Papers in the Earth and Atmospheric Sciences   Earth and Atmospheric Sciences, Department of

1995

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The dissociation quotient of benzoic acid was determined potentiometrically in a concentration cell fitted with hydrogen electrodes. The hydrogen ion molality of benzoic acid/benzoate solutions was measured relative to a standard aqueous HCl solution at seven temperatures from 5 to 250°C and at seven ionic strengths ranging from 0.1 to 5.0 molal (NaCl). The molal dissociation quotients and selected literature data were fitted in the isocoulombic (all anionic) form by a six-term equation. This treatment yielded the following thermodynamic quantities for the acid dissociation equilibrium at 25°C and 1 bar: $logK_a = -4.206 \pm 0.006$, $\Delta H_a^o = 0.3 \pm 0.3$ kJ-mol^{-1}, $\Delta S_a^o = -79.6 \pm 1.0$ J-mol^{-1}-K^{-1}, and $\Delta C_{p;a}^o = -207 \pm 5$ J-mol^{-1}-K^{-1}. A five-term equation derived to describe the dependence of the dissociation constant on solvent density is accurate to 250°C and 200 MPa.

KEY WORDS: Benzoic acid; dissociation constant; ionization constant; potentiometry; ionic strength, temperature and pressure dependence; thermodynamics.

1. INTRODUCTION

The ionization of benzoic acid is of great interest to the chemical and geological sciences. Much of the interest in the chemical community results from attempts to evaluate the validity of the Hammett equation[1] or other free-energy relationships.[2] These studies have established a discrepancy between thermodynamic properties derived from differentiation of $logK_a$ with respect to T and those measured using solution calorimetry.[3]

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Benzoic acid has been identified in a number of fluids of inter-
est to the geological community including landfill leachates,[4,5]
petrochemical wastewaters,[6] and the vadose waters found in forest
soils,[7] and at a variety of hazardous and nuclear waste sites.[8,9] High
temperature fluids, in particular those associated with petroleum,
contain significant amounts of benzoic acid. These solutions include
sedimentary basin brines,[10,11] oil shale retort and tar sand byproduct
waters,[12,13] and waters present during hydrous pyrolysis of kerogen
in the presence of limonite.[14] Benzoic acid complexes transition
metal ions and is, therefore, of importance to research related to
weathering, sedimentary diagenesis and the formation of ore de-
posits.

The dissociation of benzoic acid follows the reaction

$$C_6H_5CO_2H \leftrightarrow H^+ + C_6H_5CO_2^- \tag{1}$$

The molal dissociation quotient for this reaction Q_a is defined in
terms of molal concentrations and is related to the equilibrium dis-
sociation constant K_a as shown in Eq. (2).

$$Q_a = \frac{[H^+][C_6H_5CO_2^-]}{[C_6H_5CO_2H^-]} = K_a \frac{\gamma_{C_6H_5CO_2H}}{\gamma_{H^+}\gamma_{C_6H_5CO_2^-}} \tag{2}$$

Equation (1) can be written in its basic, or anionic, form by combin-
ing it algebraically with the water dissociation reaction

$$C_6H_5CO_2H + OH^- \leftrightarrow C_6H_5CO_2^- + H_2O \tag{3}$$
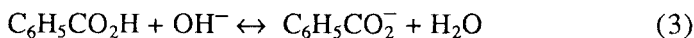
with the relevant concentration quotient defined as

$$Q_b = \frac{[C_6H_5CO_2^-]}{[C_6H_5CO_2H][OH^-]} = K_b \frac{\gamma_{OH^-}\gamma_{C_6H_5CO_2H}}{a_w\gamma_{C_6H_5CO_2^-}} \tag{4}$$

where a_w is the activity of water. Although data exist at temperatures
ranging from 0 to 250°C (Table I), few measurements have been
made in solutions of high ionic strength. The few studies performed
at higher ionic strengths have used tetraalklyammonium salts as a
supporting electrolyte[29-31] and are not directly relevant to aqueous
solutions of geochemical interest. The dissociation quotients of ben-
zoic acid have, therefore, been measured in aqueous NaCl media to
ionic strengths of 5.0m and to temperatures of 250°C, the limit of
thermal stability of benzoic acid in this experimental environment.

Table I. Summary of the Thermodynamic Data for the Dissociation of Benzoic Acid at Saturated Vapor Pressure[a]

pK_a	$\Delta H_a{}^b$	$\Delta S_a{}^c$	$\Delta C_{p;a}^{o}{}^{c}$	T (°C)	Ref.
4.223±0.010[d]				5	15
4.204±0.005[d]	0.251±0.021			25	15
4.224±0.005[d]				50	15
4.266±0.010[d]				70	15
4.336±0.015[d]				90	15
4.202[d,e]				25	16
4.390[d,e]				99.9	16
4.401[d,e]				100.0	16
4.621[d,e]				150.2	16
4.626[d,e]				150.3	16
4.965[d,e]				200.2	16
4.925[d,e]				200.2	16
5.428[d,e]				250.9	16
5.392[d,e]				251.0	16
	4.01±0.15			5.0	17
	2.51±0.15			12.5	17
	0.44±0.15			25.0	17
	-1.90±0.15			40.0	17
	-3.29±0.17			50.0	17
	-4.79±0.23			65.0	17
	-5.95±0.27			75.0	17
	-7.17±0.27			85.0	17
	-9.08±0.36			100.0	17
4.218				15	18
4.208				20	18
4.202	0.627±0.10	78.2±0.3		25	18
4.205				30	18
4.210				35	18
4.219				40	18
4.202	-0.28±0.079	-81.35±0.2	-176±12	25	19
	0.42±0.042[d]			25	20
	0.63±0.21[d]	-78.2		25	21
4.208				25	22
4.236				25	22
4.244				50	22
4.260				50	22
4.347				100	22
4.377				100	22
4.553				150	22
4.585				150	22
4.854				200	22
4.886				200	22
5.051				225	22

Table I. Continued

pK_a	$\Delta H_a{}^b$	$\Delta S_a{}^c$	$\Delta C_{p;a}^{o}{}^{c}$	$T\,(°C)$	Ref.
5.070				225	22
4.205[d]	1.41	-75.7	-198	20	23
4.201[d]	0.44	-79.1	-202	25	23
4.203[d]	-0.60	-82.4	-205	30	23
4.205[d]	-1.63	-85.8	-208	35	23
	0.38±0.21[d]			25	24
	3.080			5	25
			-115	10	25
	1.925[d]			15	25
			-143	20	25
	0.494[d]			25	25
			-163	30	25
	-1.138[d]			35	25
			-161	40	25
	-2.749[d]			45	25
			-156	50	25
	-4.306[d]			55	25
4.216[d]				10	26
4.209[d]				15	26
4.205[d]				20	26
4.201[d]				25	26
4.202[d]				30	26
4.208[d]				35	26
4.211[d]				40	26
4.218[d]				45	26
4.222[d]				50	26
4.236[d]				55	26
4.248[d]				60	26
4.262[d]				65	26
4.277[d]				70	26
4.293[d]				75	26
4.311[d]				80	26
4.330[d]				85	26
4.351[d]				90	26
4.373[d]				95	26
4.395[d]				100	26
4.214				15	27
4.212				20	27
4.213	0.502	-74.7	163	25	27
4.215				30	27
4.221				35	27
4.232				40	27
4.241				45	27
4.203				25	28

Table I. Continued

pK_a	$\Delta H_a{}^b$	$\Delta S_a{}^c$	$\Delta C_{p;a}^{o}{}^c$	T (°C)	Ref.
4.208				35	28
4.219				50	28
4.236				60	28
4.262				75	28
4.309				90	28
4.209				35	29

[a] 1 bar at T ≤ 100°C. [b] Units: kJ-mol^{-1}. [c] Units: J-mol^{-1}-K^{-1}. [d] These values were combined with the results of this study in the fitting process. [e] Values extrapolated to saturation vapor pressure, see text.

2. EXPERIMENTAL

2.1 Materials

All solutions were prepared from reagent grade chemicals and distilled, deionized water (resistivity ≥0.183 MΩm). Stock solutions of NaCl, NaOH and HCl were sparged and stored under argon in polypropylene containers. The test solutions were made using reagent grade benzoic acid (Mallinckrodt lot 0112 KVRK) combined with the NaOH and NaCl stock solutions and purified water. The protolytic purity of the benzoic acid was checked by titration against a standard NaOH solution. This titration yielded an equivalent weight for benzoic acid of 122.1 g-eq^{-1} (cf. actual equivalent weight of 122.12). The high temperature cell was pressurized with ultrapure Matheson (99.999%) hydrogen.

Two stock reference solutions with ionic strengths of 1 and 5 molal were prepared (ionic strength was determined from the stoichiometric molalities of all ions in solution) and diluted to the appropriate ionic strength prior to each experiment (Table II). The molal ratios of HCl:NaCl in these stock solutions were 1:199 and 1:999 for the 1 and 5 molal solutions, respectively. Two stock test solutions with ionic strengths of 1 and 5 molal were prepared and diluted as necessary for the experimental runs (Table II). The 5 molal solution had a ratio of benzoic acid to NaCl of 1:123 whereas the ratio in the 1 molal solution was 1:23. Although equivalent formal concentrations of NaOH and benzoic acid were used in the 1 molal stock solution, sufficient NaOH was added to the 5m stock solution to produce a benzoate:benzoic acid ratio of 8:1. As benzoic

Table II. Starting Molal Solution Compositions

Expt.	Test Cell			Ref. Cell	
	$m(NaCl)$	$m(C_6H_5CO_2H)$	$m(NaOH)$	$m(NaCl)$	$m(HCl)$
2,8,13	0.9900	0.02010	0.01006	0.9950	0.005000
9	0.09898	0.002010	0.001006	0.09950	0.0005000
10	0.4948	0.01004	0.005028	0.4975	0.002500
11	0.3300	0.006699	0.003353	0.3317	0.001667
14	0.09898	0.002010	0.001006	0.09951	0.0005000
15	0.3299	0.006697	0.003352	0.3317	0.001666
16	0.4949	0.01005	0.005029	0.4975	0.002500
18	0.9970	0.001996	0.001777	0.9950	0.005000
19	0.9969	0.001996	0.001776	0.9950	0.005000
21	2.991	0.005988	0.005330	2.997	0.003000
22	3.987	0.007984	0.007105	3.997	0.004001
23	4.993	0.009998	0.008898	4.995	0.005000

acid is sparingly soluble in NaCl solutions, this high ratio allowed sufficient benzoic acid to be dissolved to perform the experiments.

2.2 Apparatus and Procedures

The static concentration cell used in this study has been described by Mesmer et al.,[32] with modifications described by Wesolowski et al.[33] and Kettler et al.[34] The solution compositions listed in Table II define the cell configuration

$$Pt,H_2 \mid C_6H_5CO_2H,NaCl,NaOH \parallel NaCl,HCl \mid H_2,Pt$$

The porous Teflon liquid junction was saturated with stock reference solution prior to each experiment. The cell was assembled and purged at least five times by pressurizing the vessel to 1.5 MPa with hydrogen and venting to ambient room pressure. The solutions in the cell were stirred with Teflon-coated magnetic (Alnico-V) stirring bars during all phases of the experiments. The hydrogen pressure was then regulated to approximately 1.5 MPa and the system allowed to attain thermal equilibrium in either the oil or water baths. Equilibrium was considered to be achieved when the potential changed by less than 0.01 mV over a 4 minute period. After a stable potential was observed, the potential, temperature, and pressure were recorded. The bath temperature was then increased to the next setpoint and the data collection repeated. The cell was allowed to stabilize overnight (10 to 12 h) for those runs beginning at 5°C, whereas initial equilib-

rium was achieved in approximately 2.5 h for those runs beginning at 100°C and within 1 to 2 h at subsequent temperature increments.

3. RESULTS

The observed potential (Table III) is related to the cell composition by the relationship

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

where square brackets denote the molality of the enclosed species and the subscripts r and t refer to the reference and test solutions, respectively; the ideal gas and Faraday constants are designated by R and F, respectively; and the absolute temperature is denoted by T. The use of matching ionic media in both the test and reference compartments minimizes the second term in Eq. (5), reduces the ratio of activity coefficients for minor ions to unity, and permits use of molal concentrations rather than activities.

The second term in Eq. (5) is the approximation for the liquid junction potential (Table III) obtained from the Henderson equation [Eqs. (2 -12) of Baes and Mesmer.[35]] The limiting equivalent conductances for Na^+, H^+, OH^-, and Cl^- are taken from Quist and Marshall.[36] Limiting equivalent conductances for benzoate at temperatures from 5 to 100°C were obtained by subtracting the limiting equivalent conductance for $H^{+[36]}$ from those obtained for benzoic acid by Strong et al.[26] The potassium benzoate data collected by Ellis[22] were combined with the Quist and Marshall data for K^+ to obtain limiting equivalent conductances of benzoate at temperatures greater than 100°C. The liquid junction potentials in this study were less than 0.3 mV, which corresponds to a maximum correction of approximately 0.005 log units to the equilibrium quotient. If the Henderson approximation can estimate liquid junction potentials to within 25%, as suggested by Mesmer and Holmes,[37] then the uncertainty to $\log Q$ is on the order of 0.001 or less.

The hydrogen ion molality (Table III), which was calculated from Eq. (5), was used to determine the ratio of benzoate anion:total benzoate $\bar{n}$ (Table III) using the relation

$$\bar{n} = \frac{m_{NaOH}+[H^+] - [OH^-]}{m_{C_6H_5CO_2H}} \tag{6}$$

Table III. Experimental Results for the Dissociation Quotient
of Benzoic Acid

	T	I	E	$e_{lj}{}^a$	pH^b	$\bar{n}$	$s_{\bar{n}}$	pQ_a	s_a	-pQ_b	s_b
2	100.02	1.001	124.06	0.133	3.978	0.506	0.005	3.968	0.002	7.898	0.012
	150.81	1.004	151.51	0.087	4.102	0.504	0.005	4.094	0.002	7.010	0.011
	199.95	1.010	184.58	0.038	4.264	0.503	0.005	4.258	0.002	6.340	0.011
	249.94	1.022	222.88	-0.004	4.439	0.502	0.005	4.435	0.002	5.807	0.011
8	5.12	1.000	93.30	0.249	3.995	0.506	0.005	3.986	0.003	10.473	0.015
	24.90	1.000	96.85	0.208	3.942	0.506	0.005	3.932	0.003	9.785	0.014
	49.96	1.000	103.80	0.208	3.923	0.506	0.005	3.912	0.003	9.052	0.013
	100.04	1.001	123.87	0.133	3.976	0.506	0.005	3.966	0.002	7.900	0.012
	149.95	1.003	150.93	0.087	4.099	0.504	0.005	4.091	0.002	7.023	0.011
	199.84	1.009	184.55	0.038	4.264	0.503	0.005	4.259	0.002	6.340	0.011
	249.94	1.020	222.99	-0.004	4.441	0.502	0.005	4.437	0.002	5.805	0.011
9	5.08	0.100	44.37	0.201	4.108	0.539	0.005	4.040	0.003	10.474	0.016
	25.02	0.100	46.02	0.161	4.082	0.542	0.005	4.009	0.003	9.764	0.014
	50.02	0.100	50.42	0.169	4.090	0.541	0.005	4.019	0.003	9.021	0.013
	99.94	0.100	65.92	0.109	4.193	0.532	0.005	4.136	0.002	7.862	0.012
	149.76	0.100	89.84	0.073	4.371	0.522	0.005	4.334	0.002	6.995	0.011
10	5.03	0.500	75.96	0.243	3.983	0.511	0.005	3.963	0.003	10.480	0.016
	24.92	0.500	79.04	0.202	3.942	0.512	0.005	3.921	0.003	9.778	0.014
	50.00	0.500	85.26	0.203	3.935	0.512	0.005	3.913	0.003	9.039	0.013
	99.95	0.500	104.82	0.132	4.019	0.510	0.005	4.002	0.002	7.877	0.012
	149.85	0.501	132.18	0.088	4.177	0.507	0.005	4.164	0.002	6.998	0.011
	199.99	0.504	168.08	0.041	4.389	0.505	0.005	4.381	0.002	6.311	0.011
	249.94	0.509	211.20	0.000	4.629	0.503	0.005	4.624	0.002	5.778	0.011
11	4.99	0.333	66.99	0.235	3.996	0.516	0.005	3.969	0.003	10.486	0.016
	24.98	0.333	69.65	0.193	3.959	0.517	0.005	3.929	0.003	9.779	0.014
	49.98	0.333	75.77	0.196	3.963	0.517	0.005	3.934	0.003	9.033	0.013
	99.98	0.334	94.66	0.126	4.058	0.514	0.005	4.034	0.002	7.868	0.012
	149.89	0.334	121.23	0.083	4.222	0.509	0.005	4.206	0.002	6.995	0.011
	199.96	0.336	155.91	0.036	4.436	0.506	0.005	4.425	0.002	6.325	0.011
13	5.04	1.000	93.47	0.249	3.999	0.505	0.005	3.989	0.003	10.473	0.015
	24.84	1.000	96.97	0.207	3.945	0.506	0.005	3.934	0.003	9.785	0.014
	49.96	1.000	103.87	0.207	3.924	0.506	0.005	3.913	0.003	9.052	0.013
	100.10	1.001	123.96	0.132	3.976	0.506	0.005	3.966	0.002	7.899	0.012
	149.91	1.003	150.96	0.087	4.099	0.504	0.005	4.091	0.002	7.024	0.011
	199.97	1.009	185.01	0.037	4.269	0.503	0.005	4.263	0.002	6.336	0.011
14	100.02	0.100	65.95	0.110	4.193	0.532	0.005	4.137	0.002	7.861	0.012
	199.97	0.101	124.96	0.034	4.629	0.512	0.005	4.609	0.002	6.311	0.011
	249.95	0.102	171.12	-0.004	4.943	0.505	0.005	4.934	0.002	5.781	0.011
15	100.03	0.333	94.65	0.129	4.058	0.514	0.005	4.035	0.002	7.866	0.012
	201.02	0.336	158.81	0.041	4.463	0.506	0.005	4.454	0.002	6.288	0.011

Table III. Continued

	T	I	E	$e_{lj}{}^a$	pH^b	$\bar{n}$	$s_{\bar{n}}$	pQ_a	s_a	$-pQ_b$	s_b
16	100.00	0.500	104.76	0.129	4.018	0.510	0.005	4.001	0.002	7.876	0.012
	199.98	0.504	166.70	0.037	4.375	0.505	0.005	4.367	0.002	6.323	0.011
18	100.10	0.999	192.13	0.194	4.898	0.897	0.005	3.960	0.005	7.901	0.012
19	100.08	0.999	192.12	0.193	4.898	0.896	0.005	3.962	0.005	7.903	0.012
	199.98	1.006	267.98	0.126	5.154	0.891	0.005	4.239	0.005	6.360	0.012
21	5.08	2.996	141.63	0.048	5.089	0.891	0.005	4.175	0.005	10.534	0.015
	25.01	2.996	147.84	0.040	5.023	0.892	0.005	4.107	0.005	9.854	0.014
	49.95	2.997	157.02	0.039	4.973	0.892	0.005	4.056	0.005	9.144	0.013
	100.05	2.999	178.76	0.025	4.937	0.892	0.005	4.020	0.005	8.019	0.012
	149.90	3.006	204.20	0.016	4.954	0.892	0.005	4.038	0.005	7.149	0.012
22	5.06	3.994	156.78	0.044	5.239	0.891	0.005	4.328	0.005	10.539	0.015
	24.97	3.994	164.04	0.036	5.172	0.891	0.005	4.260	0.005	9.858	0.014
	49.94	3.995	172.30	0.035	5.086	0.891	0.005	4.174	0.005	9.178	0.013
	100.06	3.998	193.23	0.020	5.007	0.891	0.005	4.094	0.005	8.069	0.012
	149.90	4.006	217.53	0.011	4.988	0.891	0.005	4.075	0.005	7.191	0.012
23	4.99	5.002	175.30	0.055	5.478	0.890	0.005	4.569	0.006	10.469	0.015
	24.97	5.002	180.42	0.047	5.352	0.890	0.005	4.442	0.005	9.847	0.014
	50.00	5.003	188.43	0.046	5.240	0.891	0.005	4.330	0.005	9.185	0.013
	100.06	5.005	207.25	0.031	5.100	0.891	0.005	4.189	0.005	8.113	0.012
	149.95	5.018	229.91	0.022	5.039	0.891	0.005	4.127	0.005	7.232	0.012
	200.01	5.047	254.86	0.012	5.012	0.891	0.005	4.101	0.005	6.479	0.012

^{a} Liquid junction potential, see text. ^{b} pH is defined as the negative logarithim of the hydrogen ion molality in this study.

where m_x is the stoichiometric molality of the reagent in solution, $[H^+]$ is the measured molal hydrogen ion concentration, and $[OH^-]$ is calculated from $[H^+]$ using the data of Busey and Mesmer[38] for dissociation of water in aqueous NaCl media. The relevant dissociation quotients (Table III) are obtained from

$$Q_a = \frac{[H^+]\,\bar{n}}{1 - \bar{n}} \tag{7}$$

and

$$Q_b = \frac{\bar{n}}{(1 - \bar{n})[OH^-]} \tag{8}$$

The calculation is an iterative one involving the liquid junction potential and ionic strength. The estimated uncertainties in 16 variables (e.g., solution composition, potential, liquid junction correction, etc.)

are used to calculate the uncertainty in $\bar{n}$ and in the dissociation quotients (Table III).

Many of the experimental runs made during development of the technique did not yield stable, reproducible potentials. For example, two experimental runs were performed using aliquots of the $1m$ stock solutions and coating the electrodes with fresh platinum black before each run; the potentials measured at 25°C differed by 1 mV and those measured at 100°C differed by 3 mV. At temperatures below 100°C the potential drifted to more positive values (higher pH), whereas the drift was back toward 0 (lower pH) at temperatures or 100°C or more. If the platinum-black-coated electrodes were allowed to age and stabilize, reproducible potentials were attainable, however. A number of experiments were repeated to check the precision of the data (Expts. 2, 8 and 13; 9 and 14; 11 and 15; 10 and 16; Table III). Reproducibility of $\log Q$ was better than 0.002 at 100°C and acceptable at higher temperatures (0.005 to 0.029 at 200°C and 0.002 at 250°C) when the electrodes were allowed to age. Several previous attempts[22,23,39] to measure the dissociation quotient of benzoic acid reported difficulty in obtaining stable, reproducible results. This difficulty is postulated to have resulted either from decarboxylation of benzoic acid[16] or reduction of benzoic acid to its naphthenic counterpart (cyclohexane carboxylic acid). The latter possibility is suggested by early efforts to define suitable pH buffer solutions that describe reduction of phthalate to hexhydrophthalate in experimental systems with platinum hydrogen-electrodes.[40,41] The rate at which benzoic acids are reduced to naphthenic acids depends strongly on the amount of platinum sponge present on the electrode.[42] Although the cause of the drifting, non-reproducible potentials observed in this study is unknown, it is consistent with reduction of the aromatic ring at temperatures below 100°C and with decarboxylation at higher temperature. Reduction of benzoic acid to cyclohexane carboxylic acid should cause pH to increase: at low temperatures cyclohexane carboxylic acid is a weaker acid than benzoic acid.[43-45] The drift to lower pH observed at high temperature is consistent with decarboxylation. Aromatic acids will decarboxylate *via* either the arenium ion mechanism or by unimolecular substitution of the carboxylate anion.[46] The former mechanism requires deprotonation of the carboxylic acid immediately before cleavage of the carboxyl group, whereas the latter mechanism is relevant only to the deprotonated anion. In either case the benzoic acid will become increasingly dissociated.
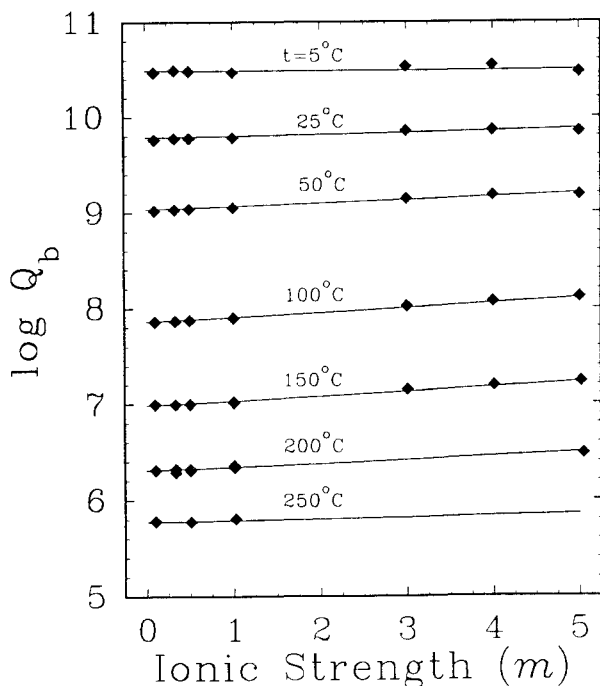
Fig. 1. The relationship between $\log Q_b$ and solution ionic strength at temperatures ranging from 5 to 250°C. The solid curves are derived from Eq. (10).

4. DISCUSSION

4.1 Regression of Experimental Data

Previous work on carboxylic acids in this laboratory[34,47-49] has shown that whereas the equilibrium quotients for the acid forms of the dissociation reaction exhibit considerable curvature as a function of ionic strength, the anionic forms of the reactions exhibit a much simpler dependence (Fig. 1). Because Δz^2 is equal to 0 when the reaction is written in the anionic or isocoulombic form, extrapolation to infinite dilution is simplified greatly. The isocoulombic form should also have small changes in heat capacity and volume,[50] thereby simplifying computation of the corresponding thermodynamic parameters. Therefore the data collected in this study and selected data from the literature (Table I) were fitted in their anionic form using the ORGLS least squares fitting program.[51] Included in the fit were the glass electrode data of Travers *et al.*,[15] the high temperature con-

Table IV. Correction of Read's Data to Saturation Vapor Pressure: Coefficients for Eq. (9) and Values of $pK_{a(sat)}$[a]

T (°C)	$pK_{a(1\ bar)}$[b]	a	b	c	$pK_{a(sat)}$[c]
25	4.203	-4.18887	10.3523	29.2065	4.202
99.9	4.388	-4.14715	13.3412	9.97004	4.390
100.0	4.399	-4.16113	13.3184	17.9923	4.401
150.2	4.623	-4.09091	15.1222	28.2202	4.621
150.3	4.625	-4.09118	15.0468	23.3914	4.626
200.2	4.964	-4.07775	16.3435	36.4860	4.965
200.2	4.927	-4.06815	16.1127	40.3257	4.925
250.9	5.446	-4.04007	16.4111	23.1312	5.428
251.0	5.409	-4.09178	15.7172	25.2252	5.392

[a] Ref. 16. [b] Extrapolated values reported by Read[16] for T and 1 bar. [c] Values at saturation vapor pressure retrieved using Eq. (9) for each isothermal data set.

ductance measurements of Read,[16] the detailed conductance measurements of Strong et al.,[26] and the emf measurements made by Jones and Parton[23] using a Pt-quinhydrone electrode in a cell without liquid junction. Although a number of calorimetric data are available, only the 25°C data of Rodante et al.[20] and Canady et al.[24] were included in the fitting process. All literature-derived data were converted to those appropriate for Eq. (3) using relevant data for the dissociation of water.[38]

The data presented by Read[16] (Table I) were corrected to the saturation vapor pressure (at $T > 100$°C) in order to be included in the fitting process. This data-set comprises the results of nine isothermal experiments with measurements from 20 to 200 MPa. Each isothermal data set can be fit precisely as a function of solvent density following

$$\log K_a = a + b \log \rho + c (\log \rho)^2 \qquad (9)$$

where ρ is the solvent density.[52] The values of a, b, and c as well as the values of pK_a at the saturation vapor pressure are reported in Table IV. The first two terms are consistent with the functional form of aqueous ionization reactions suggested by Mesmer et al.[53] Although all isothermal data can be fitted to within 0.1 to 0.2 log units using only a constant and the logarithm of solvent density, the addition of the quadratic term allows all data to be fit to within 0.005 log

units. The quadratic term may be an intrinsic property of the dissociation reaction or the manifestation of an experimental artifact.

The preferred fit of all data cited above at the saturation vapor pressure yielded the equation

$$\log Q_b = p_1 + \frac{p_2}{T} + p_3 \ln T + (p_4 + p_5 T^2 + \frac{p_6}{T})I - \log a_w \qquad (10)$$

in which a_w is derived from the data of Liu and Lindsay.[54] The form of this equation follows previous reports from this laboratory in that the first three terms define the equilibrium constant, whereas p_4 to p_6 describe the ionic strength dependence consistent with the β° parameter of the Pitzer ion-interaction treatment.[55] The values determined for the 6 adjustable parameters are $p_1 = -8.58280$, $p_2 = 3284.79$, $p_3 = 1.29055$, $p_4 = 0.436975$, $p_5 = -8.30346 \times 10^{-7}$, and $p_6 = -108.519$. The expression appropriate to Eq. (1) is obtained by adding Eq. (10) to that presented for the dissociation of water by Busey and Mesmer.[38]

Equation (10) provides a satisfactory fit of the combined data as illustrated in Figs. 1 and 2. The agreement factor

$$AF = [\{\Sigma W_i (Q_{obs} - Q_{calc})^2\} / (N - N_v)]^{1/2} \qquad (11)$$

is 1.08, where W is the squared reciprocal of the estimated error of any datum, Q_{obs} is the experimentally-determined value of Q_b, Q_{calc} is derived from Eq. (10), N is the number of observed values, and N_v is the number of independent variables. An AF of 1.08 indicates that the scatter in the data around Eq. (10) is 1.08 times greater than would be predicted solely on the statistical summation of the experimental errors. Figure 2 provides a direct comparison of the experimental results (both those obtained in this study and reported in the literature) with the model (Eq. 10) which was based on the combined results. These plots (Fig. 2) demonstrate that although a random distribution of residuals is apparent for the current results the literature data show a small positive offset.

Recently Huh et al.[56] have measured the dissociation quotient of benzoic acid using acridine as an optical indicator of pH. Their equation for the variation of pK_a from 0 to 250°C agrees neither with the values obtained in this study, nor with work published previously (Fig. 3).
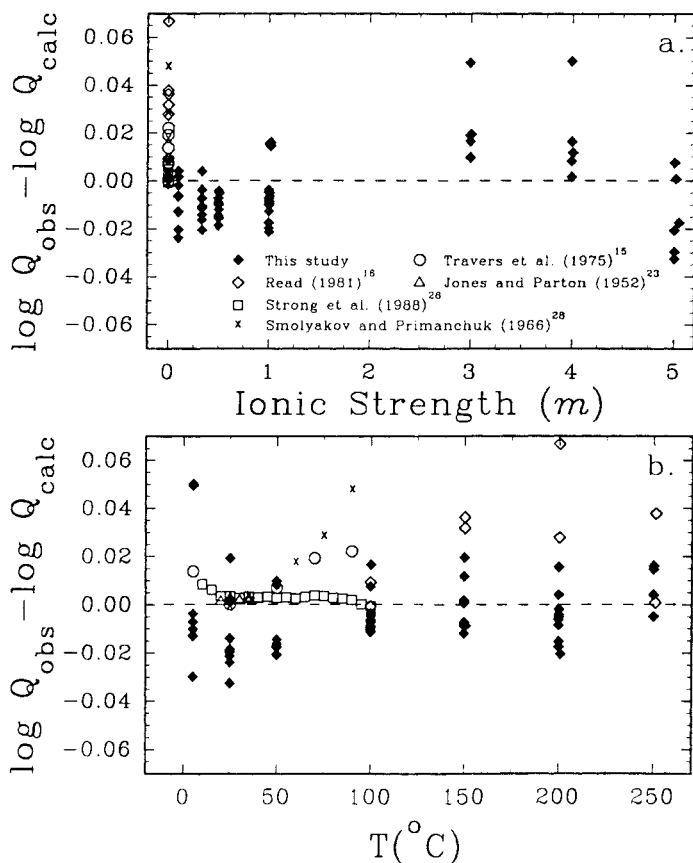
Fig. 2. Deviation plot of the differences between $\log Q_b$ values computed in Eq. (10) and those obtained experimentally. The deviations are plotted *vs.* a) ionic strength and b) temperature.

4.2 Derived Thermodynamic Quantities

Numerical differentiation of Eq. (10) yielded ΔH_b, ΔS_b, and $\Delta C_{p,b}$ data. These data were converted to values appropriate to Eq. (1) using the thermodynamic properties for water dissociation[38] and are presented in Table V. The thermodynamic data were retrieved assuming that there is no change in volume for the isocoulombic reaction. Those data retrieved at temperatures greater than 100°C will be in error if ΔV_b is large. Although the ΔH_b data obtained in the fitting process are in good agreement with $\Delta H_{b,298}$ data obtained
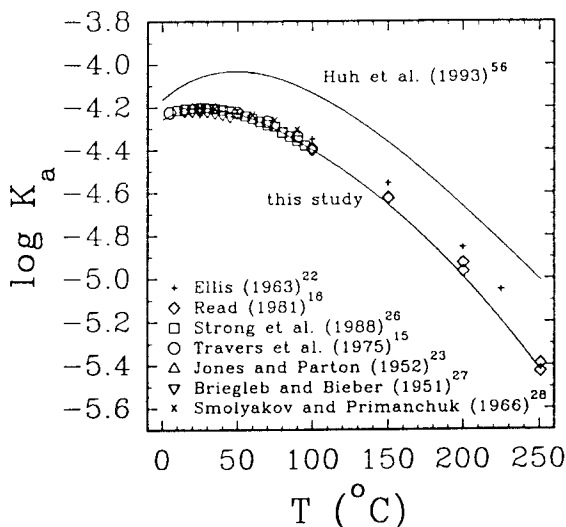
Fig. 3. Comparison of the $\log K_a$ values as determined by Eq. (10) with data published previously and with the function for $\log K_a$ proposed by Huh *et al.*[56]

using calorimetry and with the value derived by Jones and Parton[23] (Tables I and V), agreement with the high temperature calorimetric measurements of Leung and Grunwald[25] and Matsui *et al.*[17] is poor (Fig. 4). The values reported here are preferred despite this discrepancy for three reasons. First, the function describing $\log K_b$ *vs.* T is well constrained by the experimental data over the range of 0 to 250°C and is inconsistent with the high temperature ΔH data. The values of ΔH and $\log K_b$ obtained from the literature are such that the form of Eq. (10) is not changed if the high temperature calorimetric data are included in the ORGLS fitting routine; the agreement factor merely increases (indicating poorer agreement) reflecting the 2 kJ discrepancy between the 100°C value reported by Matsui *et al.*[17] and that obtained by differentiation of Eq. (10) (Fig. 4). Secondly, the high temperature calorimetric work does not consider all relevant equilibria. Strong *et al.*[26] have reported that the equilibrium constants for the dimerization of benzoic acid following

$$2C_6H_5CO_2H \leftrightarrow (C_6H_5CO_2H)_2 \tag{12}$$
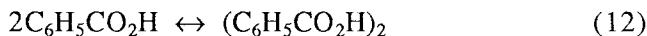
range from $10^{0.204}$ at 10°C to $10^{-0.004}$ at 100°C. The calorimetric studies in question[17,25] were performed before the work by Strong *et al.*[26] It is probable that the high temperature calorimetric data are in

Table V. Summary of Molal Thermodynamic Parameter for the Dissociation of Benzoic Acid in Aqueous Sodium Chloride Media at Saturation Vapor Pressure Retrieved From Eq. (10)[a]

T (°C)	$\log Q_a$	$\Delta H_a{}^b$	$\Delta S_a{}^c$	$\Delta C_{p,a}{}^c$
		$I = 0.0$		
0	-4.258±0.009	6.43±0.40	-58.0±1.3	-292±5
25	-4.206±0.006	0.29±0.30	-79.6±1.0	-207±5
50	-4.233±0.005	-4.23±0.22	-94.2±0.7	-161±5
75	-4.304±0.005	-8.00±0.17	-105.3±0.5	-144±5
100	-4.401±0.006	-11.64±0.18	-115.5±0.5	-150±5
125	-4.520±0.006	-15.63±0.25	-125.8±0.7	-172±5
150	-4.657±0.007	-20.36±0.35	-137.3±0.9	-208±5
175	-4.815±0.008	-26.12±0.45	-150.5±1.1	-256±5
200	-4.993±0.010	-33.25±0.55	-165.8±1.3	-316±5
225	-5.195±0.013	-42.04±0.66	-183.9±1.5	-390±5
250	-5.421±0.016	-52.93±0.77	-205.0±1.7	-487±5
		$I = 0.1$		
0	-4.056±0.009	7.10±0.39	-51.7±1.3	-286±4
25	-3.991±0.005	1.17±0.29	-72.5±0.9	-195±4
50	-4.004±0.005	-3.01±0.21	-86.0±0.7	-145±4
75	-4.058±0.005	-6.33±0.16	-95.8±0.5	-125±4
100	-4.137±0.006	-9.41±0.18	-104.4±0.5	-126±4
125	-4.233±0.006	-12.75±0.24	-113.1±0.6	-144±4
150	-4.346±0.006	-16.68±0.33	-122.6±0.8	-172±4
175	-4.474±0.008	-21.41±0.42	-133.5±1.0	-207±4
200	-4.620±0.009	-27.02±0.52	-145.5±1.2	-243±4
225	-4.782±0.012	-33.53±0.62	-158.8±1.4	-275±4
250	-4.959±0.015	-40.76±0.72	-172.8±1.6	-304±4
		$I = 0.5$		
0	-3.986±0.008	7.94±0.36	-47.3±1.2	-280±4
25	-3.907±0.005	2.22±0.27	-67.3±0.9	-185±4
50	-3.904±0.005	-1.64±0.20	-79.8±0.6	-130±4
75	-3.940±0.005	-4.54±0.15	-88.5±0.5	-106±4
100	-3.998±0.005	-7.13±0.16	-95.6±0.4	-104±4
125	-4.072±0.005	-9.88±0.21	-102.8±0.5	-118±4
150	-4.159±0.006	-13.10±0.28	-110.6±0.7	-140±4
175	-4.260±0.007	-16.92±0.37	-119.3±0.9	-165±4
200	-4.375±0.008	-21.28±0.46	-128.7±1.1	-181±4
225	-4.500±0.010	-25.85±0.55	-138.0±1.3	-182±4
250	-4.634±0.012	-30.16±0.64	-146.4±1.4	-158±4

Table V. Continued

T (°C)	$\log Q_a$	$\Delta H_a{}^b$	$\Delta S_a{}^c$	$\Delta C_{p,a}{}^c$
		$I = 1.0$		
0	-4.009±0.009	8.68±0.37	-45.0±1.2	-275±4
25	-3.917±0.005	3.12±0.29	-64.5±0.9	-177±4
50	-3.901±0.005	-0.52±0.21	-76.3±0.7	-120±4
75	-3.921±0.005	-3.13±0.16	-84.1±0.5	-93±4
100	-3.964±0.005	-5.38±0.15	-90.3±0.4	-89±4
125	-4.021±0.005	-7.74±0.20	-96.4±0.5	-101±4
150	-4.090±0.005	-10.49±0.29	-103.1±0.7	-120±5
175	-4.171±0.006	-13.72±0.40	-110.4±0.9	-138±5
200	-4.264±0.008	-17.28±0.52	-118.1±1.2	-144±6
225	-4.365±0.010	-20.72±0.66	-125.2±1.5	-128±6
250	-4.469±0.013	-23.39±0.81	-130.2±1.8	-76±7
		$I = 3.0$		
0	-4.266±0.018	11.14±0.74	-40.8±2.4	-259±6
25	-4.131±0.011	6.08±0.60	-58.7±1.9	-155±7
50	-4.071±0.009	3.05±0.45	-68.5±1.4	-93±8
75	-4.047±0.011	1.20±0.31	-74.1±1.0	-61±9
100	-4.040±0.011	-0.16±0.29	-77.9±0.8	-51±10
125	-4.047±0.011	-1.52±0.46	-81.3±1.1	-56±12
150	-4.063±0.010	-3.07±0.74	-85.0±1.8	-67±14
175	-4.086±0.012	-4.83±1.09	-89.0±2.5	-73±15
200	-4.118±0.017	-6.55±1.48	-92.7±3.4	-60±17
225	-4.153±0.025	-7.54±1.94	-94.5±4.3	-12±19
250	-4.184±0.035	-6.68±2.44	-92.9±5.3	91±22
		$I = 5.0$		
0	-4.588±0.030	13.35±1.24	-38.9±4.1	-245±9
25	-4.412±0.018	8.70±1.01	-55.4±3.3	-137±11
50	-4.312±0.016	6.18±0.76	-63.5±2.4	-70±13
75	-4.248±0.018	4.93±0.53	-67.2±1.7	-34±16
100	-4.200±0.019	4.29±0.51	-69.0±1.4	-21±18
125	-4.161±0.018	3.75±0.82	-70.2±2.0	-20±21
150	-4.131±0.018	3.15±1.31	-71.6±3.2	-25±24
175	-4.106±0.021	2.53±1.91	-73.0±4.5	-23±27
200	-4.087±0.031	2.17±2.60	-73.9±6.0	0±30
225	-4.068±0.045	2.91±3.38	-72.0±7.6	65±33
250	-4.041±0.063	6.00±4.26	-66.0±9.3	195±37

[a] At saturation vapor pressure retrieved from Eq. (10). Uncertainties listed represent 3 times the standard deviation. [b] Units: kJ-mol^{-1}. [c] Units: J-mol^{-1}-K^{-1}.

error: both groups used high concentrations of benzoic acid and the change in enthalpy for Eq. (12) ($\Delta H^{\circ}_{298} = -5.8\,\text{kJ-mol}^{-1}$)[26] is sufficiently large that dimerization must be addressed. The calorimetric data that were included in the fitting process[20,24] used low concentrations of benzoic acid (0.001 to 0.005M) with much less dimerization. And third, both high temperature calorimetric studies exhibit some irregularities. Matsui *et al.*[17] used a glass reaction calorimeter for measurements from 5 to 50°C and a stainless steel bomb calorimeter for measurements from 50 to 100°C. Although the two data-sets overlap at 50°C, they are apparently discontinuous (Fig. 4). On the other hand, values of $\Delta C^{\circ}_{p;a}$ determined by Leung and Grunwald[25] pass through a minimum near 30°C. Generally, values of $\Delta C^{\circ}_{p;a}$ for such dissociation reactions are maximized at ~75°C and move to negative infinity as the critical point of water is approached.[53] All organic acids that have been examined in this laboratory, including benzoic acid (Table V), exhibit similar behavior.[34,47-49]

4.3 A Density Model for $\log K_a$

The high pressure infinite dilution data presented by Read[16] can be combined in a global fit to obtain a model that relates the equilibrium constant for Eq. (1) to solvent density. Regression of the selected literature $\log K_b$ data, (*i.e.*, values computed using Eq. (10) from 0 to 275°C, and data from Table IV of Read,[16] for pressures greater than the saturation vapor pressure of water) using the ORGLS fitting routine[51] gave the following equation as most appropriate

$$\log K_a = a + bT + \left(c + \frac{d}{T^2}\right)\log\rho + e(\log\rho)^2 \tag{13}$$

where $a = -4.4058$, $b = 7.18399\times10^{-4}$, $c = 20.09178$, $d = -8.19026\times10^{5}$, and $e = 29.2548$. The model is in excellent agreement with all data presented by Read[16] (Fig. 5) and with Eq. (10) at the saturation vapor pressure of water (Fig. 6). The density function (Eq. 13) and the temperature function (Eq. 10) diverge only at temperatures below 25°C where we have no high pressure data. Note that the quadratic [$(\log\rho)^2$] term in Eq. (13) contributes <0.3 to the value of $\log K_a$ over the entire temperature range. Thermodynamic data retrieved by numerical differentiation of Eq. (13) are in good agreement with those retrieved by differentiation of Eq. (10) (Table VI). Equation (13) is a much better fit to Read's[16] data than a solvent density model presented recently by Anderson *et al.*[57] Use of
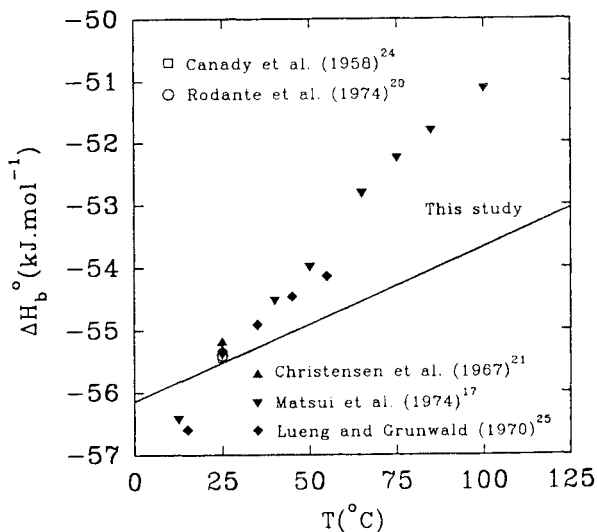
Fig. 4. Comparison of ΔH_b^o for Eq. (3) as determined in this study (solid line) with published values. Open symbols designate data that were used in the fitting process whereas filled symbols designate those data that were omitted from the fitting process.

Table VI. Summary of Molal Thermodynamic Parameters for the Dissociation of Benzoic Acid at Infinite Dilution and at Saturation Vapor Pressure Retrieved from Eq. (13)[a]

T (°C)	$\log K_a$	$\Delta H_a^{o\ b}$	$\Delta S_a^{o\ c}$	$\Delta C_{p;a}^o$ [c]	$\Delta V_a^{o\ d}$	$\Delta V_{a;w}^o$ [d,e]	$\Delta V_b^{o\ d,f}$
0	-4.210±0.007	1.5±0.2	-75.2±0.6	-95±16	-10.6±1.3	-24.1±2.2	13.5±3.5
25	-4.205±0.004	-1.0±0.2	-83.8±0.8	-104±3	-12.1±0.9	-23.0±1.9	10.9±2.8
50	-4.237±0.004	-3.8±0.2	-92.9±0.7	-123±5	-14.2±0.7	-22.8±1.7	8.6±2.4
75	-4.300±0.004	-7.2±0.2	-102.8±0.5	-144±6	-16.8±0.6	-23.7±1.6	6.9±2.2
100	-4.390±0.005	-11.0±0.2	-113.6±0.6	-167±6	-20.0±0.6	-25.8±1.6	5.8±2.2
125	-4.505±0.005	-15.5±0.3	-125.2±0.7	-192±5	-24.0±0.7	-29.2±1.6	5.2±2.3
150	-4.644±0.006	-20.7±0.3	-137.8±0.9	-223±9	-29.1±0.8	-34.0±1.7	4.9±2.5
175	-4.804±0.007	-26.7±0.5	-151.5±1.2	-262±18	-35.7±1.2	-40.3±1.8	4.6±3.0
200	-4.986±0.009	-33.8±1.0	-166.8±2.2	-314±36	-44.4±2.1	-48.5±2.3	4.1±4.4
225	-5.191±0.014	-42.3±2.2	-184.3±4.6	-387±69	-56.2±3.9	-59.6±3.3	3.4±7.2
250	-5.418±0.027	-52.8±0.4	-204.6±9.0	-494±133	-72.9±7.6	-76.4±5.1	3.5±12.7

[a] Errors listed represent 3 times the standard deviation. [b] Units: kJ-mol⁻¹. [c] Units: J-mol⁻¹-K⁻¹. [d] Units: cm³-mol⁻¹. [e] $\Delta V_{a;w}^o$ partial molar volume change for dissociation of water from Busey and Mesmer, Ref. 38 [f] Volume change for Eq. (3) computed from $V_b^o = V_a^o - V_w^o$.
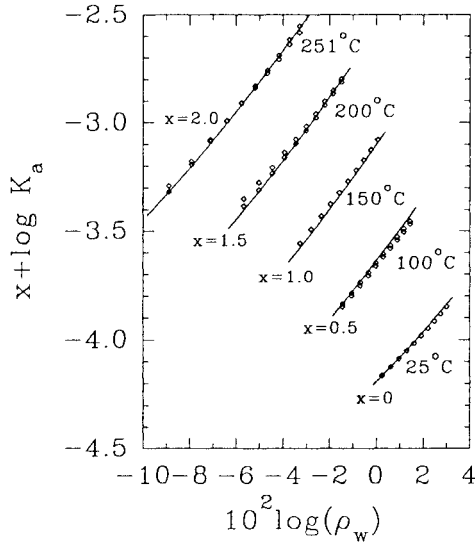
Fig. 5. Comparison of the data presented by Read, Ref. 16 (open diamonds) with Eq. (13) (solid lines). Data are plotted in $x + \log K_a$ vs. $\log \rho_w$ space where x is a constant used to prevent superimposition of the curves.
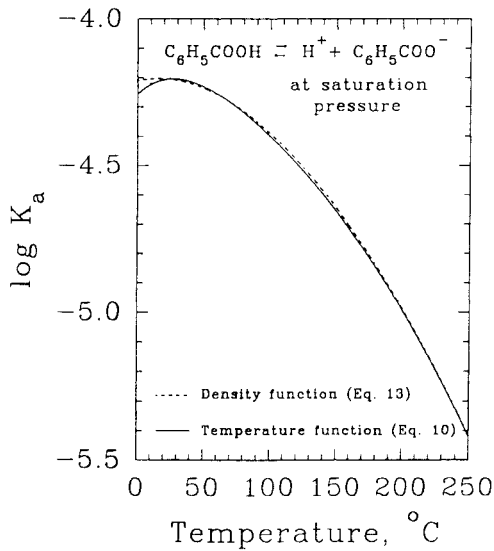

Fig. 6. Comparison of values of $\log K_a$ as determined from Eq. (13) with those determined using Eq. (10) at the saturation vapor pressure of water.

the 25°C values for $\log K_a$, ΔH, and $\Delta C^o_{p;a}$ obtained in this study does improve the fit of the Anderson *et al.*[57] model to Read's[16] data. The discrepancies are, however, still as large as 0.5 log units; much larger than the discrepancies between Eq. (13) and the high pressure data (Fig. 5).

Read[16] reported that the standard partial molar volume change for the dissociation of benzoic acid at 1 bar was -11.7 cm^3-mol^{-1} at 25°C and -60 cm^3-mol^{-1} at 250°C. These values are in good agreement with those obtained from Eq. (13), namely -12.1 ± 0.9 cm^3-mol^{-1} at 25°C and -76 ± 8 cm^3-mol^{-1} at 250°C. Values of $\Delta V^o_{a;w}$ for the dissociation of water are also presented in Table VI. The computed values of ΔV^o_b for Eq. (3) are small and approach 0 (within the stated uncertainty) at higher temperatures (Table VI). The data in Table VI provide strong support for the assumption of zero change in volume for the isocoulombic reaction (Eq. 3) that was used to calculate the thermodynamic values in Table V.

5. CONCLUSIONS

The dissociation quotients of benzoic acid have been measured in aqueous NaCl media at temperatures ranging from 0 to 250°C. The results are in quantitative agreement with most of the previous measurements made at low temperatures and low ionic strength, as well as with the general conclusions drawn from similar studies of other acids in this laboratory. Equations (10, 13) provide an accurate model for the behavior of benzoic acid in NaCl brines and can be used to predict the behavior of benzoic acid in soils, sedimentary basin brines, wastewaters, and the byproduct waters associated with enhanced oil recovery and synthetic fuels production.

ACKNOWLEDGMENT

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