

KINETICS OF CO₂ WITH PRIMARY AND SECONDARY AMINES IN AQUEOUS SOLUTIONS—I. ZWITTERION DEPROTONATION KINETICS FOR DEA AND DIPA IN AQUEOUS BLENDS OF ALKANOLAMINES

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Abstract—The deprotonation kinetics of the DEA–CO₂ and the DIPA–CO₂ zwitterions have been studied in aqueous blends of amines at 298 K. Amine mixtures investigated were: DEA–TEA, DEA–MDEA, DEA–DMMEA, DEA–DEMEA, DIPA–TEA, DIPA–MDEA, DIPA–DMMEA, DIPA–DEMEA. For each blend the zwitterion deprotonation constant of the additional base present in solution (i.e. the tertiary amine) was determined. The observed deprotonation rate constants for the DEA-zwitterion and for the DIPA-zwitterion could be summarized in two Brønsted-type relationships. These relationships can be used to estimate the overall reaction rate of CO₂ with DEA or DIPA in aqueous blends of amines. The present work on the zwitterion deprotonation kinetics of the reaction of CO₂ with DEA and DIPA in aqueous amine blends provides additional verification for the validity of the zwitterion mechanism proposed by Caplow (1968) for the description of the reaction between CO₂ and primary and secondary alkanolamines.

1. INTRODUCTION

The removal of acid components, such as H₂S, CO₂ and COS, from natural and industrial gases is a frequently encountered operation in process industry. A common method used is the chemical absorption in a basic alkanolamine solution. Industrially important alkanolamines for this operation are the secondary amines, diethanolamine (DEA) and diisopropanolamine (DIPA), and the tertiary alkanolamine N-methyldiethanolamine (MDEA). Generally, aqueous solutions of these alkanolamines are applied; however, combined solvents like water and sulfolane in the Shell Sulfinol process are also used (Kohl and Riesenfeld, 1979).

Much research has been focussed on selective absorption of H₂S (being the main sulfur compound) from gas streams in which both CO₂ and H₂S are present. Blauwhoff *et al.* (1985) showed that selective absorption of H₂S reduces the costs of the treating process considerably. Selective absorption of H₂S is, among others, achieved by reducing the reaction rate of CO₂. Generally, this reaction rate is much lower for tertiary amines than for primary and secondary amines, which explains the increasing popularity of tertiary amines for selective absorption. Also processes based on sterically hindered (secondary) amines, like the Exxon Flexsorb process, seem applicable for this purpose (Sartori *et al.*, 1987). Primary and secondary alkanolamines, however, remain very suitable for the bulk removal of CO₂ from industrial gas streams. Also aqueous blends of primary or secondary amines with tertiary amines promise to be very attractive for bulk CO₂ removal as these blends combine the higher reaction rates between CO₂ and primary or secondary amines with the easier regeneration of tertiary amines (Chakravarty *et al.*, 1985).

In order to establish the performance of treating processes, thorough knowledge is required on mechanism and kinetics of the reaction between CO₂ and alkanolamines. This reaction has been subject to many studies. For the reaction of CO₂ with primary and secondary alkanolamines the zwitterion mechanism proposed by Caplow (1968) is generally accepted. This mechanism comprises two steps: formation of the CO₂-amine zwitterion, followed by base-catalyzed deprotonation of this zwitterion. The reaction of CO₂ with tertiary amines differs essentially from that with primary and secondary alkanolamines. For tertiary amines, the reaction with CO₂ can be described by the base-catalyzed hydration mechanism proposed by Donaldson and Nguyen (1980).

Versteeg and van Swaaij (1988a) suggested a correlation between the rate constant for the zwitterion formation and the basicity of the alkanolamine for a variety of primary and secondary alkanolamines. For the reaction between CO₂ and tertiary amines a correlation between the forward reaction rate constant and the basicity of the amine has been reported also (Littel *et al.*, 1990b).

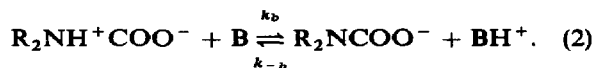
In part I of the present work, the zwitterion deprotonation step of the reaction between CO₂ and the secondary amines DEA and DIPA has been studied at 298 K in solutions comprising DEA or DIPA, water, and a tertiary alkanolamine. For both DEA and DIPA the overall reaction rate is substantially limited by the deprotonation of the zwitterion. By varying concentration and type of the tertiary alkanolamine the rate of this deprotonation step can be influenced significantly. The tertiary amines applied were triethanolamine (TEA), MDEA, dimethylmonoethanolamine (DMMEA) and diethylmonoethanolamine (DEMEA). It was attempted to derive a similar

correlation between the contribution of a base to the zwitterion deprotonation rate and the basicity of the deprotonating agent as the relation suggested by Versteeg and van Swaaij (1988a) for the zwitterion formation.

In Part II of the present work (Littel *et al.*, 1992) attention will be focussed on the temperature influence on zwitterion formation and deprotonation rates for the reaction between CO₂ and primary and secondary amines in aqueous solutions.

2. REACTION MECHANISM

The reaction of CO₂ with primary and secondary alkanolamines has been studied extensively in both aqueous and nonaqueous solutions [e.g. Alvarez-Fuster *et al.* (1980), Laddha and Danckwerts (1981), Barth *et al.* (1984), Blauwhoff *et al.* (1984), Sada *et al.* (1985, 1986), Versteeg and van Swaaij (1988a) and Versteeg and Oyevaar (1989)]. The zwitterion mechanism originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979) is generally accepted as the reaction mechanism:



This mechanism comprises two steps: formation of the CO₂-amine zwitterion [reaction (1)], followed by base-catalyzed deprotonation of this zwitterion [reaction (2)]. According to Blauwhoff *et al.* (1984) any base present in solution will contribute to the deprotonation of the zwitterion. Hence, in an aqueous solution of a single primary or secondary amine, the zwitterion deprotonation depends on R₂NH, H₂O, and OH⁻ concentrations, whereas in the aqueous amine blends studied in the present work this deprotonation also depends on the R₃N concentration. Versteeg and van Swaaij (1988a) argued that, for aqueous amine solutions, the contribution of the hydroxyl ion is only minor, due to its low concentration, and may be neglected without a substantial loss of accuracy. Under the assumption of pseudo-steady state for the zwitterion concentration, the following expression for the overall forward reaction rate can be derived (Blauwhoff *et al.*, 1984):

$$R_{\text{CO}_2} = \frac{[\text{R}_2\text{NH}][\text{CO}_2]}{\frac{1}{k_2} + \frac{k_{-1}}{k_2 \sum k_b [\text{B}]}} \quad (3)$$

Reaction rate equation (3) is a general expression which, in the case of aqueous blends of a secondary amine and a tertiary amine, can be specified as

$$R_{\text{CO}_2} = \frac{[\text{R}_2\text{NH}][\text{CO}_2]}{\frac{1}{k_2} + \frac{1}{k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{\text{R}_2\text{NH}}[\text{R}_2\text{NH}] + k_{\text{R}_3\text{N}}[\text{R}_3\text{N}]}} = k_{\text{app}, \text{R}_2\text{NH}}[\text{CO}_2] \quad (4)$$

with

$$k_{\text{H}_2\text{O}} = \frac{k_2 k_{b, \text{H}_2\text{O}}}{k_{-1}}, \quad k_{\text{R}_2\text{NH}} = \frac{k_2 k_{b, \text{R}_2\text{NH}}}{k_{-1}},$$

$$k_{\text{R}_3\text{N}} = \frac{k_2 k_{b, \text{R}_3\text{N}}}{k_{-1}}$$

Values for k_2 , $k_{\text{H}_2\text{O}}$ and $k_{\text{R}_2\text{NH}}$ for aqueous solutions of DIPA and DEA were reported by Versteeg and van Swaaij (1988a) and Versteeg and Oyevaar (1989), respectively.

Apart from the contribution of the tertiary amine to the deprotonation of the zwitterion, carbon dioxide can also react directly with the tertiary amine. The reaction between CO₂ and tertiary amines can be described as a base-catalyzed hydration of CO₂ (Donaldson and Nguyen, 1980):



with the forward reaction rate

$$R_{\text{CO}_2} = k_{2, \text{R}_3\text{N}}[\text{R}_3\text{N}][\text{CO}_2] \quad (6)$$

Littel *et al.* (1990b) presented a literature review for tertiary amines and presented also new experimental data for TEA, DMMEA and DEMA.

A third parallel reaction which takes place in aqueous solutions of secondary and tertiary amines is the reaction of CO₂ with the hydroxyl ion:



Kinetic data on this reaction were among others reported by Pohorecki and Moniuk (1988). From the work of Glasscock and Rochelle (1989) and Littel *et al.* (1991a) it can be concluded, however, that the contribution of reaction (7) to the overall reaction rate is negligible for the amine mixtures and experimental conditions applied in the present work.

The absorption of CO₂ in aqueous blends of a primary or secondary amine with a tertiary amine or carbonate, has received much attention lately (Rangwala *et al.*, 1988; Tseng *et al.*, 1988; Bosch *et al.*, 1989; Versteeg *et al.*, 1990; Glasscock *et al.*, 1991). From the point of view of chemical reaction kinetics, these systems can be divided into two classes, based on the rate-determining step of the reaction between CO₂ and the primary or secondary amine. If the zwitterion formation [reaction (1)] is rate determining, the absorption process can be described by the independently determined reaction rates of CO₂ with each reactant and the equilibria which take place among products and reactants. Consequently, calculation of gas absorption rates for these systems is relatively straightforward and requires no additional kinetic data. Examples of this class of systems are the blends of MEA-MDEA, MEA-TEA, and MMEA-MDEA which were studied by Glasscock *et al.* (1991), Rangwala *et al.* (1988) and Versteeg *et al.* (1990).

If, however, the deprotonation of the zwitterion is rate determining, the description of the absorption process is much more complicated as all bases present

in solution contribute to this zwitterion deprotonation. As a result, the overall reaction rate between CO₂ and the primary or secondary amine in an aqueous blend of amines is inherently different from that in an aqueous solution of just the primary or secondary amine. Examples of this class of systems are aqueous blends of DEA–MDEA, and DIPA–MDEA (Glasscock *et al.*, 1991; Versteeg *et al.*, 1990). Also DEA promoted carbonate solutions exhibit this behavior (Tseng *et al.*, 1988). In order to calculate absorption rates for the latter class of systems, it is necessary to determine the zwitterion deprotonation rate with respect to the various bases which are present in solution. Naturally, it would be very convenient if this zwitterion deprotonation rate could be related to the basicity of the base. Therefore, aqueous blends of DEA–R₃N and DIPA–R₃N were studied systematically in the present work.

3. EXPERIMENTAL

The kinetic experiments were carried out in a stirred cell reactor with a smooth horizontal gas–liquid interface. The operation was batchwise with respect to both gas and liquid phases. The experimental setup used (see Fig. 1) was essentially identical to that of Blauwhoff *et al.* (1984) and Versteeg and van Swaaij (1988a). A detailed description of the experimental procedure is given by Blauwhoff *et al.* (1984).

Concentrations of the alkanolamines were chosen carefully in order to determine accurate zwitterion deprotonation rate constants and to avoid a large contribution of the direct reaction between CO₂ and the tertiary amine to the overall reaction rate. In practice, this implies that the concentration ratio of

tertiary and secondary amines may not be too high, as in that case the direct reaction between CO₂ and tertiary amine would be dominant, and may also not be too low, as in that case the contribution of tertiary amine to the zwitterion deprotonation rate would be negligible.

During the experiment, the pressure decrease of pure carbon dioxide is recorded as a function of time. Based on mass balances for both gas and liquid phase, the following expression for the carbon dioxide flux can be derived:

$$J_{\text{CO}_2} = m_{\text{CO}_2} k_{L,\text{CO}_2} E P_{\text{CO}_2} / RT. \quad (10)$$

The enhancement factor E is equal to Ha if pseudo-first-order conditions are fulfilled, i.e.

$$2 < Ha \ll E^\infty \quad (11)$$

with

$$Ha = \frac{\sqrt{k_{ov} D_{\text{CO}_2}}}{k_L} \quad (12)$$

$$E = \sqrt{\frac{D_{\text{CO}_2}}{D_{R_2NH}}} + \sqrt{\frac{D_{R_2NH}}{D_{\text{CO}_2}} \frac{[R_2NH] RT}{\gamma m_{\text{CO}_2} P_{\text{CO}_2}}}. \quad (13)$$

Strictly speaking, eq. (13) is only valid for irreversible reactions. The validity of the application of eqs (11)–(13) for the interpretation of the present kinetic experiments, involving reversible reactions, was verified by means of the numerically solved absorption model presented by Littel *et al.* (1991a). From these model simulations it was concluded that pseudo-first-order conditions with regard to both secondary and tertiary amine prevailed in all kinetic experiments. The contribution to the overall reaction rate of

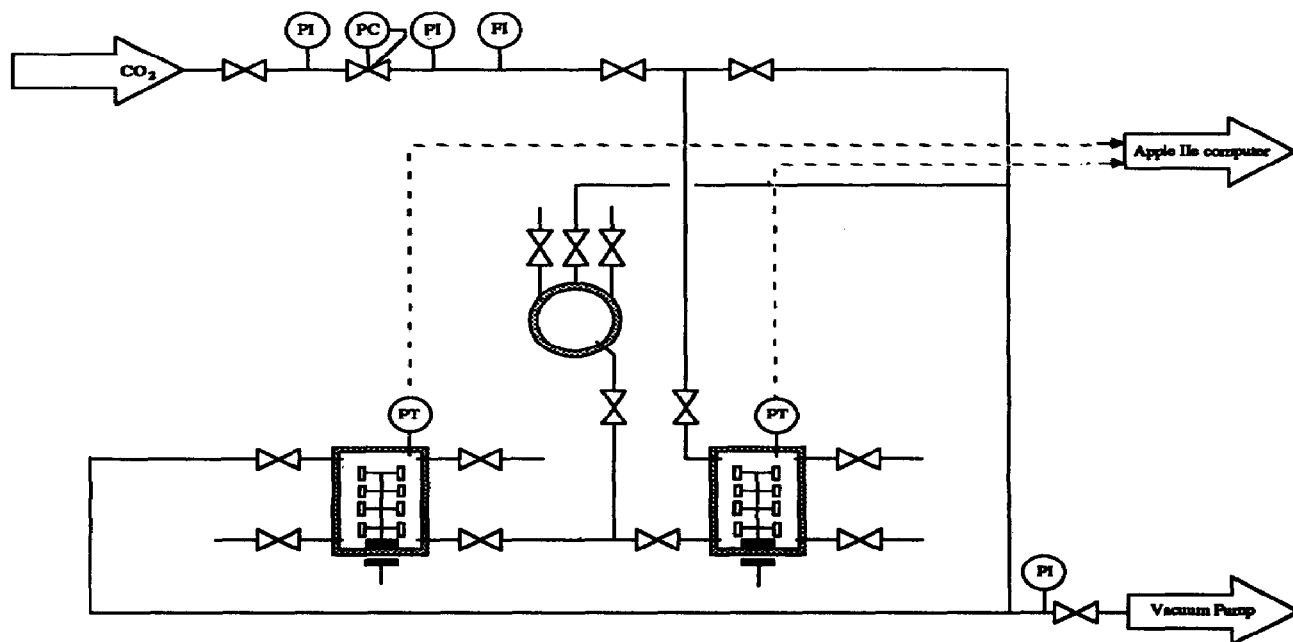


Fig. 1. Experimental setup.

the reaction between CO_2 and OH^- was negligible for all present kinetic experiments. A typical concentration profile at the end of the contact time is presented in Fig. 2 for a DIPA–MDEA blend. The validity of assuming pseudo-first-order conditions is illustrated by the flatness of curves 2 and 3 in Fig. 2.

The overall pseudo-first-order reaction rate constant, which is obtained from the kinetic experiments, consists of the contributions of the two pseudo-first-order parallel reactions between CO_2 and the secondary and tertiary amine. Hence, the apparent pseudo-first-order reaction rate constant with respect to the secondary amine can be calculated from eq. (14):

$$k_{ov} = k_{app,R_2NH} + k_{2,R_3N}[R_3N]. \quad (14)$$

The k_{2,R_3N} was obtained from the work of Littell *et al.* (1990b). The apparent reaction rate constant k_{app,R_2NH} , which follows from eq. (14), is a function of all bases present in solution as expressed by eq. (4). Fitting of the experimentally obtained reaction rate constants k_{app,R_2NH} to expression (4) by means of a Levenberg–Marquardt fitting procedure yielded the zwitterion deprotonation rate constants with respect to the various bases present in solution. In fitting the present data to expression (4), also the kinetic data for DIPA and DEA reported by Versteeg and van Swaaij (1988a) and Versteeg and Oyevaar (1989) were taken into account.

The deduction of zwitterion deprotonation rate constants from kinetic experiments in aqueous solutions of alkanolamines turns out to be not that straightforward. The concentrations of the components which take part in the zwitterion deprotonation cannot be varied independently and the variation in concentrations is rather limited as a result of experimental limitations. Consequently, the fitted deprotonation rate constants are not entirely independent of each other and tend to be rather sensitive to small variations in experimental data, although it should be noted that this sensitivity of individually fitted rate constants did not have a significant effect on the accuracy of k_{app} predictions. In the present work on aqueous blends of amines, two approaches were used to maximize the accuracy of individual fitted rate constants: applying variations in amine concentrations as widely as possible within the experimental constraints and including experimental data for aqueous solutions of DEA or DIPA alone in fitting the experiments to expression (4).

Since CO_2 reacts with the alkanolamine it is in general not possible to determine its solubility and diffusivity directly. In view of the similarities with regard to configuration, molecular volume and electronic structure, N_2O is often used as a nonreacting gas to estimate the physical properties of CO_2 . In the present study, the solubility of CO_2 was determined by means of this CO_2 – N_2O analogy (Laddha *et al.*, 1981). 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

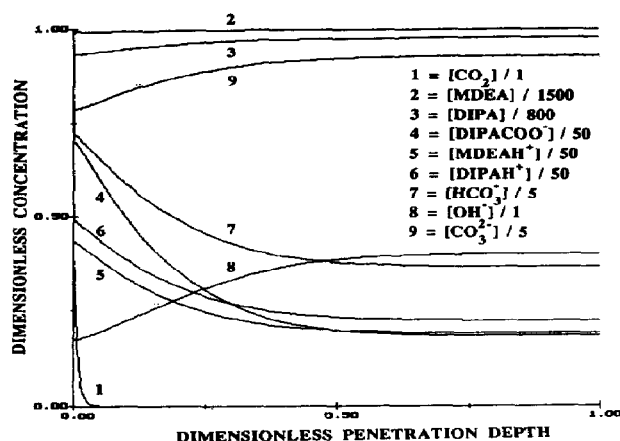


Fig. 2. Typical concentration profile at the end of the contact time for a DIPA–MDEA blend (penetration theory model, 298 K, $[\text{DIPA}] = 803 \text{ mol m}^{-3}$, $[\text{MDEA}] = 1510 \text{ mol m}^{-3}$, $P_{\text{CO}_2} = 0.015 \text{ bar}$, amine loading 0.7%).

ous amine mixtures used in the present work are reported by Littell *et al.* (1991b).

For all kinetic experiments CO_2 pressures and amine loadings were typically 0.01–0.10 bar and 0.3–2.0%, respectively.

Secondary and tertiary amine concentrations were determined by means of the titration method described by Siggia *et al.* (1950).

DEA, MDEA and TEA were obtained from Janssen Chimica; DMMEA and DEMEA were obtained from Merck; DIPA was obtained from Riedel-de Haën. All alkanolamines were pure analytical quality and used as received.

4. KINETIC RESULTS

4.1. Mixtures of DIPA and tertiary amines

In the present work the kinetics of DIPA with CO_2 has been studied in aqueous amine blends of DIPA–TEA, DIPA–MDEA, DIPA–DMMEA, and DIPA–DEMEA at 298 K. The results of these kinetic experiments, which were interpreted according to eq. (14), are reported in Tables 1–4. In Table 1 also some additional data for aqueous DIPA solutions are presented, which were obtained at relatively low DIPA concentrations. Fitting of these data together with the data published by Versteeg and van Swaaij (1988a) to the zwitterion rate expression yields the reaction rate constants reported in Table 9. The present rate constants presented for aqueous DIPA solutions agree well with those reported by Versteeg and van Swaaij (1988a). Only the fitted value for $k_{\text{H}_2\text{O}}$, which is largely determined by kinetic data obtained at low amine concentrations, is somewhat lower.

Comparison of the present kinetic results for DIPA in aqueous amine blends with the kinetic results reported for DIPA in aqueous solutions shows that the presence of an additional base results in a significant increase in k_{app} . For a blend of 200 mol m^{-3} DIPA and 2000 mol m^{-3} of the rather weak base TEA, this

Table 1. Experimental kinetic data for the DIPA-TEA system

DIPA (mol m ⁻³)	TEA (mol m ⁻³)	H ₂ O (mol m ⁻³)	k _{app} (s ⁻¹)
219	0	53,840	12
220	0	53,830	15
221	0	53,820	13
222	0	53,820	15
939	0	48,810	175
943	0	48,780	169
952	0	48,710	158
228	203	52,090	24
236	200	52,150	23
238	300	51,590	24
240	305	51,520	26
228	993	46,700	19
230	995	46,670	19
221	1991	39,830	26
238	1983	39,770	32
241	1961	39,930	28
244	1982	39,740	33
259	2169	38,080	34
238	2754	34,290	44
251	2748	34,380	35
251	2802	33,800	36
257	2744	34,370	47
258	3391	29,730	47
259	3394	29,700	43
241	4005	25,450	57
243	4078	24,800	54
820	3001	28,400	217

Table 2. Experimental kinetic data for the DIPA-MDEA system

DIPA (mol m ⁻³)	MDEA (mol m ⁻³)	H ₂ O (mol m ⁻³)	k _{app} (s ⁻¹)
327	996	47,110	60
328	999	47,090	60
329	1005	47,030	56
330	1367	44,570	84
332	1993	41,110	81
335	1975	41,210	114
335	1988	41,120	80
281	2311	39,430	75
288	2344	39,230	89
338	2749	36,490	109
338	2783	36,260	90
342	2810	36,130	110
343	2886	35,630	106
315	3533	31,960	142
323	3540	31,850	104
339	3518	31,870	134
331	4024	28,930	118
348	4194	27,640	140
785	509	46,830	189
806	525	46,570	169
796	1488	40,910	205
796	1498	40,880	248
797	1493	40,870	266
803	1510	40,740	257
805	1973	37,930	225
819	2006	37,610	239
751	2519	35,030	302
775	2467	35,200	259
786	2472	35,080	230
796	2922	32,290	262
823	3011	31,530	263

Table 3. Experimental kinetic data for the DIPA-DMMEA system

DIPA (mol m ⁻³)	DMMEA (mol m ⁻³)	H ₂ O (mol m ⁻³)	k _{app} (s ⁻¹)
975	485	46,110	378
990	493	45,980	331
1002	499	45,840	378
956	1004	43,610	412
967	965	43,750	478
982	979	43,560	518
988	986	43,450	505
936	1457	41,470	672
964	1501	41,050	604
965	1494	41,070	526
986	1970	38,500	657
993	1902	39,070	747
958	2502	35,970	862
848	3095	33,550	767
870	3174	33,000	797

Table 4. Experimental kinetic data for the DIPA-DEMEA system

DIPA (mol m ⁻³)	DEMEA (mol m ⁻³)	H ₂ O (mol m ⁻³)	k _{app} (s ⁻¹)
976	492	44,600	378
998	500	45,120	390
998	504	44,550	429
1039	509	44,750	351
958	945	42,070	500
979	964	41,780	460
994	981	41,570	521
995	1005	41,780	490
1002	1000	41,730	504
1026	1014	41,490	609
995	1973	35,090	707
1001	1981	34,970	741
1029	2000	34,850	826
1037	2023	34,640	815

increase amounts to about 45%; for a blend of 1000 mol m⁻³ DIPA and 2000 mol m⁻³ of the much stronger base DEMEA, this increase is more than 250%.

In Table 9, zwitterion formation and deprotonation rate constants are presented which were obtained by fitting the kinetic results reported in Tables 1–4 to the reaction rate expression (4). The zwitterion formation rate constants (*k*₂) show a relatively large variation as a result of the fact that the deprotonation of the zwitterion is almost entirely rate determining. The zwitterion deprotonation rate constants increase with increasing basicity of the deprotonating base. All kinetic data are fitted within 20% by the rate constants reported in Table 9.

4.2. Mixtures of DEA and tertiary amines

The kinetics between DEA and CO₂ has been studied in aqueous amine blends of DEA-TEA, DEA-MDEA, DEA-DMMEA, and DEA-DEMEA

at 298 K. The results of these kinetic experiments are presented in Tables 5–8. The presence of an additional base results in an increase in k_{app} for DEA in aqueous amine blends in comparison to the k_{app} reported for DEA in aqueous solution (Versteeg and Oyeveaar, 1989). This increase is about 100% for a mixture of 500 mol m⁻³ DEA and 2000 mol m⁻³ MDEA. For a blend of 500 mol m⁻³ DEA and 2000 mol m⁻³ DEMEA, this increase amounts even to 270%.

The kinetic results reported in Tables 5–8 were fitted to eq. (4), which follows from the zwitterion mechanism. The fitted values for k_2 and the fitted values for the zwitterion deprotonation constants for DEA, H₂O and the various tertiary amines are presented in Table 9. Most of the kinetic experiments are fitted within 15% with these constants. The value obtained for MDEA for the DEA-zwitterion deprotonation constant compares favorably to the value reported by Glasscock *et al.* (1991). The results in Table 9 show that the zwitterion deprotonation rate constants increase with increasing basicity of the deprotonating base.

4.3. Discussion

In Fig. 3, the zwitterion deprotonation rate constants for DEA, DIPA, and the tertiary amines are

Table 5. Experimental kinetic data for the DEA-TEA system

DEA (mol m ⁻³)	TEA (mol m ⁻³)	H ₂ O (mol m ⁻³)	k_{app} (s ⁻¹)
202	981	50,710	89
206	989	50,640	72
208	986	50,650	60
207	1908	47,320	65
217	1937	47,110	65
230	2933	43,330	81
499	1074	48,680	234
490	1107	48,570	208
525	2946	41,750	272

Table 6. Experimental kinetic data for the DEA-MDEA system

DEA (mol m ⁻³)	MDEA (mol m ⁻³)	H ₂ O (mol m ⁻³)	k_{app} (s ⁻¹)
197	1022	48,250	121
197	1027	48,220	133
200	2055	42,070	129
208	2001	42,390	114
195	2029	42,280	111
192	3051	36,080	202
208	3046	36,020	196
501	1037	46,580	408
502	1029	46,630	442
505	1041	46,530	346
501	3072	34,360	580
491	3102	34,220	541

plotted as a function of the pK_a-value of the deprotonating base for the DEA-CO₂ and DIPA-CO₂ zwitterion, respectively. The pK_a-values used for the alkanolamines were obtained from either Perrin (1965) or Littell *et al.* (1990a). From Fig. 3 it can be concluded that, for the same base, the zwitterion deprotonation rate constant for the DEA-zwitterion is always higher than that for the DIPA-zwitterion. The

Table 7. Experimental kinetic data for the DEA-DMMEA system

DEA (mol m ⁻³)	DMMEA (mol m ⁻³)	H ₂ O (mol m ⁻³)	k_{app} (s ⁻¹)
473	942	48,030	459
490	976	47,790	419
493	982	47,730	550
497	990	47,680	483
476	1899	43,150	673
488	1948	42,790	717
472	2826	38,460	679
494	2964	37,650	821
987	1003	45,130	1063
998	992	45,131	1205
1012	1018	44,900	1077
1016	1006	44,960	1126
1018	998	44,990	1127
1031	1036	44,710	1233
967	1932	40,490	1415
1002	2001	39,940	1574
1006	2009	39,880	1448

Table 8. Experimental kinetic data for the DEA-DEMEA system

DEA (mol m ⁻³)	DEMEA (mol m ⁻³)	H ₂ O (mol m ⁻³)	k_{app} (s ⁻¹)
503	493	49,434	322
522	498	49,290	425
486	955	46,320	429
500	985	46,050	508
512	998	46,140	491
515	995	46,140	482
485	1928	39,890	765
508	2020	39,120	793
509	2020	39,110	875
509	2023	39,110	865
513	2500	35,870	966
527	2531	35,590	789
531	2523	35,590	871
466	2787	34,000	909
489	2921	32,930	904
497	2962	32,650	912
977	776	45,154	1161
1004	743	45,210	1066
990	977	43,670	1013
993	982	43,640	1124
1000	1494	40,230	1646
1015	1505	40,060	1496
944	1877	37,890	1668
981	1945	37,170	1659
990	1966	37,020	1756
1002	2490	33,400	1682
1019	2481	33,360	1709

Table 9. Fitted reaction rate constants (298 K)

System	k_2 ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)	$10^4 \times k_{\text{H}_2\text{O}}$ ($\text{m}^6 \text{mol}^{-2} \text{s}^{-1}$)	$10^6 \times k_{\text{H}_2\text{O}}$ ($\text{m}^6 \text{mol}^{-2} \text{s}^{-1}$)	$10^4 \times k_{\text{B},\text{N}}$ ($\text{m}^6 \text{mol}^{-2} \text{s}^{-1}$)	Present work/Versteeg and van Swazij (1988a)
DIPA	2.78	2.00	0.51	—	Present work
DIPA-TEA	3.29	1.94	0.56	0.34	Present work
DIPA-MDEA	1.67	2.21	0.45	1.00	Present work
DIPA-DMMEA	2.72	2.01	0.51	3.87	Present work
DIPA-DEMEA	2.60	2.03	0.50	4.26	Present work
DEA	3.17	7.15	1.69	—	Versteeg and Oyeveaar (1989)
DEA-TEA	3.16	7.13	1.75	0.7	Present work
DEA-MDEA	—	6.37	4.10	4.57	Glasscock et al. (1991)
DEA-MDEA	3.13	7.23	1.68	3.54	Present work
DEA-DMMEA	3.29	7.02	1.72	9.74	Present work
DEA-DEMEA	3.20	7.07	1.70	11.2	Present work

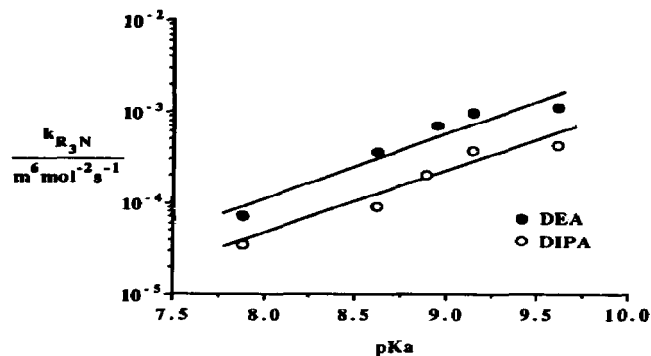


Fig. 3. Zwitterion deprotonation rate constants as a function of the basicity of the deprotonating base.

Table 10. pK_a values (298 K)

Amine	pK_a
DIPA	8.89
DEA	8.88
TEA	7.88
MDEA	8.63
DMMEA	9.11
DEMEA	9.61

experimentally determined zwitterion deprotonation rate constants can be summarized in two Brønsted-type relationships

$$\text{DEA: } \ln k_{\text{dep}} = 1.69pK_a - 22.7 \quad (15)$$

$$\text{DIPA: } \ln k_{\text{dep}} = 1.57pK_a - 22.7. \quad (16)$$

The pK_a of a base is defined as the negative logarithm of the dissociation equilibrium constant of its conjugate acid at infinite dilution. Consequently, the pK_a value of H₂O is an undefined property in water and the deprotonation constants of H₂O could not be taken into account in deriving eqs (15) and (16). Nevertheless, also for H₂O, the ratio of the deprotonation rate constants for the DIPA-zwitterion and for the DEA-zwitterion is much like that indicated by eqs (15) and (16).

The intercepts in eqs (15) and (16) have identical values, whereas the slopes differ slightly though still significantly. As yet this should be regarded coincidental and without physical meaning, as the constants in eqs (15) and (16) are rather sensitive to the exact values of the deprotonation rate constants. Equations (15) and (16) provide merely convenient expressions for a first estimation of zwitterion deprotonation rate constants as a function of the basicity of the deprotonating agents.

For DEA and DIPA, Blauwhoff *et al.* (1984) published rate constants for the zwitterion deprotonation by OH⁻. However, they assumed a constant OH⁻ concentration, equal to the bulk OH⁻ concentration,

throughout the mass transfer zone. This assumption is not correct as is illustrated by the concentration profile for OH⁻ depicted in Fig. 2. Consequently, the zwitterion deprotonation rate constants presented by Blauwhoff *et al.* (1984) for OH⁻ have been underestimated and they are indeed much lower than these predicted according to eqs (15) and (16). Nevertheless, the general dependence of the zwitterion deprotonation rate from the basicity of the deprotonating agent shown by Blauwhoff *et al.* (1984) agrees satisfactorily with the present work.

5. CONCLUSIONS

The reaction of CO₂ with the secondary alkanolamines DEA and DIPA has been studied in aqueous blends of a secondary and a tertiary amine. Amine blends investigated were: DEA-TEA, DEA-MDEA, DEA-DMMEA, DEA-DEMEA, DIPA-TEA, DIPA-MDEA, DIPA-DMMEA, DIPA-DEMEA. The overall reaction rate of CO₂ with DEA and DIPA in aqueous solutions is almost entirely determined by the zwitterion deprotonation rate. By varying concentration and type of an additional base present in solution (i.e. the tertiary alkanolamine), the rate of this zwitterion deprotonation step could be affected significantly. In this way zwitterion deprotonation rate constants were determined for various tertiary alkanolamines.

The observed deprotonation rate constants for the DEA-zwitterion and the DIPA-zwitterion were summarized in two Brønsted-type relationships. These Brønsted-type relationships can be used to estimate the overall reaction rate of CO₂ with DEA or DIPA in aqueous blends of amines.

The present work on the zwitterion deprotonation kinetics of the reaction of CO₂ with DEA and DIPA in aqueous amine blends provides strong evidence for the validity of the zwitterion mechanism proposed by Caplow (1968) for the description of the reaction between CO₂ and primary and secondary alkanolamines.

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NOTATION

D	diffusivity, $\text{m}^2 \text{s}^{-1}$
E	enhancement factor
E^∞	maximum enhancement factor
Ha	Hatta number [eq. (7)]
J	mol flux, $\text{mol m}^{-2} \text{s}^{-1}$
k_{app}	pseudo-first-order reaction rate constant, s^{-1}
k_{ov}	overall pseudo-first-order reaction rate constant, s^{-1}
k_L	liquid-phase mass transfer coefficient, m s^{-1}
m	dimensionless solubility

P	pressure, Pa
R	ideal gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
T	temperature, K

Greek letter

γ	stoichiometric coefficient
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Amine abbreviations

DEA	diethanolamine
DEMEA	diethylmonoethanolamine
DIPA	diisopropanolamine
DMMEA	dimethylmonoethanolamine
MDEA	N-methyldiethanolamine
MMEA	methylmonoethanolamine
TEA	triethanolamine
$R_2\text{NH}$	secondary amine (DEA, DIPA)
$R_3\text{N}$	tertiary amine (TEA, MDEA, DMMEA, DEMEA)

REFERENCES

- Alvarez-Fuster, C., Midoux, N., Laurent, A. and Charpentier, J. C., 1980, Chemical kinetics of the reaction of carbon dioxide with amines in pseudo m - n th order conditions in aqueous and organic solutions. *Chem. Engng Sci.* **35**, 1717–1723.
- Barth, D., Tondre, C. and Delpuech, J.-J., 1984, Kinetics and mechanism of the reactions of carbon dioxide with alkanolamines: a discussion concerning the cases of MDEA and DEA. *Chem. Engng Sci.* **39**, 1753–1757.
- Blauwhoff, P. M. M., Versteeg, G. F. and van Swaaij, W. P. M., 1984, A study on the reaction between CO₂ and alkanolamines in aqueous solutions. *Chem. Engng Sci.* **39**, 207–225.
- Blauwhoff, P. M. M., Kamphuis, B., van Swaaij, W. P. M. and Westerterp, K. R., 1985, Absorber design in sour natural gas treatment plants: impact of process variables on operation and economics. *Chem. Engng Proc.* **19**, 1–25.
- Bosch, H., Versteeg, G. F. and van Swaaij, W. P. M., 1989, Gas-liquid mass transfer with parallel reversible reactions—III. Absorption of CO₂ into solutions of blends of amines. *Chem. Engng Sci.* **44**, 2745–2750.
- Caplow, M., 1968, Kinetics of carbamate formation and breakdown. *J. Am. chem. Soc.* **90**, 6795–6803.
- Chakravarty, T., Phukan, U. K. and Weiland, R. H., 1985, Reaction of acid gases with mixtures of amines. *Chem. Engng Prog.* (4), 32–36.
- Danckwerts, P. V., 1979, The reactions of CO₂ with ethanolamines. *Chem. Engng Sci.* **34**, 443–446.
- Donaldson, T. L. and Nguyen, Y. N., 1980, Carbon dioxide reaction and transportation in aqueous amine membranes. *Ind. Engng Chem. Fundam.* **19**, 260–266.
- Glasscock, D. A. and Rochelle, G. T., 1989, Numerical simulation of theories for gas absorption with chemical reaction. *A.I.Ch.E. J.* **35**, 1271–1281.
- Glasscock, D. A., Critchfield, J. E. and Rochelle, G. T., 1991, CO₂ absorption/desorption in mixtures of methyl-diethanolamine with monoethanolamine or diethanolamine. *Chem. Engng Sci.* **46**, 2829–2845.
- Kohl, A. L. and Riesenfeld, F. C., 1979, *Gas Purification*. Gulf, Houston, TX.
- Laddha, S. S. and Danckwerts, P. V., 1981, Reaction of CO₂ with ethanolamines: kinetics from gas-absorption. *Chem. Engng Sci.* **36**, 479–482.
- Laddha, S. S., Diaz, J. M. and Danckwerts, P. V., 1981, The N₂O analogy: the solubilities of CO₂ and N₂O in aqueous solutions of organic compounds. *Chem. Engng Sci.* **36**, 228–229.
- Littel, R. J., Bos, M. and Knoop, G. J., 1990a, Dissociation constants of some alkanolamines at 293, 303, 318 and 333 K. *J. chem. Engng Data* **35**, 276–277.

- Littel, R. J., van Swaaij, W. P. M. and Versteeg, G. F., 1990b, The kinetics of carbon dioxide with tertiary amines in aqueous solution. *A.I.Ch.E. J.* **36**, 1633–1640.
- Littel, R. J., Filmer, B., Versteeg, G. F. and van Swaaij, W. P. M., 1991a, Modelling of simultaneous absorption of H₂S and CO₂ in alkanolamine solutions: the influence of parallel and consecutive reversible reactions and the coupled diffusion of ionic species. *Chem. Engng Sci.* **46**, 2303–2313.
- Littel, R. J., Versteeg, G. F. and van Swaaij, W. P. M., 1991b, Solubility and diffusivity data for the absorption of COS, CO₂, and N₂O in amine solutions. *J. chem. Engng Data* (in press).
- Littel, R. J., Versteeg, G. F. and van Swaaij, W. P. M., 1992, Kinetics of CO₂ with primary and secondary amines in aqueous solutions—II. Influence of temperature on zwitterion formation and deprotonation rates. *Chem. Engng Sci.* **47**, 2037–2045.
- Perrin, D. D., 1965, *Dissociation Constants of Organic Bases in Aqueous Solution*. Butterworths, London.
- Pohorecki, R. and Moniuk, W., 1988, Kinetics of reaction between carbon dioxide and hydroxyl ions in aqueous electrolyte solutions. *Chem. Engng Sci.* **43**, 1677–1684.
- Rangwala, H. A., Morrell, B. R., Mather, A. E. and Otto, F. D., 1988, Absorption of CO₂ into aqueous tertiary amine/MEA solutions. AIChE National Meeting, New Orleans, LA.
- Sada, E., Kumazawa, H., Han, Z. Q. and Matsuyama, H., 1985, Chemical kinetics of the reaction of carbon dioxide with ethanalamines in nonaqueous solvents. *A.I.Ch.E. J.* **31**, 1297–1303.
- Sada, E., Kumazawa, H., Osawa, Y., Matsuura, M. and Han, Z. Q., 1986, Reaction kinetics of carbon dioxide with amines in non-aqueous solvents. *Chem. Engng J.* **33**, 87–95.
- Sartori, G., Ho, W. S., Savage, D. W., Chludzinski, G. R. and Wiechert, S., 1987, Sterically-hindered amines for acid–gas absorption. *Sep. Purif. Methods* **16**, 171–200.
- Siggia, S., Hanna, J. G. and Kervenski, I. R., 1950, Quantitative analysis of mixtures of primary, secondary, and tertiary aromatic amines. *Analyt. Chem.* **12**, 1295–1297.
- Tseng, P. C., Ho, W. S. and Savage, D. W., 1988, Carbon dioxide absorption into promoted carbonate solutions. *A.I.Ch.E. J.* **34**, 922–931.
- Versteeg, G. F. and van Swaaij, W. P. M., 1988a, On the kinetics between CO₂ and alkanolamines both in aqueous and non-aqueous solutions—I. Primary and secondary amines. *Chem. Engng Sci.* **43**, 573–587.
- Versteeg, G. F. and van Swaaij, W. P. M., 1988b, Solubility and diffusivity of acid gases (CO₂, N₂O) in aqueous alkanolamine solutions. *J. chem. Engng Data* **33**, 29–34.
- Versteeg, G. F. and Oyevaar, M. H., 1989, The reaction between CO₂ and diethanolamine at 298 K. *Chem. Engng Sci.* **44**, 1264–1268.
- Versteeg, G. F., Kuipers, J. A. M., van Beckum, F. P. H. and van Swaaij, W. P. M., 1990, Mass transfer with complex reversible chemical reactions—II. Parallel reversible chemical reactions. *Chem. Engng Sci.* **45**, 183–197.