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Acidic Dissociation Constant and Related Thermodynamic Quantities for Diethanolammonium Ion in Water From 0 to 50 °C[1]

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The dissociation constants of diethanolamine (2:2′-dihydroxydiethylamine) and its conjugate acid were determined by electromotive force measurements of the cell

$$\mathrm{Pt};\ \mathrm{H_2}(\mathrm{g},\ 1\ \mathrm{atm}),(\mathrm{HOC_2H_4})_2\mathrm{NH_2Cl}(m_1),(\mathrm{HOC_2H_4})_2\mathrm{NH}\ (m_2),\ \mathrm{AgCl}\ (\mathrm{s});\ \mathrm{Ag}$$

in the temperature range 0 to 50 °C. The acidic dissociation constant (K_{bh}) of the diethanolammonium ion is given by

$$-\log K_{bh}=\frac{1830.15}{T}+4.0302-0.0043261\ T,$$

where T, the temperature on the Kelvin scale, lies between 273.15 and 323.15°. From this equation were calculated $\Delta G°$, the change in free energy; $\Delta H°$, the change in heat content; $\Delta S°$, the change in entropy; and ΔC_p°, the change in heat capacity that accompany the dissociation of 1 mole of diethanolammonium ion in the standard state. At 25 °C, $-\log K_{bh}=8.883$; $\Delta G°=50{,}682$ joule mole^{-1}; $\Delta H°=42{,}400$ joule mole^{-1}; $\Delta S°=-27.8$ joule deg^{-1}mole^{-1}; and $\Delta C_p^\circ=49$ joule deg^{-1}mole^{-1}.

1. Introduction

The effect of changes of temperature upon the dissociation constants of neutral and negatively charged acids has been the object of considerable study over the past quarter century. This effort has resulted in much useful information concerning the thermodynamic quantities associated with the dissociation process in acids of these types. Until recently, however, the systematic study of positively charged acids has received little attention.

From the electrostatic point of view, the dissociation of a positively charged monobasic acid is of unusual interest. The dissociation process is isoelectric, and consequently it might be expected that the electrostatic contribution to the change of heat capacity would be zero [1, 2][2]. This prediction was confirmed for ammonium ion [3, 4], but rather large positive values of the heat-capacity change have been found for other acids of the same charge type.[3]

From the molecular point of view, the dissociation process appears to be a reaction of considerable complexity. Although considerable progress has been made, notably by Everett and Wynne-Jones and their coworkers [6, 7, 8], Evans and Hamann [9], Laidler [10], and others,[4] in identifying the several factors involved, it is not yet possible to account theoretically for the measured thermodynamic quantities. The empirical correlation of structure with the observed changes of entropy and heat capacity, on the other hand, has revealed a considerable amount of regularity permitting useful predictions to be made.

Earlier papers have reported the dissociation constants of monoethanolammonium ion [12] and triethanolammonium ion [13] from 0 to 50 °C, as well as the changes of free energy, enthalpy, entropy, and heat capacity that accompany the dissociation process in the standard state. Similar data for diethanolammonium ion are now presented.

2. Method

The method was the same as that used in the determination of the dissociation constant of monoethanolammonium ion [12], and that of triethanolammonium ion [13, 14]. It has been described in detail in earlier publications and will only be summarized here.

Electromotive-force measurements of the cell

$$\mathrm{Pt};\ \mathrm{H_2}(\mathrm{g},1\ \mathrm{atm}),\ (\mathrm{HOC_2H_4})_2\mathrm{NH_2Cl}(m_1),\ (\mathrm{HOC_2H_4})_2\mathrm{NH}(m_2),\ \mathrm{AgCl}\ (\mathrm{s});\ \mathrm{Ag}$$

were made at intervals of 5 deg from 0 to 50 °C. The molalities m_1 and m_2 were approximately equal, and the partial pressure of diethanolamine over the buffer solutions was so low that no correction was

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[2] Figures in brackets indicate the literature references at the end of this paper.

[3] For example, the value of $\Delta C°_p$, the change of heat capacity, for trimethylammonium ion is +183 j deg^{-1}mole^{-1} at 25 °C [5].

[4] See, for example, reference [11].

applied for volatility of the solute (diethanolamine boils at about 140 °C under a pressure of 2 mm Hg). It was also found that the correction for the complexing of silver chloride by the amine was negligible, and it was therefore omitted.[5]

The thermodynamic acidity function $p(a_H\gamma_{Cl})$ was computed for each buffer solution at each temperature by the equation

$$p(a_H\gamma_{Cl}) \equiv -\log(\gamma_H\gamma_{Cl}m_H)$$
$$=(E-E^\circ)F/(2.3026RT)+\log m_{Cl} \quad (1)$$

where E is the emf of the cell and E° the standard potential of the cell [15]. In addition, F is the Faraday, R the gas constant, T the temperature on the Kelvin scale, m is molality, and γ is the molal activity coefficient. Values of $2.3026RT/F$ have been tabulated elsewhere [16].

The acidity function $p(a_H\gamma_{Cl})$ is the same quantity for which the symbol pwH was earlier suggested [17] and has been widely used. In order to clarify the nature of this quantity, it has now been proposed that $p(a_H\gamma_{Cl})$ be used instead of pwH [18].

The hydrolysis (dissociation) of diethanolamine as a base is sufficiently extensive that the true equilibrium concentrations of diethanolammonium ion (BH^+) and of diethanolamine (B) in the solution differ somewhat from the stoichiometric molalities m_1 and m_2. This hydrolysis reaction is written as follows:

$$B+H_2O=BH^++OH^-. \quad (2)$$

It is evident from this equation that the molality of BH^+ will be equal to (m_1+m_{OH}) whereas that of B will be (m_2-m_{OH}). Accordingly the ionic strength (I) will be given by

$$I=m_1+m_{OH}. \quad (3)$$

It has been shown earlier [19] that the concentration of hydroxyl ion can be computed very conveniently and with sufficient accuracy by the approximation

$$\log m_{OH}\approx\log K_w+p(a_H\gamma_{Cl}), \quad (4)$$

where K_w is the ion product constant for water [20].

Experience has shown that the determination of the dissociation constant is facilitated by estimating the magnitude of the activity coefficient of the ionized diethanolammonium chloride in each of the solutions. The complete expression for the acidic dissociation constant of the diethanolammonium ion is therefore obtained by combining the mass-law expression for the dissociation process with the acidity function $p(a_H\gamma_{Cl})$ and with the Hückel expression for the activity coefficients. The resulting equation is

$$-\log K'_{bh}\equiv-\log K_{bh}-\beta I=p(a_H\gamma_{Cl})$$
$$+\log\frac{m_1+m_{OH}}{m_2-m_{OH}}-\frac{2A\sqrt{I}}{1+Ba^*\sqrt{I}}. \quad (5)$$

The apparent value of K_{bh} in any solution is designated K'_{bh}; A and B are constants of the Debye-Hücke theory [21], and a^* and β are adjustable parameters.

The thermodynamic constant was obtained by plotting the values of $-\log K'_{bh}$ as a function of ionic strength and extending the line so obtained to an ionic strength of zero. When too large a value of a^* was selected, the plot of the right side of eq (5) as a function of ionic strength was concave downward; when a^* was too small, the function was concave upward. For the measurements of diethanolamine, straight lines easily extrapolated to zero ionic strength were obtained by using a value of zero for a^*. The last term of eq (5) thus takes the form of the Debye-Hückel limiting law.

3. Experimental Procedures and Results

Diethanolamine was distilled at 143° C±3° at a pressure of 2 mm Hg. The middle third of the distillate was collected and subjected to another distillation at the same pressure and temperature, and the middle third of this new distillate was collected. This final sample was found by electrometric titration with a standard solution of hydrochloric acid to assay 100.1 percent, if assumed to contain only diethanolamine.[6]

The buffer solutions were prepared and studied in groups of five. The last four of each series were prepared by weight dilution of the first. This stock solution was prepared, for each series, by pipeting into a 0.1-m hydrochloric acid solution (standardized by weighing the chloride as silver chloride) an amount of diethanolamine sufficient to produce a solution about 0.1 m in diethanolamine hydrochloride and 0.1 m in uncombined diethanolamine. The exact molality of the hydrochloride was, of course, the same as that of the hydrochloric acid used in making the solution. The exact molality of the free amine was determined by weight titration.

The observed values of the electromotive force (the averages for two pairs of electrodes in each cell) were corrected in the usual way to the standard reference state for 1 atm partial pressure of hydrogen. The corrected average values are given in table 1. Values of $p(a_H\gamma_{Cl})$ were calculated by eq (1) from each corrected value of the emf and the chloride molality (m_1).

The quantity $-\log K'_{bh}$ was evaluated by eq (5) for each solution and was plotted at each temperature as a function of ionic strength. The calculated points at each temperature fell on a straight line when $a^*=0$ was chosen. By the method of least squares, the equations for these lines were determined and the intercepts ($-\log K_{bh}$) at $I=0$ were obtained. The values of $-\log K_{bh}$ from 0 to 50° C are listed in table 2 together with the standard deviation of the intercept.

The basic dissociation constant (K_b) of diethanolamine is also given in table 2. This is the equilibrium constant for eq (2) and was obtained by the

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[5] The solubility of silver chloride in a 0.1 m solution of diethanolamine was found to be 0.0002 mole/liter. The corresponding correction to the emf can be calculated in the manner outlined by Bates and Pinching [4].

[6] An estimate of the effect of monoethanolamine as an impurity is given in the appendix, section 5 of this paper.

TABLE 1. *Electromotive force of the cell:* Pt;H_2(*g,1 atm*), *diethanolammonium chloride* (m_1), *diethanolamine* (m_2), AgCl;Ag *from 0 to 50° C*

Series	m_1	m_2	0	5	10	15	20	25	30	35	40	45	50
A	0.10066	0.10833	0.82349	0.82387	0.82410	0.82411	0.82396	0.82364	0.82320	0.82254	0.82165	0.82068	0.81962
	.06207	.06680	.83254	.83285	.83327	.83333	.83394	.83363	.83320	.83260	.83194	.83114	.83018
	.03922	.04220	.84134	.84203	.84263	.84294	.84313	.84325	.84304	.84263	.84191	.84124	.84051
	.02924	.03147	.84704	.84762	.84854	.84908	.84911	.84961	.84918	.84893	.84847	.84795	.84724
	.02097	.02257	.85385	.85481	.85573	.85628	.85669	.85694	.85699	----------	----------	----------	----------
B	.10239	.09148	.81879	.81904	.81917	.81902	.81883	.81877	.81781	.81675	.81583	.81490	.81364
	.09114	.08143	.82095	.82124	.82139	.82132	.82108	.82096	.82019	.81939	.81842	.81729	.81621
	.07174	.06410	.82543	.82584	.82608	.82613	.82600	.82588	.82533	.82466	.82387	.82294	.82161
	.05182	.04630	.83165	.83213	.83254	.83274	.83278	.83270	.83224	.83165	.83099	.83007	.82909
	.03138	.02804	.84125	.84192	.84250	.84287	.84305	.84320	.84285	.84254	.84196	.84130	.84048
C	.10239	.10575	.82202	.82236	.82256	.82253	.82246	.82230	----------	----------	----------	----------	----------
	.08678	.08963	.82526	.82570	.82597	.82603	.82594	.82573	----------	----------	----------	----------	----------
	.013163	.013595	.86239	.86352	.86444	.86508	.86573	.86612	----------	----------	----------	----------	----------
	.009087	.009385	.87017	.87143	.87250	.87334	.87407	.87475	----------	----------	----------	----------	----------
D	.10239	.10460	----------	----------	----------	----------	----------	----------	.82129	.82056	.81980	.81892	.81763
	.012161	.012423	----------	----------	----------	----------	----------	----------	.86739	.86743	.86734	.86718	.86671
	.008791	.008981	----------	----------	----------	----------	----------	----------	.87496	.87517	.87510	.87499	.87469
	.007109	.007262	----------	----------	----------	----------	----------	----------	.87979	.87998	.88013	.88008	.87980
	.005248	.005361	----------	----------	----------	----------	----------	----------	.88720	.88755	.88775	.88781	.88762
E	.08643	.07830	.82236	.82268	.82288	.82286	.82269	.82243	.82190	.82112	.82001	.81907	.81792
	.06103	.05529	.82881	.82917	.82946	.82954	.82950	.82958	.82902	.82838	.82757	.82658	.82560
	.04569	.04139	.83436	.83492	.83531	.83552	.83556	.83562	.83525	.83469	.83403	.83308	.83214
	.03521	.03190	.83950	.84018	.84062	.84093	.84111	.84117	.84092	.83959	.83993	.83916	.83829
	.02521	.02284	.84605	.84657	.84709	.84746	.84782	.84830	.84814	.84760	.84709	.84649	.84577

TABLE 2. *Summary of the dissociation constants of diethanolammonium ion* (K_{bh}) *and diethanolamine* (K_b) *from 0 to 50 °C*

t	$-\log K_{bh}$	σ_i	$-\log K_b$
°C			
0	9.550	0.001	5.394
5	9.404	.002	5.330
10	9.268	.001	5.267
15	9.133	.001	5.213
20	9.005	.001	5.162
25	8.883	.001	5.113
30	8.759	.001	5.074
35	8.632	.002	5.048
40	8.518	.001	5.017
45	8.406	.001	4.990
50	8.297	.001	4.965

formula

$$K_b = K_w / K_{bh}. \tag{6}$$

The constants given in the second column of table 2 may be expressed by the following equation, valid from 0 to 50 °C:

$$-\log K_{bh} = \frac{1830.15}{T} + 4.0302 - 0.0043261\,T, \tag{7}$$

where T is temperature in °K: $T = {}^\circ\mathrm{C} + 273.15$. The constants of eq (7) were computed by the method of least squares. The standard deviation of a single value of $-\log K_{bh}$ from eq (7) was 0.003. Equation (7) is of the form proposed by Harned and Robinson [22].

Hall and Sprinkle [23], using a cell with a hydrogen electrode and a liquid junction, found a value of 8.88 for $-\log K_{bh}$ for diethanolammonium ion at 25 °C. In recent work [24], Chremos and Zimmerman have reported a value of 8.96 at the same temperature. This value was calculated from pH measurements made with a pH meter of the glass-electrode type. Our result agrees well with the earlier work of Hall and Sprinkle.

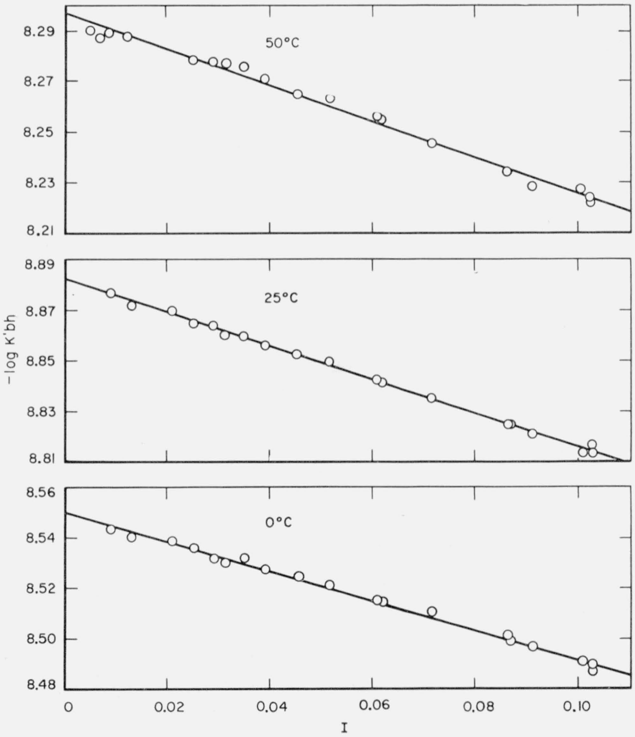

FIGURE 1. *Plots of* $-\log K'_{bh}$ *as a function of ionic strength at 0, 25, and 50 °C.*

4. Derived Thermodynamic Quantities

The changes of free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°), and heat capacity (ΔC_p°) for the dissociation for one mole of diethanolammonium ion in the standard state were calculated in the usual way from the change of the dissociation constant with temperature as given in eq (7). The results are summarized in table 3. The thermodynamic quantities for the dissociation of monoethanolammonium ion [12], diethanolammonium ion, and triethanolammonium ion [13] at 25 °C are compared in table 4.

TABLE 3. *Thermodynamic quantities for the dissociation of diethanolammonium ion:* $BH^+ \leftrightarrows B + H^+$

t	ΔG°	ΔH°	ΔS°	ΔC_p°
°C	*j mole⁻¹*	*j mole⁻¹*	*j deg⁻¹mole⁻¹*	*j deg⁻¹mole⁻¹*
0	49, 936	41, 220	−31. 9	45
5	50, 094	41, 440	−31. 1	46
10	50, 247	41, 680	−30. 3	47
15	50, 396	41, 910	−29. 4	48
20	50, 541	42, 160	−28. 6	49
25	50, 682	42, 400	−27. 8	49
30	50, 819	42, 650	−27. 0	50
35	50, 952	42, 910	−26. 1	51
40	51, 079	43, 160	−25. 3	52
45	51, 204	43, 420	−24. 5	53
50	51, 325	43, 690	−23. 6	53

TABLE 4. *Comparison of the thermodynamic quantities for the dissociation of monoethanolammonium, diethanolammonium, and triethanolammonium ions at 25 °C*

Acid (BH^+)	$-\log K_{bh}$	ΔG°	ΔH°	ΔS°	ΔC_p°
		j mole⁻¹	*j mole⁻¹*	*j deg⁻¹mole⁻¹*	*j deg⁻¹mole⁻¹*
Monoethanolammonium [12]	9. 498	54, 205	50, 540	−12. 3	−5
Diethanolammonium (present work)	8. 883	50, 682	42, 400	−27. 8	49
Triethanolammonium [13]	7. 762	44, 305	33, 450	−36. 4	52

5. Appendix. Effects of Impurities in the Diethanolamine

The effect of small amounts of monoethanolamine or other bases present as an impurity may be gaged as follows. In the measurements described above, a solution was made of diethanolamine (D) and hydrogen chloride in water. Let a be the weight of diethanolamine in 1 kg of water. The molality of D, on the assumption that this base was 100 percent pure, would be a/M_D, where M_D is the molecular weight of D, and hydrochloric acid would be added to a molality $a/(2\mathrm{M}_D)$; thus

$$m'_D = m'_{D\mathrm{H}} = \frac{a}{2\mathrm{M}_D}. \tag{8}$$

Hence, the apparent concentration dissociation constant, $k'_{D\mathrm{H}}$, can be written

$$k'_{D\mathrm{H}} = \frac{m_\mathrm{H} m'_D}{m'_{D\mathrm{H}}} = m_\mathrm{H}. \tag{9}$$

A relation between $k'_{D\mathrm{H}}$ and the true concentration dissociation constant is sought.

If a fraction x (by weight) of the base added is present as another base (e.g., monoethanolamine, M) whose conjugate acid has the dissociation constant $k_{M\mathrm{H}}$, the total concentration of diethanolamine (as free base and hydrochloride) is

$$m_D + m_{D\mathrm{H}} = \frac{(1-x)a}{\mathrm{M}_D} \tag{10}$$

and the total concentration of monoethanolamine is

$$m_M + m_{M\mathrm{H}} = \frac{xa}{\mathrm{M}_M} \tag{11}$$

From the definition of the dissociation constants,

$$m_D = \frac{k_{D\mathrm{H}}}{m_\mathrm{H}}\, m_{D\mathrm{H}} \tag{12}$$

and

$$m_M = \frac{k_{M\mathrm{H}}}{m_\mathrm{H}}\, m_{M\mathrm{H}} \tag{13}$$

Hence, from eq (8), (10), and (12) one can write

$$m_{D\mathrm{H}}\left(1 + \frac{k_{D\mathrm{H}}}{m_\mathrm{H}}\right) = \frac{(1-x)a}{\mathrm{M}_D} = 2(1-x)m'_D \tag{14}$$

and from eq (8), (11), and (13) one finds

$$m_{M\mathrm{H}}\left(1 + \frac{k_{M\mathrm{H}}}{m_\mathrm{H}}\right) = \frac{xa}{\mathrm{M}_M} = 2x\frac{\mathrm{M}_D}{\mathrm{M}_M}\, m'_D. \tag{15}$$

Electroneutrality imposes the following condition:

$$m_\mathrm{H} + m_{M\mathrm{H}} + m_{D\mathrm{H}} = m_\mathrm{Cl} + m_\mathrm{OH} \tag{16}$$

or

$$m_{M\mathrm{H}} + m_{D\mathrm{H}} \approx m_\mathrm{Cl}, \tag{16a}$$

inasmuch as the hydroxyl ion concentration is very much smaller than the molality of the added hydrochloric acid. Hence, with the aid of eq (14) and (15) one obtains

$$\frac{2(1-x)m'_D}{1 + k_{D\mathrm{H}}/m_\mathrm{H}} + \frac{2x\mathrm{M}_D m'_D}{\mathrm{M}_M(1 + k_{M\mathrm{H}}/m_\mathrm{H})} = m_\mathrm{Cl}. \tag{17}$$

Remembering that $m_\mathrm{H} = k'_{D\mathrm{H}}$ and that $m_\mathrm{Cl} = m'_D = m'_{D\mathrm{H}}$, one can then write

$$\frac{1-x}{1 + k_{D\mathrm{H}}/k'_{D\mathrm{H}}} + \frac{x\mathrm{M}_D}{\mathrm{M}_M(1+\epsilon)} = 0.5, \tag{18}$$

where $\epsilon \equiv k_{M\mathrm{H}}/k'_{D\mathrm{H}}$. Finally, eq (18) can be rearranged to

$$\frac{k_{D\mathrm{H}}}{k'_{D\mathrm{H}}} = \frac{(1+\epsilon)(2-2x)}{(1+\epsilon) - 2x(\mathrm{M}_D/\mathrm{M}_M)} - 1. \tag{18a}$$

It is now possible, with the aid of eq (18a), to compute the error in the dissociation constant resulting from the presence of small amounts of a second base in the diethanolamine used. Inasmuch as the assay (100.1 percent) exceeded the theoretical value, it is evident that the impurity was a base of equivalent weight less than that of diethanolamine. It is likely, therefore, that it was monoethanolamine (molecular weight=61.08) rather than triethanolamine (mol wt=149.19). The value of x is readily shown to be

$$x = \frac{\Delta A}{100} \frac{M_M}{M_D - M_M} \tag{19}$$

where ΔA is the observed assay value (in percent) minus 100, due consideration being given to sign.

For the measurements reported here, ΔA was $+0.1$, and x is therefore 0.0015. The value of k'_{DH} at 25 °C is 1.31×10^{-9} and k_{MH} is 3.18×10^{-10} [12]; hence ϵ is 0.243. The ratio of molecular weights, M_D/M_M, is 1.721. Substitution of these values in eq (18a) gives 1.0051 for k_{DH}/k'_{DH}. It may be concluded, therefore, that the presence of monoethanolamine ($x=0.0015$) could result in values of $-\log K_{bh}$ for diethanolamine that are too high by about 0.002 unit. This correction was not made in reporting the values of $-\log K_{bh}$ given in table 2.

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