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Potentiometric Study of the Dissociation Quotients of Aqueous Dimethylammonium Ion As a Function of Temperature and Ionic Strength

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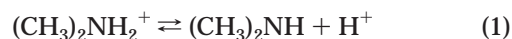
The acid dissociation equilibria involving aqueous dimethylammonium ion in the reaction $(\text{CH}_3)_2\text{NH}_2^+ \rightleftharpoons (\text{CH}_3)_2\text{NH} + \text{H}^+$ were measured potentiometrically with a hydrogen-electrode concentration cell from (0 to 290) °C in sodium trifluoromethanesulfonate (NaTr) solutions at ionic strengths of (0.1, 0.3, and 1) molal. The molal dissociation quotients and selected literature data at infinite dilution were fitted by an empirical equation involving six adjustable parameters involving functions of temperature, solvent density, and ionic strength. This treatment yielded the following thermodynamic quantities at 25 °C and infinite dilution: $\log K_d = -10.77 \pm 0.02$, $\Delta H_d = (50.8 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S_d = (-35.8 \pm 2.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\Delta C_{p,d} = (116 \pm 11) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $\Delta V_d = (-4.3 \pm 2.5) \text{ cm}^3\cdot\text{mol}^{-1}$.

Introduction

Amines, such as dimethylamine (DMA), can be found in a number of ambient environments such as air, water, soil, and foods, as well as in biological fluids and industrial process streams.¹ Amines (dimethylamine, morpholine, ...) have also been used extensively to minimize corrosion by nuclear power utilities in the secondary water-steam cycles. However, the dissociation constants of DMA are poorly known at high temperatures. They have been determined previously in dilute solutions, mainly by potentiometric measurements, at 25 °C by Harned and Robinson,² and from (0 to 50) °C at (0.05, 0.1, 0.15, and 0.20) molal ionic strengths by Everett and Wynne-Jones.³ Conductometric measurements have also been performed by Van der Linde and Robertson,⁴ and Hamann and Strauss.⁵ The thermodynamic data for the ionization of DMA have been reviewed in detail.⁶ In the results reported by Harned and Robinson,² recalculated by Harned and Owen,⁷ the means of extrapolation to infinite dilution was not described and no mention was made of the purity of the amine employed. Thus, the published results are not always directly comparable with one another due to the different extrapolation techniques used. The values obtained by Everett and Wynne-Jones³ appear to be the most reliable data in the literature. More recently, Cobble and Turner⁸ reported estimated values for the acid ionization at infinite dilution and Shvedov and Tremaine⁹ reported the apparent molar volumes and heat capacities of dimethylamine and dimethylammonium chloride at temperatures from (10 to 250) °C. Note that the hydrogen-electrode concentration cell (HECC) used in our experiments is not suitable for measuring the pressure dependence of the hydrolysis reaction, and consequently a comprehensive treatment of the hydrolysis thermodynamics must rely on independent measurements of ΔV .^{5,9}

The present investigation is part of a systematic approach to provide consistent sets of thermodynamic measurements of amines such as morpholinium ion, $(\text{C}_4\text{H}_8\text{N}_2^+)$.

$\text{ONH}_2^+)$.¹⁰ In the present paper, the equilibrium quotients for reaction 1



$$\text{with } Q_d = [(\text{CH}_3)_2\text{NH}][\text{H}^+]/[(\text{CH}_3)_2\text{NH}_2^+] \quad (2)$$

were measured potentiometrically with a hydrogen-electrode concentration cell from (0 to 290) °C in sodium trifluoromethanesulfonate (NaTr) solutions at ionic strengths of (0.1, 0.3, and 1) molal.

Experimental Section

Materials. All solutions were prepared from reagent grade chemicals and distilled, deionized water (resistivity < 0.18 MΩm). 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 dimethylamine stock solution was prepared either from reagent grade material (26% mass per volume, J. T. Baker, lot L23415) or by dissolving the pure gas (Aldrich, DMA anhydrous, 99%, lot 01511TQ) in pure water. In each case the stock solution was titrated to know precisely the concentration of the dimethylamine ($\pm 0.2\%$). Compositions of the solutions used for the experimental runs are given in Table 1.

Apparatus. The HECC and the general experimental procedure have been described in numerous publications.^{10–14} The initial configuration of the cell was as follows:



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 ~10 bar and purged in five cycles with ultrapure hydrogen gas (Matheson, 99.999%). After the purging process, the hy-

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Table 1. Starting Molal Solution Compositions

run no.	test/reference			titrant	
	m_{HTr}^a (mol·kg ⁻¹)	m_{NaTr}^a (mol·kg ⁻¹)	m_{DMA} (mol·kg ⁻¹)	m_{DMA} (mol·kg ⁻¹)	m_{NaTr} (mol·kg ⁻¹)
1–6	0.0100	0.9950	0	0.2050	0.9963
7–9	0.0030	0.2984	0	0.0614	0.3000
10, 11	0.0030	0.2974	0	0.0614	0.3000
12	0.0010	0.1000	0	0.0205	0.0999
13, 14	0.0010 (test)	0.1004 (test)	0.0102 (test)	0	0
	0.0010 (ref)	0.0992 (ref)			
15	0.0010	0.0103	0	0.0201	0.1002 (NaCl)
16, 17	0.0027 (HCl, test)	0.098 (test)	0.0049 (test)	0	0
	0.0010 (ref)	0.0992 (ref)			
18	0.0010	0.0992	0	0.0201	0.0999
19–22	0.0010	0.0990	0	0.0201	0.0999
23	0.0027 (test)	0.2984 (test)	0.0050 (test)	0	0
	0.0030 (ref)	0.2982 (ref)			
24	0.0010	0.0989	0	0.0194	0.0999
25	0.0096 (test)	0.9593 (test)	0.0223 (test)	0	0
	0.0100	0.9950			
26	0.0029 (test)	0.2948 (test)	0.0071 (test)	0	0
	0.0030 (ref)	0.2982 (ref)			
27	0.0009 (test)	0.1004 (test)	0.0022 (test)	0	0
	0.0010 (ref)	0.1002 (ref)			

^a Experimental uncertainty = 0.1%.Table 2. Experimental Results for the Dissociation Quotient of DMAH⁺ at Saturation Vapor Pressure

run no.	t^a (°C)	m_{DMAH^+} (mol·kg ⁻¹)	m_{DMA} (mol·kg ⁻¹)	I (mol·kg ⁻¹)	E^b (mV)	E_{ij} (mV)	pH _m ^c	–log Q_d
17	0.19	0.0031	0.0019	0.101	447.17	0.67	11.26	11.48 ± 0.02
16	24.87	0.0033	0.0017	0.101	441.30	0.48	10.47	10.76 ± 0.02
27	24.85	0.0014	0.0008	0.101	442.17	0.79	10.49	10.73 ± 0.02
14	25.19	0.0117	0.0003	0.101	423.07	0.84	10.16	10.78 ± 0.02
15	25.68	0.0116	0.0003	0.104	417.33	0.83	10.04	10.71 ± 0.02
13	25.68	0.0031	0.0071	0.104	477.05	1.39	11.07	10.71 ± 0.02
17	25.70	0.0033	0.0017	0.101	439.98	0.78	10.43	10.71 ± 0.02
18	25.74	0.0013	0.0006	0.101	435.75	0.90	10.36	10.71 ± 0.02
19	25.99	0.0014	0.0007	0.101	439.16	0.91	10.42	10.72 ± 0.02
19	26.02	0.0012	0.0003	0.100	420.26	0.83	10.09	10.70 ± 0.02
16	49.66	0.0033	0.0017	0.102	433.54	0.87	9.78	10.08 ± 0.02
27	49.76	0.0014	0.0008	0.101	433.12	0.53	9.78	10.03 ± 0.02
13	51.06	0.0031	0.0071	0.104	469.92	1.50	10.33	9.97 ± 0.02
14	51.17	0.0012	0.0003	0.101	413.31	0.92	9.44	10.09 ± 0.02
12	51.45	0.0012	0.0003	0.101	413.10	0.92	9.43	10.10 ± 0.02
19	100.01	0.0013	0.0007	0.101	416.58	1.12	8.64	8.90 ± 0.02
16	101.35	0.0032	0.0018	0.102	415.66	0.96	8.61	8.86 ± 0.02
16	125.14	0.0031	0.0019	0.102	404.37	0.96	8.13	8.34 ± 0.02
16	126.26	0.0031	0.0019	0.102	404.76	0.97	8.13	8.35 ± 0.02
20	150.04	0.0011	0.0005	0.100	372.97	0.46	7.45	7.75 ± 0.02
16	150.65	0.0030	0.0020	0.102	390.86	0.99	7.66	7.83 ± 0.02
21	200.00	0.0010	0.0004	0.101	321.70	0.35	6.43	6.86 ± 0.02
21	250.14	0.0010	0.0004	0.101	281.15	0.38	5.71	6.10 ± 0.02
22	290.18	0.0009	0.0006	0.103	237.98	0.22	5.12	5.35 ± 0.02
24	290.18	0.0009	0.0006	0.103	244.30	0.22	5.18	5.41 ± 0.02
23	–0.02	0.0032	0.0018	0.302	476.32	0.74	11.33	11.56 ± 0.02
26	0.01	0.0037	0.0035	0.299	487.28	0.79	11.53	11.56 ± 0.02
26	25.82	0.0040	0.0032	0.299	482.91	0.89	10.68	10.78 ± 0.02
23	25.93	0.0034	0.0017	0.302	471.83	0.83	10.49	10.80 ± 0.02
23	49.04	0.0035	0.0016	0.302	467.00	0.90	9.84	10.18 ± 0.02
26	49.39	0.0041	0.0031	0.299	478.62	0.97	10.02	10.14 ± 0.02
7	100.07	0.0033	0.0015	0.302	448.55	0.56	8.56	8.92 ± 0.02
26	150.05	0.0035	0.0037	0.299	451.29	1.18	7.91	7.88 ± 0.02
8	200.04	0.0029	0.0016	0.303	390.02	0.35	6.68	6.94 ± 0.02
11	200.07	0.0029	0.0016	0.302	395.75	0.36	6.74	7.01 ± 0.02
9	250.10	0.0026	0.0014	0.304	340.95	0.28	5.80	6.11 ± 0.02
10	290.18	0.0028	0.0012	0.303	301.91	0.22	5.22	5.60 ± 0.02
25	–0.03	0.0111	0.0113	0.970	531.60	0.81	11.83	11.82 ± 0.02
1	25.80	0.0107	0.0092	1.006	526.52	0.81	10.89	10.95 ± 0.02
25	25.82	0.0115	0.0109	0.971	529.54	0.90	10.94	10.97 ± 0.02
25	49.57	0.0116	0.0107	0.971	528.25	0.98	10.27	10.30 ± 0.02
1	49.57	0.0107	0.0091	1.006	524.53	0.88	10.21	10.28 ± 0.02
5	100.02	0.0101	0.0067	1.006	506.24	0.54	8.85	9.02 ± 0.02
1	151.10	0.0097	0.0102	1.007	500.62	1.10	7.96	7.94 ± 0.02
3	200.05	0.0095	0.0055	1.011	445.55	0.35	6.75	6.98 ± 0.02
2	200.11	0.0093	0.0113	1.009	479.27	0.35	7.11	7.03 ± 0.02
2	200.11	0.0084	0.0122	1.008	482.34	0.38	7.14	6.98 ± 0.02
4	250.09	0.0094	0.0055	1.017	398.60	0.28	5.84	6.073 ± 0.02
6	290.11	0.0094	0.0050	1.017	363.19	0.23	5.25	5.52 ± 0.02

^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.

drogen pressure was regulated to approximately 10 bar, whereupon the vessel was sealed and immersed in a thermostated water bath (the bath contained a water/ice mixture for $t = 0$ °C) for experiments at ($0 \leq t \leq 50$) °C or

placed into an aluminum block furnace for $t > 50$ °C.

Two experimental methods were used in this study to measure the dissociation quotients of DMAH⁺. (1) In most of the experiments, the cell initially contained the same

Table 3. Literature Values of the Dimethylammonium Dissociation Quotients

$-\log Q_d$	t (°C)	I (mol·kg ⁻¹)	ref
11.58 ± 0.005	0.0	0.05	3
11.25 ± 0.005	10.0	0.05	3
10.95 ± 0.005	20.0	0.05	3
10.65 ± 0.005	30.0	0.05	3
10.37 ± 0.005	40.0	0.05	3
10.11 ± 0.005	50.0	0.05	3
11.60 ± 0.005	0.0	0.10	3
11.27 ± 0.005	10.0	0.10	3
10.96 ± 0.005	20.0	0.10	3
10.67 ± 0.005	30.0	0.10	3
10.39 ± 0.005	40.0	0.10	3
10.12 ± 0.005	50.0	0.10	3
11.62 ± 0.005	0.0	0.15	3
11.30 ± 0.005	10.0	0.15	3
10.99 ± 0.005	20.0	0.15	3
10.69 ± 0.005	30.0	0.15	3
10.41 ± 0.005	40.0	0.15	3
10.14 ± 0.005	50.0	0.15	3
11.64 ± 0.005	0.0	0.20	3
11.31 ± 0.005	10.0	0.20	3
10.99 ± 0.005	20.0	0.20	3
10.70 ± 0.005	30.0	0.20	3
10.42 ± 0.005	40.0	0.20	3
10.15 ± 0.005	50.0	0.20	3
10.76 ± 0.005	25.0	0.0	5

Table 4. Literature Values of the Apparent Molar Heat Capacities and Volumes of Dimethylammonium Dissociation

$\Delta C_{p,d}$ (J·K ⁻¹ ·mol ⁻¹)	t (°C)	I (mol·kg ⁻¹)	ref
72.7 ± 9	10.0	0.0	9
77.0 ± 9	25.0	0.0	9
66.4 ± 9	40.0	0.0	9
68.1 ± 9	55.0	0.0	9

ΔV_d (cm ³ ·mol ⁻¹)	t (°C)	I (mol·kg ⁻¹)	ref
-4.3 ± 3	25.0	0.0	5
-5.1 ± 3	5.0	0.0	9
-4.4 ± 3	10.0	0.0	9
-2.7 ± 3	25.0	0.0	9
-1.6 ± 3	40.0	0.0	9
-0.9 ± 3	55.0	0.0	9
-2.2 ± 3	125.0	0.0	9
-7.8 ± 3	175.0	0.0	9
-20.8 ± 3	225.0	0.0	9
-32.1 ± 3	250.0	0.0	9

acidic solution in both compartments (see configuration of the cell above), whereas the titrant consisted of dimethylamine and NaTr. NaTr was used as a noncomplexing supporting electrolyte to maintain constant ionic strength.¹⁴ The cell was allowed to equilibrate at temperature (controlled by an aluminum-block furnace), after which the DMA was titrated into the cell at temperature, using a displacement pump. The experiment was terminated either after a stable potential reading was observed or when the potential started to drift back, due to either DMA decomposition or vaporous transport. Note that the decomposition kinetics and limits of stability of DMA are unknown under the conditions of these experiments to our knowledge, so the implication of decomposition is supposition. Thus, this titration method yielded only one dissociation constant per experiment. (2) In some experiments performed at temperatures from (0 to 50) °C (runs # 13, 14, 17, 23, 25, 26, 27, Tables 1 and 2), buffer mixtures of almost equal molal concentrations of DMA and DMAH⁺ were initially equilibrated in the test compartment of the cell with an acidic reference solution at 25 °C in the thermostated bath. Upon attainment of a stable cell potential, the cell was then placed into an ice/water mixture to measure the constant

Table 5. Thermodynamic Quantities for the Dissociation Constants of Dimethylammonium Ion (Reaction 1) in Aqueous Sodium Trifluoromethanesulfonate Media at the Saturation Vapor Pressure^a

t (°C)	$-\log Q_d$	ΔH_d^b (kJ·mol ⁻¹)	ΔS_d^c (J·K ⁻¹ ·mol ⁻¹)	$\Delta C_{p,d}^c$ (J·K ⁻¹ ·mol ⁻¹)	ΔV_d (cm ³ ·mol ⁻¹)
I (mol·kg ⁻¹) = 0.0					
0	11.56 ± 0.02	48.2 ± 0.9	-45 ± 3	88 ± 11	-4 ± 3
25	10.77 ± 0.02	50.8 ± 0.7	-36 ± 3	116 ± 11	-4 ± 3
50	10.06 ± 0.02	53.8 ± 0.6	-26 ± 2	128 ± 13	-5 ± 3
75	9.42 ± 0.02	57.1 ± 0.6	-16 ± 2	137 ± 13	-5 ± 3
100	8.83 ± 0.03	60.6 ± 0.8	-6 ± 3	143 ± 13	-6 ± 3
125	8.28 ± 0.03	64.3 ± 1.0	3 ± 3	147 ± 13	-7 ± 4
150	7.76 ± 0.04	68.0 ± 1.3	12 ± 4	148 ± 15	-8 ± 5
175	7.28 ± 0.05	71.6 ± 1.6	20 ± 4	143 ± 19	-10 ± 6
200	6.83 ± 0.05	75.1 ± 2.0	28 ± 5	130 ± 29	-13 ± 8
225	6.41 ± 0.06	78.1 ± 2.5	34 ± 6	102 ± 48	-18 ± 10
250	6.00 ± 0.07	80.2 ± 3.6	38 ± 8	44 ± 85	-25 ± 14
275	5.63 ± 0.08	80.4 ± 5.9	39 ± 12	-81 ± 161	-36 ± 21
300	5.29 ± 0.10	76.6 ± 11	32 ± 20	-397 ± 350	-59 ± 34
I (mol·kg ⁻¹) = 0.1					
0	11.60 ± 0.02	47.9 ± 0.9	-47 ± 3	90 ± 10	-4 ± 3
25	10.82 ± 0.01	50.6 ± 0.7	-38 ± 2	116 ± 10	-4 ± 3
50	10.11 ± 0.01	53.6 ± 0.6	-28 ± 2	128 ± 12	-4 ± 3
75	9.47 ± 0.02	56.9 ± 0.6	-18 ± 2	137 ± 13	-5 ± 3
100	8.88 ± 0.02	60.4 ± 0.7	-8 ± 2	143 ± 13	-5 ± 3
125	8.33 ± 0.03	64.1 ± 0.9	1 ± 3	148 ± 13	-6 ± 4
150	7.82 ± 0.03	67.8 ± 1.2	11 ± 3	149 ± 14	-8 ± 5
175	7.34 ± 0.04	71.5 ± 1.4	19 ± 4	146 ± 18	-10 ± 6
200	6.89 ± 0.05	75.1 ± 1.7	27 ± 4	134 ± 28	-13 ± 8
225	6.46 ± 0.05	78.2 ± 2.3	33 ± 5	108 ± 47	-17 ± 10
250	6.06 ± 0.06	80.5 ± 3.4	38 ± 7	55 ± 84	-23 ± 14
275	5.69 ± 0.07	81.1 ± 5.7	39 ± 12	-61 ± 160	-34 ± 21
300	5.35 ± 0.09	77.8 ± 11	33 ± 20	-356 ± 346	-55 ± 34
I (mol·kg ⁻¹) = 0.3					
0	11.66 ± 0.02	47.6 ± 0.9	-49 ± 3	94 ± 10	-4 ± 3
25	10.87 ± 0.02	50.3 ± 0.7	-39 ± 2	118 ± 10	-4 ± 3
50	10.17 ± 0.02	53.4 ± 0.6	-29 ± 2	130 ± 12	-4 ± 3
75	9.53 ± 0.02	56.8 ± 0.5	-19 ± 2	139 ± 12	-4 ± 3
100	8.94 ± 0.02	60.2 ± 0.6	-10 ± 2	146 ± 12	-5 ± 3
125	8.40 ± 0.03	64.1 ± 0.8	0.2 ± 2	151 ± 12	-6 ± 4
150	7.89 ± 0.03	67.9 ± 1.2	10 ± 3	154 ± 13	-7 ± 5
175	7.40 ± 0.04	71.8 ± 1.2	18 ± 3	152 ± 17	-8 ± 6
200	6.95 ± 0.04	75.5 ± 1.5	27 ± 4	144 ± 27	-11 ± 8
225	6.52 ± 0.04	78.9 ± 2.0	34 ± 5	123 ± 47	-14 ± 10
250	6.12 ± 0.05	81.7 ± 3.2	39 ± 7	79 ± 85	-20 ± 14
275	5.74 ± 0.06	83.0 ± 5.6	42 ± 11	-19 ± 162	-29 ± 21
300	5.38 ± 0.07	81.0 ± 11	38 ± 19	-271 ± 350	-47 ± 34
I (mol·kg ⁻¹) = 0.5					
0	11.69 ± 0.03	47.4 ± 0.9	-50 ± 3	99 ± 10	-3 ± 3
25	10.91 ± 0.03	50.2 ± 0.7	-41 ± 3	120 ± 10	-3 ± 3
50	10.21 ± 0.03	53.4 ± 0.6	-30 ± 2	132 ± 11	-3 ± 3
75	9.57 ± 0.03	56.8 ± 0.5	-20 ± 2	142 ± 12	-3 ± 3
100	8.98 ± 0.03	60.4 ± 0.6	-10 ± 2	150 ± 12	-4 ± 3
125	8.44 ± 0.03	64.3 ± 0.8	-0.1 ± 2	156 ± 12	-5 ± 4
150	7.92 ± 0.03	68.2 ± 1.0	10 ± 3	160 ± 13	-6 ± 5
175	7.44 ± 0.03	72.2 ± 1.2	19 ± 3	160 ± 18	-7 ± 6
200	6.98 ± 0.04	76.2 ± 1.6	27 ± 4	155 ± 29	-9 ± 8
225	6.55 ± 0.04	80.0 ± 2.0	35 ± 5	140 ± 50	-12 ± 11
250	6.14 ± 0.05	83.2 ± 3.5	42 ± 7	104 ± 89	-17 ± 15
275	5.75 ± 0.06	85.3 ± 6.0	46 ± 12	24 ± 168	-24 ± 22
300	5.39 ± 0.07	84.6 ± 11	38 ± 19	-271 ± 350	-47 ± 34
I (mol·kg ⁻¹) = 1.0					
0	11.75 ± 0.04	47.0 ± 0.9	-53 ± 3	112 ± 16	-2 ± 3
25	10.97 ± 0.04	50.1 ± 0.7	-42 ± 3	128 ± 11	-2 ± 3
50	10.27 ± 0.04	53.4 ± 0.6	-31 ± 2	140 ± 13	-2 ± 3
75	9.63 ± 0.04	57.1 ± 0.7	-21 ± 2	151 ± 13	-2 ± 3
100	9.04 ± 0.04	60.9 ± 0.8	-10 ± 2	160 ± 14	-2 ± 4
125	8.49 ± 0.04	65.1 ± 1.1	0.9 ± 3	169 ± 16	-2 ± 5
150	7.97 ± 0.04	69.4 ± 1.5	11 ± 4	177 ± 20	-3 ± 6
175	7.47 ± 0.05	73.9 ± 2.0	22 ± 5	182 ± 26	-4 ± 7
200	7.00 ± 0.05	78.5 ± 2.6	32 ± 6	185 ± 40	-5 ± 9
225	6.56 ± 0.06	83.1 ± 4.0	41 ± 8	183 ± 64	-6 ± 12
250	6.13 ± 0.08	87.6 ± 5.4	50 ± 11	170 ± 108	-9 ± 17
275	5.72 ± 0.10	91.7 ± 9	58 ± 17	134 ± 198	-13 ± 24
300	5.33 ± 0.13	94.5 ± 15	63 ± 27	32 ± 420	-20 ± 40

^a Uncertainties represent three times the standard deviation.^{b,c} These thermodynamic quantities were not corrected to constant pressure in view of the small ΔV_d of reaction and the uncertainty in this value at high temperatures.

at 0 °C. After equilibrium was obtained, the temperature was raised to 50 °C and another reading was taken after the system had reequilibrated. One additional experiment

was also performed the same way as (2) starting at 25 °C and raising the temperature to (50, 100, 125, and 150) °C (run #16).

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:

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

where $[\text{H}^+]_t$ and $[\text{H}^+]_r$ 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,¹⁵ which involves the molar ionic conductivities (λ°) of the individual ions. The values for Na^+ , H^+ , and OH^- ions were taken from Quist and Marshall;¹⁶ that for Tr^- was taken from Ho and Palmer.¹⁷ It was assumed that $\lambda^\circ(\text{DMAH}^+) = \lambda^\circ(\text{Na}^+)$. 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%.¹⁸

The potentiometric results obtained in this study were treated with existing "in-house" computer programs, which calculate the liquid junction potentials and other correction factors to yield the dissociation quotients reported in Table 2. A weighted fit of these values was carried out, including 49 $\log Q_d$ values from this study (Table 2), 24 $\log Q_d$ values, (0 to 50) °C and 0.05 to 0.2 ionic strength, from Everett and Wynne-Jones³ as reported in Table 3, a $\log K_d$ and ΔV_d value (25 °C, infinite dilution) from Hamann and Strauss⁵ (Tables 3 and 4, respectively), and 4 $\Delta C_{p,d}$ values (10 to 55 °C, infinite dilution) and 9 ΔV_d values (5 to 250 °C, infinite dilution) from Shvedov and Tremaine⁹ (Table 4). Table 2 shows that some experiments were performed several times at the same conditions (especially at low temperatures), with excellent agreement and reproducibility among the values obtained.

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

$$\log Q_d = p_1 + p_2/(TK) + p_3(T/K) + (p_4 + p_5 I/(\text{mol}\cdot\text{kg}^{-1}) \ln(\rho_w/g\cdot\text{cm}^{-3}) + p_6 F(I)(TK) \quad (4)$$

where $F(I) = 1 - e^{-2\sqrt{I}(1 + 2\sqrt{I})}$, I is the stoichiometric molal ionic strength, T is the absolute temperature, and ρ_w is the density of pure water taken from Haar et al.¹⁹ The values of the parameters are $p_1 = -9.4416$, $p_2 = -1542.3$, $p_3 = 0.012\,918$, $p_4 = 1.6621$, $p_5 = -1.0848$, and $p_6 = -0.001\,179\,5$. The thermodynamic parameters for reaction 1 at 25 °C and infinite dilution are $\log K_d = -10.77 \pm 0.02$, $\Delta H_d = (50.8 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S_d = (-35.8 \pm 2.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\Delta C_{p,d} = (116 \pm 11) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $\Delta V_d = (-4.3 \pm 2.5) \text{ cm}^3\cdot\text{mol}^{-1}$. The smoothed values calculated as a function of temperature are reported in Table 5 at (0, 0.1, 0.3, 0.5, and 1.0) molal ionic strengths.

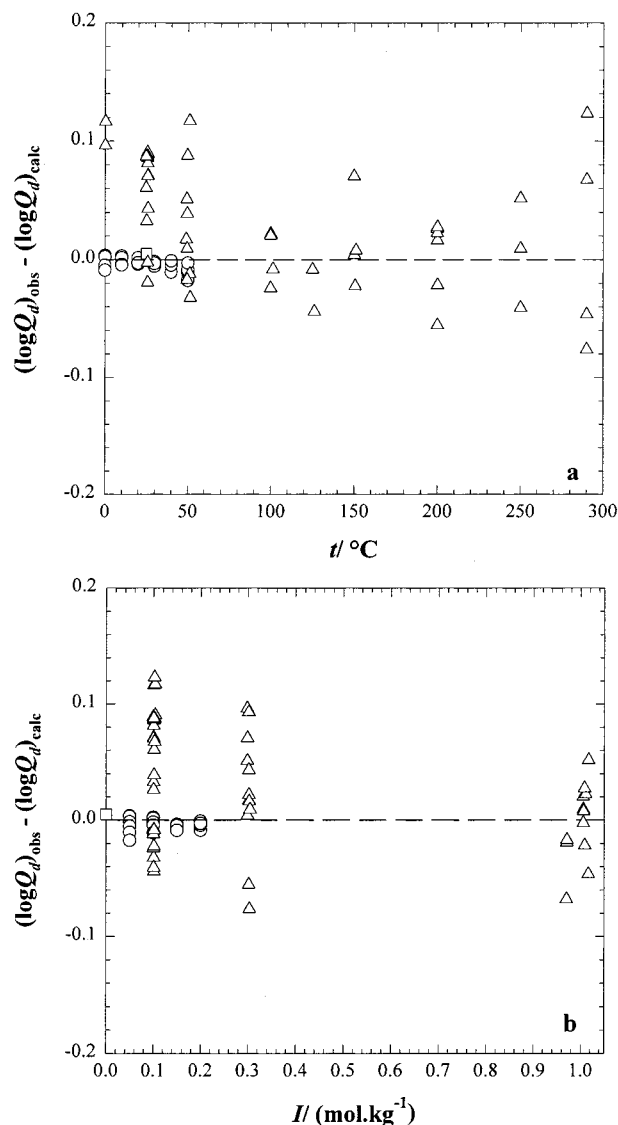
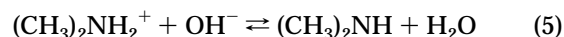


Figure 1. Deviation plot of experimental values of $\log Q_d$ as a function of temperature (a) and ionic strength (b). Symbols: (○) Everett and Wynne-Jones;³ (□) Hamann and Strauss;⁵ (△) this study.

The deviations between eq 4 and the experimental values of $\log Q_d$, as a function of temperature and ionic strength are reported in parts a and b, respectively, of Figure 1 and those for the values of ΔV_d and $\Delta C_{p,d}$ are reported in Figure 2 as a function of temperature. As can be seen in Figure 1, the deviations are random for the dissociation quotient with respect to both temperature and ionic strength and the maximum deviation for $\log Q_d$ is less than 0.14 log units. Note that this deviation is much larger than normally obtained from potentiometry but reflects the difficulties in handling volatile and thermally unstable DMA. Whereas the deviations in ΔV_d from Shvedov and Tremaine⁹ are random (Figure 2), the values of $\Delta C_{p,d}$ from these authors show a systematic diverging trend that may indicate a problem with these measurements.

The previous literature data were reported in terms of the corresponding base hydrolysis equilibrium, namely:



The equilibrium constants for reactions 1 and 5 are related by the dissociation constant for water (Q_w). To convert the

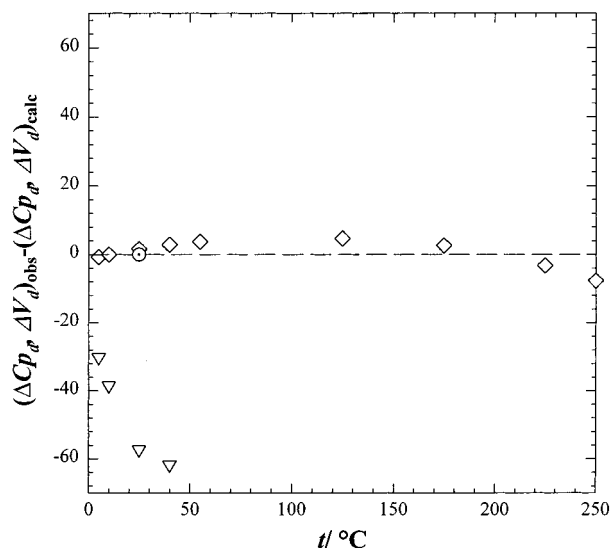


Figure 2. Deviation plot of $\Delta C_{p,d}$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and ΔV_d ($\text{cm}^3\cdot\text{mol}^{-1}$) as a function of temperature. Symbols: (∇) ($\Delta C_{p,d}$) and (\diamond) (ΔV_d) Shvedov and Tremaine;⁹ (\odot) ($\Delta C_{p,d}$) Hamann and Strauss.⁵

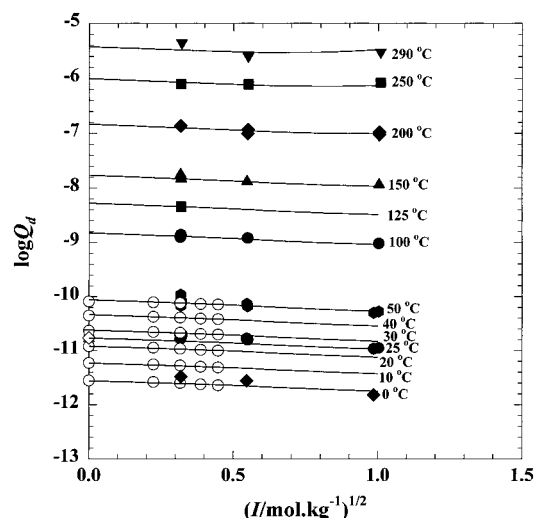


Figure 3. $\log Q_d$ values as a function of the square root of ionic strength. The filled symbols and the solid lines represent the experimental values and the fit from this study. Symbols: (\odot) Everett and Wynne-Jones;³ (\square) Harned and Robinson;² (\triangle) Jones and Arnett;⁶ (\diamond) Hamann and Strauss.⁵

literature values for reaction 5 to the constant for reaction 1, Q_w values were taken from Busey and Mesmer,²⁰ who measured Q_w in NaCl media.

The results of the present study are compared with literature values in Figure 3 as a function of the square root of ionic strength and in Figure 4 as a function of the reciprocal temperature. These results are clearly in good agreement with the low-temperature data ($\leq 50^\circ\text{C}$) from previous studies. Also it can be seen from these figures that the temperature dependence of $\log Q_d$ is almost linear with reciprocal temperature to 300°C and also nearly independent of ionic strength. These advantages support the approach taken here of fitting the data for reaction 1, which is an isocoulombic reaction, rather than for reaction 5. Despite the good agreement with the existing low-temperature data and the recent calorimetric measurements, this study gives significantly different $\log Q_d$ values at the high temperature than those estimated previously by Cobble and Turner.⁸

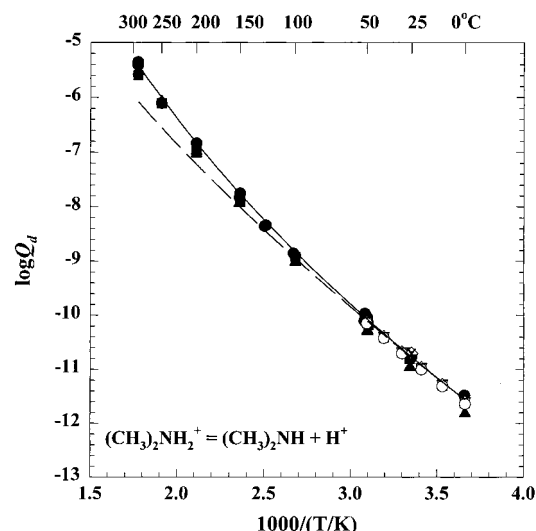


Figure 4. $\log Q_d$ values as a function of reciprocal absolute temperature. The solid curve represents the fit from this study at infinite dilution (eq 4). Symbols: (\bullet , \blacksquare , \blacktriangle) 0.1, 0.3, and 1.0 m NaTr, respectively, from this study; (\diamond) Harned and Robinson;² (+) Jones and Arnett;⁶ (\times) Hamann and Strauss;⁵ (∇ , \triangle , \square , \odot) Everett and Wynne-Jones³ (0.05, 0.1, 0.15, 0.2 m ionic strength, respectively); (dashed line) estimation of Cobble and Turner⁸ (at infinite dilution).

Conclusion

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

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