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Determination of Dissociation Constants of Hexanoic, Heptanoic, and Benzoic Acids to 673 K and 30 MPa by Potentiometric pH Measurements

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Potentiometric pH measurements of 0.01 mol·kg^{-1} aqueous solutions of hexanoic, heptanoic, and benzoic acids in 0.1 mol·kg^{-1} NaCl media were performed using a flow-through electrochemical cell with two pressure-balanced hydrogen platinum electrodes. The dissociation constants of these carboxylic acids were determined on the basis of pH values measured at temperatures from (322 to 673) K and pressures of (23 and 30) MPa. The dissociation constants were consistent with the literature values determined from calorimetry, electrical conductivity, and potentiometry at temperatures up to 523 K. A simple Born model for describing temperature and pressure dependence of the dissociation constants was used to correlate the data.

Introduction

Water at high-temperature and high-pressure conditions including the supercritical state has been attracting much attention as new reaction fields from the viewpoint of green chemistry.[1] In many cases, carboxylic acids are used as not only starting materials, intermediates, and products for organic reaction[2] but also pH control agents and effective surface modifiers for preparing functional metal oxide nanoparticles.[3] Dissociation constants of carboxylic acids have been one of the indispensable thermodynamic properties for controlling and understanding these chemical phenomena in aqueous systems. For acetic and β-naphthoic acids, dissociation constants were reported up to 673 K by potentiometric and spectroscopic measurements, respectively.[4,5] In contrast, for other carboxylic acids, no measurements have been carried out at higher temperatures above 623 K.[6,7]

In this work, the dissociation constants of hexanoic, heptanoic, and benzoic acids were determined at temperatures up to 673 K and pressures of (23 and 30) MPa on the basis of pH values obtained using a flow-through electrochemical cell for potentiometric measurements.[8,9] The temperature and pressure dependence of the dissociation constants was analyzed by a simple Born model.[10]

Experimental Sections

Materials. The reference solution consisted of 10^{-3} mol·kg^{-1} HCl + 10^{-1} mol·kg^{-1} NaCl aqueous solution, and it was prepared by diluting 1.0 mol·kg^{-1} HCl standardized solution (Wako Pure Chemical) with distilled and deionized water (resistivity > 0.18 MΩ·m) and then adding crystalline NaCl (purity > 99.5 %, Wako Pure Chemical). The test solution consisted of 10^{-2} mol·kg^{-1} carboxylic acid (RCOOH) + 10^{-1} mol·kg^{-1} NaCl aqueous solution, and it was prepared by dissolving precise amounts of hexanoic acid (purity > 99.0 %, Wako Pure Chemical), heptanoic acid (purity > 97.0 %, Kanto Chemical), and benzoic acid (purity > 99.5 %, Kanto Chemical) with distilled and deionized water and then adding crystalline NaCl. These solutions were continuously purged with H_2 gas (purity > 99.99 %, Suzuki Shokan) to remove dissolved O_2 and to maintain constant H_2 molality around the electrodes.

Apparatus and Measurements. A flow-through apparatus with pressure-balanced hydrogen platinum reference and test electrodes and general experimental procedure are described in our previous publications.[8,9] The flow-through cell configuration during potentiometric measurements was

$$\underbrace{\mathrm{H_2, Pt|NaCl\ (10^{-1}\ mol\cdot kg^{-1}),\ RCOOH\ (10^{-2}\ mol\cdot kg^{-1})}}_{\text{Test solution}}||\underbrace{\mathrm{NaCl\ (10^{-1}\ mol\cdot kg^{-1}),\ HCl\ (10^{-3}\ mol\cdot kg^{-1})}}_{\text{Reference solution}}\mathrm{|Pt, H_2}$$

The H_2 activity and the molal activity coefficients of ions in the reference and test compartments are assumed to be almost equal at the given conditions for keeping same pressure in cell and adding same amount of NaCl into 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 measured potentials between the electrodes, E, are listed in Table 1, depending on the relative hydrogen ion molalities and the measured temperature, and are given by the Nernst equation:

$$E = -\frac{RT}{F}\ln\frac{m_{\mathrm{H^+,test}}}{m_{\mathrm{H^+,ref}}} - E_{\mathrm{LJ}} \qquad (1)$$

where R and F are the gas and Faraday constants, T is the absolute temperature, and E_{LJ} represents the liquid junction potential. m is (relative) molality, m/m^0 where $m^0 = 1$ mol·kg^{-1}.

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Table 1. Experimental Value of E and log K_a for (a) Hexanoic Acid, (b) Heptanoic Acid, and (c) Benzoic Acid

T/K	P/ MPa	E/mV	log(K_a/−)	T/K	P/MPa	E/mV	log(K_a/−)
			(a)				
472.7	23.0	62.0 ± 0.1	−5.68 ± 0.03	572.1	30.0	110.5 ± 0.2	−6.60 ± 0.03
522.6	23.0	87.9 ± 0.2	−6.17 ± 0.04	622.3	30.0	130.5 ± 0.1	−7.18 ± 0.02
572.3	23.0	120.8 ± 0.1	−6.81 ± 0.03	633.1	30.0	134.4 ± 0.1	−7.37 ± 0.01
622.7	23.1	133.3 ± 0.1	−7.34 ± 0.03	642.0	30.0	129.5 ± 0.2	−7.45 ± 0.01
632.9	23.1	131.3 ± 0.1	−7.51 ± 0.03	648.0	30.0	126.8 ± 0.2	−7.54 ± 0.02
643.4	23.1	108.9 ± 0.3	−7.57 ± 0.03	653.0	30.0	121.3 ± 0.2	−7.61 ± 0.02
652.2	23.1	105.9 ± 3.2	−10.74 ± 0.25	662.9	30.0	108.8 ± 0.3	−7.90 ± 0.02
472.3	30.0	56.9 ± 0.2	−5.56 ± 0.04	673.4	30.0	74.5 ± 1.1	−8.51 ± 0.08
522.6	30.0	83.2 ± 0.2	−6.07 ± 0.04				
			(b)				
321.6	23.0	22.1 ± 0.0	−4.89 ± 0.02	663.1	23.0	99.2 ± 1.4	−12.52 ± 0.10
372.2	23.2	28.7 ± 0.0	−5.01 ± 0.02	668.1	23.0	106.5 ± 1.3	−12.99 ± 0.11
421.5	23.2	42.0 ± 0.0	−5.31 ± 0.03	472.0	30.0	60.1 ± 0.3	−5.64 ± 0.05
447.9	23.1	49.8 ± 0.1	−5.44 ± 0.02	521.7	30.0	84.0 ± 0.2	−6.09 ± 0.03
471.7	23.0	58.9 ± 0.2	−5.61 ± 0.04	571.2	30.0	113.0 ± 0.2	−6.65 ± 0.04
497.6	23.0	68.4 ± 0.1	−5.80 ± 0.03	625.8	30.1	134.9 ± 0.2	−7.29 ± 0.03
522.3	23.0	83.7 ± 0.1	−6.09 ± 0.03	631.9	30.2	134.5 ± 0.3	−7.35 ± 0.02
547.3	23.0	96.1 ± 0.1	−6.34 ± 0.03	642.9	30.0	127.2 ± 0.2	−7.43 ± 0.02
570.9	23.1	121.7 ± 0.1	−6.82 ± 0.03	647.8	30.1	126.0 ± 0.2	−7.52 ± 0.02
621.8	23.1	136.1 ± 0.1	−7.38 ± 0.01	652.6	30.0	123.5 ± 0.2	−7.63 ± 0.02
642.5	23.1	122.8 ± 0.3	−7.73 ± 0.03	658.4	30.0	118.6 ± 0.2	−7.80 ± 0.02
648.8	23.1	113.9 ± 0.2	−8.23 ± 0.03	663.2	30.0	112.7 ± 0.3	−7.99 ± 0.02
653.9	23.0	110.1 ± 5.7	−11.54 ± 0.59	667.5	30.1	88.2 ± 0.4	−7.95 ± 0.03
658.2	23.0	106.9 ± 2.1	−12.17 ± 0.17	672.9	30.0	92.2 ± 0.4	−8.76 ± 0.03
			(c)				
476.5	23.0	26.3 ± 0.0	−4.91 ± 0.02	614.4	23.0	88.2 ± 0.0	−6.49 ± 0.02
486.9	22.9	31.0 ± 0.0	−5.02 ± 0.02	624.1	23.1	85.6 ± 0.0	−6.59 ± 0.03
494.0	23.0	36.6 ± 0.0	−5.14 ± 0.03	633.7	23.0	77.0 ± 0.0	−6.58 ± 0.05
503.6	23.0	40.9 ± 0.0	−5.23 ± 0.03	638.5	23.1	72.3 ± 0.1	−6.66 ± 0.07
513.4	23.0	45.3 ± 0.0	−5.33 ± 0.04	643.5	23.0	63.2 ± 0.0	−6.78 ± 0.03
523.7	23.0	49.9 ± 0.0	−5.43 ± 0.04	648.3	23.1	73.1 ± 0.0	−7.48 ± 0.02
533.6	23.0	56.2 ± 0.0	−5.57 ± 0.03	655.0	23.1	53.9 ± 0.1	−10.78 ± 0.07
543.7	23.1	61.3 ± 0.0	−5.68 ± 0.04	471.4	30.0	21.2 ± 0.1	−4.79 ± 0.02
553.3	23.1	66.6 ± 0.0	−5.80 ± 0.04	571.4	30.0	67.5 ± 0.2	−5.84 ± 0.03
563.6	23.1	74.2 ± 0.0	−5.96 ± 0.04	622.1	30.0	91.2 ± 0.2	−6.54 ± 0.02
574.6	23.0	75.9 ± 0.0	−6.02 ± 0.04	632.0	30.0	88.8 ± 0.1	−6.63 ± 0.01
584.9	23.0	82.0 ± 0.0	−6.17 ± 0.03	642.8	30.0	83.4 ± 0.2	−6.74 ± 0.01
594.5	23.0	85.7 ± 0.0	−6.28 ± 0.03	648.7	30.0	78.7 ± 0.1	−6.81 ± 0.01
605.4	23.1	87.5 ± 0.0	−6.39 ± 0.03	653.4	30.0	75.4 ± 0.2	−6.91 ± 0.01

The subscripts, test and ref, refer to the test and reference solutions, respectively.

All of these measurements were carried out at the flow rate of 1.5 $g\cdot min^{-1}$ having maximum standard uncertainties (i.e., estimated standard deviations) of flow rate (± 2.0 %), pressure (± 0.1 MPa), temperature (± 0.1 K), potential difference (± 5.7 mV), and initial concentration of HCl, NaCl, and RCOOH (± 0.2 %), which gives an maximum uncertainty in the logarithms of the dissociation constants of ± 0.59 as shown in Table 1b (653.9 K and 23.0 MPa).

Stability of carboxylic acids at high-temperature conditions was analyzed by gas chromatography/mass spectrometry (GC-MS; Shimadzu, GCMS-QP2010) and total organic carbon (Shimadzu, TOC-V) analyses. No significant difference between starting and recovered solutions was observed in GC-MS analysis. The decomposition rate of organic carbon to inorganic carbon was evaluated on the basis of TOC analysis and was determined to be from (0.0 to 1.8) % depending on temperature. These results showed an advantage of the flow-through technique for the potentiometric measurements of thermally unstable organic acids.

Analysis

Dissociation constants of the carboxylic acids at each temperature and pressure, K_a, were determined on the basis of estimated $m_{H+,test}$ values from eq 1, related dissociation constants in RCOOH and NaCl aqueous systems, and activity coefficients of ions as well as an activity of water. For estimation of $m_{H+,test}$ values, $m_{H+,ref}$ values were calculated using literature values. Detailed procedures are described in our previous publications.[4,7−9,11] In this study, the molalities of H^+, OH^-, and carboxylate anions ($RCOO^-$) are assumed to be at least 2 orders of magnitude lower than that of Na^+ and Cl^- at a given temperature and pressure for both reference and test compartments considering the fact that the dissociation constants of HCl and RCOOH are apparently lower than that of NaCl. Then, solutions involve only monovalent ions. In these cases, E_{LJ} in eq 1 is typically calculated to be less than 0.5 mV.[12,13] Here, E_{LJ} at given conditions was estimated by the Henderson equation with the limiting conductance of H^+, OH^-, Na^+, Cl^-, and $RCOO^-$ and the molal concentration of the ions, which was calculated on the basis of dissociation constant of H_2O, HCl, NaCl, NaOH, and RCOOH, activity coefficient formulation, mass balance, and charge balance equations. The conductance and the dissociation constant were estimated using empirical functions of temperature and water density as described in previous work.[9] The following two approximations were used for this analysis that the dissociation constant of RCOOH and the conductance of $RCOO^-$ were similar to that of ethanoic acid[4] and that of Cl^-, respectively. The estimated E_{LJ} values were in the ranges from (0.01 to 0.25) mV. The value corresponds to an estimated uncertainty of the measured potentials in this work from (0.1 to 1.1) %.

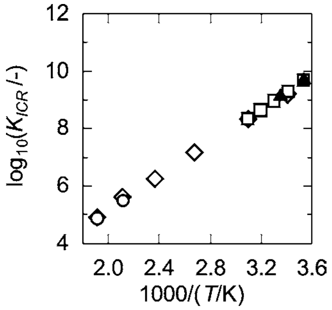

Figure 1. log K_{ICR} for hexanoic acid dissociation as a function of $1/T$ at the subcritical region. The open circle represents the experimental data from this study at 23 MPa. The open square, the open rhombus, and the closed triangle represent the literature data from Everett et al.,[14] Sue et al.,[7] and Christensen et al.,[15] respectively.

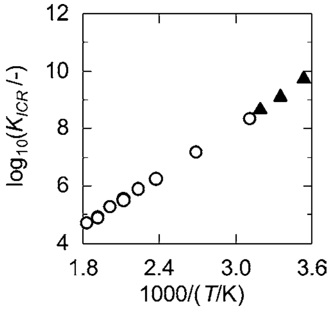

Figure 2. log K_{ICR} for heptanoic acid dissociation as a function of $1/T$ at the subcritical region. The open circle represents the experimental data from this study at 23 MPa. The closed triangle represents the literature data from Christensen et al.[15]

Results

The determined molal dissociation constants of hexanoic, heptanoic, and benzoic acids, K_a, were summarized in Table 1. The K_a values decreased with increasing temperature on each pressure due to the decrease in dielectric constant of water. A comparison of the K_a values obtained in this work with literature data[7,14−24] is shown in Figures 1 to 3. In the figures, the K_a values were converted into the equilibrium constants of the isoCoulombic reactions ($RCOOH + OH^- = RCOO^- + H_2O$), K_{ICR}, by dividing using the ion product of water, K_W, at given temperatures and pressures. The conversion can minimize the effect of ionic strength, temperature, and pressure, and it is useful for comparing data at different conditions. As shown in Figures 1 to 3, the log K_{ICR} values linearly decreased with decreasing the reciprocal temperature (increasing the temperature) and were clearly in good agreement with the literature data.

The temperature and pressure dependence of the K_{ICR} values is shown in Figure 4. In the figure, K_{ICR} for acetic acid reported in our previous work[4] is also shown for comparison. With increasing temperature, the log K_{ICR} values linearly decreased in proportion to the reciprocal temperature at subcritical region but drastically increased at supercritical region. Then, the increase in the K_{ICR} values at 23 MPa is more remarkable than that at 30 MPa. For four carboxylic acids, similar behavior was observed. For understanding the temperature and pressure dependence, a following simple Born model[10] was used for correlation,

$$\log K_{ICR}(T,\rho) = \log K_{ICR}(T_r,\rho_r) + \left(\frac{\partial \log K_{ICR}}{\partial(1/T)}\right)_{\rho_r}\left(\frac{1}{T}-\frac{1}{T_r}\right) + \frac{36278}{T}\left(\frac{1}{R^*_{OH^-}}-\frac{1}{R^*_{RCOO^-}}\right)\left(\frac{1}{\varepsilon(T,\rho)}-\frac{1}{\varepsilon(T,\rho_r)}\right) \quad (2)$$

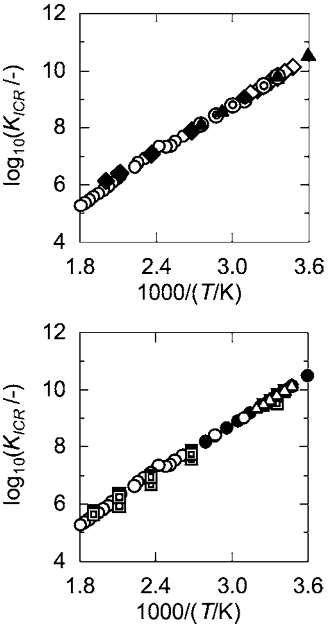

Figure 3. log K_{ICR} for benzoic acid dissociation as a function of $1/T$ at the subcritical region. The open circle represents the experimental data from this study at 23 MPa. The open rhombus, the closed rhombus, the open square, the double circle, the closed triangle, the closed circle, the double square, the closed square, and the open triangle represent the literature data from Briegleb and Bleber,[16] Ellis,[17] Matsui et al.,[18] Smolyakov and Primanchuk,[19] Travers et al.,[20] Strong et al.,[21] Read,[22] Jones and Parton,[23] and Wilson et al.,[24] respectively.

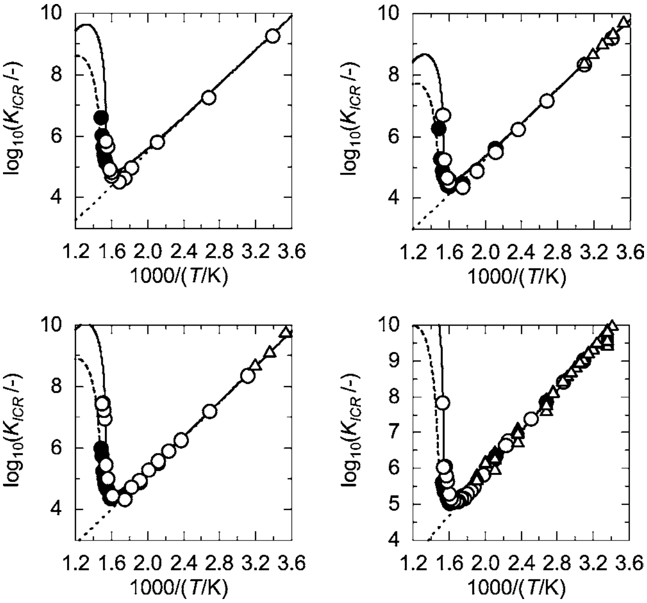

Figure 4. log K_{ICR} for dissociation of (a) acetic acid, (b) hexanoic acid, (c) heptanoic acid, and (d) benzoic acid as a function of $1/T$ at subcritical and supercritical regions. The open circle and the closed circle represent the experimental data at (23 and 30) MPa, respectively. All data for acetic acid were taken from our previous work.[4] The open triangle represents the literature data shown in Figures 1 to 3.[7,14−24]

where K_{ICR} is the equilibrium constant for the isoCoulombic reaction and is expressed as K_a/K_W. T, ρ, and ε are absolute temperature, density, and dielectric constant. R^* denotes an ionic radius. T_r and ρ_r are 298.15 K and 0.997 $g \cdot cm^{-3}$, respectively. On the right-hand side of eq 2, the first and second terms denote log K_{ICR} at T_r and ρ_r and the change in log K_{ICR} from T_r to T at ρ_r. The third term denotes the change in log K_{ICR} from ρ_r to ρ at T and is evaluated by Born theory for ionic hydration on the basis of the assumption that the hydration energies for the ions ($RCOO^-$ and OH^-) are relatively large compared to those of the neutral molecules (RCOOH and H_2O). The log K_{ICR} values at T_r and ρ_r were evaluated to be 9.238 for acetic acid, 9.115 for hexanoic acid, 9.101 for heptanoic acid, and 9.790 for benzoic acid from literature data of K_a[4,15,22] and K_W. The $(\partial \log K_{ICR}/\partial(1/T))\rho_r$ values were determined through the correlation to log K_{ICR} data up to 573 K and were 2776 for acetic acid, 2841 for hexanoic acid, 2893 for heptanoic acid, and 2912 for benzoic acid. The $(1/R^*_{OH^-} - 1/R^*_{RCOO^-})$ values were determined through the correlation to log K_{ICR} data from (573 to 673) K and were 0.219 for acetic acid, 0.193 for hexanoic acid, 0.247 for heptanoic acid, and 0.265 for benzoic acid. The results are shown in Figure 4 as the dotted line at ρ_r, the dashed line at 23 MPa, and solid line at 30 MPa. The Born model could describe the temperature and pressure dependence of the K_{ICR} values. At supercritical conditions, the $(1/\varepsilon(T, \rho) - 1/\varepsilon(T, \rho_r))$ values greatly increase due to the drastic decrease in dielectric constant of water, especially at lower pressure conditions, and the effect of the difference between $R^*_{OH^-}$ and $R^*_{RCOO^-}$ becomes remarkable. For further discussion, the $R^*_{RCOO^-}$ values were obtained using literature values for $R^*_{OH^-}$, 1.39 Å,[25] and were 2.0 Å for acetic acid, 1.9 Å for hexanoic acid, 2.1 Å for heptanoic acid, and 2.2 Å for benzoic acid. No significant difference was observed in spite of large difference in molecular structure and length. Considering that $R^*_{RCOO^-}$ for acetic acid is reported to be 2.12 Å,[26] the local radius around hydroxyl terminal may become the dominant factor for changing the hydration energies of the carboxylate anions.

Conclusion

New data of the molal dissociation constants of hexanoic, heptanoic, and benzoic acids were reported at temperatures from (323 to 673) K and pressures of (23 and 30) MPa. The values at low temperatures agreed well with literature data. A simple Born model could correlate the data as a function of temperature and dielectric constant of water.

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