J. Chem. Eng. Data **2003,** *48,* 171−175

Potentiometric Study of the Dissociation Quotient of the Aqueous Ethanolammonium Ion as a Function of Temperature and Ionic Strength

Pascale Bénézeth,* David J. Wesolowski, and Donald A. Palmer

Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6110

The acid dissociation equilibrium involving aqueous ethanolammonium ion in the reaction, $HO(CH_2)_2NH_3^+ \rightleftarrows HO(CH_2)_2NH_2 + H^+$, was measured potentiometrically with a hydrogen-electrode concentration cell from (0 to 290) °C in sodium trifluoromethanesulfonate (NaTr) solutions at ionic strengths of (0.03, 0.1, and 0.3) molal. The molal dissociation quotients and selected literature data at infinite dilution were fitted by an empirical equation with five adjustable parameters involving functions of temperature, solvent density, and ionic strength. This treatment yielded the following thermodynamic quantities at 25 °C and infinite dilution: $\log K_a = -9.48 \pm 0.03$, $\Delta H_a = (51.3 \pm 1.5)$ kJ·mol^{-1}, $\Delta S_a = (-9 \pm 5)$ J·K^{-1}·mol^{-1}, $\Delta C_{pa} = (8 \pm 17)$ J·K^{-1}·mol^{-1}.

Introduction

Alkanolamines, such as monoethanolamine or ethanolamine (ETA), contain both hydroxyl and amino functional groups. ETA is used for example as an acid−gas absorbent in fossil-fueled power plants to remove impurities (e.g., carbon dioxide and hydrogen sulfide) in natural gas processing and to minimize corrosion by nuclear power utilities in the secondary water−steam cycle. However, the dissociation constants of ETA are poorly known at high temperatures and have been determined previously only at temperatures up to 50 °C and in very dilute solutions, mostly by emf measurements in cells without liquid junction. The available literature data are from Bates and Pinching[1] from (0 to 50) °C, Lotz et al.[2] from (10 to 40) °C, and Datta and Grzybowski[3] from (5 to 45) °C. The enthalpy of ionization of ETA has also been measured by Levi et al.[4] at (10, 20, and 30) °C. The thermodynamic data for the ionization of ETA have been reviewed in detail by Jones and Arnett.[5] More recently, Cobble and Turner[6] reported estimated values for the acid ionization constant at infinite dilution.

The present investigation is part of a systematic effort to provide consistent sets of thermodynamic measurements of amines such as morpholinium ion, $(C_4H_8ONH_2^+)$,[7] and dimethylammonium ion.[8] In the present paper, the equilibrium quotients for reaction 1:

$$HO(CH_2)_2NH_3^+ \rightleftarrows HO(CH_2)_2NH_2 + H^+ \qquad (1)$$

$$(\text{or, } ETAH^+ \rightleftarrows ETA + H^+)$$

with

$$Q_{ETAH^+} = [HO(CH_2)_2NH_2][H^+]/[HO(CH_2)_2NH_3^+] \qquad (2)$$

involving the aqueous ethanolammonium ion, were measured potentiometrically with a hydrogen-electrode concentration cell (HECC) from (0 to 290) °C in sodium trifluoromethanesulfonate (NaTr) solutions at ionic strengths of (0.1, 0.3, and 1) molal. Note that the stoichiometric molal dissociation constant, Q_{ETAH^+}, approaches the thermodynamic equilibrium constant, K_{ETAH^+}, in the limit of infinite dilution. The reason for choosing to express ETA ionization as the dissociation of the protonated amine is because reaction 1 is “isocoulombic”, meaning that there is no change in the number, magnitudes, or signs of charges from reactants to products. The dissociation quotients of reactions written in this form typically have very simple temperature and pressure dependencies, and the logarithm of the dissociation quotient is often found to be linearly and weakly dependent on ionic strength.

Experimental Section

Materials. All solutions were prepared from reagent grade chemicals and distilled, deionized water (resistivity > 0.18 MΩ m). Stock solutions of NaTr, NaOH, and trifluoromethanesulfonic acid (HCF_3SO_3 or HTr) used to make up the desired experimental solutions were stored under argon in polypropylene containers. The ethanolamine stock solution was prepared from redistilled 99.5+% ethanolamine (Aldrich Chemical Co.). The stock solution was titrated to know precisely the concentration of the ethanolamine (± 0.2%). Compositions of the solutions used for the experimental runs are given in Table 1.

Apparatus. The HECC and the general experimental procedure to measure the dissociation quotients of amines have been described in numerous publications.[7,8] The initial configuration of the cell in a typical homogeneous amine buffer experiment at low temperature (ca. 50 °C or less) is as follows:

$$\mathrm{Pt, H_2 \,|\, HTr, NaTr \,||\, HTr, NaTr, Amine \,|\, H_2, Pt}$$

$$m_1 \quad m_2 \qquad m_3 \quad m_4 \quad m_5$$

Reference　　Test

with $m_2 \approx m_4$, and $m_3 \approx m_5/2$ at the start of the experiment and the ratio of m_1 to m_2 (or m_3 to m_4) is <0.1 in order to minimize both liquid junction (E_{LJ}) contributions to the measured potential, and activity coefficient differences

---

* To whom correspondence should be addressed. Phone: 865 574-4960. Fax: 865 574-4961. E-mail: benezethp@ornl.gov.

10.1021/je0201424 CCC: $25.00

Table 1. Starting Molal Solution Compositions

	test/reference			titrant	
I/(mol·kg^{-1})	m_{HTr}/(mol·kg^{-1})^a	m_{NaTr}/(mol·kg^{-1})^a	m_{ETA}/(mol·kg^{-1})	m_{ETA}/(mol·kg^{-1})	m_{NaTr}/(mol·kg^{-1})^a
0.03	0.00034 (ref) 0.0008 (test)	0.03400 (ref) 0.03400 (test)	0 (ref) 0.00164 (test)	0	0
0.03	0.00199	0.0300	0	0.02085	0.03060
0.1	0.00199	0.10000	0	0.02041	0.09998
0.1	0.00104	0.10434	0	0.02041	0.09998
0.3	0.00202	0.30225	0	0.02186	0.29993
0.3	0.00489 (ref) 0.00496 (test)	0.2999 (ref) 0.3002 (test)	0 (ref) 0.01001(test)	0	0

[a] Experimental uncertainty = 0.1%

Table 2. Experimental Results for the Dissociation Quotient of ETAH$^+$ at Saturation Vapor Pressure

t^a/(°C)	m_{ETAH^+}/(mol·kg^{-1})	m_{ETA}/(mol·kg^{-1})	I/(mol·kg^{-1})	E^b/(mV)	E_{lj}/(mV)	pH$_m$^{c}	$-\log Q_a$	$-\log Q_b$
−0.08	0.0005	0.0005	0.030	386.97	2.579	10.15	10.18 ± 0.02	4.64 ± 0.02
24.53	0.0005	0.0005	0.030	375.88	2.821	9.37	9.42 ± 0.02	4.45 ± 0.02
24.84	0.0009	0.0008	0.034	350.79	0.128	9.40	9.43 ± 0.02	4.42 ± 0.02
49.51	0.0005	0.0005	0.030	364.11	3.062	8.69	8.75 ± 0.02	4.39 ± 0.02
50.08	0.0009	0.0008	0.034	335.08	0.141	8.69	8.73 ± 0.02	4.39 ± 0.02
100.07	0.0009	0.0008	0.034	306.15	0.156	7.60	7.63 ± 0.02	4.47 ± 0.02
101.82	0.0005	0.0005	0.030	339.76	3.553	7.57	7.62 ± 0.02	4.46 ± 0.02
106.73	0.0005	0.0005	0.030	333.89	3.596	7.44	7.48 ± 0.02	4.53 ± 0.02
151.25	0.0005	0.0005	0.030	319.44	4.006	6.80	6.83 ± 0.02	4.62 ± 0.02
149.83	0.0016	0.0025	0.030	356.78	2.821	6.98	6.79 ± 0.02	4.67 ± 0.02
150.03	0.0009	0.0008	0.034	276.81	0.161	6.76	6.78 ± 0.02	4.67 ± 0.02
149.84	0.0018	0.0006	0.030	295.31	2.774	6.25	6.76 ± 0.02	4.71 ± 0.02
200.03	0.0008	0.0008	0.034	239.15	0.159	6.01	6.02 ± 0.02	5.04 ± 0.02
200.03	0.0018	0.0006	0.030	272.28	2.244	5.62	6.06 ± 0.02	5.01 ± 0.02
200.11	0.0016	0.0026	0.030	337.77	2.280	6.32	6.10 ± 0.02	4.97 ± 0.02
249.59	0.0018	0.0006	0.031	245.87	1.819	5.08	5.54 ± 0.02	5.36 ± 0.02
249.59	0.0016	0.0026	0.031	314.21	1.852	5.74	5.53 ± 0.02	5.37 ± 0.02
289.48	0.0018	0.0006	0.031	217.86	1.440	4.65	5.13 ± 0.05	5.78 ± 0.05
289.14	0.0018	0.0014	0.031	263.84	1.464	5.06	5.16 ± 0.05	5.76 ± 0.05
−0.03	0.0025	0.0025	0.103	394.46	0.642	10.27	10.28 ± 0.05	4.45 ± 0.05
4.93	0.0025	0.0025	0.103	390.12	0.785	10.07	10.08 ± 0.05	4.44 ± 0.05
24.95	0.0025	0.0025	0.103	382.78	0.846	9.47	9.48 ± 0.02	4.29 ± 0.02
26.52	0.0026	0.0026	0.103	382.37	0.709	9.43	9.44 ± 0.02	4.28 ± 0.02
50.07	0.0026	0.0025	0.103	371.11	0.767	8.78	8.80 ± 0.02	4.24 ± 0.02
100.03	0.0025	0.0025	0.103	345.45	0.881	7.66	7.67 ± 0.02	4.33 ± 0.02
150.04	0.0025	0.0025	0.103	322.85	0.993	6.84	6.85 ± 0.02	4.49 ± 0.02
150.73	0.0017	0.0006	0.100	300.36	0.869	6.28	6.74 ± 0.02	4.59 ± 0.02
150.76	0.0016	0.0025	0.100	360.98	0.889	7.00	6.80 ± 0.02	4.53 ± 0.02
195.91	0.0025	0.0025	0.104	296.53	0.342	6.17	6.17 ± 0.02	4.78 ± 0.02
200.11	0.0025	0.0025	0.104	297.78	1.103	6.16	6.16 ± 0.02	4.76 ± 0.02
200.93	0.0009	0.0014	0.105	309.88	0.385	6.28	6.09 ± 0.02	4.82 ± 0.02
200.68	0.0009	0.0022	0.105	328.44	0.401	6.47	6.09 ± 0.02	4.83 ± 0.02
250.40	0.0017	0.0014	0.102	282.68	0.556	5.42	5.53 ± 0.02	5.19 ± 0.02
250.46	0.0018	0.0005	0.102	240.98	0.548	5.02	5.56 ± 0.02	5.16 ± 0.02
289.00	0.0018	0.0003	0.103	204.07	0.439	4.52	5.25 ± 0.05	5.44 ± 0.05
289.64	0.0019	0.0005	0.104	218.02	0.434	4.64	5.19 ± 0.05	5.50 ± 0.05
289.57	0.0018	0.0014	0.104	262.09	0.443	5.04	5.15 ± 0.05	5.54 ± 0.05
289.98	0.0018	0.0011	0.103	255.77	0.450	4.98	5.17 ± 0.05	5.52 ± 0.05
−0.03	0.0050	0.0050	0.300	432.02	1.122	10.30	10.30 ± 0.05	4.36 ± 0.05
24.82	0.0050	0.0050	0.300	425.29	1.226	9.53	9.53 ± 0.02	4.18 ± 0.02
24.82	0.0050	0.0050	0.300	422.36	1.126	9.48	9.48 ± 0.02	4.23 ± 0.02
50.14	0.0050	0.0050	0.300	417.18	1.332	8.84	8.84 ± 0.02	4.12 ± 0.02
50.26	0.0050	0.0050	0.300	417.03	1.332	8.83	8.84 ± 0.02	4.12 ± 0.02
100.01	0.0050	0.0050	0.300	400.36	0.830	7.73	7.73 ± 0.02	4.18 ± 0.02
100.08	0.0050	0.0050	0.300	399.34	1.536	7.73	7.73 ± 0.02	4.18 ± 0.02
150.07	0.0050	0.0050	0.301	381.17	1.739	6.87	6.87 ± 0.02	4.35 ± 0.02
151.43	0.0016	0.0013	0.303	332.07	0.297	6.64	6.77 ± 0.02	4.44 ± 0.02
154.22	0.0050	0.0050	0.301	380.98	0.948	6.81	6.81 ± 0.02	4.36 ± 0.02
200.09	0.0017	0.0015	0.305	309.19	0.241	5.98	6.07 ± 0.02	4.70 ± 0.02
200.16	0.0050	0.0050	0.302	360.79	1.941	6.17	6.17 ± 0.02	4.61 ± 0.02
200.17	0.0018	0.0006	0.305	263.51	0.236	5.50	5.99 ± 0.02	4.78 ± 0.02
248.85	0.0018	0.0005	0.307	279.82	0.198	5.39	5.51 ± 0.02	5.02 ± 0.02
248.87	0.0018	0.0014	0.308	230.98	0.193	4.92	5.48 ± 0.02	5.05 ± 0.02
288.27	0.0019	0.0007	0.314	231.08	0.151	4.76	5.17 ± 0.05	5.27 ± 0.05
288.31	0.0019	0.0009	0.314	231.18	0.149	4.76	5.10 ± 0.05	5.33 ± 0.05
288.30	0.0018	0.0016	0.313	266.32	0.157	5.07	5.11 ± 0.05	5.32 ± 0.05
288.36	0.0018	0.0018	0.313	266.70	0.155	5.08	5.08 ± 0.05	5.35 ± 0.05

[a] Experimental uncertainty = 0.1 °C. [b] Experimental uncertainty = 0.1 mV. [c] pH$_m$ = −log[H$^+$], where [H$^+$] is the measured molality of H$^+$ in solution.

between the two solutions. For systems involving only monovalent ions and with a significant excess of inert electrolyte, as is the case in these experiments, the liquid junction potential is typically calculated to be less than 1 mV, with an approximately 25% estimated uncertainty, translating into an error of less than 0.005 pH units. Prior to each experiment, the porous Teflon liquid junction was saturated with the same test/reference solution. The cell was pressurized at room temperature to about 10 bar and purged in five cycles with ultrapure hydrogen gas (Matheson, 99.999%). After the purging process, the hydrogen pressure was regulated to approximately 10 bar.

In most of the experiments, buffer mixtures of almost equal molal concentrations of ETA and ETAH$^+$ ion were

Table 3. ETAH$^+$ Dissociation Constants at Infinite Dilution and Thermodynamic Quantities from Literature

t		ΔH_a	ΔS_a	ΔC_{pa}	
°C	$-\log K_a$	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	ref no.
10		50.1		35	4
20		50.4		35	4
30		50.6		17	4
0.0	10.31	50.7	−12	−5	1
5.0	10.13	50.6	−12	−5	1
10.0	9.97	50.6	−12	−5	1
15.0	9.80	50.6	−12	−5	1
20.0	9.65	50.6	−12	−5	1
25.0	9.50	50.4	−12	−5	1
30.0	9.35	50.5	−12	−5	1
35.0	9.21	50.5	−12	−5	1
40.0	9.07	50.5	−12	−5	1
45.0	8.94	50.4	−13	−5	1
50.0	8.81	50.4	−13	−5	1
10.0	9.97	48.1	−21		2
20.0	9.66	48.1	−21		2
30.0	9.36	48.1	−21		2
40.0	9.11	48.1	−21		2
5.0	10.14	50.0	−14	42	3
15.0	9.81	50.5	−13	43	3
25.0	9.50	50.9	−11	45	3
35.0	9.21	51.3	−10	46	3
45.0	8.93	51.8	−8	48	3
25.0	9.496	50.54	−12.3	26.4	5

initially equilibrated in the test compartment of the cell with an acidic reference solution at 25 °C in a thermostated bath, and a stable potential was achieved in approximately 12 h. This time is required for all free oxygen to be consumed at the electrode surfaces, with a rate dependent on temperature. Upon attainment of a stable cell potential measurement, the cell was then placed into an ice/water mixture to measure the constant at 0 °C, and then the temperature was raised to 50 °C, with stable potential readings recorded after a few hours at each temperature. The cell was then transferred to an aluminum-block tube furnace and heated successively to (100, 150, 200, 250, and 290) °C. Drifting potentials were observed at the higher temperatures, and so an alternative cell configuration was adopted for the higher temperature experiments, wherein the starting test and reference solutions were identical NaTr + HTr solutions, and the unprotonated ETA in an NaTr solution of the same ionic strength was titrated into the test compartment at temperature to establish the buffer mixture.[7,8]

Results

The measured cell potentials, E, at each experimental condition are listed in Table 2. The potential depends on the relative hydrogen ion molalities in the two compartments (activity coefficients are assumed to be equal because of the presence of excess supporting electrolyte) as dictated by the Nernst relationship:

$$E = -\frac{RT}{F}\ln\left\{\frac{[\mathrm{H}^+]_t}{[\mathrm{H}^+]_r}\right\} - E_{lj} \qquad (3)$$

where $[\mathrm{H}^+]_t$ and $[\mathrm{H}^+]_r$ refer to the molalities of hydrogen ions in the test and reference compartments, respectively. The ideal gas and Faraday constants are designated by R and F, respectively; T denotes the absolute temperature. E and E_{lj} represent the measured potential and liquid junction potential, respectively. The value of E_{lj} was calculated according to the Henderson equation,[9] which involves the molar ionic conductivities ($\lambda°$) of the individual ions. The values for Na$^+$, H$^+$, and OH$^-$ ions were taken from Quist and Marshall;[10] that for Tr$^-$ was taken from Ho and Palmer.[11] It was assumed that $\lambda°$ (ETAH$^+$) = $\lambda°$(Na$^+$). The calculated liquid junction potentials were less than 1.8 mV, which gives an uncertainty in the logarithms of the dissociation quotients of ± 0.01 (depending on temperature), assuming that the Henderson equation predicts the value of E_{lj} to within 25%.[12]

Table 4. Thermodynamic Quantities for the Dissociation Constants of Ethanolammonium Ion (Reaction 1) in Aqueous Sodium Trifluoromethanesulfonate Media at the Saturation Vapor Pressure[a]

t		ΔH_a	ΔS_a	ΔC_{pa}
°C	$-\log Q_a$	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}
		I/(mol·kg^{-1})=0.0		
0	10.30 ± 0.05	51.1 ± 1.9	−10 ± 6	7 ± 16
25	9.48 ± 0.03	51.3 ± 1.5	−9 ± 5	8 ± 17
50	8.78 ± 0.02	51.5 ± 1.2	−9 ± 4	8 ± 18
75	8.18 ± 0.03	51.7 ± 0.8	−8 ± 3	9 ± 20
100	7.66 ± 0.03	51.9 ± 0.7	−7 ± 2	10 ± 21
125	7.20 ± 0.03	52.2 ± 0.9	−7 ± 2	10 ± 23
150	6.80 ± 0.03	52.5 ± 1.4	−6 ± 3	11 ± 24
175	6.44 ± 0.03	52.8 ± 1.9	−6 ± 5	11 ± 25
200	6.11 ± 0.04	53.0 ± 2.6	−5 ± 6	12 ± 27
225	5.82 ± 0.05	53.4 ± 3.2	−4 ± 7	13 ± 28
250	5.55 ± 0.06	53.7 ± 3.9	−4 ± 9	13 ± 30
275	5.30 ± 0.08	54.0 ± 4.7	−3 ± 10	14 ± 31
300	5.08 ± 0.10	54.4 ± 5.5	−2 ± 11	15 ± 33
		I/(mol·kg^{-1})=0.03		
0	10.30 ± 0.05	51.1 ± 1.9	−10 ± 6	8 ± 15
25	9.48 ± 0.03	51.4 ± 1.5	−9 ± 5	8 ± 16
50	8.78 ± 0.02	51.6 ± 1.2	−9 ± 4	9 ± 18
75	8.18 ± 0.03	51.8 ± 0.8	−8 ± 3	10 ± 19
100	7.66 ± 0.03	52.1 ± 0.7	−7 ± 2	11 ± 20
25	7.20 ± 0.03	52.3 ± 0.8	7 ± 2	11 ± 22
150	6.79 ± 0.03	52.6 ± 1.2	−6 ± 3	12 ± 23
175	6.43 ± 0.03	52.9 ± 1.8	−5 ± 4	13 ± 24
200	6.11 ± 0.03	53.3 ± 2.4	−4 ± 5	15 ± 25
225	5.81 ± 0.04	53.7 ± 3.0	−4 ± 7	16 ± 26
250	5.54 ± 0.05	54.1 ± 3.6	−3 ± 8	19 ± 26
275	5.29 ± 0.07	54.6 ± 4.3	−2 ± 9	23 ± 26
300	5.06 ± 0.08	55.2 ± 4.9	−0.6 ± 10	31 ± 27
		I/(mol·kg^{-1})=0.1		
0	10.31 ± 0.05	51.1 ± 1.9	−10 ± 6	11 ± 13
25	9.49 ± 0.03	51.4 ± 1.6	−9 ± 5	10 ± 15
50	8.79 ± 0.02	51.7 ± 1.2	−8 ± 4	11 ± 17
75	8.19 ± 0.03	51.9 ± 0.8	−8 ± 3	12 ± 18
100	7.66 ± 0.03	52.3 ± 0.6	−7 ± 2	13 ± 19
125	7.20 ± 0.03	52.6 ± 0.6	−6 ± 2	14 ± 20
150	6.79 ± 0.03	52.9 ± 1.0	−5 ± 2	16 ± 21
175	6.43 ± 0.03	53.4 ± 1.5	−4 ± 3	18 ± 22
200	6.10 ± 0.03	53.8 ± 2.0	−3 ± 4	21 ± 23
225	5.80 ± 0.03	54.4 ± 2.5	−2 ± 5	25 ± 23
250	5.52 ± 0.04	55.1 ± 3.1	−0.5 ± 7	31 ± 25
275	5.27 ± 0.05	55.9 ± 3.7	1 ± 8	43 ± 33
300	5.04 ± 0.07	57.2 ± 4.3	3 ± 9	70 ± 62
		I/(mol·kg^{-1})=0.3		
0	10.35 ± 0.07	51.1 ± 1.9	−11 ± 6	19 ± 14
25	9.53 ± 0.05	51.5 ± 1.6	−10 ± 5	16 ± 14
50	8.83 ± 0.05	51.9 ± 1.3	−8 ± 4	16 ± 15
75	8.23 ± 0.04	52.3 ± 1.0	−7 ± 3	18 ± 16
100	7.70 ± 0.04	52.8 ± 0.9	−6 ± 2	20 ± 18
125	7.23 ± 0.04	53.3 ± 0.9	−5 ± 2	23 ± 19
150	6.82 ± 0.04	53.9 ± 1.3	−3 ± 3	26 ± 21
175	6.44 ± 0.03	54.6 ± 1.7	−1 ± 4	31 ± 24
200	6.10 ± 0.04	55.5 ± 2.4	0.4 ± 5	38 ± 29
225	5.79 ± 0.04	56.5 ± 3.2	3 ± 7	48 ± 39
250	5.51 ± 0.05	57.9 ± 4.2	5 ± 9	66 ± 58
275	5.24 ± 0.07	59.8 ± 5.9	9 ± 12	101 ± 100
300	4.99 ± 0.10	62.8 ± 8.8	14 ± 17	182 ± 204

[a] The uncertainties represent three times the standard deviation.

The measured potentials of the ETA/ETAH$^+$ buffer mixtures obtained in this study were treated with existing "in-house" computer programs, which calculate the liquid junction potentials and provide a numerical analysis of the overall error associated with the liquid junction calculation and uncertainties in solution compositions and potential measurements,[7,8] to yield the dissociation quotients reported in Table 2. As can be seen in this table, some experiments were performed several times at the same

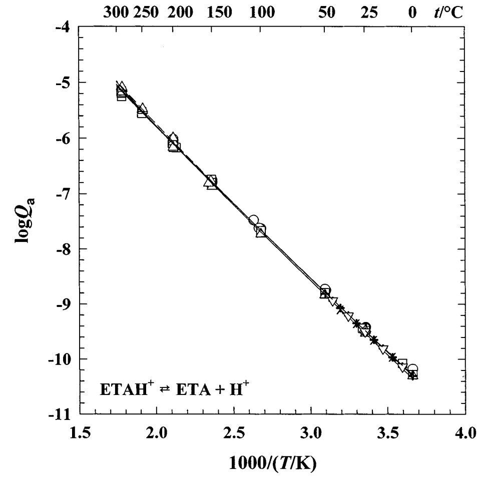

Figure 1. Acid dissociation quotients of $ETAH^+$ as a function of reciprocal temperature. The solid curve represents the fit from this study (eq 4); the symbols represent: ○, □, and △, (0.03, 0.1, and 0.3) m NaTr, respectively, from this study; ◇, Jones and Arnett;[5] +, Bates and Pinching[1]; ×, Lotz et al.[2]; ▽, Datta and Grzybowski[3]; and the dashed line represents the estimation of Cobble and Turner.[6]

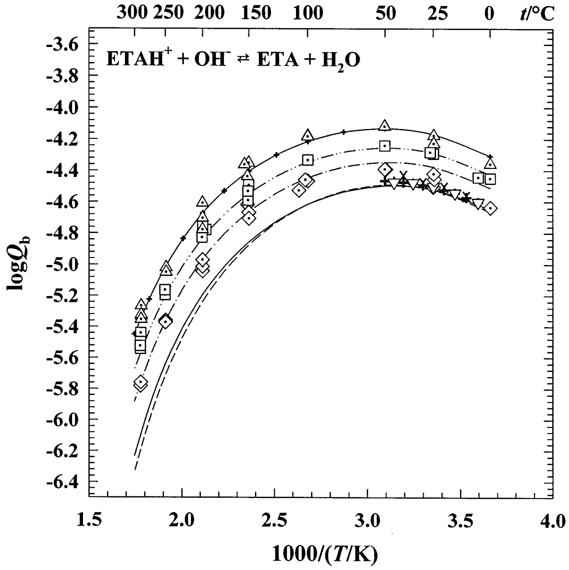

Figure 2. Base association quotients ($\log Q_b$) of ETA. The dotted symbols represent the experimental data from this study. The curves represent the fit from this study: (—), at infinite dilution; (—•—), at 0.03 m NaTr; (—••—), at 0.1 m NaTr; (-+-), at 0.3 m NaTr. The other symbols represent ◇, Jones and Arnett;[5] +, Bates and Pinching[1]; ×, Lotz et al.[2]; ▽, Datta and Grzybowski[3]; and the dashed line represents the estimation of Cobble and Turner[6] at infinite dilution.

conditions, with excellent agreement and reproducibility among the values obtained. A weighted fit of these values was carried out, including 57 $\log Q_a$ values from this study (Table 2) and one $\log K_a$ value at 25 °C (−9.496) from Jones and Arnett,[5] as reported in Table 3. Table 3 also includes the literature values for $\log K_a$ and thermodynamic properties for reaction 1 (ΔH_a, ΔS_a, and ΔC_{pa}) from other sources mentioned above. These latter quantities were not included in the overall fit because our results over this wide temperature range provide a more reliable database for calculating these derivative properties. Also, earlier studies suffered from a lack of availability of high purity ethanolamine reagents.

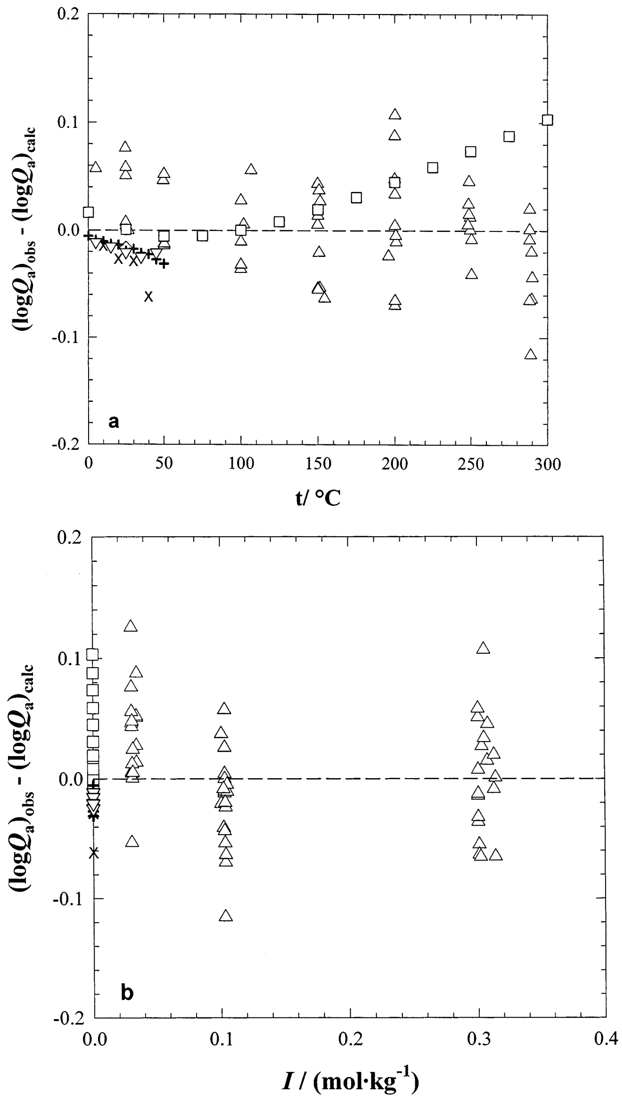

Figure 3. Deviation plots of experimental values of $\log Q_a$ as a function of temperature (a) and ionic strength (b). The symbols represent +, Bates and Pinching[1]; ×, Lotz et al.[2]; ▽, Datta and Grzybowski[3]; ◇, Jones and Arnett;[5] □, Cobble and Turner;[6] and △, this study.

The resulting equation, which gave the "best fit" to the combined data with the minimum number of adjustable parameters, was found to be:

$$\log Q_{\mathrm{ETAH^+}} = p_1 + p_2/T + p_3T + p_4(I)\ln(\rho_w) + p_5I^2 \qquad (4)$$

where I is the stoichiometric molal ionic strength, T is the temperature in Kelvin, and ρ_w is the density in kg·m^{-3} of pure liquid water at each experimental temperature.[13] The values of the parameters are $p_1 = -0.882749$; $p_2 = -2622.09$; $p_3 = 6.63648 \cdot 10^{-4}$; $p_4 = -1.365598$; and $p_5 = -0.576199$. The thermodynamic parameters for reaction 1 at 25 °C, 1 bar and infinite dilution are $\log K_a = -9.48 \pm 0.03$; $\Delta H_a = (51.3 \pm 1.5)$ kJ·mol^{-1}; $\Delta S_a = (-9 \pm 5)$ J·K^{-1}·mol^{-1}; $\Delta C_{pa} = (8 \pm 17)$ J·K^{-1}·mol^{-1}. The smoothed values calculated as a function of temperature are reported in Table 4 at (0, 0.03, 0.1, and 0.3) molal ionic strengths.

Similar functions were previously found adequate to fit our results for $MORH^+$ and $DMAH^+$:

$$\log Q_{\mathrm{MORH^+}} = p_1 + p_2/T + p_3\ln(T) + p_4\ln(\rho_w) + p_5I/T \qquad (5)$$

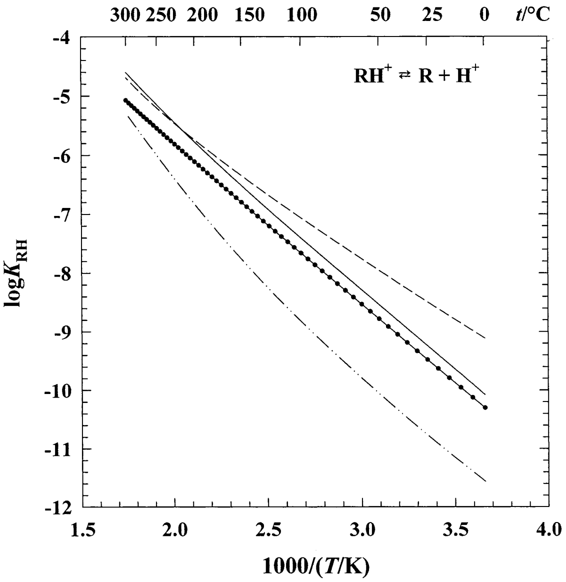

Figure 4. Comparison of log K_{RH} values for amines versus reciprocal temperature (1000/K). The curves represent (- - -), morpholine;[7] (—), ammonia;[15] (—••—), dimethylamine;[8] and (-+-), ethanolamine from this study.

with $p_1 = -7.9813$; $p_2 = -1738.8$; $p_3 = 0.93352$; $p_4 = -1.1546$; and $p_5 = -33.917$ from Ridley et al.[7] and

$$\log Q_{DMAH^+} = p_1 + p_2/T + p_3T + (p_4 + p_5I)\ln(\rho_w) + p_6f(I)(T) \quad (6)$$

with $p_1 = -9.4416$; $p_2 = -1542.3$; $p_3 = 0.012918$; $p_4 = 1.6621$; $p_5 = -1.0848$; and $p_6 = -0.0011795$ from Bénézeth et al..[8] In eq 6, the function $f(I)$ is related to the Pitzer ion interaction treatment, $f(I) = 1 - e^{-x}(1 + x)$, where $x = 2I^{1/2}$.

The equilibrium constants for $ETAH^+$ dissociation are compared with literature values (at infinite dilution) in Figure 1 as a function of the reciprocal temperature. These results are clearly in good agreement with the low-temperature data (≤50 °C) from previous studies. Also, it can be seen from this figure that the temperature dependence of log Q_{ETAH^+} is almost linear to 300 °C and is also nearly independent of ionic strength, which further supports the use of the isocoulombic nature of reaction 1.

However, to compare our experimental data with eq 4, as well as with the literature data, we converted the dissociation quotients to the base form (Q_b) by combining the log Q_{ETAH^+} values with the appropriate dissociation quotients for water (Q_w) to obtain the base form reaction:

$$HO(CH_2)_2NH_3^+ + OH^- = (HOCH_2)_2NH_2 + H_2O \quad (7)$$

Q_w values were taken from Palmer and Drummond.[14] The experimental values of log Q_b (Table 2), the smoothed values from Table 3, as well as the literature values converted to the base form are compared in Figure 2 as a function of the reciprocal of absolute temperature.

The deviations between eq 4 and the experimental values of log Q_a, obtained in this study and reported in the literature as a function of temperature and ionic strength are shown in Figure 3a–b, respectively. As can be seen in this figure, the deviations are random for the dissociation quotient with respect to both temperature and ionic strength and the maximum deviation for log Q_a is less than 0.13 log units. In Figure 4, we compare the infinite dilution log K_a values for the dissociation constants of MOR, DMA, and ETA from this study with the equivalent constant for ammonium ion dissociation[15] as a function of reciprocal temperature. The log K_a values for these amines show a large variation in their temperature dependencies, and DMA is a weaker acid than the others.

Conclusion

This study has yielded a complete and precise database for the dissociation quotients of the ethanolammonium ion that is completely compatible with previous data at low temperatures. Equation 4 can now been used to predict the dissociation quotients at conditions relevant to industrial systems.

Literature Cited

(1) Bate, R. G.; Pinching, G. D. Acidic dissociation constant and related thermodynamic quantities for monoethanolammonium ion in water from 0 to 50 °C. *J. Res. Nat. Bur. Stand.* **1951**, *46*, 349–352.
(2) Lotz, J. R.; Block, B. P.; Fernelius, W. C. A thermodynamic study of some coordination compounds of metal ions with amines containing oxygen. *J. Chem. Phys.* **1959**, *63*, 541–544.
(3) Datta, S. P.; Grzybowski, A. K. Acid dissociation contants of the ammonium group in 2-aminoethanol, 2-aminoethyl phosphate, and 2-aminoethyl sulphate. *J. Chem. Soc.* **1962**, 3068–3077.
(4) Levi, D. L.; McEwan, W. S.; Wolfenden, J. H. The thermochemistry of solutions. Part VII. The heats of ionisation of some substituted ammonium ions. *J. Chem. Soc.* **1949**, 761–761.
(5) Jones, F. M., III.; Arnett, E. M. Thermodynamics of ionization and solution of aliphatic amines in water. *Prog. Phys. Org. Chem.* **1974**, *11*, 263–322.
(6) Cobble, J. W.; Turner, P. J. Temperature dependence of acid ionization and steam volatility of dimethylamine and ethanolamine. PWR Advanced all-volatile treatment additives, byproducts and boric acid, EPRI Report TR-100755, July 1992.
(7) Ridley, M. K.; Xiao, C.; Palmer, D. A.; Wesolowski, D. J. Thermodynamic properties of the hydrolysis of morpholine as a function of temperature and ionic strength. *J. Chem. Eng. Data* **2000**, *45*, 502–507.
(8) Bénézeth, P.; Palmer, D. A.; Wesolowski D. J. Potentiometric study of the dissociation quotients of aqueous dimethylammonium ion as a function of temperature and ionic strength. *J. Chem., & Eng. Data* **2001**, *46*, 202–207.
(9) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations,* (Reprint with corrections of the 1976 edition by John Wiley and Sons); Robert E. Krieger Publishing Co., Inc.: Melbourne, FL, 1986; p 489.
(10) Quist, A. S.; Marshall, W. L. Assignment of limiting equivalent conductances for single ions to 400 °C. *J. Phys. Chem.* **1965**, *69*, 2984–2987.
(11) Ho, P. C.; Palmer, D. A. Electrical conductivity measurements of dilute aqueous sodium trifluoromethanesulfonate solutions at temperatures 0–450 °C and pressures up to 250 MPa. *J. Solution Chem.* **1995**, *24*, 753–769.
(12) Mesmer, R. E.; Palmer, D. A., Simonson, J. M. *Ion Association at High Temperatures and Pressures*. In Activity coefficients in Electrolyte Solutions; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; p 491.
(13) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables*; Hemisphere Publishing Corp.; New York, 1984; 320p.
(14) Palmer, D. A.; Drummond S. E. The molal dissociation quotients of water in sodium trifluoromethanesulfonate solutions to high temperatures. *J. Solution Chem.* **1988**, *17*, 153–164.
(15) Hitch, B. F.; Mesmer, R. E. The ionization of aqueous ammonia to 300°C in KCl media. *J. Solution Chem.* **1976**, *5*, 667–680.

Received for review July 24, 2002. Accepted October 7, 2002. Research sponsored by EPRI, Inc., and by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC05-00OR22725, Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. The EPRI project managers were Drs. P. Frattini and K. Fruzzetti, and this work will be published as an EPRI report project No. 1003179.

JE0201424