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Dissociation Quotients of Malonic Acid in Aqueous Sodium Chloride Media to 100°C¹

Richard M. Kettler,² David J. Wesolowski,³ and Donald A. Palmer²

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The first and second molal dissociation quotients of malonic acid were measured potentiometrically in a concentration cell fitted with hydrogen electrodes. The hydrogen ion molality of malonic acid/bimalonate solutions was measured relative to a standard aqueous HCl solution from 0 to 100°C over 25° intervals at five ionic strengths ranging from 0.1 to 5.0 molal (NaCl). The molal dissociation quotients and available literature data were treated in the all anionic form by a seven-term equation. This treatment yielded the following thermodynamic quantities for the first acid dissociation equilibrium at 25°C: $\log K_{1a} = -2.852 \pm 0.003$, $\Delta H_{1a}^\circ = 0.1 \pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S_{1a}^\circ = -54.4 \pm 1.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and $\Delta C_{p,1a}^\circ = -185 \pm 20 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Measurements of the bimalonate/malonate system were made over the same intervals of temperature and ionic strength. A similar regression of the present and previously published equilibrium quotients using a seven-term equation yielded the following values for the second acid dissociation equilibrium at 25°C: $\log K_{2a} = -5.697 \pm 0.001$, $\Delta H_{2a}^\circ = -5.13 \pm 0.11 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S_{2a}^\circ = -126.3 \pm 0.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and $\Delta C_{p,2a}^\circ = -250 + 10 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

KEY WORDS: Malonic acid; propanedioic acid; dissociation constants; thermodynamics; potentiometry; ionic strength

1. Introduction

Malonic (propanedioic) acid is an important difunctional carboxylic acid in geological systems. It is one of the most abundant of this class of acids in soils, and has received considerable attention be-

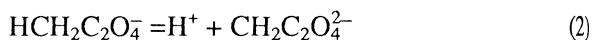
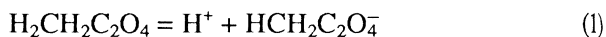
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cause of its effect on nutrient availability,⁽¹⁾ aluminum toxicity,⁽²⁾ and the release of aluminum and sulfate from soils.⁽³⁾ Although malonic acid is known to decarboxylate readily at temperatures near 100°C,⁽⁴⁾ its importance may not be limited to near-surface environments. Concentrations of malonate in excess of 2500 mg-L⁻¹ have been reported in basinal brines;⁽⁵⁾ thus, malonate may be an important species in the transport of aluminum and other metals in sedimentary basins. Malonic acid is important to geochemical and industrial processes because its anion forms strong complexes with di- and trivalent metal cations. The thermodynamic behavior and activity-concentration relationships of malonic acid in all its forms must be understood in order to model geological or industrial systems, to use malonate species as pH buffers, or to measure the association constants of metal-malonate complexes.

The dissociation of malonic acid proceeds as follows:



Although reactions (1) and (2) have been studied extensively at temperatures from 0-60°C at low ionic strengths (Table I), no data exist at higher ionic strengths and temperatures.

2. Experimental

2.1. Materials

All solutions were prepared from reagent grade chemicals and distilled, deionized water (resistivity greater than 0.18 MΩm). Stock solutions of NaCl, NaOH and HCl were sparged and stored under argon in polypropylene containers. Solutions used in the experiments listed in Table II were prepared by combining reagent grade H₂CH₂C₂O₄ (Aldrich lot BE 100297) with the NaOH and NaCl stock solutions. The malonic acid was dried at 50°C in a vacuum oven for at least two hours, whereupon titration with a standard NaOH solution yielded an equivalent weight of 52.03 g-eq⁻¹ (*cf.* calculated equivalent weight of 52.03). The high temperature cell was pressurized with ultrapure Matheson (99.999%) hydrogen.

Three stock reference solutions with ionic strengths of 0.1, 1 and 5 molal were prepared (ionic strength was determined from the stoichiometric molalities of all ions in solution) and diluted to the appropriate ionic strength prior to each experiment (Table II). The molal

Table I. Summary of the Thermodynamic Data for the Dissociation of Malonic Acid

| pK_{1a}^a | $\Delta H_{1a}^{\circ b}$ | $\Delta S_{1a}^{\circ c}$ | $\Delta C_{p,1a}^{\circ c}$ | pK_{2a}^a | $\Delta H_{2a}^{\circ b}$ | $\Delta S_{2a}^{\circ c}$ | $\Delta C_{p,2a}^{\circ c}$ | $T(^{\circ}C)$ | Ref. |
|-------------|---------------------------|---------------------------|-----------------------------|-------------|---------------------------|---------------------------|-----------------------------|----------------|------|
| 2.881 | | | | 5.664 | | | | 5 | 6 |
| 2.867 | | | | 5.664 | | | | 5 | 6 |
| 2.867 | | | | 5.666 | | | | 10 | 6 |
| 2.855 | | | | 5.673 | | | | 15 | 6 |
| 2.849 | | | | 5.683 | | | | 20 | 6 |
| 2.847 | 0.071 | -54.4 | -255 | 5.696 | -4.77 | -125 | -243 | 25 | 6 |
| 2.849 | | | | 5.711 | | | | 30 | 6 |
| 2.855 | | | | 5.730 | | | | 35 | 6 |
| 2.862 | | | | 5.752 | | | | 40 | 6 |
| 2.875 | | | | 5.775 | | | | 45 | 6 |
| 2.882 | | | | 5.663 | | | | 5 | 7 |
| 2.869 | | | | 5.666 | | | | 10 | 7 |
| 2.857 | | | | 5.673 | | | | 15 | 7 |
| 2.851 | | | | 5.683 | | | | 20 | 7 |
| 2.847 | | | | 5.696 | | | | 25 | 7 |
| 2.849 | | | | 5.710 | | | | 30 | 7 |
| 2.855 | | | | 5.729 | | | | 35 | 7 |
| 2.863 | | | | 5.751 | | | | 40 | 7 |
| 2.876 | | | | 5.774 | | | | 45 | 7 |
| | | | | 5.770 | 1.35 | -104 | -239 | 0 | 8 |
| | | | | 5.664 | 0.14 | -108 | -243 | 5 | 8 |
| | | | | 5.667 | -1.08 | -112 | -246 | 10 | 8 |
| | | | | 5.673 | -2.33 | -117 | -250 | 15 | 8 |
| | | | | 5.683 | -3.58 | -121 | -253 | 20 | 8 |
| | | | | 5.696 | -4.86 | -125 | -256 | 25 | 8 |
| | | | | 5.710 | -6.15 | -130 | -259 | 30 | 8 |
| | | | | 5.730 | -7.45 | -134 | -262 | 35 | 8 |
| | | | | 5.752 | -8.77 | -138 | -265 | 40 | 8 |
| | | | | 5.777 | -9.96 | -142 | -268 | 45 | 8 |
| | | | | 5.803 | -11.45 | -146 | -270 | 50 | 8 |
| | | | | 5.833 | -12.80 | -151 | -272 | 55 | 8 |
| | | | | 5.866 | -14.17 | -154 | -275 | 60 | 8 |
| | 1.21 ± 0.21 | -50.2 | | | -3.85 ± 0.21 | -122 | | 25 | 9 |

^a These values were combined with the results of this study in the fitting process.

^b Units: kJ·mol⁻¹. ^c Units: J·K⁻¹·mol⁻¹.

ratios of HCl to NaCl were less than 1:990, 1:195 and 1:988 for the 0.1, 1, and 5 molal solutions, respectively. Four stock test solutions were prepared and diluted as necessary for the experimental runs (Table II). Two stock solutions with molal ratios of malonic acid to NaOH of 2:1 and ionic strengths of 1 and 5 molal were prepared for determination of the first dissociation quotient. The 5 molal solution had a ratio of

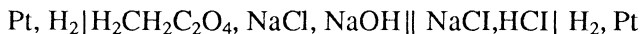
Table II. Starting Molal Solution Compositions

| Run No. | Test Cell | | | Reference Cell | |
|---------|------------------|--|------------------|------------------|-----------------|
| | $m(\text{NaCl})$ | $m(\text{H}_2\text{CH}_2\text{C}_2\text{O}_4)$ | $m(\text{NaOH})$ | $m(\text{NaCl})$ | $m(\text{HCl})$ |
| 1 | 0.9190 | 0.03995 | 0.06000 | 0.9953 | 0.005028 |
| 2 | 0.9800 | 0.04000 | 0.02000 | 0.9953 | 0.005028 |
| 3 | 0.09191 | 0.003996 | 0.006001 | 0.09913 | 0.0009994 |
| 4,5 | 0.09797 | 0.003998 | 0.001999 | 0.09913 | 0.0009994 |
| 6 | 4.980 | 0.04000 | 0.02018 | 4.994 | 0.005050 |
| 7 | 4.924 | 0.04003 | 0.06020 | 4.994 | 0.005050 |
| 8 | 2.988 | 0.02400 | 0.01211 | 2.997 | 0.003030 |
| 9 | 2.954 | 0.02402 | 0.03612 | 2.977 | 0.003030 |
| 10 | 0.3065 | 0.01332 | 0.02001 | 0.3332 | 0.001675 |
| 11 | 0.3265 | 0.01333 | 0.006661 | 0.3332 | 0.001675 |

malonic acid to NaCl of 1:123 whereas the ratio in the 1 molal solution was 1:23. Similar ratios of malonic acid to NaCl were used in preparation of the 1 and 5 molal solutions used for determination of the second dissociation quotient. Ratios of malonic acid to NaOH were *ca.* 2:3 in these latter solutions.

2.2. Apparatus and Procedures

The concentration cell was described by Mesmer *et al.*⁽¹⁰⁾, with modifications described by Wesolowski *et al.*⁽¹¹⁾, and Kettler *et al.*⁽¹²⁾ The porous Teflon liquid junction was saturated with a 5.4*m* NaCl solution prior to each experiment. The platinum electrodes were coated with platinum black. The solution compositions listed in Table II refer to the cell configuration:



The experiments were initiated by placing the cell in an ethylene glycol bath at 0°C (except for Expt. 5 which was initiated at 25 °C). The cell was then purged five times with hydrogen by pressurizing the vessel to 3.3 MPa and venting to ambient room pressure. The hydrogen pressure was then regulated to approximately 3.3 MPa. After a stable potential was observed, the potential, temperature, and pressure were recorded. The bath temperature was then increased by 25°C and the process repeated. Both sets of experiments finally exhibited drifting potentials at 100°C. This behavior was attributed to thermal decomposition of malonic acid and a linear correction was applied by back extrapolation

of the potential to the time at which the vessel reached thermal equilibrium. The drift rates were reproducible and small, averaging 0.033 mV·min⁻¹ in measurements of the first dissociation quotient and 0.012 mV·min⁻¹ in measurements of the second quotient.

3. Results

The observed potential (Tables III and IV) is related to the cell composition by

$$E = -(RT/F)\ln([H^+]_t/[H^+]_r) - \sum_i D_i([i]_r - [i]_t) \quad (3)$$

where square brackets denote the molality of the enclosed species and the subscripts r and t refer to the reference and test solutions, respectively; the ideal gas and Faraday constants are designated by R and F , respectively; and the absolute temperature is denoted by T . Matching ionic strengths in the test and reference compartments reduces the ratio of activity coefficients of the component minor ions to approximately unity and permits use of molal concentrations rather than activities. The last term in Eq. (3) is an approximation for the liquid junction potential ($e|j$ in Tables III and IV) obtained from the Henderson equation.⁽¹³⁾ The limiting equivalent conductances are taken from Quist and Marshall⁽¹⁴⁾, while those for malonate and bimalonate are assigned the values of sulfate and bisulfate.⁽¹⁴⁾ This assumption, which follows previous reports from this laboratory,^(11,12,15) contributes little to the uncertainty in determining the dissociation quotients. The absolute value of the liquid junction potential is less than 0.34 mV over the entire range of temperature and ionic strength examined, and is less than 0.1 mV for 32 of the 53 measurements reported here (Tables III and IV).

The respective stoichiometric reaction quotients for equilibria (1) and (2) are

$$Q_{1a} = ([H^+][HCH_2C_2O_4^-]) / [H_2CH_2C_2O_4] \quad (4)$$

$$Q_{2a} = ([H^+][CH_2C_2O_4^{2-}]) / [HCH_2C_2O_4^-] \quad (5)$$

These reaction quotients are related to the observed potential

$$\begin{aligned} \log Q_{xa} = & \log [H^+]_r - F/(2.3026RT) \{ E + \sum_i D_i([i]_r - [i]_t) \} \\ & + \log ([H_{2-x}CH_2C_2O_4^{x-}] / [H_{3-x}CH_2C_2O_4^{1-x}]) \end{aligned} \quad (6)$$

where $x = 1$ or 2 . The exact concentration of each malonate species is

computed from the total concentration of malonate (Table II), the reference hydrogen ion molality (Table II) and the cell potential (Tables III and IV) by an iterative calculation involving the distribution of malonate species, the liquid junction potential, and ionic strength.^(11,15-17) The results of this calculation are presented in Tables III and IV and include values for pH (defined as the negative logarithm of the molal concentration of H⁺), ionic strength, liquid junction potential, the degree of association of malonate \bar{n} , and $\log Q_x$. For the purposes of these calculations the degree of association is defined as

$$\bar{n} = \{ (2m_{\text{H}_2\text{CH}_2\text{C}_2\text{O}_4} - m_{\text{NaOH}} + m_{\text{HCl}}) - [\text{H}^+] + [\text{OH}^-] \} / m_{\text{H}_2\text{CH}_2\text{C}_2\text{O}_4} \quad (7)$$

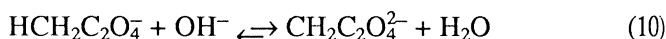
where m_x represents the stoichiometric molalities of the reagents in solution, while the terms in brackets represent the measured molality of protons and the corresponding value for hydroxide ions [as calculated using Ref. (18)]. The experiments reported here were performed under acidic conditions such that $[\text{OH}^-]$ was negligible. The sum of the terms enclosed in parentheses is the formal acidity of a malonic acid solution to which strong acid (*e.g.* HCl) or base (*e.g.* NaOH) could have been added (Table II). Only base was added to the starting solution in these experiments (*i.e.* $m_{\text{HCl}} = 0$ in all cases). Note that in the previous paper on oxalic acid,⁽¹²⁾ the equation defining \bar{n} is reported incorrectly and an equation analogous to equation (7) should have been used, namely

$$\bar{n} = \{ (2m_{\text{H}_2\text{C}_2\text{O}_4} - m_{\text{NaOH}} + m_{\text{HCl}}) - [\text{H}^+] + [\text{OH}^-] \} / m_{\text{H}_2\text{C}_2\text{O}_4} \quad (8)$$

The values of uncertainties in \bar{n} , $\sigma_{\bar{n}}$, and hence those in $\log Q_x$ (*i.e.* σ_x) were computed from the statistical combination of 18 estimated experimental and computational errors, including those derived from the liquid junction potential calculation.

4. Discussion

Combination of the reaction for the dissociation of water⁽¹⁸⁾ with equilibria (1) and (2) yields the malonic acid and bimalonate hydrolysis equilibria in their base, or anionic, forms



The respective equilibrium quotients for these equilibria are

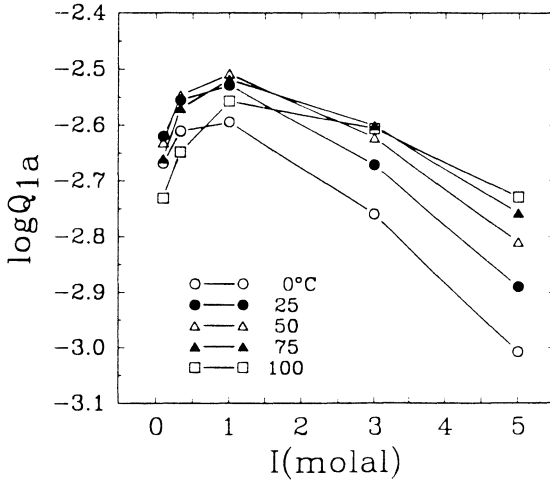


Fig. 1. $\log Q_{1a}$ obtained in this study plotted against solution ionic strength. Lines connecting the data points have been drawn for reference.

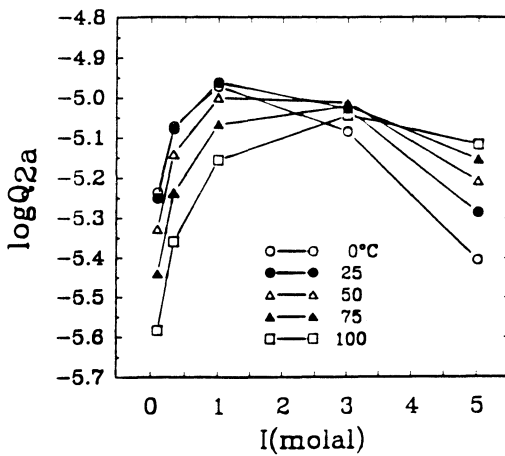


Fig. 2. $\log Q_{2a}$ obtained in this study plotted against solution ionic strength. Lines connecting the data points have been drawn for reference.

$$Q_{1b} = [\text{HCH}_2\text{C}_2\text{O}_4^-] / ([\text{H}_2\text{CH}_2\text{C}_2\text{O}_4][\text{OH}^-]) \quad (11)$$

$$Q_{2b} = [\text{CH}_2\text{C}_2\text{O}_4^{2-}] / ([\text{HCH}_2\text{C}_2\text{O}_4][\text{OH}^-]) \quad (12)$$

Whereas the the equilibrium quotients for the acid form of the dissociation reaction exhibit considerable curvature as a function of ionic strength (Figs. 1,2), the constants in the anionic form of the reactions exhibit a much simpler relationship (Figs. 3,4). The anionic forms are isocoulombic with respect to total anionic charge and consequently have small changes in heat capacity and volume,⁽¹⁹⁾ thereby simplifying extrapolation to infinite dilution and computation of the corresponding thermodynamic parameters. Figures 1 and 2 are presented to illustrate two points: (1) The dissociation of bimalonate is nearly independent of temperature in a 3*m* NaCl solution. This behavior makes a bimalonate/malonate solution at this ionic strength particularly useful as a pH buffer in low temperature aqueous systems. (2) The temperature dependence of both dissociation quotients in the acidic form is reversed as ionic strength increases. Although malonic acid and bimalonate become stronger acids as temperature increases from 0 to 100°C at low ionic strengths, they become more associated with increasing temperature at high ionic strengths. This behavior is particularly pronounced for the dissociation of bimalonate, but like all acids it must revert to becoming more associated as the critical temperature is approached.

The equilibrium quotients for reaction⁽⁹⁾ were fit as functions of temperature and ionic strength using the general equation

$$\begin{aligned} \log Q_{1b} = & p_1 + p_2/T + p_3T + p_4/I + p_5\{1 - (1+2\sqrt{I}) \exp(-2\sqrt{I})\}T \\ & + p_6I + p_7IT - \log(a_w) \end{aligned} \quad (13)$$

where a_w is the activity of water.⁽²⁰⁾ The weighted regression was performed using the ORGLS general least squares computer program⁽²¹⁾ incorporating the data in Tables I and III. The form of this equation follows previous reports from this laboratory,^(15,16) in that the equilibrium constant K_{1b} is determined by the first three terms. The values determined for these parameters are $p_1 = -1.0652$, $p_2 = 3275.1$, $p_3 = 4.0951 \times 10^{-3}$, $p_4 = -108.25$, $p_5 = 8.9741 \times 10^{-5}$, $p_6 = 0.62986$, and $p_7 = -7.9435 \times 10^{-4}$.

The agreement factor

$$\text{AF} = \{[\sum W_i(Q_{\text{obs}} - Q_{\text{calc}})^2] / (N - N_v)\}^{1/2} \quad (14)$$

for the fit is 1.19, where W is the squared reciprocal of the estimated

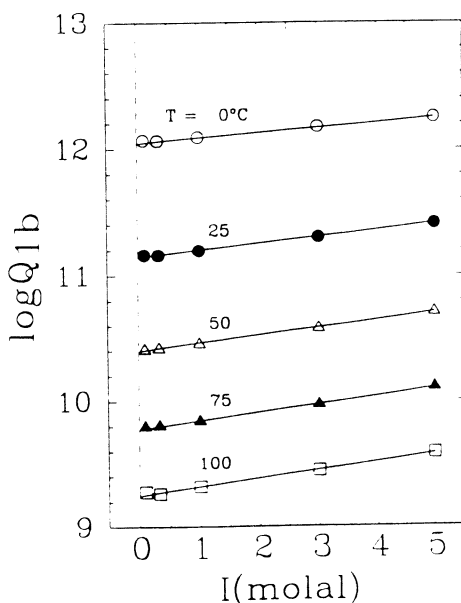


Fig. 3. The relationship between $\log Q_{1b}$ and solution ionic strength at temperatures ranging from 0-100°C. The solid curves are derived from Eq. (13).

error of any datum point, Q_{obs} is the experimentally determined value of Q_{1b} , Q_{calc} is derived from Eq. (13), N is the number of observed values, and N_v is the number of independent variables. An AF of 1.19 indicates that the scatter in the data around Eq. (13) is 1.19 times greater than would be predicted based on the statistical summation of 18 sources of error in the experimental technique.

The isothermal fits of the first dissociation quotient are shown in Fig. 3. The agreement between the data collected in this study and the published ionization constants is excellent (Fig. 5). The average deviation of the $\log Q_{1b}$ values, given in Table III from Eq. (13), is 0.0087 as compared with 0.0028 for data obtained from the literature (Fig. 5). None of these deviations exhibit a systematic relationship to ionic strength or temperature (Fig. 5).

Numerical differentiation of Eq. (13) yielded the values ΔH_{1b} , ΔS_{1b} and $\Delta C_{p,1b}$. The anionic equilibrium quotients and derived thermodynamic data were converted to the corresponding values for reaction (1) by adding the corresponding thermodynamic quantities for the dissociation of water.⁽¹⁸⁾ These latter values are presented in Table V. The $\Delta H_{1a,298}$ and $\Delta S_{1a,298}$ values are in excellent agreement with

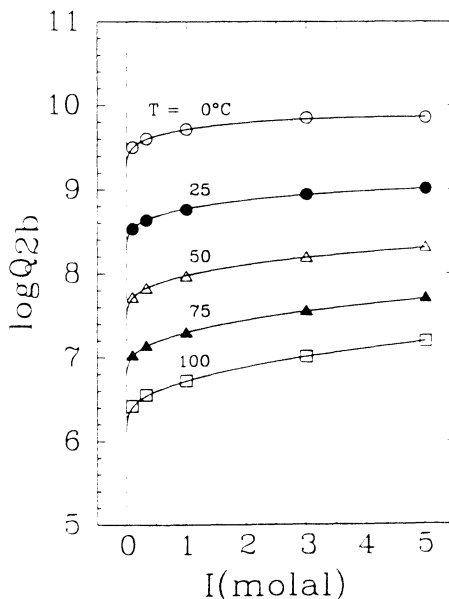


Fig. 4. The relationship between $\log Q_{2b}$ and solution ionic strength at temperatures ranging from 0-100°C. The solid curves are derived from Eq. (15).

those reported by Das and Ives⁽⁶⁾, while the corresponding ΔC_p value is slightly outside the combined experimental uncertainties (Tables I and V). The discrepancy of 1.1 kJ mol^{-1} in the $\Delta H_{1a,298}^0$ with that published by Christensen *et al.*⁽⁹⁾ (Tables I and V) is a concern as their result is based on direct titration calorimetric experiments.

A similar treatment of the data for $\log Q_{2b}$ yields the equation,

$$\log Q_{2b} = 2A_\phi \left[\frac{\sqrt{I}}{(1+1.2\sqrt{I})} + (2/1.2)\ln(1+1.2\sqrt{I}) \right] / \ln(10) - \log a_w + p_1 + p_2/T + p_3T + p_4I/T + p_5I + p_6 \{ 1 - (1+2\sqrt{I}) \exp(-2\sqrt{I}) \} T + p_7I^2/T \quad (15)$$

where the first term is the Debye-Hückel expression⁽²²⁾ and the p_1 - p_3 terms define the equilibrium constant such that $p_1 = -1.4093$, $p_2 = 3038.5$, and $p_3 = -1.6287 \times 10^{-3}$. The values determined for the remaining parameters are $p_4 = -66.211$, $p_5 = 0.22664$, $p_6 = -7.9149 \times 10^{-4}$ and $p_7 = -1.5016$. AF for this fit is 0.876 indicating that both the present and previously-published equilibrium quotients are compatible (Fig. 6). The average difference between $\log Q_{2b}$ as determined in this study and the

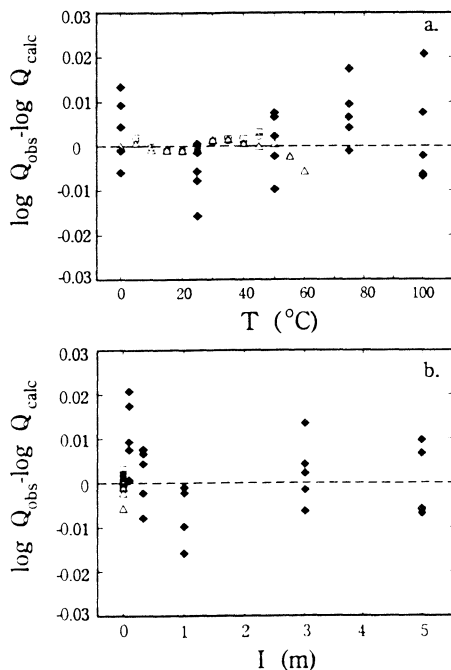


Fig. 5. Deviation plot of the differences between $\log Q_{1b}$ values computed in Eq. (13) and those obtained experimentally. The deviations are plotted against a.) temperature and b.) ionic strength. The symbols represent: \blacklozenge , this study; \circ , Ref. 6; \square , Ref. 7.

calculated fit is 0.0071 compared with an average deviation of 0.0013 for the data obtained from the literature. The residuals of the regression exhibit no systematic relation to temperature or ionic strength (Fig. 6).

Values of ΔH_{1b} , ΔS_{2b} , and $\Delta C_{p,2b}$ were obtained from numerical differentiation of Eq. (15). The values of $\log Q_{2b}$ and the associated thermodynamic quantities were converted to forms appropriate to Eq. (2) by addition of the corresponding values for the dissociation of water⁽⁸⁾ and these data are presented in Table VI. The ΔC_p values reported by Hamer *et al.*⁽⁸⁾ show close agreement with those presented here at ambient temperatures, but diverge at both lower and higher temperatures. The value of $\Delta H_{2a,298}^0$ given in Table VI lies outside the experimental uncertainty given by Christensen *et al.*⁽⁹⁾ by $1.28 \text{ kJ}\cdot\text{mol}^{-1}$. Interestingly, this positive deviation is almost identical to that found in $\Delta H_{1a,298}$ indicating that some systematic error exists in one of the two data sets.

Table. III. Experimental Results for the First Dissociation Quotient of Malonic Acid

| Expt. | T (°C) | I (m) | E (mV) | elj^a (mV) | pH | \bar{n} | $\sigma_{\bar{n}}$ | pQ_{1a} | σ_{1a} | $-pQ_{1b}$ | σ_{1b} |
|-------|-------------|------------|-------------|-----------------|-------|-----------|--------------------|-----------|---------------|------------|---------------|
| 2 | 0.00 | 1.002 | 20.82 | 0.100 | 2.685 | 1.448 | 0.005 | 2.594 | 0.008 | 12.090 | 0.018 |
| | 24.90 | 1.002 | 19.58 | 0.059 | 2.631 | 1.442 | 0.005 | 2.528 | 0.008 | 11.193 | 0.018 |
| | 49.84 | 1.002 | 20.22 | 0.033 | 2.615 | 1.439 | 0.005 | 2.509 | 0.008 | 10.464 | 0.018 |
| | 74.80 | 1.003 | 22.35 | 0.010 | 2.622 | 1.440 | 0.005 | 2.518 | 0.008 | 9.852 | 0.018 |
| | 99.80 | 1.003 | 26.31 | -0.010 | 2.654 | 1.445 | 0.005 | 2.557 | 0.008 | 9.319 | 0.018 |
| 4 | 0.01 | 0.101 | 3.59 | -0.012 | 3.066 | 1.286 | 0.005 | 2.668 | 0.011 | 12.068 | 0.017 |
| | 24.89 | 0.101 | 2.60 | -0.050 | 3.043 | 1.274 | 0.005 | 2.620 | 0.012 | 11.163 | 0.018 |
| | 49.84 | 0.101 | 3.16 | -0.056 | 3.049 | 1.277 | 0.005 | 2.631 | 0.011 | 10.418 | 0.017 |
| 5 | 24.90 | 0.101 | 2.59 | -0.051 | 3.043 | 1.274 | 0.005 | 2.620 | 0.012 | 11.162 | 0.018 |
| | 49.85 | 0.101 | 3.05 | -0.058 | 3.047 | 1.276 | 0.005 | 2.628 | 0.011 | 10.421 | 0.017 |
| | 74.84 | 0.101 | 4.36 | -0.061 | 3.062 | 1.284 | 0.005 | 2.660 | 0.011 | 9.810 | 0.017 |
| | 99.81 | 0.101 | 7.28 | -0.055 | 3.098 | 1.301 | 0.005 | 2.731 | 0.010 | 9.275 | 0.016 |
| 6 | 0.00 | 5.001 | 40.98 | 0.039 | 3.054 | 1.474 | 0.005 | 3.007 | 0.008 | 12.246 | 0.038 |
| | 24.90 | 5.001 | 38.38 | 0.028 | 2.946 | 1.467 | 0.005 | 2.889 | 0.008 | 11.406 | 0.038 |
| | 49.85 | 5.002 | 37.04 | 0.021 | 2.875 | 1.462 | 0.005 | 2.809 | 0.008 | 10.714 | 0.038 |
| | 74.82 | 5.003 | 36.79 | 0.013 | 2.830 | 1.459 | 0.005 | 2.757 | 0.008 | 10.116 | 0.038 |
| | 99.78 | 5.005 | 37.61 | 0.006 | 2.805 | 1.456 | 0.005 | 2.729 | 0.008 | 9.582 | 0.038 |
| 8 | 0.00 | 3.001 | 18.85 | 0.019 | 2.867 | 1.439 | 0.005 | 2.760 | 0.008 | 12.171 | 0.024 |
| | 24.89 | 3.002 | 16.39 | 0.009 | 2.796 | 1.429 | 0.005 | 2.671 | 0.008 | 11.298 | 0.024 |
| | 49.85 | 3.002 | 15.35 | 0.003 | 2.758 | 1.423 | 0.005 | 2.623 | 0.009 | 10.585 | 0.025 |
| | 74.83 | 3.003 | 15.42 | -0.003 | 2.742 | 1.420 | 0.005 | 2.601 | 0.009 | 9.978 | 0.025 |
| | 99.79 | 3.004 | 16.81 | -0.008 | 2.745 | 1.421 | 0.005 | 2.606 | 0.009 | 9.443 | 0.025 |
| 11 | 0.00 | 0.335 | 2.14 | -0.073 | 2.814 | 1.385 | 0.005 | 2.611 | 0.009 | 12.063 | 0.018 |
| | 24.90 | 0.335 | 0.19 | -0.101 | 2.777 | 1.375 | 0.005 | 2.555 | 0.009 | 11.160 | 0.018 |
| | 49.81 | 0.335 | -0.17 | -0.110 | 2.772 | 1.373 | 0.005 | 2.546 | 0.009 | 10.429 | 0.018 |
| | 74.84 | 0.335 | 0.88 | -0.113 | 2.787 | 1.378 | 0.005 | 2.570 | 0.009 | 9.816 | 0.018 |
| | 99.80 | 0.335 | 4.82 | -0.103 | 2.840 | 1.392 | 0.005 | 2.648 | 0.009 | 9.262 | 0.018 |

^a Junction potential, see text.

The equations describing the dissociation of malonic acid at infinite dilution can be derived from Eqs. (13,15) and a similar relation for the dissociation of water⁽¹⁸⁾ to yield

$$\log K_{1a} = -607.587 + 34561/T - 0.093516T + 94.9734 \ln T - 2.17087 \times 10^6/T^2 \quad (16)$$

$$\log K_{2a} = -607.931 + 34324/T - 0.099240T + 94.9734 \ln T - 2.17087 \times 10^6/T^2 \quad (17)$$

Table IV. Experimental Results for the Second Dissociation Quotient of Malonic Acid

| Expt. | <i>T</i> (°C) | <i>I</i> (<i>m</i>) | <i>E</i> (mV) | elj ^a (mV) | pH | <i>n</i> | σ _{<i>n</i>} | p <i>Q</i> _{2a} | σ _{2a} | -p <i>Q</i> _{2b} | σ _{2b} |
|-------|------------------|--------------------------|------------------|--------------------------|-------|----------|-----------------------|--------------------------|-----------------|---------------------------|-----------------|
| 1 | 0.00 | 0.999 | 145.09 | -0.149 | 4.973 | 0.499 | 0.006 | 4.972 | 0.011 | 9.712 | 0.021 |
| | 24.90 | 0.999 | 157.78 | -0.209 | 4.963 | 0.499 | 0.006 | 4.962 | 0.011 | 8.759 | 0.021 |
| | 49.83 | 0.999 | 173.45 | -0.250 | 5.001 | 0.500 | 0.006 | 5.000 | 0.011 | 7.973 | 0.021 |
| | 74.82 | 0.999 | 191.48 | -0.295 | 5.068 | 0.500 | 0.006 | 5.067 | 0.011 | 7.303 | 0.021 |
| | 99.78 | 0.999 | 211.82 | -0.340 | 5.156 | 0.500 | 0.006 | 5.156 | 0.011 | 6.720 | 0.021 |
| 3 | 0.01 | 0.0999 | 121.34 | 0.188 | 5.242 | 0.497 | 0.006 | 5.237 | 0.011 | 9.500 | 0.017 |
| | 24.91 | 0.0999 | 133.39 | 0.088 | 5.257 | 0.497 | 0.006 | 5.251 | 0.011 | 8.531 | 0.017 |
| | 49.83 | 0.0999 | 149.49 | 0.016 | 5.333 | 0.497 | 0.006 | 5.328 | 0.011 | 7.722 | 0.017 |
| | 74.82 | 0.0999 | 168.90 | -0.057 | 5.446 | 0.497 | 0.006 | 5.441 | 0.011 | 7.030 | 0.017 |
| | 100.03 | 0.0999 | 191.76 | -0.130 | 5.588 | 0.498 | 0.006 | 5.584 | 0.011 | 6.419 | 0.017 |
| 7 | 0.00 | 5.005 | 168.84 | -0.022 | 5.412 | 0.496 | 0.006 | 5.404 | 0.011 | 9.850 | 0.041 |
| | 24.90 | 5.005 | 177.21 | -0.034 | 5.293 | 0.496 | 0.006 | 5.286 | 0.011 | 9.010 | 0.041 |
| | 49.84 | 5.005 | 187.04 | -0.042 | 5.215 | 0.496 | 0.006 | 5.207 | 0.011 | 8.316 | 0.041 |
| | 74.82 | 5.006 | 197.80 | -0.051 | 5.161 | 0.496 | 0.006 | 5.154 | 0.011 | 7.721 | 0.041 |
| | 99.79 | 5.009 | 209.25 | -0.060 | 5.123 | 0.496 | 0.006 | 5.116 | 0.011 | 7.195 | 0.041 |
| 9 | 0.00 | 3.002 | 139.48 | -0.025 | 5.092 | 0.496 | 0.006 | 5.084 | 0.011 | 9.847 | 0.027 |
| | 24.91 | 3.002 | 148.86 | -0.036 | 5.035 | 0.496 | 0.006 | 5.028 | 0.011 | 8.941 | 0.027 |
| | 49.86 | 3.003 | 160.33 | -0.044 | 5.019 | 0.496 | 0.006 | 5.012 | 0.011 | 8.195 | 0.027 |
| | 74.83 | 3.003 | 173.26 | -0.053 | 5.027 | 0.496 | 0.006 | 5.020 | 0.011 | 7.560 | 0.027 |
| | 99.80 | 3.005 | 187.48 | -0.062 | 5.051 | 0.496 | 0.006 | 5.044 | 0.011 | 7.005 | 0.027 |
| 10 | 0.00 | 0.333 | 124.87 | -0.144 | 5.077 | 0.497 | 0.006 | 5.072 | 0.011 | 9.602 | 0.020 |
| | 24.92 | 0.333 | 136.71 | -0.203 | 5.084 | 0.497 | 0.006 | 5.079 | 0.011 | 8.635 | 0.020 |
| | 49.85 | 0.333 | 152.19 | -0.245 | 5.147 | 0.497 | 0.006 | 5.142 | 0.011 | 7.833 | 0.020 |
| | 74.82 | 0.333 | 170.57 | -0.289 | 5.242 | 0.497 | 0.006 | 5.238 | 0.011 | 7.149 | 0.020 |
| | 99.81 | 0.333 | 191.85 | -0.334 | 5.364 | 0.497 | 0.006 | 5.359 | 0.011 | 6.551 | 0.020 |

^a See footnote of Table III.

The temperature dependencies of the ionization constants of malonic acid and bimalonate mirror those of other acids that have been studied in this laboratory.⁽²³⁾ The trend to increasing association with increasing temperature results from a change in Δ*S*_a to more negative values which counters a similar change in Δ*H*_a. The Δ*C*_{p,2a}^o values presented by Hamer *et al.*⁽⁸⁾ are maximized at 0°C and become progressively more negative as temperature increases, whereas values of Δ*C*_{p,2a}^o reported in Table VI reach a maximum at approximately 75°C. A similar trend in Δ*C*_{p,a}^o for a wide variety of acids⁽²³⁾ lends support to the data presented here compared those presented by Hamer⁽⁸⁾. The dependence of the dissociation quotient on ionic strength is also similar to that exhibited by other acids. Malonic acid and bimalonate become increas-

Table V. Summary of Thermodynamic Quantities for the First Acid Dissociation Quotient of Malonic Acid in Aqueous Sodium Chloride Media at the Saturation Vapor Pressure^a

| $T(^{\circ}\text{C})$ | $\log Q_{1a}$ | ΔH_{1a}^b | ΔS_{1a}^c | $\Delta C_{p,1a}^c$ |
|-----------------------|--------------------|-------------------|-------------------|---------------------|
| $I = 0.0$ | | | | |
| 0 | -2.897 ± 0.007 | 5.7 ± 0.7 | -34.6 ± 2.3 | -274 ± 19 |
| 25 | -2.852 ± 0.003 | 0.1 ± 0.3 | -54.4 ± 1.0 | -185 ± 20 |
| 50 | -2.879 ± 0.005 | -3.8 ± 0.5 | -67.0 ± 1.6 | -135 ± 22 |
| 75 | -2.941 ± 0.012 | -6.9 ± 1.0 | -76.1 ± 3.1 | -114 ± 24 |
| 100 | -3.024 ± 0.024 | -9.8 ± 1.6 | -84.1 ± 4.8 | -116 ± 25 |
| $I = 0.1$ | | | | |
| 0 | -2.688 ± 0.007 | 6.4 ± 0.6 | -28.3 ± 2.3 | -268 ± 18 |
| 25 | -2.631 ± 0.005 | 0.9 ± 0.3 | -47.3 ± 1.0 | -173 ± 20 |
| 50 | -2.644 ± 0.005 | -2.7 ± 0.5 | -58.8 ± 1.5 | -119 ± 21 |
| 75 | -2.689 ± 0.009 | -5.3 ± 1.0 | -66.6 ± 3.0 | -94 ± 23 |
| 100 | -2.754 ± 0.021 | -7.5 ± 1.6 | -72.9 ± 4.6 | -92 ± 25 |
| $I = 0.5$ | | | | |
| 0 | -2.596 ± 0.010 | 7.0 ± 0.6 | -24.0 ± 2.2 | -262 ± 16 |
| 25 | -2.527 ± 0.010 | 1.8 ± 0.3 | -42.3 ± 1.0 | -162 ± 18 |
| 50 | -2.526 ± 0.010 | -1.4 ± 0.4 | -52.8 ± 1.2 | -104 ± 19 |
| 75 | -2.556 ± 0.010 | -3.6 ± 0.9 | -59.4 ± 2.5 | -75 ± 21 |
| 100 | -2.600 ± 0.017 | -5.4 ± 1.4 | -64.2 ± 4.0 | -69 ± 22 |
| $I = 1.0$ | | | | |
| 0 | -2.595 ± 0.012 | 7.5 ± 0.6 | -22.0 ± 2.3 | -258 ± 16 |
| 25 | -2.517 ± 0.012 | 2.5 ± 0.3 | -39.9 ± 1.1 | 155 ± 17 |
| 50 | -2.506 ± 0.012 | -0.5 ± 0.4 | -49.7 ± 1.1 | -93 ± 18 |
| 75 | -2.523 ± 0.011 | -2.4 ± 0.8 | -55.3 ± 2.2 | -62 ± 20 |
| 100 | -2.554 ± 0.015 | -3.8 ± 1.3 | -59.2 ± 3.6 | -53 ± 21 |
| $I = 3.0$ | | | | |
| 0 | -2.768 ± 0.016 | 9.1 ± 1.2 | -19.8 ± 1.3 | -244 ± 24 |
| 25 | -2.693 ± 0.012 | 4.5 ± 0.7 | -36.1 ± 2.7 | -134 ± 26 |
| 50 | -2.621 ± 0.013 | 2.0 ± 0.4 | -43.9 ± 4.8 | -65 ± 28 |
| 75 | -2.605 ± 0.011 | 0.9 ± 1.0 | -47.2 ± 0.0 | -27 ± 30 |
| 100 | -2.596 ± 0.016 | 0.5 ± 1.7 | -48.4 ± 0.0 | -11 ± 32 |
| $I = 5.0$ | | | | |
| 0 | -3.010 ± 0.026 | 10.3 ± 2.0 | -19.9 ± 7.1 | -232 ± 40 |
| 25 | -2.881 ± 0.018 | 6.1 ± 1.1 | -34.9 ± 3.8 | -117 ± 43 |
| 50 | -2.813 ± 0.020 | 4.1 ± 0.7 | -41.1 ± 2.2 | -42 ± 47 |
| 75 | -2.767 ± 0.017 | 3.7 ± 1.6 | -42.4 ± 4.6 | 2 ± 50 |
| 100 | -2.727 ± 0.026 | 4.0 ± 2.8 | 41.4 ± 8.0 | 24 ± 54 |

^a Errors listed represent three times the standard deviation. ^b Units: $\text{kJ}\cdot\text{mol}^{-1}$. ^c Units: $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

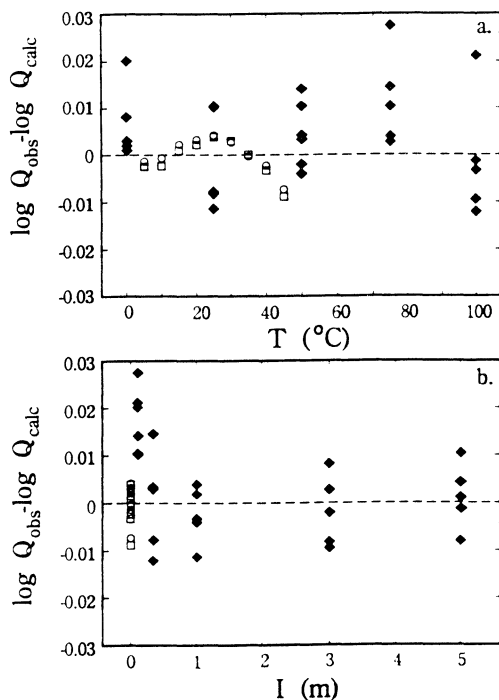


Fig. 6. Deviation plot of the differences between $\log Q_{2b}$ computed in Eq. (15) and those obtained experimentally. The deviations are plotted against a.) temperature and b.) ionic strength. The symbols represent: \blacklozenge , this study; \circ , Ref. 6; \square , Ref. 7; \triangle , Ref. 8.

ingly dissociated then reassociate as ionic strength increases, at least at these moderate temperatures. Similar behavior has been observed for water,⁽¹⁸⁾ bicarbonate,⁽²⁴⁾ and acetic acid⁽²⁵⁾ and occurs because the ΔH_a becomes more positive, outstripping the conflicting contribution made by the increase in the $T\Delta S_a$ term as the ionic strength increases. The salt competes with protons and acid anions for water; thus, at high ionic strengths ΔH_a will be dominated by the breaking of the H-anion bond and will be positive.⁽²³⁾ Although the dominance of the ΔH_a term at low temperatures is not unusual, reassociation at high temperatures is always driven by the $T\Delta S_a$ term.⁽²³⁾ The reversal of the temperature dependence of the dissociation quotient with increasing ionic strength has been observed for acetic acid⁽²⁵⁾ and bioxalate⁽¹²⁾

Table VI. Summary of Thermodynamic Quantities for the Second Dissociation Quotient of Malonic Acid in Aqueous Sodium Chloride Media at Saturation Vapor Pressure^a

| $T(^{\circ}\text{C})$ | $\log Q_{2a}$ | ΔH_{2a}^b | ΔS_{2a}^c | $\Delta C_{p,2a}^a$ |
|-----------------------|--------------------|-------------------|-------------------|---------------------|
| $I = 0.0$ | | | | |
| 0 | -5.671 ± 0.003 | 2.07 ± 0.29 | -101.0 ± 1.0 | -334 ± 9 |
| 25 | -5.697 ± 0.001 | -5.13 ± 0.11 | -126.3 ± 0.4 | -250 ± 10 |
| 50 | -5.805 ± 0.002 | -10.76 ± 0.26 | -144.5 ± 0.8 | -206 ± 11 |
| 75 | -5.958 ± 0.006 | -15.68 ± 0.53 | -159.0 ± 1.6 | -191 ± 12 |
| 100 | -6.138 ± 0.012 | -20.52 ± 0.83 | -172.6 ± 2.5 | -199 ± 13 |
| $I = 0.1$ | | | | |
| 0 | -5.247 ± 0.004 | 2.57 ± 0.31 | -91.1 ± 1.1 | -329 ± 9 |
| 25 | -5.253 ± 0.004 | -4.43 ± 0.11 | -115.4 ± 0.4 | -239 ± 10 |
| 50 | -5.336 ± 0.004 | -9.73 ± 0.24 | -132.3 ± 0.7 | -190 ± 11 |
| 75 | -5.459 ± 0.006 | -14.19 ± 0.51 | -145.3 ± 1.5 | -172 ± 12 |
| 100 | -5.605 ± 0.011 | -18.49 ± 0.81 | -156.8 ± 2.3 | -175 ± 13 |
| $I = 0.5$ | | | | |
| 0 | -5.026 ± 0.007 | 3.04 ± 0.36 | -85.1 ± 1.3 | -322 ± 9 |
| 25 | -5.016 ± 0.009 | -3.74 ± 0.18 | -108.6 ± 0.7 | -228 ± 10 |
| 50 | -5.077 ± 0.010 | -8.69 ± 0.23 | -124.1 ± 0.8 | -174 ± 11 |
| 75 | -5.174 ± 0.010 | -12.71 ± 0.47 | -135.6 ± 1.4 | -151 ± 12 |
| 100 | -5.286 ± 0.013 | -16.45 ± 0.76 | -145.2 ± 2.2 | -151 ± 12 |
| $I = 1.0$ | | | | |
| 0 | -4.971 ± 0.009 | 3.51 ± 0.42 | -82.3 ± 1.5 | -315 ± 9 |
| 25 | -4.946 ± 0.010 | -3.04 ± 0.25 | -104.9 ± 0.9 | -217 ± 10 |
| 50 | -4.992 ± 0.010 | -7.69 ± 0.26 | -119.4 ± 0.8 | -161 ± 11 |
| 75 | -5.066 ± 0.011 | -11.34 ± 0.46 | -129.5 ± 1.4 | -135 ± 11 |
| 100 | -5.154 ± 0.013 | -14.63 ± 0.74 | -137.9 ± 2.1 | -132 ± 12 |
| $I = 3.0$ | | | | |
| 0 | -5.098 ± 0.018 | 5.58 ± 0.58 | -77.1 ± 1.9 | -286 ± 9 |
| 25 | -5.056 ± 0.014 | -0.15 ± 0.44 | -96.7 ± 1.4 | -181 ± 10 |
| 50 | -5.014 ± 0.012 | -3.79 ± 0.40 | -107.8 ± 1.2 | -116 ± 10 |
| 75 | -5.024 ± 0.012 | -6.20 ± 0.51 | -114.1 ± 1.5 | -82 ± 11 |
| 100 | -5.037 ± 0.014 | -8.06 ± 0.73 | -118.1 ± 2.1 | -70 ± 12 |
| $I = 5.0$ | | | | |
| 0 | -5.398 ± 0.022 | 7.83 ± 0.77 | -74.6 ± 2.5 | -259 ± 9 |
| 25 | -5.279 ± 0.015 | 2.90 ± 0.66 | -91.4 ± 2.1 | -146 ± 10 |
| 50 | -5.213 ± 0.013 | 0.20 ± 0.62 | -99.2 ± 1.9 | -74 ± 10 |
| 75 | -5.162 ± 0.015 | -1.09 ± 0.68 | -102.0 ± 2.1 | -33 ± 11 |
| 100 | -5.109 ± 0.019 | -1.62 ± 0.84 | -102.2 ± 2.5 | -13 ± 12 |

^a See footnotes for Table V.

5. Conclusions

The dissociation quotients of malonic acid were measured in aqueous NaCl media at temperatures ranging from 0 to 100°C. The results are in quantitative agreement with most of the previous measurements made at low temperatures and low ionic strength, as well as with the general conclusions drawn from similar studies of other acids in this laboratory. Equations (13, 15, 16, 17) provide an accurate model for the behavior of malonic acid in NaCl brines and can be used to represent the behavior of malonic acid in soils, sedimentary basin brines, and in solutions used or produced in industrial applications.

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