>2</sub> into a 1.36 molal MDEA–0.61 molal MEA solution at 304 K and a CO<sub>2</sub> pressure of 96 kPa by following the liquid composition in a stirred-cell batch reactor.

They presented a theoretical treatment of the absorption of CO<sub>2</sub> into amine blends. By substituting the sum of all pseudo-first-order reaction rates in the definition of the Hatta number a simple solution was obtained. Because this solution is restrictive in its applicability a more realistic situation for which the MEA–CO<sub>2</sub> reaction approaches equilibrium at the interface and the MDEA reaction is fast was considered. There are two asymptotic cases comparable to those pointed out by Astarita *et al.* (1981). The authors state that the rate of carbamate reversion determines what model is best. Although no actual reaction equations were presented we assume the authors considered reactions (2), (13), (14) and (3), in which reaction (13) is the carbamate reversion. Note

that the overall effect of the first three reactions is reaction (3) and that reactions (2) and (14) are assumed to be instantaneous with respect to mass transfer. Now if the reversion reaction is also instantaneous with respect to mass transfer the reactions of MEA and MDEA can both be treated as instantaneous and reversible. In this case the solution is rather simple and corresponds to the homogeneous-catalysis solution given by Astarita *et al.* (1981). If the reversion reaction is slow it occurs only in the bulk of the liquid. In this case there is an extra path for CO<sub>2</sub> to the bulk of the liquid as in the shuttle mechanism. The authors calculate the shuttle mechanism enhancement factor as the sum of the instantaneous enhancement factor for MEA and the (corrected) pseudo-first-order enhancement factor for MDEA. In the intermediate range the reversibility of the reactions has to be taken into account.



The authors used only these two asymptotic models for the interpretation of their experiments. The experimental data were best predicted by the shuttle mechanism solution. It slightly underpredicts the absorption rate. The homogeneous-catalysis solution predicts far too high absorption rates. The authors conclude that the reversion reaction has to be taken into account to describe the experiments presented.

Rangwala *et al.* (1988) also studied the absorption of CO<sub>2</sub> into MEA–MDEA mixtures in a stirred-cell apparatus. The experiments were executed at rather high gas phase concentrations. Therefore there were gradients in the amine concentrations near the gas–liquid interface. So the simple pseudo-first-order model could not be used for the interpretation of the data. Rangwala *et al.* (1988) used a modified pseudo-first-order film model, in which cubic concentration profiles for the amines were assumed and the concentrations of the amines in the rate equations were set equal to the interfacial concentrations, and called this a shuttle model, because it includes shuttle effects. This model is different from the model discussed by Critchfield and Rochelle, however. The experimental absorption rates were predicted well with the model.

## 4. DISCUSSION OF THE WORK OF PHUKAN (1985)

The simulations of Phukan could not be reproduced due to insufficient availability of data. It is hard to say if the analytical approximation of Phukan is valid for a wide range of conditions. He took the simple approach of adding the reaction rates for the two amines with CO<sub>2</sub> in his differential equations. This has to be done with care because the reaction rates in blends of amines may be different from those in the single-amine systems. For the DEA–MDEA mixture this is very important because MDEA can

deprotonate the zwitterion formed in the reaction of DEA with  $\text{CO}_2$ . This is also stated by Laddha and Danckwerts (1982) and Bosch *et al.* (1989b) for  $\text{CO}_3^{2-}$ , and by Versteeg *et al.* (1990) for mixtures of amines. Tseng *et al.* (1988) presented experimental proof of this effect for DEA-promoted carbonate solutions, as did Critchfield and Rochelle (1988) for the MDEA-DEA system.

A second reservation that must be made about Phukan's analytical solution is that reactions can be coupled by mechanisms not taken into account in the reaction model. For instance the protonation equilibria and the hydration of  $\text{CO}_2$  are not incorporated in his model. One should be very careful in applying restricted reaction models to complicated problems as was shown for amine-promoted carbonate solutions (Bosch *et al.*, 1989b) and sterically hindered amine solutions (Bosch *et al.*, 1989a).

So there is some doubt about whether Phukan's model can be used for the prediction of absorption

rates under practical conditions. This matter is discussed in more detail by Bosch (1989).

## 5. SIMULATIONS OF THE EXPERIMENTS BY CRITCHFIELD AND ROCHELLE (1987)

### 5.1. Data

The experiments of Critchfield and Rochelle were simulated with the numerical film model using primarily data published by them. The data used are listed in Table 1. The diffusivities of species other than  $\text{CO}_2$  were estimated in the same way as in Part I (Bosch *et al.*, 1989a).

### 5.2. Results

In Fig. 1 the results of Critchfield and Rochelle are shown together with the results of our simulation. The complicated numerical model and the much simpler model of Critchfield and Rochelle (1987) both represent the data well over the whole range of liquid

Table 1. Parameters used in simulation of experiments by Critchfield and Rochelle (1987)

Parameter	Value		Source	
	MDEA	MEA	MDEA	MEA
$T$ (K)	304		Critchfield and Rochelle (1987)	
$C_{Am}$ ( $\text{mol m}^{-3}$ )	1150	517	Critchfield and Rochelle (1987)	
$C_{\text{CO}_2, g}$ ( $\text{mol m}^{-3}$ )	$3.70 \times 10^{-1}$		Critchfield and Rochelle (1987)	
$k_L$ ( $\text{m s}^{-1}$ )	$1.05 \times 10^{-5}$		Critchfield and Rochelle (1987)	
$m$	0.7		Critchfield and Rochelle (1987)	
$k_g$ ( $\text{m s}^{-1}$ )	100		No gas phase resistance	
$K_{c1}$ ( $\text{m}^3 \text{mol}^{-1}$ )	$3.10 \times 10^4$		Chakravarty (1985)	
$K_{c2}$ ( $\text{mol m}^{-3}$ )	$5.16 \times 10^{-8}$		Chakravarty (1985)	
$K_w$ ( $\text{mol}^2 \text{m}^{-6}$ )	$1.52 \times 10^{-8}$		Harned (1958)	
$K_p$ ( $\text{mol m}^{-3}$ )	$3.94 \times 10^{-6}$	$4.61 \times 10^{-7}$	Perrin (1965)	
$K_c$ ( $\text{m}^3 \text{mol}^{-1}$ )	0	$2.32 \times 10^{-2}$	No carbamate formation	Chan and Danckwerts (1982)
$k_{OH}$ ( $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ )	12.6		Pinsent <i>et al.</i> (1956)	
$k_2$ ( $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ )	$4.0 \times 10^{-3}$	7.93	Critchfield and Rochelle (1987)	Blauwhoff <i>et al.</i> (1984)
$D_{\text{CO}_2}$ ( $\text{m}^2 \text{s}^{-1}$ )	$1.42 \times 10^{-9}$		Critchfield and Rochelle (1987)	
$D_{AMP}$ ( $\text{m}^2 \text{s}^{-1}$ )	$0.97 \times 10^{-9}$	$1.12 \times 10^{-9}$	$D = V_b^{-0.6}$	
$D_{ion}$ ( $\text{m}^2 \text{s}^{-1}$ )	$1.08 \times 10^{-9}$		$V_b$ from Perry and Chilton (1973)	

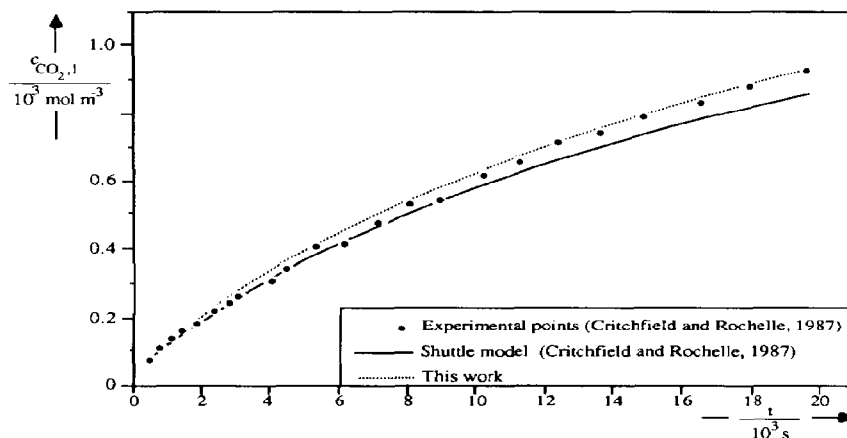


Fig. 1. Comparison of experimental and theoretical results of Critchfield and Rochelle (1987) and this work.

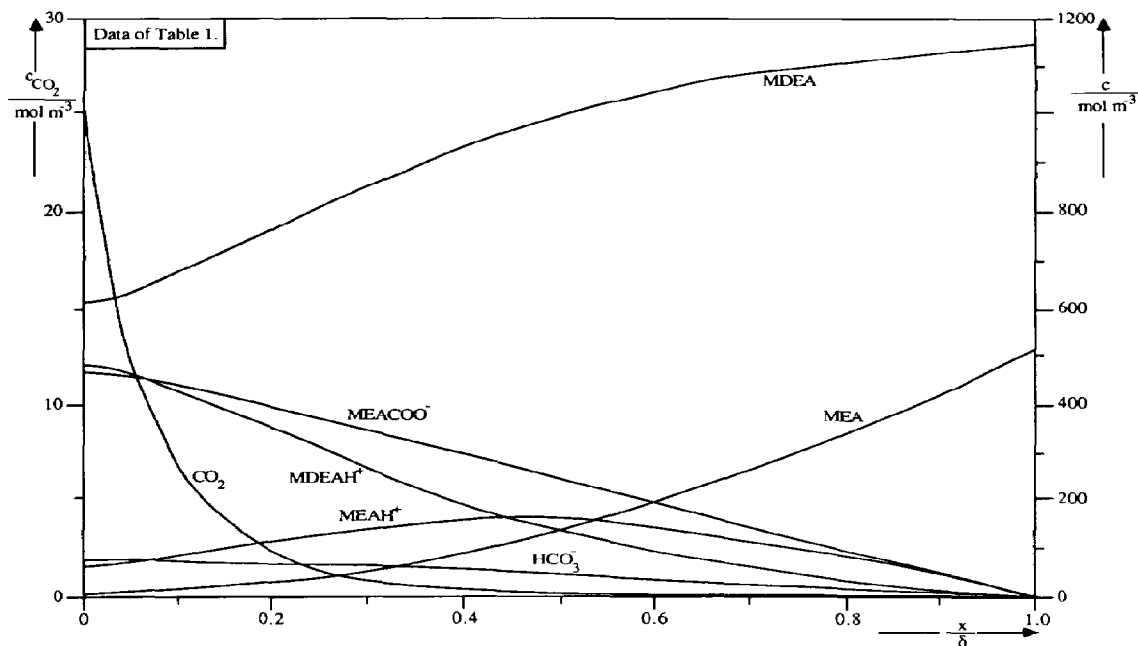


Fig. 2. Calculated concentration profiles for absorption of  $\text{CO}_2$  into an MDEA-MEA blend.

loadings. The simple model is partly correct as can be seen in Fig. 2, in which the concentration profiles calculated with the numerical model for zero liquid loading are plotted. MEA indeed provides an additional path for  $\text{CO}_2$  into the bulk of the liquid. The assumption of no concentration gradient for MDEA however, does not hold because MDEA is needed to neutralize the protons produced by the reactions of  $\text{CO}_2$ .

### 5.3. Discussion

The experimental results of Critchfield and Rochelle (1987) are predicted very well with the numerical film model. The model of Critchfield and Rochelle also works well for these conditions, but the fit seems to be partly fortuitous. Their model overestimates the mass transfer rate because it assumes that the concentration of MDEA in the film is equal to the bulk concentration, whereas in fact it is lower. Moreover the solution presented for the shuttle mechanism model does not coincide with the solution presented by Jhaveri (1969). If reversibility is taken into account the enhancement factor can be calculated (Bosch, 1989; Bosch *et al.*, 1989c). This enhancement factor is not equal to the sum of the enhancement factors of the independent reactions, but to the product of enhancement factor for MDEA and the square root of the enhancement factor for MEA. Therefore the solution of Critchfield and Rochelle (1987) underestimates the mass transfer rate. The under- and overestimation effects seem to cancel in this case.

It should be stressed that analytical approximations cannot be expected to predict the absorption rates in

this case because of the complicated nature of the absorption process.

From the concentration profiles it can be seen that the reversibility of the reactions is important as Critchfield and Rochelle (1987) stated. We have taken the reversion of carbamate into account by assuming that it proceeds by the reversal of the formation reaction, as was suggested by Danckwerts and McNeil (1967a). There might be other paths for this reversion, but no experimental proof has been given, and the path described here can explain all effects observed. This issue is discussed in more detail by Bosch (1989).

### 5.4. Conclusion

For the calculation of the absorption rates of  $\text{CO}_2$  into mixtures of amines it is important to take into account all reversible reactions simultaneously. Also one must be aware of the fact that reaction rates in mixtures can be different from reaction rates in a pure amine solution.

## 6. DISCUSSION OF THE WORK OF RANGWALA *ET AL.* (1988)

The experiments of Rangwala *et al.* (1988) were executed under conditions comparable to those of Critchfield and Rochelle (1987). Unfortunately the driving force was not specified for their experiments on the absorption into amine mixtures, preventing direct comparison with the results of Critchfield and Rochelle (1987) and numerical simulation. The shuttle model Rangwala *et al.* (1988) used for the explanation of the absorption rate data should be applicable over

as a wider range of conditions as that of Critchfield and Rochelle (1987), because it includes diffusion and reaction effects for both amines, whereas the model of Critchfield and Rochelle (1987) includes only diffusion effects for MEA and only a reaction effect for MDEA. The model of Rangwala *et al.* (1988) is more in accordance with the numerically calculated concentration profiles in Fig. 1. However, both models will fail to represent the effects of the reversibility that are clearly visible in Fig. 1.

## 7. CONCLUSIONS

For absorption processes in which more than one reaction occurs in the liquid phase a rigorous approach to the solution of the differential equations describing the mass transfer is the most fertile one. The processes occurring are often oversimplified if analytical approximations are used.

For absorption of CO<sub>2</sub> into mixtures of absorbing species (water, amines and carbonate) this means the reactions of all absorbing species have to be taken into account.

It was shown that such an approach can explain effects that could not be understood using approximate models.

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## NOTATION

$c$	concentration, mol m <sup>-3</sup>
$D$	diffusion coefficient, m <sup>2</sup> s <sup>-1</sup>
$E$	enhancement factor
$E^\infty$	enhancement factor for instantaneous reaction
$E_p$	promotion factor ( $J_{\text{promoted}}/J_{\text{unpromoted}}$ )
$k_g$	gas phase mass transfer coefficient, m s <sup>-1</sup>
$k_L$	liquid phase mass transfer coefficient, m s <sup>-1</sup>
$k_{\text{OH}}$	reaction rate constant for CO <sub>2</sub> hydration, m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
$k_1$	first-order reaction rate constant, s <sup>-1</sup>
$k_2$	second-order reaction rate constant, m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
$K_c$	carbamate stability constant $\{K_c = [\text{AmR}_2\text{COO}^-]/([\text{AmR}_2\text{H}][\text{HCO}_3^-])\}$ , m <sup>3</sup> mol <sup>-1</sup>
$K_{c1}$	equilibrium constant for CO <sub>2</sub> hydrolysis $\{K_{c1} = [\text{HCO}_3^-]/([\text{OH}^-][\text{CO}_2])\}$ , m <sup>3</sup> mol <sup>-1</sup>
$K_{c2}$	bicarbonate dissociation constant $\{K_{c2} = ([\text{CO}_3^{2-}][\text{H}^+])/[\text{HCO}_3^-]\}$ , mol m <sup>-3</sup>
$K_{\text{eq}}$	equilibrium constant for CO <sub>2</sub> -amine reaction ( $K_{\text{eq}} = K_c K_{c1} K_w/K_p$ ), m <sup>3</sup> mol <sup>-1</sup>
$K_p$	primary- or secondary-amine protonation constant ( $K_p = [\text{AmR}_2\text{H}][\text{H}^+]/[\text{AmR}_2\text{H}_2^+]$ ), mol m <sup>-3</sup>
$K_w$	dissociation constant of water ( $K_w = [\text{H}^+][\text{OH}^-]$ ), mol <sup>2</sup> m <sup>-6</sup>

$m$	distribution coefficient ( $m = [\text{CO}_2]_L/[\text{CO}_2]_g$ at equilibrium)
$r$	reaction rate, mol m <sup>-3</sup> s <sup>-1</sup>
$t$	time, s
$T$	temperature, K
$V_b$	molecular volume at normal boiling point, m <sup>3</sup> mol <sup>-1</sup>
$x$	spatial coordinate, m

## Greek letter

$\delta$	thickness of laminar film, m
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## Amine abbreviations

MEA	monoethanolamine
MDEA	methyldiethanolamine

## Subscripts

Am	amine
$g$	gas
ion	ionic products
$L, l$	liquid
$t$	total

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