Thermodynamic Properties of the Ionization of Morpholine as a Function of Temperature and Ionic Strength

Moira K. Ridley*,[†]

Texas Tech University, Department of Geosciences, P.O. Box 41053, Lubbock, Texas 79409-1053

Caibin Xiao,[‡] Donald A. Palmer,[§] and David J. Wesolowski[||]

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

A hydrogen−electrode concentration cell was used to monitor pH in a study of morpholine ionization in aqueous solutions to temperatures of 290 °C and to ionic strengths of 1 *m*, maintained with either sodium trifluoromethanesulfonate or sodium chloride. The resulting hydrolysis quotients were combined with values from two previous potentiometric investigations of this reaction, as well as existing heat capacity and apparent molar volume data, to provide a global fitting equation. The computed thermodynamic parameters for the acid dissociation of the morpholinium ion at 25 °C and infinite dilution are $\log K = (-8.491 \pm 0.003)$; $\Delta H = (39 \pm 1)\ \mathrm{kJ \cdot mol^{-1}}$; $\Delta S = (-31 \pm 1)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$; $\Delta C_p = (40 \pm 7)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$; and $\Delta V = (3 \pm 1)\ \mathrm{cm^3 \cdot mol^{-1}}$. At low ionic strengths, including values at infinite dilution, the log *Q* data were found to be near linear with respect to the reciprocal temperature in Kelvin over the measured temperature range of 0 °C to 300 °C.

Introduction

Morpholine, $O(C_2H_4)_2(NH)$, is widely used in many industrial applications as a pH buffering agent and corrosion inhibitor; in particular, it is utilized at elevated temperatures in nuclear power plants.[1−3] Morpholine is a highly soluble, volatile, weak base that can maintain a mildly basic environment and has sufficient thermal stability to survive to a large extent at high temperatures.[1] In this context, the behavior of morpholine at elevated temperatures has been of significant interest.[1,4−6]

Three major independent potentiometric studies have been performed in the past by Hetzer et al.,[7] Mesmer and Hitch,[5] and Czerminiski et al.[8] The first study utilized platinum/hydrogen and silver/silver chloride electrodes in cells without liquid junctions (i.e, so-called Harned cells) and extended from (0 to 50) °C at 5 K intervals in very dilute solutions. The investigation by Mesmer and Hitch[5] involved measurements from (50 to 294) °C in 0.081 *m* KCl using a flow-through hydrogen-electrode concentration cell. Czerminiski et al.[8] also employed Harned cells in the range (5 to 40) °C in synthetic seawater containing NaCl, $MgCl_2$, Na_2SO_4, $CaCl_2$, and KCl in amounts corresponding to ca. 10, 20, 30, 35, and 40 parts per 1000 (equivalent to 0.2 to 0.8 *m* ionic strength). Tremaine et al.[6] recently reported the apparent molar volumes and heat capacities of morpholine and morpholinium chloride from (10 to 300) °C and (10 to 55) °C, respectively. Excellent agreement for the standard partial molar heat capacity and standard partial molar volume properties for the ionization of morpholine was found between the study of Tremaine et al.[6] and the values calculated from the potentiometric data of Mesmer and Hitch.[5]

The purpose of this investigation was to provide consistent hydrolysis quotients for the ionization of the morpholinium ion to temperatures of 300 °C and to ionic strengths of 1 *m*. The ionization of the morpholinium ion can be represented by

$$C_4H_8ONH_2^+ \leftrightarrows C_4H_8ONH + H^+ \tag{1}$$

The stoichiometric equilibrium quotient for this reaction is

$$Q = \frac{[C_4H_8ONH][H^+]}{[C_4H_8ONH_2^+]} \tag{2}$$

Equation 1 contains a single positive charge on each side of the equilibrium, which is commonly referred to as an isocoulombic reaction[9] and as such is expected to exhibit minimal ionic strength effects and only small changes in heat capacities.

Experimental Section

Materials. All experimental solutions were prepared from reagent-grade chemicals and distilled, deionized water. The general procedures followed in preparing all solutions have been described previously.[10−12] The morpholine stock solution was prepared from redistilled 99.5% reagent (Aldrich, lot 03010 JR) and was purified further by distillation at (55 ± 0.2) °C. The exact morpholine content was quantified by acidimetric titration against standardized HCl stock solution. The stoichiometric molal compositions of the solutions used in each experiment are listed in Tables 1 and 2.

[†] Telephone: 806-742-0627. Fax: 806-742-0100. E-mail: Moira.Ridley@ttu.edu.
[‡] Telephone: 865-576-2749. Fax: 865-574-4961. E-mail: xiaoc@ornl.gov.
[§] Telephone: 865-576-5209. Fax: 865-574-4961. E-mail: ddp@ornl.gov.
[||] Telephone: 865-574-6903. Fax: 865-574-4961. E-mail: dqw@ornl.gov.

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Table 1. A Summary of Starting Molal Solution Compositions for Measurements in NaTr Media

reference		test			titrant	
$10^3\ m_{\mathrm{HTr}}$ / mol·kg^{-1}	m_{NaTr} / mol·kg^{-1}	$10^3 m_{\mathrm{Morph}}$ / mol·kg^{-1}	$10^3\ m_{\mathrm{HTr}}$ / mol·kg^{-1}	m_{NaTr} / mol·kg^{-1}	m_{Morph} / mol·kg^{-1}	m_{NaTr} / mol·kg^{-1}
20.00	0.9802	39.99	20.00	0.98001		
1.000	0.04901	2.000	1.000	0.04901		
2.001	0.09804	4.002	2.001	0.09806		
6.000	0.2940	12.00	6.000	0.29401		
2.000	0.09803	3.999	2.000	0.09800		
0.9999	0.04900	1.999	0.9999	0.04899		
0.9998	0.04900	1.999	0.9999	0.04899		
0.9998	0.04900		0.9998	0.04900	0.02000	0.05040
0.9915	0.04892		0.9915	0.04892	0.01996	0.04990
1.040	0.04900		1.040	0.04900	0.01996	0.04990
1.003	0.04851		1.003	0.04851	0.04996	0.05036
0.9905	0.04844		0.9905	0.04844	0.04996	0.05036
0.9964	0.04890		0.9964	0.04890	0.04996	0.05036

Table 2. A Summary of Starting Molal Solution Compositions for Measurements in NaCl Media

reference		test				titrant		
$10^3\ m_{\mathrm{NaOH}}$ / mol·kg^{-1}	m_{NaCl} / mol·kg^{-1}	$10^3\ m_{\mathrm{Morph}}$ / mol·kg^{-1}	$10^3\ m_{\mathrm{HCl}}$ / mol·kg^{-1}	$10^3\ m_{\mathrm{NaOH}}$ / mol·kg^{-1}	m_{NaCl} / mol·kg^{-1}	m_{Morph} / mol·kg^{-1}	m_{NaCl} / mol·kg^{-1}	m_{HCl} / mol·kg^{-1}
1.010	0.04907			1.010	0.04907	0.03710	0.01118	0.03701
1.008	0.09895	4.017	3.011		0.09700			
1.008	0.09895			1.008	0.09895	0.04005	0.06988	0.03023

Apparatus and Procedures. All experiments (40 individual equilibrium constants were measured) performed in this study utilized a stirred hydrogen–electrode concentration cell, which has been described in detail previously.[11–16] In addition, duplicate measurements at 25 °C (0.05 *m* sodium trifluoromethanesulfonate, NaTr) were performed using a commercial Ross glass combination electrode.

Titrations to determine the ionization quotients for reaction 1 were performed at ionic strengths of (0.05, 0.1, 0.3, and 1.0) *m* in (NaTr) media, over a temperature range of (25 to 290) °C at ca. 50 K intervals. The titrations carried out at and above 200 °C exhibited drifting cell potentials, which were ascribed to the decomposition of morpholine.[1] However, there was concern that this effect could partially result from the decomposition of NaTr. Independent measurements confirmed that the trifluoromethanesulfonate anion (Tr^-) decomposes in relatively strong basic conditions at elevated temperatures, but even after 3 days at 250 °C, no observable (in terms of pH) decomposition was found. The decomposition rate of trifluoromethanesulfonate at high acid and base concentrations, which were much higher than those used in the present study, was investigated by Fabes and Swaddle,[17] and was found to be first order with respect to acid and base concentrations. An additional series of morpholine hydrolysis measurements were performed in 0.1 *m* NaCl media, to eliminate any possible effects caused by the decomposition of the supporting electrolyte.

Two cell configurations were employed in this investigation. The initial cell configuration was as follows:

$$\underset{\text{test}}{\mathrm{Pt, H_2 \mid C_4H_8ONH, C_4H_8ONH_2^+, NaTr}} \parallel \underset{\text{reference}}{\mathrm{HTr, NaTr \mid H_2, Pt}}$$

In this case, the test solutions consisted of near equal molal concentrations of morpholine and morpholinium and were equilibrated with acidic reference solutions at either (25 or 50) °C. Upon attainment of a stable cell potential reading, the temperature of the furnace was raised and an additional potential measurement taken once the system had reequilibrated. Experimental evidence indicated that the morpholine decomposed slowly at and above 250 °C, within the time required to equilibrate the cell thermally. This raised concern that some degree of decomposition may occur at lower temperatures. Therefore, in all remaining experiments the initial cell configuration was simply:

$$\underset{\text{test}}{\mathrm{Pt, H_2 \mid HTr, NaTr}} \parallel \underset{\text{reference}}{\mathrm{HTr, NaTr \mid H_2, Pt}}$$

These experiments proceeded by the equilibration of identical acidic solutions in the test and reference compartments, whereupon titrant containing morpholine at the same ionic strength was metered into the cell (Table 1). The experiments were terminated after either a stable potential reading was observed, or in the case of experiments at 250 °C and above, after a constant drift rate of the potential was recorded. This method yielded a single hydrolysis constant per titration. Although this approach was more tedious, it ensured minimum decomposition and vaporous transport of morpholine during the course of an equilibration.

Two series of experiments were performed in NaCl media and involved equilibration of test solutions comprising a 3:1 *m* ratio of morpholinium to morpholine in contact with basic reference solutions. This cell configuration yielded hydrolysis constants at three to four temperatures per experiment. In the second series, a morpholinium/morpholine (3:1 *m* ratio) titrant was added to basic test solutions, producing a single hydrolysis constant per titration. Use of a basic reference solution is preferable in that the effects of vaporous carryover of morpholine on the pH of the reference solution are minimal.

In the experiments using a commercial Ross glass combination electrode, the electrode was first equilibrated at 25 °C and then calibrated on the molality scale, such that acidity is defined in terms of the negative logarithm of hydrogen ion molality, pH_m.[18] The electrode was calibrated with solutions containing 0.001 *m* trifluoromethanesulfonic acid (HTr) and 0.001 *m* NaOH in NaTr media at 0.05 *m* ionic strength. A calibration curve, incorporating a

Table 3. Experimental Results for the Ionization of Morpholium

t	I	E	E_{LJ}				
°C	mol·kg^{-1}	mV	mV	pH	$\bar{n}$	log Q	σ^a
NaTr Media							
25.00	0.0500	325.90	1.616	8.536	0.4553	−8.459	0.02
25.33	0.0499	325.52	1.606	8.527	0.4565	−8.452	0.02
50.73	0.0500	315.73	1.445	7.936	0.4932	−7.924	0.02
50.65	0.0499	312.92	1.438	7.897	0.5108	−7.915	0.02
51.08	0.0500	314.76	1.501	7.899	0.5058	−7.909	0.02
100.10	0.0500	274.91	1.186	6.711	0.6674	−7.013	0.02
102.16	0.0500	291.44	1.676	6.936	0.5041	−6.943	0.02
150.12	0.0501	275.62	1.890	6.303	0.5038	−6.310	0.02
200.11	0.0503	252.01	2.107	5.704	0.5016	−5.707	0.02
250.08	0.0505	227.84	2.316	5.212	0.4983	−5.209	0.03
250.10	0.0503	225.56	0.676	5.177	0.4799	−5.142	0.03
250.19	0.0498	251.26	0.683	5.423	0.3605	−5.174	0.03
100.19	0.1001	316.22	1.577	6.989	0.5025	−6.993	0.03
150.08	0.1003	302.14	1.787	6.317	0.5024	−6.321	0.03
200.08	0.1006	280.24	1.995	5.702	0.5011	−5.704	0.03
50.09	0.1000	329.90	1.449	7.865	0.5018	−7.868	0.03
100.08	0.1000	316.65	1.675	6.997	0.5026	−7.002	0.03
150.39	0.1002	298.98	1.900	6.278	0.5022	−6.282	0.03
50.21	0.3000	367.84	1.447	7.978	0.5010	−7.979	0.03
100.09	0.3001	359.34	1.671	7.097	0.5014	−7.099	0.03
150.12	0.3007	340.76	1.894	6.301	0.5011	−6.303	0.03
200.05	0.3018	329.39	2.117	5.750	0.5008	−5.751	0.03
50.36	1.000	410.69	1.446	8.119	0.5005	−8.120	0.03
100.15	1.000	403.06	1.668	7.163	0.5006	−7.164	0.03
150.19	1.003	395.45	1.892	6.428	0.5006	−6.429	0.03
200.23	1.007	378.34	2.115	5.747	0.5004	−5.747	0.03
253.29	1.015	371.96	2.351	5.276	0.5002	−5.277	0.05
NaCl Media							
25.73	0.1000	−161.41	−0.246	8.027	0.7499	−8.504	0.02
25.52	0.0990	−121.55	−0.297	8.704	0.3768	−8.485	0.02
50.29	0.1000	−164.26	−0.244	7.474	0.7501	−7.951	0.02
50.05	0.1000	−161.88	−0.265	7.514	0.7502	−7.992	0.02
50.01	0.0990	−119.10	−0.320	8.181	0.3788	−7.966	0.02
50.12	0.0990	−116.00	−0.294	8.227	0.3509	−7.960	0.02
99.99	0.1000	−178.85	−0.282	6.584	0.7503	−7.062	0.02
99.96	0.0991	−126.25	−0.367	7.293	0.3812	−7.082	0.02
150.18	0.0992	−136.15	−0.243	6.706	0.2941	−6.326	0.02
150.03	0.0992	−146.84	−0.244	6.579	0.3912	−6.387	0.02
199.96	0.0993	−155.18	−0.228	6.269	0.2475	−5.786	0.02
290.06	0.0491	−347.20	−0.386	4.690	0.6318	−4.925	0.06
Glass Cell							
25.00	0.05					−8.510	0.02

[a] The error estimates, σ, associated with log Q result from the nonlinear least-squares fitting routine for each titration.

liquid junction correction,[19] was then established. Titrations were performed by the addition of a morpholine titrant into an acid test solution.

Results

The measured cell potentials, E, at each experimental condition are listed in Table 3 together with other relevant details. The molal concentration of hydrogen ions in the test solution [H^+_{test}] can be related to the measured cell potentials by the Nernst expression:

$$-\log [H^+_{test}] = \frac{2.303F}{RT}(E + E_{LJ}) - \log [H^+_{ref}] \qquad (3)$$

where R is the gas constant, F is the Faraday constant, T is the temperature in Kelvin, [H^+_{ref}] is the known molal concentration of hydrogen ions in the reference compartment, and E_{LJ} is the calculated liquid junction potential. Implicit in these calculations is the assumption that the activity coefficient of the H^+ ion is identical in the test and reference compartments because the ionic strengths are similar and the supporting electrolyte is in excess of the other ions.

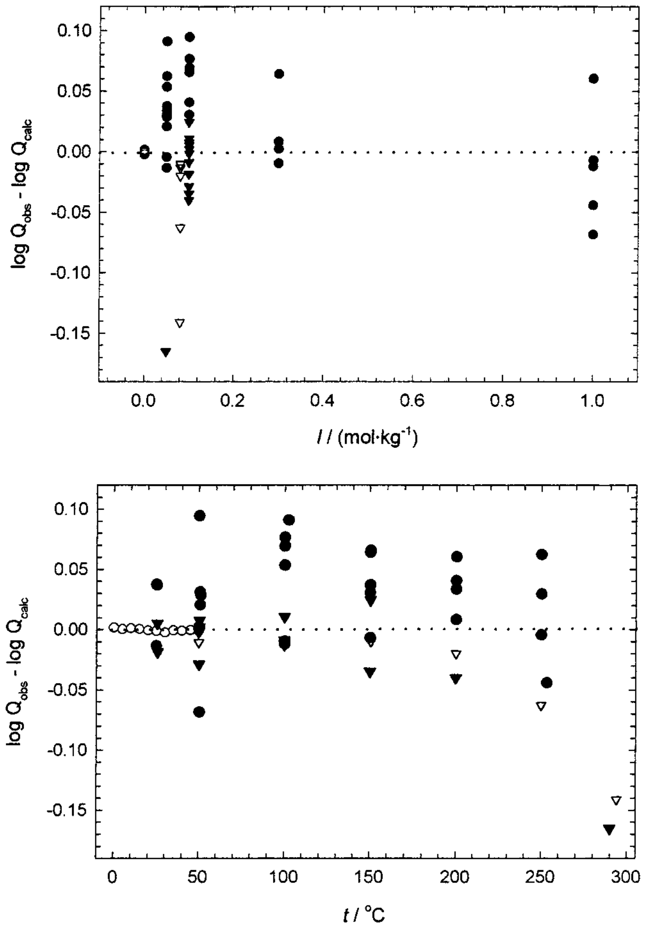

Figure 1. Deviation plots of the experimentally determined log Q values from those calculated from eq 6 plotted vs ionic strength and temperature. The symbols represent the following: ● and ▼, results of this study in NaTr and NaCl media, respectively; ○, Hetzler et al.;[7] and ▽, Mesmer and Hitch.[5]

The liquid junction potential, E_{LJ}, (Table 3) is based on the Henderson equation (eq 2−12 in Baes and Mesmer[19]), which requires the limiting equivalent conductance data for the individual ions. Conductance data for H^+, OH^-, Na^+, and Cl^- were obtained from Quist and Marshall,[20] whereas those for Tr^- were obtained from Ho and Palmer.[21] Limiting equivalent conductance values for the monovalent, positively charge morpholonium ion were assumed equivalent to values for Na^+. For all experiments, the calculated liquid junction potentials were small, and contributed an uncertainty of <0.005 in the pH of the test solutions.

The degree of protonation ($\bar{n}$, Table 3) was calculated from

$$\bar{n} = \frac{m_{HTr} - m_{NaOH} - [H^+] + [OH^-]}{m_{C_4H_9NO}} \qquad (4)$$

where m_X represents the stoichiometric molality of the designated species, and the terms in brackets represent the calculated molality of hydrogen ions and the corresponding concentration of hydroxide ions contributed by the dissociation of water.[10,22]

Discussion

The ORGLS[23] general least-squares routine was used to perform a weighted regression of the data; the fitting process is iterative and has been described previously.[12,16,24,25] This weighted fit included 11 log K values ((0−50) °C,

Table 4. Literature Data Included in the Fitting Routine

log Q	ΔC_p	ΔV	t	I	reference
	J·K^{-1}·mol^{-1}	cm^3·mol^{-1}	°C	mol·kg^{-1}	
−9.108 ± 0.002			0.0	0.0	Hetzler et al.[7]
−8.978 ± 0.002			5.0	0.0	
−8.850 ± 0.002			10.0	0.0	
−8.727 ± 0.002			15.0	0.0	
−8.608 ± 0.002			20.0	0.0	
−8.492 ± 0.002			25.0	0.0	
−8.380 ± 0.002			30.0	0.0	
−8.268 ± 0.002			35.0	0.0	
−8.161 ± 0.002			40.0	0.0	
−8.056 ± 0.002			45.0	0.0	
−7.955 ± 0.002			50.0	0.0	
−7.973 ± 0.02			50.0	0.081	Mesmer and Hitch[5]
−7.084 ± 0.02			100.0	0.081	
−6.356 ± 0.02			150.4	0.081	
−5.764 ± 0.02			200.0	0.081	
−5.270 ± 0.02			250.0	0.081	
−4.902 ± 0.05			294.0	0.081	
	29.60 ± 6.3		10.0	0.0	Tremaine et al.[6]
	41.23 ± 6.3		25.0	0.0	
	44.55 ± 6.3		40.0	0.0	
	43.48 ± 6.3		55.0	0.0	
		6.08 ± 4.0	10.0	0.0	
		5.44 ± 4.0	25.0	0.0	
		6.28 ± 4.0	40.0	0.0	
		7.65 ± 4.0	55.0	0.0	
		9.74 ± 4.0	100.0	0.0	
		10.23 ± 4.0	150.0	0.0	
		15.67 ± 4.0	200.0	0.0	
		28.23 ± 4.0	250.0	0.0	
		38.62 ± 4.0	300.0	0.0	

infinite dilution) from Hetzer et al.,[7] six log Q values ((50−294) °C, 0.081 m ionic strength in KCl media) from Mesmer and Hitch,[5] four ΔC_p values ((10−55) °C, infinite dilution), and nine ΔV values ((10−300) °C, infinite dilution) from Tremaine et al.[6] The data of Mesmer and Hitch[5] were reported in terms of the base hydrolysis equilibrium, namely

$$C_4H_8ONH_2^+ + OH^- \leftrightarrows C_4H_8ONH + H_2O \quad (5)$$

The equilibrium quotients for this reaction and for the reaction represented in eq 1 are related by the dissociation constants for water (Q_w). Therefore, the data of Mesmer and Hitch[5] were recast in the form of eq 1 using Q_w values from Busey and Mesmer.[22] The Q_w of Busey and Mesmer[22] were measured in NaCl media. However, at 0.081 m ionic strength the differences between NaCl and KCl media are trivial.

All data included in the final fitting procedure are summarized in Table 4. The following equation, which is a function of temperature, T, and ionic strength, I, gave the "best fit" [15,26] to the data with the minimum number of adjustable parameters:

$$\log Q = p_1 + p_2/(T/\mathrm{K}) + p_3 \ln(T/\mathrm{K}) + p_4 \ln(\rho_w) + p_5 I/T(\mathrm{mol}\cdot(\mathrm{kg}\cdot\mathrm{K})^{-1}) \quad (6)$$

The density of pure water, ρ_w, was taken from IAPWS 1995 scientific formulation for water, tabulated by Harvey.[27] The values determined for the five parameters are $p_1 = -7.9813$, $p_2 = -1738.8$, $p_3 = 0.93352$, $p_4 = -1.1546$, and $p_5 = -33.917$. The adequacy of this overall fit was determined by the agreement factor, which is the ratio of the observed deviation over the experimental uncertainty (σ in Table 3) is 1.5818. Moreover, the average deviation of the log Q values show no systematic trends when plotted against temperature and ionic strength (Figure 1). The data of Mesmer and Hitch,[5] however, do show a slight systematic trend with respect to temperature. The deviation of data at 290 °C from this study and Mesmer and Hitch,[5] is significantly larger than at all other temperatures.

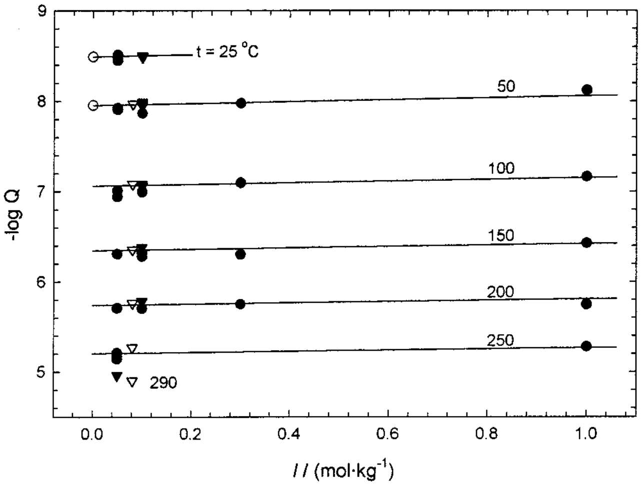

Figure 2. log Q values are shown as a function of ionic strength. The isothermal curves were computed from eq 6. The symbols represent the following: ● and ▼, results of this study in NaTr and NaCl media, respectively; ○, Hetzler et al.;[7] and ▽, Mesmer and Hitch.[5]

Isothermal curves generated from eq 6 are shown in Figure 2. These modeled curves provide an excellent fit to measured ionization quotients from the present study (Table 3), and with the data of Hetzer et al.[7] and Mesmer and Hitch.[5] In addition, Figure 2 clearly illustrates the isocoulombic nature of the morpholine ionization reaction (eq 1) in minimizing ionic strength and specific ion effects. Equilibrium quotients generated from eq 6, at selected temperatures and ionic strengths, are presented in Table 5.

Table 5. Summary of Equilibrium Quotients for the Ionization of Morpholine

t	log Q			
°C	I/(mol·kg^{-1}) = 0.0	I/(mol·kg^{-1}) = 0.1	I/(mol·kg^{-1}) = 0.5	I/(mol·kg^{-1}) = 1.0
0	−9.110 ± 0.006	−9.122 ± 0.011	−9.172 ± 0.049	−9.234 ± 0.096
25	−8.491 ± 0.003	−8.502 ± 0.009	−8.548 ± 0.044	−8.605 ± 0.088
50	−7.954 ± 0.005	−7.965 ± 0.009	−8.007 ± 0.040	−8.059 ± 0.080
100	−7.064 ± 0.010	−7.073 ± 0.010	−7.109 ± 0.033	−7.154 ± 0.068
150	−6.345 ± 0.017	−6.353 ± 0.016	−6.385 ± 0.030	−6.425 ± 0.058
200	−5.738 ± 0.026	−5.746 ± 0.025	−5.774 ± 0.031	−5.810 ± 0.053
250	−5.202 ± 0.038	−5.209 ± 0.037	−5.235 ± 0.039	−5.267 ± 0.053
300	−4.694 ± 0.060	−4.700 ± 0.059	−4.724 ± 0.059	−4.754 ± 0.067

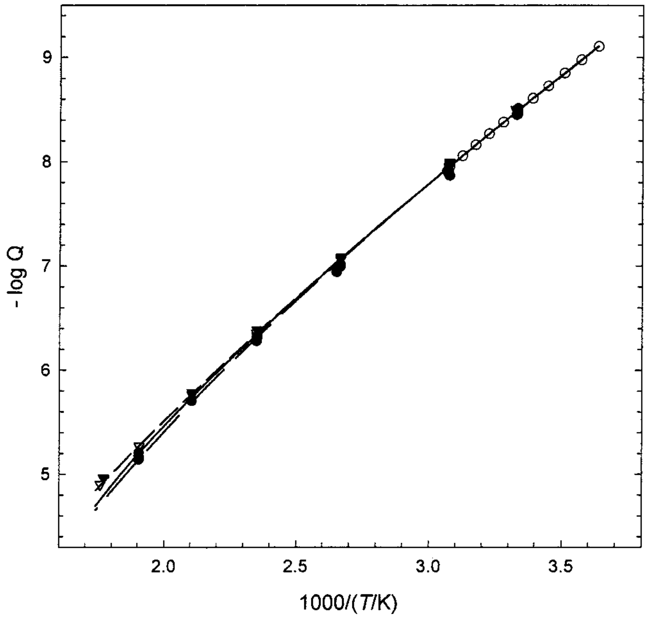

Figure 3. log Q values for the hydrolysis of morpholine at ionic strengths ≤0.1 m, taken from this study and the literature are presented as a function of the reciprocal temperature in Kelvin. The symbols represent the following: ● and ▼, results of this study in NaTr and NaCl media, respectively; ○, Hetzler et al.;[7] and ▽, Mesmer and Hitch.[5] The curves represent infinite dilution fits from this study (—), Hetzler et al.[7] (– –), and Czerminski et al.[8] (- - -).

The low ionic strength (≤0.1 m) results of the present study are compared with literature values in Figure 3 and are clearly very compatible. Moreover, Figure 3 shows the almost linear dependence of log Q on the reciprocal temperature in Kelvin to 300 °C, that further supports the use of the isocoulombic approach. Note that in neither the fit of Hetzer et al.[7] nor Czerminiski et al.[8] shown in Figure 3, were the high-temperature data of Mesmer and Hitch[5] used. The fits of Hetzer et al.[7] and Czerminiski et al.[8] have clearly been extrapolated well beyond the experimental range of the two studies, yet they remain in agreement with the present data to high temperatures. However, it is important to note that the ionic strength dependence of log Q determined by Czerminiski et al.[8] based on a synthetic seawater mixture of electrolytes, was excluded from the fit of the present study because it was significantly larger than found in other studies.

Numerical differentiation of eq 6 using the ORGLS program[22] yielded thermodynamic parameters for reaction 1 at 25 °C and infinite dilution. These values are: log $K = -8.491 \pm 0.003$; $\Delta H = (39 \pm 1)$ kJ·mol^{-1}; $\Delta S = (-31 \pm 1)$ J·K^{-1}·mol^{-1}; $\Delta C_p = (40 \pm 7)$ J·K^{-1}·mol^{-1}; and $\Delta V = (3 \pm 1)$ cm^3·mol^{-1}.

Conclusions

The present study yielded a complete and precise database for the acid dissociation of morpholinium ion from (0 to 300) °C and to 1.0 m ionic strength. Moreover, the results of this study are compatible with previously published data. Finally, the fitting expression (eq 6) based on temperature, ionic strength and the density of pure water, allows for the behavior of morpholine to be modeled at elevated temperatures such as those encountered in industrial settings where morpholine is utilized as a pH buffering agent and possible corrosion inhibitor.

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