GAS–LIQUID MASS TRANSFER WITH PARALLEL REVERSIBLE REACTIONS—II. ABSORPTION OF CO$_2$ INTO AMINE-PROMOTED CARBONATE SOLUTIONS

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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$_2$ into amine-promoted carbonate solutions. The experimental results of Savage *et al.* (1984, *Faraday Discuss. chem. Soc.* **77**, 17–31) 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 and numerical approximations based on a reduction of the number of reactions by neglecting or lumping reactions.
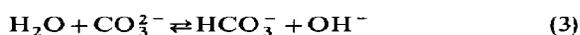
1. INTRODUCTION

In Part I (Bosch *et al.*, 1989a) the available solutions of the models which describe absorption with multiple parallel reversible reactions were discussed. It was concluded that only numerical solutions are sufficiently detailed to explain the experimental observations. The numerical method developed by Versteeg *et al.* (1989) was applied to the absorption of CO$_2$ into aqueous solutions of a sterically hindered amine. In this part the absorption of CO$_2$ into mixtures of carbonate and amines will be discussed.

These processes were extensively studied by Jeffreys and Bull (1964), McNeil and Danckwerts (1964), Shrier and Danckwerts (1969), Leder (1971), Astarita *et al.* (1981, 1982), Laddha and Danckwerts (1982), Mahajani and Danckwerts (1983a,b), Sartori and Savage (1983), Savage *et al.* (1984) and Tseng *et al.* (1988). The data of Savage *et al.* (1984) will be simulated with the numerical mass transfer model, because in this case the conditions were such that diffusion as well as the reaction rate influenced the results, and application of the numerical model offers the largest advantages. Also the mechanisms of promotion are discussed in Savage *et al.* (1984).

2. REACTION MODEL

Usually primary or secondary amines are used as rate promotors. Tertiary amines do not seem to give rise to promotion (Laddha and Danckwerts, 1982; Savage *et al.*, 1984). For primary and secondary amines the following reactions occur:

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \tag{1}$$

$$CO_2 + 2NR_2H \rightleftharpoons NR_2COO^- + NR_2H_2^+ \tag{2}$$

$$H_2O + CO_3^{2-} \rightleftharpoons HCO_3^- + OH^- \tag{3}$$

$$H_2O + NR_2H_2^+ \rightleftharpoons NR_2H + H_3O^+ \tag{4}$$
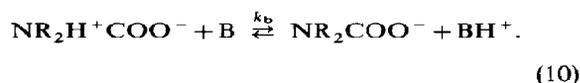
$$2H_2O \rightleftharpoons H_3O^+ + OH^-. \tag{5}$$

The reactions that involve only the transfer of a proton [reactions (3)–(5)] are regarded to be instantaneous with respect to mass transfer, and are therefore considered to be at equilibrium:

$$K_p = \frac{[NR_2H][H_3O^+]}{[NR_2H_2^+]} \tag{6}$$

$$K_{c2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} \tag{7}$$

$$K_w = [OH^-][H_3O^+]. \tag{8}$$

Reaction (2) seems to imply that all zwitterions formed in the first step [reaction (9)] of the zwitterion mechanism for the reaction of CO$_2$ with the amine [reactions (9) and (10)] are deprotonated by the amine. For the stoichiometry of the reactions this assumption is not important because all bases are equilibrated by reactions (3)–(5). From a kinetic point of view it is important to notice that all bases, including CO$_3^{2-}$, can deprotonate the zwitterion produced by reaction (9). Blauwhoff *et al.* (1984) suggested that a relation between the strength of the base and the rate of step (10) exists. Since CO$_3^{2-}$ is a strong base its contribution to the rate of step (10) can be large. This means that step (9) possibly becomes the rate-determining step in the reaction of CO$_2$ with the amine in amine-promoted carbonate solutions.

$$CO_2 + NR_2H \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} NR_2H^+COO^- \tag{9}$$

$$NR_2H^+COO^- + B \overset{k_b}{\rightleftharpoons} NR_2COO^- + BH^+. \tag{10}$$

If the reaction rate of this step is not available it can be estimated with correlation (11) (Versteeg and van Swaaij, 1988):

$$\ln k_2 = 16.26 + pK_a - \frac{7188}{T}. \tag{11}$$

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3. REVIEW OF LITERATURE

3.1. General

The rate promotion effect of the addition of amines to carbonate solutions was discovered more than 50 years ago (Killefer, 1937). The effect was attributed to the changes in surface tension caused by amines. Later, Jeffreys and Bull (1964) determined the rate of absorption of CO_2 in water, sodium carbonate solutions and sodium carbonate solutions with glycine as an additive in a laminar jet apparatus. An increase in the mass transfer rate upon addition of glycine was found and this effect was related to a decrease in the surface tension. McNeil and Danckwerts (1964) pointed out that the reaction of CO_2 with the amine could also influence the mass transfer rate.
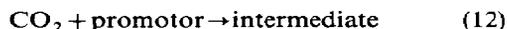
In a study on the effect of arsenite catalysts on the absorption rate of CO_2 into aqueous amine solutions Danckwerts and McNeil (1967a) suggested that amine spent in the reaction with CO_2 near the gas–liquid interface might be regenerated in the bulk by reversion of the carbamate formation reaction followed by the hydration of CO_2. This work is the first reference to a shuttle mechanism. The mechanism is schematically represented in Fig. 1. Danckwerts and McNeil (1967a) ascribed the rate-promoting effect of the addition of arsenite to catalysis of the hydration of CO_2. In amine–carbonate systems, this implies that more amine is available for reaction with CO_2 near the interface, and therefore gives rise to increased enhancement factors.

Shrier and Danckwerts (1969) studied the promotion of CO_2 absorption into potash solutions by the addition of a number of amines. Absorption rates into CO_3^{2-}/HCO_3^- buffer solutions in a stirred cell apparatus were determined. A considerable increase in the absorption rates upon addition of small amounts of amines was observed even when there was already enhancement of mass transfer in the unpromoted solutions. 2-Ethylaminoethanol proved to be an especially effective promotor. The results were interpreted in terms of shuttle mechanism.

Leder (1971) studied the absorption of CO_2 into amine-promoted potash solutions at 353 K and observed results similar to those of Shrier and Danckwerts.

Astarita et al. (1981) studied the promotion of mass transfer in carbonate solutions theoretically and pro-

posed a general mechanism of the form

$$CO_2 + promotor \rightarrow intermediate \qquad (12)$$

$$Intermediate + OH^- \rightarrow HCO_3^- + promotor. \qquad (13)$$

It was stated that for inorganic promotors such as arsenite ions both reactions are very fast and the second one is much faster than the first one. In this case the promotor is regenerated at the same location at which it is spent. In this case the mechanism resembles homogeneous catalysis. For amine promotors they stated that the intermediate is carbamate and the first step [step (12)] is faster than the second one [step (13)]. If the second reaction is slow and takes place only in the bulk of the liquid a shuttle mechanism describes the mass transfer process better. Furthermore, Astarita et al. (1981) found that a shuttle mechanism rate promotor cannot produce rate promotion in desorption. Danckwerts (1981) showed, however, that this last conclusion was incorrect.

Laddha and Danckwerts (1982) conducted experiments with mixtures of carbonate and monoethanolamine (MEA), and of carbonate or sulphate and diethanolamine (DEA). The absorption rates in DEA solutions were increased more than they were in MEA solutions upon the addition of carbonate. DEA had also been proven to be a more effective rate promotor in carbonate solutions in the experiments of Shrier and Danckwerts (1969). These results were explained with the fact that carbonate ions can deprotonate the zwitterion. In DEA solutions reaction step (10) is rate-limiting and therefore the reaction rate can be increased by addition of carbonate. Ultimately it is possible that reaction step (9) becomes rate-limiting. For MEA solutions this first step is already rate-limiting, so the reaction rate cannot be increased very much by carbonate. An increase in the rate of step (9) with the addition of sulphate and carbonate to DEA and of carbonate to MEA was observed too. This effect was related to the ionic strength, similar to its influence on the rate of the hydration of CO_2 (Savage et al., 1980). The effect was larger for the DEA–carbonate system than for the other two systems. The difference could not be explained.

Mahajani and Danckwerts (1983a,b) studied the stripping of CO_2 from amine-promoted potash solutions. Experiments with MEA, DEA, diisopropanolamine (DIPA), triethanolamine (TEA) and 2-amino-2-methylpropanol (AMP) were carried out. Desorption rates were determined in a stirred cell containing a batch of CO_2-loaded liquid at 373 K. The results were interpreted by assuming that both the reaction of CO_2 with the amine and the hydration of CO_2 were fast compared to mass transfer, and no gradients for other species than CO_2 occurred. DEA was found to be a more effective promotor than MEA. This could be explained by the fact that the rate of the desorption reaction for DEA is much higher than it is for MEA. This was concluded from the much higher equilibrium constant for MEA and the only slightly higher rate constant for the absorption reaction, under the as-
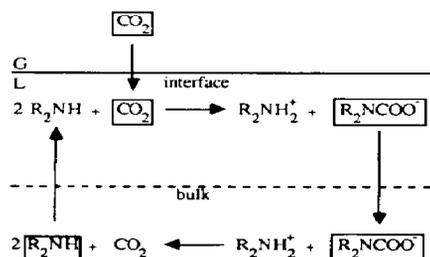

Fig. 1. Schematic representation of shuttle mechanism.

sumption that the equilibrium constant is equal to the ratio of the forward and backward reaction rate constants. TEA promoted mass transfer only very marginally which was explained by the fact that tertiary amines cannot form carbamates. No explanation of the observed promotion factors for AMP and DIPA, which were similar to those for MEA, was given.

Tseng et al. (1988) discussed the rate promotion effect of the addition of 2 or 5 wt% DEA to 25 wt% potassium carbonate solutions more rigorously. Small deviations from pseudo-first-order behaviour were corrected for by an approximate analytical model. With this model the interfacial concentration of various components needed in the reaction rate expressions could be estimated. The observed absorption rate could be explained satisfactorily. At low liquid loadings the rate of the reaction of CO_2 with DEA was controlled by the zwitterion formation step: at larger liquid loadings the deprotonation of the zwitterion became rate-limiting. The reaction rate constants for the deprotonation of the zwitterion of DEA by the various bases in the solution were determined from the absorption rate data.

3.2 Sterically hindered amines as rate promotors

Sartori and Savage (1983) and Savage et al. (1984) studied the absorption of CO_2 into and the desorption of CO_2 from amine-promoted potash solutions. They reported results for equilibrium experiments and mass transfer experiments for absorption and desorption with a sterically hindered diamine (HDA) and DEA as promotors. The data presented by Savage et al. (1984) which include the data presented by Sartori and Savage (1983) will be discussed. Sterically hindered amines are dealt with in Part I (Bosch et al., 1989a).

By fitting a plot of the equilibrium partial pressure of CO_2 vs the fractional loading of HDA- and DEA-promoted solutions with theoretical ones the stability of the carbamate was determined. From the low stability it could be concluded that HDA is indeed sterically hindered.

The rate experiments were carried out in a one-sphere absorber. Both amines increased the absorption rate even though considerable enhancement already occurred in the unpromoted solutions. A strong influence of the liquid flow rate and only a small influence of the CO_2 partial pressure on the magnitude of the absorption rates for HDA-promoted carbonate solutions was observed. From this observation it was concluded that the absorption takes place in the instantaneous regime, and therefore that the catalytic effect must be very large.

The results were interpreted in terms of the general mechanism presented by Astarita et al. (1981). Instead of OH^- in reaction (13) CO_3^{2-} was taken. They presumed the promotor was the free amine and did not give their opinion upon the form of the intermediate. The rate promotion effect was expressed as a promotion factor defined as the ratio of the absorption

rates with and without addition of the promotor. A maximum promotion factor for the shuttle mechanism was derived, based on the assumptions of an irreversible instantaneous reaction (12) and a maximum concentration of free amine in the liquid bulk. Solving this mass transfer problem gave eq. (14). The actual promotion factors were about as high as the ones predicted by this equation, so the authors concluded that the promotion effect is too large to be explained by a shuttle mechanism, and therefore a homogeneous-catalysis mechanism must be responsible for the observed effects. Another argument for this conclusion is that promotion was also observed during desorption, and, according to Astarita et al. (1981), in this case the shuttle mechanism cannot account for promotion.

$$F = \sqrt{1 + \frac{k_L^2 c_{Am}^2 K_{c2}[HCO_3^-]}{\mathbb{D}_{CO_2} k_{OH} K_W [CO_3^{2-}]([CO_2]_i - [CO_2]_b)}}.$$
(14)

An expression for the maximum absorption rate for a homogeneous-catalysis mechanism based on the assumption of instantaneous reversible reactions was derived. This relation implied that the absorption rate should be proportional to the difference between the loading in equilibrium with the interfacial CO_2 concentration and the actual liquid loading, which is generally higher for HDA-promoted solutions, and therefore HDA should be a better promotor.

A chemical mechanism for the observed effects was not presented, and the fact that tertiary amines are not effective rate promotors could not be explained.

4. SIMULATIONS

4.1. Data

Unfortunately, some of the conditions of the experiments reported by Savage et al. (1984) were not presented; however, for our purpose estimates were sufficiently accurate. The concentrations of carbonate and amine chosen were confirmed by private communication with the authors (Savage et al., 1984). The physicochemical data were those at a temperature of 363 K. The reaction rates of the amines were based on reaction (9) as the rate-limiting step: at low liquid loadings this is probably justified (Tseng et al., 1988). For HDA the value of k_2 was estimated using correlation (11). The value of k_{OH} corrected for the ionic strength was obtained from Savage et al. (1980). The rate constants for HDA and DEA were taken to vary with the ionic strength proportionally to k_{OH}. It should be noted that the exact values of the rate constants for the amines are not very important since the reactions are essentially instantaneous with respect to mass transfer at the present conditions, as can be concluded from the results below. Errors introduced for instance by deviation of the actual reaction rate from eq. (11) are therefore not important. The values for the constants used are presented in Table 1.

Liquid compositions were calculated by solving the relevant equilibrium equations. Non-idealities in the liquid phase equilibria were not taken into account.

Table 1. Parameters used in evaluation of absorption experiments by Savage *et al.* (1984).

Parameter	Value		Source	
	DEA	HDA	DEA	HDA
c_{Am} (mol m^{-3})	600		Estimated from Savage *et al.* (1984)	
c_{carb} (mol m^{-3})	2000		Estimated from Savage *et al.* (1984)	
k_L (m s^{-1})	1.5×10^{-4}		Estimated from Savage *et al.* (1980)	
m	0.1		Savage *et al.* (1980)	
k_g (m s^{-1})	100		No gas phase resistance	
K_{c1} (m^3 mol^{-1})	1.09×10^3		Chakravarty (1985)	
K_{c2} (mol m^{-3})	7.29×10^{-8}		Chakravarty (1985)	
K_w (mol^2 m^{-6})	3.33×10^{-7}		Harned (1958)	
K_p (mol m^{-3})	3.17×10^{-5}	3.17×10^{-7}	Perrin (1965)	Savage *et al.* (1984)
K_c (m^3 mol^{-1})	7.06×10^{-4}	1.41×10^{-4}	Mahajani and Danckwerts (1982)	Savage *et al.* (1984)
k_{OH} (m^3 mol^{-1} s^{-1})	1.87×10^3		Savage *et al.* (1980)	
k_2 (m^3 mol^{-1} s^{-1})	214	1581	Blauwhoff *et al.* (1984)	Versteeg and van Swaaij (1988)
$\mathbb{D}_{CO_2}$ (m^2 s^{-1})	2.5×10^{-9}		Savage *et al.* (1980)	
$\mathbb{D}_{Am}$ (m^2 s^{-1})	1.69×10^{-9}		$\mathbb{D} \div V_b^{-0.6}$	
$\mathbb{D}_{ion}$ (m^2 s^{-1})	1.96×10^{-9}		V_b from Perry and Chilton (1973)	
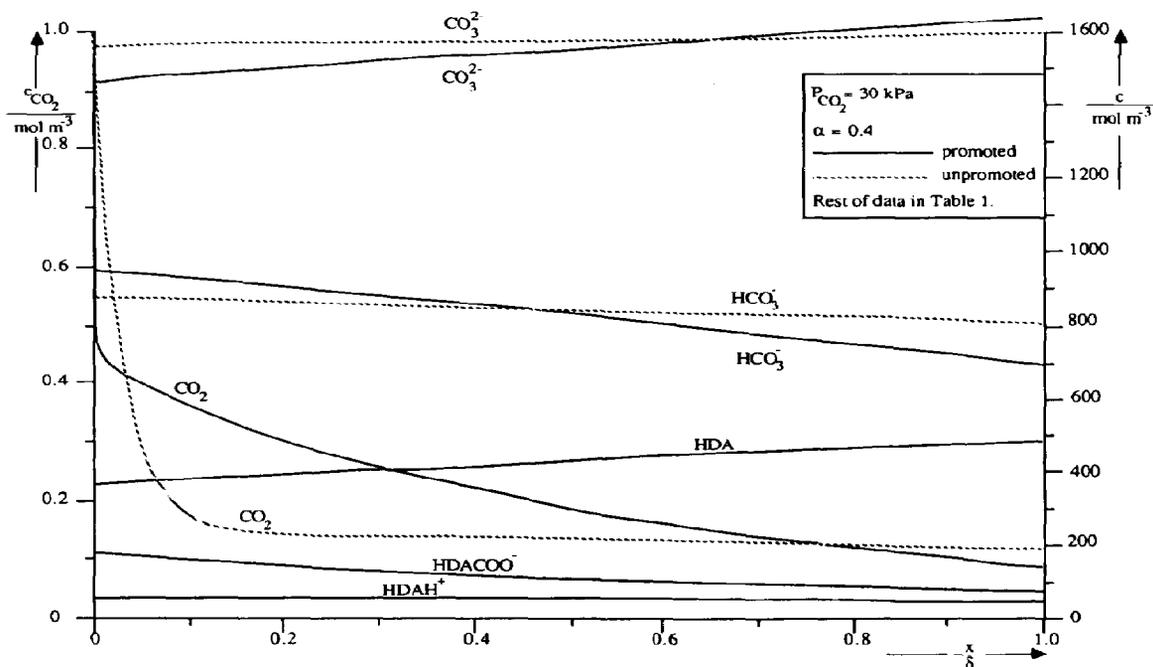
Fig. 2. Calculated concentration profiles for absorption of CO_2 into unpromoted and HDA-promoted carbonate solutions at 363 K.

The diffusivities were estimated as described in Part I (Bosch *et al.*, 1989a).

4.2. *Results*

In Fig. 2 the film model concentration profiles in the interfacial film for HDA-promoted and unpromoted potash solutions are compared. The concentration profile of CO_2 at the interface gets steeper with the addition of HDA, which means that there is a significant promotion effect. The concentration profiles of the other components show that several mechanisms are involved in the generation of this effect. Because

there is a concentration gradient for HDACOO$^-$ part of the CO_2 is transported to the liquid bulk in this form. This can be considered as a shuttle mechanism effect.

The HDACOO$^-$ present in the mass transfer film also causes promotion by another mechanism. Due to the high concentration of this unstable carbamate the CO_2 concentration rises with respect to the unpromoted case. This causes the hydration of CO_2 [reaction (1)] to become more effective in enhancing mass transfer, leading to more diffusion of CO_2 in the HCO$_3^-$ form compared with the unpromoted case.

Figure 3 gives the same comparison for a DEA-promoted solution. Here the shuttle mechanism is also active. The second mechanism of promotion does not occur since $DEACOO^-$ is much more stable than $HDACOO^-$, and therefore the concentration of CO_2 in the interfacial film does not rise, so that the influence of the hydration reaction on mass transfer is not increased in this case.

In Table 2 the results of the simulations for absorption for a number of liquid loadings and partial pressures of CO_2 are shown. Considerable promotion occurs for both amines and the promotion factors for HDA are much higher than those for DEA.

Figure 4 shows the concentration profiles for a simulation of desorption from a loaded HDA solution. Again a shuttle mechanism effect is observed combined with a large effect of a decreasing CO_2 concentration in the interfacial film. The promotion factor obtained at a loading of $\alpha = 0.6$ was 3.81. This is very high considering the fact that addition of the amine lowers the driving force for desorption by about one third.

5. DISCUSSION

5.1. General literature

In many cases the approximations necessary to allow analytical solution of the mass transfer model for multiple reversible reactions introduce the risk of oversimplifications and may cause the results of experiments to be either unexplainable or misinterpreted. Often a more complete model solved numerically is necessary to check the assumptions. For example the reason why Laddha and Danckwerts (1982) measured and could not explain the large increase in the reaction rate of step (9) for DEA upon the addition of carbonate might be that in the interpretation of the results they neglected the contribution of bases other than the amine and carbonate to the deprotonation of the zwitterion as well as the interaction of the hydration of CO_2 and the reaction of CO_2 with the amine in the mass transfer film.

For the interpretation of their desorption experiments Danckwerts and Mahajani (1983a) took into account kinetic factors only. They discussed the influ-
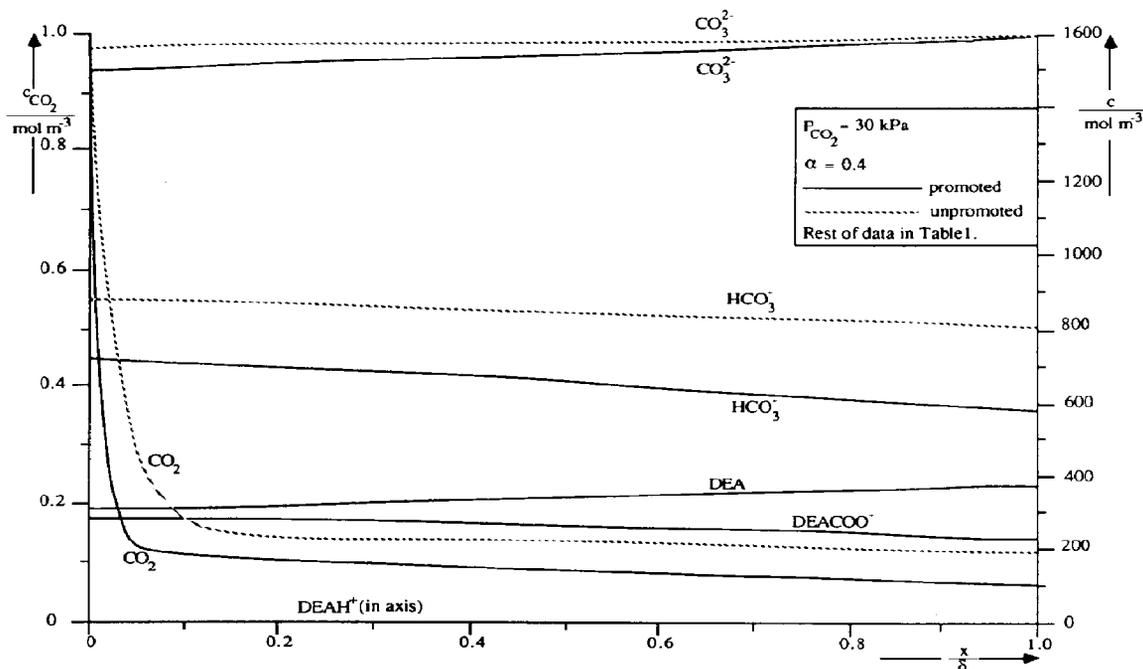

Fig. 3. Calculated concentration profiles for absorption of CO_2 into unpromoted and DEA-promoted carbonate solutions at 363 K.

Table 2. Numerical results for absorption of CO_2 into amine-promoted carbonate solutions

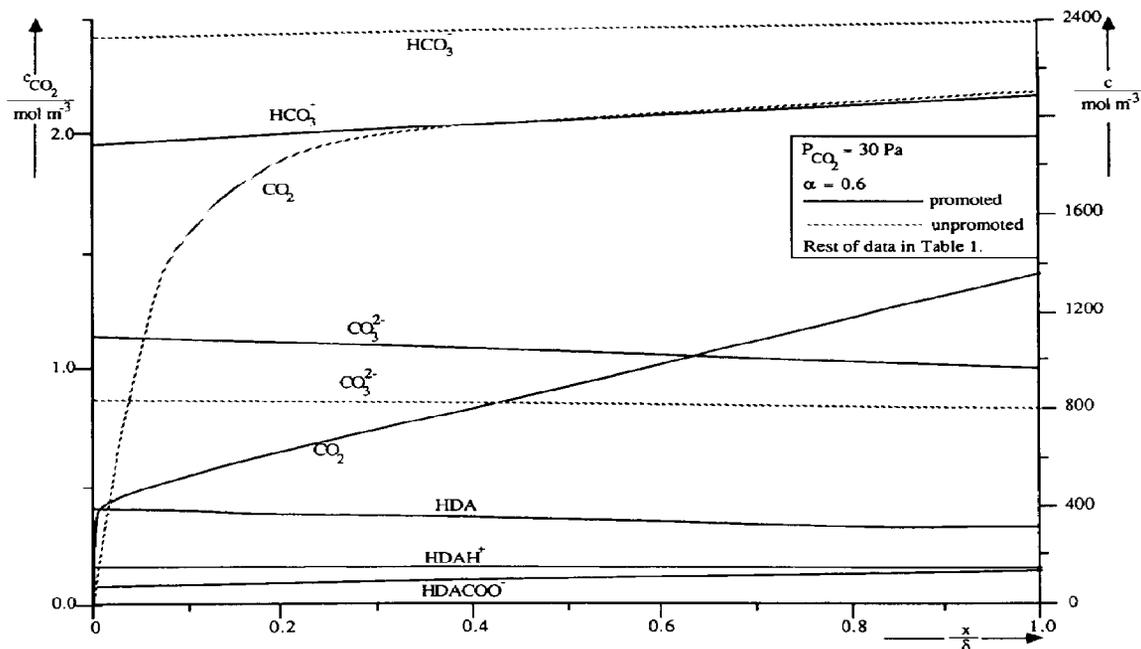| α	P_{CO_2} (kPa)	J_u (mol m^{-2} s^{-1})	E_u	J_{DEA} (mol m^{-2} s^{-1})	E_{DEA}	F_{DEA}	J_{HDA} (mol m^{-2} s^{-1})	E_{HDA}	F_{HDA}
0.2	30	4.34×10^{-3}	33.0	1.19×10^{-2}	84.4	2.74	2.16×10^{-2}	158	4.98
0.4	30	1.10×10^{-3}	20.6	5.51×10^{-3}	60.8	5.00	8.80×10^{-3}	106	8.00
0.4	120	9.69×10^{-3}	19.2	2.43×10^{-2}	45.0	2.51	3.64×10^{-2}	68.3	3.76
0.6	120	3.53×10^{-3}	12.9	1.19×10^{-2}	31.6	3.37	1.80×10^{-2}	46.3	5.10

Fig. 4. Calculated concentration profiles for desorption of CO_2 from unpromoted and HDA-promoted carbonate solutions at 363 K.

ence of equilibrium and depletion qualitatively, but did not recognize that MEA might be a poor promotor because its carbamate is very stable compared to the other amines, and that a major part of the MEA in the solution is present in the form of carbamate, and therefore has no effect on the desorption rate.

5.2. Sterically hindered amines

The omission of presenting the molecular formula of HDA in the work of Savage et al. (1984) give rise to many uncertainties. HDA is presented as a diamine with one secondary hindered amino group and one primary unhindered amino group. The latter merely serves to increase the solubility. The formula given (HNRR'NH), however, is of a ring-structured diamine with two secondary amino groups. This must have been a printing error and presumably $H_2NRR'NH$ was meant.

The thermodynamical description of the equilibria of the HDA is complicated by its bifunctionality. The authors made some assumptions in order to treat HDA thermodynamically as a monoamine. The doubly protonated $(H_3^+NRR'NH_2^+)$ and the doubly carbamated $(^-OOCHNRR'NCOO^-)$ forms were regarded as unstable and their formation was neglected. Linear equilibrium equations between the two singly protonated $(H_3^+NRR'NH$ and $H_2NRR'NH_2^+)$ and between the two singly carbamated $(^-OOCHNRR'NH$ and $H_2NRR'NCOO^-)$ were assumed to exist, the concentration of either form being proportional to the sum of both. Finally, the formation of the two amphoteric forms

$(^-OOCHNRR'NH_2^+$ and $H_3^+NRR'NCOO^-)$ was neglected and so the same equilibrium description as for monoamines was considered to hold. The last assumption is based on the fact that "severe bending of the stiff organic backbone" is required for the amphoteric forms. We think these forms do exist, and that bending of the backbone would only stabilize these forms because the opposing charges get closer. If bending is prevented, it does not necessarily imply that the forms are not stable. Moreover, reaction at one side of the molecule would make the other side more likely to react towards the amphoteric form because of electronic effects. Formation of a species of this kind, mostly with the primary unhindered side carbamated and the other side protonated $(^-OOCHNRR'NH_2^+)$, would yield an equilibrium behaviour even better (higher capacity for CO_2) than that of a singular hindered amine, even though a considerable amount of carbamate exists. It should also be a good rate promotor simply because the effective amine concentration (counted as the number of amine groups) is higher than the HDA concentration.

Apart from the observed absorption rates some additional arguments for the selection of a homo-geneous-catalysis mechanism to account for the observations were given (see Section 3.2); however, some of these are questionable.

The argument that a promotor acting via a shuttle mechanism in absorption cannot promote mass transfer at desorption was already refuted by Danckwerts (1981). Whether a shuttle mechanism promotor in absorption can also be a shuttle mechanism promotor

in desorption depends on the way in which the equilibria and the reaction rates change on going from absorption to desorption conditions.

The influence of the liquid flow rate on the promotion factor is not clear from the graph presented by Savage et al. (1984), so the conclusion that absorption takes place in the instantaneous regime is largely based on the observed effects of varying the driving force. Moreover, the consequences of instantaneous reversible and irreversible reactions were confused. Using an irreversible model of mass transfer the conclusion that the reactions must be instantaneous was drawn from the experiments with different driving forces, whereas a model with reversible reactions, was used to calculate the maximum enhancement factor for this case. This last model predicts a linear dependence of the absorption rate on the driving force. So the homogeneous-catalysis model also results in a different behaviour than the one observed.

5.3. Simulations

With a numerical simulation, the experimental results obtained by Savage et al. (1984) can be approximated rather well using independently determined and estimated parameters only. In Table 3 the experimental promotion factors of Savage et al. (1984) are compared with our numerical results. Both DEA and HDA are effective rate promotors. HDA is a better promotor, probably owing to its steric hindrance, as Savage et al. (1984) proposed. A considerable promotion effect is also observed for desorption.

For HDA the results of the simulations are less reliable than for DEA, since the structural formula of HDA is not given and the equilibrium behaviour of HDA is unclear. Moreover, some of the parameters could not be estimated accurately. The concentrations used had to be guessed on the basis of previous work referred to by the authors and from the equilibrium experiments reported. This does not seem to invalidate our conclusions however.

The results of the simulations of the absorption experiments give some new insights. They indicate that both mechanisms discussed by Savage et al., the shuttle mechanism and homogeneous catalysis, are not realistic. The shuttle mechanism is much too simple, especially for HDA. The homogeneous-catalysis mechanism does not take into account the effect of the established reactions of the amine on mass transfer.

In terms of the general mechanism proposed by Astarita et al. (1981) it can also be demonstrated that neither of the two models apply. In the general mechanism reaction (11) should be comparatively slow. In fact for HDA this reaction is almost instantaneous, compared to mass transfer, if at least the order of magnitude of the reaction rate constants assumed is correct. This means that the conditions for neither a homogeneous-catalysis mechanism nor the shuttle mechanism given by Astarita et al. (1981) are fulfilled for this situation.

As explained before, the present simulations (Figs 2–4) clearly show some shuttle activity for absorption as well as desorption. These simulations cannot be used to resolve the differences between Astarita et al. (1981) and Danckwerts (1981). As Astarita et al. (1981) pointed out the homogeneous-catalysis and shuttle mechanism models are extreme manifestations of the same process, and therefore in actual processes a mixture of the two effects occurs. So a discussion about the extreme models is of little value for the understanding of the real process.

Just as in the experimental observations of Savage et al. (1984) there was only a small influence of k_L on the observed promotion factors. Also the influence of the driving force is reduced in the promoted solution. The enhancement factor changes little with the driving force in the unpromoted case, whereas it decreases with the driving force when a promotor is added. The effect is smaller than suggested by the results presented by Savage et al. (1984), even though the lines with which they prove their point are drawn rather tentatively.

A strong support for the present mechanism is the fact that tertiary amines do not give rise to significant promotion if they are added to carbonate solutions, a fact that could not be explained by Savage et al. (1984). The explanation in terms of the mechanisms revealed by the numerical simulations is simple, and was already suggested by Mahajani and Danckwerts (1983a). Tertiary amines do not form carbamates at all and therefore cannot act as a shuttle, nor can they give rise to an increase in the CO_2 concentration in the mass transfer film at some distance from the interface, and so they do not promote mass transfer.

With the considerations above it is possible to derive an approximate analytical model for describing the promotion effect. This model assumes that reaction (1) is fast pseudo-first-order and irreversible, while reaction (2) is instantaneous and reversible. An expression for the promotion factor for this model [eq. (15)] was derived by Bosch et al. (1989b):

$$F = \sqrt{1 + \frac{[NR_2H]^2 K_{eq}}{[NR_2H_2^+]}}. \qquad (15)$$

This expression suggests no influence of k_L and the driving force on the promotion factor. So this model does not correctly describe the observed behaviour either. The most important reason is that the reaction of the promotor is not at equilibrium very close to the interface. Expression (15) therefore gives much to high values for the promotion factor.

It might be possible to explain the observed behav-

Table 3. Comparison of experimental promotion factors of Savage et al. (1984) and numerical results

	DEA	HDA
Experimental	±4	±6
Numerical	2.7–5.0	3.8–8.0

iour with an approximate model comparable to the one described by Tseng *et al.* (1988).

5.4. *Conclusion*

Both mechanisms, the shuttle mechanism and homogeneous catalysis, proposed to explain the promotion of mass transfer by addition of amines to carbonate solutions oversimplify the mechanisms which are actually occurring. In any interpretation of experimental results the influence of all established reactions should be taken into account. Generally, this can only be done by numerically solving the equations that describe the phenomenon of mass transfer with parallel reversible reactions.

6. 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 and numerical approximations are used.

For absorption of CO_2 into mixtures of absorbing species (water, amines and carbonate) this means that 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 explained using approximated models based on the mechanism presented by Astarita *et al.* (1981).

NOTATION

B	base
c	concentration mol m^{-3}
$\mathbb{D}$	diffusion coefficient, m^2 s^{-1}
E	enhancement factor
F	promotion factor ($J_{promoted}/J_{unpromoted}$)
J	molar absorption flux, mol m^{-2} s^{-1}
k_b	reaction rate constant for zwitterion deprotonation, m^3 mol^{-1} s^{-1}
k_g	gas phase mass transfer coefficient, m s^{-1}
k_L	liquid phase mass transfer coefficient, m s^{-1}
k_{OH}	reaction rate constant for CO_2 hydration, m^3 mol^{-1} s^{-1}
k_1	first-order reaction rate constant, s^{-1}
k_{-1}	reverse reaction rate constant, s^{-1}
k_2	second-order reaction rate constant, m^3 mol^{-1} s^{-1}
K_c	carbamate stability constant $\{K_c = [AmR_2COO^-]/([AmR_2H][HCO_3^-])\}$, m^3 mol^{-1}
K_{c1}	equilibrium constant for CO_2 hydrolysis $\{K_{c1} = [HCO_3^-]/([OH^-][CO_2])\}$, m^3 mol^{-1}
K_{c2}	bicarbonate dissociation constant $\{K_{c2} = ([CO_3^{2-}][H^+])/[HCO_3^-]\}$, mol m^{-3}

K_{eq}	equilibrium constant for CO_2–amine reaction ($K_{eq} = K_c K_{c1} K_w/K_p$), m^3 mol^{-1}
K_p	primary or secondary amine protonation constant ($K_p = [AmR^2H][H^+]/[AmR_2H_2^+]$), mol m^{-3}
K_w	dissociation constant of water ($K_w = [H^+][OH^-]$), mol^2 m^{-6}
m	distribution coefficient $\{m = ([CO_2]_L/CO_2]_g)$ at equilibrium$\}$
P	pressure, N m^{-2}
r	reaction rate, mol m^{-3} s^{-1}
T	temperature, K
V_b	molecular volume at normal boiling point, m^3 mol^{-1}

Greek letter

α	liquid loading, mol CO_2 (mol primary absorbent)$^{-1}$

Amine abbreviations

MEA	monoethanolamine
DEA	diethanolamine
TEA	triethanolamine
AMP	2-amino-2-methylpropanol
HDA	hindered diamine
DIPA	diisopropanolamine

Subscripts

Am	amine
b	bulk
carb	carbonate
g	gas
i	interface
ion	ionic products
L	liquid
max	maximum
u	unpromoted

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