ELECTRICAL CONDUCTIVITY MEASUREMENTS OF AQUEOUS ELECTROLYTE SOLUTIONS AT HIGH TEMPERATURES AND HIGH PRESSURES

Patience C. Ho and Donald A. Palmer
Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, Tennessee 37831, USA

ABSTRACT: In aqueous solutions all electrolytes tend to associate at high temperatures (low dielectric constants). Ion association results in the formation of uncharged substrates, which are substantially more volatile than their precursor ions. Thus knowledge of the association constants is important in interpreting the thermodynamics of the partitioning of electrolytes to the vapor phase in a fully speciated approach. Electrical conductance measurements provide a unique window into ionic interactions of solutions at high temperatures and pressures.

In this study, the electrical conductivities of dilute ($<$0.1 molal) aqueous solutions of NaCl (100-600°C to 300 MPa) and sodium and potassium hydroxides (0-600 and 100-600°C, respectively, and to 300 MPa) were measured. The results show that the extent of association of Na$^+$ and Cl$^-$ is similar to those for Na$^+$ and K$^+$ with OH$^-$ in solution from subcritical to supercritical conditions.

INTRODUCTION

Knowledge of the electrical conductivity of electrolytes has considerable practical value. All electrolytes tend to associate at high temperatures (i.e. low densities). Electrical conductance measurements provide a convenient means for determining the degree of association of electrolytes at extreme conditions of temperature and pressure, including the supercritical region. The conductometric data not only provide a basic understanding of the behavior of electrolytes under supercritical conditions, but also yield complementary information for various thermodynamic studies (such as volatility, isopiestic, and calorimetry measurements).[1-3] The information are also invaluable in modelling processes, such as metal corrosion, the behavior of deep hydrothermal fluids, and in the fast emerging field of supercritical treatment of waste streams.

Electrical conductance measurements of many inorganic salt solutions, such as dilute aqueous NaCl , at elevated temperatures and pressures were initiated at ORNL during the 1960's.[4] In the present study we re-measured the conductance of dilute NaCl solutions with an updated conductance apparatus to 600°C and 300 MPa. Measurements were emphasized at temperatures close to the critical point of water in order to investigate the possible occurence of extremes under these

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conditions.

For many years, electrical conductances of dilute (<0.01 molal) aqueous alkali hydroxides at high temperatures and pressures, were unable to be measured due to the corrosive nature of these bases. Modifications of the existing apparatus involving constructing a doubly-insulated electrode permitted the determination of the extent of ion association in solutions for Na^+, K^+ and OH^-.

EXPERIMENTS AND CALCULATION

The electrical conductances of aqueous NaOH solutions at 0-75°C and saturation pressure were measured with conventional glass cells. At temperatures $\geq$ 100°C and pressures up to 300 MPa, the conductances of NaCl, NaOH, and KOH solutions were determined with a high-pressure conductance cell. The design of the apparatus, including the high-pressure conductance cell and experimental procedures are described in detail in a previous paper.[5] The accuracy of temperature measurement is better than 0.01°C for 0-75°C and ±0.1°C for temperatures > 100°C; accuracy for pressure and conductance measurements are better than ±0.1%.

After correcting for water specific conductance, the specific conductance of NaCl, NaOH, and KOH solutions were used to calculate the equivalent conductance (Λ) from Eq. 1

$$\Lambda = \{1000 + mM_{wt}\}\kappa/m\rho_s$$ (1)

where m is the molality of the solute, M_{wt} is the molecular weight of the solute, and ρ_s is the density of solution (water at temp. > 100°C) at the same temperature and pressure.[6]

The limiting equivalent conductance (Λ_0) (at infinite dilution) and molar association constant (K_M) of the electrolyte solutions at various temperatures and densities were calculated with the Shedlovsky equation:

$$1/\Lambda S(z) = 1/\Lambda_0 + M\Lambda S(z)f_\pm^2 K_M/\Lambda_0^2$$ (2)

where M is the molar concentration of electrolyte, $f_\pm$ is the mean molar activity coefficient of the constituent ions, S(z) is a function of M, Λ_0, and the limiting Onsager slope. As in previous conductance studies with this high-temperature apparatus the results are insufficient to permit application of more sophisticated equations.

RESULTS AND DISCUSSION

At temperatures below 300°C, the equivalent conductance (Λ) increases with increasing temperature and decreasing density. Above 300°C, Λ values increase linearly at first with decreasing density until reaching a maximum. The maxima occur from 0.5-0.75 $g \cdot cm^{-3}$ for NaCl and 0.6-0.75 $g \cdot cm^{-3}$ for NaOH and KOH depending on solution concentrations. However, in the temperature region of 370-390°C, Λ increases with decreasing density and no obvious maxima exist.

Table 1 presents the comparison of limiting equivalent conductance (Λ_0) of NaOH of this study and the reported values at 0 to 100°C and saturation pressures.[7,8] The results at 25, 50, 75, and 100°C are in excellent agreement with one another. Figures 1a-c present the values of Λ_0 of NaCl, NaOH and KOH solutions as a function of density of water at 100-600°, 0-600°, and 100-600°C, respectively, where Λ_0 is seen to increase with increasing temperature to 300°C and decreasing density. At temperatures $\geq$ 400°C, Λ_0 is virtually temperature-independent but increase linearly with decreasing density at densities between 0.8 to 0.3 $g \cdot cm^{-3}$ for NaCl, and at densities between 0.8 to 0.6 $g \cdot cm^{-3}$ for NaOH and KOH.

For the purposes of fitting the molal association constants as a function of temperature and water density as proposed by Marshall and Franck, the values of K_M were converted to molal quantities, K_m, using the density of pure water.[9] The best weighted least-squares fit is given Eq.3:

$$\log K_m = a + b/T + (c + d/T) \log \rho_w \qquad (3)$$

As an unidentified experimental problem, there was an apparent discontinuity observed in the 350 to 395°C data of NaCl below a density of 0.6 g·cm^{-3}, thus only the values of K_m obtained at temperatures $\geq$ 400°C were included in the final weighted least-squares fit, with the exception of NaOH which was calculated both in the temperature range at 400-600°C and 75-600°C (for the purpose of elevating the long extrapolation to 75°C and saturation pressures). The fitting parameters of Eq.3 for NaCl, NaOH, and KOH at 400-600°C are given in Table 2. The dependence of K_m on density and temperature are graphically presented in Figs. 2a-c and 3a-c, respectively.

Fig. 4a presents a comparison of K_m values of NaCl from this study and from the reported values by Quist and Marshall.[4] The two sets of data are generally in reasonable agreement in the intermediate density range at 100-600°C. The descrepancy is more obvious in the extrapolation to lower temperatures at the saturation pressure as illustrated in Fig. 4b, in which, K_m values were obtained by extrapolation (using Eq.3) at the discrete experimental conditions studied by Zimmerman whereas the other points were calculated either from the reported fitting equation, or by interpolation of tabulated K_m values fitted by Eq. 3. [4,11-13] The results of this study are in excellent agreement with the log K_m values reported by Zimmerman.[10]

Fig.5 shows the extrapolated K_m values of NaOH at temperatures 75-373°C and saturation pressure, whereas the other points were either obtained from estimation or by actual conductance measurements.[14-16] The values of K_m of NaOH at 250-325°C were measured by titration calorimetry and are included for comparison.[17] In Fig.5 it can be seen that the results of this study are in reasonalbe agreement with Bianchi et al. at 75-150°C, Noyes at 218°C and the estimated values from Plyasunov et al. at 75-350°C.[8,14-15] However, K_m values of Lukashov et al. are about 1.5 to 0.5 log units higher, whereas K_m values of NaOH measured by calorimetry are ca. 1.5 to 0.7 log units lower than the predicted values from this study.[16,17]

Figs. 6a,b present a comparison of log K_m values of KOH of this study with results from Franck and Lukaskov.[16,18] At temperatures $\leq$ 400°C (Fig.6a) and saturation pressure, the results from Lukashov are about 0.5 to 2 log units higher and values of Franck are systematically about 0.5 log units higher than the values of this study. Under supercritical conditions at 400-600°C and densities at 0.4-0.7 g·cm^{-3} (Fig.6b), the results of this study show good agreement with the log K_m values reported by Franck.

Table 3 gives the thermodynamics quantities calculated by differentiation of Eq. 3 with respect to temperature and pressure at chosen temperatures and pressures. The increase in association with temperature is clearly demonstrated by the increases of ΔS^0, ΔC_p^0, and ΔV^0 of reaction.[19]

Hydrolysis of sodium chloride leads to a change in the pH of solution, depending on the relative magnitudes of the ion-pair association constants. Based on this concept the concentration of H^+ in NaCl solutions at temperatures from 300 to 600°C , densities 0.4, 0.5, 0.6, and 0.75 g·cm^{-3} were calculated from the following equations:

$$Na^+_{(aq)} + Cl^-_{(aq)} \rightleftarrows NaCl_{(aq)} \qquad K_s \qquad (4)$$

$$Na^+_{(aq)} + OH^-_{(aq)} \rightleftarrows NaOH_{(aq)} \qquad K_b \qquad (5)$$

$$H^+_{(aq)} + Cl^-_{(aq)} \rightleftarrows HCl_{(aq)} \qquad K_a \qquad (6)$$

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \qquad\qquad K_w \qquad (7)$$

$$H^+_{(aq)} + Na^+_{(aq)} = OH^-_{(aq)} + Cl^-_{(aq)} \qquad\qquad (8)$$

$$\Sigma Na^+ = Na^+_{(aq)} + NaCl_{(aq)} + NaOH_{(aq)} \qquad\qquad (9)$$

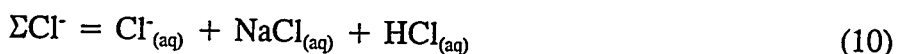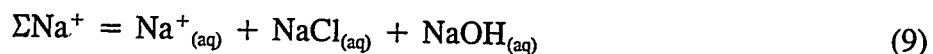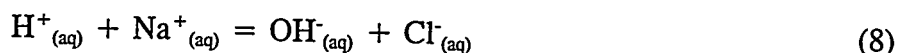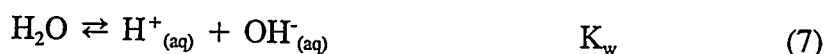$$\Sigma Cl^- = Cl^-_{(aq)} + NaCl_{(aq)} + HCl_{(aq)} \qquad\qquad (10)$$

Fig.7 presents pH values of a 0.01 m NaCl solution at various temperatures and densities as a function of temperature (Kelvin) using the values of association constants of NaCl, NaOH and HCl from Franck (Fig.7a) and from Frantz/Marshall (Fig.7b) compared to the pH values of water (i.e. 1/2 pKw).[18,20] The pH values of NaCl solutions are on the basic side of neutral, especially at density < 0.5 g·cm^{-3}, due to the fact that $K_a > K_b$. At constant temperature the pH values of water and NaCl solutions increase with decreasing density.

From Figs 7a,b it can be seen that the relative values of the association constants of acid and base control in the shift in pH, so that uncertainties in K_a can lead to an uncertainty in pH of one unit. The design of the current conductance apparatus can not preclude possibility of corrision due to the static nature of the apparatus. Therefore in collaboration with Prof. R. H. Wood (University of Delaware), we are in the process of constructing a flow-through high-pressure conductance apparatus, which will be used initially to reinvestigate the electrical conductance of HCl.

ACKNOWLEDGMENTS

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Table 1. Comparison of Limiting Conductance (cm^2·S·equiv^{-1}) of Aqueous NaOH Solutions at Saturation Pressure

Temp (°C)	Λ_0			
	This Study	Noyes [15]	Marsh/ Stokes [7]	Bianchi [8]
25	250±3		249	249
50	362±4		365	365
75	477±70		484	484
100	599±12	596		604

Table 2. Parameters of Eq. 3 (400-600°C)

Parameter	NaCl	NaOH	KOH
a	0.997	1.620	1.132
b	-650.07	-370.40	-205.02
c	-10.42	-13.91	-13.19
d	2600.5	6765.0	6051.2

Table 3. Thermodynamics Parameters for NaCl$_{(aq)}$, NaOH$_{(aq)}$, KOH$_{(aq)}$ Association

Electro-lyte	Pressure	Temp	log K_a	ΔH^0	ΔS^0	ΔC_p^0	ΔV^0
NaCl	sat.	25	-1.18	12.8	20	25	1.9
	sat.	100	-0.68	16.4	31	70	5.3
	sat.	200	-0.07	28.2	58	190	17.
	sat.	300	0.73	72.3	140	1200	90.
	sat.	370	2.18	1510	2400	1400000	5800
	300	300	0.05	27.	48	100	12.
	300	400	0.48	39.	67	140	22.
	300	500	0.95	55.	89	180	39.
NaOH	sat.	25	0.37	5.6	26.	-44	-9 8
	sat.	100	0.55	5.8	26.	38	-6.4
	sat.	200	0.81	14.3	46.	144	-1.4
	sat.	300	1.28	45.	103	743	32.
	sat.	370	2.21	841	1350	750000	3084
	300	300	1.04	15.6	47.	113	4.3
	300	400	1.33	29.5	69.	165	13.
	300	500	1.72	48.6	96.	215	29.
KOH	sat.	25	0.44	2.7	17.	-33	-8.0
	sat.	100	0.53	3.4	19.	43	-4 6
	sat.	200	0 72	12.3	40	150	1 4
	sat.	300	1 16	44.5	100.	798	40
	sat.	370	2.11	924	1479	830000	3441
	300	300	0 98	6.7	30.	112	5 1
	300	400	1.15	20.3	52.	163	14.
	300	500	1 44	39.	78.	211	29.

* Units: Pressure. MPa; temp. °C: ΔH^0. kJ·mol^{-1}; ΔS^0. J·mol^{-1}: ΔC_p^0. J·K^{-1}·mol^{-1}: ΔV^0. cm^3·r

(1a) NaCl

Limiting Equivalent Conductance ($cm^2 \cdot S \cdot equiv^{-1}$)

Temp (°C)

■ 100	△ 200
▲ 300	◇ 350
○ 370	● 375
▽ 380	▼ 385
□ 390	▪ 395
△ 400	▲ 450
◇ 500	○ 550

Density of Water ($g.cm^{-3}$)

(1b) NaOH

Limiting Equivalent Conductance ($cm^2 \cdot S.equiv^{-1}$)

Temp (°C)

▽ 100	▼ 200
□ 300	■ 375
▲ 400	▲ 450
◇ 500	◆ 550
○ 600	
○ 0–75 (at saturation)	

Density of Water ($g.cm^{-3}$)

(1c) KOH

Limiting Equivalent Conductance ($cm^2.S.equiv^{-1}$)

Temp (°C)

○ 100	● 200
▽ 300	▼ 375
□ 400	■ 450
△ 500	▲ 550
◇ 600	

Density of Water ($g.cm^{-3}$)

Figures 1a-c. Λ_0 of NaCl$_{(aq)}$, NaOH$_{(aq)}$, and KOH$_{(aq)}$ as a function of ρ_w at constant temperature.

(2a)

$\log K_m$

$[Na^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons NaCl_{(aq)}]$

Temp (°C)

▽ 350	□ 370
■ 375	△ 380
▲ 385	◇ 390
◆ 395	○ 400
● 450	▽ 500
▼ 550	□ 600

$\log \rho_w$

(2b)

$\log K_m$

$[Na^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons NaOH_{(aq)}]$

Temp (°C)

○ 375	
● 400	
▽ 450	
▼ 500	
□ 550	
■ 600	

$\log \rho_w$

(2c)

$\log K_m$

$[K^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons KOH_{(aq)}]$

Temp (°C)

○ 375	
● 400	
▽ 450	
▼ 500	
□ 550	
■ 600	

$\log \rho_w$

Figure 2a-c. Log K_m for NaCl$_{(aq)}$, NaOH$_{(aq)}$, and KOH$_{(aq)}$ as a function of log ρ_w.

Figures 3a-c. Log K_m for $NaCl_{(aq)}$, $NaOH_{(aq)}$, and $KOH_{(aq)}$ as a function of 1000/T (K^{-1}) at constant densities.
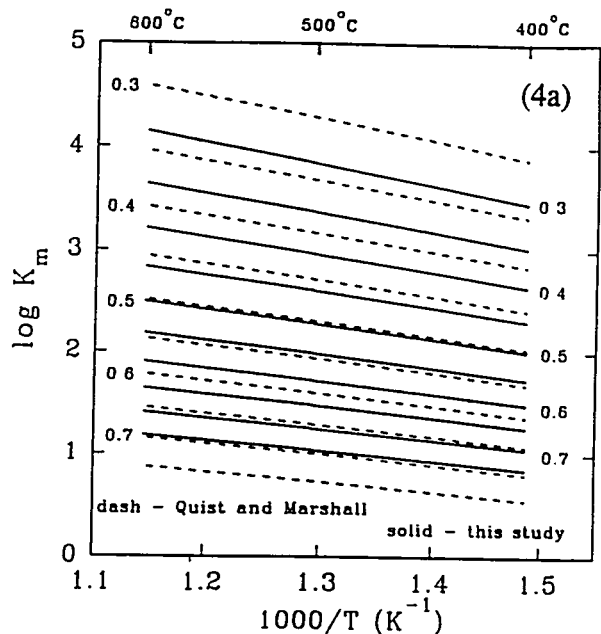
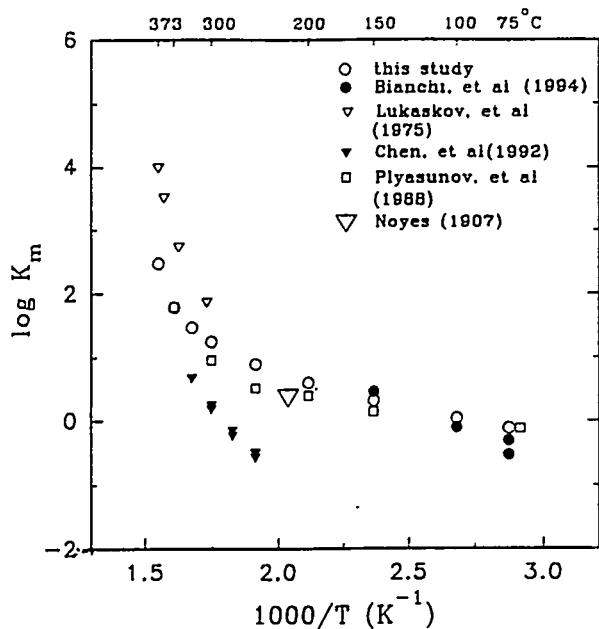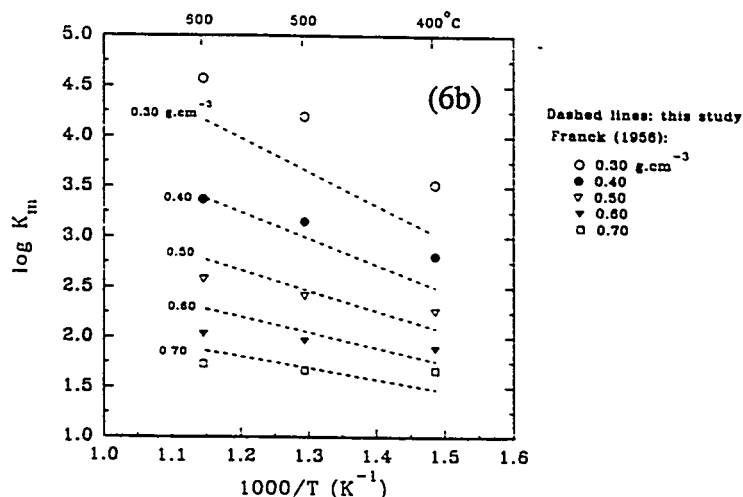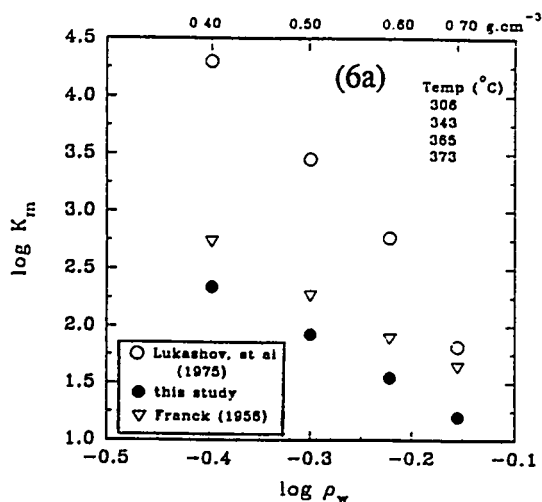Figure 4a,b. A comparison of the log K_m values for $NaCl_{(aq)}$ as a function of 1000/T (K^{-1}).

Figure 5. A comparison of the log K_m values for $NaOH_{(aq)}$ as a function of 1000/T (K^{-1}).

Figures 6. A comparison of the log K_m values for $KOH_{(aq)}$ as a function of log ρ_w (6a) and of 1000/T (K^{-1}) at constant density (6b).
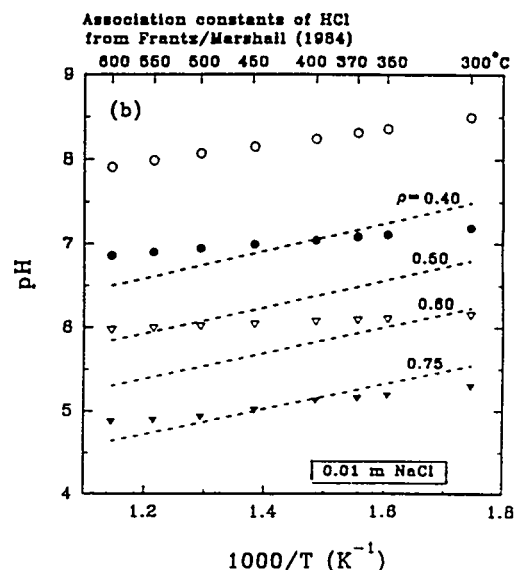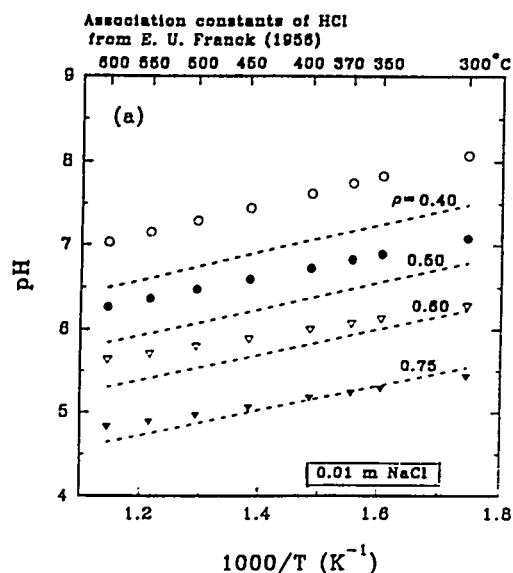

Figure 7. A comparison of the pH values for a 0.01 m NaCl solution and 1/2 pK_w at temperatures 300-600°C and densities 0.4-0.75 g·cm⁻³.