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Determination of Acetic Acid Dissociation Constants to 400 °C and 32 MPa by Potentiometric pH Measurements

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pH of 0.01 mol·kg^{-1} CH_3COOH aqueous solutions at subcritical and supercritical conditions was measured at temperatures from (21.8 to 400.4) °C and pressures from (23.0 to 32.3) MPa by a flow-through electrochemical cell, and it changed from 3.38 at 21.8 °C and 23.0 MPa to 6.90 at 400.4 °C and 28.1 MPa. The molal equilibrium constant for the dissociation reaction of CH_3COOH was determined on the basis of the measured pH, and the value varied from 4.29×10^{-10} at 400.4 °C and 28.1 MPa to 1.79×10^{-5} at 21.8 °C and 23.0 MPa. At subcritical conditions, the values showed good agreement with the literature values determined from potentiometry with a static cell, from calorimetry, and from electrical conductivity. An empirical density model for the description of the temperature and pressure dependence of the equilibrium constants was used to correlate the data.

Introduction

Acetic acid is the simplest carboxylic acid that is relatively stable up to around 450 °C,[1] and the knowledge of its dissociation constants has long been a basis for understanding fundamental physical and chemical phenomena in aqueous solutions. Further, acetic acid + acetate buffers are widely used for pH control in several research fields. Much research has been carried out on dissociation of aqueous acetic acid up to 350 °C by measurements of potentiometry,[2] calorimetry,[3] and electrical conductivity.[4] However, no measurements have been carried out beyond 350 °C.

Over the past few decades, in parallel with the establishment of a measurement apparatus for dissociation constants of several compounds in aqueous solutions at the saturation vapor pressure, advantages of new flow-through techniques, such as in-situ UV−vis spectroscopy,[5] electrical conductivity,[6] and potentiometry,[7,8] for an accurate measurement of those properties at near critical and supercritical water conditions have been outlined by several researchers.

Potentiometric pH measurement is a useful tool for evaluating ionization behavior. In the 1990s, a flow-through technique with a pressure balanced hydrogen platinum electrode was proposed by Lvov et al.[7] for the measurement at near critical and supercritical regions. Recently, Sue et al.[8−11] improved the apparatus for measuring the potentials more precisely and the pH directly and demonstrated that the apparatus operates successfully in supercritical aqueous solutions (HCl + NaCl system) at temperatures up to 400.2 °C and at pressures up to 35.1 MPa.

In this work, we focus on pH measurements of subcritical and supercritical acetic acid aqueous solutions and an evaluation of the molal dissociation constant of acetic acid with an empirical 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 aqueous solution as reference and test (1) solutions, 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 a precise amount of crystalline NaCl (purity > 99.5%, Wako Pure Chemicals, Osaka, Japan). The second solution consisted of 10^{-2} mol·kg^{-1} CH_3COOH (HAc) + 10^{-1} mol·kg^{-1} NaCl aqueous solution as a test (2) solution, and it was prepared by diluting 1.0 mol·kg^{-1} CH_3COOH standardized solution (Wako Pure Chemicals, Osaka, Japan) with ultrapure water and then adding a precise amount of crystalline NaCl. These solutions were continuously purged with hydrogen gas (purity > 99.99%, Nihon Sanso, Sendai, Japan) for at least 1 day priori to use, 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.[8−11] The cell has a Y type passage, and pressure balanced hydrogen platinum reference and test electrodes are placed on the left and right side, respectively. These electrodes were sealed by a packing type high-pressure CONAX fitting with Teflon sealant.

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

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

Each electrode responds to the half cell reaction $H_2 = 2H^+ + 2e^-$. Since the hydrogen activity can be assumed to be constant over both solutions for keeping the same pressure in the cell and adding the same amount of NaCl into both solutions, the potentials between the electrode are given

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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 $E_{\mathrm{test(1)}}$ and E_{ref} are the emf, R/J·mol^{-1}·K^{-1} and F/C·mol^{-1} are the gas and Faraday constants, T/K is the temperature, and E_{LJ} represents the liquid junction potential based on the full Henderson equation.[12] $m_{\mathrm{H^+,test(1)}}$ and $m_{\mathrm{H^+,ref}}$ refer to the molalities of hydrogen ions in the test and reference compartments, 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. Then, the feed solution was changed from test (1) solution (HCl + NaCl) to test (2) solution (CH_3COOH + NaCl). After this change, the cell configuration was

H_2,Pt|NaCl (10^{-1} mol·kg^{-1}), HAc (10^{-2} mol·kg^{-1})|
test (2) solution
|NaCl (10^{-1} mol·kg^{-1}), HCl (10^{-3} mol·kg^{-1})|Pt,H_2
reference solution

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 eqs1 and 2, the potential difference ΔE_{ap} was evaluated from

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

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 a 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 these measurements were carried out at the flow rate 1.5 g·min^{-1} having the following uncertainties of flow rate (±2.0%); pressure (±0.1 MPa); temperature (±0.1 K); potential reading (±3.2 mV); and initial concentration of HCl, NaCl, and CH_3COOH (±0.2%).

Results

The experimental ΔE_{ap} values were measured for test solutions at temperatures ranging from (21.8 to 400.4) °C and at pressures ranging from (23.0 to 32.3) MPa. The data obtained for both test solutions at given temperatures and pressures are shown in Table 1 with the experimental uncertainties during potential readings.

Table 1. Experimental Results for the Acetic Acid Dissociation Constant

t/°C	P/MPa	ΔE/mV	$\mathrm{pH}_{\mathrm{test(1)}}$	$\mathrm{pH}_{\mathrm{test(2)}}$	$\log(K_{\mathrm{HAc}}/-)$
21.8	23.0	16.5 ± 0.8	3.10	3.38	−4.75 ± 0.05
100.0	23.0	25.6 ± 0.7	3.12	3.47	−4.92 ± 0.04
200.2	23.2	48.4 ± 1.0	3.18	3.70	−5.37 ± 0.05
275.1	23.4	85.8 ± 0.6	3.28	4.07	−6.07 ± 0.02
299.8	23.1	111.2 ± 0.3	3.34	4.32	−6.54 ± 0.01
320.5	23.2	125.6 ± 0.6	3.42	4.49	−6.83 ± 0.02
350.2	23.3	134.5 ± 2.4	3.66	4.75	−7.17 ± 0.08
351.3	23.4	127.6 ± 0.3	3.68	4.71	−7.07 ± 0.02
360.2	23.3	130.8 ± 0.7	3.83	4.87	−7.26 ± 0.02
369.8	23.2	101.2 ± 0.6	4.13	4.92	−7.12 ± 0.02
374.9	23.2	107.5 ± 1.0	4.49	5.33	−7.64 ± 0.03
375.0	26.0	112.8 ± 0.9	4.13	5.00	−7.29 ± 0.03
375.2	28.1	115.7 ± 1.3	4.01	4.91	−7.20 ± 0.05
375.2	30.3	118.1 ± 1.0	3.93	4.84	−7.13 ± 0.03
375.2	32.3	117.2 ± 1.3	3.87	4.78	−7.05 ± 0.04
380.1	26.2	112.9 ± 0.6	4.36	5.23	−7.55 ± 0.02
380.2	28.1	114.7 ± 0.6	4.18	5.06	−7.36 ± 0.02
379.9	30.2	117.2 ± 0.6	4.04	4.95	−7.24 ± 0.02
380.1	32.1	118.3 ± 0.7	3.97	4.88	−7.17 ± 0.02
385.0	26.1	112.7 ± 0.5	4.89	5.75	−8.17 ± 0.02
385.0	28.1	114.3 ± 0.4	4.41	5.29	−7.62 ± 0.01
385.0	30.1	115.2 ± 0.5	4.21	5.10	−7.40 ± 0.02
385.1	32.3	116.9 ± 0.5	4.09	4.98	−7.27 ± 0.02
389.9	26.0	99.8 ± 1.1	6.04	6.80	−9.39 ± 0.03
390.1	27.9	108.7 ± 0.3	4.91	5.73	−8.11 ± 0.01
390.0	30.2	109.7 ± 0.4	4.44	5.27	−7.57 ± 0.02
390.0	32.2	110.2 ± 0.4	4.25	5.09	−7.36 ± 0.01
394.9	28.0	99.0 ± 0.3	5.57	6.32	−8.76 ± 0.01
395.2	30.0	102.8 ± 0.4	4.85	5.63	−7.94 ± 0.01
395.1	32.1	105.2 ± 0.3	4.49	5.29	−7.55 ± 0.01
400.4	28.1	77.1 ± 3.2	6.32	6.90	−9.37 ± 0.09
400.1	30.0	85.3 ± 0.3	5.37	6.01	−8.29 ± 0.01
399.9	32.1	93.7 ± 0.2	4.79	5.49	−7.71 ± 0.01

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 of the concentration and the different transport numbers of the ions (H^+, Na^+, OH^-, Cl^-, CH_3COO^-). In these solutions, the concentrations of H^+, OH^-, and CH_3COO^- are at least 2 orders of magnitude lower than those of Na^+ and Cl^- at a given temperature and pressure, considering the fact that the dissociation constants of HCl and CH_3COOH are apparently lower than that of NaCl.[3] Considering that there are no data for the transport number for CH_3COO^- at higher temperatures, we adopted the assumption that the effects on the liquid junction potential by H^+, OH^-, and CH_3COO^- were probably very small.[8,11,13]

From the above description, the relationship follows:

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

where pH is defined as the following relation:

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

Evaluation of the pH in the test (1) solution (HCl + NaCl), $\mathrm{pH}_{\mathrm{test(1)}}$, is necessary for estimating the pH in the test (2) solution (CH_3COOH + 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 ionic activity coefficient and water activity with electroneutrality and mass balance constraints.

The dissociation constants of these reactions were expressed as follows:

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

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

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

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

where the activity coefficients of the neutral aqueous species HCl, NaCl, and NaOH were assumed to be unity.[14]

The mean ionic activity coefficient $\gamma\pm$ and the activity of water a_{H_2O} were calculated using the extended Debye–Hückel theory.[15]

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

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

where A_{γ} and B_{γ} stand for the coefficients that are a function of the water density, ρ_{H_2O}, and the dielectric constant of water, ϵ_{H_2O}, which can be taken from literature data,[16–18] and the coefficients are defined by

$$A_{\gamma} = \frac{(1.8248 \times 10^6)\rho_{H_2O}{}^{1/2}}{(\epsilon_{H_2O} T)^{3/2}} \tag{12}$$

and

$$B_{\gamma} = \frac{(50.29 \times 10^8)\rho_{H_2O}{}^{1/2}}{(\epsilon_{H_2O} T)^{1/2}} \tag{13}$$

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

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

where the summation is over all ionic species in solution. In eqs 10 and 11, a stands for the ion size parameter, and it is a linear function of temperature, as reported by Lvov et al.,[7] and is expressed as

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

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

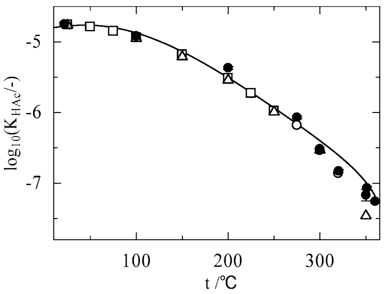

Figure 1. Dissociation constants ($K_{HAc}/-$) of acetic acid at subcritical conditions. The closed circles represent the experimental data from this study at 23 MPa. The other symbols represent (□) Mesmer et al.,[2] (○) Oscarson et al.,[3] and (△) Fisher and Barnes[4] at saturation vapor pressure, and the solid line represents calculated results from eq 20.

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

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

$$m^{\circ}_{Na} = m_{Na^+} + m_{NaCl} + m_{NaOH} \tag{17}$$

$$m^{\circ}_{Cl} = m_{Cl^-} + m_{NaCl} + m_{HCl} \tag{18}$$

The dissociation constants of HCl, NaOH, and H_2O at subcritical and supercritical conditions can be calculated with the empirical functions of temperature and water density reported by Ho et al.,[5] Ho et al.,[19] and Marshall and Franck,[20] respectively. The dissociation constant of NaCl at subcritical and supercritical conditions can also be calculated with the following empirical function of temperature and water density correlated in this work with the data from Ho et al.[21]

$$\log_{10}(K_{NaCl}/-) = -3.487089 + \frac{1788.105}{(T/\mathrm{K})} + 4.97196 \log_{10}(\rho_{H_2O}/\mathrm{g{\cdot}cm^{-3}}) \tag{19}$$

Then $pH_{test(2)}$ was calculated on the basis of eq 4 with the calculated $pH_{test(1)}$ 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 $pH_{test(2)}$, equilibrium constant data of the 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 CH_3COOH, K_{HAc}, at given temperatures and pressures was determined. The results are shown in Figures 1 and 2 and Table 1 with the experimental uncertainty in $\log_{10} K_{HAc}$ estimated from the one during potential readings. The present results below the critical temperature, 374 °C, were compared with the literature data from Mesmer et al.,[2] Oscarson et al.,[3] and Fisher and Barnes[4] in Figure 1. The temperature dependence of these values showed a similar trend quantitatively.

The temperature and pressure dependence dissociation constants of CH_3COOH are correlated with the following empirical model as a function of water density, ρ_{H_2O}, and temperature, T.

$$\log_{10}(K_{HAc}/-) = q_1 + \frac{q_2}{(T/\mathrm{K})} + q_3 \log_{10}(T/\mathrm{K}) + \left(q_4 + \frac{q_5}{(T/\mathrm{K})} + q_6(T/\mathrm{K})\right)\log_{10}(\rho_{H_2O}/g{\cdot}cm^{-3}) \tag{20}$$

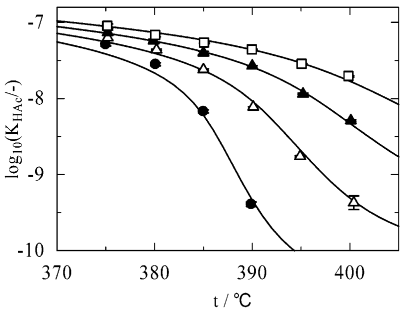

Figure 2. Dissociation constants (K_{HAc}/−) of acetic acid at supercritical conditions as a function of temperature and pressure. The symbols represent (●) 26 MPa, (△) 28 MPa, (▲) 30 MPa, and (□) 32 MPa, and the solid line represents calculated results from eq 20.

where q_1, q_2, q_3, q_4, q_5, and q_6 are reaction dependent parameters and the values are -1.9193, -1.0367×10^2, -1.0065, 1.3963×10^2, -3.2319×10^4, and -1.2491×10^{-1}, respectively. The correlation results are shown in Figures 1 and 2 as a solid line, and the model could well describe the temperature and pressure dependences of the dissociation constants.

Conclusion

A flow-through electrochemical cell was used to measure the pH of subcritical and supercritical acetic acid aqueous solutions at temperatures ranging from (21.8 to 400.4) °C and pressures ranging from (23.0 to 32.3) MPa. On the basis of the measured pH, the molal dissociation constants of acetic acid were determined and the values at subcritical conditions agreed well with literature data from potentiometric, calorimetric, and electrical conductivity measurements. A semiempirical density model could correlate the data at subcritical and supercritical conditions as a function of water density and temperature.

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