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Determination of Carboxylic Acid Dissociation Constants to 350 °C at 23 MPa by Potentiometric pH Measurements

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The dissociation constants of aqueous ethanoic, propanoic, butanoic, pentanoic, and hexanoic acids were determined in 0.1 mol·kg^{-1} NaCl media at temperatures from (19.4 to 350.4) °C and 23 MPa by a flow-through electrochemical cell with a pressure-balanced hydrogen platinum electrode. Temperature dependence of K values shown by each acid were qualitatively similar. The values are consistent with the literature values determined from potentiometry, calorimetry, and electrical conductivity. An empirical density model for the description of the temperature dependence of the equilibrium constants was used to correlate the data.

Introduction

Knowledge of the dissociation constants of carboxylic acids at hydrothermal conditions has long been a basis for understanding not only fundamental physical and chemical phenomena[1] but also organic and inorganic reaction mechanisms in several applications.[2−5] Many studies have been carried out on the dissociation of aqueous ethanoic acid up to 400 °C and 32 MPa by measurements of potentiometry,[6,7] calorimetry,[8] and electrical conductivity.[9] In contrast, some studies have been carried out for propanoic and butanoic acids up to 225 °C[10−13] and for pentanoic and hexanoic acids up to 60 °C.[12,14] No measurements have been carried out at higher temperatures.

In this work, we focus on pH measurements of aqueous ethanoic, propanoic, butanoic, pentanoic, and hexanoic acids solutions by a recently developed flow-through potentiometric apparatus[7,15−18] at temperatures up to 350 °C and an evaluation of the molal dissociation constants as a function of temperature and water density.

Experimental Section

Materials. Two different stock solutions were prepared. The first solution consisted of 10^{-3} mol·kg^{-1} HCl + 10^{-1} mol·kg^{-1} NaCl as the reference and test (1) solution, and it was prepared by diluting 1.0 mol·kg^{-1} HCl standardized solution (Wako Pure Chemicals, Osaka, Japan) with ultrapure water (resistivity > 0.18 MΩ·m) and then adding known masses of crystalline NaCl (purity > 99.5%, Wako Pure Chemicals, Osaka, Japan). The second solution consisted of 10^{-2} mol·kg^{-1} carboxylic acid (CA) + 10^{-1} mol·kg^{-1} NaCl aqueous solution as the test (2) solution, and it was prepared by diluting 1.0 mol·kg^{-1} carboxylic acid standardized solution (Wako Pure Chemicals, Osaka, Japan) with ultrapure water and then adding precise amounts of crystalline NaCl. These solutions were continuously purged with hydrogen gas (purity > 99.99%, Nihon Sanso, Sendai, Japan) to remove dissolved oxygen and to maintain a constant H_2 concentration around the electrodes.

Apparatus. The flow-through cell and apparatus and general procedure are described in our previous publications.[7,15−18] The cell has a Y-type passage, and pressure-balanced hydrogen platinum reference and test electrodes are placed on the left and right sides, respectively. These electrodes were sealed by a packing-type high-pressure CONAX fitting with a Teflon sealant.

The flow-through cell configuration at the start of each experiment was

$$\underset{\text{test (1) solution}}{H_2, \mathrm{Pt}|\mathrm{NaCl}(10^{-1}\ \mathrm{mol{\cdot}kg^{-1}}), \mathrm{HCl}(10^{-3}\ \mathrm{mol{\cdot}kg^{-1}})|}$$

$$\underset{\text{reference solution}}{|\mathrm{NaCl}(10^{-1}\ \mathrm{mol{\cdot}kg^{-1}}), \mathrm{HCl}(10^{-3}\ \mathrm{mol{\cdot}kg^{-1}})|\mathrm{Pt}, H_2}$$

Each electrode responds to the half-cell reaction $2H^+ + 2e^- = H_2$. The hydrogen activity can be assumed to be constant over both solutions when keeping the same pressure in the cell and adding the same amount of NaCl to both solutions. Note that we use a standard state of unit activity of H_2 in a hypothetical 1 mol·kg^{-1} solution referenced to infinite dilution at any temperature and pressure rather than the customary unit fugacity. The potential between the electrodes is given by the Nernst equation

$$\Delta E_{\mathrm{ap(1)}} = E_{\mathrm{test(1)}} - E_{\mathrm{ref}} = \frac{RT}{F}\ln\frac{m_{\mathrm{H^+,test(1)}}\gamma_{\pm,\mathrm{test(1)}}}{m_{\mathrm{H^+,ref}}\gamma_{\pm,\mathrm{ref}}} + E_{\mathrm{LJ(1)}} \quad (1)$$

where E is the emf. R and F are the gas and Faraday constants, T is the absolute temperature, and E_{LJ} represents the liquid junction potential. In this work, the liquid junction potential was calculated by the full Henderson equation.[19] m is the (relative) molality in $m/(m^0)$, where $m^0 = 1$ mol·kg^{-1}. Subscripts test(1) and ref refer to the test(1) and reference solutions, respectively. The molal activity coefficients of ions $\gamma_\pm$ in the reference and test compartments are assumed to be almost equal at the given conditions.

At the beginning of each experiment, the reference and test (1) solutions were pumped through the cell from the inlet placed on the left and right ends of the cell, respectively, until the potentials between the reference and test electrodes attained a steady value within ca. ±1.0 mV.

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Table 1. Experimental Results for the Carboxylic Acid Dissociation Constant[a]

	t	P	ΔE	I_m		
solutes	°C	MPa	mV	mol kg^{-1}	pH$_{\text{test(2)}}$	$\log_{10} K_{\text{CA}}$
CH_3COOH	21.8	23.0	16.5 ± 0.5	0.101	3.38 −	−4.75 ± 0.03[a]
	49.7	23.2	18.3 ± 0.1	0.101	3.39 ± 0.00	−4.77 ± 0.01
	100.0	23.0	25.6 ± 0.7	0.101	3.47 −	−4.92 ± 0.00[a]
	150.2	23.2	36.1 ± 0.1	0.100	3.58 ± 0.00	−5.14 ± 0.01
	200.2	23.2	48.4 ± 1.0	0.097	3.70 −	−5.37 ± 0.05[a]
	250.2	23.4	83.7 ± 0.3	0.091	4.40 ± 0.00	−6.05 ± 0.01
	299.8	23.1	111.2 ± 0.3	0.080	4.32 −	−6.54 ± 0.01[a]
	350.2	23.3	134.5 ± 0.9	0.062	4.75 −	−7.17 ± 0.05[a]
C_2H_5COOH	23.8	23.2	19.2 ± 0.1	0.101	3.43 ± 0.00	−4.84 ± 0.00
	49.9	23.2	21.9 ± 0.1	0.101	3.45 ± 0.00	−4.88 ± 0.00
	100.3	23.2	28.8 ± 0.2	0.101	3.51 ± 0.00	−5.01 ± 0.00
	150.0	23.2	42.3 ± 0.1	0.100	3.65 ± 0.00	−5.29 ± 0.00
	199.8	23.2	57.3 ± 0.1	0.097	3.79 ± 0.00	−5.56 ± 0.00
	250.0	23.1	80.8 ± 0.5	0.091	4.01 ± 0.00	−5.99 ± 0.01
	300.4	23.2	119.8 ± 0.2	0.080	4.39 ± 0.00	−6.69 ± 0.00
	350.4	23.2	136.5 ± 0.8	0.062	4.77 ± 0.01	−7.20 ± 0.01
C_3H_7COOH	23.6	23.1	18.9 ± 0.1	0.101	3.42 ± 0.00	−4.83 ± 0.01
	50.6	23.1	20.2 ± 0.2	0.101	3.42 ± 0.00	−4.83 ± 0.01
	100.1	23.1	28.4 ± 0.1	0.101	3.51 ± 0.00	−5.00 ± 0.00
	150.1	23.1	42.2 ± 0.1	0.100	3.65 ± 0.00	−5.28 ± 0.00
	200.2	23.1	57.4 ± 0.2	0.097	3.79 ± 0.00	−5.56 ± 0.00
	250.1	23.2	87.0 ± 0.8	0.091	4.07 ± 0.02	−6.06 ± 0.04
	300.1	23.3	118.6 ± 0.3	0.080	4.38 ± 0.00	−6.67 ± 0.01
	350.4	23.3	140.0 ± 0.0	0.062	4.79 ± 0.00	−7.25 ± 0.00
C_4H_9COOH	19.4	23.1	19.5 ± 0.0	0.101	3.44 ± 0.00	−4.86 ± 0.00
	50.5	23.2	20.7 ± 0.1	0.101	3.43 ± 0.00	−4.84 ± 0.00
	99.9	23.3	28.1 ± 0.1	0.101	3.50 ± 0.00	−4.99 ± 0.00
	150.5	23.2	41.8 ± 0.1	0.100	3.65 ± 0.00	−5.27 ± 0.00
	200.7	23.2	58.2 ± 0.1	0.097	3.80 ± 0.00	−5.58 ± 0.00
	250.0	23.0	87.5 ± 0.2	0.091	4.08 ± 0.00	−6.12 ± 0.00
	300.3	23.2	116.8 ± 0.1	0.080	4.37 ± 0.00	−6.64 ± 0.00
	350.1	23.2	137.0 ± 0.7	0.062	4.77 ± 0.01	−7.19 ± 0.01
$C_5H_{11}COOH$	20.5	23.3	19.6 ± 0.1	0.101	3.44 ± 0.00	−4.86 ± 0.00
	49.9	23.2	21.3 ± 0.2	0.101	3.44 ± 0.00	−4.86 ± 0.01
	100.2	23.2	29.0 ± 0.1	0.101	3.52 ± 0.00	5.01 ± 0.00
	150.1	23.2	42.9 ± 0.1	0.100	3.66 ± 0.00	−5.30 ± 0.00
	200.3	23.3	56.8 ± 0.2	0.097	3.79 ± 0.00	−5.55 ± 0.00
	250.2	23.3	87.4 ± 0.2	0.091	4.08 ± 0.00	−6.11 ± 0.00
	300.3	23.3	119.3 ± 0.2	0.080	4.39 ± 0.00	−6.68 ± 0.00
	350.1	23.4	140.3 ± 0.7	0.062	4.79 ± 0.01	−7.24 ± 0.01

[a] Literature data[7] determined with the same experimental apparatus.

Then, the feed solution was changed from the test (1) solution (HCl + NaCl) to the test (2) solution (CA + NaCl). After this change, the cell configuration was

$$\underset{\text{test (2) solution}}{\mathrm{H_2,\ Pt|NaCl(10^{-1}\ mol{\cdot}kg^{-1}),\ CA(10^{-2}\ mol{\cdot}kg^{-1})|}}$$

$$\underset{\text{reference solution}}{\mathrm{|NaCl(10^{-1}\ mol{\cdot}kg^{-1}),\ HCl(10^{-3}\ mol{\cdot}kg^{-1})|Pt,\ H_2}}$$

and the measured potential difference was given by following equation:

$$\Delta E_{\mathrm{ap(2)}} = E_{\mathrm{test(2)}} - E_{\mathrm{ref}} = \frac{RT}{F}\ln\frac{m_{\mathrm{H^+,test(2)}}\gamma_{\pm,\mathrm{test(2)}}}{m_{\mathrm{H^+,ref}}\gamma_{\pm,\mathrm{ref}}} + E_{\mathrm{LJ(2)}} \quad (2)$$

In this work, with eqs 1 and 2, the molality term for the test (2) solution was evaluated from the potential difference ΔE_{ap} according to the following equation:

$$\Delta E_{\mathrm{ap}} = \Delta E_{\mathrm{ap(2)}} - \Delta E_{\mathrm{ap(1)}} = \frac{RT}{F}\ln\frac{m_{\mathrm{H^+,test(2)}}\gamma_{\pm,\mathrm{test(2)}}}{m_{\mathrm{H^+,test(1)}}\gamma_{\pm,\mathrm{test(1)}}} + E_{\mathrm{LJ(2)}} - E_{\mathrm{LJ(1)}} \quad (3)$$

During the experiment, the reference and test solutions were mixed in the center of the cell and then the mixed solution was withdrawn after cooling and depressurization. The temperatures in the center of the cell were measured with an Inconel-sheathed K-type thermocouple and kept at a given value by the electric furnace and ribbon heater. The pressure in the cell was controlled by a back-pressure regulator. All of these measurements were carried out at a flow rate of 1.5 g·min^{-1} having standard uncertainties (i.e., estimated standard deviations) of flow rate (±2.0%), pressure (±0.1 MPa); temperature (±0.1 K), potential difference (±0.8 mV), and initial concentration of HCl, NaCl, and CA(±0.2%).

Results

The experimental ΔE_{ap} values were measured for test solutions at temperatures ranging from (19.4 to 350.4) °C and at 23 MPa. The potentiometric data obtained for both test solutions at given temperatures are shown in Table 1 with experimental uncertainties.

Here, the liquid junction potential between the reference solution and the test (1) solution in eq 3 can be assumed to be negligible because of the same concentration of HCl and NaCl. The liquid junction potential between the reference solution and the test (2) solution exists because of the difference in the concentration and the different transport numbers of the ions (H^+, Na^+, OH^-, Cl^-, CH_3COO^-, $C_2H_5COO^-$, $C_3H_7COO^-$, $C_4H_9COO^-$, $C_5H_{11}COO^-$). In these solutions, the concentrations of H^+, OH^-, and carboxylate anions are at least 2 orders of magnitude lower than those of Na^+ and Cl^- at a given temperature. There is no data for transport numbers of carboxylate anions at higher temperatures. We adopted the same assumption with our previous work[7,16,18] that the effects on the liquid junction potential for H^+, OH^-, and carboxylate anions were probably very small.[19,20]

From the above description, the following relationship is derived:

$$\mathrm{pH}_{\mathrm{test}(2)} = -\frac{\Delta E_{\mathrm{ap}} F}{2.303RT} + \mathrm{pH}_{\mathrm{test}(1)} \tag{4}$$

where pH is defined as

$$\mathrm{pH} = -\log_{10}(m_{\mathrm{H}^+}\gamma_{\pm}) \tag{5}$$

An evaluation of the pH in the test (1) solution (HCl + NaCl), $\mathrm{pH}_{\mathrm{test}(1)}$, is necessary for the estimation of pH in the test (2) solution (CA + NaCl), $\mathrm{pH}_{\mathrm{test}(2)}$, from the measured potential differences, ΔE_{ap}. $\mathrm{pH}_{\mathrm{test}(1)}$ can be estimated with the dissociation constant data of HCl, NaCl, NaOH, and H_2O and formulations for the ionic activity coefficient and water activity with electroneutrality and mass balance constraints.

Dissociation constants of these reactions were expressed as follows:

$$K_{\mathrm{H_2O}} = \frac{m_{\mathrm{H}^+} m_{\mathrm{OH}^-} \gamma_{\pm}^2}{a_{\mathrm{H_2O}}} \tag{6}$$

$$K_{\mathrm{HCl}} = \frac{m_{\mathrm{H}^+} m_{\mathrm{Cl}^-} \gamma_{\pm}^2}{m_{\mathrm{HCl}^0}} \tag{7}$$

$$K_{\mathrm{NaCl}} = \frac{m_{\mathrm{Na}^+} m_{\mathrm{Cl}^-} \gamma_{\pm}^2}{m_{\mathrm{NaCl}^0}} \tag{8}$$

$$K_{\mathrm{NaOH}} = \frac{m_{\mathrm{Na}^+} m_{\mathrm{OH}^-} \gamma_{\pm}^2}{m_{\mathrm{NaOH}^0}} \tag{9}$$

where the activity coefficient of neutral aqueous species HCl, NaCl, and NaOH were assumed to be unity.[7]

The mean ionic activity coefficient $\gamma\pm$ and the activity of water $a_{\mathrm{H_2O}}$ were calculated using extended Debye–Hückel theory.[21]

$$\log_{10}\gamma_{\pm} = \frac{-A_{\gamma} z_i^2 \sqrt{I_m}}{1 + B_{\gamma} a \sqrt{I_m}} - \log_{10}\left(1 + \frac{m_{\mathrm{tot}}}{55.51}\right) \tag{10}$$

$$\ln a_{\mathrm{H_2O}} = -\frac{m_{\mathrm{tot}}}{55.51} \times \left\{1 - \frac{z_i^2 A_{\gamma}\sqrt{I_m}}{B_{\gamma}^3 a^3 (\sqrt{I_m})^3}[(1 + B_{\gamma} a\sqrt{I_m}) - 2\ln(1 + B_{\gamma} a\sqrt{I_m}) - (1 + B_{\gamma} a \sqrt{I_m})^{-1}] + \frac{55.51}{m_{\mathrm{tot}}}\log_{10}\left(1 + \frac{m_{\mathrm{tot}}}{55.51}\right)\right\} \tag{11}$$

where A_{γ} and B_{γ} stand for the coefficients that are functions of the water density, ρ, and dielectric constant of water, ϵ, respectively, which can be taken from literature data.[22−24] The coefficients are defined by

$$A_{\gamma} = \frac{1.8248 \times 10^6 \rho^{1/2}}{(\epsilon T)^{3/2}} \tag{12}$$

and

$$B_{\gamma} = \frac{50.291 \times 10^8 \rho^{1/2}}{(\epsilon T)^{1/2}} \tag{13}$$

In eqs 10 and 11, z_i represents the ionic charge of the species, and I_m denote the molal ionic strength of the solution. I_m is calculated from

$$I_m = \frac{1}{2}\sum_i m_i z_i^2 \tag{14}$$

where the summation is over all ionic species in solution. In eqs 10 and 11, a stand for the ion size parameter, which is a linear function of temperature as reported by Lvov et al.[25] and is expressed as

$$(a/10^{-10} m) = -0.0103T + 8.6638 \tag{15}$$

Furthermore, m_{tot} in eqs 10 and 11 is the sum of the molalities of all solute species in solution.

In this system, charge balance and mass balance equations are expressed by

$$m_{\mathrm{Na}^+} + m_{\mathrm{H}^+} = m_{\mathrm{Cl}^-} + m_{\mathrm{OH}^-} \tag{16}$$

$$m_{\mathrm{Na}}^0 = m_{\mathrm{Na}^+} + m_{\mathrm{NaCl}^0} + m_{\mathrm{NaOH}^0} \tag{17}$$

$$m_{\mathrm{Cl}}^0 = m_{\mathrm{Cl}^-} + m_{\mathrm{NaCl}^0} + m_{\mathrm{HCl}^0} \tag{18}$$

The dissociation constants of HCl, NaOH, NaCl, and H_2O at subcritical and supercritical conditions can be calculated with empirical functions of temperature and water density reported by Ho et al.,[26] Sue et al.,[7] Ho et al.,[27] and Marshall and Franck,[28] respectively.

$\mathrm{pH}_{\mathrm{test}(1)}$ was calculated by solving a system of nonlinear equations with an iterative method. These equations are the chemical equilibrium equations (eqs 6–9), the mass balance equations of Na^+ and Cl^- (eqs 17 and 18), and the charge balance equation (eq 16). First, we assumed a value for the ionic strength, I_m, and solved the equations (eqs 6–11, 16–18). Ionic strength was recalculated by eq 14 with the concentrations of all species obtained, and the iteration was repeated until the difference between two consecutive values of the ionic strength was less than 0.1% of the assumed value.

Then, $\mathrm{pH}_{\mathrm{test}(2)}$ was calculated on the basis of eq 4 with the calculated $\mathrm{pH}_{\mathrm{test}(1)}$ and the experimentally determined ΔE_{ap} value at given temperatures and pressures. The results are shown in Table 1.

On the basis of the evaluated $\mathrm{pH}_{\mathrm{test}(2)}$, molal equilibrium constant data of dissociation reaction of HCl, NaCl, NaOH, and H_2O and the formulations of ionic activity coefficient and water activity together with mass and charge balance constraints, the molal dissociation constant of CA, K_{CA}, as a thermodynamic activity product, at given temperatures was determined. The results are shown in Figures 1–5 and Table 1 with experimental uncertainty in $\log_{10} K_{\mathrm{CA}}$. The uncertainty was defined as a maximum error in $\log_{10} K_{\mathrm{CA}}$ estimated within standard uncertainties of temperature, pressure, and potential difference.

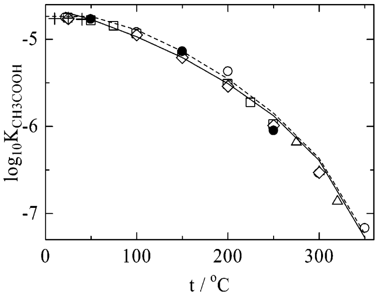

Figure 1. Dissociation constants of ethanoic acid. Solid circles represent the experimental data from this study at 23 MPa. The other symbols represent ○, Sue et al.[7] at 23 MPa; ◇, Fisher and Barnes[9]; △, Oscarson et al.[8]; □, Mesmer et al.[6]; and +, Christensen et al.[12] at saturation vapor pressure. Solid and dashed lines represent the calculated results from eq 19 and from the revised HKF equation of state[29] at 23 MPa.

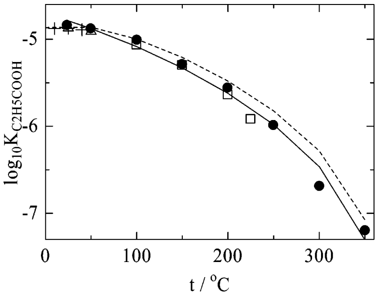

Figure 2. Dissociation constants of propanoic acid. Solid circles represent the experimental data from this study at 23 MPa. The other symbols represent △, Harned and Ehlers[10]; □, Ellis[11]; and +, Christensen et al.[12] at saturation vapor pressure. Solid and dashed lines represent the calculated results from eq 19 and from the revised HKF equation of state[29] at 23 MPa.

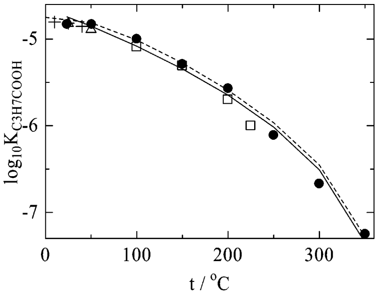

Figure 3. Dissociation constants of butanoic acid. Solid circles represent the experimental data from this study at 23 MPa. The other symbols represent △, Harned and Sutherland[13]; □, Ellis[11]; and +, Christensen et al.[12] at saturation vapor pressure. Solid and dashed lines represent the calculated results from eq 19 and from the revised HKF equation of state[29] at 23 MPa.

The present results were compared with the literature data from potentiometry, calorimetry, and electrical conductivity, and the calculated results by the revised HKF equation of state[29] in Figures 1−5. The temperature dependence of these experimental values showed a similar trend.

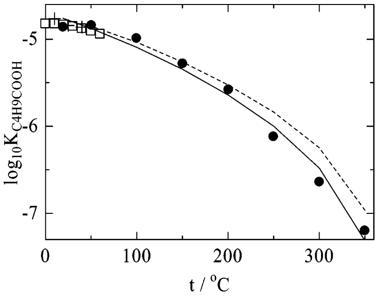

Figure 4. Dissociation constants of pentanoic acid. Solid circles represent the experimental data from this study at 23 MPa. The other symbols represent □, Everett et al.[14] and +, Christensen et al.[12] at saturation vapor pressure. Solid and dashed lines represent the calculated results from eq 19 and from the revised HKF equation of state[29] at 23 MPa.

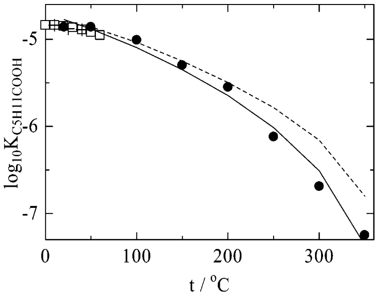

Figure 5. Dissociation constants of hexanoic acid. Solid circles represent the experimental data from this study at 23 MPa. The other symbols represent □, Everett et al.[14] and +, Christensen et al.[12] at saturation vapor pressure. Solid and dashed lines represent the calculated results from eq 19 and from the revised HKF equation of state[29] at 23 MPa.

The temperature dependence dissociation constant of carboxylic acids is correlated with the following empirical density model[26] as a function of water density, ρ, and temperature, T.

$$\log_{10} K_{\mathrm{CA}} = p_1 + \frac{p_2}{T} + p_3 \log_{10} \rho \qquad (19)$$

where p_1, p_2, and p_3 are constant in each reaction. Table 2 gives the fitted values for each reaction and the estimated and literature values of $\log_{10} K_{\mathrm{CA}}$ at reference conditions (25 °C and 0.1 MPa). Estimated $\log_{10} K_{\mathrm{CA}}$ at reference conditions shows agreement with the literature data within the standard deviation. The correlation results are shown in Figures 1−5 as a solid line, and the model could well describe the temperature dependence of the dissociation constants. The differences in the dissociation constants between this work and the revised HKF equation of state[29] for the pentanoic acid and hexanoic acid systems increased with increasing temperature. The main reason for this is assumed to be that the parameters in the HKF equation of state were determined with the data at lower temperature and the predicted value at higher temperature had a large uncertainty. No significant difference was observed among these carboxylic acids at the given conditions.

Table 2. Fitted Parameters in the Density Model (eq 19) with Estimated and Literature Values of log *K* at 25 °C and 0.1 MPa

solutes	p_1	p_2	p_3	$\log_{10} K_r$	$\log_{10} K_{r,\mathrm{lit}}$
CH_3COOH	−5.186	136.6	11.05	−4.74 ± 0.12	$-4.757,^{6,29}$ $-4.756,^{9,30,31,34}$ $-4.763,^{11}$ $-4.74,^{32}$ -4.62^{33}
C_2H_5COOH	−5.427	180.9	10.40	−4.83 ± 0.11	$-4.889,^{29}$ -4.87^{10}
C_3H_7COOH	−5.575	237.0	10.33	−4.79 ± 0.10	$-4.809,^{29}$ -4.82^{13}
C_4H_9COOH	−5.517	210.4	10.20	−4.82 ± 0.11	$-4.845,^{29}$ -4.842^{14}
$C_5H_{11}COOH$	−5.471	193.9	10.58	−4.83 ± 0.11	$-4.860,^{29}$ -4.879^{14}

Finally, to control the temperature and pressure and to measure the potential difference more accurately, we plan to improve the apparatus by decreasing the size of the electrode and the electrochemical cell. We also plan to carry out the potentiometric pH measurement of those carboxylic acids at the supercritical state and discuss the differences in the determined dissociation constants.

Conclusions

A flow-through electrochemical cell was used to measure the pH of carboxylic acid aqueous solutions at temperatures ranging from (19.4 to 350.4) °C and 23 MPa. On the basis of the measured pH, new data of the molal dissociation constants of propanoic, butanoic, pentanoic, and hexanoic acids were reported at higher temperatures, and the values agreed well with literature data from potentiometric, calorimetric, and electrical conductivity measurements. A semiempirical density model could correlate the data as a function of temperature and water density.

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