Equilibrium Constant for Carbamate Formation from Monoethanolamine and Its Relationship with Temperature

Mohammed Kheireddine Aroua, Abdelbaki Benamor, and Mohd Zaki Haji-Sulaiman*

Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

The equilibrium constant for the formation of carbamate from monoethanolamine was evaluated at various temperatures of 298, 308, 318, and 328 K and ionic strengths up to 1.7 M. From the plot of $\log_{10} K$ versus $I^{0.5}$, the variation of the thermodynamical constant with temperature follows the relationship $\log_{10} K_1 = -0.934 + (0.671 \times 10^3)K/T$.

Introduction

Removal of acid gases such as CO_2 and H_2S using aqueous solutions of alkanolamines is an industrially important process. The presence of the alkanolamine enhances the removal of the acid gas components through reactions in the liquid phase. The reactions of H_2S with an aqueous alkanolamine proceed according to parallel acid–base reactions. However, CO_2 reacts directly with a primary or secondary alkanolamine to form carbamate, which is one of the major reaction products. This step in the reaction mechanism has been argued to be responsible for the high rate of CO_2 absorption by primary and secondary alkanolamines as compared to those for tertiary alkanolamines. This reaction limits the ultimate stoichiometric loading to 0.5 mol of CO_2/mol of amine. At high CO_2 partial pressures, hydrolysis of carbamate can occur to yield free amines which would further react with additional CO_2 to give loadings higher than 0.5.

Despite the importance of the carbamate-forming reactions, reliable values of the equilibrium constant for its formation are not readily available in the literature. The data on the apparent equilibrium constants for diethanolamine (DEA) and monoethanolamine (MEA) reported by Jensen et al. (1954) and Chan and Danckwerts (1981) were obtained over a very limited range of operating conditions and could not be used in VLE models where thermodynamic constants are generally required. Due to the scarcity of this important data, it is a common approach among investigators to consider the equilibrium constants as adjustable parameters to be fitted together with other interaction parameters to alkanolamine + CO_2 VLE data. The values of equilibrium constants generated in this manner were found to give erroneous results when used to determine the species concentrations such as that of carbamate in the system (Haji-Sulaiman and Aroua, 1996). Recently, the authors (Aroua et al., 1997) applied the technique developed by Haji Sulaiman et al. (1996) to study the temperature dependence of the equilibrium constant for the formation of carbamate from DEA. In this technique, equilibrium solutions of DEA + $NaHCO_3$ with different ionic strengths were titrated with NaOH. This information, together with equations describing the equilibrium of the system and mass and charge balances, was used to evaluate the concentrations of the different species

and subsequently the equilibrium constants. From the plot of apparent equilibrium constant expressed in terms of species concentration versus the square root of the ionic strength, the equilibrium constants at infinite dilution at various temperatures were estimated. In a related work, Haji-Sulaiman et al. (1998) used these values of equilibrium constant for carbamate formation to analyze their equilibrium data for CO_2 in DEA and DEA + MDEA mixtures as well as other data reported in the literature using the modified Kent–Eisenberg model. Within reasonable accuracy, they obtained excellent agreement between experimental and predicted CO_2 loading.

The results to be discussed in this paper are an extension of the earlier work which estimates the equilibrium constant of carbamate formation from MEA. A relationship on its variations with temperature is also proposed.

Experimental Setup and Procedure

The chemicals used in the investigation were obtained from Merck (98% monoethanolamine and 99% sodium perchlorate monohydrate), May & Baker (99% sodium bicarbonate), and Reagecon (standard 1.0 M aqueous sodium hydroxide solution). All these chemicals were of p.a. quality and were used as received.

A similar experimental procedure to that employed in the previous work was used here (Aroua et al., 1997). Equilibrium experiments were performed by adding a predetermined amount of $NaHCO_3$ to exactly 100 mL of 0.100 ± 0.005 M MEA solution. The concentration of the MEA solution was checked by titration with a standard 0.1 M HCl solution. Experimental runs were conducted at different ratios (0.5, 1.0, and 1.5 mol of $NaHCO_3$ per mol of MEA) of bicarbonate to total amine. The ionic strength of the solution was varied by adding various amounts of inert salt $NaClO_4$ (0.0, 0.5, 1.0, and 1.5 M), and the system was left to equilibrate at (298, 308, 318, and 328) ± 0.5 K for about 24 h. A Labb-Line Orbit air bath shaker was used to control the temperature of the reacting mixtures. Finally, the equilibrated solution was titrated with 1.0 M NaOH solution using a PC-controlled Metrohm 716 DMS Titrino autotitrator which utilized the DET (Dynamic Equivalence-point Titration) technique for the determination of the end point from the first derivative of the titration curve. The analysis requires less than 5 min to perform, and within this short analysis period, the equilibrium of the system was not expected to be disturbed. All determinations were carried out in triplicate.

* To whom correspondence should be sent. Telephone: 3-7595292. Fax: 3-7595319. E-mail: mzaki@fk.um.edu.my.

Theory

The reaction of an aqueous solution of MEA with bicarbonate would result in the formation of carbamate, as represented by the equation

$$RNH_2 + HCO_3^- \leftrightarrow RNHCOO^- + H_2O \qquad \text{(i)}$$

where RNH_2 refers to MEA ($R = C_2H_4OH$). The apparent equilibrium constant K_C for this reaction is given by

$$K_C = \frac{[RNHCOO^-]_e}{[HCO_3^-]_e[RNH_2]_e} \qquad \text{(1)}$$

The subscripts e and t in the above and subsequent equations refer to the equilibrium and total species concentrations. The equilibrium constant given by eq 1 can be rewritten as a thermodynamical equilibrium constant K_1 as follows

$$K_1 = K_C \frac{\gamma_{RNHCOO^-}}{\gamma_{HCO_3^-}\gamma_{RNH_2}} \qquad \text{(2)}$$

In addition to reaction i, the following chemical equilibria are also established in the system:

$$RNH_3^+ \leftrightarrow RNH_2 + H^+ \qquad \text{(ii)}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad \text{(iii)}$$
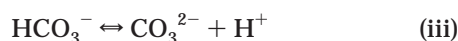
$$H_2O \leftrightarrow OH^- + H^+ \qquad \text{(iv)}$$

Each of the above reactions is characterized by a thermodynamical constant K_i similar to that of eq 2 according to the following expressions:

$$K_2 = \frac{[RNH_2]_e[H^+]_e}{[RNH_3^+]_e} \frac{\gamma_{RNH_2}\gamma_{H^+}}{\gamma_{RNH_3^+}} \qquad \text{(3)}$$

$$K_3 = \frac{[CO_3^{2-}]_e[H^+]_e}{[HCO_3^-]_e} \frac{\gamma_{CO_3^{2-}}\gamma_{H^+}}{\gamma_{HCO_3^-}} \qquad \text{(4)}$$

$$K_4 = \frac{[OH^-]_e[H^+]_e}{a_{H_2O}} \gamma_{OH^-}\gamma_{H^+} \qquad \text{(5)}$$

where a_{H_2O} is the activity of water. The following material and charge balance equations must also be satisfied:

Amine Balance

$$[RNH_2]_t = [RNH_2]_e + [RNH_3^+]_e + [RNHCOO^-]_e \qquad \text{(6)}$$

CO$_2$ Balance

$$[NaHCO_3]_t = [HCO_3^-]_e + [CO_3^{2-}]_e + [RNHCOO^-]_e \qquad \text{(7)}$$

Charge Balance

$$[Na^+]_t + [H^+]_e + [RNH_3^+]_e = [HCO_3^-]_e + 2[CO_3^{2-}]_e + [RNHCOO^-]_e + [OH^-]_e + [ClO_4^-]_t \qquad \text{(8)}$$

Sodium Balance

$$[Na^+]_t = [NaHCO_3]_t + [NaClO_4]_t \qquad \text{(9)}$$

By substituting $[Na^+]_t$ as given by eq 9 into eq 8 and

Table 1. Dissociation Constants Used in This Work (Various Units but Based on mol·dm^{-3})

parameter	a	b	c	d	range of validity, T/K
$K_2{}^a$	−3 071.15	6.776904	0	−48.7594	273−353
$K_3{}^b$	−12 431.70	−35.4819	0	220.067	273−498
$K_4{}^b$	−13 445.90	−22.4773	0	140.932	273−498

[a] Perrin, 1965. [b] Edwards et al., 1978.

replacing $[ClO_4^-]_t = [NaClO_4]_t$, we obtain

$$[NaHCO_3]_t + [H^+]_e + [RNH_3^+]_e = [HCO_3^-]_e + 2[CO_3^{2-}]_e + [RNHCOO^-]_e + [OH^-]_e \qquad \text{(10)}$$

As discussed by Aroua et al. (1997), the concentration of free CO_2 in carbonated aqueous amine solutions is generally small and has been ignored in this work.

If an aliquot of the solution is titrated with a strong base such as NaOH, only the bicarbonate and the protonated MEA ions will react with hydroxide ions. Thus, the concentration B of NaOH at the end point can be related to the concentrations of the two ionic species by the equation

$$B = [RNH_3^+]_e + [HCO_3^-]_e \qquad \text{(11)}$$

The set of eqs 3−7, 10, and 11 was solved simultaneously to obtain the concentrations of the seven species for given values of K_2, K_3, K_4, γ_j, a_{H_2O}, $[RNH_2]_t$, $[NaHCO_3]_t$, and B. The apparent equilibrium constant for carbamate formation can then be calculated using eq 1. Literature values for the equilibrium constants K_2-K_4 which were expressed in the form

$$\ln K = a/T + b \ln T + cT + d \qquad \text{(12)}$$

were used in the calculation. The constants a, b, c, and d are given in Table 1. The activity of water was assumed to be that of water in $NaClO_4$ solutions, and the corresponding values were taken from the literature (Aroua, 1992). To compute the activity coefficients of the other species, the equation proposed by Guggenheim (1935) was used, with the contribution from the binary interactions neglected, as supported by the data published by Haji-Sulaiman and Aroua (1996)

$$\ln \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + b_i\sqrt{I}} \qquad \text{(13)}$$

In the equation, z_i is the electrical charge of the corresponding species and I is the ionic strength of the solution. In this work the value of A, as a function of temperature, was taken from Lewis et al. (1961) and b_i was set equal to 1.2, a value suggested by Pitzer (1973) and Pitzer and Kim (1974). Under the conditions employed in this study, the contribution of the binary interaction to the activity coefficient as given by eq 13 was found to be small (Haji-Sulaiman and Aroua, 1996a; Aroua et al., 1997) and has been neglected. The system of equations was solved using commercially available MathCad Software.

Results and Discussion

The experimental NaOH volumes obtained by titrating 100 mL of the carbonated MEA solutions are given in Table 2 as the average values of three replicates. The relative

Table 2. Equilibrium Data for the H_2O + MEA + $NaHCO_3$ System[a]

| α	V_{NaOH}/mL	$10^5[RNH_2]_e$/ mol·dm^{-3}	$10^5[RNH_3^+]_e$/ mol·dm^{-3}	$[RNHCOO^-]_e$/ mol·dm^{-3}	$[HCO_3^-]_e$/ mol·dm^{-3}	$10^5[CO_3^{2-}]$/ mol·dm^{-3}	K_c/dm^3·mol^{-1}
				T = 298 K			
				$[NaClO_4]$ = 0.0 mol·dm^{-3}			
0.5	2.31 ± 0.05	0.0730 ± 0.0010	0.3128 ± 0.2461	0.0270 ± 0.0010	0.0230 ± 0.0010	0.3128 ± 0.2461	15.89 ± 1.50
1.0	5.09 ± 0.04	0.0510 ± 0.0010	1.3558 ± 1.6362	0.0490 ± 0.0010	0.0510 ± 0.0010	1.3558 ± 0.0693	19.00 ± 1.13
1.5	9.00 ± 0.16	0.0400 ± 0.0020	0.6127 ± 0.3327	0.0596 ± 0.0020	0.0900 ± 0.0020	0.6127 ± 0.3327	16.73 ± 1.77
				$[NaClO_4]$ = 0.5 mol·dm^{-3}			
0.5	2.89 ± 0.02	0.0790 ± 0.0001	7.5180 ± 8.9020	0.0210 ± 0.0001	0.0290 ± 0.0001	7.5180 ± 1.4240	9.19 ± 0.08
1.0	5.91 ± 0.04	0.0590 ± 0.0001	3.2877 ± 0.8940	0.0410 ± 0.0001	0.0590 ± 0.0001	3.2877 ± 2.0313	11.57 ± 0.06
1.5	9.86 ± 0.08	0.0490 ± 0.0001	5.2123 ± 1.1870	0.0510 ± 0.0001	0.0990 ± 0.0001	5.2123 ± 1.0577	10.56 ± 0.05
				$[NaClO_4]$ = 1.0 mol·dm^{-3}			
0.5	3.34 ± 0.05	0.0830 ± 0.0001	17.5940 ± 5.4000	0.0160 ± 0.0001	0.0330 ± 0.0001	17.5940 ± 4.6760	5.84 ± 0.06
1.0	6.49 ± 0.04	0.0650 ± 0.0010	28.5360 ± 0.1600	0.0350 ± 0.0001	0.0650 ± 0.0010	28.5360 ± 0.9860	8.17 ± 0.27
1.5	10.61 ± 0.08	0.0560 ± 0.0010	24.0900 ± 11.730	0.0440 ± 0.0010	0.1060 ± 0.0010	24.0900 ± 7.0800	7.22 ± 0.36
				$[NaClO_4]$ = 1.5 mol·dm^{-3}			
0.5	3.57 ± 0.11	0.0850 ± 0.0010	27.0230 ± 0.5800	0.0140 ± 0.0010	0.0350 ± 0.0010	27.0230 ± 1.723	4.53 ± 0.50
1.0	6.67 ± 0.04	0.0660 ± 0.0010	22.9430 ± 9.8400	0.0330 ± 0.0010	0.0660 ± 0.0010	32.9430 ± 1.003	7.21 ± 0.44
1.5	10.81 ± 0.03	0.0580 ± 0.0001	39.5000 ± 0.1900	0.0420 ± 0.0001	0.1080 ± 0.0001	39.5000 ± 2.540	6.43 ± 0.03
				T = 308 K			
				$[NaClO_4]$ = 0.0 mol·dm^{-3}			
0.5	2.28 ± 0.01	0.0730 ± 0.0010	0.3953 ± 0.6407	0.0270 ± 0.0001	0.0230 ± 0.0001	0.3953 ± 0.0871	16.44 ± 0.36
1.0	5.35 ± 0.05	0.0530 ± 0.0010	0.1195 ± 0.0223	0.0470 ± 0.0010	0.0530 ± 0.0010	1.1949 ± 0.2041	16.22 ± 0.96
1.5	9.13 ± 0.15	0.0410 ± 0.0010	0.3731 ± 0.1897	0.0590 ± 0.0010	0.0910 ± 0.0020	0.3731 ± 0.15498	15.59 ± 0.99
				$[NaClO_4]$ = 0.5 mol·dm^{-3}			
0.5	3.05 ± 0.06	0.0800 ± 0.0010	18.6730 ± 0.2600	0.0190 ± 0.0010	0.0300 ± 0.0010	18.6730 ± 0.217	7.87 ± 0.77
1.0	6.10 ± 0.13	0.0610 ± 0.0010	2.5886 ± 0.9490	0.0390 ± 0.0010	0.0610 ± 0.0010	2.5886 ± 0.8624	10.37 ± 0.61
1.5	9.87 ± 0.06	0.0490 ± 0.0010	3.8500 ± 3.4930	0.0510 ± 0.0010	0.0990 ± 0.0010	3.8500 ± 1.508	10.53 ± 0.53
				$[NaClO_4]$ = 1.0 mol·dm^{-3}			
0.5	3.24 ± 0.04	0.0820 ± 0.0010	16.5900 ± 14.530	0.0180 ± 0.0010	0.0320 ± 0.0010	16.5900 ± 7.14	6.46 ± 0.64
1.0	6.54 ± 0.04	0.0650 ± 0.0001	30.5530 ± 0.1900	0.0350 ± 0.0010	0.0650 ± 0.0001	30.5530 ± 0.479	7.92 ± 0.25
1.5	10.64 ± 0.07	0.0560 ± 0.0010	36.6900 ± 0.3400	0.0430 ± 0.0010	0.1060 ± 0.0010	36.6900 ± 0.200	7.12 ± 0.36
				$[NaClO_4]$ = 1.5 mol·dm^{-3}			
0.5	3.31 ± 0.01	0.0830 ± 0.0010	27.2700 ± 8.1600	0.0170 ± 0.0001	0.0330 ± 0.0001	27.2700 ± 0.030	5.91 ± 0.12
1.0	6.74 ± 0.03	0.0670 ± 0.0001	35.3730 ± 5.7700	0.0330 ± 0.0010	0.0670 ± 0.0001	35.3730 ± 0.157	6.93 ± 0.23
1.5	10.61 ± 0.14	0.0560 ± 0.0010	40.8800 ± 0.5400	0.0440 ± 0.0010	0.1060 ± 0.0010	40.8800 ± 0.540	7.12 ± 0.36
				T = 318 K			
				$[NaClO_4]$ = 0.0 mol·dm^{-3}			
0.5	2.62 ± 0.08	0.0760 ± 0.0010	2.0312 ± 3.3050	0.0240 ± 0.0010	0.0260 ± 0.0010	2.0312 ± 3.3048	11.92 ± 1.11
1.0	5.58 ± 0.09	0.0560 ± 0.0010	1.6676 ± 1.0560	0.0440 ± 0.0010	0.0560 ± 0.0010	1.6676 ± 0.0826	14.24 ± 0.83
1.5	9.29 ± 0.16	0.0430 ± 0.0010	0.9742 ± 1.1828	0.0570 ± 0.0020	0.0930 ± 0.0010	0.9743 ± 0.5145	14.34 ± 0.99
				$[NaClO_4]$ = 0.5 mol·dm^{-3}			
0.5	2.93 ± 0.03	0.0800 ± 0.0010	2.0235 ± 0.4720	0.0200 ± 0.0010	0.0300 ± 0.0010	2.0235 ± 0.3185	8.70 ± 0.84
1.0	6.20 ± 0.08	0.0620 ± 0.0010	9.3123 ± 15.6380	0.0380 ± 0.0010	0.0620 ± 0.0010	9.3123 ± 15.6277	9.75 ± 0.57
1.5	10.40 ± 0.19	0.0540 ± 0.0010	31.1900 ± 0.8200	0.0460 ± 0.0020	0.1040 ± 0.0010	31.1900 ± 0.820	8.17 ± 0.58
				$[NaClO_4]$ = 1.0 mol·dm^{-3}			
0.5	3.23 ± 0.03	0.0830 ± 0.0010	10.8150 ± 13.950	0.0170 ± 0.0010	0.0330 ± 0.0010	10.8150 ± 3.131	6.51 ± 0.66
1.0	6.37 ± 0.13	0.0630 ± 0.0010	31.2360 ± 0.6700	0.0360 ± 0.0010	0.0630 ± 0.0010	31.2360 ± 0.666	8.79 ± 0.52
1.5	10.40 ± 0.90	0.0540 ± 0.0010	37.2530 ± 0.4900	0.0460 ± 0.0010	0.1040 ± 0.0010	37.2530 ± 0.453	8.05 ± 0.40
				$[NaClO_4]$ = 1.5 mol·dm^{-3}			
0.5	3.43 ± 0.09	0.0840 ± 0.0010	19.9300 ± 9.9400	0.0160 ± 0.0010	0.0340 ± 0.0010	19.9300 ± 9.10	5.23 ± 0.54
1.0	6.68 ± 0.03	0.0660 ± 0.0010	36.8500 ± 2.7800	0.0330 ± 0.0001	0.0660 ± 0.0010	36.8500 ± 0.14	7.16 ± 0.24
1.5	10.61 ± 0.14	0.0560 ± 0.0020	42.9300 ± 0.8400	0.0440 ± 0.0010	0.1050 ± 0.0020	42.9300 ± 0.27	7.12 ± 0.55
				T = 328 K			
				$[NaClO_4]$ = 0.0 mol·dm^{-3}			
0.5	2.71 ± 0.05	0.0780 ± 0.0010	0.1803 ± 0.4162	0.0220 ± 0.0010	0.0280 ± 0.0010	0.1803 ± 0.0219	10.92 ± 1.03
1.0	5.98 ± 0.17	0.0600 ± 0.0020	0.5386 ± 0.0479	0.0400 ± 0.0020	0.0600 ± 0.0020	0.5386 ± 0.0579	11.28 ± 1.31
1.5	9.63 ± 0.07	0.0460 ± 0.0010	2.2644 ± 2.1550	0.0540 ± 0.0010	0.0960 ± 0.0010	2.2644 ± 0.5564	12.04 ± 0.61
				$[NaClO_4]$ = 0.5 mol·dm^{-3}			
0.5	3.15 ± 0.05	0.0810 ± 0.0010	7.8733 ± 13.1370	0.0190 ± 0.0010	0.0310 ± 0.0010	7.8733 ± 6.5523	7.15 ± 0.69
1.0	6.31 ± 0.20	0.0630 ± 0.0020	10.8090 ± 15.370	0.0370 ± 0.0020	0.0630 ± 0.0020	10.8090 ± 6.823	9.19 ± 1.08
1.5	10.11 ± 0.26	0.0510 ± 0.0020	21.7460 ± 19.110	0.0490 ± 0.0030	0.1010 ± 0.0020	21.7460 ± 4.734	9.41 ± 1.11
				$[NaClO_4]$ = 1.0 mol·dm^{-3}			
0.5	3.30 ± 0.03	0.0820 ± 0.0010	14.1200 ± 20.180	0.0170 ± 0.0001	0.0320 ± 0.0010	14.1200 ± 7.58	6.06 ± 0.30
1.0	6.69 ± 0.05	0.0670 ± 0.0010	34.0630 ± 0.2200	0.0330 ± 0.0010	0.0670 ± 0.0010	34.0630 ± 0.237	7.23 ± 0.44
1.5	10.09 ± 0.21	0.0510 ± 0.0020	36.9530 ± 1.1700	0.0490 ± 0.0020	0.1010 ± 0.0020	36.9530 ± 0.803	9.42 ± 0.94
				$[NaClO_4]$ = 1.5 mol·dm^{-3}			
0.5	3.50 ± 0.13	0.0850 ± 0.0010	30.8600 ± 0.8100	0.0150 ± 0.0010	0.0350 ± 0.0010	30.8600 ± 0.25	4.89 ± 0.52
1.0	6.83 ± 0.14	0.0680 ± 0.0010	39.0500 ± 0.8000	0.0320 ± 0.0010	0.0680 ± 0.0010	39.0500 ± 0.23	6.57 ± 0.39
1.5	10.27 ± 0.15	0.0520 ± 0.0020	30.6700 ± 23.370	0.0480 ± 0.0020	0.1020 ± 0.0020	30.6700 ± 12.69	8.44 ± 0.84

[a] α = mol of $NaHCO_3$/total mol of MEA.
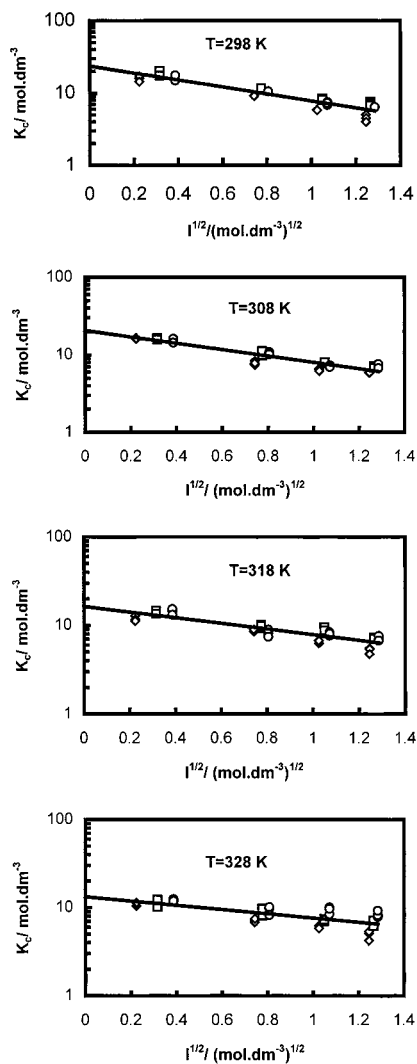
Figure 1. Effect of temperature and ionic strength on the apparent carbamate formation constant K_c: $\diamond$, 0.1 mol·dm^{-3} NaHCO$_3$; $\square$, 0.2 mol·dm^{-3} NaHCO$_3$; $\bigcirc$, 0.3 mol·dm^{-3} NaHCO$_3$.

error of these measurements is estimated to be less than 1.6%, which indicates excellent reproducibility and accuracy of the determinations despite a small change (approximately 2 units) in the pH values at the end points. These volumes are incorporated in the system of equations to be solved for the equilibrium concentrations of the different species. The calculated concentrations are also included in Table 2 along with their uncertainties, taken as the maximum deviation from the average of the three determinations. The concentrations of free amine, carbamate, and bicarbonate are substituted into eq 1 to calculate the apparent equilibrium constant for the formation of carbamate. As shown in the table, the calculated K_c values depend on temperature as well as the ionic strength of the solution and have relative errors of 6.5%. The relative errors of K_c were estimated as the sum of the relative errors of free amine, carbamate, and bicarbonate concentrations. A linear relationship between log K_c and $I^{0.5}$ was observed at all temperatures investigated, as shown in Figure 1. Extrapolating the plot to zero ionic strength gives an estimate of the corresponding equilibrium constant K_1, and these values are given in Table 3 at temperatures of (298, 318, 328, and 338) K. For comparison, the corresponding values for DEA are also included. As expected, the stability of MEA carbamate is higher than that of DEA carbamate, as indicated by the higher values of K_1. This comparison

Table 3. Equilibrium Constant K_1 for the Carbamate Formation at Different Temperatures

	K_1/dm^3·mol^{-1}	
T/K	DEA	MEA
298	7.19	20.19
308	4.60	18.43
318	3.02	15.30
328	2.04	12.64

Table 4. Carbamate Hydrolysis Constant (Comparison of Data)

T/K	this study (mol·dm^{-3})	lit. (mol·dm^{-3})	ref
291	0.042	0.018[a]	Jensen et al., 1954
298	0.048	0.030[b]	Kent and Eisenberg, 1976
		0.013[a]	Chan and Danckwerts, 1981
313	0.062	0.042[b]	Kent and Eisenberg, 1976
		0.080[a]	Chan and Danckwerts, 1981

[a] Extrapolated to infinite dilution in this work. [b] Fitted to VLE data.

also shows that DEA carbamate is more sensitive to temperature than that of MEA.

The relationship between the carbamate equilibrium constant and temperature was fitted by linear regression to the relationship

$$\log_{10} K_1 = -0.934 + (0.671 \times 10^3)K/T \qquad (14)$$

with the value of r^2 (mean residual squares) equal to 0.97. The first and second coefficients in eq 14 have standard errors of 0.272 and 0.085 × 10^3, respectively. A comparison between the equilibrium constant for carbamate hydrolysis $(1/K_1)$ obtained from eq 14 and literature values at three different temperatures is shown in Table 4. The data reported by Kent and Eisenberg (1976) were obtained by fitting the equilibrium constant along with the interaction parameters to the MEA + CO$_2$ VLE data. The data of Jensen et al. (1954) were only at 18 °C and the two ionic strengths 0.04 and 0.14 mol·dm^{-3}. The data presented by Chan and Danckwerts (1981) covered a very narrow range of ionic strength, 0.531−0.686 mol·dm^{-3} at 25 °C and 0.624 and 0.931 mol·dm^{-3} at 40 °C. For meaningful comparison, these data were extrapolated to zero ionic strength using the linear relationship described in this work. The estimated equilibrium constants thus generated are given in Table 4. Differences between these values and those obtained from this work are expected since the literature data were gathered over a very narrow range of ionic strength. Furthermore, the total ionic strength of the solution in the work conducted by Jensen et al. (1954) and Chan and Danckwerts (1981) was fixed by the concentration of the ionic species in the experiments. In such cases, the binary interaction parameters for evaluating the activity coefficient (eq 13) which have been ignored in this work should have been included. The inclusion of this term would generate a nonlinear relationship in the plot of log K versus $I^{0.5}$. In the present investigation, an inert salt was used as the ionic strength buffer for the solution, which made the contribution of the interaction parameters to the activity coefficient negligible.

Conclusion

The equilibrium constant for the formation of carbamate from MEA has been estimated by extrapolating the value of the calculated apparent equilibrium constant to zero ionic strength. The estimated values could not be compared

directly with literature data, as most of the reported values refer to the apparent constant at a specified ionic strength. Comparison with DEA, a secondary alkanolamine, showed that the MEA carbamate is more stable and less temperature sensitive.

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