Thermochimica Acta, 154 (1989) 119–127
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF PROTONATION OF ALKANOLAMINES IN AQUEOUS SOLUTION TO 325 °C *

J.L. OSCARSON, G. WU, P.W. FAUX, R.M. IZATT ** and J.J. CHRISTENSEN

Departments of Chemistry and Chemical Engineering, Brigham Young University, Provo, UT 84602 (U.S.A.)

(Received 12 December, 1988)

ABSTRACT

Equilibrium quotients (K') for the protonation of diethanolamine (DEA), 2-(2-aminoethoxy)ethanol or diglycolamine (DGA), and *N*-methyldiethanolamine (MDEA) were determined potentiometrically over the ionic strength range 0.004–4.0 at 298.2 K. Corresponding ΔH values were determined by a flow calorimetric procedure at six temperatures from 299.9 to 422.1 K. At 299.9 K the protonation reactions become less exothermic, i.e. $-\Delta H$ decreases, in the order DGA (primary amine), DEA (secondary amine), MDEA (tertiary amine). From 299.9 to 422.1 K this order remains unchanged but the differences among the ΔH values decrease. The ΔH results are used, together with the 298.2 K lg K values (valid at ionic strength, $\mu = 0$), to calculate the dissociation constants of the corresponding protonated alkanolamines from 298.2 to 423.2 K. The effect of μ on the lg K value (valid at $\mu = 0$) for proton ionization from protonated alkanolamines is large. The change of lg K' with μ is nearly insensitive to substitution of functional groups on the nitrogen atom. The isocoulombic reaction principle was used to extrapolate K and ΔH to 423.2 K. Equations are given describing lg K, ΔH, ΔS and ΔC_p at $\mu = 0$ from 298.2 to 423.2 K.

INTRODUCTION

A knowledge of the thermodynamic quantities associated with the absorption of acid gases in aqueous alkanolamine solutions is valuable in evaluating the potential uses of such solutions in removing these gases from industrial and natural gas streams [1,2]. Absorption of acid gases in alkanolamine solutions involves (i) dissolution of the gas in water, (ii) gas–water interaction to form H^+ and an anion, (iii) amine–H^+ interaction, and (iv) in some cases, gas–amine interaction, i.e. carbamate formation between CO_2 and either a primary or a secondary amine. Processes (i) and

---

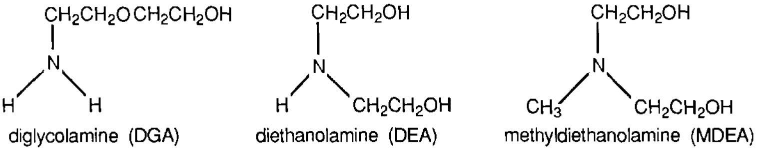
* Dedicated to Professor James J. Christensen (deceased 5 September 1987) in memory of his contribution to innovation in calorimetry.

** Author to whom correspondence should be addressed.

0040-6031/89/$03.50

(ii) have been well characterized for CO_2 [3,4]. The remaining processes have received little study. The objective of the present work is to investigate process (iii) over a wide temperature range.

The change in basicity of aqueous alkanolamines has been investigated as a function of successive alkanol substitution on the nitrogen atom at 298 K [5]. However, little attention has been paid to the effects of temperature and ionic strength (μ) on the equilibrium quotients (K'), enthalpy changes (ΔH), entropy changes (ΔS), and heat capacity changes (ΔC_p) for protonation of aqueous alkanolamines. In the present study calorimetric and potentiometric determinations are reported for the interaction of H^+ with 2-(2-aminoethoxy)ethanol or diglycolamine (DGA), diethanolamine (DEA), and *N*-methyldiethanolamine (MDEA). The potentiometric measurements were made at 298.2 K and the calorimetric measurements were made at six temperatures covering the range 299.9–422.1 K. DGA, DEA, and MDEA were chosen for this study to represent primary, secondary, and tertiary alkanolamines, respectively, in order to observe the effect of alkanol substitution on the nitrogen atom on the thermodynamic quantities associated with H^+–alkanolamine interaction.



EXPERIMENTAL

Materials

DGA (Aldrich) was fractionally distilled twice and dried using molecular sieves. Both gravimetric and chromatographic analyses showed the resulting DGA to be 99.5 wt.% pure. DEA (Aldrich) and MDEA (Aldrich) were 99 wt.% pure. These amines were stored over sodalime in desiccators prior to use. Solutions of HCl (Fisher) and $HClO_4$ (Fisher) were used as titrants in potentiometric and calorimetric measurements, respectively. The KCl (MCB) and KNO_3 (MCB) were reagent grade. The solutions prepared for potentiometric and calorimetric measurements were standardized by potentiometric titrations using tri(hydroxymethyl)amino-methane (Fisher) as an alkalimetric standard. Distilled, deionized water was used in all experiments.

Procedures

Potentiometric titration measurements were carried out with an Orion Model 701A pH meter using Sargent Welch glass electrodes. All titrations were carried out in a sealed, thermostatically controlled vessel (298.2 ± 0.2 K) under a CO_2-free nitrogen atmosphere using standardized 0.1 M HCl. The calibration of the glass electrode–pH meter system was accomplished both before and after each experiment by using buffer solutions traceable to the National Bureau of Standards (RICCA and Fisher). The titration procedure was computer controlled. At least three duplicate measurements were made at each of the six μ values studied. The μ values were maintained using KNO_3 in the case of DGA, and KCl in the cases of DEA and MDEA.

The calorimetric measurements were made using a Hart Scientific Model 5004 Isothermal flow calorimeter. The measurements were made in a steady-state, fixed-composition mode. The flow rate of the alkanolamine solution was constant at 0.0833 $cm^3\ s^{-1}$. Each run consisted of varying the flow rate of the acidic solution from 0.00217 $cm^3\ s^{-1}$ to 0.00783 $cm^3\ s^{-1}$ in 0.00112 $cm^3\ s^{-1}$ increments, giving heat generation values at six different flow rates. These flow rates corresponded to acid : amine molar ratios ranging from approximately 0.27 : 1 to 0.93 : 1. For each run, the measured heat values were plotted versus acidic solution flow rate. The enthalpy of protonation was determined by multiplying the slope of the best linear fit through these points by the acid concentration. Each run was repeated at least three times and the results of all the runs at a particular temperature were averaged.

RESULTS AND DISCUSSION

The reaction studied may be represented as

$$H^+ + Am(aq) = AmH^+ \tag{1}$$

The lg K value for eqn. (1) is given by

$$\lg K = pH + \lg (a_{AmH^+}/a_{Am}) \tag{2}$$

in which a_{AmH^+} and a_{Am} represent the activities of AmH^+ and Am, respectively. At finite μ values, eqn. (2) may be written as

$$\lg K' - \lg \gamma_{H^+} = pH + \lg([AmH^+]/[Am]) \tag{3}$$

where γ is the activity coefficient of the indicated species. The quantities on the right-hand side of eqn. (3) were determined experimentally. Equation (2) can also be written as

$$\lg K = pH + \lg([AmH^+]/[Am]) + \lg \gamma_{AmH^+} - \lg \gamma_{Am} \tag{4}$$

The methods used in the determinations of lg K and lg K', and in the modelling procedure are as follows. Three sets of (lg $K' - \lg \gamma_{H^+}$) values for each of the compounds DGA, DEA, and MDEA, at each of several μ values, were determined experimentally. Lg K values for protonation of DGA, DEA, and MDEA were derived by extrapolating these three sets of

TABLE 1

Experimental (exp) [a] and calculated (calc) proton ionization constants for alkanolamines at 292.4 K

Amine (lg K[c], $\mu = 0$)	Ionic strength (KCl or KNO_3) [b]						
	0.004	0.01	0.04	0.1	1.0	3.0	4.0
DGA [b] (9.42)							
$(\lg K' - \lg \gamma_{H^+})_{exp}$	9.44	9.47	9.54	9.62	9.85	10.01	–
$(\lg K' - \lg \gamma_{H^+})_{calc}$	9.45	9.47	9.51	9.56	9.81	10.05	–
$\lg K'$ [d]	9.41	9.43	9.47	9.52	9.76	10.13	–
DEA (8.88)							
$(\lg K' - \lg \gamma_{H^+})_{exp}$	–	8.93	8.98	9.03	9.27	9.53	9.61
$(\lg K' - \lg \gamma_{H^+})_{calc}$	–	8.93	8.97	9.02	9.27	9.53	9.61
$\lg K'$ [d]	–	8.89	8.91	8.93	9.18	9.69	9.86
MDEA (8.56)							
$(\lg K' - \lg \gamma_{H^+})_{exp}$	–	8.64	8.68	8.73	8.98	9.24	9.33
$(\lg K' - \lg \gamma_{H^+})_{calc}$	–	8.63	8.67	8.72	8.97	9.23	9.31
$\lg K'$ [d]	–	8.60	8.61	8.63	8.89	9.36	9.58

[a] Standard deviations are less than ±0.03.

[b] KNO_3 was used to adjust μ.

[c] Values obtained by extrapolation of $(\lg K' - \lg \gamma_{H^+})$ to $\mu = 0$.

[d] Lg K' values are estimated by adding literature values for the common lgarithms of the mean HCl μ value to the experimental $(\lg K' - \lg \gamma_{H^+})$ values.

$(\lg K' - \lg \gamma_{H^+})$ values to $\mu = 0$. By comparison of eqns. (3) and (4) the differences between the experimental $(\lg K' - \lg \gamma_{H^+})$ values and the extrapolated lg K values can be attributed to the effects of the activity coefficients of AmH^+ and Am(aq). As expected, a plot of $(\lg K' - \lg \gamma_{H^+})$ versus $- Az^+z^- \cdot \mu^{1/2}/(1 + \mu^{1/2})$ is linear at low μ values showing that the data follow the Debye–Hückel relationship. In addition, this linear relationship allows the precise extrapolation of $(\lg K' - \lg \gamma_{H^+})$ to $\mu = 0$ giving lg K. As μ increases, the values of $(\lg K' - \lg \gamma_{H^+})$ increase gradually which can be attributed in part to the salting-out effects of unprotonated alkanolamines. A semi-empirical model has been developed

$$(\lg K' - \lg \gamma_{H^+}) = \lg K + (0.5115\mu^{1/2})(1 + \mu^{1/2})^{-1} + 0.139847\mu - 1.1857 \times 10^{-2}\mu^2 \qquad (5)$$

which gives $(\lg K' - \lg \gamma_{H^+})$ at 298 K as a function of μ for all three amines. The correlation coefficient of eqn. (5) is larger than 0.97.

In Table 1 the experimental and predicted $(\lg K' - \lg \gamma_{H^+})$ values are compared. The good agreement between the experimental and calculated values is shown in Fig. 1. The lg K' values in Table 1 were obtained using literature γ_{H^+} values [6]. The lg K values at $\mu = 0$ decrease in the order primary alkanolamine > secondary alkanolamine > tertiary alkanolamine,

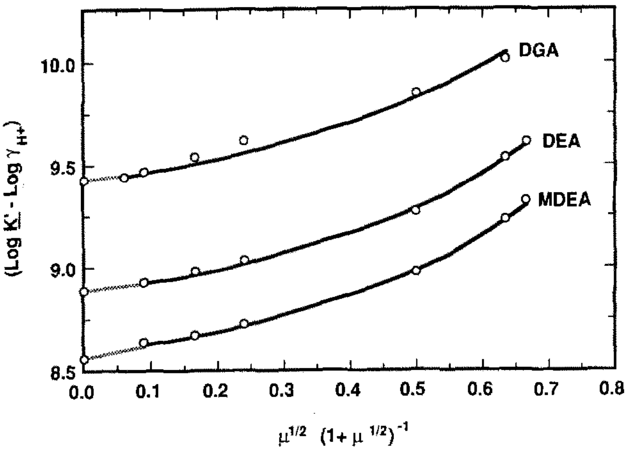


Fig. 1. Plot of ($\lg K' - \lg \gamma_{H^+}$) versus $\mu^{1/2}/(1+\mu^{1/2})$ for the alkanolamines studied. Lines are based on calculations using eqn. (5).

which is different from the sequence of aliphatic amines, tertiary > secondary > primary [5,7].

In Table 2 experimental and calculated values of enthalpies of protonation (ΔH) for DGA, DEA, and MDEA over the temperature range 299.9–422.1 K are given. The experimental ΔH values for each amine were fitted well by linear regression to give equations of the form such as

$$-\Delta H(T) = C_0 + C_1 T \qquad (6)$$

where T represents temperature in K. The values of the parameters C_0 and C_1, as well as the standard deviations, are listed in Table 3. The ΔH values calculated from eqn. (6) are listed in Table 2. The good agreement between the experimental and calculated ΔH values is seen in Fig. 2. The linear relationships in Fig. 2 are expected because of the isocoulombic nature of

TABLE 2

Experimental (exp) and calculated (calc) enthalpies of protonation of DGA, DEA, and MDEA[a]

Temp. (K)	$-\Delta H$, DGA (kJ mol^{-1})		$-\Delta H$, DEA (kJ mol^{-1})		$-\Delta H$, MDEA (kJ mol^{-1})	
	exp	calc	exp	calc	exp	calc
299.9	50.1	50.2	42.1	41.8	34.9	35.2
311.0	50.6	50.3	42.1	42.2	36.2	35.9
333.2	50.4	50.6	42.7	43.0	37.2	37.3
361.0	51.1	51.0	43.6	43.9	39.0	39.0
388.8	51.1	51.3	45.0	44.9	41.0	40.8
422.1	51.8	51.7	46.3	46.1	42.7	42.9

[a] Estimated uncertainties are ±1 kJ mol^{-1}.

TABLE 3

Summary of parameters obtained by linear regression of enthalpies of protonation of alkanolamines by eqn. (6)

Alkanolamine	C_0 (kJ mol^{-1})	C_1 (kJ mol^{-1} K^{-1})	Standard deviation (kJ mol^{-1})
DGA	46.551	0.012182	0.167
DEA	31.111	0.035524	0.261
MDEA	16.416	0.062632	0.236

the reactions involved, i.e. equal numbers of positive and negative charges are present on each side of each reaction. This linear relationship also makes possible the extrapolation with confidence of ΔH to temperatures higher than 422.1 K. Using appropriate thermodynamic relationships the following temperature-dependent equations were derived for ln K, ΔS, and ΔC_p

$$\ln K = \ln K_{298} + C_0(RT)^{-1} - C_0(298R)^{-1} - C_1R^{-1}\ln(T298^{-1}) \qquad (7)$$

$$\Delta S = R\ln K_{298} - C_0(298)^{-1} - C_1 - C_1\ln(T298^{-1}) \qquad (8)$$

$$\Delta C_p = -C_1 \qquad (9)$$

In Table 4, lg K, ΔH, ΔS, and ΔC_p values are given from 298 to 598 K. These values were calculated using eqn. (7), eqn. (6), eqn. (8), and eqn. (9), respectively.

Lg K and ΔS values from Table 4 for DEA, DGA, and MDEA are plotted versus temperature in Figs. 3 and 4, respectively. These plots together with corresponding ΔH plots in Fig. 2 show that as temperature increases each of the quantities decreases and each of them approaches a

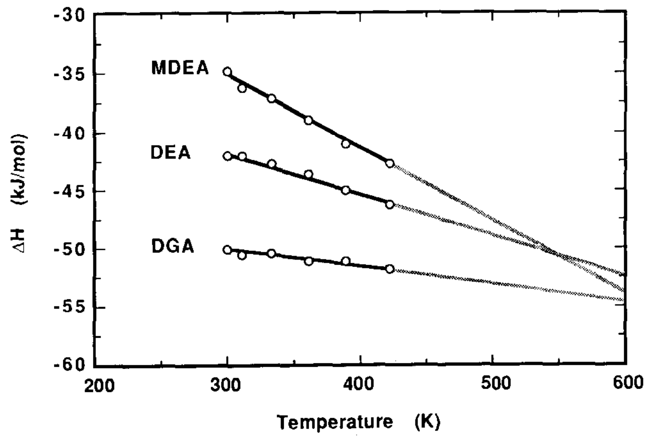


Fig. 2. Plot of ΔH of protonation values versus temperature. Solid lines are based on calculations using eqn. (6). Dashed lines are based on extrapolated values using eqn. (6).

TABLE 4

Calculated thermodynamic values for the indicated reaction

System	Temp. (K)	Lg K	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔC_p (J mol^{-1} K^{-1})
$DGA + H^+ = DGAH^+$	298.2	9.42	−50.2	12.0	−12.2
	323.2	8.74	−50.5	11.0	−12.2
	348.2	8.15	−50.8	10.1	−12.2
	373.2	7.64	−51.1	9.3	−12.2
	398.2	7.19	−51.4	8.5	−12.2
	423.2	6.79	−51.7	7.8	−12.2
	448.2	6.43	−52.0	7.1	−12.2
	473.2	6.11	−52.3	6.4	−12.2
	498.2	5.82	−52.6	5.8	−12.2
	523.2	5.55	−52.9	5.2	−12.2
	548.2	5.31	−53.2	4.6	−12.2
	573.2	5.09	−53.5	4.1	−12.2
	598.2	4.89	−53.8	3.5	−12.2
$DEA + H^+ = DEAH^+$	298.2	8.88	−41.7	30.1	−35.5
	323.2	8.31	−42.6	27.3	−35.5
	348.2	7.81	−43.5	24.6	−35.5
	373.2	7.37	−44.4	22.2	−35.5
	398.2	6.96	−45.3	19.9	−35.5
	423.2	6.62	−46.1	17.7	−35.5
	448.2	6.30	−47.0	15.7	−35.5
	473.2	6.01	−47.9	13.7	−35.5
	498.2	5.74	−48.8	11.9	−35.5
	523.2	5.49	−49.7	10.2	−35.5
	548.2	5.26	−50.9	8.5	−35.5
	573.2	5.05	−51.5	6.9	−35.5
	598.2	4.85	−52.4	5.4	−35.5
$MDEA + H^+ = MDEAH^+$	298.2	8.56	−35.1	46.2	−62.6
	323.2	8.07	−36.7	41.1	−62.6
	348.2	7.64	−38.2	36.5	−62.6
	373.2	7.25	−39.8	32.1	−62.6
	398.2	6.89	−41.4	28.1	−62.6
	423.2	6.57	−42.9	24.3	−62.6
	448.2	6.26	−44.5	20.7	−62.6
	473.2	5.99	−46.1	17.3	−62.6
	498.2	5.73	−47.6	14.0	−62.6
	523.2	5.48	−49.2	11.0	−62.6
	548.2	5.26	−50.8	8.1	−62.6
	573.2	5.04	−52.3	5.3	−62.6
	598.2	4.84	−53.9	2.6	−62.6

common value. These trends can be explained qualitatively using the model for ion–water interaction given earlier [8]. As temperature increases this model predicts that, for ions of equal charge, ion radius and structure

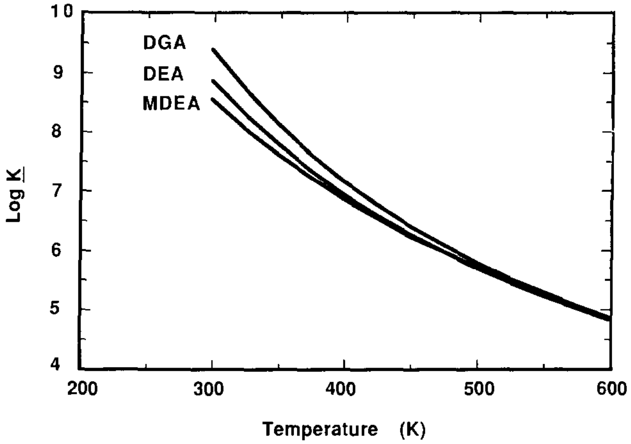


Fig. 3. Plot of calculated lg K values of protonation versus temperature.

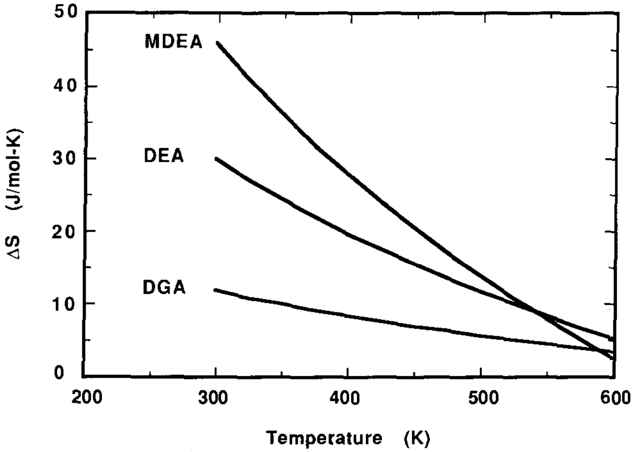


Fig. 4. Plot of calculated ΔS values of protonation versus temperature.

TABLE 5

Comparison of the results of this study with those of other investigations [a]

Amine type	Alkanolamine [b]	lg K	$-\Delta H$ (kJ mol^{-1})	Reference
Primary	DGA	9.42 ± 0.02	50.1 (299.9 K)	This study
	MEA	9.508	50.55	[11]
Secondary	DEA	8.88 ± 0.01	42.1 (299.9 K)	This study
	DEA	–	41.93	[11]
	DEA	8.883	42.4	[10]
	DIPA	8.88	42.7	[11]
Tertiary	MDEA	8.56 ± 0.02	34.9 (299.9 K)	This study
	MDEA	8.52	35.2	[11]
	MDEA	8.52	–	[9]
	TEA	7.80	33.91	[11]

[a] Values are valid at 298.2 K unless otherwise noted. Reaction; $H^+ + L = HL^+$.

[b] Abbreviations are as follows: MEA, monoethanolamine; DIPA, diisopropylamine; TEA, triethanolamine. The remaining abbreviations are defined in the text.

become less important in determining thermodynamic properties. Therefore, in high temperature aqueous solutions, the same thermodynamic quantities for different isocoulombic reactions of the same type will become similar.

Lg K, ΔH, and ΔS values for the protonation of DEA and MDEA as well as some other alkanolamines at 298 K have been reported [9–11]. Corresponding thermodynamic values for the protonation of DGA have not been determined. A comparison of the results of this study and those of other investigations is summarized in Table 5. The agreement between our data and those of others is excellent.

ACKNOWLEDGEMENTS

This work was supported by the Gas Processor's Association as part of GPA Project 821. The authors are grateful to Dennis Cordray, Paul Harding, Keith Merkley and Teresa Walker for their assistance with data measurement and reduction.

REFERENCES

1 G. Astarita, D.W. Savage and A. Bisio, Gas Treating with Chemical Solvents, Wiley, New York, 1983, p. 3.
2 R.D. Deshmukh and A.E. Mather, Chem. Eng. Sci., 36 (1981) 355.
3 A.J. Ellis and R.M. Golding, Am. J. Sci., 261 (1963) 47.
4 A.J. Read, J. Solution Chem., 4 (1975) 53.
5 D.D. Perrin, B. Dempsey and E.P. Serjeant, pK_a Prediction for Organic Acids and Bases, Chapman & Hall, London, 1981, p. 22.
6 R.A. Robinson and R.H. Stokes, Electrolyte Solutions, Butterworth, London, 1959, p. 547.
7 S. Bergström and G. Olofsson, J. Solution Chem., 4 (1975) 535.
8 J.L. Oscarson, R.M. Izatt, P.R. Brown, Z. Pawlak, S.E. Gillespie and J.J. Christensen, J. Solution Chem., 17 (1988) 841.
9 K. Schwabe, W. Graichen and D. Spiethoff, Z. Phys. Chem. N.F., 20 (1959) 68.
10 V.E. Bower, R.A. Robinson and R.G. Bates, J. Res. Natl. Bur. Stand., Sect. A, 66 (1962) 71.
11 J.H. Kim, C. Dobrogowska and L.G. Hepler, Can J. Chem., 65 (1987) 1726.