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Cadmium Malonate Complexation in Aqueous Sodium Trifluoromethanesulfonate Media to 75°C; Including Dissociation Quotients of Malonic Acid

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The molal formation quotients for cadmium–malonate complexes were measured potentiometrically from 5 to 75°C, at ionic strengths of 0.1, 0.3, 0.6 and 1.0 molal in aqueous sodium trifluoromethanesulfonate (NaTr) media. In addition, the stepwise dissociation quotients for malonic acid were measured in the same medium from 5 to 100°C, at ionic strengths of 0.1, 0.3, 0.6, and 1.0 molal by the same method. The dissociation quotients for malonic acid were modeled as a function of temperature and ionic strength with empirical equations formulated such that the equilibrium constants at infinite dilution were consistent, within the error estimates, with the malonic acid dissociation constants obtained in NaCl media. The equilibrium constants calculated for the dissociation of malonic acid at 25°C and infinite dilution are $\log K_{1a} = -2.86 \pm 0.01$ and $\log K_{2a} = -5.71 \pm 0.01$. A single Cd–malonate species, $CdCH_2C_2O_4$, was identified from the complexation study and the formation quotients for this species were also modeled as a function of temperature and ionic strength. Thermodynamic parameters obtained by differentiating the equation with respect to temperature for the formation of $CdCH_2C_2O_4$ at 25°C and infinite dilution are: $\log K = 3.45 \pm 0.09$, $\Delta H° = 7 \pm 6$ kJ-mol^{-1}, $\Delta S° = 91 \pm 22$ J-K^{-1}-mol^{-1}, and $\Delta C_p° = 400 \pm 300$ J-K^{-1}-mol^{-1}.

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1. INTRODUCTION

The bioavailability and geochemical cycling of toxic elements, such as cadmium, in the environment is strongly dependent on the chemical speciation of the element. This is apparent from the numerous studies showing that the uptake of Cd by aquatic organisms and plants is controlled by the concentration of free Cd^{2+} in natural solutions rather than the total Cd concentration.[1–4] Complexation and sorption reactions, therefore, play an important role in regulating the bioavailability and toxicity of Cd.[5–7] In particular, it has been observed that organic acid–Cd complexes reduce the uptake of Cd by aquatic organisms and plants.[1,2,4,5] Although an understanding of the interaction between Cd and organic ligands is required in order to assess the impact of Cd on the environment, few organic acid–Cd complexes have been studied extensively. The most studied organic ligands are the humic and fulvic acids, whereas potential organic ligands such as the dicarboxylic acids have rarely been examined, despite their occurrence in a variety of natural aqueous solutions.[2,4,5,8] Numerous studies have emphasized the potential for the formation of metal–carboxylate complexes to increase the mobility of metal ions in natural waters, and to increase the capacity of geologic fluids to transport metals in basin brines, hydrothermal fluids, and ore solutions, e.g., Mississippi Valley-type (MVT) deposits.[9–13] Moreover, cadmium is found principally related to Zn, Pb–Zn and Pb–Cu-Zn ores such as those in basinal brines and MVT deposits.[1,4,14]

If the role of the dicarboxylic acids, for example, malonic acid, in controlling the speciation of Cd is to be understood and assessed, then formation quotients and thermodynamic data are required over a wide range of temperature and salinity conditions. Equilibrium data for the formation of Cd–malonate complexes are, however, limited to ambient conditions and low ionic strengths, and agreement between studies is poor (Table I). Furthermore, experimental measurements of the association quotients for Cd–malonate complexes have often involved NaCl as a supporting electrolyte and it is known that Cl^- ions complex Cd^{2+}.[23–25] The use of NaCl will yield reasonable results only if the association quotients for the $CdCl_n^{2-n}$ complexes are known accurately.

This paper presents the results of a potentiometric study undertaken to determine the speciation and association quotients for the complexation of Cd with malonate, and provides an empirical model describing the temperature and ionic strength dependence of the formation quotients at geologically and environmentally relevant conditions. The potentiometric titrations were performed using sodium trifluoromethanesulfonate, $NaCF_3SO_3$ (NaTr), as a supporting electrolyte, thus avoiding the formation of Cd–Cl complexes. The thermodynamic behavior of NaTr has been well established [26,27] and it has

Table I. Summary of Available Data for the Formation of Cd-Malonate Complexes at 20°C

Reaction	log Q^a	Ionic Medium	Ref.
$Cd^{2+} + CH_2C_2O_4^{2-} \rightleftharpoons CdCH_2C_2O_4$	2.51	0.1 M NaClO$_4$	15
	2.89^c	0.01 M NaCl	16
	3.29^c	NSE^b	17
	2.7	0.1 M NaCl	18
	3.25^c	0.04 M NaCl	19
	2.3^c	0.1 M NaCl	20
	1.7	2 M NaClO$_4$	21
$Cd^{2+} + 2CH_2C_2O_4^{2-} \rightleftharpoons Cd(CH_2C_2O_4)_2^{2-}$	3.6	2 M NaClO$_4$	21
$Cd^{2+} + HCH_2C_2O_4^{-} \rightleftharpoons CdHCH_2C_2O_4^{+}$	1.05	0.1 M NaClO$_4$	15
	0.72	2 M NaClO$_4$	21
$Cd^{2+} + 2HCH_2C_2O_4^{-} \rightleftharpoons Cd(HCH_2C_2O_4)_2$	1.66	2 M NaClO$_4$	21
$Cd^{2+} + HCH_2C_2O_4^{-} + CH_2C_2O_4^{2-} \rightleftharpoons$ $Cd(HCH_2C_2O_4)(CH_2CH_2O_4)^{-}$	2.28	2 M NaClO$_4$	22
$Cd^{2+} + 2HCH_2C_2O_4^{-} + CH_2C_2O_4^{2-} \rightleftharpoons$ $Cd(HCH_2C_2O_4)(2CH_2C_2O_4)^{2-}$	2.95	2 M NaClO$_4$	22
$Cd^{2+} + HCH_2C_2O_4^{-} + 2CH_2C_2O_4^{2-} \rightleftharpoons$ $Cd(HCH_2C_2O_4)(CH_2C_2O_4)_2^{3-}$	4.41	2 M NaClO$_4$	22

^{a} Molar units.
^{b} No supporting electrolyte used in these experiments.
^{c} 25°C.

been used successfully as a noncomplexing supporting electrolyte in previous metal–acetate complexation studies.[28,29] Sodium perchlorate (NaClO$_4$)—a more conventional supporting electrolyte—could not be used in this study, because perchlorate is unstable in the hydrogen atmosphere of the potentiometric concentration cell.

The success of any metal–complexation study requires accurate speciation of the ligand, so that knowledge of the acid dissociation quotients of the ligand in the relevant electrolyte media is essential. Therefore, equilibrium quotients for the stepwise dissociation of malonic acid, which proceeds as follows

$$H_2CH_2C_2O_4 \rightleftharpoons H^+ + HCH_2C_2O_4^{-} \tag{1}$$

$$HCH_2C_2O_4^{-} \rightleftharpoons H^+ + CH_2C_2O_4^{2-} \tag{2}$$
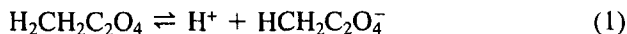
were measured in NaTr media in order to interpret accurately the results of the Cd-malonate complexation study.

2. EXPERIMENTAL

2.1. Dissociation of Malonic Acid

The preparation, standardization, and storage of trifluoromethanesulfonic acid (HTr), malonic acid (H_2Ma), NaOH, and NaTr stock solutions have been described previously.[27,29,30,31] In addition to the procedure outlined by Palmer and Drummond[27,29], the NaTr stock solution was further acidified with an aliquot of HTr, purged with argon for 2 hr to remove possible carbonate impurities, then neutralized with NaOH and stored under a positive pressure of argon. Two test solutions and a reference solution were prepared at each ionic strength (0.1, 0.3, 0.6, and 1.0 m), by diluting the relevant stock solutions with purified water. The test solutions used to measure the first dissociation of malonic acid (Eq. 1) were prepared with a 2:1 molal ratio of stoichiometric malonic acid to NaOH (equivalent to pH values of 2.5 to 3); whereas test solutions with a 2:3 molal ratio of stoichiometric malonic acid to NaOH (equivalent to pH values of 4.9 to 5.3) were used to measure the second dissociation reaction (Eq.2). {Note that throughout this study pH = $-\log[H^+]$, in molal concentration units (mol-kg^{-1})}. The stoichiometric molal compositions of the test and reference solutions used in each experiment are listed in Table II.

The hydrogen-electrode concentration cell and auxiliary equipment used in this study have been described previously.[28,32] In the present study, the configuration of the concentration cell was:

Table II. Summary of Starting Molal Solution Compositions for the Dissociation of Malonic Acid

Exp. #	Test			Ref.	
	$10^3 m_{\Sigma H2Ma}$	$10^3 m_{NaOH}$	m_{NaTr}	$10^3 m_{HTr}$	m_{NaTr}
1	4.04	5.98	0.0919	5.00	0.0950
2	4.04	5.98	0.0919	5.00	0.0950
3	4.03	1.70	0.0979	5.00	0.0950
4	12.8	18.9	0.291	5.26	0.311
5	40.4	59.9	0.921	4.90	0.996
6	40.4	17.0	0.980	4.90	0.996
7	12.8	5.37	0.309	5.26	0.311
8	12.1	5.10	0.294	1.47	0.299
9	4.04	1.70	0.0980	1.67	0.0983
10	24.3	10.2	0.588	2.94	0.597
11	40.4	17.0	0.980	4.90	0.996
12	12.8	18.9	0.291	5.26	0.311
13	24.3	36.0	0.552	30.0	0.570

$$Pt, H_2|H_2CH_2C_2O_4, NaOH, NaCF_3SO_3\|HCF_3SO_3, NaCF_3SO_3|H_2, Pt$$

<div align="center">Test   Reference</div>

The dissociation of malonic acid was measured from 5 to 100°C, following the procedure used by Kettler et al.[30] to measure the dissociation of malonic acid in NaCl media. All experiments exhibited drifting cell potentials at 100°C, which have been ascribed previously to the thermal decomposition of malonic acid.[30]

2.2 Association of Cadmium-Malonate

Test, reference, and titrant solutions were prepared by diluting the same stock solutions as used in the malonic acid dissociation experiments with purified water. In addition, a Cd-Triflate, $Cd(CF_3SO_3)_2$ (CdTr$_2$), stock solution was prepared by dissolving cadmium oxide (EM Science, Lot # 6101) in a stoichiometric amount of HTr, and then diluting the solution with purified water. The exact Cd^{2+} content was quantified using a cation-exchange column (H^+ form), and then titrating the eluate with standardized NaOH stock solution. The compositions of the test, reference, and titrant solutions, prepared at 0.1, 0.3, 0.6 and 1.0 m ionic strengths, are given in Table III. The hydrogen ion concentration and ionic strength of corresponding test and reference solutions were closely matched, whereas the ionic strength of the titrant solutions was slightly higher. By increasing the ionic strength of the titrant solutions, it

Table III. Summary of Starting Molal Solution Compositions for the Complexation of Cd^{2+} with Malonate

Titration #	Ref.		Test			Titrant		
	$10^3 m_{HTr}$	$10^2 m_{NaTr}$	$10^3 m_{HTr}$	$10^3 m_{CdTr2}$	$10^2 m_{NaTr}$	$10^2 m_{\Sigma H2Ma}$	$10^2 m_{NaOH}$	$10^2 m_{NaTr}$
14,17,18	2.00	9.80	2.00	2.00	9.20	2.02	4.00	8.16
19	2.00	9.80	2.00	2.00	9.20	2.02	4.00	8.16
20	2.00	9.78	2.00	2.00	9.20	2.02	4.00	8.16
21,22,23, 24,25	4.00	29.8	4.00	4.00	28.6	4.04	8.00	30.0
28,29,30, 31,32	4.92	101.1	4.45	4.51	99.8	10.1	20.0	100.0
33,34,36, 37	5.00	99.5	5.00	15.0	95.0	10.1	20.0	100.0
38,39,40	5.00	99.5	5.00	5.00	98.0	10.1	20.0	100.0
41,42,43, 44	5.00	59.5	5.00	5.00	58.0	6.05	12.0	57.9
45	5.00	59.5	4.98	5.01	57.9	6.05	12.0	57.9
46	5.00	59.5	5.00	5.00	58.0	6.05	12.0	57.9

was possible to compensate for changes in ionic strength arising from the formation of Cd–malonate species, and therefore it was possible to maintain a near constant ionic strength throughout the titration. (With the exception of one titration, the ionic strength of the test solutions varied less than 5% from their initial values. A 6.2% change in ionic strength was observed for a titration performed at $0.1m$ and 50°C.) Titrant solutions were prepared with a 1:2 molal ratio of stoichiometric malonic acid to NaOH, such that the malonic acid was almost fully dissociated, and the solution pH ranged between 6.6 and 7.0. All titrant solutions were stored under a positive pressure of argon.

Experiments were performed at 5, 25, 50, and 75°C following the titration procedure described by Palmer and Bell.[33] As in the earlier studies, the cell potential was recorded by signal averaging, which included 50 readings taken over a 2-minute period. During a titration, the cell potential was considered stable when three consecutive readings were identical (approximately 6 minutes, ±0.01 mV). The cell potential of a titration performed at 100°C was unstable throughout the experiment, most likely resulting from the decomposition of malonic acid, thereby constraining the upper temperature limit of this study. The configuration of the hydrogen-electrode concentration cell used in this complexation study was:

$$\text{Pt, } H_2|Cd(CF_3SO_3)_2, \text{ } HCF_3SO_3, \text{ } NaCF_3SO_3\|HCF_3SO_3, \text{ } NaCF_3SO_3|H_2, \text{ Pt}$$

<div align="center">Test   Reference</div>

with malonate-bearing titrant added to the Cd-bearing test solution. Approximately 12 ml of titrant was added to the Cd test solution in aliquots increasing in size from 0.5 to 2 ml over the course of a titration. The final ratio of total malonate to total Cd in the test solutions ranged between 1 and 6.5; within this range it was possible to complex nearly all available Cd.

3. RESULTS AND DISCUSSION

3.1 Dissociation of Malonic Acid

The molal concentration of hydrogen ions in the test solution ($[H^+_{test}]$) can be related to the observed cell potential by applying the Nernst equation:

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

where F is the Faraday constant; R is the universal gas constant; T is temperature in Kelvin; $[H^+_{ref}]$ is the known hydrogen ion concentration of the reference solution; and E and E_{LJ} represent the measured cell potential and the liquid junction potential, respectively. The liquid junction potential was calculated

using the full Henderson equation (Eq. [2–12] in Baes and Mesmer,[34]) which is assumed accurate to within 25% if the limiting equivalent conductances of the relevant species are known.[35] Limiting equivalent conductance data are known for H^+, Na^+, and $Tr,^-$[26,36] but data for the malonate species have not been measured over the temperature ranges considered in this study. The limiting equivalent conductance data for sulfate and bisulfate[36] were used to represent the conductance values of malonate and bimalonate, respectively. Computed liquid junction potentials of less than 1.0 mV were typical for measurements of the first acid dissociation (Table IV), whereas higher values were computed for the second acid dissociation (Table V). The higher calculated liquid junction potentials result from differences in the concentration of hydrogen ions between the test and reference solutions used to measure the second dissociation reaction (Table II). The malonate species, however, contributes relatively little to the liquid junction potential.

The concentrations of each malonate species in the test solution were calculated from the known concentration of total malonic acid, the hydrogen ion molality of the reference solution ($[H^+_{ref}]$), and the measured cell potential, using an iterative process involving Eq. (3), the speciation of malonic acid, and refinement of the liquid junction potential and ionic strength terms. The results of this iterative process were used to calculate the stoichiometric reaction quotients for the dissociation of malonic acid, Eqs. (1, 2). The equilibrium quotients for the dissociation of malonic acid are defined as:

$$Q_{1a} = \frac{[H^+][HCH_2C_2O_4^-]}{[H_2CH_2C_2O_4]} \tag{4}$$

$$Q_{2a} = \frac{[H^+][CH_2C_2O_4^{2-}]}{[HCH_2C_2O_4^-]} \tag{5}$$

All experimental results, including the measured cell potential and temperature, and the calculated ionic strength, liquid junction potential, pH, log Q_{na} and the degree of association of malonic acid ($\bar{n}$), are presented in Tables IV and V. The degree of association is defined as:

$$\bar{n} = \frac{(2m_{H_2CH_2C_2O_4} - m_{NaOH} + m_{HTr}) - [H^+] + [OH^-]}{m_{H_2CH_2C_2O_4}} \tag{6}$$

where m_x represents the stoichiometric molality of the reagents in solution, and the terms in brackets represent the calculated molality of hydrogen ions and the corresponding concentration of hydroxide ions, calculated from the dissociation of water in NaTr media.[27] For all experiments, m_{HTr} was zero as only m_{NaOH} was added to the test solutions (Table II).

The dissociation quotients listed in Tables IV and V have a strong ionic strength dependence, as is apparent from Fig. 1, which may be simplified

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

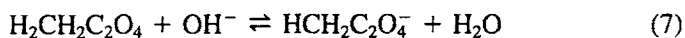| Exp. #	°C	I^a	E^b	$E_{LJ}{}^b$	pH	$\bar{n}^c$	$\log Q_{1a}$	$10^3\sigma_{1a}$	$\log Q_{1b}{}^d$
3	5.07	0.1006	34.68	3.303	2.989	1.325	−2.681	17	11.834
	24.86	0.1007	36.86	2.999	2.975	1.316	−2.650	16	11.129
	49.86	0.1007	40.61	2.730	2.977	1.318	−2.653	15	10.391
	74.87	0.1006	45.41	2.481	2.994	1.328	−2.689	13	9.780
	100.13	0.1005	53.42	2.272	3.053	1.360	−2.806	12	9.199
6	5.04	0.9999	15.23	0.249	2.590	1.515	−2.622	8	11.833
	24.88	1.0001	14.38	0.218	2.557	1.510	−2.579	8	11.132
	49.90	1.0003	15.07	0.204	2.548	1.509	−2.568	8	10.397
	74.94	1.0004	17.30	0.194	2.563	1.511	−2.586	8	9.786
7	5.02	0.3167	24.28	0.992	2.737	1.435	−2.630	9	11.812
	24.85	0.3168	24.81	0.882	2.713	1.427	−2.592	10	11.109
	49.89	0.3168	26.98	0.802	2.712	1.427	−2.589	10	10.370
	74.96	0.3168	30.41	0.735	2.730	1.433	−2.616	9	9.759
	100.09	0.3166	37.32	0.696	2.792	1.452	−2.712	9	9.192
8	5.01	0.3008	−4.48	−0.058	2.751	1.432	−2.640	9	11.805
	24.86	0.3009	−6.31	−0.070	2.726	1.424	−2.598	9	11.105
	49.87	0.3009	−6.88	−0.051	2.725	1.424	−2.597	9	10.367
	74.74	0.3009	−6.20	−0.026	2.743	1.430	−2.625	9	9.758
	100.11	0.3007	−1.73	0.029	2.810	1.451	−2.729	8	9.179
9	5.04	0.1007	11.50	0.611	2.998	1.330	−2.700	11	11.816
	24.84	0.1007	11.40	0.532	2.980	1.320	−2.661	11	11.118
	49.83	0.1007	12.63	0.494	2.983	1.321	−2.666	11	10.379
	74.78	0.1007	14.81	0.468	2.999	1.331	−2.700	10	9.770
	100.08	0.1006	19.97	0.479	3.054	1.360	−2.809	10	9.196
10	5.06	0.6007	5.08	0.122	2.626	1.482	−2.601	8	11.826
	24.56	0.6009	3.81	0.099	2.598	1.476	−2.561	8	11.134
	49.87	0.6010	3.80	0.097	2.593	1.474	−2.553	8	10.389
	74.81	0.6010	5.22	0.102	2.609	1.478	−2.575	8	9.780
	100.08	0.6007	10.32	0.124	2.673	1.492	−2.662	8	9.212
11	5.04	0.9993	14.52	0.243	2.577	1.514	−2.606	8	11.848
	24.85	0.9996	13.64	0.213	2.544	1.509	−2.564	8	11.148
	49.89	0.9997	14.26	0.200	2.536	1.507	−2.552	8	10.412
	74.77	0.9998	16.38	0.191	2.550	1.510	−2.570	8	9.805
	100.09	0.9996	22.32	0.195	2.614	1.519	−2.650	8	9.238

[a] $mol\text{-}kg^{-1}$.

[b] mV.

[c] $\sigma_{\bar{n}}$ are 5×10^{-3} except for the first 5 entries which are $7 \pm 1 \times 10^{-3}$.

[d] $\sigma_{\bar{n}}$ was $17 \pm 1 \times 10^{-3}$ except for the first four entries which were $21.5 \pm 1.5 \times 10^{-3}$.

Table V. Experimental Results for the Second Dissociation Quotient of Malonic Acid[a,b]

Exp. #	°C	I	E	E_{LJ}	pH	$\log Q_{2a}{}^c$	$\log Q_{2b}$	$10^3\sigma_{2b}$
1	5.09	0.0999	154.32	3.960	−5.168	−5.193	9.322	17
	24.88	0.0999	168.29	3.556	−5.207	−5.233	8.546	17
	49.89	0.0999	189.46	3.168	−5.306	−5.333	7.711	17
	74.72	0.0999	212.66	2.786	−5.422	−5.450	7.022	17
2	5.07	0.0999	156.28	3.961	−5.204	−5.229	9.287	17
	24.91	0.0999	169.44	3.556	−5.226	−5.252	8.525	17
	49.90	0.0999	189.47	3.168	−5.306	−5.333	7.711	17
	74.83	0.0999	212.75	2.784	−5.422	−5.450	7.020	17
	100.07	0.0999	241.01	2.396	−5.588	−5.617	6.390	17
4	5.06	0.3157	152.41	1.162	−5.061	−5.087	9.354	20
	24.90	0.3157	164.23	0.994	−5.073	−5.099	8.600	20
	49.85	0.3157	182.55	0.843	−5.140	−5.168	7.794	20
	74.77	0.3158	203.89	0.690	−5.242	−5.270	7.109	20
	100.12	0.3158	229.18	0.535	−5.380	−5.409	6.495	20
5	5.06	1.0005	147.21	0.094	−4.978	−5.004	9.450	21
	24.91	1.0005	158.05	0.029	−4.983	−5.009	8.701	21
	49.93	1.0006	174.48	−0.023	−5.031	−5.058	7.905	21
	74.92	1.0008	193.36	−0.082	−5.108	−5.136	7.236	21
	100.43	1.0009	214.60	−0.145	−5.203	−5.231	6.651	21
12	5.04	0.3156	150.28	1.162	−5.022	−5.048	9.394	20
	24.87	0.3156	162.47	0.995	−5.043	−5.069	8.631	20
	49.87	0.3156	181.36	0.844	−5.122	−5.148	7.812	20
	74.79	0.3156	202.99	0.691	−5.229	−5.257	7.122	20
	100.09	0.3157	220.23	0.535	−5.260	−5.287	6.618	20
13	5.02	0.5998	187.28	3.960	−4.988	−5.013	9.415	20
	24.85	0.5998	201.88	3.553	−4.997	−5.023	8.662	20
	49.78	0.5998	223.32	3.165	−5.057	−5.084	7.860	20
	74.80	0.6000	247.52	2.778	−5.148	−5.176	7.179	20
	100.10	0.6000	274.72	2.388	−5.264	−5.292	6.582	20

[a] Units as in Table IV.
[b] ñ for all entries is 0.517 ± 0.006.
[c] $\sigma_{\bar{n}}$ is 11×10^{-3} for all entries.

by combining the reaction for the dissociation of water with equilibrium reactions Eqs. (1, 2) (Fig. 2). This combination yields an isocoulombic equilibrium reaction for the first dissociation reaction Eq. (1), and a "pseudo-isocoulombic" equilibrium reaction for the second dissociation reaction Eq. (2) of malonic acid in the base, or anionic, form
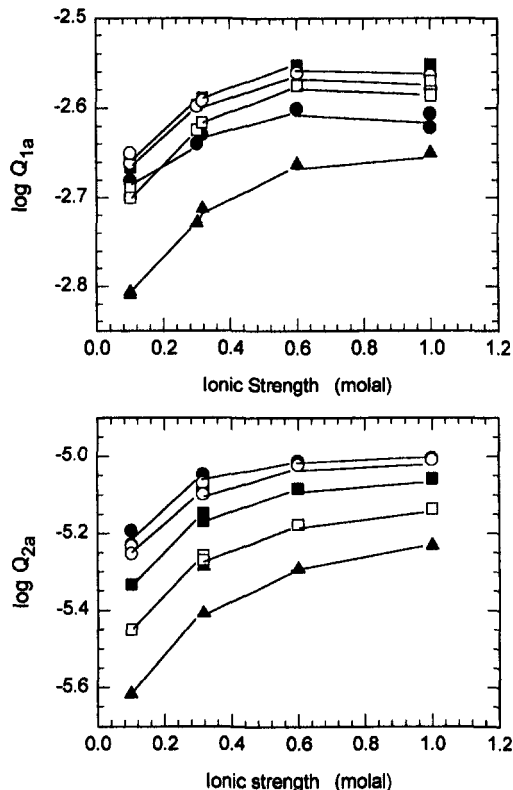
$$H_2CH_2C_2O_4 + OH^- \rightleftharpoons HCH_2C_2O_4^- + H_2O \tag{7}$$

$$HCH_2C_2O_4^- + OH^- \rightleftharpoons CH_2C_2O_4^{2-} + H_2O \tag{8}$$

Fig. 1. Dissociation quotients of malonic acid in the acid form, log Q_{1a} and log Q_{2a}, plotted as functions of ionic strength, where the symbols define the measured log Q_n values at temperatures of (●) 5, (○) 25, (■) 50, (□) 75, and (▲) 100°C. (The connecting lines have been drawn for reference only.)

The respective equilibrium quotients for these equilibrium reactions are

$$Q_{1b} = \frac{[HCH_2C_2O_4^-]}{[H_2CH_2C_2O_4][OH^-]} \tag{9}$$

$$Q_{2b} = \frac{[CH_2C_2O_4^{2-}]}{[HCH_2C_2O_4^-][OH^-]} \tag{10}$$

The equilibrium quotients for these two reactions (Tables IV and V) were modeled as a function of temperature and ionic strength using ORGLS, a nonlinear least-squares fitting routine.[37] The equation that best described the first dissociation reaction is
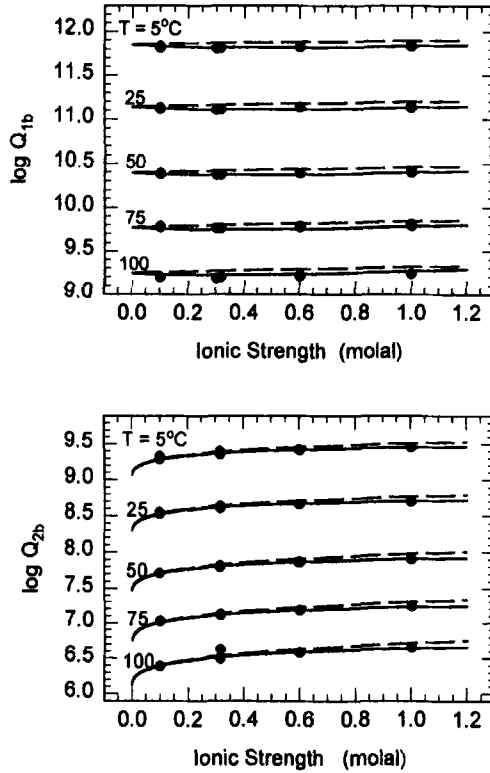
Fig. 2. The relationship between log Q_{1b} and log Q_{2b} and ionic strength, where the symbols define the measured log Q_{nb} values. The solid curves represent the dissociation of malonic acid in NaTr media and were derived from Eqs. (11, 12) for log Q_{1b} and log Q_{2b}, respectively; whereas the dashed curves were generated from the fits of Kettler et al.[30] for the dissociation of malonic acid in NaCl media.

$$\log Q_{1b} = -1.0652 + 3275.1/T + (4.0951 \times 10^{-3})T + (4.2354$$

$$\times 10^{-4})(IT) - 0.24516[1 - (1 + 2\sqrt{I})exp(-2\sqrt{I})] - \log(a_w) \quad (11)$$

whereas the second dissociation reaction is best described by

$$\log Q_{2b} = 2A_\varphi[\sqrt{I}/(1 + 1.2\sqrt{I}) + (2/1.2)\ln(1 + 1.2\sqrt{I})]/(\ln 10)$$

$$- 1.4093 + 3038.5/T - (1.6287 \times 10^{-3})T - (7.5316 \times 10^{-2})I$$

$$- 0.22111[1 - (1 + 2\sqrt{I})exp(-2\sqrt{I})] - \log(a_w) \quad (12)$$

where a_w is the activity of water, and the first term of Eq. (12) comprises the extended Debye–Hückel expression.[38] The first three terms in Eq. (11) and the second, third, and fourth terms in Eq. (12) determine the equilibrium

constants K_{1b} and K_{2b} at infinite dilution, respectively. These temperature terms are the same terms as defined by Kettler *et al.*[30] for the dissociation of malonic acid in NaCl media at infinite dilution, thereby maintaining consistent equilibrium constants (K_{1b} and K_{2b}) between this study and that of Kettler *et al.*[30] Isothermal curves generated from Eqs. (11, 12), and equivalent curves generated from the fits of Kettler *et al.*[30] for the dissociation of malonic acid in NaCl media are compared in Fig.2.

Differentiation of Eqs. (11, 12) with respect to temperature yields values for ΔH_b, ΔS_b, and ΔC_{pb}. The anionic equilibrium quotients and thermodynamic data were converted to the corresponding values for the dissociation reactions in Eqs. (1, 2) by adding the appropriate thermodynamic quantities for the dissociation of water in NaTr media.[27] These data, at selected temperatures and ionic strengths, are presented in Tables VI and VII, and exhibit the same trends as reported by Kettler *et al.*[30] for NaCl media. The estimated uncertainties recorded in Tables VI and VII represent three times the standard deviation derived from the measured dissociation quotients, combined with the error estimates reported for the dissociation of water.[27] Despite combining the error uncertainties in this manner, they are still small.

3.2. Association of Cadmium–Malonate

The effectiveness of the potentiometric technique as applied in determining the complexation of Cd^{2+} with malonate relies on the competition between H^+ and Cd^{2+} ions for association with the malonate anions. The concentration of hydrogen ions in the test solution, therefore, provides a quantitative indication of the degree of Cd–malonate complexation. As for experiments involving the measurement of the dissociation of malonic acid, the molal concentration of hydrogen ions in the test solution ($[H_{test}^+]$) can be calculated from the cell potential[39] and the Nernst equation, Eq. (3), with the liquid junction potential calculated from the Henderson equation.[34] Limiting equivalent conductance data for Cd^{2+} are required, but have not been measured over the conditions considered in this study. Therefore, limiting equivalent conductance data for Mg^{2+} were used to model the conductance values of Cd^{2+}.[40] The calculated liquid junction potentials were typically less than 2.0 mV, which contributed an uncertainty of <0.010 in the pH of the test solution, assuming that the Henderson equation predicts E_{LJ} to within 25%.[35]

The concentrations of hydrogen and malonate ($[Ma^{2-}]$) ions were calculated using an iterative process involving the Nernst expression, Eq. (3), the dissociation quotients of malonic acid, and a stepwise refinement of the E_{LJ} and ionic strength terms. Included in this algorithm were error estimates for temperature ($\pm$ 0.1°C), pump readings ($\pm$ 0.002 cm^{-3}), emf readings ($\pm$ 0.1 mV), and the dissociation of water and malonic acid. The expressions for

Table VI. Summary of Thermodynamic Quantities for the First Dissociation of Malonic
Acid at the Saturation Vapor Pressure of Water

°C	log Q_1	ΔH^a	ΔS^b	ΔC_p^b
		$I = 0.0$		
0	-2.909 ± 0.012	5.6 ± 0.3	-35.1 ± 0.9	-250 ± 14
25	-2.863 ± 0.007	0.2 ± 0.1	-54.3 ± 0.4	-190 ± 7
50	-2.889 ± 0.010	-4.0 ± 0.2	-67.6 ± 0.5	-146 ± 4
75	-2.954 ± 0.017	-7.3 ± 0.2	-77.4 ± 0.6	-119 ± 5
100	-3.041 ± 0.030	-10.1 ± 0.3	-85.3 ± 0.7	-110 ± 6
		$I = 0.1$		
0	-2.708 ± 0.012	5.6 ± 0.3	-31.1 ± 1.0	-250 ± 15
25	-2.652 ± 0.011	0.2 ± 0.2	-50.1 ± 0.5	-189 ± 7
50	-2.665 ± 0.011	-3.9 ± 0.2	-63.2 ± 0.6	-145 ± 4
75	-2.715 ± 0.011	-7.2 ± 0.2	-72.7 ± 0.7	-119 ± 6
100	-2.783 ± 0.011	-10.0 ± 0.3	-80.1 ± 0.8	-110 ± 6
		$I = 0.3$		
0	-2.651 ± 0.019	5.7 ± 0.4	-30.0 ± 1.2	-249 ± 15
25	-2.590 ± 0.017	0.3 ± 0.2	-48.7 ± 0.7	-187 ± 8
50	-2.595 ± 0.016	-3.9 ± 0.3	-61.6 ± 0.7	-144 ± 5
75	-2.635 ± 0.014	-7.1 ± 0.3	-70.8 ± 0.8	-117 ± 6
100	-2.692 ± 0.013	-9.8 ± 0.4	-77.9 ± 1.0	-108 ± 7
		$I = 0.5$		
0	-2.637 ± 0.021	5.7 ± 0.5	-29.7 ± 1.4	-247 ± 16
25	-2.571 ± 0.018	0.3 ± 0.4	-48.1 ± 1.0	-186 ± 8
50	-2.572 ± 0.016	-3.8 ± 0.4	-60.8 ± 1.1	-142 ± 6
75	-2.606 ± 0.014	-6.9 ± 0.4	-69.8 ± 1.1	-115 ± 7
100	-2.655 ± 0.015	-9.7 ± 0.5	-76.7 ± 1.4	-106 ± 7
		$I = 1.0$		
0	-2.643 ± 0.025	5.8 ± 0.7	-29.4 ± 2.5	-244 ± 17
25	-2.571 ± 0.022	0.5 ± 0.6	-47.6 ± 2.2	-182 ± 10
50	-2.563 ± 0.023	-3.5 ± 0.7	-59.8 ± 2.2	-138 ± 8
75	-2.586 ± 0.027	-6.6 ± 0.7	-68.3 ± 2.3	-111 ± 9
100	-2.623 ± 0.031	-9.2 ± 0.8	-74.8 ± 2.5	-101 ± 9

^{a}kJ-mol^{-1}.
^{b}J-K^{-1}-mol^{-1}.

the dissociation of malonic acid were included in the iterative algorithm in
order to speciate the malonic acid in the test solutions. Establishing the
speciation of malonic acid was most significant at the start of the experiments
when the pH of the test solution was low (pH <3), because malonate added
from the titrant solution is largely protonated to form malonic acid and
bimalonate (Fig. 3). As a titration proceeded, the pH increased and Ma^{2-}
became the dominant species (Fig. 3).[39] The degree of complexation $\bar{n}$,

Table VII. Summary of Thermodynamic Quantities for the Second Dissociation of Malonic Acid at the Saturation Vapor Pressure of Water[a]

°C	log Q_2	ΔH	ΔS	ΔC_p
		$I = 0.0$		
0	−5.682 ± 0.008	2.0 ± 0.3	−101.5 ± 0.9	−310 ± 14
25	−5.707 ± 0.005	−5.0 ± 0.1	−126.2 ± 0.4	−255 ± 7
50	−5.815 ± 0.007	−10.9 ± 0.2	−145.0 ± 0.5	−217 ± 4
75	−5.971 ± 0.011	−16.0 ± 0.2	−160.3 ± 0.6	−196 ± 5
100	−6.155 ± 0.018	−20.8 ± 0.3	−173.7 ± 0.7	−192 ± 6
		$I = 0.1$		
0	−5.247 ± 0.011	1.9 ± 0.3	−93.3 ± 1.0	−310 ± 14
25	−5.253 ± 0.010	−5.1 ± 0.1	−117.6 ± 0.5	−255 ± 7
50	−5.336 ± 0.010	−10.9 ± 0.2	−136.0 ± 0.6	−216 ± 4
75	−5.462 ± 0.011	−16.1 ± 0.2	−150.7 ± 0.7	−195 ± 5
100	−5.611 ± 0.011	−20.9 ± 0.3	−163.3 ± 0.8	−192 ± 6
		$I = 0.3$		
0	−5.091 ± 0.015	1.8 ± 0.3	−90.7 ± 1.2	−310 ± 14
25	−5.089 ± 0.014	−5.2 ± 0.1	−114.8 ± 0.7	−254 ± 7
50	−5.159 ± 0.014	−11.0 ± 0.2	−132.9 ± 0.7	−216 ± 4
75	−5.270 ± 0.014	−16.1 ± 0.2	−147.2 ± 0.7	−195 ± 5
100	−5.400 ± 0.014	−20.9 ± 0.2	−159.4 ± 0.9	−191 ± 6
		$I = 0.5$		
0	−5.036 ± 0.016	1.8 ± 0.3	−90.0 ± 1.3	−310 ± 14
25	−5.028 ± 0.015	−5.3 ± 0.2	−113.9 ± 0.8	−254 ± 7
50	−5.092 ± 0.014	−11.1 ± 0.2	−131.8 ± 0.8	−215 ± 4
75	−5.194 ± 0.014	−16.2 ± 0.2	−145.9 ± 0.7	−194 ± 6
100	−5.313 ± 0.015	−21.0 ± 0.2	−157.8 ± 0.9	−191 ± 6
		$I = 1.0$		
0	−5.015 ± 0.030	1.5 ± 0.4	−90.4 ± 1.7	−308 ± 15
25	−5.001 ± 0.026	−5.4 ± 0.3	−114.0 ± 1.2	−253 ± 8
50	−5.056 ± 0.025	−11.2 ± 0.3	−131.5 ± 1.1	−214 ± 5
75	−5.145 ± 0.025	−16.3 ± 0.2	−145.2 ± 1.0	−193 ± 6
100	−5.249 ± 0.025	−21.0 ± 0.2	−156.8 ± 1.0	−189 ± 6

[a]Unit as in Table VI.

defined as the average number of malonate ions bound per Cd^{2+} ion, was calculated from:

$$\bar{n} = \frac{\Sigma n \, [Cd(Ma)_n^{2-2n}]}{m_{Cd^{2+}}}$$

$$= \frac{m_{Ma} - ([Ma^{2-}] + [HMa^-] + [H_2Ma])}{m_{Cd^{2+}}} \tag{13}$$
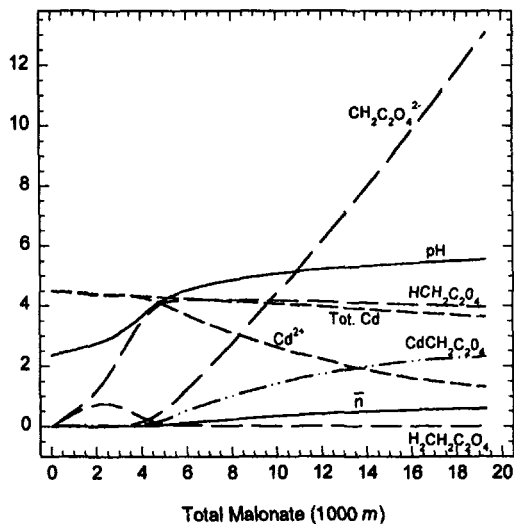
Fig. 3. Progress of a typical titration is shown on the ordinate as concentration, plotted as $1000m$ total Cd; free Cd^{2+}, malonic acid, bimalonate, malonate, Cd–malonate. Also included are the pH and the ligand number $\bar{n}$. The abscissa is $1000 \times$ total concentration of malonate. The results are for a titration performed at 50°C, 1.0 m ionic strength, and an initial total Cd concentration of 4.5×10^{-3} m.

$$= \frac{m_{Ma} - [Ma^{2-}]\left(1 + \dfrac{[H^+]^2}{Q_1 Q_2} + \dfrac{[H^+]}{Q_2}\right)}{m_{Cd^{2+}}}$$

where the numerator reflects all malonate bound to Cd^{2+}, and the denominator is the total stoichiometric concentration of Cd^{2+}, $m_{Cd^{2+}}$. The concentration of associated malonate is given by the initial stoichiometric concentration of malonic acid, m_{Ma}, minus the calculated molality of malonate, bimalonate, and malonic acid; $[H^+]$, Q_1, and Q_2 represent the calculated molality of hydrogen ions and the dissociation quotients of malonic acid, respectively. No corrections for the effect of Cd hydrolysis were included in the above expression, as the concentrations of Cd-hydrolysis species were insignificant at the pH conditions considered in this study:[24,34] the ratio of $[CdOH^+]$ to $[Cd^{2+}]$ will exceed 1:1000 only when the solution pH exceeds 7 at all temperatures studied. The maximum calculated $\bar{n}$ values were typically <0.8. In order to establish the speciation and formation quotients of complexes formed between Cd^{2+} and malonate, all $\bar{n}$ values <0.6, computed for a given titration, were regressed using the simultaneous nonlinear least-squares fitting routine of Busing and Levy.[37] A single Cd-malonate complex was identified and is represented by the formation equilibrium:

$$Cd^{2+} + CH_2C_2O_4^{2-} \rightleftharpoons CdCH_2C_2O_4 \qquad (14)$$

The stoichiometric formation quotient Q for this reaction is

$$Q = \frac{[CdCH_2C_2O_4]}{[Cd^{2+}][CH_2C_2O_4^{2-}]} \qquad (15)$$

The molal formation quotients resulting from these calculations are given in Table VIII. The formation of Cd–bimalonate species $(Cd(HMa)_n^{2-n})$ was expected to be negligible at the pH conditions employed in this study. The titration data were, however, fitted such that $\bar{n}$, Eq. (13), was defined as the average number of bimalonate ions bound per Cd ion; negative $\bar{n}$ values were obtained at all conditions. These negative $\bar{n}$ values indicate that Cd–

Table VIII. Experimental Association Quotients for the Formation of $CdCH_2C_2O_4$ Complexes

Titr. #	$\log Q^a$	°C	I^b	$E_{LJ}max^c$
14	2.574 ± 0.025	49.98	0.1006	1.73
17	2.523 ± 0.022	5.09	0.0999	2.02
18	2.477 ± 0.017	24.87	0.1006	1.85
19	2.835 ± 0.008	74.69	0.1005	1.59
20	2.624 ± 0.018	49.92	0.1006	1.72
21	2.282 ± 0.045	24.89	0.3075	1.22
22	2.332 ± 0.044	49.92	0.3076	1.12
23	2.734 ± 0.029	74.92	0.3065	1.10
24	2.182 ± 0.056	5.02	0.3079	1.33
25	2.181 ± 0.047	5.02	0.3079	1.33
41	1.821 ± 0.121	24.80	0.6060	0.78
42	1.889 ± 0.069	4.96	0.6029	0.86
43	2.144 ± 0.031	74.77	0.6057	0.66
44	1.829 ± 0.098	49.80	0.6241	0.73
45	1.644 ± 0.204	24.81	0.6062	0.79
46	1.924 ± 0.046	49.76	0.6050	0.72
29	2.062 ± 0.013	49.92	1.0276	0.42
30	2.127 ± 0.056	74.85	1.0257	0.38
31	1.721 ± 0.080	4.98	1.0280	0.50
32	1.777 ± 0.012	24.79	1.0513	0.46
33	1.938 ± 0.035	24.79	1.0100	0.61
34	2.167 ± 0.020	74.79	1.0078	0.56
36	2.005 ± 0.021	49.90	1.0105	0.59
37	1.847 ± 0.060	5.00	1.0083	0.66
38	2.015 ± 0.078	74.77	1.0119	0.40

^{a} The error estimates associated with Q result from the nonlinear least-squares fitting routine for each titration.
^{b} mol-kg^{-1}.
^{c} mV.

bimalonate is not a viable species, thus confirming the identification of a Cd–malonate species.

The derived CdMa association quotients were then regressed as a function of temperature and ionic strength. The empirical equation that best described the data is

$$\log Q = \frac{-\Delta z^2 A_\varphi}{\ln(10)} \left\{ \frac{\sqrt{I}}{(1 + b\sqrt{I})} + \left(\frac{\alpha}{b}\right) \ln(1 + b\sqrt{I}) \right\} - 127.77 + \frac{5510.4}{T}$$

$$+ 19.787 \log(T) + (3.4478 \times 10^{-3})\, IT - 70.862\, I^2/T \qquad (16)$$

where the first term is the extended Debye–Hückel expression from Pitzer,[38] and includes α, b and A_φ taken from Bradley and Pitzer,[41] and $\Delta z^2 = -8$. The equilibrium constant at infinite dilution is defined by the second, third, and fourth terms of Eq. (16), with the fifth and sixth terms required to fit the deviation from the Debye–Hückel expression. Results of this fitting procedure are shown in Fig. 4. Agreement between the modeled and observed values is good at 0.1 m ionic strength, but becomes poorer at higher ionic strengths. The poorer agreement at 0.6 and 1.0 m ionic strength results from the large experimental uncertainties and the poor reproducibility between titrations (Table VIII, Fig. 4), which result largely from the small $\bar{n}$ values, reflective of the weakness of the complex at high ionic strength. Although the association quotients increase in stability with increasing temperature and
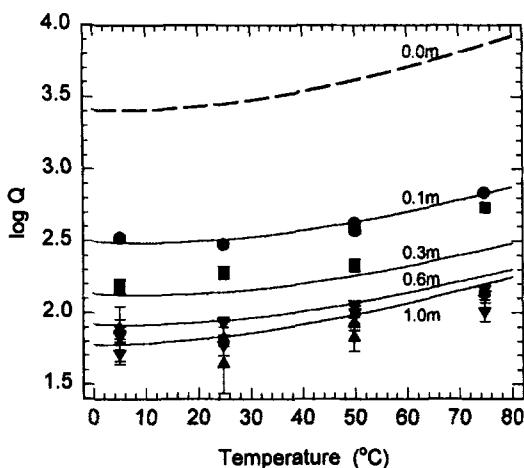

Fig. 4. Association quotients, log Q, for the formation of Cd–malonate (CdCH$_2$C$_2$O$_4$) plotted as a function of temperature, where the symbols define the measured log Q values at ionic strengths of (●) 0.1, (■) 0.3, (▲) 0.6, and (▼) 1.0 molal. The curves were computed from Eq. (16), and the dashed line represents association constants at infinite dilution, also computed from Eq. (16).

decreasing ionic strength, the temperature dependence is small: less than 0.5 log units separates the 5°C association quotient values from those at 75°C (Table VIII).

The association quotients listed in Table IX, at selected temperatures and ionic strengths, were calculated from Eq. (16); whereas the thermodynamic quantities, ΔH, ΔS, and ΔC_p were determined by differentiating Eq. (16) with respect to temperature. It is clearly apparent from the thermodynamic parameters that the complexation reaction is driven by the large positive changes in entropy, which offset the positive ΔH values. This behavior is typical of complexation reactions in which electrostricted water is released.[28,33] An extensive comparison of these data with literature values was not possible, because as previously noted, literature data are limited (Table I) and measurements performed in NaCl media

Table IX. Summary of Thermodynamic Quantities for the Formation of $CdCH_2C_2O_4$ at the Saturation Vapor Pressure of Water[a]

°C	log Q^b	ΔH	ΔS	ΔC_p
		$I = 0.0$		
0	3.41 ± 0.16	−2 ± 14	58 ± 49	400 ± 300
25	3.45 ± 0.09	7 ± 6	91 ± 22	400 ± 300
50	3.62 ± 0.09	17 ± 4	122 ± 14	400 ± 300
75	3.87 ± 0.09	26 ± 12	150 ± 34	400 ± 300
		$I = 0.1$		
0	2.50 ± 0.16	−2 ± 14	42 ± 49	400 ± 300
25	2.51 ± 0.08	80 ± 6	75 ± 22	400 ± 300
50	2.63 ± 0.08	18 ± 4	105 ± 13	400 ± 300
75	2.83 ± 0.06	27 ± 12	132 ± 34	400 ± 300
		$I = 0.3$		
0	2.14 ± 0.17	−1 ± 14	39 ± 49	400 ± 300
25	2.14 ± 0.10	9 ± 6	72 ± 22	400 ± 300
50	2.26 ± 0.09	19 ± 4	102 ± 12	400 ± 300
75	2.44 ± 0.07	29 ± 11	130 ± 33	400 ± 300
		$I = 0.5$		
0	1.98 ± 0.18	1 ± 14	41 ± 49	400 ± 300
25	1.99 ± 0.11	11 ± 6	74 ± 22	400 ± 300
50	2.11 ± 0.11	21 ± 4	104 ± 12	400 ± 300
75	2.30 ± 0.10	31 ± 11	132 ± 33	400 ± 300
		$I = 1.0$		
0	1.78 ± 0.20	4 ± 15	50 ± 50	400 ± 300
25	1.84 ± 0.06	15 ± 7	84 ± 24	400 ± 300
50	1.99 ± 0.07	25 ± 5	116 ± 16	400 ± 300
75	2.20 ± 0.11	36 ± 12	145 ± 35	400 ± 300

[a] Units as in Table VI.
[b] The errors listed represent three times the standard deviation.

may underestimate the formation quotients. However, Campi[15] reported an association quotient of log $Q = 2.51$ for CdMa, at 20°C and $0.1M$ ionic strength in NaClO$_4$ media (Table I), which is in exact agreement with the value calculated in this study of log $Q = 2.50$, at 20°C and $0.1m$ ionic strength. In addition, Campi[15] reported an association quotient of log $Q = 1.05$ for the formation of CdHMa$^+$ (Table I). The CdHMa$^+$ species should be significant at low pH, corresponding to conditions at the start of each titration performed in this study (Fig. 3).[39] However, the total malonate concentration is low and the formation of a Cd–bimalonate complex could not be detected in the regression analysis of the titration curves.

The equilibrium quotients obtained in this study can be combined with similar quantities for competing reactions to model the speciation of cadmium as a function of temperature and ionic strength. For example, the effect of Cd–Cl complexation and Cd hydrolysis on the speciation of cadmium is shown in the speciation plots in Fig. 5, at 25°C and infinite dilution; equilibrium constants used to construct the plots are given in Table X. The formation of Cd-hydrolysis species are negligible at pH values typically encountered in natural waters (Fig. 5a), as CdOH$^+$ starts forming above a pH of 7 to 7.5, and additional hydrolysis species form only above pH 9. At a pH of 6 (Figs. 5b and 5c) there is considerable competition between CH$_2$C$_2$O$_4^{2-}$ and Cl$^-$ ions for complexation with Cd^{2+}. The speciation of Cd is dominated by the formation of Cd–chloride species when [Cl$^-$] exceeds [CH$_2$C$_2$O$_4^{2-}$] by two orders of magnitude, as would be the case in most natural waters. The contribution of free Cd^{2+} to the total concentration of Cd is typically small, even at low concentrations of CH$_2$C$_2$O$_4^{2-}$ and Cl$^-$ ions. It must be noted that changing any variable, such as pH, temperature, ionic strength, and the total concentration of malonic acid, used to compute the plots in Fig. 5(a–c) would change the Cd speciation. Furthermore, the addition of competing metals would significantly influence the speciation of Cd. It is apparent from these speciation plots that even low concentrations of malonic acid (and by analogy other dicarboxylic acids) in natural aqueous solutions may influence the speciation, hence the bioavailability and toxicity, of cadmium.

4. CONCLUSIONS

In a two-part potentiometric study, the dissociation quotients of malonic acid were measured in NaTr media, allowing the association quotients for the complexation of Cd^{2+} with malonate to be determined. The temperature and ionic strength dependencies of the malonic acid dissociation reactions were modeled by empirical equations, such that the equilibrium constants (K_1 and K_2) were consistent with the dissociation constants of malonic acid in NaCl media.[30] These equations provide an accurate model for the behavior of malonic acid
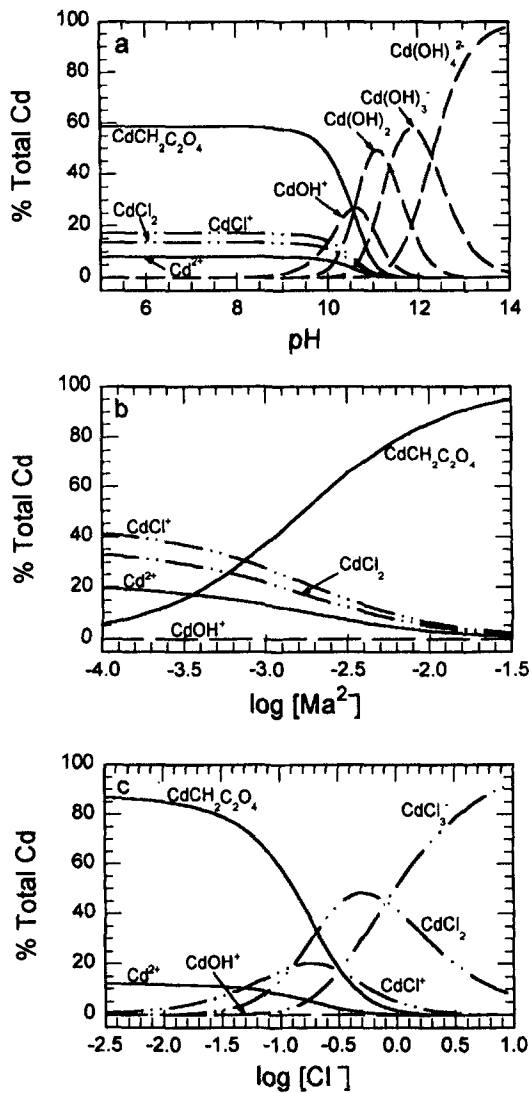
Fig. 5. Cadmium speciation at 25°C, infinite dilution and $[\Sigma Cd] = 0.005$ m; plotted as a function of pH, the logarithm of chloride, and the logarithm of free malonate: (a) $[Cl^-] = 0.1$ m and $[CH_2C_2O_4^{2-}] = 0.0025$ m; (b) pH = 6 and $[Cl^-] = 0.1$ m; and (c) pH = 6 and $[CH_2C_2O_4^{2-}] = 0.0025$ m.

Table X. Equilibrium Constants, at 25°C and Infinite Dilution, Used in Speciation Calculations

Reaction	log K	Ref.
$H_2O \rightleftharpoons H^+ + OH^-$	-13.993	42
$Cd^{2+} + CH_2C_2O_4^{2-} \rightleftharpoons CdCH_2C_2O_4$	3.453	This study
$Cd^{2+} + Cl^- \rightleftharpoons CdCl^+$	1.32	24
$Cd^{2+} + 2Cl^- \rightleftharpoons CdCl_2$	2.22	24
$Cd^{2+} + 3Cl^- \rightleftharpoons CdCl_3^-$	2.31	24
$Cd^{2+} + OH^- \rightleftharpoons CdOH^+$	4.30	24
$Cd^{2+} + 2OH^- \rightleftharpoons Cd(OH)_2$	7.70	24
$Cd^{2+} + 3OH^- \rightleftharpoons Cd(OH)_3^-$	10.30	24
$Cd^{2+} + 4OH^- \rightleftharpoons Cd(OH)_4^{2-}$	12.00	24

over a wide range of temperatures and ionic strength; such data were necessary to interpret accurately the results of the Cd–malonate complexation study.

A single Cd–malonate species ($CdCH_2C_2O_4$) was identified from the complexation study. The Cd–malonate association quotients were modeled by an empirical equation, comprising the extended Debye–Hückel expression and variable temperature and ionic strength parameters. The thermodynamic quantities (ΔH, ΔS, and ΔC_p) obtained by differentiating the empirical equation with respect to temperature showed the trends typical of previous complexation studies.[28,29,33] The results of this study provide a model for the behavior and speciation of Cd–malonate in aqueous solutions and can be used to understand the importance and effects of malonic acid (and by analogy other dicarboxylic acids) on the bioavailability, and, hence, the toxicity of Cd^{2+} in the environment.

ACKNOWLEDGMENT

REFERENCES

1. D. C. Adriano, *Trace Elements in the Terrestrial Environment*, (Springer-Verlag, NY, 1986), p. 106.
2. R. Blust, M. Baillieul, and W. Decleir, *Marine Biol.* **123**, 65 (1995).
3. S. L. Brown, R. L. Chaney, J. S. Angle, and A. J. M. Baker, *Environ. Sci. Technol.* **29**, 1581 (1995).

4. A. P. Jackson and B. J. Alloway, in *Biogeochemistry of Trace Metals*, D. C. Adriano, ed. (Lewis Publishers, 1992), p. 109.

5. M. F. Benedetti, W. H. Van Riemsdijk, L. K. Koopal, D. G. Kinniburgh, D. C. Gooddy, and C. J. Milne, *Geochim. Cosmochim. Acta* **60**, 2503 (1996).

6. M. G. Hickey and J. A. Kittrick, *J. Environ. Qual.* **13**, 372 (1984).

7. C. Papelis, *Environ. Sci. Technol.* **29**, 1526 (1995).

8. S. Bardhan and S. Aditya, *J. Indian Chem. Soc.* **32**, 102 (1955).

9. J. I. Drever and G. F. Vance, in *Organic Acids in Geological Processes* (E. D. Pittman and M. D. Lewan, Eds.) (Springer-Verlag, NY, 1994), p. 138

10. J. B. Fein, *Geochim. Cosmochim. Acta* **55**, 955 (1991).

11. J. B. Fein and P. V. Brady, *Chem. Geol.* **121**, 11 (1995).

12. T. H. Giordano, in *Organic Acids in Geological Processes*, E. D. Pittman and M. D. Lewan, Eds.) (Springer-Verlag, NY, 1994), p. 319.

13. R. J. C. Hennet, D. A. Crerar, and J. Schwartz, *Economic Geol.* **83**, 742 (1988).

14. H. Morgan and D. L. Simms, *Sci. Total Environ.* **75**, 135 (1988).

15. E. Campi, *Ann. Chim.* **53**, 96 (1963).

16. H. L. Riley and N. I. Fisher, *J. Chem. Soc.*, p. 2006 (1929).

17. R. W. Money and C. W. Davies, *Trans. Faraday Soc.* **28**, 609 (1932).

18. E. Ferrel, J. H. Ridgion, and H. L. Riley, *J. Chem. Soc.*, p. 1440 (1934).

19. D. I. Stock and C. W. Davies, *J. Chem. Soc.*, p. 1371 (1949).

20. M. Yasada, K. Yamaskai, and H. Ohtaki, *Bull. Chem. Soc. Jpn.* **33**, 1067 (1960).

21. G. D'Amore and G. Sergi, *Ann. Chim.* **54**, 327 (1964).

22. G. D'Amore and G. Sergi, *Ann. Chim.* **54**, 424 (1964).

23. J. J. Christensen and R. M. Izatt, *Handbook of Metal Ligand Heats and Related Thermodynamic Quantities* (Marcel Decker, NY, 1970), p. 234.

24. H. C. H. Hahne and W. Kroontje, *J. Environ. Qual.* **2**, 444 (1973).

25. J. F. W. Mosslemans, P. F. Schofield, J. M. Charnock, C. D. Garner, R. A. D. Pattrick, and D. J. Vaughan, *Chem. Geol.* **127**, 339 (1996).

26. P. C. Ho and D. A. Palmer, *J. Solution Chem.* **24**, 753 (1995).

27. D. A. Palmer and S. E. Drummond, *J. Solution Chem.* **17**, 153 (1988).

28. T. H. Giordano and S. E. Drummond, *Geochim. Cosmochim. Acta* **55**, 2401 (1991).

29. D. A. Palmer and S. E. Drummond, *J. Phys. Chem.* **92**, 6795 (1988).

30. R. M. Kettler, D. J. Wesolowski, and D. A. Palmer, *J. Solution Chem.* **21**, 883 (1992).

31. D. A. Palmer and D. J. Wesolowski, *Geochim. Cosmochim. Acta* **57**, 2929 (1993).

32. R. M. Kettler, D. A. Palmer, and D. J. Wesolowski, *J. Solution Chem.* **20**, 905 (1991).

33. D. A. Palmer and J. L. S. Bell, *Geochim. Cosmochim. Acta* **58**, 651 (1994).

34. C. F. Baes, Jr. and R. E. Mesmer, *The Hydrolysis of Cations* (Krieger, 1976), p. 489.

35. R. E. Mesmer and H. F. Holmes, *J. Solution Chem.* **21**, 725 (1992).

36. A. S. Quist and W. L. Marshall, *J. Phys. Chem.* **69**, 2984 (1965).

37. W. R. Busing and H. A. Levy, *A General Fortran Least Squares Program*, Oak Ridge National Laboratory Report ORNL-TM-271 (1962).

38. K. S. Pitzer, *J. Phys. Chem.* **77**, 268 (1973).

39. M. K. Ridley, Ph.D. dissertation, (Univ. Nebraska, 1997).

40. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths, 1959).

41. D. J. Bradley and K. S. Pitzer, *J. Phys. Chem.* **83**, 1599 (1979).

42. R. H. Busey and R. E. Mesmer, *J. Chem. Eng. Data* **23**, 175 (1978).