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KINETICS OF CO$_2$ WITH PRIMARY AND SECONDARY AMINES IN AQUEOUS SOLUTIONS—II. INFLUENCE OF TEMPERATURE ON ZWITTERION FORMATION AND DEPROTONATION RATES

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Abstract—The kinetics of the reaction of CO$_2$ with various alkanolamines (MEA, DGA, DIPA, DEA, MMEA) in aqueous solutions has been studied as a function of temperature. Also kinetic data at 303 K were obtained for the reaction between CO$_2$ and the cyclic amine morpholine in aqueous solutions. All observed phenomena can be explained very satisfactorily with the zwitterion mechanism proposed by Caplow. With respect to the temperature influence on the overall reaction rate for primary and secondary amines, two classes can be distinguished: when the zwitterion formation is rate determining a significant temperature influence is observed whereas only a slight temperature dependence is observed when the zwitterion deprotonation is rate determining. All kinetic experiments were interpreted with the aid of a numerically solved absorption model which describes gas absorption accompanied by reversible chemical reactions. For fast reversible reactions like those in the present study, only in this way reliable reaction-rate data can be deduced from absorption experiments. The Brønsted relationship between the zwitterion-formation rate constant and the acid dissociation constant of the alkanolamine, as proposed by Versteeg and van Swaaij (1988a), seems to be valid over a wide range of temperatures and for a great variety of alkanolamines. This relationship is not valid for cyclic amines like MOR.
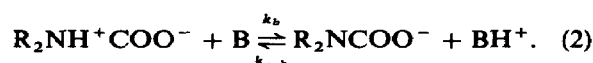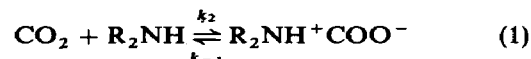
1. INTRODUCTION

The removal of acid gases (e.g. hydrogen sulfide carbonyl sulfide, and carbon dioxide) from industrial and natural gas streams is a very important and frequently encountered operation in process industry In many cases the removal of sulfur-containing compounds like H$_2$S, COS, and mercaptans, is required whereas CO$_2$ may remain in the gas. Improvement of the selectivity of the treating process towards H$_2$S, being the main sulfur compound, can be achieved by reducing the reaction rate between CO$_2$ and the alkanolamine. Obviously, information on the reaction rate constants and knowledge of the reaction mechanism for the reaction between CO$_2$ and (aqueous) solutions of alkanolamines are indispensable for an adequate design of treating processes.

Part I of the present work (Littel *et al.*, 1992) dealt with the zwitterion deprotonation kinetics for diethanolamine (DEA) and diisopropanolamine (DIPA) in aqueous blends of alkanolamines. In Part II, i.e. the present work, the kinetics and mechanism of the reaction of CO$_2$ with primary and secondary amines in aqueous solutions have been studied as a function of temperature. Kinetic experiments were carried out with monoethanolamine (MEA), diglycolamine (DGA), DEA, DIPA, methylmonoethanolamine (MMEA), and morpholine (MOR) at temperatures ranging from 293 to 333 K. All experiments were interpreted by means of a numerical flux model which describes mass transfer accompanied by multiple reversible chemical reactions (Littel *et al.*, 1991a).

2. REACTION MECHANISM

For the reaction of CO$_2$ with primary and secondary alkanolamines, the zwitterion reaction mechanism, originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979), is generally accepted as the reaction mechanism:

$$CO_2 + R_2NH \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} R_2NH^+COO^- \qquad (1)$$

$$R_2NH^+COO^- + B \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} R_2NCOO^- + BH^+. \qquad (2)$$

This mechanism comprises two steps: formation of the CO$_2$–amine zwitterion [reaction (1)], followed by base-catalyzed deprotonation of this zwitterion [reaction (2)].

The contribution of the hydroxyl ions to the deprotonation of the zwitterion may be neglected without a substantial loss of accuracy (Versteeg and van Swaaij, 1988a). Assuming pseudo-steady state for the zwitterion concentration, the following expression for the forward reaction rate can be derived:

$$R_{CO_2} = \cfrac{[R_1R_2NH][CO_2]}{\cfrac{1}{k_2} + \cfrac{1}{k_{H_2O}[H_2O] + k_{R_1R_2NH}[R_1R_2NH]}} = k_{app}[CO_2] \qquad (3)$$

with

$$k_{H_2O} = \frac{k_2 k_{b,H_2O}}{k_{-1}} \qquad k_{R_1R_2NH} = \frac{k_2 k_{b,R_1R_2NH}}{k_{-1}}.$$

Although the reaction of CO_2 with primary and secondary alkanolamines has been studied extensively [e.g. Alvarez-Fuster *et al.* (1980), Laddha and Danckwerts (1981), Blauwhoff *et al.* (1984), Barth *et al.* (1984), Sada *et al.* (1985, 1986), Versteeg and van Swaaij (1988a) and Versteeg and Oyevaar (1989)] only very limited information is available for temperatures different from 293 or 298 K. A review of literature data for MEA, DEA, and DIPA was presented by Blauwhoff *et al.* (1984). Kinetic data for MEA up to 308 K, and for DEA up to 313 K, were reported by Hikita *et al.* (1977a). Leder (1971) presented rate data for MEA at 353 K which were inferred from CO_2 absorption rates into a carbonate–bicarbonate buffer solution containing MEA. Several authors presented kinetic data for MEA for temperatures lower than 298 K (Penny and Ritter, 1983; Alper, 1990a). For aqueous DGA solutions, Hikita *et al.* (1977b) published kinetic data for temperatures ranging from 278 to 313 K and Alper (1990b) gives data at 278, 288 and 298 K.

van Krevelen and Hoftijzer (1948) interpreted packed-column absorption data of Cryder and Maloney (1941) for aqueous DEA solutions up to 328 K. They concluded from these data that the overall reaction rate seemed to be nearly independent of temperature. Nunge and Gill (1963) studied the absorption of carbon dioxide in pure diethanolamine at 302, 308 and 314 K. Blanc and Demarais (1984) reported kinetic data for DEA at temperatures ranging from 293 to 333 K. As pointed out by Versteeg and van Swaaij (1988a), the data provided by Blanc and Demarais (1984) are questionable as a result of incorrect physical constants used in the interpretation of the experiments. For aqueous DEA and DIPA solutions at 323 K, Savage and Kim (1985) reported kinetic experiments in which the free amine concentration was varied by varying the amine loading. However, if the free amine concentration is varied in this way, the interpretation of the kinetic experiments becomes questionable as physical constants needed for interpretation of the experiments as well as the reaction rates themselves are likely to be affected considerably by the ionic strength. Therefore, only the kinetic data reported by Savage and Kim (1985) at low amine loadings should be regarded reliable. For aqueous DEA at 298 K, extensive kinetic data, together with a comparison of these data to literature data, are presented by Versteeg and Oyevaar (1989).

Recently, Crooks and Donnellan (1989) questioned the validity of the zwitterion mechanism and proposed a single-step, termolecular mechanism (see Fig. 1) which postulates a loosely bound encounter complex as initial product. For this mechanism the forward reaction rate can be calculated according to

$$R_{CO_2} = \{k_{AM}[R_1R_2NH]^2$$

$$+ k_w[R_1R_2NH][H_2O]\}[CO_2]. \quad (4)$$

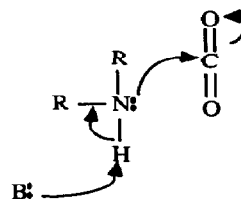Reaction rate expression (4) for the single-step, termolecular mechanism according to Crooks and

Fig. 1. Single-step, termolecular reaction mechanism for the formation of carbamate according to Crooks and Donnellan (1989).

Donnellan (1989) can be regarded as a limiting case of the zwitterion mechanism, because if zwitterion deprotonation is entirely rate determining, reaction rate expression (3) reduces to rate expression (4). However, the termolecular reaction mechanism is not able to explain the occurrence of fractional orders for the reaction between CO_2 and alkanolamines in non-aqueous solutions as has been reported by Sada *et al.* (1985, 1986) and Versteeg and van Swaaij (1988a), because according to Crooks and Donellan (1989) a second order in the alkanolamine should have been observed. Moreover, the experimental data presented in Part I by Littel *et al.* (1992) on the zwitterion deprotonation kinetics in blends of secondary and tertiary amines cannot be understood in terms of the reaction mechanism proposed by Crooks and Donnellan (1989), whereas they can be elegantly explained in terms of the zwitterion mechanism proposed by Caplow (1968). Also the kinetic data reported by Versteeg and Oyevaar (1989) for the reaction between CO_2 and aqueous DEA solutions with amine concentrations ranging from 86 to 4358 mol m^{-3} can only be described accurately with the zwitterion mechanism for all concentrations studied. Regarding these extensive experimental data, it must be concluded that the single-step, termolecular mechanism suggested by Crooks and Donnellan (1989) is not able to explain all phenomena observed and therefore it is not necessary to reject the zwitterion mechanism proposed by Caplow (1968).

3. EXPERIMENTAL

Experimental setup and procedure were identical to those described in Part I of the present work (Littel *et al.*, 1992).

Since in the present study the temperature dependence of the reaction-rate constants was studied and the equilibrium constants for the reaction between CO_2 and alkanolamines are known to decrease with increasing temperature, it was considered that the possibility of reversibility effects should be taken into account. Furthermore, it was considered unlikely that in all kinetic experiments, for all amines and temperatures studied, true pseudo-first-order conditions could be attained in view of the high reaction rates to be expected from strongly basic amines in combination with high temperatures.

Therefore, all experimental data were interpreted by means of a numerically solved absorption model

which describes gas absorption accompanied by multiple reversible chemical reactions (Littel et al., 1991a). In this numerical flux model, which describes the absorption process according to Higbie's penetration theory, the following reversible chemical reactions were taken into account:

$$CO_2 + 2R_1R_2NH \rightleftharpoons R_1R_2NH_2^+ + R_1R_2NCOO^- \quad (5)$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \quad (6)$$

$$HCO_3^- + OH^- = CO_3^{2-} + H_2O \quad (7)$$

$$R_1R_2NH_2^+ + OH^- = R_1R_2NH + H_2O. \quad (8)$$
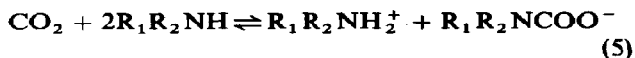
The expression for the reverse reaction rate was derived from the assumption that at equilibrium the net reaction rate equals zero. Detailed information concerning the absorption model and the numerical techniques used can be found elsewhere (Littel et al., 1991a; Versteeg et al., 1989).

For each experiment, for some well-defined conditions (P_{CO_2}, k_L, liquid composition), the enhancement factor calculated with the absorption model was fitted to the experimentally observed enhancement factor with the reaction rate constant as an adjustable parameter. Two simulations were carried out for each experiment: one with the reaction order in amine set to one and one with the reaction order in amine set to two. Differences, with respect to the fitted apparent reaction-rate constants, between these two extreme situations were usually less than 15%. As under true pseudo-first-order conditions both extreme situations would have coincided, this difference also indicates that diffusion limitation was not entirely avoided in the kinetic experiments. The situation which resembled most the dependence of the apparent reaction rate constants on the amine concentrations was assumed to be correct.

In Fig. 2 a concentration profile at the end of the contact time is shown for an aqueous solution of

1000 mol m^{-3} MMEA at 318 K. This concentration profile clearly shows the significant depletion of free MMEA towards the gas–liquid interface and illustrates the necessity of applying a numerical model to deduce reaction kinetics from the present experiments. Naturally, the accuracy of the deduced kinetic data decreases with increasing depletion of free amine towards the gas–liquid interface, because the absorption flux is increasingly determined by diffusion. Therefore, very low CO_2 pressures were applied in order to minimize the effect of diffusion limitation and, consequently, even for the highly reactive amines like MEA, DGA, and MMEA, differences between bulk and interface concentrations of free amine were usually not more than 10 to 20%. The apparent reaction rate constants obtained from the absorption model were fitted to reaction rate expression (3) in order to obtain zwitterion formation and deprotonation reaction-rate constants. The fitting procedure used was based on the Levenberg–Marquardt method.

In the present study, the solubility of CO_2 was determined by means of the CO_2–N_2O analogy (Laddha et al., 1981; Versteeg and van Swaaij, 1988b). The diffusivity of CO_2 was estimated using the modified Stokes–Einstein relationship reported by Versteeg and van Swaaij (1988b) for aqueous amine solutions. Viscosity and N_2O-solubility of the aqueous amine solutions applied in the present work are presented by Versteeg and van Swaaij (1988b) and Littel et al. (1991b).

For all kinetic experiments, CO_2 pressures and amine loadings were typically 0.005–0.05 bar and 1–10%, respectively.

DEA, MMEA, MOR, and MEA were obtained from Janssen Chimica; DGA was provided by Texaco Chemical Company; DIPA was obtained from Riedel-de Haën. All alkanolamines were at least 99% pure and used as received.

Fig. 2. Concentration profile at the end of the contact time for an aqueous MMEA solution ($T = 318$ K, [MMEA] = 1000 mol m^{-3}, $P_{CO_2} = 1.5$ kPa, amine loading = 3%, k_L = 2.3 × 10^{-5} m s^{-1}).

1 = $[CO_2] / 0.5$
2 = $[MMEA] / 950$
3 = $[MMEACOO^-] / 300$
4 = $[MMEAH^+] / 300$
5 = $[HCO_3^-] / 5$
6 = $[OH^-] / 5$
7 = $[CO_3^{2-}] / 5$

4. RESULTS

4.1. Aqueous MEA solutions

In the present work the reaction between carbon dioxide and MEA in aqueous solutions has been studied at 318 and 333 K. The experimental results are presented in Fig. 3. For both temperatures studied, the apparent pseudo-first-order reaction-rate constant showed a first-order behavior in the amine concentration. A definite temperature dependence of the overall reaction rate was observed. The experimental data indicate that the reaction rate is entirely determined by the zwitterion-formation rate, which reduces the general rate expression (3) to the rate expression (9). The fitted reaction-rate constants k_2 are presented in Table 1.

$$R_{CO_2} = k_2[R_1R_2NH][CO_2]. \quad (9)$$

In Fig. 4, the present data are compared to data published by Hikita et al. (1977a), Penny and Ritter (1983), and Alper (1990a). All these authors applied a
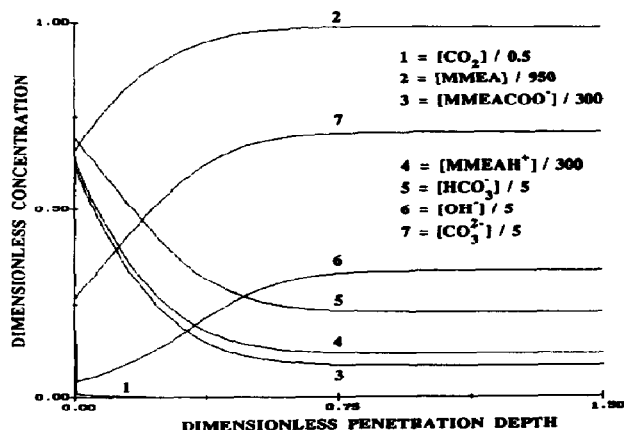
Table 1. Fitted reaction rate constants

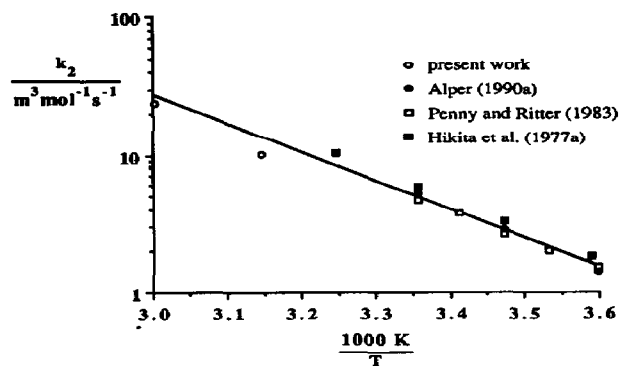| Amine	T (K)	pK_a	k_2 (m^{3}mol^{-1}s^{-1})	$k_{R_1R_2NH}$ (m^{6}mol^{-2}s^{-1})	k_{H_2O} (m^{6}mol^{-2}s^{-1})	Reference
MEA	318	8.94	10.4	—	—	Present work
MEA	333	8.56	25.7	—	—	Present work
DIPA	293	9.01	2.09	1.80×10^{-4}	0.75×10^{-6}	Versteeg and van Swaaij (1988a)
DIPA	298	8.89	2.70	1.98×10^{-4}	0.84×10^{-6}	Versteeg and van Swaaij (1988a)
			2.44	1.75×10^{-4}	0.60×10^{-6}	Blauwhoff *et al.* (1984)
			2.78	2.00×10^{-4}	0.51×10^{-6}	Littel *et al.* (1992)
DIPA	308	8.76	—	2.06×10^{-4}	0.68×10^{-6}	Present work
DIPA	318	8.41	—	1.56×10^{-4}	1.39×10^{-6}	Present work
DIPA	333	8.09	—	1.10×10^{-4}	2.99×10^{-6}	Present work
DEA	298	8.88	3.17	0.72×10^{-3}	0.17×10^{-5}	Versteeg and Oyevaar (1989)
DEA	303	8.75	4.36	1.30×10^{-3}	0.85×10^{-5}	Present work
DEA	318	8.41	7.31	1.36×10^{-3}	1.82×10^{-5}	Present work
DEA	333	8.10	—	1.31×10^{-3}	0.43×10^{-5}	Present work
DGA	298	9.46	3.99	—	—	Present work
DGA	318	8.98	10.3	—	—	Present work
DGA	333	8.60	—	1.05×10^{-3}	1.71×10^{-4}	Present work
MMEA	293	9.95	5.34	—	—	Present work
MMEA	318	9.35	21.8	—	—	Present work
MOR	303	8.24*	12.4	1.21×10^{-2}	—	Present work

*Estimated from pK_a value at 298 K.
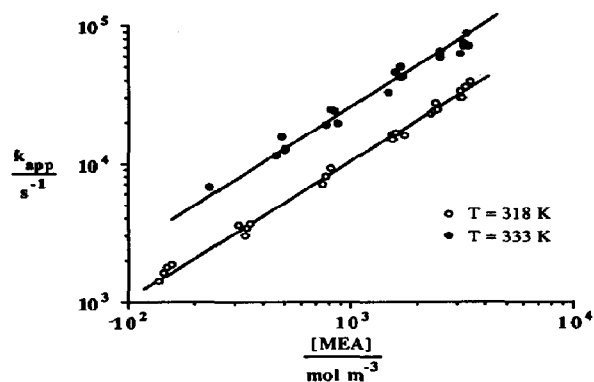
Fig. 3. Experimental results for aqueous MEA solutions.

stopped-flow technique, whereas in the present work stirred-cell reactors were used. The agreement between the present results and these literature data is satisfactory. Also data provided by Alvarez-Fuster *et al.* (1980) at 293 K and Sada *et al.* (1985) at 303 K are in good agreement with the data presented in Fig. 4.

4.2. *Aqueous DIPA solutions*

For aqueous DIPA solutions kinetic experiments were carried out at 308, 318 and 333 K. The results of these experiments are presented in Fig. 5. For all temperatures investigated, the reaction order was found to be equal to about 1.7. In the present work almost no temperature influence on the apparent reaction-rate constants was observed. Moreover, the
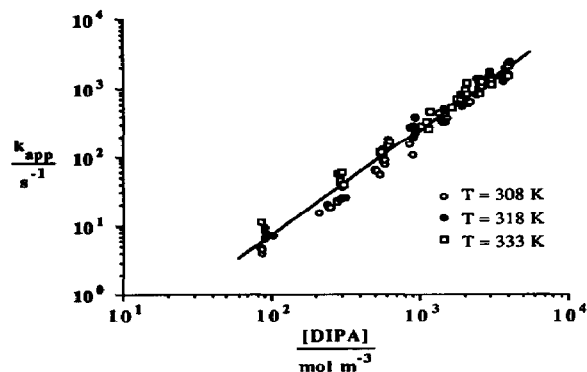

Fig. 4. Arrhenius plot for aqueous MEA solutions.

Fig. 5. Experimental results for aqueous DIPA solutions.

kinetic data at 293 and 298 K presented by Blauwhoff et al. (1984), Versteeg and van Swaaij (1988a), and Littel et al. (1992) also are only slightly lower than the present kinetic data. Apparently the overall forward reaction rate for the reaction between CO_2 and DIPA in aqueous solutions is almost independent of temperature over a temperature range from 293 to 333 K.

The absence of a temperature influence on the apparent reaction rate was also observed by Versteeg and van Swaaij (1988a). They suggested that this peculiar behavior may be attributed to the effect of reversibility on the absorption rate. This conclusion was based on simulations with the absorption model in which the kinetic constants were estimated by means of an Arrhenius extrapolation of their results at 293 and 298 K. In the present work the effect of reversibility on absorption has been explicitly taken into account as all kinetic experiments were interpreted by means of the numerically solved absorption model. Consequently, the provisional explanation of Versteeg and van Swaaij (1988a) for the observed absence of a temperature influence on the apparent reaction rate should be considered incorrect.

As can be concluded from the observed reaction order in amine, the reaction rate for the reaction between CO_2 and DIPA in aqueous solutions is primarily determined by the zwitterion deprotonation in which both water and amine take part. Moreover, the zwitterion-deprotonation rate constants are a combination of elementary rate constants and, consequently, may be independent of temperature or even decrease with temperature.

A closer look at the experimental results plotted in Fig. 5 appears to suggest that at low amine concentrations a slight temperature dependence is still observed, whereas at high amine concentrations the k_{app}s obtained at various temperatures coincide within experimental accuracy. This may indicate that zwitterion deprotonation by water, which determines largely the reaction rate at low amine concentrations, is affected by temperature and that the zwitterion deprotonation by amine, which determines largely the reaction rate at high amine concentrations, is seemingly temperature independent. The fitted reaction-rate constants are presented in Table 1, together with the experimental results published by Blauwhoff et al. (1984), Versteeg and van Swaaij (1988a) and Littel et al. (1992). All experimental data are fitted within 20% by the rate constants reported in Table 1.

The only literature data for temperatures higher than 298 K for the reaction between CO_2 and DIPA seems to be the work of Savage and Kim (1985), who published some data, obtained in a single-sphere absorber, for a 1 M DIPA solution at 323 K. However, they varied the free-amine concentration by varying the amine loading and applied estimated physical data in the interpretation of their experiments. For this method of concentration variation, the interpretation is questionable because physical constants needed for the interpretation of the kinetic experi-

ments as well as the reaction rates themselves will be affected considerably by the ionic strength. Reinterpretation of the data of Savage and Kim (1985) at the lowest amine loading applied with the physical data reported by Versteeg and van Swaaij (1988b) leads to a value for k_{app} of about 750 s^{-1}. This value is about 100% higher than that expected from the present results.

4.3. Aqueous DEA solutions

The reaction between CO_2 and DEA in aqueous solutions has been studied at 303, 318 and 333 K. The experimental results are shown in Fig. 6. A reaction order in amine of about 1.5 is observed for all temperatures investigated. From this observed reaction order in amine it can be concluded that the overall reaction rate is considerably affected by the deprotonation rate of the DEA–CO_2 zwitterion.

The fitted reaction-rate constants obtained in the present work are presented in Table 1 together with rate constants reported by Versteeg and Oyevaar (1989). The reaction-rate constants reported in Table 1 fit all experimental data within 15%. Zwitterion-formation rate constants (k_2), which could be obtained up to 318 K, show a definite temperature dependence. The fitted zwitterion-deprotonation constants by amine $(k_{R_1R_2NH})$ are almost constant at 303, 318 and 333 K, but considerably higher than the value at 298 K given by Versteeg and Oyevaar (1989). The zwitterion-deprotonation constants by water (k_{H_2O}) show a rather large spread. Hence, it must be concluded that the fitted zwitterion-deprotonation rate constants presented in Table 1 do not exhibit a definite temperature dependence.

For the reaction between CO_2 and DEA, some data concerning the temperature dependence of the reaction rate have been presented in literature. van Krevelen and Hoftijzer (1948) concluded from an analysis of the data of Cryder and Maloney (1941) that the overall reaction rate seemed to be nearly independent of temperature. This is in good agreement with the present observations. Also the kinetic results at low amine loadings $(T = 323 K)$ presented by Savage and Kim (1985) agree satisfactorily with the present work.
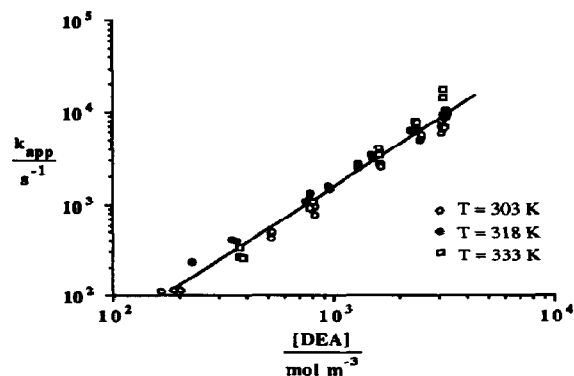
Fig. 6. Experimental results for aqueous DEA solutions.

Hikita *et al.* (1977a) presented kinetic data for the CO_2–DEA system for temperatures ranging from 278.8 to 313.3 K. For their kinetic experiments they applied a rapid mixing method in which the temperature rise due to reaction was detected. They assumed that reaction-rate constants could be obtained directly from the measured temperature differences without knowledge of the heats of reaction and the specific heats of the reaction fluids. They observed a second-order behavior in amine and a considerable temperature dependence of the overall reaction rate. Both are in disagreement with the observations in the present work.

4.4. *Aqueous DGA solutions*

The reaction between carbon dioxide and DGA in aqueous solutions has been studied at 298, 318 and 333 K. The experimental results are shown in Fig. 7. For all temperatures investigated an overall reaction order in amine was observed which was about equal to one. The experimental results at 298 K indicate that the reaction rate is entirely determined by the zwitterion-formation rate [reaction-rate expression (9)]. In Fig. 7 it is striking that the apparent reaction rate constants at 333 K coincide with those at 318 K. The experimental results at 333 K in comparison to those at 318 K suggest a similar behavior for DGA as observed for DIPA and DEA. Apparently, for DGA at 333 K, zwitterion deprotonation is entirely rate determining and, from the observed reaction order in amine, it can be concluded that water contributes very substantially to the zwitterion deprotonation. Because of this and rather limited water concentration variations, it could not be determined reliably if, and to what extent, zwitterion deprotonation contributed to the overall reaction rate at 318 K. Consequently, in fitting the experimental results at 318 K to reaction-rate expression (4), it was assumed that zwitterion formation was entirely rate determining. The fitted reaction rate constants are presented in Table 1.

In Fig. 8 the present results for the zwitterion-formation rate constants (k_2) are compared to data published by Hikita *et al.* (1977b) and Alper (1990b).
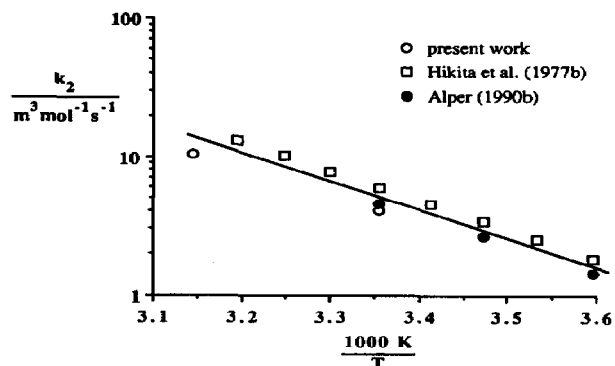

Fig. 8. Arrhenius plot for aqueous DGA solutions.

Hikita *et al.* (1977b) and Alper (1990b) used a stopped-flow method, whereas in the present work the stirred-cell reactor technique has been applied. From Fig. 8 it can be concluded that satisfactory agreement exists between the present and literature results, although the data of Hikita *et al.* (1977b) are systematically somewhat higher than the other results.

4.5. *Aqueous MMEA solutions*

In the present work, the reaction between CO_2 and MMEA in aqueous solutions has been studied at 293 and 318 K. The experimental data are presented in Fig. 9. For both temperatures investigated a first-order behavior in the amine concentration has been observed. From the experimental data it was concluded that the zwitterion-formation rate was rate determining. The fitted reaction-rate constants are presented in Table 1.

Also some kinetic experiments were carried out at 333 K. However, the reaction rate between CO_2 and MMEA at 333 K was too high for a reliable determination of the the reaction-rate constants with the present stirred-cell reactor method.

No data on the reaction between CO_2 and MMEA in aqueous solutions seem to be available in the open literature.
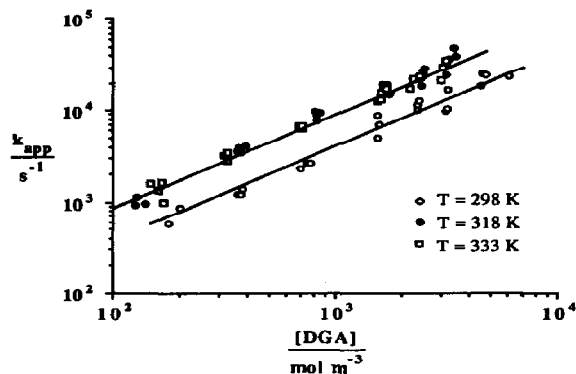

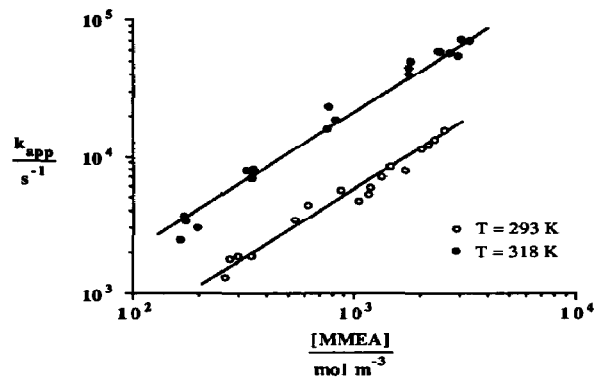Fig. 7. Experimental results for aqueous DGA solutions.

Fig. 9. Experimental results for aqueous MMEA solutions.

4.6. Aqueous MOR solutions

Kinetic experiments for the reaction between CO_2 and MOR in aqueous solutions have been carried out at 303 K. The experimental results, which are presented in Fig. 10, showed a reaction order in amine equal to 1.6. In fitting the experimental results to rate expression (3), it was concluded that the contribution of H_2O to the zwitterion deprotonation is negligible and that the overall reaction rate depends on both the zwitterion-formation rate and the zwitterion-deprotonation rate by amine. The fitted reaction-rate constants are reported in Table 1.

Alper (1990b) reported kinetic data at 298 K obtained by a stopped-flow technique with conductrimetric detection. In the interpretation of his experiments, Alper (1990b) assumed a priori that the overall reaction rate was entirely determined by the zwitterion-deprotonation rate. This assumption seems to be premature and possibly incorrect; Alper (1990b) did not attempt to fit his experimental data to the general rate expression [eq. (4)]. The present results at 303 K obtained with the stirred-cell reactor technique are considerably lower than the results at 298 K reported by Alper (1990b). The causes for this discrepancy are not clear.

5. DISCUSSION

Several authors have suggested a relationship between the zwitterion-formation rate constant and the basicity of the alkanolamine (Caplow, 1968; Penny and Ritter, 1983; Versteeg and van Swaaij, 1988a). Recently Versteeg and van Swaaij (1988a) presented such a Brønsted relationship for temperatures ranging from 293 to 303 K:

$$\ln k_2 = pK_a - \frac{7188}{T} + 16.26. \tag{10}$$

The kinetic results reported by Penny and Ritter (1983) for a series of primary alkylamines and alkanolamines at 293 K compare favorably to eq. (10). In the present study, additional information on the values of k_2, especially at higher temperatures, is available. This offers the possibility of validation of eq. (10) over a
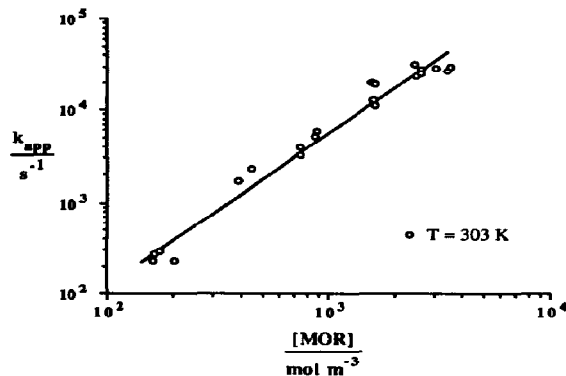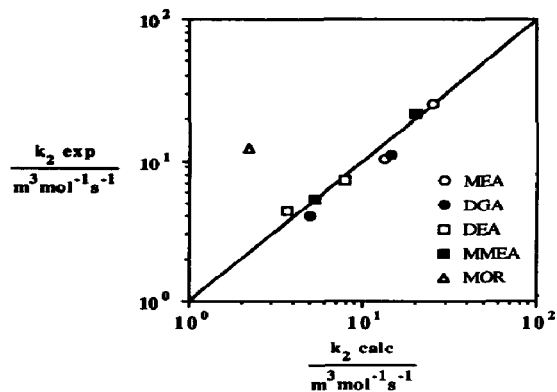
Fig. 11. Parity plot for zwitterion-formation rate constants.

broader temperature range. In Fig. 11 the presently obtained values for k_2 are compared to values calculated according to eq. (10). Extensive information on pK_a values has been presented in literature (e.g. Perrin, 1965; Littel et al., 1990). From Fig. 11 it seems reasonable to conclude that eq. (10) may be used for the estimation of the reaction-rate constant for the zwitterion-formation step in the reaction between CO_2 and alkanolamines in aqueous solutions. The validity of eq. (10) seems to be limited to noncyclic amines as is clearly illustrated by the large deviation observed for the cyclic amine MOR in Fig. 11.

Considering the deprotonation constants presented in Table 1 it does not seem possible to derive a generalized expression for these rate constants. This observation is supported by the conclusions reached in Part I of the present study (Littel et al., 1992).

For engineering purposes, however, it is convenient to derive expressions for the zwitterion-deprotonation rate constants as a function of temperature for DEA and DIPA separately. For this purpose the present data were used in combination with literature data reported by Versteeg and van Swaaij (1988a) and Versteeg and Oyevaar (1989) for DIPA and DEA, respectively. Fitting these data to reaction-rate expression (3) with k_2 given by eq. (10) and allowing for temperature dependence of the zwitterion-deprotonation constants yielded for DIPA

$$k_{DIPA} = 1.55 \times 10^{-4} \quad (m^6 \, mol^{-2} \, s^{-1}) \tag{11}$$

$$k_{H_2O} = 3.05 \times 10^{-2} \exp\left(\frac{-3188}{T}\right) \quad (m^6 \, mol^{-2} \, s^{-1}). \tag{12}$$

The zwitterion-deprotonation constant by amine (k_{DIPA}) was found to be independent of temperature, whereas the zwitterion-deprotonation constant by water (k_{H_2O}) is slightly temperature dependent. These results are in good agreement with tentative observations from the experimental data in Fig. 5. All DIPA data reported in the present work and those presented by Blauwhoff et al. (1984) and Versteeg and van

Fig. 10. Experimental results for aqueous MOR solutions.

Swaaij (1988a) are fitted within 30% with the kinetic-rate constants given by eqs (10)–(12).

For DEA all present kinetic data together with the kinetic data reported by Versteeg and Oyevaar (1989) were fitted to rate expression (3) with the k_2-values given by eq. 10. This procedure gave the following equations for the zwitterion-deprotonation rate constants:

$$k_{DEA} = 1.92 \exp\left(\frac{-2296}{T}\right) \quad (m^6 \, mol^{-2} \, s^{-1}) \quad (13)$$

$$k_{H_2O} = 1.74 \times 10^{-3} \exp\left(\frac{-2127}{T}\right) \quad (m^6 \, mol^{-2} \, s^{-1}). \quad (14)$$

The present kinetic data and those data reported by Versteeg and Oyevaar (1989) are all fitted within 40% with the rate constants given by eqs (10), (13), and (14).

A commonly applied experimental method for the determination of reaction kinetics for the reaction between CO_2 and primary or secondary amines is the stopped-flow or rapid-mixing method. In this method the advancement of the reaction is detected by conductometry (Crooks and Donnellan, 1989; Alper, 1990a, b), temperature rise (Hikita *et al.*, 1977a, b) or indicator colour change (Penny and Ritter, 1983). In the present work, the stirred-cell reactor technique was used which is also a widely applied method for the determination of reaction kinetics in amine systems [e.g. Sharma (1965), Laddha and Danckwerts (1981), Blauwhoff *et al.* (1984), Sada *et al.* (1985, 1986), Haimour *et al.* (1987) and Versteeg and Oyevaar (1989)]. From Figs 4 and 8 it can be concluded that the agreement between both methods is very satisfactory for reactions in which the zwitterion-formation is rate determining. However, substantial disagreement exists between both experimental techniques for reactions in which the overall reaction rate is, at least partially, determined by the zwitterion-deprotonation rate (DEA, MOR).

A reason for this disagreement might be that in the stopped-flow experiments a single irreversible reaction is assumed (Hikita *et al.*, 1977a, b; Alper, 1990a, b), whereas effects due to parallel and consecutive reactions are not taken into account. Especially, relatively rapid consecutive reactions might complicate the interpretation of stopped-flow experiments as they can yield extra ions or additional heat effects. The detection of the advancement of the rate-determining reaction by means of conductometry or temperature rise can be affected significantly by these effects and, as a result, the overall forward reaction rate for the reaction between CO_2 and amine may seriously be over- or underestimated. Therefore, stability of the reaction products of the rate-determining reaction seems to be a strict requirement for a correct interpretation of stopped-flow experiments. For primary and secondary amines, these reaction products consist of carbamate and protonated amine. From these products, the carbamate can be hydrolyzed to

yield bicarbonate and eventually carbonate. The carbamate stability, which decreases substantially with temperature, is for primary amines, like MEA, considerably higher than for secondary amines like DEA. Consequently, the assumptions underlying the stopped-flow method might have been fulfilled for the primary amines MEA and DGA, whereas they have not been entirely fulfilled for the secondary amines DEA and MOR. However, additional research is necessary in order to explain unambiguously the discrepancy between stopped-flow and stirred-cell technique for amine reactions in which the zwitterion deprotonation is rate determining.

6. CONCLUSIONS

The kinetics of the reaction of CO_2 with various alkanolamines in aqueous solutions has been studied as a function of temperature. Also kinetic data were obtained for the reaction between CO_2 and the cyclic amine MOR in aqueous solutions. All these reactions can be described by the zwitterion mechanism originally proposed by Caplow (1968).

With respect to the temperature influence on the overall reaction rate for primary and secondary amines, two classes can be distinguished: when the zwitterion formation is rate determining a significant temperature influence is observed, whereas only a slight temperature dependence is observed when the zwitterion deprotonation is rate determining. Since the zwitterion-deprotonation rate constants are a combination of elementary reaction-rate constants, this phenomenon can be described satisfactorily by the zwitterion-reaction mechanism. Depending on the relative values of zwitterion-formation and deprotonation rates an amine can shift from the first class to the second with increasing temperature, resulting in a decreasing temperature dependence of the overall reaction rate.

In the present work, all kinetic experiments were interpreted with the aid of a numerical flux model which describes gas absorption accompanied by reversible chemical reactions (Littel *et al.*, 1991a). For fast reversible reactions like those in the present study, only in this way can reliable reaction-rate data be deduced from absorption experiments.

The relationship between the zwitterion-formation rate constant and the acid-dissociation constant of the alkanolamine, as proposed by Versteeg and van Swaaij (1988a), seems to be valid over a wide range of temperatures and for a great variety of alkanolamines. This relationship is not valid for cyclic amines like MOR.

For DIPA and DEA, Arrhenius-type expressions for the zwitterion-deprotonation rate constants were presented which describe all kinetic data within 30% and 40%, respectively.

NOTATION

k_{app}	apparent pseudo-first-order reaction-rate constant, s^{-1}
k_2	zwitterion-formation-rate constant, $m^3\,mol^{-1}\,s^{-1}$
k_{H_2O}	zwitterion-deprotonation-rate constant, $m^6\,mol^{-2}\,s^{-1}$
$k_{R_1R_2NH}$	zwitterion-deprotonation-rate constant, $m^6\,mol^{-2}\,s^{-1}$
k_L	liquid-phase mass transfer coefficient, $m\,s^{-1}$
P	pressure, Pa

Amine abbreviations

DEA	diethanolamine
DGA	diglycolamine
DIPA	diisopropanolamine
MEA	monoethanolamine
MMEA	methylmonoethanolamine
MOR	morpholine
R_1R_2NH	primary or secondary amine

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