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Dissociation Constants of Oxalic Acid in Aqueous Sodium Chloride and Sodium Trifluoromethanesulfonate Media to 175 °C

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The first and second molal dissociation constants of oxalic acid were measured potentiometrically in a concentration cell fitted with hydrogen electrodes. Measurements were made at six temperatures ranging from 5 °C to 125 °C at four ionic strengths ranging from 0.1 mol·kg^{-1} to 1.0 mol·kg^{-1} (NaCl and $NaCF_3SO_3$). The second molal dissociation constant was measured in $NaCF_3SO_3$ media only. The data obtained in this study were combined with the corresponding literature values, including a number of recalculated Harned cell and concentration cell measurements and previous results from this laboratory. Data for first molal dissociation constant obtained in the two ionic media were regressed simultaneously to yield a five-term equation that describes the dissociation in the anionic form. The thermodynamic properties obtained at 25 °C and infinite dilution are: $\log K_{1a}^{\ominus} = -1.401 \pm 0.052$, $\Delta H_{1a} = (-0.7 \pm 0.7)$ kJ·mol^{-1}, $\Delta S_{1a} = (-29 \pm 2)$ J·K^{-1}·mol^{-1}, and $\Delta C_{p,1a} = (-231 \pm 6)$ J·K^{-1}·mol^{-1}. Similar treatment of the original and recalculated data for the second molal dissociation constant yielded a nine-term equation and the following values at 25 °C and infinite dilution: $\log K_{2a}^{\ominus} = -4.264 \pm 0.014$, $\Delta H_{2a} = (-7.3 \pm 0.5)$ kJ·mol^{-1}, $\Delta S_{2a} = (-106 \pm 2)$ J·K^{-1}·mol^{-1}, and $\Delta C_{p,2a} = (-229 \pm 27)$ J·K^{-1}·mol^{-1}.

Introduction

Ethanedioic acid (oxalic acid) is an important biochemical and industrial compound. It is ubiquitous in soils where its concentration is buffered by the presence of the minerals whewellite ($CaC_2O_4{\cdot}H_2O$) and weddelite ($CaC_2O_4{\cdot}2H_2O$), and it plays a significant role in nutrient availability (Graustein et al., 1977). Because of its ability to form strong complexes with metals, oxalic acid is used to decontaminate the cooling circuits of water-cooled nuclear reactors (Ayres, 1970), and there is considerable interest in the use of oxalic acid to clean kaolin and quartz sand for use by the ceramic industry (Vegliò et al., 1996; Ubaldini et al., 1996). The biochemical, geochemical, and industrial significance of oxalic acid have led to significant interest in the behavior of the compound in high-temperature water (e.g., Bayri et al. (1996)). A recent report (Kettler et al., 1991) from this laboratory examined the dissociation of oxalic acid following the reactions

$$H_2C_2O_4 = HC_2O_4^- + H^+ \tag{1}$$

and

$$HC_2O_4{}^- = C_2O_4^{2-} + H^+ \tag{2}$$

in aqueous sodium chloride media to 175 °C. The respective molal dissociation constants for eqs 1 and 2 are defined as

$$K_{m,1a} = [HC_2O_4^-][H^+]/[H_2C_2O_4] \tag{3}$$

and

$$K_{m,2a} = [C_2O_4^{2-}][H^+]/[HC_2O_4^-] \tag{4}$$

The standard equilibrium constants for eqs 1 and 2 are $K_{1a}^{\ominus}$ and $K_{2a}^{\ominus}$, respectively, and are defined in the usual way (Mills et al., 1993). The standard state used in this paper is a 1 mol·kg^{-1} solution behaving as though it were infinitely dilute at the saturation vapor pressure for water at the temperature of interest.

It is difficult to prepare oxalic acid solutions that have low ionic strength: the acid is a strong one and contributes hydrogen, bioxalate, and oxalate ions to the solution. Therefore, the fitting process in the earlier report (Kettler et al., 1991) relied heavily on previously published data (Table 1) in order to extrapolate the molal dissociation constants to infinite dilution. These data included conductance measurements at 25 °C (Darken, 1941), glass electrode measurements (Kurz and Farrar, 1969), potentiometric data obtained using electrochemical cells without liquid junctions (Parton and Gibbons, 1939; McAuley and Nancollas, 1961), and titration calorimetry measurements (Christensen et al. 1967). The generally accepted value for $pK_{1a,298}^{\ominus}$ is 1.25 (Martell and Smith, 1977) and is derived largely from the McAuley and Nancollas (1961) measurements (Table 1). The acceptance of a single value for $pK_{1a,298}^{\ominus}$ belies the wide variety of results reported for the first dissociation at 25 °C and low values of ionic strength. Measurements in 0.1 mol·kg^{-1} $NaClO_4$ yield $pK_{m,1a}$ values as high as 1.37 (Table 1) (McAuley and Nancollas, 1960), a value that will increase if extrapolated to infinite dilution.

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Table 1. Selected Thermodynamic Data for the Dissociation of Oxalic Acid

$-\log K_{m,1a}$	ΔH_{1a}/(kJ·mol^{-1})	$-\log K_{m,2a}$	ΔH_{2a}/(kJ·mol^{-1})	t/°C	I/(mol·kg^{-1})	reference
1.299[a]		4.300		25	0	Parton and Gibbons (1939)
1.271[a]		4.275[a]		25	0	Darken (1941)
1.42		4.28		25	0	Choppin and Chen (1996)
1.28		3.65		25	0.529 ($NaClO_4$)	Choppin and Chen (1996)
1.33		3.60		25	1.073 ($NaClO_4$)	Choppin and Chen (1996)
1.244[a]				0	0	McAuley and Nancollas (1961)
1.252[a]				15	0	McAuley and Nancollas (1961)
1.252[a]				25	0	McAuley and Nancollas (1961)
1.286[a]				35	0	McAuley and Nancollas (1961)
1.295[a]				45	0	McAuley and Nancollas (1961)
1.30[a]	−3.35			25	0	Kurz and Farrar (1969)
1.31[a]				30	0	Kurz and Farrar (1969)
1.32[a]				35	0	Kurz and Farrar (1969)
1.33[a]				40	0	Kurz and Farrar (1969)
1.34[a]				45	0	Kurz and Farrar (1969)
1.36[a]				50	0	Kurz and Farrar (1969)
1.36[a]				55	0	Kurz and Farrar (1969)
		4.228[a]	−1.16	0	0	Harned and Fallon (1939)
		4.235[a]	−2.10	5	0	Harned and Fallon (1939)
		4.244[a]	−4.15	10	0	Harned and Fallon (1939)
		4.255[a]	−5.29	15	0	Harned and Fallon (1939)
		4.268[a]	−5.29	20	0	Harned and Fallon (1939)
		4.286[a]	−6.49	25	0	Harned and Fallon (1939)
		4.308[a]	−7.77	30	0	Harned and Fallon (1939)
		4.331[a]	−9.11	35	0	Harned and Fallon (1939)
		4.356[a]	−10.54	40	0	Harned and Fallon (1939)
		4.388[a]	−12.04	45	0	Harned and Fallon (1939)
		4.417[a]	−13.62	50	0	Harned and Fallon (1939)
		4.201[a]	−1.447	0	0	Pinching and Bates (1948)
		4.207[a]	−2.508	5	0	Pinching and Bates (1948)
		4.218[a]	−3.587	10	0	Pinching and Bates (1948)
		4.231[a]	−4.686	15	0	Pinching and Bates (1948)
		4.247[a]	−5.804	20	0	Pinching and Bates (1948)
		4.266[a]	−6.941	25	0	Pinching and Bates (1948)
		4.287[a]	−8.098	30	0	Pinching and Bates (1948)
		4.312[a]	−9.274	35	0	Pinching and Bates (1948)
		4.338[a]	−10.47	40	0	Pinching and Bates (1948)
		4.369[a]	−11.68	45	0	Pinching and Bates (1948)
		4.399[a]	−12.92	50	0	Pinching and Bates (1948)
	−4.27 ± 0.21[a]		−6.28 ± 0.21[a]	25	0	Christensen et al. (1967)
1.37		3.81		25	0.10 ($NaClO_4$)	McAuley and Nancollas (1960)
1.33		3.94		25	0.15 ($NaClO_4$)	de Bruin et al. (1962)
1.20		3.67		25	0.50 ($NaClO_4$)	Bauer and Smith (1965)
1.07		3.57		25	1.0 ($NaClO_4$)	Bottari and Ciavatta (1965)
1.08		3.554		25	1.0 ($NaClO_4$)	Moorhead and Sutin (1966)
1.1		3.62		25	1.0 (KNO_3)	Rajan and Martell (1967)
0.89		3.51		25	1.0 (NaCl)	Cruywagen et al. (1986)

[a] Datum was used in the fitting process by Kettler et al. (1991).

Moreover, Choppin and Chen (1996) have reported a value of 1.42 for p$K^{\ominus}_{1a,298}$ recently.

Subsequent to the earlier report (Kettler et al., 1991), measurements of $K_{m,1a}$ and $K_{m,2a}$ were made in aqueous sodium trifluoromethanesulfonate (Na-triflate) media in this laboratory. These later measurements are inconsistent with the low-temperature (<75 °C) extrapolations published in the earlier report and have prompted a reexamination of the data in the earlier report as well as those data available in the literature for this system. This paper reports the measurement of $K_{m,1a}$ and $K_{m,2a}$ in Na-triflate media, the results of additional measurements of $K_{m,1a}$ in aqueous NaCl media, and the results of a fitting process that incorporates values obtained by recalculating and refitting previously published data. An improved set of equations describing the dissociation of oxalic acid is given as is a significant revision in the widely accepted value for p$K^{\ominus}_{1a}$ at 25 °C.

Experimental Section

Materials. Stock solutions of HCl, NaOH, and NaCl were prepared using reagent-grade chemicals and water that had been purified in a Barnstead four-stage deionizing/purification system to yield water with a resistivity of 0.18 MΩ·m (Palmer and Wesolowski, 1993). The stock solutions were sparged and stored under argon. Concentrated reagent-grade (Aldrich Chemical Co., lot AQ06628DN) trifluoromethanesulfonic (triflic) acid was purified by vacuum distillation (Palmer and Drummond, 1988). Crystalline Na-triflate was synthesized by reacting concentrated triflic acid with an equivalent amount of concentrated NaOH and recrystallizing the resulting solid from an ethanolic solution (Palmer and Drummond, 1988). Stock solutions of the acid and salt were prepared by combining the purified analyte with water. Stock solutions of oxalic acid were prepared from reagent-grade $H_2C_2O_4{\cdot}2H_2O$ (Mallinckrodt, lot NTP) and water. The concentrations of all stock solutions were measured by acidimetric titration (after cation exchange when necessary) with the NaOH stock solution.

Ratios of total oxalate to supporting electrolyte ranged from 1:8.6 in the most dilute solutions to 1:94 in the more concentrated solutions (Tables 2 and 3). Ratios of acid to supporting electrolyte in the reference solutions were varied depending on whether the experiments were designed to measure the first or second molal dissociation

Table 2. Starting Molal Solution Compositions for Experiments in Aqueous Sodium Chloride Media

	test cell			reference cell	
expt	m(NaCl)/(mol·kg^{-1})	m($H_2C_2O_4$)/(mol·kg^{-1})	m(HCl)/(mol·kg^{-1})	m(HCl)/(mol·kg^{-1})	m(NaCl)/(mol·kg^{-1})
20, 40	0.086 483	0.010 01	0.004 999	0.005 143	0.094 864
37, 38	0.301 76	0.009 993 5	0.005 103 8	0.004 999 8	0.310 02
49	0.942 41	0.014 993	0.049 957	0.050 019	0.950 69
51	0.564 99	0.008 989	0.029 950	0.029 992	0.570 04
52	0.564 55	0.008 982	0.029 927	0.029 980	0.569 82

Table 3. Starting Molal Solution Compositions for Experiments in Aqueous Sodium Trifluoromethanesulfonate Media

	test cell				reference cell	
expt	m(NaTr)/(mol·kg^{-1})	m($H_2C_2O_4$)/(mol·kg^{-1})	m(HTr)/(mol·kg^{-1})	m(NaOH)/(mol·kg^{-1})	m(HTr)/(mol·kg^{-1})	m(NaTr)/(mol·kg^{-1})
6	0.079 57	0.010 24		0.015 27	0.005 018	0.095 06
8	0.079 38	0.010 25		0.015 37	0.005 018	0.095 07
16, 17	0.087 90	0.010 20	0.005 097		0.005 018	0.095 07
18, 19	0.087 90	0.010 20	0.005 097		0.004 999	0.095 05
21, 22	0.301 9	0.010 00	0.005 004		0.005 263	0.310 6
23, 24	0.585 8	0.010 01	0.005 004		0.004 999	0.594 9
25, 26	0.944 4	0.009 999	0.049 99		0.05 000	0.950 0
27	0.079 98	0.010 01		0.015 02	0.099 99	0.098 33
28	0.079 98	0.010 01		0.015 02	0.000 833 1	0.099 14
44	0.969 8	0.014 99		0.022 09	0.004 898	0.996 3
45	0.582 2	0.008 998		0.013 26	0.002 934	0.596 8
46	0.253 0	0.009 995		0.014 79	0.001 335	0.271 6
47	0.582 4	0.009 002		0.013 26	0.004 999	0.594 9
48	0.306 5	0.004 737		0.006 980	0.005 263	0.310 6

Table 4. Experimental Results for the First Dissociation of Oxalic Acid in Aqueous Sodium Chloride Media

expt	t/°C	I/(mol·kg^{-1})	E·10^3/V	$E_{lj}{}^{a}$·10^3/V	pH^b	$\bar{n}$	$\sigma_{\bar{n}}$	log $K_{m,1a}$	σ_{1a}	log $K_{m,1b}$	σ_{1b}
20	4.96	0.100	−17.83	−4.68	1.881	1.185	0.108	−1.271	0.296	13.249	0.302
	24.89	0.100	−19.64	−4.40	1.882	1.190	0.089	−1.282	0.235	12.497	0.241
	49.77	0.100	−21.73	−4.07	1.886	1.201	0.072	−1.310	0.183	11.738	0.189
	74.81	0.099	−23.69	−3.73	1.891	1.217	0.059	−1.351	0.142	11.117	0.148
	100.10	0.099	−25.65	−3.41	1.896	1.231	0.048	−1.385	0.112	10.613	0.118
	125.12	0.099	−26.78	−3.10	1.910	1.272	0.039	−1.489	0.083	10.136	0.089
37	5.03	0.316	−22.66	−1.88	1.856	1.118	0.035	−1.051	0.098	13.402	0.107
	24.84	0.316	−24.46	−1.73	1.858	1.123	0.029	−1.068	0.080	12.645	0.089
	49.85	0.316	−26.65	−1.57	1.861	1.132	0.025	−1.089	0.066	11.882	0.075
	74.90	0.316	−28.52	−1.41	1.868	1.154	0.020	−1.159	0.051	11.222	0.060
	100.03	0.315	−30.21	−1.25	1.876	1.180	0.017	−1.238	0.039	10.665	0.048
	124.98	0.315	−31.51	−1.13	1.887	1.215	0.014	−1.338	0.031	10.178	0.040
38	5.12	0.316	−22.67	−1.88	1.856	1.118	0.035	−1.050	0.098	13.399	0.107
	24.96	0.316	−24.49	−1.73	1.858	1.122	0.029	−1.064	0.081	12.645	0.090
	49.91	0.316	−26.65	−1.57	1.861	1.132	0.025	−1.090	0.066	11.879	0.075
	75.01	0.316	−28.55	−1.41	1.867	1.153	0.020	−1.156	0.051	11.223	0.060
	100.03	0.315	−30.20	−1.25	1.876	1.180	0.017	−1.240	0.039	10.663	0.048
	125.01	0.315	−31.49	−1.13	1.887	1.216	0.014	−1.340	0.031	10.175	0.040
40	5.06	0.100	−18.20	−4.81	1.872	1.158	0.114	−1.183	0.369	13.329	0.375
	24.94	0.100	−20.10	−4.53	1.872	1.159	0.095	−1.184	0.294	12.590	0.300
	49.84	0.100	−22.25	−4.19	1.876	1.171	0.077	−1.216	0.222	11.826	0.228
	74.82	0.100	−24.13	−3.82	1.884	1.194	0.061	−1.284	0.162	11.180	0.168
	100.08	0.099	−25.78	−3.43	1.894	1.225	0.049	−1.369	0.116	10.626	0.122
	125.02	0.099	−26.94	−3.12	1.908	1.265	0.040	−1.472	0.086	10.150	0.092
49	5.06	1.002	−3.65	−0.60	1.224	1.349	0.036	−0.961	0.066	13.499	0.076
	24.89	1.002	−4.05	−0.57	1.223	1.339	0.032	−0.941	0.059	12.775	0.069
	49.84	1.002	−4.29	−0.50	1.226	1.369	0.027	−1.000	0.047	11.967	0.057
	74.63	1.002	−4.48	−0.44	1.229	1.400	0.022	−1.059	0.039	11.309	0.049
	100.10	1.001	−4.61	−0.39	1.233	1.435	0.019	−1.124	0.033	10.739	0.043
	125.02	1.002	−4.56	−0.34	1.238	1.484	0.017	−1.214	0.029	10.241	0.039
51	5.07	0.602	−4.15	−0.69	1.435	1.250	0.042	−0.974	0.089	13.466	0.098
	24.88	0.602	−4.56	−0.64	1.435	1.246	0.036	−0.966	0.078	12.732	0.087
	49.89	0.602	−4.86	−0.57	1.438	1.277	0.030	−1.033	0.061	11.918	0.070
	74.94	0.601	−5.04	−0.50	1.443	1.319	0.025	−1.122	0.047	11.233	0.056
	100.06	0.601	−5.27	−0.44	1.446	1.347	0.021	−1.178	0.039	10.690	0.048
	125.00	0.601	−5.28	−0.39	1.451	1.396	0.019	−1.272	0.033	10.198	0.042
52	5.04	0.601	−4.11	−0.68	1.436	1.256	0.041	−0.989	0.086	13.453	0.095
	24.89	0.601	−4.58	−0.65	1.435	1.241	0.037	−0.953	0.079	12.745	0.088
	49.91	0.601	−4.85	−0.57	1.439	1.276	0.030	−1.033	0.061	11.918	0.070
	74.91	0.601	−5.03	−0.50	1.443	1.318	0.025	−1.121	0.047	11.234	0.056
	100.07	0.601	−5.26	−0.44	1.446	1.347	0.021	−1.177	0.039	10.690	0.048
	124.91	0.601	−5.26	−0.39	1.451	1.397	0.019	−1.273	0.033	10.199	0.042

[a] Liquid junction potential, see text. [b] Defined as −log [H$^+$].

Table 5. Experimental Results for the First Dissociation of Oxalic Acid in Aqueous Sodium Trifluoromethanesulfonate Media[a]

expt	t/°C	I/(mol·kg^{-1})	E·10^3/V	E_{lj}·10^3/V	pH	$\bar{n}$	$\sigma_{\bar{n}}$	log $K_{m,1a}$	σ_{1a}	log $K_{m,1b}$	σ_{1b}
16	24.87	0.101	−20.02	−5.36	1.870	1.178	0.052	−1.236	0.150	12.557	0.156
	49.87	0.101	−22.46	−4.93	1.872	1.184	0.043	−1.248	0.122	11.811	0.128
	75.03	0.101	−24.66	−4.33	1.880	1.207	0.034	−1.311	0.088	11.166	0.094
	100.09	0.101	−26.49	−3.70	1.892	1.242	0.026	−1.405	0.060	10.607	0.066
	124.88	0.101	−27.84	−3.27	1.905	1.281	0.021	−1.503	0.045	10.138	0.051
17	5.00	0.101	−17.79	−5.42	1.879	1.204	0.055	−1.318	0.142	13.215	0.148
	24.83	0.101	−19.98	−5.35	1.871	1.180	0.052	−1.244	0.147	12.551	0.153
	49.90	0.101	−22.49	−4.93	1.872	1.182	0.043	−1.242	0.123	11.817	0.129
	74.87	0.101	−24.68	−4.35	1.879	1.205	0.034	−1.305	0.089	11.176	0.095
18	4.98	0.101	−17.98	−5.49	1.876	1.194	0.056	−1.290	0.150	13.243	0.156
	24.83	0.102	−20.22	−5.43	1.867	1.169	0.053	−1.206	0.160	12.588	0.166
	49.91	0.102	−22.77	−5.02	1.868	1.170	0.044	−1.203	0.134	11.855	0.140
	74.91	0.101	−24.92	−4.40	1.876	1.197	0.034	−1.282	0.093	11.198	0.099
	100.11	0.101	−26.71	−3.74	1.890	1.236	0.026	−1.390	0.062	10.622	0.068
	125.03	0.101	−28.01	−3.29	1.904	1.279	0.021	−1.498	0.045	10.140	0.051
19	5.02	0.101	−17.99	−5.50	1.876	1.194	0.056	−1.289	0.151	13.243	0.157
	24.89	0.101	−20.12	−5.38	1.870	1.176	0.052	−1.231	0.152	12.561	0.158
	49.99	0.101	−22.61	−4.96	1.871	1.181	0.043	−1.238	0.124	11.818	0.130
	74.87	0.101	−24.69	−4.34	1.881	1.209	0.034	−1.319	0.087	11.161	0.093
	100.09	0.101	−26.63	−3.72	1.891	1.240	0.026	−1.400	0.061	10.611	0.067
21	5.03	0.316	−20.87	−2.14	1.862	1.126	0.018	−1.084	0.065	13.381	0.074
	24.86	0.316	−22.71	−2.03	1.860	1.121	0.017	−1.060	0.062	12.664	0.071
	49.89	0.316	−24.84	−1.81	1.863	1.130	0.014	−1.082	0.051	11.902	0.060
	74.87	0.316	−26.69	−1.55	1.870	1.151	0.012	−1.150	0.037	11.248	0.046
	100.10	0.315	−28.19	−1.30	1.880	1.184	0.009	−1.253	0.026	10.667	0.035
22	4.94	0.316	−20.86	−2.14	1.862	1.126	0.018	−1.085	0.065	13.385	0.074
	24.78	0.316	−22.75	−2.04	1.859	1.118	0.017	−1.048	0.063	12.679	0.072
	49.86	0.316	−24.83	−1.81	1.863	1.130	0.014	−1.084	0.051	11.902	0.060
23	5.02	0.600	−23.09	−1.23	1.861	1.123	0.011	−1.082	0.039	13.374	0.048
	24.87	0.600	−25.04	−1.16	1.858	1.114	0.010	−1.044	0.039	12.668	0.048
	49.90	0.600	−27.23	−1.03	1.860	1.122	0.009	−1.060	0.033	11.909	0.042
	74.78	0.600	−29.23	−0.89	1.865	1.136	0.008	−1.105	0.026	11.276	0.035
24	5.04	0.600	−23.40	−1.25	1.854	1.103	0.011	−1.002	0.046	13.453	0.055
	24.78	0.600	−25.23	−1.18	1.854	1.103	0.011	−0.995	0.043	12.720	0.052
	49.90	0.600	−27.42	−1.04	1.857	1.111	0.009	−1.019	0.036	11.950	0.045
	74.91	0.600	−29.31	−0.89	1.864	1.133	0.008	−1.092	0.027	11.286	0.036
	100.12	0.600	−30.97	−0.74	1.873	1.161	0.006	−1.184	0.020	10.710	0.029
	125.06	0.600	−32.24	−0.65	1.884	1.198	0.006	−1.293	0.015	10.209	0.024
25	5.08	1.001	−2.35	−0.46	1.250	1.377	0.033	−1.040	0.061	13.441	0.071
	24.89	1.001	−2.66	−0.46	1.248	1.354	0.031	−0.995	0.058	12.744	0.068
	49.92	1.001	−2.80	−0.39	1.251	1.391	0.027	−1.066	0.049	11.927	0.059
	74.92	1.001	−2.93	−0.33	1.254	1.425	0.024	−1.127	0.043	11.271	0.053
	100.07	1.000	−3.00	−0.27	1.257	1.464	0.022	−1.197	0.038	10.712	0.048
	125.07	1.001	−2.87	−0.21	1.261	1.528	0.020	−1.313	0.034	10.196	0.044
26	5.03	1.001	−2.35	−0.46	1.250	1.377	0.033	−1.040	0.061	13.443	0.071
	24.83	1.001	−2.63	−0.45	1.249	1.361	0.031	−1.010	0.058	12.731	0.068
	49.90	1.001	−2.79	−0.39	1.251	1.394	0.027	−1.070	0.049	11.924	0.059
	74.81	1.000	−2.89	−0.32	1.254	1.433	0.024	−1.142	0.042	11.259	0.052
	100.09	1.000	−3.00	−0.27	1.257	1.464	0.022	−1.197	0.038	10.712	0.048
	125.04	1.001	−2.90	−0.22	1.261	1.523	0.020	−1.303	0.034	10.206	0.044

[a] See footnotes for Table 4.

constants. Although these ratios were typically ~1:18 in experiments to measure $K_{m,1a}$, in experiments at ionic strengths of 0.3 mol·kg^{-1} the ratio was ~1:60 (Tables 2 and 3). Sufficient acid was added to the corresponding test solutions to produce a formal concentration of 0.005 mol·kg^{-1} to 0.05 mol·kg^{-1} (Tables 2 and 3); the addition of acid was required to maintain sufficiently high degrees of association to permit accurate measurement of $K_{m,1a}$.

The reference solutions used in experiments to measure $K_{m,2a}$ had triflic acid to sodium triflate ratios 1:59 or less and were typically less than 1:119 (Table 3). The corresponding test solutions were prepared by combining the oxalic acid and sodium hydroxide stock solutions in a 2:3 molal ratio (Table 3).

Apparatus and Procedures. The modified hydrogen-electrode concentration cell used in these experiments has been described in detail previously (Mesmer et al., 1970; Wesolowski et al., 1984; Kettler et al., 1991; Palmer and Hyde, 1993) The solution compositions listed in Tables 2 and 3 refer to the cell configuration

$$\text{Pt, } H_2|H_2C_2O_4\text{, HX, NaOH, NaX}||\text{HX, NaX}|H_2\text{, Pt}$$

where X refers to chloride or triflate. The experimental procedure described previously (Kettler et al., 1991) was used in this study with two modifications: (1) the porous Teflon liquid junction was saturated with reference solution prior to each experiment, and (2) the cell was allowed to equilibrate overnight at 5 °C. The upper temperature limit (125 °C) was imposed by drifting potentials produced by decomposition of oxalic acid. Stable potentials were achieved at all temperatures reported in this study.

Results

The measured potentials (Tables 4−6) can be related to the molal concentration of hydrogen ions by the Nernst equation

$$E = -(RT/F)\ln([H^+]_t/[H^+]_r) - E_{lj} \tag{5}$$

Table 6. Experimental Results of the Second Dissociation of Oxalic Acid in Aqueous Sodium Trifluoromethanesulfonate Media[a]

expt	t/°C	I/(mol·kg^{-1})	E·10^3/V	E_{lj}·10^3/V	pH	$\bar{n}$	$\sigma_{\bar{n}}$	log $K_{m,2a}$	σ_{2a}	log $K_{m,2b}$	σ_{2b}
6	5.03	0.100	77.56	3.97	3.777	0.492	0.006	−3.760	0.011	10.772	0.017
	24.93	0.100	86.49	4.21	3.833	0.494	0.006	−3.821	0.011	9.971	0.017
	49.87	0.100	101.22	4.06	3.942	0.498	0.006	−3.936	0.011	9.125	0.017
	49.87	0.100	101.32	4.06	3.944	0.498	0.006	−3.937	0.011	9.122	0.017
	75.06	0.100	119.87	3.59	4.086	0.501	0.006	−4.086	0.011	8.391	0.017
	100.10	0.100	141.60	3.03	4.252	0.503	0.006	−4.256	0.011	7.755	0.017
	125.02	0.100	166.43	2.94	4.443	0.505	0.006	−4.450	0.011	7.187	0.017
8	5.06	0.100	78.77	3.98	3.799	0.485	0.006	−3.769	0.011	10.761	0.017
	24.95	0.100	87.58	4.22	3.851	0.487	0.006	−3.826	0.011	9.965	0.017
	100.05	0.100	142.69	3.03	4.267	0.495	0.006	−4.257	0.011	7.755	0.017
27	5.08	0.100	54.85	1.28	3.795	0.484	0.006	−3.764	0.011	10.767	0.017
	24.93	0.100	61.57	1.62	3.847	0.486	0.006	−3.819	0.011	9.974	0.017
	49.84	0.100	73.57	1.69	3.952	0.489	0.006	−3.931	0.011	9.131	0.017
	74.99	0.100	89.13	1.50	4.090	0.492	0.006	−4.074	0.011	8.406	0.017
	100.08	0.100	108.12	1.21	4.254	0.494	0.006	−4.243	0.011	7.771	0.017
	124.98	0.100	130.52	1.26	4.446	0.496	0.006	−4.438	0.011	7.203	0.017
28	5.02	0.100	39.19	0.56	3.799	0.484	0.006	−3.769	0.011	10.763	0.017
	24.88	0.100	44.44	0.93	3.847	0.486	0.006	−3.819	0.011	9.974	0.017
	49.88	0.100	54.86	1.07	3.952	0.489	0.006	−3.930	0.011	9.129	0.017
	74.75	0.100	68.85	0.96	4.090	0.492	0.006	−4.074	0.011	8.409	0.017
	100.08	0.100	86.50	0.75	4.257	0.494	0.006	−4.246	0.011	7.766	0.017
	125.01	0.100	107.31	0.83	4.447	0.496	0.006	−4.440	0.011	7.198	0.017
44	4.99	1.000	66.02	0.41	3.514	0.506	0.006	−3.520	0.011	10.964	0.021
	24.99	1.000	71.91	0.45	3.533	0.507	0.006	−3.541	0.011	10.193	0.021
	49.97	1.000	82.38	0.45	3.602	0.510	0.006	−3.615	0.011	9.375	0.021
	74.93	1.000	95.73	0.39	3.702	0.513	0.006	−3.721	0.011	8.675	0.021
	100.09	1.000	111.78	0.32	3.824	0.517	0.006	−3.849	0.011	8.059	0.021
	125.01	1.001	130.18	0.32	3.961	0.519	0.006	−3.992	0.011	7.517	0.021
45	5.08	0.600	55.87	0.39	3.552	0.495	0.006	−3.539	0.011	10.913	0.020
	25.06	0.600	61.49	0.43	3.579	0.497	0.006	−3.571	0.011	10.134	0.020
	49.89	0.600	71.57	0.43	3.656	0.502	0.006	−3.656	0.011	9.312	0.020
	74.98	0.600	84.79	0.38	3.765	0.507	0.006	−3.775	0.011	8.600	0.020
	100.09	0.600	100.94	0.31	3.900	0.513	0.006	−3.919	0.011	7.975	0.020
	124.99	0.601	119.55	0.31	4.049	0.517	0.006	−4.076	0.011	7.426	0.020
46	5.09	0.273	41.92	0.35	3.640	0.498	0.006	−3.633	0.011	10.836	0.017
	24.94	0.273	47.09	0.48	3.679	0.500	0.006	−3.675	0.011	10.053	0.017
	49.91	0.273	56.80	0.52	3.769	0.504	0.006	−3.772	0.011	9.218	0.017
	74.87	0.273	69.92	0.47	3.894	0.508	0.006	−3.905	0.011	8.501	0.017
	100.06	0.273	86.08	0.38	4.042	0.512	0.006	−4.060	0.011	7.870	0.017
	125.00	0.273	105.23	0.40	4.211	0.515	0.006	−4.234	0.011	7.312	0.017
47	5.05	0.600	68.35	0.69	3.552	0.495	0.006	−3.540	0.011	10.914	0.020
	24.95	0.600	74.96	0.72	3.581	0.497	0.006	−3.573	0.011	10.137	0.020
	49.97	0.600	86.29	0.69	3.658	0.502	0.006	−3.658	0.011	9.309	0.020
	75.06	0.600	100.72	0.60	3.767	0.508	0.006	−3.778	0.011	8.597	0.020
	100.08	0.600	117.81	0.51	3.899	0.512	0.006	−3.918	0.011	7.977	0.020
	125.01	0.601	137.72	0.49	4.050	0.517	0.006	−4.076	0.011	7.426	0.020
48	5.13	0.316	73.81	1.38	3.641	0.478	0.006	−3.599	0.011	10.860	0.020
	24.94	0.316	81.21	1.39	3.675	0.482	0.006	−3.641	0.011	10.079	0.020
	50.01	0.316	93.66	1.30	3.760	0.490	0.006	−3.739	0.011	9.240	0.020
	74.94	0.316	109.18	1.14	3.876	0.498	0.006	−3.871	0.011	8.524	0.020
	100.07	0.316	127.83	0.97	4.018	0.506	0.006	−4.027	0.011	7.892	0.020
	125.02	0.316	149.32	0.92	4.180	0.513	0.006	−4.200	0.011	7.333	0.020

[a] See footnotes for Table 4.

where E is the measured potential, R is the gas constant, F is the Faraday constant, T is the thermodynamic temperature, and $[H^+]_t$ and $[H^+]_r$ refer to the molal concentration of hydrogen ions in the test and reference compartments, respectively. The E_{lj} term designates the liquid junction potential. The value of $[H^+]_t$ can be calculated (Tables 4−6), given that the value of $[H^+]_r$ is known. This simplified version of the Nernst equation requires the presence of matching ionic media on both sides of the liquid junction so that the calculated ratio of activity coefficients for H^+ in the test and reference compartments approaches unity. This equation is solved using an iterative process that considers partial vaporization of the solutions at elevated temperature, speciation of the test solution, and the consequent effects of vaporization and solution speciation on ionic strength and the liquid junction potential.

The liquid junction potential (Tables 4−6) is evaluated using the full Henderson approximation (eq 2-12 in Baes and Mesmer (1976)). Conductance data for H^+, OH^-, Cl^-, Na^+, HSO_4^-, and SO_4^{2-} were obtained from Quist and Marshall (1965), whereas those for $CF_3SO_3^-$ were obtained from Ho and Palmer (1995). The limiting molar conductances of bioxalate and oxalate were assumed to be identical to bisulfate and sulfate, respectively. Uncertainties introduced by this approximation are probably small: the conductances of oxalate and bioxalate at 25 °C are within 25% of those for sulfate and bisulfate (Robinson and Stokes, 1959). The calculated liquid junction potential changes by less than 10% if the conductances assigned to bioxalate and oxalate are doubled. This value is well within the 25% error assigned to the liquid junction potential by using the Henderson equation (Mesmer and Holmes, 1992).

Table 7. Experimental Results for the First Dissociation of Oxalic Acid in Aqueous Sodium Chloride Media Published Previously (Kettler et al., 1991) and Recalculated as Part of This Study[a]

exptl	t/°C	I/(mol·kg^{-1})	E·10^3/V	E_{lj}·10^3/V	pH	$\bar{n}$	$\sigma_{\bar{n}}$	log $K_{m,1a}$	σ_{1a}	log $K_{m,1b}$	σ_{1b}
19	0.00	4.998	−27.30	−0.32	1.490	1.417	0.008	−1.351	0.012	13.893	0.042
	24.88	4.999	−31.00	−0.30	1.471	1.345	0.007	−1.203	0.012	13.084	0.042
	49.85	5.000	−34.18	−0.28	1.462	1.314	0.007	−1.135	0.011	12.380	0.041
	74.81	5.001	−36.93	−0.25	1.461	1.311	0.006	−1.127	0.010	11.739	0.040
	99.79	5.003	−39.49	−0.23	1.463	1.318	0.006	−1.143	0.009	11.160	0.039
20	24.86	2.001	25.83	1.89	1.452	1.234	0.041	−0.957	0.089	12.863	0.105
	49.83	2.002	27.55	1.68	1.439	1.181	0.036	−0.808	0.092	12.255	0.108
	74.82	2.002	30.23	1.51	1.443	1.197	0.031	−0.851	0.075	11.596	0.091
	99.79	2.002	33.06	1.35	1.448	1.218	0.027	−0.909	0.061	11.023	0.077
	124.77	2.003	36.16	1.27	1.457	1.255	0.024	−1.002	0.050	10.493	0.066
21	49.85	0.101	−25.88	−5.67	1.792	1.187	0.066	−1.174	0.178	11.864	0.184
	74.83	0.101	−27.90	−5.16	1.805	1.212	0.051	−1.248	0.125	11.210	0.131
	99.79	0.100	−29.49	−4.62	1.823	1.243	0.038	−1.339	0.087	10.655	0.093
	124.77	0.099	−30.54	−4.18	1.844	1.280	0.030	−1.438	0.063	10.182	0.069
22	49.84	3.172	−56.23	−0.72	1.310	1.329	0.032	−1.010	0.060	12.214	0.076
	74.77	3.173	−60.44	−0.64	1.314	1.361	0.028	−1.075	0.050	11.520	0.066
	99.80	3.173	−64.69	−0.56	1.317	1.386	0.024	−1.123	0.042	10.937	0.058
	124.77	3.175	−68.78	−0.52	1.321	1.421	0.022	−1.188	0.037	10.411	0.053
23	49.85	1.030	2.74	0.22	1.321	1.270	0.022	−0.901	0.043	12.063	0.053
	74.82	1.030	3.14	0.21	1.323	1.294	0.020	−0.953	0.039	11.409	0.049
	99.79	1.030	3.67	0.19	1.327	1.335	0.019	−1.036	0.035	10.830	0.045
	124.77	1.030	4.34	0.20	1.332	1.392	0.018	−1.146	0.033	10.308	0.043
24	49.89	0.332	0.23	−0.22	1.767	1.138	0.007	−1.009	0.013	11.955	0.022
	74.82	0.332	0.94	−0.18	1.778	1.159	0.007	−1.080	0.012	11.296	0.021
	99.79	0.331	2.02	−0.15	1.792	1.186	0.007	−1.169	0.013	10.731	0.022
	124.77	0.331	3.52	−0.09	1.810	1.220	0.007	−1.270	0.014	10.240	0.023
25	49.86	1.982	16.42	1.21	1.264	1.262	0.040	−0.826	0.086	12.234	0.096
	74.82	1.982	18.08	1.09	1.267	1.279	0.035	−0.864	0.072	11.581	0.082
	99.79	1.982	19.90	0.98	1.271	1.307	0.031	−0.925	0.060	11.005	0.070
	124.77	1.982	21.97	0.93	1.279	1.357	0.028	−1.028	0.051	10.467	0.061
26	0.00	3.172	−47.28	−0.91	1.310	1.325	0.045	−1.001	0.086	13.948	0.102
	24.93	3.172	−51.44	−0.79	1.316	1.376	0.036	−1.104	0.065	12.882	0.081
	49.89	3.172	−56.19	−0.72	1.311	1.335	0.032	−1.024	0.060	12.200	0.076
	74.82	3.172	−60.26	−0.64	1.317	1.385	0.027	−1.121	0.048	11.474	0.064
	99.80	3.173	−64.55	−0.56	1.319	1.403	0.024	−1.154	0.041	10.906	0.057
	124.78	3.175	−68.76	−0.52	1.321	1.423	0.022	−1.192	0.037	10.407	0.053
27	24.92	4.002	−32.77	−0.33	1.537	1.230	0.008	−1.033	0.014	13.085	0.044
	49.89	4.002	−35.57	−0.30	1.537	1.231	0.008	−1.034	0.012	12.317	0.042
	74.86	4.003	−38.25	−0.27	1.539	1.238	0.007	−1.051	0.010	11.662	0.040
	99.81	4.004	−40.67	−0.24	1.544	1.257	0.006	−1.100	0.009	11.067	0.039
	124.77	4.007	−42.69	−0.22	1.553	1.293	0.006	−1.185	0.008	10.505	0.038
28	24.86	3.002	−33.69	−0.35	1.646	1.165	0.009	−0.981	0.013	12.981	0.029
	49.93	3.002	−36.60	−0.32	1.646	1.164	0.008	−0.978	0.013	12.219	0.029
	74.84	3.003	−39.25	−0.28	1.649	1.178	0.007	−1.017	0.011	11.554	0.027
	99.80	3.004	−41.81	−0.25	1.653	1.195	0.007	−1.064	0.009	10.976	0.025
	124.78	3.006	−44.27	−0.23	1.658	1.214	0.006	−1.114	0.008	10.468	0.024

[a] See footnotes for Table 4.

The degree of association ($\bar{n}$, Tables 4−6) is calculated from

$$\bar{n} = (2m(\mathrm{H_2C_2O_4}) - m(\mathrm{NaOH}) + m(\mathrm{HX}) - [\mathrm{H^+}]_t + [\mathrm{OH^-}]_t)/m(\mathrm{H_2C_2O_4}) \tag{6}$$

where m(X) denotes the stoichiometric molal concentrations of the designated species. For measurements of the first molal dissociation constant, the molal concentration of bioxalate was calculated from the proton balance expression

$$[\mathrm{HC_2O_4^-}] = ([\mathrm{H^+}] - [\mathrm{OH^-}] - m(\mathrm{HX}))/(1 + 2K_{m,2a}/[\mathrm{H^+}]) \tag{7}$$

whereas the concentration of undissociated oxalic acid was calculated from mass balance considerations

$$[\mathrm{H_2C_2O_4}] = m(\mathrm{H_2C_2O_4}) - [\mathrm{HC_2O_4^-}](1 + K_{m,2a}/[\mathrm{H^+}]) \tag{8}$$

The parallel equations for the second molal dissociation constant are

$$[\mathrm{HC_2O_4^-}] = (2m(\mathrm{H_2C_2O_4}) - m(\mathrm{NaOH}) - [\mathrm{H^+}] + [\mathrm{OH^-}])/(2[\mathrm{H^+}]/K_{m,1a} + 1) \tag{9}$$

and

$$[\mathrm{C_2O_4^{2-}}] = m(\mathrm{H_2C_2O_4}) - [\mathrm{HC_2O_4^-}]([\mathrm{H^+}]/K_{m,1a} + 1) \tag{10}$$

Values of $K_{m,1a}$ and $K_{m,2a}$ (Tables 4−6) were then calculated using eqs 3 and 4.

Discussion

Fitting Process. In a number of previous reports (Kettler et al., 1991, 1992, 1995a; Bell et al., 1993; Bénézeth et al., 1997) from this laboratory, it has become apparent that the fitting process is simplified if the dissociation reactions are iso-Coulombic or pseudo-iso-Coulombic. This serves to minimize Δz^2 and hence reduce the degree of electrostriction (Lindsay, 1980). The Debye−Hückel limiting slope, changes in heat capacity, and changes in volume are thus minimized. This approach is achieved by recast-

Table 8. Experimental Results of the Second Dissociation of Oxalic Acid in Aqueous Sodium Chloride Media Published Previously (Kettler et al., 1991) and Recalculated as Part of this Study[a]

exptl	t/°C	I/(mol·kg^{-1})	E·10^3/V	E_{lj}·10^3/V	pH	$\bar{n}$	$\sigma_{\bar{n}}$	log $K_{m,2a}$	σ_{2a}	log $K_{m,2b}$	σ_{2b}
1	99.79	2.003	198.77	2.02	3.696	0.491	0.008	−3.678	0.014	8.254	0.030
	124.79	2.004	219.91	1.87	3.792	0.493	0.008	−3.777	0.014	7.719	0.030
	149.76	2.006	242.40	1.73	3.892	0.495	0.008	−3.880	0.014	7.244	0.030
	174.81	2.009	265.49	1.58	3.986	0.496	0.008	−3.977	0.014	6.829	0.030
2	24.93	2.002	145.74	2.85	3.496	0.485	0.008	−3.467	0.014	10.351	0.030
	49.89	2.002	157.91	2.56	3.487	0.485	0.008	−3.457	0.014	9.604	0.030
	74.81	2.002	177.78	2.29	3.591	0.489	0.008	−3.568	0.014	8.878	0.030
	99.81	2.003	198.57	2.02	3.694	0.491	0.008	−3.675	0.014	8.256	0.030
3	99.80	1.002	183.77	2.01	3.795	0.485	0.008	−3.767	0.014	8.099	0.024
	124.77	1.002	206.18	1.87	3.919	0.489	0.008	−3.898	0.014	7.556	0.024
	149.77	1.003	230.59	1.73	4.052	0.492	0.008	−4.036	0.014	7.075	0.024
	174.77	1.005	260.00	1.58	4.226	0.495	0.008	−4.216	0.014	6.612	0.024
4	24.90	1.001	133.32	2.85	3.587	0.475	0.008	−3.541	0.015	10.169	0.025
	49.87	1.001	146.15	2.56	3.604	0.476	0.008	−3.561	0.014	9.400	0.024
	74.80	1.001	163.49	2.29	3.685	0.481	0.008	−3.649	0.014	8.711	0.024
5	24.88	0.334	112.66	2.82	3.714	0.443	0.009	−3.613	0.015	10.093	0.024
	49.88	0.334	127.52	2.55	3.791	0.453	0.009	−3.706	0.015	9.258	0.024
	74.84	0.334	145.24	2.28	3.898	0.463	0.008	−3.832	0.015	8.544	0.024
	99.79	0.334	165.79	2.01	4.029	0.473	0.008	−3.980	0.014	7.919	0.023
	124.77	0.334	189.04	1.86	4.179	0.481	0.008	−4.145	0.014	7.366	0.023
	149.76	0.334	215.11	1.72	4.345	0.488	0.008	−4.322	0.014	6.873	0.023
	174.77	0.335	242.80	1.58	4.510	0.492	0.008	−4.495	0.014	6.448	0.023
6	24.92	0.100	97.76	2.79	3.985	0.398	0.006	−3.803	0.010	9.969	0.016
	49.84	0.100	111.35	2.53	4.061	0.415	0.005	−3.910	0.009	9.130	0.015
	74.77	0.100	127.88	2.26	4.169	0.434	0.005	−4.052	0.008	8.410	0.014
	99.79	0.100	147.46	2.00	4.304	0.452	0.004	−4.219	0.008	7.778	0.014
	124.77	0.100	170.27	1.86	4.464	0.467	0.004	−4.406	0.008	7.217	0.014
	149.76	0.100	196.25	1.72	4.643	0.479	0.004	−4.605	0.007	6.719	0.013
	174.78	0.100	227.30	1.58	4.858	0.488	0.004	−4.836	0.007	6.254	0.013
7	24.91	0.334	112.92	2.82	3.719	0.444	0.009	−3.618	0.015	10.086	0.024
	0.00	0.334	101.08	3.19	3.685	0.439	0.009	−3.577	0.016	11.089	0.025
8	24.90	2.002	147.32	2.85	3.523	0.486	0.008	−3.496	0.014	10.326	0.030
	0.00	2.002	134.94	3.22	3.532	0.487	0.008	−3.506	0.014	11.279	0.030
	49.89	2.002	162.59	2.57	3.560	0.488	0.008	−3.535	0.014	9.530	0.030
9	24.91	1.001	133.93	2.85	3.597	0.476	0.008	−3.553	0.015	10.159	0.025
10	24.95	1.001	134.11	2.85	3.600	0.476	0.008	−3.556	0.015	10.155	0.025
11	74.80	5.002	117.10	0.07	3.697	0.484	0.008	−3.665	0.014	9.202	0.044
12	49.87	5.001	109.40	0.08	3.708	0.484	0.008	−3.677	0.014	9.837	0.044
	74.82	5.002	117.13	0.07	3.697	0.484	0.008	−3.665	0.014	9.201	0.044
	99.79	5.004	125.63	0.06	3.698	0.484	0.008	−3.666	0.014	8.637	0.044
	124.77	5.006	135.79	0.05	3.720	0.485	0.008	−3.690	0.014	8.114	0.044
	149.77	5.012	146.22	0.05	3.742	0.486	0.008	−3.713	0.014	7.642	0.044
	174.77	5.020	157.82	0.04	3.775	0.487	0.008	−3.749	0.014	7.202	0.044
13	49.89	3.149	89.16	0.08	3.593	0.463	0.008	−3.526	0.014	9.694	0.030
	74.82	3.150	98.18	0.07	3.624	0.466	0.008	−3.562	0.014	9.030	0.030
	99.83	3.151	108.83	0.06	3.672	0.470	0.008	−3.617	0.014	8.440	0.030
	124.83	3.153	120.77	0.05	3.730	0.474	0.008	−3.683	0.014	7.913	0.030
	149.76	3.156	134.39	0.05	3.802	0.479	0.008	−3.762	0.014	7.432	0.030
	174.78	3.161	149.50	0.04	3.882	0.483	0.008	−3.850	0.014	6.991	0.030
14	24.89	5.000	103.99	0.09	3.760	0.486	0.008	−3.733	0.014	10.554	0.044
	0.00	5.000	100.41	0.11	3.855	0.490	0.008	−3.834	0.014	11.411	0.044
	49.85	5.001	109.79	0.08	3.714	0.484	0.008	−3.684	0.014	9.831	0.044
15	24.92	3.149	81.80	0.09	3.586	0.462	0.008	−3.517	0.014	10.463	0.030
	0.00	3.149	76.60	0.11	3.616	0.465	0.008	−3.553	0.014	11.389	0.030
	49.87	3.149	89.32	0.08	3.596	0.463	0.008	−3.529	0.014	9.689	0.030
	74.83	3.150	98.88	0.07	3.634	0.467	0.008	−3.573	0.014	9.016	0.030
16	0.00	0.185	93.55	3.22	3.803	0.417	0.005	−3.655	0.010	11.034	0.016
	24.93	0.185	104.95	2.86	3.841	0.424	0.005	−3.706	0.009	10.027	0.015
	49.87	0.185	118.94	2.60	3.914	0.436	0.005	−3.801	0.008	9.196	0.014
	74.86	0.185	136.41	2.33	4.027	0.451	0.004	−3.940	0.008	8.472	0.014
	99.77	0.185	157.42	2.07	4.173	0.466	0.004	−4.112	0.008	7.831	0.014
	124.77	0.185	180.86	1.94	4.333	0.477	0.004	−4.291	0.007	7.271	0.013
	149.77	0.185	208.22	1.80	4.520	0.486	0.004	−4.494	0.007	6.760	0.013
	174.73	0.185	241.66	1.66	4.755	0.493	0.004	−4.741	0.007	6.270	0.013

[a] See footnotes for Table 4.

ing eqs 1 and 2 in the base or anionic forms

$$H_2C_2O_4 + OH^- = HC_2O_4^- + H_2O \tag{11}$$

and

$$HC_2O_4^- + OH^- = C_2O_4^{2-} + H_2O \tag{12}$$

for which the molal dissociation constants are defined by

$$K_{m,1b} = [HC_2O_4^-]/([H_2C_2O_4][OH^-]) \tag{13}$$

and

$$K_{m,2b} = [C_2O_4^{2-}]/([HC_2O_4^-][OH^-]) \tag{14}$$

Table 9. Values Obtained for Parameters for Eq 17

term	Harned and Fallon	Pinching and Bates 1−4	Pinching and Bates 5	Pinching and Bates 6	Pinching and Bates 7
p_1	−1.314 325	−1.310 412	−1.290 979	−1.324 607	−1.310 050
p_2	3293.019	3288.747	3285.281	3294.901	3290.594
p_3	0.051 580 81	0.081 379 41	0.028 718 44	0.021 732 94	0.065 092 61
p_4	0.526 362 9	0.101 700 3	0.124 808 0	0.141 295 1	0.155 631 2
AF[a]	0.234 6	0.390 5	0.256 1	0.338 7	0.259 5

[a] Agreement factor (eq 18).

The values for log $K_{m,n\mathrm{a}}$ are converted to the respective values for log $K_{m,n\mathrm{b}}$ by the subtraction of the appropriate values for log $K_{m,\mathrm{w}}$ as measured in Na-triflate (Palmer and Drummond, 1988) or NaCl media (Busey and Mesmer, 1978). The standard equilibrium constants for eqs 11 and 12 are designated by $K^{\ominus}_{1\mathrm{b}}$ and $K^{\ominus}_{2\mathrm{b}}$, respectively, are defined in the usual way (Mills et al., 1993), and are equal to the products of the equilibrium activities of the species listed in eqs 11 and 12 raised to the respective stoichiometric numbers.

The ORGLS (Busing and Levy, 1963) general least-squares routine was used to perform a weighted regression of the data. The fitting process was an iterative one because the solution speciation can only be calculated if one of the molal dissociation constants is known and because five separate data sets were used in the fitting process. These data sets comprised measurements of (1) $K_{m,1\mathrm{b}}$ and $K_{m,2\mathrm{b}}$ made in Na-triflate media (Tables 5 and 6), (2) $K_{m,1\mathrm{b}}$ made in NaCl media (Table 4), (3) $K_{m,1\mathrm{b}}$ and $K_{m,2\mathrm{b}}$ in NaCl reported by Kettler et al. (1991) (Tables 7 and 8), (4) $K_{m,2\mathrm{b}}$ made by Harned and Fallon (1939), and (5) $K_{m,2\mathrm{b}}$ made by Pinching and Bates (1948). The latter two sets of measurements were made using Harned cells.

Several of the data sets that were used in the previous fitting process (Kettler et al., 1991) have been omitted here. Although the glass electrode measurements of Kurz and Farrar (1969) (Table 1) were utilized previously, those authors did not publish sufficient data to permit recalculation of the values of $K^{\ominus}_{1\mathrm{a}}$ reported originally. The titration calorimetry measurements of Christensen et al. (1967) were not reported in sufficient detail to permit recalculation of ΔH on the basis of the results of this study. Measurements by Parton and Gibbons (1939) using a cell without a liquid junction were limited to a few values collected at 25 °C (Table 1), and although McAuley and Nancollas (1961) reported results obtained from Harned cell measurements at five temperatures from 0 °C to 45 °C, solution compositions and potentials were presented only for the measurements at 25 °C.

The fitting process involved (1) calculation of values for $K_{m,2\mathrm{b}}$ using the most recent equations describing $K_{m,1\mathrm{b}}$, (2) extrapolation of the Harned and Fallon (1939) and Pinching and Bates (1948) data to infinite dilution to obtain values of $K^{\ominus}_{2\mathrm{b}}$ at temperatures from 0 °C to 50 °C, (3) fitting the data for $K_{m,2\mathrm{b}}$ collected in NaCl and Na-triflate media simultaneously with the values for $K^{\ominus}_{2\mathrm{b}}$ obtained in the previous step, (4) calculation of values for $K_{m,1\mathrm{b}}$ using the models developed for $K_{m,2\mathrm{b}}$ in NaCl and Na-triflate media, and (5) performing a simultaneous fit of the data for $K_{m,1\mathrm{b}}$ in NaCl and Na-triflate media. This process was repeated until the values of $K_{m,1\mathrm{b}}$ and $K_{m,2\mathrm{b}}$ obtained in consecutive iterations agreed to within 0.0001 log units.

Recalculation of Data Published Previously. Because the fitting process is iterative, the experimental values of $K_{m,n\mathrm{a}}$ and $K_{m,n\mathrm{b}}$ obtained in our previous study (Kettler et al., 1991) have been recalculated using eqs 9−14 and are presented in Tables 7 and 8. The Harned cell data (Harned and Fallon, 1939; Pinching and Bates, 1948) are well-documented and recognized to be of high quality and should therefore be included in the fitting process. To ensure consistency with the data presented in this study, particularly with regard to calculation of activity coefficients, the Harned cell data have been recalculated using the Nernst equation

$$E = E^\circ - RT/F\,(\ln\,[\mathrm{Cl}^-][\mathrm{H}^+] + \ln\,\gamma(\mathrm{Cl}^-)\,\gamma(\mathrm{H}^+)) \qquad (15)$$

where $\gamma(\mathrm{X})$ refers to the activity coefficient of the designated ion. Values for the standard potential ($E°$) of the AgCl electrode have been taken from Bates (1964). The activity coefficients are calculated using the extended Debye−Hückel equation of Pitzer (1973) where

$$\ln\,\gamma(\mathrm{H}^+)\,\gamma(\mathrm{Cl}^-) = 2A_\phi((I/\mathrm{kg{\cdot}mol^{-1}})^{0.5}/(1 + 1.2(I/\mathrm{kg{\cdot}mol^{-1}})^{0.5}) + (2/1.2)\ln(1 + 1.2(I/\mathrm{kg{\cdot}mol^{-1}})^{0.5})) \qquad (16)$$

and A_ϕ is the Debye−Hückel osmotic coefficient parameter (calculated using eq 9 in Dickson et al. (1990)), whereas the ionic strength is represented by I. After eq 15 was solved for [H$^+$], the oxalate species were distributed according to eqs 11−14 and $K_{m,2\mathrm{a}}$ was calculated from $K_{m,2\mathrm{b}}$ using the molal dissociation constant of water (Busey and Mesmer, 1978).

Fitting of Harned Cell Data. The Harned and Fallon (1939) data set comprises 87 measurements made at 11 different temperatures from 0 °C to 50 °C in 8 different solutions with ionic strengths ranging from ~0.03 mol·kg^{-1} to ~0.15 mol·kg^{-1}. Each solution had the same ratio of oxalate to chloride (2:1), so that all of the data could be treated as a single set. Regression of the log $K_{m,2\mathrm{b}}$ values as a function of temperature and ionic strength yielded

$$\log K_{m,2\mathrm{b}} = 2(A_\phi((I(\mathrm{kg/mol}))^{0.5})/(1 + 1.2(I(\mathrm{kg/mol}))^{0.5}) + (2/1.2)\ln(1 + 1.2(I(\mathrm{kg/mol}))^{0.5})/\ln 10) + p_1 + p_2(K/T) + p_3 f(I) + p_4(I(\mathrm{kg/mol}))^2 - \log a_\mathrm{w} \qquad (17)$$

where

$$f(I) = 1 - (1 + 2(I(\mathrm{kg/mol}))^{0.5})\exp(-2(I(\mathrm{kg/mol}))^{0.5}) \qquad (18)$$

and a_w is the activity of water (Busey and Mesmer, 1976). The first term in eq 17 defines the extended Debye−Hückel limiting slope (Pitzer, 1973), whereas parameters p_1 and p_2 define log $K^{\ominus}_{2\mathrm{b}}$ and the remaining quantify the deviation from the limiting law. The values of parameters p_1−p_4 are shown in Table 9. The goodness of fit is quantified using the agreement factor

$$\mathrm{AF} = \left(\left(\sum W_i(\log K_{m,i(\mathrm{obs})} - \log K_{m,i(\mathrm{calc})}\right)^2\right)\Big/(N - N_\mathrm{v}))^{0.5} \qquad (19)$$

where W is the squared reciprocal of the estimated error assigned to any individual determination of log K_m, N is

Table 10. Values of p$K_{2a}^{\ominus}$ for Oxalic Acid Obtained by Recalculating the Data of Harned and Fallon (1939) and Pinching and Bates (1948)

t/°C	Harned and Fallon	Pinching and Bates series 1−4	Pinching and Bates series 5	Pinching and Bates series 6	Pinching and Bates series 7
0	4.200 ± 0.004	4.211 ± 0.002	4.204 ± 0.013	4.203 ± 0.004	4.204 ± 0.004
5	4.203 ± 0.004	4.215 ± 0.002	4.208 ± 0.013	4.207 ± 0.004	4.208 ± 0.004
10	4.212 ± 0.004	4.223 ± 0.002	4.216 ± 0.013	4.216 ± 0.004	4.217 ± 0.004
15	4.226 ± 0.004	4.237 ± 0.002	4.230 ± 0.013	4.230 ± 0.004	4.230 ± 0.004
20	4.242 ± 0.004	4.252 ± 0.002	4.245 ± 0.013	4.246 ± 0.004	4.246 ± 0.004
25	4.262 ± 0.004	4.273 ± 0.002	4.265 ± 0.013	4.266 ± 0.004	4.266 ± 0.004
30	4.285 ± 0.004	4.295 ± 0.002	4.287 ± 0.013	4.289 ± 0.004	4.288 ± 0.004
35	4.310 ± 0.004	4.320 ± 0.002	4.312 ± 0.013	4.314 ± 0.004	4.313 ± 0.004
40	4.336 ± 0.004	4.346 ± 0.002	4.338 ± 0.013	4.341 ± 0.004	4.340 ± 0.004
45	4.366 ± 0.004	4.375 ± 0.002	4.367 ± 0.013	4.370 ± 0.004	4.369 ± 0.004
50	4.396 ± 0.004	4.405 ± 0.002	4.396 ± 0.013	4.400 ± 0.004	4.399 ± 0.004

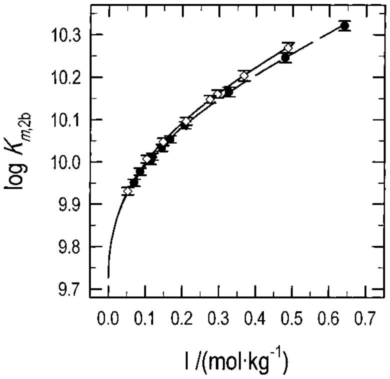

Figure 1. Comparisons of Harned cell data obtained in two different ionic media by Pinching and Bates (1948) at 25 °C. The filled circles (●) and dashed line designate the results from series 6 measurements and the resulting regression equation (eq 17), respectively, whereas the open diamonds (◇) and solid line designate the results from series 7.

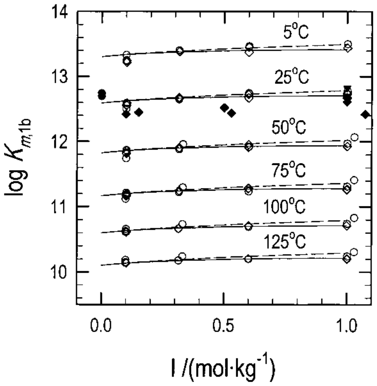

Figure 2. Relation between log $K_{m,1b}$ and solution ionic strength to 1 mol·kg^{-1}. The dashed curves are generated from eq 20 when solved for NaCl media, whereas the solid curves are generated when eq 20 is solved for Na-triflate media. The symbols represent measurements made in NaCl media reported in Tables 4 and 6 (○), measurements made in Na-triflate media reported in Table 5 (◇), the 25 °C measurements reported by McAuley and Nancollas (1961) and Parton and Gibbons (1939), (●), the value reported by Cruywagen et al. (1986) (▼), and measurements made in $NaClO_4$ and KNO_3 media listed in Table 1 (◆). Measurements reported as $K_{m,1a}$ in $NaClO_4$ and KNO_3 solutions were converted to $K_{m,1b}$ using values for $K_{m,w}$ in $NaClO_4$ and KNO_3 solutions as reported by Maeda et al. (1987).

the number of observations, and N_v is the number of independent variables in the fit. The agreement factor for the Harned and Fallon (1939) regression is 0.23 and indicates that the actual scatter around eq 17 is 0.23 times the anticipated scatter using the uncertainties in solution composition and potentials given by Harned and Fallon. The values of $K_{2a}^{\ominus}$ derived from this regression after multiplication by the standard dissociation constant of water (Busey and Mesmer, 1978) differ from the values originally reported by Harned and Fallon (1939) by ca. −0.03 log units (cf. Table 10 with Table 1).

The data collected by Pinching and Bates (1948) comprised 617 measurements made at 11 temperatures in 4 different ionic media. These experiments were classified into seven different series. Series 1−4 were performed in solutions in which the ratio of total oxalate to chloride was 2.4:1. Series 5 was performed with solutions in which this ratio was 6:1, whereas the ratios for series 6 and 7 were 10:1 and 2:1, respectively. The values obtained are sufficiently different in the various ionic media (Figure 1) that four different extrapolations to infinite dilution were performed to correspond to the different ionic media. The best fit in each case was provided by eq 17 using the parameters listed in Table 9. The values of p$K_{2a}^{\ominus}$ obtained from the series 5−7 data were in excellent agreement with the values obtained by recalculation and regression of the Harned and Fallon (1939) data (Table 10). The values of p$K_{2a}^{\ominus}$ obtained from the series 1−4 data are ca. 0.01 log units greater than those reported in the original study. The overall effect is that the difference between the values of p$K_{2a}^{\ominus}$ obtained from these two groups decreases from ca. 0.025 log units to 0.01 log unit (cf. Table 10 with Table 1).

Fitting of the First Molal Dissociation Constant of Oxalic Acid. The fitting process for the first dissociation of oxalic acid in the base form (eq 13) utilized only those data in Tables 4, 5, and 7. The data, which were obtained in NaCl and Na-triflate media, were fitted simultaneously yielding a five-parameter function of temperature and ionic strength

$$\log K_{m,1b} = p_1 + p_2(\mathrm{K}/T) + p_3 f(I) + p_4 I(\mathrm{kg/mol}) + p_5(I(\mathrm{kg/mol}))^2 - \log a_w \quad (20)$$

where p_1 and p_2 define the logarithm of the standard equilibrium constant ($K_{1b}^{\ominus}$), p_3 applies to both NaCl and Na-triflate media, p_4 is used only in NaCl media, and p_5 applies only to Na-triflate solutions. The values determined for the five parameters are p_1 = 2.683 85, p_2 = 2954.02, p_3 = 0.234 331, p_4 = 0.040 461 8, and p_5 = −0.041 847 3. This function provides an excellent fit to data in both NaCl and Na-triflate media (Figures 2 and 3); the agreement factor for this model is 0.79, and the residuals of the regression are distributed randomly when plotted against ionic strength and temperature (Figure 4). Values of log $K_{m,1a}$ obtained by adding the results of eq 20 to the logarithm of molal dissociation constant of water (Palmer and Drummond, 1988; Busey and Mesmer, 1978) are presented in Tables 11 and 12. Although eq 20 is

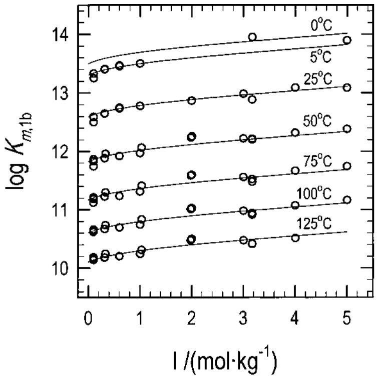

Figure 3. Relation between log $K_{m,1b}$ and solution ionic strength to 5 mol·kg^{-1}. The lines are generated by solving eq 20 for NaCl media. The symbols represent the measurements made in NaCl media reported in Tables 4 and 7.

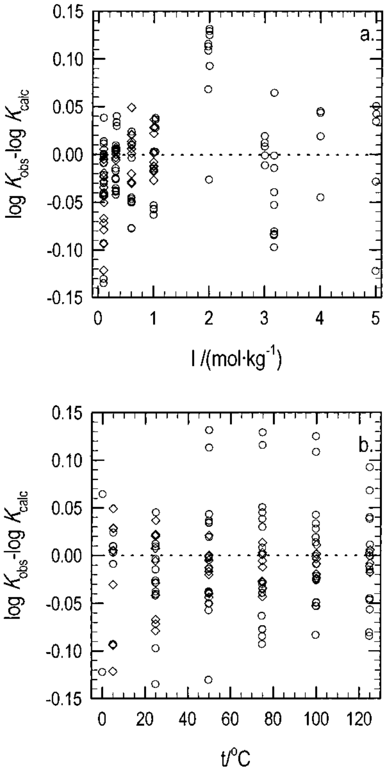

Figure 4. Deviation plots of the difference between experimentally determined values of log $K_{m,1b}$ presented in Tables 4 and 7 and eq 20 as a function of (a) ionic strength and (b) temperature. Symbols designate measurements made in NaCl media (○, Tables 4 and 7) and Na-triflate media (◇, Table 5).

Table 11. Summary of Thermodynamic Quantities for the First Dissociation of Oxalic Acid in Aqueous Sodium Chloride Media at the Saturation Vapor Pressure[a]

t/°C	log $K_{m,1a}$	ΔH_{1a}/ (kJ·mol^{-1})	ΔS_{1a}/ (J·mol^{-1}·K^{-1})	$\Delta C_{p,1a}$/ (J·mol^{-1}·K^{-1})
		I = 0 mol·kg^{-1}		
0	−1.443 ± 0.057	6.0 ± 0.9	−6 ± 3	−317 ± 18
25	−1.401 ± 0.052	−0.7 ± 0.7	−29 ± 2	−231 ± 6
50	−1.447 ± 0.047	−5.9 ± 0.8	−46 ± 2	−186 ± 5
75	−1.540 ± 0.046	−10.3 ± 0.9	−59 ± 3	−169 ± 5
100	−1.664 ± 0.050	−14.5 ± 1.0	−71 ± 3	−174 ± 5
125	−1.811 ± 0.051	−19.1 ± 1.0	−83 ± 3	−197 ± 5
		I = 0.1 mol·kg^{-1}		
0	−1.203 ± 0.044	6.5 ± 0.9	1 ± 3	−310 ± 18
25	−1.152 ± 0.038	0.0 ± 0.7	−22 ± 2	−219 ± 6
50	−1.184 ± 0.035	−4.8 ± 0.8	−37 ± 2	−169 ± 5
75	−1.262 ± 0.034	−8.7 ± 0.9	−49 ± 3	−148 ± 5
100	−1.367 ± 0.034	−12.3 ± 1.0	−59 ± 3	−149 ± 4
125	−1.491 ± 0.039	−16.3 ± 1.0	−69 ± 3	−167 ± 5
		I = 0.5 mol·kg^{-1}		
0	−1.042 ± 0.040	6.8 ± 0.9	5 ± 3	−301 ± 18
25	−0.985 ± 0.029	0.6 ± 0.8	−17 ± 2	−205 ± 6
50	−1.008 ± 0.023	−3.8 ± 0.8	−31 ± 3	−150 ± 5
75	−1.072 ± 0.023	−7.2 ± 0.9	−41 ± 3	−125 ± 5
100	−1.159 ± 0.024	−10.2 ± 1.0	−50 ± 3	−122 ± 5
125	−1.262 ± 0.029	−13.4 ± 1.1	−58 ± 3	−135 ± 5
		I = 1.0 mol·kg^{-1}		
0	−0.991 ± 0.043	6.8 ± 0.9	6 ± 3	−293 ± 2
25	−0.932 ± 0.035	0.9 ± 0.9	−15 ± 3	−193 ± 3
50	−0.949 ± 0.031	−3.2 ± 0.8	−28 ± 2	−135 ± 3
75	−1.003 ± 0.029	−6.1 ± 0.8	−37 ± 2	−107 ± 3
100	−1.077 ± 0.030	−8.7 ± 0.8	−44 ± 2	−101 ± 4
125	−1.165 ± 0.032	−11.3 ± 0.8	−51 ± 2	−110 ± 4
		I = 3.0 mol·kg^{-1}		
0	−1.061 ± 0.048	6.4 ± 1.5	3 ± 5	−262 ± 6
25	−1.002 ± 0.035	1.3 ± 1.3	−15 ± 4	−154 ± 7
50	−1.005 ± 0.033	−1.6 ± 1.2	−24 ± 4	−87 ± 8
75	−1.034 ± 0.035	−3.4 ± 1.1	−29 ± 3	−51 ± 10
100	−1.071 ± 0.038	−4.5 ± 1.0	−32 ± 3	−36 ± 11
125	−1.113 ± 0.042	−5.5 ± 1.2	−34 ± 3	−36 ± 13
		I = 5.0 mol·kg^{-1}		
0	−1.238 ± 0.073	5.8 ± 2.1	−2 ± 7	−234 ± 10
25	−1.182 ± 0.061	1.5 ± 1.8	−18 ± 6	−119 ± 12
50	−1.177 ± 0.062	−0.5 ± 1.6	−24 ± 5	−45 ± 14
75	−1.185 ± 0.067	−1.0 ± 1.3	−26 ± 5	−1 ± 16
100	−1.193 ± 0.072	−0.7 ± 1.3	−25 ± 4	21 ± 18
125	−1.194 ± 0.075	−0.1 ± 1.6	−23 ± 5	31 ± 21

[a] Errors listed represent three times the standard deviation.

strictly valid only to I = 1 mol·kg^{-1} in Na-triflate media, it applies up to I = 5 mol·kg^{-1} in NaCl media and is valid from 0 °C to 125 °C in both media.

The model presented in eq 20 is in good agreement with a value obtained by Cruywagen et al. (1986) at 25 °C in 1 mol·kg^{-1} NaCl solution (Figure 2). On the other hand, measurements made in $NaClO_4$ and KNO_3 media differ significantly from those reported here (Figures 2 and 3), and the media-dependent variations noted in the first paper (Kettler et al., 1991) are preserved in these data. A potentially greater problem results from the fact that the value of p$K^{\ominus}_{1a,298}$ obtained from eq 20 is in poor agreement with the generally accepted value of p$K^{\ominus}_{1a,298}$ obtained by McAuley and Nancollas (1961) and the similar value reported by Parton and Gibbons (1939) (Table 1). These two data sets were recalculated to better compare them with the model presented in eq 20. The former set comprises nine measurements made in oxalate−NaCl solutions with ionic strengths ranging from 0.003 mol·kg^{-1} to 0.012 mol·kg^{-1}, whereas the latter set comprises eight measurements made in oxalate−KCl solutions with ionic strengths ranging from 0.008 mol·kg^{-1} to 0.131 mol·kg^{-1}. These data were recalculated using eqs 15 and 16 after adjustment of the standard potential. McAuley and Nancollas (1961) reported the difference in potential after subtraction of the standard potential of the Ag−AgCl electrode; the source of their standard potential values was not cited. Their potential data were used as reported. Parton and Gibbons (1939) performed their experiments in cells equipped with Pt−quinhydrone and Ag−AgCl electrodes; this report uses the standard potential values of Harned and Wright (1933). The resulting values of $K_{m,1b}$ were extrapolated independently to infinite dilution using an isothermal form of eq 20

$$\log K_{m,1b} = p_1 + p_2 f(I) + p_3 I(\text{kg/mol}) - \log a_w \quad (21)$$

The errors associated with the values of p$K^{\ominus}_{1b}$ obtained

Table 12. Summary of Thermodynamic Quantities for the First Dissociation of Oxalic Acid in Aqueous Sodium Trifluoromethanesulfonate Media at the Saturation Vapor Pressure[a]

t/°C	log $K_{m,1a}$	ΔH_{1a}/ (kJ·mol^{-1})	ΔS_{1a}/ (J·mol^{-1}·K^{-1})	$\Delta C_{p,1a}$/ (J·mol^{-1}·K^{-1})
		I = 0.1 mol·kg^{-1}		
0	−1.207 ± 0.044	6.5 ± 0.9	1 ± 3	−310 ± 18
25	−1.156 ± 0.037	0.0 ± 0.7	−22 ± 2	−219 ± 6
50	−1.189 ± 0.034	−4.8 ± 0.8	−37 ± 2	−169 ± 5
75	−1.266 ± 0.032	−8.7 ± 0.9	−49 ± 3	−148 ± 5
100	−1.372 ± 0.033	−12.3 ± 1.0	−59 ± 3	−149 ± 4
125	−1.496 ± 0.038	−16.3 ± 1.0	−69 ± 3	−167 ± 5
		I = 0.5 mol·kg^{-1}		
0	−1.073 ± 0.039	6.8 ± 0.9	4 ± 3	−301 ± 18
25	−1.016 ± 0.028	0.6 ± 0.8	−18 ± 2	−205 ± 6
50	−1.038 ± 0.022	−3.8 ± 0.8	−32 ± 3	−150 ± 5
75	−1.103 ± 0.023	−7.2 ± 0.9	−42 ± 3	−125 ± 5
100	−1.189 ± 0.024	−10.2 ± 1.0	−50 ± 3	−122 ± 5
125	−1.292 ± 0.029	−13.4 ± 1.1	−58 ± 3	−135 ± 5
		I = 1.0 mol·kg^{-1}		
0	−1.074 ± 0.051	6.8 ± 0.9	4 ± 3	−293 ± 2
25	−1.014 ± 0.045	0.9 ± 0.9	−17 ± 3	−193 ± 3
50	−1.032 ± 0.044	−3.2 ± 0.8	−30 ± 3	−135 ± 3
75	−1.085 ± 0.043	−6.1 ± 0.8	−38 ± 3	−107 ± 3
100	−1.160 ± 0.045	−8.7 ± 0.8	−45 ± 2	−101 ± 4
125	−1.247 ± 0.047	−11.3 ± 0.8	−52 ± 3	−110 ± 4

[a] Errors listed represent three times the standard deviation.

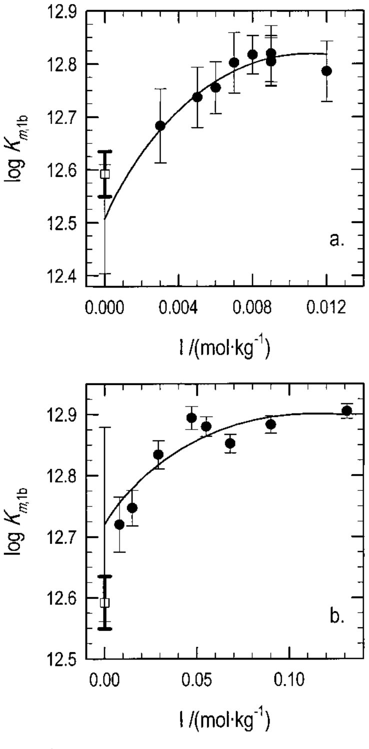

Figure 5. Plots of recalculated experimental data published by (a) McAuley and Nancollas (1961) and (b) Parton and Gibbons (1939). The experimental data are represented by the solid circles (●), whereas the value of $K_{1b}^{\ominus}$ obtained in this study and its associated error is designated by the open square (□) and bold error bar. The solid line designates the model obtained by regressing the experimental data according to eq 21 and the error in this model at I = 0 mol·kg^{-1} is shown by the thin error bar.

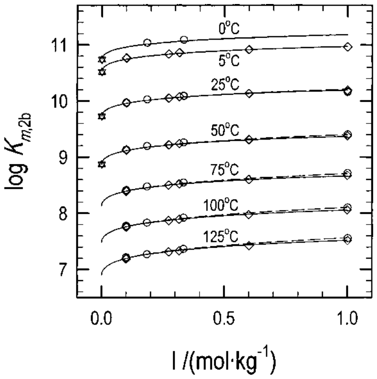

Figure 6. Relation between log $K_{m,2b}$ and solution ionic strength to 1 mol·kg^{-1}. The dashed curves are generated from eq 22 when solved for NaCl media, whereas the solid curves are generated when eq 20 is solved for Na-triflate media. The symbols represent measurements made in NaCl media reported in Table 8 (○), measurements made in Na-triflate media reported in Table 6 (◇), and the recalculated results of Harned and Fallon (1939) (▽) and Pinching and Bates (1948) (△, series 1−4 only).

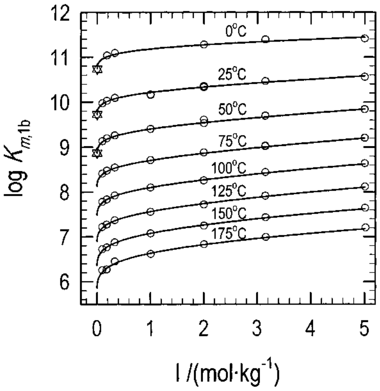

Figure 7. Relation between log $K_{m,2b}$ and solution ionic strength to 5 mol·kg^{-1}. The lines are generated by solving eq 22 for NaCl media. The symbols represent the measurements made in NaCl media reported in Table 8.

using these two small data sets are large: the value obtained for p$K_{1b}^{\ominus}$ using the McAuley and Nancollas data is 12.51 ± 0.10, whereas the results of Parton and Gibbons yield a value of 12.72 ± 0.16. When these errors are considered, however, the values of p$K_{1b}^{\ominus}$ obtained by these isothermal regressions do agree with the value of p$K_{1b}^{\ominus}$ at 25 °C obtained in this study (12.592 ± 0.043) (Figure 5). Therefore, no significant discrepancy exists between the data used to produce the generally accepted value of p$K_{1a,298}^{\ominus}$ and the model developed in this study when the former are recalculated using a more modern activity coefficient model and more recent measurements of $K_{m,2a}$.

Values of ΔH_{1b}, ΔS_{1b}, and $\Delta C_{p,1b}$ can be obtained by differentiation of eq 20. These values are converted to those appropriate for the acid form of the dissociation reaction (Tables 11 and 12) by adding the corresponding values for the dissociation of water (Palmer and Drummond, 1988; Busey and Mesmer, 1978). The available enthalpy data (Table 1) are in poor agreement with those determined in this study (Christensen et al., 1967). The values of p$K_{1a,298}^{\ominus}$ used or obtained in those previous studies are significantly different from the value measured in this study. The values of $\Delta C_{p,1a}$ (Tables 11 and 12) obtained are identical in the two media and are equal owing to the functional form of eq 20, which invokes zero heat capacity change for the iso-Coulombic reaction.

Fitting of the Second Molal Dissociation Constant of Oxalic Acid. A model to describe the dependence of $K_{m,2b}$ as a function of temperature and ionic strength was developed by regressing the measurements made in Na-triflate media (Table 6) simultaneously with the recalculated measurements made in NaCl media (Table 8) and

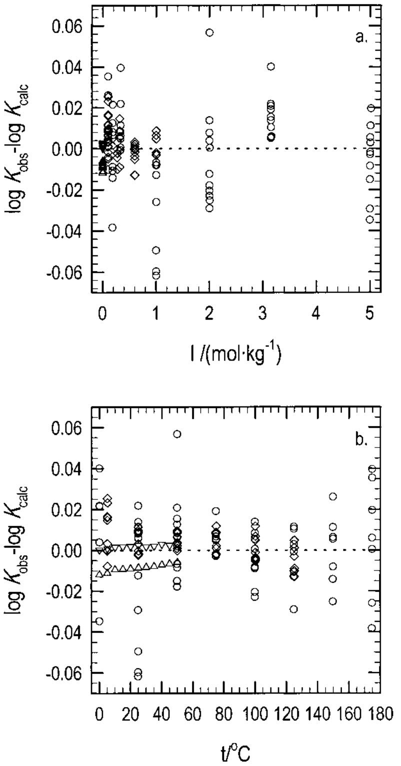

Figure 8. Deviation plots of the difference between eq 20 and the experimentally determined values of log $K_{m,2b}$ presented in Tables 6 and 8 as a function of (a) ionic strength and (b) temperature. Symbols designate measurements made in NaCl media (○, Table 8) and Na-triflate media (◇, Table 6) and the recalculated measurements of Harned and Fallon (1939) (▽) and Pinching and Bates (1948) (△, series 1−4 only).

values of $K^{\ominus}_{2b}$ obtained by regression of the recalculated Harned cell data (Table 10). Only a subset of these $K^{\ominus}_{2b}$ values was used; specifically, the results of the Harned and Fallon regression and the results of the Pinching and Bates series 1−4 measurements. Use of the results of all the Harned cell regressions would have given excessive weight to these previously published data. The series 1−4 measurements were used because they comprise 394 of the 617 measurements made by Pinching and Bates (1948) and were the sole data used by those authors to calculate $K^{\ominus}_{2a}$.

The model obtained from this simultaneous fit is

$$K_{m,2b} = 2(A_{\phi}((I(\text{kg/mol}))^{0.5}/(1 + 1.2(I(\text{kg/mol}))^{0.5}) + (2/1.2)\ln(1 + 1.2(I(\text{kg/mol}))^{0.5}))/\ln 10) - \log a_{w} + p_1 + p_2(\text{K}/T) + p_3(T^2/\text{K}^2) + p_4(T/\text{K}) + p_5 f(I) + p_6 I(\text{kg/mol}) + p_7 I/T(\text{K·kg/mol}) + p_8 I T^2(\text{kg/(mol·K}^2)) + p_9(I(\text{kg/mol}))^2 \tag{22}$$

where the first term is the Debye−Hückel contribution (Pitzer, 1973), the logarithm of the standard equilibrium constant ($K^{\ominus}_{2b}$) is defined by parameters p_1 through p_4, p_5 applies to both NaCl and Na-triflate media, parameters p_6 through p_8 apply to NaCl media only, and p_9 applies to Na-triflate media only. The values for the nine parameters are $p_1 = -7.812\ 93$, $p_2 = 3946.02$, $p_3 = -2.386\ 096 \times 10^{-5}$, $p_4 = 0.021\ 557\ 7$, $p_5 = -0.225\ 671$, $p_6 = 0.551\ 945$, $p_7 = -130.451$, $p_8 = -1.236\ 42 \times 10^{-6}$, and $p_9 = -0.015\ 935\ 8$. Comparisons of the model shown in eq 22 and the data used in the regression are shown in Figures 6 and 7. The agreement factor for this fit is 0.80. The residuals of the regression exhibit no systematic relationship to ionic strength or temperature (Figure 8). Values of $K_{m,2a}$ are derived from eq 22 and the appropriate values for the dissociation of water (Palmer and Drummond, 1988; Busey and Mesmer, 1978). These values are reported in Tables 13 and 14 and are in good agreement with the recalculated Harned cell data, particularly with the recalculated Harned and Fallon (1939) measurements. Whereas eq 22 is strictly valid for Na-triflate solutions at temperatures up to 125 °C and values of ionic strength to 1.0 mol·kg^{-1}, the limits in NaCl solutions are 175 °C and 5.0 mol·kg^{-1}, respectively.

Table 13. Summary of Thermodynamic Quantities for the Second Dissociation of Oxalic Acid in Aqueous Sodium Chloride Media at the Saturation Vapor Pressure[a]

t/°C	log $K_{m,2a}$	ΔH_{2a}/ (kJ·mol^{-1})	ΔS_{2a}/ (J·mol^{-1}·K^{-1})	$\Delta C_{p,2a}$/ (J·mol^{-1}·K^{-1})
		$I = 0$ mol·kg^{-1}		
0	−4.199 ± 0.018	−0.8 ± 1.1	−83 ± 4	−296 ± 44
25	−4.264 ± 0.014	−7.3 ± 0.5	−106 ± 2	−229 ± 27
50	−4.399 ± 0.012	−12.6 ± 0.5	−126 ± 2	−205 ± 18
75	−4.574 ± 0.014	−17.8 ± 0.7	−143 ± 2	−214 ± 13
100	−4.780 ± 0.019	−23.5 ± 0.8	−160 ± 2	−248 ± 19
125	−5.015 ± 0.020	−30.4 ± 1.0	−180 ± 3	−302 ± 32
150	−5.280 ± 0.024	−38.8 ± 1.7	−202 ± 4	−374 ± 54
175	−5.580 ± 0.031	−49.2 ± 2.9	−162 ± 7	−461 ± 73
		$I = 0.1$ mol·kg^{-1}		
0	−3.776 ± 0.015	0.3 ± 1.1	−71 ± 4	−278 ± 45
25	−3.819 ± 0.011	−5.6 ± 0.5	−92 ± 2	−206 ± 27
50	−3.927 ± 0.011	−10.3 ± 0.4	−107 ± 1	−174 ± 18
75	−4.070 ± 0.012	−14.6 ± 0.6	−120 ± 2	−175 ± 13
100	−4.240 ± 0.014	−19.2 ± 0.7	−133 ± 2	−201 ± 18
125	−4.431 ± 0.018	−24.8 ± 1.0	−147 ± 3	−245 ± 31
150	−4.647 ± 0.022	−31.6 ± 1.7	−164 ± 4	−300 ± 53
175	−4.890 ± 0.030	−39.8 ± 2.9	−183 ± 7	−363 ± 71
		$I = 0.5$ mol·kg^{-1}		
0	−3.558 ± 0.022	1.6 ± 1.2	−62 ± 4	−263 ± 45
25	−3.578 ± 0.015	−3.9 ± 0.6	−82 ± 2	−186 ± 27
50	−3.659 ± 0.015	−8.0 ± 0.5	−95 ± 2	−148 ± 18
75	−3.774 ± 0.017	−11.6 ± 0.7	−106 ± 2	−142 ± 13
100	−3.908 ± 0.018	−15.4 ± 0.8	−116 ± 2	−161 ± 19
125	−4.061 ± 0.021	−19.8 ± 1.0	−127 ± 3	−196 ± 31
150	−4.233 ± 0.025	−25.2 ± 1.6	−141 ± 4	−240 ± 51
175	−4.426 ± 0.032	−31.8 ± 2.8	−156 ± 7	−282 ± 69
		$I = 1.0$ mol·kg^{-1}		
0	−3.501 ± 0.026	2.6 ± 1.3	−57 ± 4	−254 ± 30
25	−3.503 ± 0.020	−2.7 ± 0.7	−76 ± 2	−174 ± 24
50	−3.566 ± 0.020	−6.4 ± 0.6	−88 ± 2	−133 ± 17
75	−3.658 ± 0.020	−9.6 ± 0.6	−98 ± 2	−124 ± 12
100	−3.770 ± 0.021	−12.8 ± 0.6	−107 ± 2	−138 ± 18
125	−3.898 ± 0.021	−16.6 ± 0.7	−116 ± 2	−168 ± 30
150	−4.043 ± 0.021	−21.3 ± 1.5	−128 ± 4	−205 ± 45
175	−4.206 ± 0.029	−26.8 ± 2.7	−140 ± 6	−236 ± 61
		$I = 3.0$ mol·kg^{-1}		
0	−3.591 ± 0.053	5.7 ± 2.6	−48 ± 9	−233 ± 38
25	−3.540 ± 0.031	1.0 ± 2.0	−65 ± 6	−150 ± 35
50	−3.548 ± 0.032	−2.1 ± 1.4	−74 ± 5	−102 ± 32
75	−3.587 ± 0.035	−4.4 ± 1.2	−81 ± 4	−85 ± 32
100	−3.640 ± 0.038	−6.5 ± 1.3	−87 ± 4	−92 ± 37
125	−3.707 ± 0.039	−9.1 ± 1.9	−94 ± 5	−112 ± 47
150	−3.787 ± 0.043	−12.2 ± 2.9	−101 ± 7	−134 ± 61
175	−3.880 ± 0.057	−15.7 ± 4.5	−1091 ± 1	−146 ± 78
		$I = 5.0$ mol·kg^{-1}		
0	−3.809 ± 0.095	8.3 ± 4.2	−421 ± 4	−221 ± 48
25	−3.711 ± 0.062	4.0 ± 3.2	−581 ± 1	−135 ± 48
50	−3.676 ± 0.060	1.3 ± 2.4	−66 ± 8	−82 ± 50
75	−3.670 ± 0.067	−0.4 ± 1.8	−71 ± 6	−61 ± 54
100	−3.680 ± 0.070	−1.9 ± 2.1	−76 ± 6	−63 ± 61
125	−3.701 ± 0.071	−3.7 ± 3.2	−80 ± 8	−77 ± 73
150	−3.734 ± 0.078	−5.9 ± 4.9	−851 ± 2	−92 ± 86
175	−3.778 ± 0.100	−8.2 ± 7.0	−911 ± 7	−93 ± 103

[a] Errors listed represent three times the standard deviation.

Table 14. Summary of Thermodynamic Properties for the Second Dissociation of Oxalic Acid in Aqueous Sodium Trifluoromethanesulfonate Media at the Saturation Vapor Pressure of Water[a]

t/°C	log $K_{m,2a}$	ΔH_{2a}/ (kJ·mol^{-1})	ΔS_{2a}/ (J·mol^{-1}·K^{-1})	$\Delta C_{p,2a}$/ (J·mol^{-1}·K^{-1})
		I = 0.1 mol·kg^{-1}		
0	−3.768 ± 0.010	−0.5 ± 0.9	−74 ± 3	−259 ± 27
25	−3.814 ± 0.005	−6.5 ± 0.4	−95 ± 1	−221 ± 20
50	−3.924 ± 0.006	−11.7 ± 0.3	−111 ± 1	−200 ± 13
75	−4.072 ± 0.006	−16.6 ± 0.4	−126 ± 1	−199 ± 8
100	−4.247 ± 0.008	−21.8 ± 0.4	−140 ± 1	−218 ± 14
125	−4.441 ± 0.009	−27.7 ± 0.6	−154 ± 2	−257 ± 27
		I = 0.5 mol·kg^{-1}		
0	−3.532 ± 0.012	−0.3 ± 0.9	−69 ± 3	−248 ± 27
25	−3.564 ± 0.009	−6.0 ± 0.4	−88 ± 1	−210 ± 20
50	−3.655 ± 0.009	−11.0 ± 0.3	−104 ± 1	−186 ± 13
75	−3.779 ± 0.008	−15.5 ± 0.4	−117 ± 1	−182 ± 8
100	−3.924 ± 0.008	−20.1 ± 0.4	−129 ± 1	−197 ± 14
125	−4.084 ± 0.009	−25.4 ± 0.6	−142 ± 2	−230 ± 27
		I = 1.0 mol·kg^{-1}		
0	−3.486 ± 0.021	−0.3 ± 0.9	−68 ± 3	−241 ± 27
25	−3.513 ± 0.019	−5.8 ± 0.4	−87 ± 1	−203 ± 20
50	−3.594 ± 0.019	−10.5 ± 0.3	−101 ± 1	−177 ± 13
75	−3.705 ± 0.019	−14.8 ± 0.4	−113 ± 1	−171 ± 8
100	−3.834 ± 0.019	−19.2 ± 0.4	−125 ± 1	−183 ± 14
125	−3.974 ± 0.020	−24.1 ± 0.6	−137 ± 2	−213 ± 27

[a] Errors listed represent three times the standard deviation.

Numerical differentiation of eq 22 using the ORGLS program yields ΔH_{2b}, ΔS_{2b}, and $\Delta C_{p,2b}$ which were converted to the equivalent values for the acid form (Tables 13 and 14). Although the value obtained for ΔH°_{2a} at 25 °C is not in good agreement with the value reported by Christensen et al. (1967), it is preferred because it is constrained tightly by the precise Harned cell measurements (Table 10). On the other hand, the titration calorimetry experiments were performed over a very narrow temperature range, and ΔH was assumed to be independent of I over the narrow range of ionic strength in which the titrations were performed (Christensen et al., 1967).

Conclusions

Although the revisions proposed here to the generally accepted values describing the dissociation of oxalic acid are relatively minor, they do clarify the apparently anomalous behavior of the dissociation constants of oxalic acid at low temperatures. Previous work in this laboratory (Mesmer et al., 1989; Bell et al., 1993; Kettler et al., 1991, 1992, 1995a,b) has shown that most carboxylic acids become increasingly dissociated with increasing temperature followed by reassociation at higher temperatures (viz., the temperature dependence of log $K_{m,\mathrm{na}}$ reverses with increasing temperature). As the concentration of a supporting electrolyte increases, the temperature at which this reversal occurs also increases. The reassociation is driven by the decline in the value of $T\Delta S_a$ that is a consequence of hydration of the product ions (Mesmer et al., 1988). The negative value of $T\Delta S_a$ is offset by ΔH_a in solutions with high ionic strength and low temperatures: ΔH_a is dominated by the breaking of the H-anion bond rather than by the hydration of the product ions (Mesmer et al., 1988). The first dissociation of oxalic acid had been an exception to this trend: values of log $K_{m,1a}$ became more negative with increasing temperature irrespective of the solution ionic strength (Kettler et al., 1991; McAuley and Nancollas, 1961; Kurz and Farrar, 1969). The data in Tables 11 and 12 are evidence that the behavior of oxalic acid is not anomalous, but rather that previously published schemes were inadequate for treating a diprotic acid with closely spaced $\mathrm{p}K^{\ominus}_{1a}$ and $\mathrm{p}K^{\ominus}_{1b}$ values; a problem exacerbated by the relatively low $\mathrm{p}K^{\ominus}_{1a}$ value.

The differences in the values of log $K_{m,na}$ in the two different ionic media are very small and exceed the assigned errors only at temperatures above 50 °C and values of ionic strength of 1 mol·kg^{-1}. The small differences result from similarities in ΔS_{1a}. On the other hand, values of ΔH_{2a} and ΔS_{2a} in the two media do differ by amounts exceeding the combined errors even when the values of log $K_{m,2a}$ are not significantly different. Values of ΔH_{2a} obtained in NaCl media are greater than those obtained in Na-triflate media. The difference in ΔH_{2a} values is partially offset by the differences in ΔS_{2a} values; the latter are also greater in NaCl media than in Na-triflate media.

The results of this study revise the generally accepted values for the dissociation of oxalic acid at low temperatures and ionic strengths and present some new measurements for the dissociation of oxalic acid in Na-triflate media. These revisions clarify the thermodynamics of the first dissociation of oxalic acid and are evidence that oxalic acid behaves similarly to other carboxylic acids in aqueous solutions. The measurement of the molal dissociation constants of oxalic acid in Na-triflate solutions provides the information necessary to measure the association quotients of a variety of metal−oxalate complexes in a noncomplexing electrolyte.

Literature Cited

Ayres, J. A. *Decontamination of nuclear reactors and equipment*; Ronald Press: New York, 1970.

Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976.

Bates, R. G. *Determination of pH, Theory and Practice*; Wiley: New York, 1964.

Bauer, R. F.; Smith, W. M. The mono-oxalato complexes of iron(III). Part I. Equilibria. *Can. J. Chem.* **1965**, *43*, 2755−2762.

Bayri, B.; Rosset, R.; Desbarres, J.; Jardy, A.; Noel, D.; Kerrec, O.; Lantes, B. Complexing properties of the main organic acids used in decontamination solutions for nuclear power plants and reactions involving their degradation or elimination. *Nucl. Eng. Des.* **1996**, *160*, 159−170.

Bell, J. L. S.; Wesolowski, D. J.; Palmer, D. A. The dissociation of formic acid in sodium chloride solutions to 200 °C. *J. Solution Chem.* **1993**, *22*, 125−136.

Bénézeth, P.; Palmer, D. A.; Wesolowski, D. J. Dissociation quotients for citric acid in aqueous sodium chloride media to 150 °C. *J. Solution Chem.* **1997**, *26*, 63−84.

Bottari, E.; Ciavatta, L. Potentiometric study of iron(II)-oxalate complexes. *Gazz. Chim. Ital.* **1965**, *95*, 908−920.

Busey, R. H.; Mesmer, R. E. The ionization of water in NaCl media to 300 °C. *J. Solution Chem.* **1976**, *5*, 147−152.

Busey, R. H.; Mesmer, R. E. Thermodynamic quantities for the ionization of water in NaCl media to 300 °C. *J. Chem. Eng. Data* **1978**, *23*, 175−176.

Busing, W. R.; Levy, H. A. *ORGLS: A general fortran least-squares program*; Oak Ridge National Laboratory Report, ORNL-TM (U.S.) ORNL-TM-271, Oak Ridge National Laboratory, Oak Ridge, TN, 1963.

Choppin, G. R.; Chen, J. F. Complexation of Am(III) by oxalate in NaClO$_4$ media. *Radiochim. Acta* **1996**, *74*, 105−110.

Christensen, J. J.; Izatt, R. M.; Hansen, L. D. Thermodynamics of proton ionization in dilute aqueous solution. VII. $\Delta H°$ and $\Delta S°$ values for proton ionization from carboxylic acids at 25°. *J. Am. Chem. Soc.* **1967**, *89*, 213−222.

Cruywagen, J. J.; Heyns, J. B.; van der Water, R. F. A potentiometric, spectrophotometric, and calorimetric investigation of molybdenum-(VI)-oxalate complex formation. *J. Chem. Soc., Dalton Trans.* **1986**, 1857−1862.

Darken, L. S. The ionization constants of oxalic acid at 25 °C from conductance measurements. *J. Am. Chem. Soc.* **1941**, *63*, 1007−1011.

de Bruin, H. J.; Kairaitis, D.; Temple, R. B. The extraction of anionic beryllium complexes by tri-iso-octylamine. *Aust. J. Chem.* **1962**, *15*, 457−466.

Dickson, A.; Wesolowski, D. J.; Palmer, D. A.; Mesmer, R. E. Dissociation constant of bisulfate in aqueous sodium chloride solutions to 250 °C. *J. Phys. Chem.* **1990**, *94*, 7978−7985.

Graustein, W. C.; Cromack, K., Jr.; Sollins, P. Calcium oxalate: Occurrence in soils and effect on nutrient and geochemical cycles. *Science* **1977**, *198*, 1252−1254.

Harned, H. S.; Wright, D. D. A study of the cell, Pt/quinhydrone, HCl (0.01 *M*)/AgCl/Ag, and the normal electrode potential of the quinhydrone electrode from 0 to 40°. *J. Am. Chem. Soc.* **1933**, *55*, 4849−4857.

Harned, H. S.; Fallon, L. D. The second ionization constant of oxalic acid from 0 to 50 °C. *J. Am. Chem. Soc.* **1939**, *61*, 3111−3113.

Ho, P. C.; Palmer, D. A. Electrical conductances of dilute aqueous trifluoromethanesulfonate solutions at temperatures 0−450 °C and pressure up to 250 MPa. *J. Solution Chem.* **1995**, *24*, 753−769.

Kettler, R. M.; Palmer, D. A.; Wesolowski, D. J. Dissociation quotients of oxalic acid in aqueous sodium chloride media to 175 °C. *J. Solution Chem.* **1991**, *20*, 905−927.

Kettler, R. M.; Wesolowski, D. J.; Palmer, D. A. Dissociation quotients of malonic acid in aqueous sodium chloride media to 100 °C. *J. Solution Chem.* **1992**, *21*, 883−900.

Kettler, R. M.; Wesolowski, D. J.; Palmer, D. A. Dissociation quotient of benzoic acid in aqueous sodium chloride media to 250 °C. *J. Solution Chem.* **1995a**, *24*, 385−407.

Kettler, R. M.; Palmer, D. A.; Wesolowski, D. J. Dissociation quotients of succinic acid in aqueous sodium chloride media to 250 °C. *J. Solution Chem.* **1995b**, *24*, 65−87.

Kurz, J. L.; Farrar, J. M. The entropies of dissociation of some moderately strong acids. *J. Am. Chem. Soc.* **1969**, *91*, 6057−6062.

Lindsay, W. T., Jr. Estimation of concentration quotients for ionic equilibria in high temperature water. *Proc. Int. Water Conf. Eng. Soc. W. Pa.* **1980**, *41*, 284−294.

Maeda, M.; Hisada, O.; Kinjo, Y.; Ito, K. Estimation of salt and temperature effects on ion product of water in aqueous solution. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3233−3239.

Martell, A. E.; Smith, R. M. *Critical Stability Constants. Volume 3: Other Organic Ligands*; Plenum: New York, 1977.

McAuley, A.; Nancollas, G. H. Complex formation in solutions of copper oxalate. *Trans. Faraday Soc.* **1960**, *56*, 1165−1171.

McAuley, A.; Nancollas, G. H. Thermodynamics of ion association. Part VII. Some transition- metal oxalates. *J. Chem. Soc. A* **1961**, 2215−2221.

Mesmer, R. E.; Holmes, H. F. pH, definition and measurement at high temperatures. *J. Solution Chem.* **1992**, *21*, 725−744.

Mesmer, R. E.; Baes, C. F., Jr.; Sweeton, F. H. Acidity measurements at elevated temperatures. IV. Apparent dissociation of water in 1 m potassium chloride up to 292 °C. *J. Phys. Chem.* **1970**, *74*, 1937−1942.

Mesmer, R. E.; Marshall, W. L.; Palmer, D. A.; Simonson, J. M.; Holmes, H. F. Thermodynamics of aqueous association and ionization reactions at high temperatures and pressures. *J. Solution Chem.* **1988**, *17*, 699−718.

Mesmer, R. E.; Patterson, C. S.; Busey, R. H.; Holmes, H. F. Ionization of acetic acid in NaCl(aq) media: A potentiometric study to 573 K and 130 bar. *J. Phys. Chem.* **1989**, *93*, 7483−7490.

Mills, I.; Cvitaš, T.; Homann, K.; Kallay, N.; Kuchitsu, K. *Quantities, units and symbols in physical chemistry*; Blackwell Scientific Publications: Oxford, 1993.

Moorhead, E. G.; Sutin, N. Rate and equilibrium constants for the formation of the monooxalate complex of iron (III). *Inorg. Chem.* **1966**, *5*, 1866−1871.

Palmer, D. A.; Drummond, S. E. The molal dissociation quotients of water in sodium trifluoromethanesulfonate solutions to high temperatures. *J. Solution Chem.* **1988**, *17*, 153−164.

Palmer, D. A.; Hyde, K. E. Ferrous chloride and acetate complexation in aqueous solutions at high temperatures. *Geochim. Cosmochim. Acta* **1993**, *57*, 1393−1408.

Palmer, D. A.; Wesolowski, D. J. Aluminum speciation and equilibria in aqueous solution. III. Potentiometric determination of the first hydrolysis constant of aluminum(III) in sodium chloride solutions to 125 °C. *Geochim. Cosmochim. Acta* **1993**, *57*, 2929−2938.

Parton, H. N.; Gibbons, R. C. The thermodynamic dissociation constants of oxalic acid. *Trans. Faraday Soc.* **1939**, *35*, 542−545.

Pinching, G. D.; Bates, R. G. Second dissociation constant of oxalic acid from 0° to 50 °C, and the pH of certain oxalate buffer solutions. *J. Res. Natl. Bur. Stand. (U.S.)* **1948**, *40*, 405−416.

Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **1973**, *77*, 268−277.

Quist, A. S.; Marshall, W. L. Assignment of limiting equivalent conductances for single ions to 400 °C. *J. Phys. Chem.* **1965**, *69*, 2984−2987.

Rajan, K. S.; Martell, A. E. Equilibrium studies of uranyl complexes-IV. Reactions with carboxylic acids. *J. Inorg. Nucl. Chem.* **1967**, *29*, 523−529.

Robinson, R. A.; Stokes, R. H. *Electrolyte solutions*; Butterworth: London, 1959.

Ubaldini, S.; Piga, L.; Fornari, P.; Massidda, R. Removal of iron from quartz sands: A study of column leaching using a complete factorial design. *Hydrometallurgy* **1996**, *40*, 369−379.

Vegliò, F.; Passariello, B.; Toro, L.; Marabini, A. M. Development of a bleaching process for a kaolin of industrial interest by oxalic, ascorbic, and sulfuric acids: Preliminary study using statistical methods of experimental design. *Ind. Eng. Chem. Res.* **1996**, *35*, 1680−1687.

Wesolowski, D. J.; Drummond, S. E.; Mesmer, R. E.; Ohmoto, H. Hydrolysis equilibria of tungsten(VI) in aqueous sodium chloride solutions to 300 °C. *Inorg. Chem.* **1984**, *23*, 1120−1132.

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