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Temperature Dependency of the Equilibrium Constant for the Formation of Carbamate From Diethanolamine

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The equilibrium constant for the formation of diethanolamine carbamate was determined experimentally at (303, 313, 323, and 331) K for ionic strengths up to 1.8 mol dm^{-3}, the inert electrolyte being $NaClO_4$. A linear relationship was found to hold between log K and $I^{0.5}$. The thermodynamical constant has been determined and expressed by the equation $\log K_1 = -5.12 + 1.781 \times 10^3$ K/T.

Introduction

Aqueous alkanolamine solutions are frequently used to remove acidic components such as H_2S and CO_2 from process gas streams. Among the industrially important alkanolamines which have been used for this purpose are monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) (Astarita et al., 1983). When primary or secondary amines such as DEA or MEA react with CO_2, stable carabamates are usually formed. As a result, the maximum CO_2 loading that can be attained is 0.5 mol of CO_2/mol of amine. However, at high CO_2 partial pressures carbamates may hydrolyze to generate free amines which can further react with additional CO_2 to give loadings higher than 0.5. The carbamate-forming reaction is thus an important step in the reaction mechanism especially for those involving primary and secondary amines. The instability of these carbamate ions that are formed in an aqueous system of tertiary amines has been argued to be responsible for the high sorption capacity of such solutions. For the same reason, sterically hindered amine which has been designed to induce such instability showed excellent performance for removing CO_2 (Sartory and Savage, 1983). Despite the importance of this carbamate-forming reaction for the absorption of CO_2 in alkanolamine solutions, experimental data on the equilibrium constant for its formation is still scarce in the literature. It is a common approach among investigators to consider the equilibrium constant as an additional parameter to be fitted along with the interaction parameters to the VLE data (Kent and Eisenberg, 1976; Deshmukh and Mather, 1981; Austgen et al., 1989; Haji-Sulaiman and Aroua, 1986). This procedure is likely to introduce significant errors in predicting the equilibrium concentrations of bicarbonate and carbamate ions especially at low CO_2 loading (Haji-Sulaiman et al., 1986).

The lack of experimental data on the equilibrium constant of carbamate formation in the literature is mainly attributed to the difficulty in measuring the carbamate ion concentration accurately. Chan and Danckwert (1981) have proposed an experimental technique to determine the concentrations of carbamate ion and thus the equilibrium constant for its formation. In this method, barium chloride and an excess of sodium hydroxide are added to an aliquot sample of the solution which precipitates carbonate and bicarbonate but leaves carbamate in the solution. The clear solution is further titrated by HCl for the final determination of the carbamate ions. As claimed by the investigators, the equilibrium of the system was not disturbed during the analysis. This method requires the separation of the precipitate from the filtrate, which is a rather tedious technique and gives poor reproducibility. Recently Haji Sulaiman et al. (1986) developed another technique based on titration with NaOH to determine species concentration in CO_2 + alkanoamine + water systems. This technique is simple to perform and gives reproducible results. The method is used in this work to study the effects of temperature and ionic strength on the equilibrium constant for the formation of carbamate from DEA.

Experimental Setup and Procedure

The chemicals used in the investigation were obtained from Merck (98% diethanolamine and 99% sodium perchlorate monohydrate) and May & Baker (99% sodium bicarbonate). All these compounds were of p.a. quality and were used as received. Standard aqueous sodium hydroxide (1.0 mol·dm^{-3}) solution was provided by Reagecon.

Equilibrium experiments were carried out by adding a predetermined amount of powder $NaHCO_3$ to 100 cm^3 of 0.2 mol·dm^{-3} DEA solution. Experimental runs were performed at different ratios (0.5, 1.0, and 1.5 mol $NaHCO_3$ per mol DEA) of bicarbonate to total amine. In order to vary the ionic strength of the solution, various amounts of inert salt $NaClO_4$ (0.0, 0.5, 1.0, and 1.5 mol·dm^{-3}) were added. The system was left to equilibrate at (303, 313, 323, and 331) ± 0.5 K for about 24 h and finally titrated with 1.0 mol·dm^{-3} NaOH solution using a PC controlled Metrohm 716DMS Titrino autotitrator which utilized the DET (Dynamic Equivalence-point Titration) technique for the determination of the end point. In this technique the volume increments are adopted to the slope of the titration curve, thus providing accurate results in the shortest possible time (less than 5 min). Due to the short analysis time, the equilibrium of the system is not expected to be disturbed (Haji-Sulaiman et al., 1986). The end points are determined automatically from the first derivative of the titration curve where the largest change in the solution pH with the addition of an incremental volume of NaOH is detected. All determinations were carried out in triplicate, and the results were reproducible within 4% of NaOH volume as shown by the data in Table 2.

Theory

When an aqueous solution of DEA is reacted with bicarbonate, the carbamate is formed according to the following reaction (reaction i)

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$$R_2NH + HCO_3^- \leftrightarrow R_2NCOO^- + H_2O \qquad \text{(i)}$$

where R_2NH refers to DEA ($R = -C_2H_4OH$). The apparent equilibrium constant, K_C, for this reaction is given by

$$K_C = \frac{[R_2NCOO^-]_e}{[HCO_3^-]_e[R_2NH]_e} \qquad (1)$$

The subscripts e and t in the above equation and in the following equations respectively refer to the concentrations of species at equilibrium and the total concentrations. The thermodynamic equilibrium constant, K_1, which can be related to the activity coefficients and the concentration of the different species, can be written as

$$K_1 = K_C \frac{\gamma_{R_2NCOO^-}}{\gamma_{HCO_3}\gamma_{R_2NH}} \qquad (2)$$

In addition to reaction i the following chemical equilibria are also established (reactions ii, iii, and iv respectively)

$$R_2NH_2^+ \leftrightarrow R_2NH + H^+ \qquad \text{(ii)}$$

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

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

Each equilibrium reaction is characterized by a thermodynamic constant K_i which is given by the following expressions

$$K_2 = \frac{[R_2NH]_e[H^+]_e}{[R_2NH_2^+]_e} \frac{\gamma_{R_2NH}\gamma_{H^+}}{\gamma_{R_2NH_2^+}} \qquad (3)$$

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

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

where a_{H_2O} is the activity of water.

The following material and charge balance equations also hold for this system:

Amine balance

$$[R_2NH]_t = [R_2NH]_e + [R_2NH_2^+]_e + [R_2NCOO^-]_e \qquad (6)$$

CO_2 balance

$$[NaHCO_3]_t = [HCO_3^-]_e + [CO_3^{2-}]_e + [R_2NCOO^-]_e \qquad (7)$$

Charge balance

$$[Na^+]_t + [H^+]_e + [R_2NH_2^+]_e = [HCO_3^-]_e + 2[CO_3^{2-}]_e + [R_2NCOO^-]_e + [OH^-]_e + [ClO_4^-]_t \qquad (8)$$

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

parameters	*a*	*b*	*c*	*d*	range of validity *T*/K
K_2[a]	−3071.15	6.776904	0	−48.7594	273−353
K_3[b]	−12431.70	−35.4819	0	220.067	273−498
K_4[b]	−1344.90	−22.4773	0	140.932	273−498

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

Sodium balance

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

By substituting eq 8 and $[ClO_4^-]_t = [NaClO_4]_t$ eq 9 reduces to

$$[NaHCO_3]_t + [H^+]_e + [R_2NH_2^+]_e = [HCO_3^-]_e + 2\,[CO_3^{2-}]_e + [R_2NCOO^-]_e + [OH^-]_e \qquad (10)$$

The pH of carbonated DEA solution is generally higher than 9, and the value of p*K* for the dissociation of CO_2 is of the order of 6. Under these conditions, and without introducing any significant error, the concentration of free CO_2 in the system has been neglected.

If an aliquot of the solution is titrated with a strong base such as NaOH, only the bicarbonate and the protonated DEA 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

$$B = [R_2NH_2^+]_e + [HCO_3^-]_e \qquad (11)$$

The set of equations 3−7, 10, and 11 can be solved simultaneously to calculate the concentration of the seven species for given values of K_2, K_3, K_4, γ_j, $[R_2NH]_t$, $[NaHCO_3]_t$, $[NaClO_4]_t$, and *B*. The apparent equilibrium constant for carbamate formation can then be calculated using eq 2.

In this work, literature values for the equilibrium constants K_2−K_4 were used in the calculation and were expressed in the form

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

The coefficients *a*, *b*, *c*, and *d* for these different constants are given in Table 1. The activity of water was assumed to be that of pure $NaClO_4$ 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)

$$\ln \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + b_i\sqrt{I}} + 2\sum_j [j]\beta_{ij} \qquad (13)$$

where β_{ij} refers to the binary interaction parameters, z_i is the electrical charge of the corresponding species, and *I* is the ionic strength. In this work *A* is taken as a function of temperature as proposed by Lewis et al. (1961) and b_i equals 1.2, a value proposed by Pitzer (1973) and Pitzer and Kim (1974). Using the data published by Haji-Sulaiman and Aroua (1996), it has been found that the second term on the right-hand side of eq 13 contributed less than 6% to the value of γ. Thus the contribution from this term is considered minimal and has been ignored in

Table 2. Equilibrium Data in H_2O + DEA + $NaHCO_3$ Systems[a]

α	V_{NaOH}/ mL	$[R_2NH]_e$/ mol·dm^{-3}	$[R_2NH_2^+]_e$/ mol·dm^{-3}	$[R_2NCOO^-]_e$/ mol·dm^{-3}	$[HCO_3^-]_e$/ mol·dm^{-3}	$[CO_3^{2-}]_e$/ mol·dm^{-3}	K_c/ dm^3·mol^{-1}
T = 303 K							
$NaClO_4$ = 0.0 mol·dm^{-3}							
0.5	6.71 ± 0.05	0.143 ± 0.001	0.024 ± 0.001	0.033 ± 0.001	0.043 ± 0.001	0.024 ± 0.001	5.367 ± 0.542
1.0	14.33 ± 0.02	0.106 ± 0.001	0.038 ± 0.001	0.057 ± 0.001	0.106 ± 0.001	0.038 ± 0.001	5.073 ± 0.512
1.5	23.00 ± 0.50	0.082 ± 0.004	0.049 ± 0.001	0.070 ± 0.005	0.182 ± 0.004	0.049 ± 0.001	4.690 ± 0.126
$NaClO_4$ = 0.5 mol·dm^{-3}							
0.5	7.39 ± 0.10	0.138 ± 0.001	0.035 ± 0.001	0.026 ± 0.001	0.038 ± 0.001	0.035 ± 0.001	4.958 ± 0.357
1.0	14.96 ± 0.14	0.099 ± 0.001	0.051 ± 0.001	0.05 ± 0.002	0.099 ± 0.001	0.051 ± 0.001	5.102 ± 0.312
1.5	23.96 ± 0.09	0.078 ± 0.001	0.062 ± 0.001	0.06 ± 0.001	0.178 ± 0.001	0.062 ± 0.000	4.322 ± 0.152
$NaClO_4$ = 1.0 mol·dm^{-3}							
0.5	7.54 ± 0.11	0.135 ± 0.001	0.040 ± 0.001	0.025 ± 0.001	0.035 ± 0.001	0.040 ± 0.001	5.296 ± 0.402
1.0	15.48 ± 0.09	0.097 ± 0.001	0.058 ± 0.001	0.045 ± 0.001	0.097 ± 0.001	0.058 ± 0.001	4.783 ± 0.205
1.5	24.53 ± 0.02	0.075 ± 0.001	0.070 ± 0.001	0.055 ± 0.0001	0.175 ± 0.001	0.070 ± 0.001	4.191 ± 0.016
$NaClO_4$ = 1.5 mol·dm^{-3}							
0.5	7.88 ± 0.01	0.134 ± 0.001	0.044 ± 0.000	0.021 ± 0.001	0.035 ± 0.001	0.044 ± 0.001	4.478 ± 0.037
1.0	15.80 ± 0.02	0.095 ± 0.001	0.063 ± 0.001	0.042 ± 0.001	0.095 ± 0.001	0.063 ± 0.001	4.654 ± 0.209
1.5	24.80 ± 0.02	0.073 ± 0.001	0.075 ± 0.001	0.052 ± 0.000	0.173 ± 0.001	0.075 ± 0.001	4.118 ± 0.016
T = 313 K							
$NaClO_4$ = 0.0 mol·dm^{-3}							
0.5	6.96 ± 0.05	0.145 ± 0.001	0.025 ± 0.001	0.03 ± 0.001	0.045 ± 0.001	0.025 ± 0.001	4.598 ± 0.036
1.0	15.31 ± 0.06	0.113 ± 0.001	0.040 ± 0.001	0.047 ± 0.001	0.113 ± 0.001	0.04 ± 0.001	3.681 ± 0.039
1.5	24.14 ± 0.16	0.096 ± 0.001	0.046 ± 0.001	0.059 ± 0.002	0.196 ± 0.001	0.046 ± 0.001	3.136 ± 0.049
$NaClO_4$ = 0.5 mol·dm^{-3}							
0.5	7.56 ± 0.14	0.14 ± 0.001	0.036 ± 0.0001	0.025 ± 0.001	0.040 ± 0.001	0.036 ± 0.001	4.464 ± 0.072
1.0	15.94 ± 0.07	0.106 ± 0.001	0.054 ± 0.001	0.040 ± 0.001	0.106 ± 0.001	0.054 ± 0.001	3.560 ± 0.044
1.5	24.72 ± 0.03	0.090 ± 0.001	0.058 ± 0.001	0.053 ± 0.000	0.190 ± 0.001	0.058 ± 0.001	3.100 ± 0.018
α	V_{NaOH}/ mL	DEA/ mol·dm^{-3}	$DEAH^+$/ mol·dm^{-3}	$DEACOO^-$/ mol·dm^{-3}	HCO_3^-/ mol·dm^{-3}	CO_3^{2-}/ mol·dm^{-3}	K_c/ dm^3·mol^{-1}
$NaClO_4$ = 1.0 mol·dm^{-3}							
0.5	7.86 ± 0.09	0.137 ± 0.001	0.042 ± 0.001	0.021 ± 0.001	0.037 ± 0.001	0.042 ± 0.001	4.143 ± 0.058
1.0	16.27 ± 0.09	0.102 ± 0.001	0.061 ± 0.001	0.037 ± 0.001	0.102 ± 0.001	0.061 ± 0.001	3.556 ± 0.047
1.5	25.08 ± 0.21	0.086 ± 0.001	0.065 ± 0.001	0.049 ± 0.002	0.186 ± 0.001	0.065 ± 0.001	3.063 ± 0.058
$NaClO_4$ = 1.5 mol·dm^{-3}							
0.5	8.05 ± 0.1	0.135 ± 0.001	0.045 ± 0.001	0.020 ± 0.001	0.035 ± 0.001	0.045 ± 0.001	4.233 ± 0.086
1.0	16.51 ± 0.06	0.107 ± 0.001	0.058 ± 0.001	0.035 ± 0.001	0.107 ± 0.001	0.058 ± 0.001	5.640 ± 0.047
1.5	25.33 ± 0.13	0.084 ± 0.001	0.070 ± 0.001	0.047 ± 0.001	0.184 ± 0.001	0.070 ± 0.001	3.041 ± 0.038
T = 323 K							
$NaClO_4$ = 0.0 mol·dm^{-3}							
0.5	7.83 ± 0.02	0.158 ± 0.001	0.020 ± 0.001	0.022 ± 0.001	0.058 ± 0.001	0.020 ± 0.001	2.400 ± 0.165
1.0	16.03 ± 0.09	0.128 ± 0.001	0.032 ± 0.001	0.040 ± 0.001	0.128 ± 0.001	0.032 ± 0.001	2.440 ± 0.099
1.5	25.47 ± 0.06	0.112 ± 0.001	0.043 ± 0.001	0.045 ± 0.001	0.212 ± 0.001	0.043 ± 0.001	1.895 ± 0.068
$NaClO_4$ = 0.5 mol·dm^{-3}							
0.5	8.22 ± 0.01	0.152 ± 0.001	0.030 ± 0.001	0.018 ± 0.001	0.052 ± 0.001	0.030 ± 0.001	2.277 ± 0.182
1.0	16.63 ± 0.11	0.123 ± 0.001	0.044 ± 0.001	0.034 ± 0.001	0.123 ± 0.001	0.044 ± 0.001	2.247 ± 0.088
1.5	25.87 ± 0.05	0.105 ± 0.001	0.054 ± 0.001	0.041 ± 0.001	0.205 ± 0.001	0.054 ± 0.001	1.905 ± 0.074
$NaClO_4$ = 1.0 mol·dm^{-3}							
0.5	8.51 ± 0.09	0.149 ± 0.001	0.035 ± 0.01	0.015 ± 0.001	0.050 ± 0.001	0.035 ± 0.001	2.013 ± 0.188
1.0	16.87 ± 0.05	0.119 ± 0.001	0.050 ± 0.001	0.031 ± 0.001	0.119 ± 0.001	0.050 ± 0.001	2.189 ± 0.107
1.5	26.61 ± 0.34	0.103 ± 0.003	0.062 ± 0.001	0.034 ± 0.003	0.203 ± 0.003	0.062 ± 0.001	1.626 ± 0.215
$NaClO_4$ = 1.5 mol·dm^{-3}							
0.5	8.64 ± 0.01	0.148 ± 0.001	0.039 ± 0.001	0.014 ± 0.001	0.048 ± 0.001	0.038 ± 0.001	1.971 ± 0.105
1.0	17.09 ± 0.06	0.116 ± 0.001	0.054 ± 0.001	0.029 ± 0.001	0.116 ± 0.001	0.054 ± 0.001	2.155 ± 0.133
1.5	26.20 ± 0.16	0.097 ± 0.001	0.065 ± 0.001	0.038 ± 0.002	0.197 ± 0.001	0.065 ± 0.001	1.999 ± 0.136
T = 331 K							
$NaClO_4$ = 0.0 mol·dm^{-3}							
0.5	8.05 ± 0.11	0.162 ± 0.001	0.018 ± 0.001	0.020 ± 0.001	0.062 ± 0.001	0.018 ± 0.001	1.991 ± 0.144
1.0	17.77 ± 0.06	0.148 ± 0.001	0.030 ± 0.001	0.022 ± 0.001	0.148 ± 0.001	0.030 ± 0.001	1.000 ± 0.059
15	27.12 ± 0.17	0.131 ± 0.002	0.040 ± 0.001	0.028 ± 0.002	0.231 ± 0.002	0.039 ± 0.001	0.925 ± 0.088
$NaClO_4$ = 0.5 mol·dm^{-3}							
0.5	8.19 ± 0.07	0.154 ± 0.001	0.027 ± 0.001	0.019 ± 0.001	0.054 ± 0.001	0.027 ± 0.001	2.285 ± 0.177
1.0	17.87 ± 0.18	0.138 ± 0.001	0.040 ± 0.001	0.021 ± 0.002	0.138 ± 0.001	0.040 ± 0.001	1.103 ± 0.121
1.5	27.67 ± 0.02	0.125 ± 0.001	0.052 ± 0.001	0.023 ± 0.001	0.225 ± 0.001	0.052 ± 0.001	0.818 ± 0.046
$NaClO_4$ = 1.0 mol·dm^{-3}							
0.5	8.19 ± 0.07	0.154 ± 0.001	0.027 ± 0.001	0.019 ± 0.001	0.054 ± 0.001	0.027 ± 0.001	2.285 ± 0.177
1.0	17.87 ± 0.18	0.138 ± 0.001	0.040 ± 0.001	0.021 ± 0.002	0.138 ± 0.001	0.040 ± 0.001	1.103 ± 0.069
1.5	27.67 ± 0.02	0.125 ± 0.001	0.052 ± 0.001	0.023 ± 0.001	0.225 ± 0.001	0.052 ± 0.001	0.818 ± 0.046
$NaClO_4$ = 1.5 mol·dm^{-3}							
0.5	8.35 ± 0.07	0.149 ± 0.001	0.034 ± 0.001	0.016 ± 0.001	0.050 ± 0.001	0.034 ± 0.001	2.147 ± 0.192
1.0	18.18 ± 0.11	0.13 ± 0.001	0.051 ± 0.001	0.018 ± 0.001	0.131 ± 0.001	0.051 ± 0.001	1.057 ± 0.075
1.5	27.12 ± 0.09	0.11 ± 0.001	0.060 ± 0.001	0.029 ± 0.001	0.210 ± 0.001	0.06 ± 0.001	1.255 ± 0.061

[a] α = mol of $NaHCO_3$/total mol of DEA.

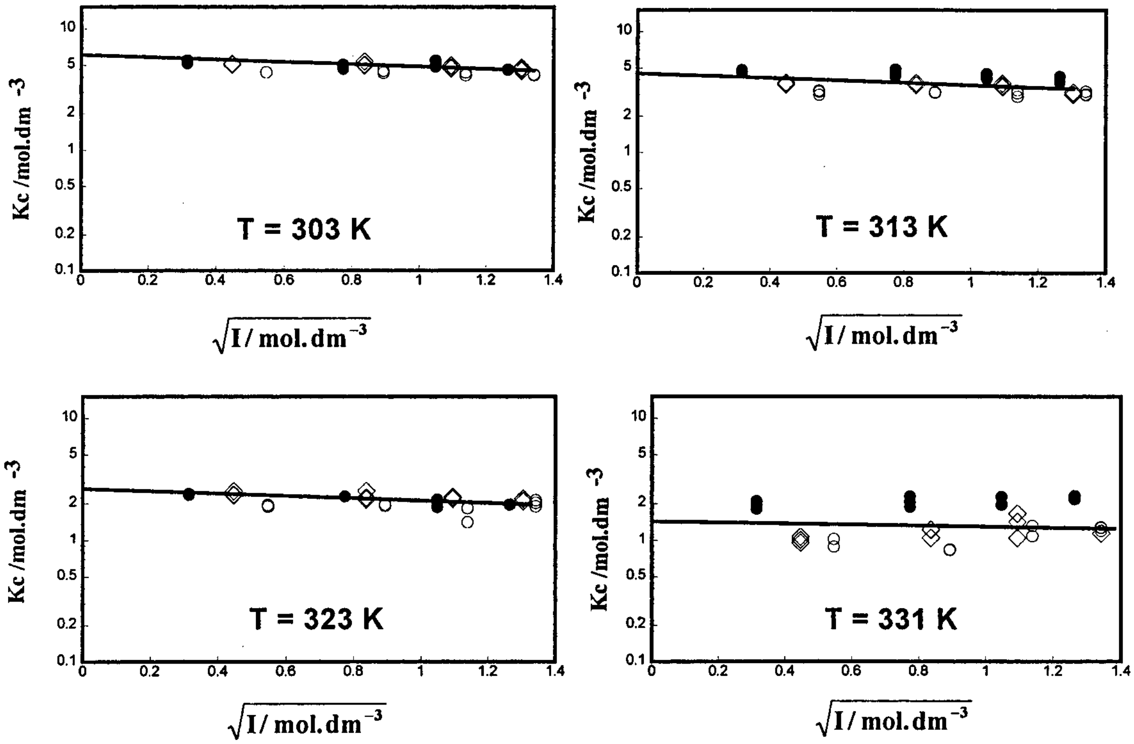

Figure 1. Effect of temperature and ionic strength on the apparent carbamate formation constant K_C; ●, 0.1 mol·dm^{-3} DEA; ◇, 0.2 mol·dm^{-3} DEA; ○, 0.3 mol·dm^{-3} DEA.

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

T/K	K_1/mol·dm^{-3}
303	5.42 ± 0.27
313	3.91 ± 0.17
323	2.41 ± 0.15
331	1.78 ± 0.12

the analysis. The system of equations was solved using a commercially available MathCad Software.

Results and Discussion

The concentrations of different species generated by solving the different equations as discussed earlier are given in Table 2. Equation 1 can be used to determine the apparent equilibrium constant from the concentration of the relevant species at various temperatures. As shown in this table, the K_C values are obtained with an average relative error of about 7%. From eq 2 and by substituting the activity coefficients using eq 13, to a good approximation, a plot of log of K_C versus $\sqrt{I}$ would generate a straight line with Y intercept equal to log K_1. This linear relationship has been observed at all the temperatures investigated as shown in Figure 1. The values of the corresponding K_1 at (303, 313, 323 and 331) K are given in Table 3. As expected, the stability of carbamate decreases with increasing temperature as indicated by the decreasing values of K_1. The relationship between the equilibrium constant (on molality scale) and the temperature can be expressed by the equation

$$\log K_1 = -5.12 + 1.781 \times 10^3\ \mathrm{K}/T \qquad (14)$$

with an average deviation of 3% and a maximum deviation of 6%. The standard errors of the coefficients in eq 14 are 0.36 and 114. A comparison between the equilibrium constant of carbamate hydrolysis ($1/K_1$) obtained from eq 14 and the literature values is shown in Table 4. Except for the data obtained from this work and that reported by Chan and Danckwerts (1981) and Jensen et al. (1954), all of the others were obtained by fitting the equilibrium constant along with the interaction parameters to the DEA + CO_2 VLE data. Thus meaningful comparison can only be made with data of Chan and Danckwerts and Jensen et al. The values reported by Chan and Danckwerts were obtained at two different ionic strengths and not that of $1/K_1$ reported here. The values at 298 K are questionable since the constant decreases with ionic strength instead of increasing as observed in this work. By applying the linear relationship to those data at 313 K, it is possible to determine the value of $1/K_1$ at this temperature. In this case $1/K_1$ has been estimated to be 0.25, which is relatively close when compared to the value of 0.268 obtained in this work. Data provided by Jensen et al. was measured at 291 K and ionic strength 0.1 mol·dm^{-3}. The value of $1/K_1$ could not be computed as only a single value was presented.

Table 4. Carbamate Hydrolysis Constant (Comparison of Data)

T/K	this study	literature	references
291	0.100 ± 0.014	0.152[a]	Jensen et al., 1954
298	0.140 ± 0.019	0.224[b]	Kent and Eisenberg, 1976
		0.262[c]	Chan and Danckwerts, 1981
		0.218[d]	Chan and Danckwerts, 1981
313	0.268 ± 0.038	0.303[b]	Kent and Eisenberg, 1976
		0.379[b]	Austgen et al., 1989
		0.322[b]	Haji-Sulaiman and Aroua, 1996
			Chan and Danckwerts, 1981
			Chan and Danckwerts, 1981

[a] Apparent constant at ionic strength 0.1 M. [b] Fitted to VLE data. [c] Apparent constant at ionic strength 0.531 M. [d] Apparent constant at ionic strength 0.624 M.

Conclusion

The titration technique which has been employed in this work can be used to estimate the equilibrium constant for carbamate formation. The apparent equilibrium constant for this reaction depends strongly on the ionic strength of the solution and temperature. The estimated thermodynamic equilibrium constant at 313 K is relatively close the value reported in the literature. However, there is no data available for comparison at other temperatures.

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