

Conductivity Measurements of Dilute Aqueous LiOH, NaOH, and KOH Solutions to High Temperatures and Pressures Using a Flow-Through Cell

Patience C. Ho,^{*,†} Donald A. Palmer,[†] and Robert H. Wood[‡]

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6110, and Department of Chemistry and Biochemistry and Center for Molecular and Engineering Thermodynamics, University of Delaware, Newark, Delaware 19716

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The limiting molar conductance (Λ_0) and molal ion association constant ($K_A(m)$) of dilute (10^{-5} to 10^{-3} mol kg^{-1}) aqueous LiOH, NaOH, and KOH solutions were determined by a flow-through conductance cell from 50 to 410 °C and pressures up to 33 MPa. The flow-through cell is designed to measure molar conductances of dilute aqueous electrolytes with a high degree of accuracy at high temperatures and pressures. The results are complementary to our previously reported results measured with a static high-pressure cell, which was incapable of yielding reliable measurements at concentrations < 0.001 mol kg^{-1} and densities < 0.4 g cm^{-3} . The new Λ_0 values of all three hydroxides at densities (ρ) ≥ 0.5 g cm^{-3} are in good agreement with those measured using the static cell. However, at densities below 0.5 g cm^{-3} the new results are slightly higher and less scattered than the previous results at comparable conditions. On the other hand, the $K_A(m)$ values of all three hydroxides are in excellent agreement with the static cell results under analogous conditions.

1. Introduction

In dilute aqueous solutions, the degree of ionic association of LiOH, NaOH, and KOH is relatively stronger than their common salts at high temperatures and low densities,^{1–3} while LiOH(aq) is significantly higher than for NaOH(aq) and KOH(aq). Electrical conductance measurements of dilute aqueous alkali hydroxide solutions at high temperatures provide a unique means of determining the extent of the association of alkali metal ions with OH^- ions. Knowledge of the association constants of these hydroxides is important in interpreting the thermodynamics of ion–ion and ion–water interactions, as well as providing a fundamental parameter in determining the pH of the solutions at extreme conditions, which in combination with the ion association values, affects such behavior as the relative volatility of HCl, and alkali chlorides and hydroxides to the vapor phases.

Because of their corrosive nature, the conductance data of the alkali hydroxides at high temperatures are scattered. In past studies, using a doubly insulated ($\text{Al}_2\text{O}_3/\text{ZrO}_2$) inner electrode of a static high-pressure cell,^{1–3} the electric conductances of the dilute aqueous LiOH, NaOH, and KOH solutions were measured over the concentration range 10^{-2} to 10^{-3} mol kg^{-1} , at temperatures to 600 °C and pressures to 300 MPa. The major disadvantages of this design are its limited accuracy at lower concentrations and densities, because of the high solvent conductance, the potential for ionic impurities to concentrate or adsorb in the cell, and the inherently large temperature gradient along the vertical axis of the static cell. These effects, coupled with the high residence time of the solutions in the cell and auxiliary tubing, limit reliability of measurements at concentrations < 0.001 mol kg^{-1} and densities < 0.4 and < 0.55 g cm^{-3} for NaOH, KOH, and LiOH solutions. For highly

TABLE 1: Corrosion Test of Insulating Materials

material	°C	solutions (mol \cdot kg $^{-1}$)	days	weight loss (%)
rutile crystal (TiO_2)	216	HCl, 0.1	7	0.05
	210	HCl, 0.1	7	0.05
	210	HCl, 0.28	6	0.06
	210	NaOH, 0.2	7	0.0
	70	NaOH, 0.96	6	0.04
	70	NaOH, 0.96	12	0.06
sapphire	216	HCl, 0.1	7	0.16
	210	HCl, 0.28	6	0.21
	210	NaOH, 0.2	7	0.18
sintered Al_2O_3	216	HCl, 0.28	7	1.12
	216	NaOH, 0.2	6	21.7
silicon nitride (Si_3N_4)	216	HCl, 0.1	8	43.2
	216	NaOH, 0.1	8	2.7
	70	NaOH, 0.96	6	0.01

associated electrolytes, such as the alkali hydroxides, accurate measurements need to be made at much lower concentrations, especially at low densities. The flow-through cell configuration permits high precision conductance measurements⁴ and extends the concentrations to as low as 10^{-5} mol kg^{-1} at densities less than 0.4 g cm^{-3} .

2. Experimental Section

2.1. Experimental Procedures. The design of the flow-through conductance cell has been described in detail in previous papers.^{5,6} However, a minor modification was made by replacing the sapphire insulation disk with a rutile (TiO_2) disk because of the corrosive nature of aqueous hydroxide solutions. The inner electrode protrudes from this rutile disk by about 0.8 cm into the Pt/Rh cup (the outer electrode). The rutile insulator was fabricated from a 1.27-cm long and 0.622-cm OD rutile single crystal (Atomergic Chemicals, Farmingdale, NY) with a 0.165-cm hole drilled in the center (Chand Assoc., Worcester, MA). Rutile proved to be an excellent insulating material in terms of corrosion resistance to acidic and basic solutions at high

* To whom correspondence should be sent. E-mail: HoPC@ORNL.GOV. Fax: 865-574-4961.

[†] Oak Ridge National Laboratory.

[‡] University of Delaware.

TABLE 2: Experimental Value of Λ of LiOH, NaOH, and KOH and % Average Relative Errors $\Delta\Lambda$ from Value Calculated by Eq 1

$^{\circ}\text{C}$	P (MPa)	$10^{-7}\chi_s^a$ ($10^{-7}\text{S}\cdot\text{cm}^{-1}$)	10^5 m (mol/kg)	10^5 c (mol/dm ³)	Λ ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)	$\delta\Lambda$ (%)	$^{\circ}\text{C}$	P (MPa)	$10^{-7}\chi_s^a$ ($10^{-7}\text{S}\cdot\text{cm}^{-1}$)	10^5 m (mol/kg)	10^5 c (mol/dm ³)	Λ ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)	$\delta\Lambda$ (%)
LiOH													
50.00	4.42	18.1	33.751	33.41	331.76	0.03	300.00	12.87	32.5	10.537	7.6032	1148.8	-0.02
	4.37		50.894	50.379	330.97	0.07		12.88		18.246	13.166	1143.1	0.06
	4.42		75.054	74.297	329.4	-0.07		12.84		26.238	18.931	1136.2	-0.04
	4.37		93.694	92.746	328.84	-0.02		12.88		36.427	26.286	1130.2	0.01
	4.4		134.55	133.19	326.84	-0.19		12.85		53.417	38.542	1120	-0.04
	4.42		165.41	163.74	327.01	0.16		12.88		65.96	47.597	1114.4	0.03
100.00	4.88	21.7	13.465	12.934	537.24	0.22	350.00	23.91	21.7	37.287	23.152	1217.2	-0.02
	4.88		24.791	23.814	533.39	-0.08		23.84		47.184	29.282	1206.6	-0.1
	4.88		33.35	32.036	531.82	-0.18		23.81		67.533	41.903	1190.1	0.0002
	4.88		45.499	43.707	531.16	-0.002		23.96		98.884	61.425	1168.2	0.14
	4.9		54.505	52.358	530.11	0.01		23.75		166.9	103.52	1125.9	0.07
	4.88		69.806	67.056	528.78	0.09		23.87		255.08	158.38	1081.7	-0.09
150.00	9.4	21.7	12.381	11.415	748.22	0.21	350.00	27.46	22	19.114	12.143	1218.8	0.09
	9.44		23.387	21.563	742.46	-0.08		27.47		30.626	19.458	1205.2	-0.13
	9.42		31.442	28.99	739.81	-0.13		27.37		37.845	24.031	1200.1	-0.04
	9.35		40.486	37.328	736.87	-0.21		27.47		49.469	31.431	1192.5	0.07
	9.38		57.583	53.093	735.97	0.21	370.00	28.74	14.6	10.438	5.9647	1246.1	-0.01
200.00	9.86	21.4	12.882	11.219	907.98	0.13		28.78		23.782	13.598	1202.8	0.02
	9.85		22.318	19.436	902.21	-0.07		28.86		33.099	18.944	1178.3	0.01
	9.86		30.89	26.902	898.92	-0.09		28.85		45.602	26.099	1150	-0.04
	9.97		39.048	34.01	896.95	-0.01		28.70		58.182	33.246	1127	0.02
	9.96		52.354	45.599	892.7	-0.04	380.00	29.82	4.72	11.889	6.3252	1236.8	0.03
	9.95		69.742	60.743	888.9	0.07		29.84		20.295	10.802	1208.8	-0.09
250.00	10.95	19.5	13.463	10.863	1037.1	0.04		29.86		31.673	16.864	1180.3	0.09
	11.03		22.311	18.004	1032.2	0.06		29.86		44.532	23.71	1149.4	-0.02
	10.93		30.957	24.978	1028.5	0.12		29.86		64.254	34.228	1110.8	-0.01
	11.21		40.475	32.671	1021.7	-0.12	390.00	28.89	4.45	5.1521	2.2849	1175.8	-0.01
	10.95		50.457	40.713	1016.8	-0.21		28.87		12.605	5.5843	1121.7	-0.18
	11.08		68.091	54.952	1012.1	-0.02		28.89		23.808	10.561	1064.6	0.06
	10.96		90.351	72.906	1006.2	0.13		28.88		42.695	18.933	993.89	0.37
300.00	9.5	32.5	44.752	31.971	1150.5	-0.11		28.88		63.816	28.306	926.94	-0.22
	9.5		64.866	46.341	1141	-0.19	400.00	32.50	2.16	4.6941	2.0327	1366.2	-0.02
	9.5		90.992	65.006	1136.1	0.23		32.49		10.581	4.5802	1295.5	-0.09
	9.54		136.75	97.715	1120.5	0.12		32.50		23.309	10.096	1187.5	0.06
	9.51		202.8	144.9	1103.8	0.17		32.47		37.039	16.023	1104	-0.03
	9.56		259.88	185.72	1086.5	-0.23	400.00	30.56	2.71	18.102	6.8665	792.97	0.25
300.00	10.39	32	10.512	7.5305	1118.7	0.19		30.57		45.637	17.334	682.32	-0.21
	10.36		15.06	10.788	1110.5	-0.18		30.56		71.884	27.287	620.47	-0.17
	10.37		23.742	17.006	1104.9	-0.09		30.57		90.066	34.424	589.19	0.03
	10.48		36.381	26.069	1098.3	0.06	410.00	32.21	1.86	27.393	8.9795	679.38	0.27
	10.39		49.617	35.554	1090.2	0.01		32.21		35.419	11.62	641.51	-0.34
								32.18		50.83	16.618	594.46	0.04
NaOH													
100.00	9.96	31.5	46.879	45.142	577.67	0.03	370.00	25.83	19.1	24.451	13.41	1339	-0.13
	9.96		59.779	57.564	576.42	0.004		25.84		43.156	23.673	1321.9	-0.04
	9.93		85.139	81.983	574.41	-0.02		25.92		65.915	36.208	1305.4	0.06
	9.86		105.38	101.47	572.89	-0.06		25.86		102.6	56.317	1282.5	0.1
	10.00		141.22	135.99	571.45	0.05		25.76		148.31	81.263	1260.1	0.21
200.00	15.46	57.4	28.669	25.082	935.33	-0.03		25.76		224.35	122.95	1222.8	-0.2
	15.36		31.076	27.186	934.29	0.09	390.00	28.76	5.54	23.696	10.475	1332.8	-0.08
	15.39		49.639	43.427	931.25	0.02		28.65		40.155	17.633	1297.3	0.14
	15.33		77.845	68.099	925.61	-0.21		28.64		61.045	26.795	1255.9	0.005
	15.35		112.54	98.456	918.3	0.1		28.74		93.421	41.278	1204.3	-0.1
	15.47		175.87	153.87	913.48	0.02		28.72		135.37	59.767	1153.3	0.03
300.00	9.65	32.5	54.622	39.048	1220	0.11		28.72		214.2	94.653	1075.4	0.006
	9.77		72.378	51.764	1211.3	-0.14	405.00	31.28	2.59	13.092	4.5493	1309.9	0.02
	9.69		104.2	74.51	1204.4	-0.002		31.28		24.858	8.6393	1231.2	-0.01
	9.61		175.82	125.73	1189.6	0.05		31.18		39.213	13.483	1159.1	-0.13
	9.72		267.06	191.11	1173.7	-0.01		31.26		54.643	18.958	1102.9	0.22
350.00	23.88	21.7	27.167	16.865	1324.9	0.11		31.27		71.966	25.001	1045.12	-0.1
	23.97		42.053	26.122	1311.6	-0.02							
	23.98		77.031	47.856	1288.2	-0.14							
	23.86		154.88	96.148	1253.9	0.01							
	23.91		254.74	152.63	1222.2	0.04							

temperatures. Table 1 shows test results for several insulators after exposure to hydrochloric acid and sodium hydroxide at high temperatures. The tests were performed by sealing weighed amounts of each insulator in either HCl or NaOH solutions at 70 to 216 $^{\circ}\text{C}$ for 6 to 12 days in a Teflon-lined autoclave. The concentrations employed were 10^2 to 10^4 times higher than the actual experimental solutions used in the conductance cell. After

cooling, the materials were rinsed with distilled water, dried, and weighed again to determine weight losses.

The experimental procedures were similar to those described in detail,⁵ except the flow rates of the very diluted hydroxide solutions were modified. To eliminate errors due to small amounts of adsorption of ionic species by TiO_2 surfaces,⁷ at temperatures ≤ 350 $^{\circ}\text{C}$, an initial flow rate was set at 0.4

TABLE 2: Continued

°C	P (MPa)	χ_s^a ($10^{-7} \text{ S}\cdot\text{cm}^{-1}$)	10^5 m (mol/kg)	10^5 c (mol/dm ³)	Λ ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)	$\delta\Lambda$ (%)	°C	P (MPa)	χ_s^a ($10^{-7} \text{ S}\cdot\text{cm}^{-1}$)	10^5 m (mol/kg)	10^5 c (mol/dm ³)	Λ ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)	$\delta\Lambda$ (%)
KOH													
100.00	13.76	8.03	31.876	30.75	630.27	0.004	28.27			147.69	94.274	1311.1	0.04
	13.77		49.521	47.772	629.01	0.07	28.26	21.7		25.622	16.352	1358.5	0.12
	13.67		82.291	79.38	626.01	-0.03	28.28			43.53	27.785	1346.5	-0.02
	13.65		126.12	121.66	623.28	-0.06	28.31			73.152	46.702	1333.7	0.01
	13.72		190.38	183.65	620.56	-0.02	370.00	17.7		23.081	13.022	1358.3	-0.004
	13.65		256.02	246.96	618.46	0.04	27.70			35.956	20.282	1346.9	-0.14
200.00	15.65	57.4	58.459	51.154	997.44	-0.11	27.73			66.132	37.309	1333.6	0.14
	15.53		82.103	71.835	995.62	0.09	27.72			99.255	55.993	1317.2	-0.03
	15.56		126.99	111.12	988.28	-0.04	27.75			142.15	80.231	1304.8	0.16
	15.56		26.43	23.127	1004.9	-0.05	27.80			207.77	117.36	1283.1	-0.12
	15.58		43.428	37.998	1001.1	-0.03	380.00	4.72		27.957	14.036	1332.8	0.03
	15.67		71.387	62.466	998.21	0.18	27.24			40.838	20.518	1318.4	0.19
	15.66		123.11	107.72	988.93	-0.02	27.19			61.524	30.88	1294.7	-0.03
	15.69		179.63	157.19	982.72	-0.02	27.13			93.635	46.954	1271.8	0.003
300.00	16.49	36.1	36.175	26.359	1282.2	0.03	27.12			36.801	18.421	1317.9	-0.2
	16.51		63.554	46.311	1273.5	0.07	390.00	9.47		13.035	5.5366	1355.3	-0.05
	16.52		141.56	103.16	1256.7	0.16	28.15			26.574	10.575	1328.6	0.07
	16.48		231.2	168.48	1241	0.07	28.18			24.915	11.252	1324.6	0.05
	16.64		45.397	33.091	1278.8	0.03	28.15			43.047	18.231	1292.2	-0.09
	16.64		65.124	47.471	1270.7	-0.11	28.21			70.306	29.93	1252.5	0.02
	16.53		103.87	75.698	1260.8	-0.13	28.19			105.48	44.849	1208.7	-0.001
	16.59		179.81	131.06	1246.8	-0.09	405.00	31.34	2.59	11.788	4.1171	1393.5	-0.1
	16.61		258.26	188.27	1236	-0.03	31.34			17.361	6.0642	1374.1	0.06
350.00	28.28	22.7	30.841	19.685	1352.8	-0.06	31.31			25.984	9.0492	1346	0.05
	28.28		48.55	30.989	1345.4	0.09	31.28			36.162	12.556	1318.3	-0.07
	28.31		61.476	39.247	1335.9	-0.19	31.28			48.396	16.79	1288.3	0.07
	28.25		101.13	64.544	1324.3	0.02							

^a χ_s Solvent specific conductance.

mL·min⁻¹ for 15 min, then reduced to 0.15 mL·min⁻¹ for another 30–40 min before the resistance measurement was taken. At higher temperatures this initial flushing could be reduced. In the range 350–390 °C, the cell was flushed for only ca. 5 min at 0.4 mL·min⁻¹ before the flow was reduced to 0.15 mL·min⁻¹, whereas at temperatures ≥ 390 °C, the flow was reduced to 0.18 mL·min⁻¹ and resistance was measured 40 to 50 min later. It appears that at higher temperatures adsorption was not as significant as at low temperatures, which conflicts with direct adsorption measurements of Mashkesky et al.,⁷ but the latter were confined to $T < 350$ °C. Normally after 20 min, the resistance readings of the sample reached a constant value for the next 30 min. Generally, the differences in conductances measured at flow rates of either 0.4 or 0.15 mL·min⁻¹ at temperature from 50 to 400 °C agree well within experimental errors. This indicates that thermal equilibrium was reached under the conditions studied.⁴ The lower flow rate was adopted in order to achieve better thermal equilibration. After the conductance of the water (background) was measured, the injector valve was returned to the load position with a flow rate of 0.2 mL·min⁻¹ until the next solution was ready for injection. Each sample solution was prepared by adding an aliquot of stock solution from a weighed polyethylene syringe into a bottle containing a weighed quantity of degassed water under helium. The empty syringe was then reweighed to determine the amount of stock solution delivered. After mixing, the sample solution was forced into the sample loop with the valve set on load, then injected in the same manner described earlier before the resistance is measured.

For each sample series, the resistance of the solvent water is measured before measuring the sample solutions at frequencies from 0.5 to 10 kHz. The frequency dependence was extrapolated (resistance versus the reciprocal square root of frequency) to infinite frequency by means of a simple linear regression.

To reduce thermal gradients in the cell at temperatures > 400 °C, the vessel is located in the central portion of the furnace, but this severely limits the extent to which the inflowing solution

can be preheated, especially at high temperatures and pressures. The problem will be minimized in the future by increasing the volume of preheated solution in the inlet path by means of lengthening the high-pressure vessel and the tube furnace, and enlarging the inner diameter of the inlet Pt/Ph tubing within the vessel.

2.2. Solutions. The stock solutions of NaOH and KOH were obtained by diluting concentrated NaOH (50% w/w, Baker) and KOH (45% w/w, Baker) solutions with conductivity water⁵ to achieve the desired concentrations. The concentrated NaOH and KOH were standardized by weight with potassium biphthalate (dried at 120 °C, Baker) and with standardized HCl (versus Na₂CO₃) using weight burets under argon. Lithium hydroxide solution was treated with solid barium hydroxide and filtrated to yield a clear supernatant liquid² (standardized at 1.0049 mol·kg⁻¹ LiOH), which was subsequently diluted with conductivity water to the desired concentration. The concentrated stock solutions are stored in polyethylene bottles under helium. Dilute solutions were prepared by adding aliquots of the concentrated stock solution from polyethylene syringes into “confirmed,” conductivity-grade water under helium.⁵ A series of sample solutions in the concentration range of 10⁻⁵ to 10⁻³ mol·kg⁻¹ was prepared by consecutively adding stock solution to the most dilute sample solution.

2.4. Cell Constant. The cell constant at 25 °C was approximately 0.2 cm⁻¹ as determined by measuring the resistance of 10⁻⁴ to 10⁻³ mol·kg⁻¹ KCl solutions, calculated according to equations given by Justice⁸ adjusted to ITS90 scale. The exact value of the cell constant is dependent upon the specific dimensions of the electrode assembly. Note that molality was converted to molarity using density data for KCl at 25 °C calculated from the partial molar volumes of KCl⁹ at 25 °C. The cell constants obtained at 25 °C from seven samples are in agreement within $\pm 0.2\%$. The cell was then heated to 400 °C (30 MPa) and allowed to cool to 25 °C, whereupon the cell constant was generally observed to change less than 0.3%. To

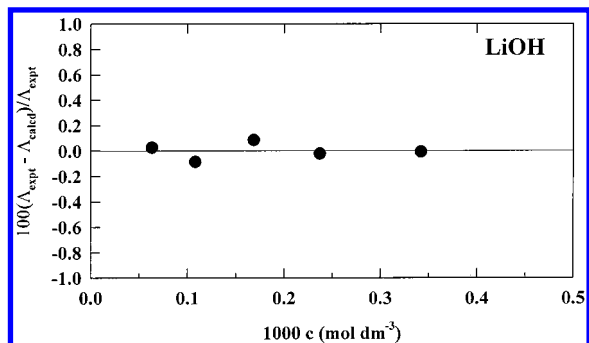


Figure 1. Deviations of experimental and fit values of molar conductance of LiOH at 380 °C and 29.85 MPa as a function of molarity.

estimate the cell constant at higher temperatures, it was corrected for the thermal expansion of rutile and platinum (less than 0.1% at 400 °C).

3. Results and Discussion

The current measurements were carried out with a commercial injector valve, pump and tubing that are rated to 50, 69, and 104 MPa, respectively. Thus, studies of the conductivity of dilute aqueous LiOH, NaOH, and KOH were made over a concentration range from 10^{-5} to 10^{-3} mol·kg $^{-1}$ at temperatures 50 to 410 °C and pressures up to 33 MPa. As mentioned above, because accurate conductance measurement of aqueous alkali hydroxides in the concentration ranges below 10^{-3} mol·kg $^{-1}$ could not be attained using the static cell, the new results are important in correlating with studies of ion association of these electrolytes at high temperatures and low densities. Table 2 gives the experimental values of the molar conductances Λ of LiOH, NaOH, and KOH, and percentage deviation $\delta\Lambda$ from values (Λ_{calcd}) calculated by the FHFP (Fuoss–Hsia–Fernández–Prini) equation¹⁰

$$\Lambda =$$

$$\alpha(\Lambda_0 - S(\alpha c)^{1/2} + E\alpha c \ln(\alpha c) - J_1\alpha c + J_2(\alpha c)^{3/2}) \quad (1)$$

where α is the degree of dissociation calculated from the mass action equation with the mean activity coefficient γ_{\pm} of the free ions calculated based on the Debye–Hückel limiting law

$$K_A(M) = \rho K_A(m) = (1 - \alpha)/(\alpha^2 \gamma_{\pm}^2) \quad (2)$$

$$\ln \gamma_{\pm} = -\kappa q \alpha^{1/2}/(1 + \kappa a \alpha^{1/2}) \quad (3)$$

and constants S , E , J_1 , and J_2 in eq 1 carry the same definitions and are calculated according to equations given in ref 10; whereas in eqs 2 and 3, $K_A(M)$ and $K_A(m)$ are the molar and molal association constants, respectively; ρ is the solvent density; κ is the reciprocal radius of the ionic atmosphere; q is the Bjerrum distance, a is the distance of the closest approach set equal to q according to the recommendation of Justice.⁸ The values of dielectric constant ϵ and viscosity η used for calculating constants S and E in eq 1 are obtained from Archer and Wang,¹¹ Uematsu and Franck,¹² and from the NBS/NRC steam tables.¹³

The solution densities are computed from the partial molar volumes of LiOH, NaOH, and KOH at temperatures up to 350 °C^{14–17} and with water densities¹⁸ at the experimental temperatures and pressures. At temperatures > 350 °C, the partial molar volumes of alkali halides and hydroxide are not too different from one another, and, therefore, the partial molar volumes of

TABLE 3: Limiting Molar Conductances Λ_0 , $\log K_A(m)$, and σ of Aqueous LiOH, NaOH, and KOH Solutions

T (K)	P (MPa)	ρ (g·cm $^{-3}$)	Λ_0 (S·cm 2 mol $^{-1}$)	$\log K_A$	σ (S·cm 2 mol $^{-1}$)
LiOH					
323.15	4.4	0.9899	335.33 \pm 0.42	0.53 \pm 0.17	0.4
373.15	4.88	0.9606	540.78 \pm 0.86	1.03 \pm 0.17	0.9
423.15	9.4	0.922	754.33 \pm 1.8	1.29 \pm 0.19	1.7
473.15	9.91	0.8709	1017.4 \pm 0.8	1.28 \pm 0.1	0.8
523.15	11.02	0.8069	1051.4 \pm 1.2	1.41 \pm 0.15	1.4
573.15	9.52	0.7144	1188.7 \pm 2.2	1.36 \pm 0.04	2.5
	10.39	0.7164	1134.0 \pm 1.8	1.56 \pm 0.1	1.8
	12.87	0.7216	1166.6 \pm 0.4	1.6 \pm 0.02	0.5
623.15	23.86	0.6206	1277.3 \pm 0.9	2 \pm 0.03	1.2
	27.44	0.6352	1251.3 \pm 2.6	1.81 \pm 0.07	1.5
643.15	28.79	0.5715	1291.0 \pm 1.5	2.49 \pm 0.06	1.4
653.15	29.85	0.5323	1294.8 \pm 0.9	2.67 \pm 0.15	0.9
663.15	28.88	0.4433	1233.4 \pm 2.1	3.18 \pm 0.03	2.7
673.15	32.49	0.4328	1452.5 \pm 53.4	3.1 \pm 0.23	1.9
673.15	30.57	0.3794	948.05 \pm 1.5	3.48 \pm 0.03	1.9
683.15	32.2	0.3273	930.41 \pm 3.5	3.75 \pm 0.2	2.9
NaOH					
373.15	9.94	0.9629	585.62 \pm 0.37	0.28 \pm 0.19	0.3
473.15	15.39	0.8748	949.17 \pm 0.92	0.66 \pm 0.13	1.1
573.15	9.69	0.7148	1255.4 \pm 1.3	0.89 \pm 0.3	1.3
623.15	23.93	0.621	1364.3 \pm 1.1	1.65 \pm 0.01	1.4
643.15	25.83	0.5484	1388.5 \pm 1.7	1.83 \pm 0.02	2.2
663.15	28.71	0.4385	1429.8 \pm 9.2	2.46 \pm 0.1	1.4
678.15	31.25	0.346	1463.2 \pm 35.4	2.9 \pm 0.13	2.2
KOH					
373.15	13.7	0.9646	636.91 \pm 0.26	-0.3 \pm 0.3	0.3
473.15	15.63	0.875	1018.8 \pm 0.8	0.4 \pm 0.18	1
573.15	16.55	0.7288	1310.1 \pm 0.9	0.58 \pm 0.4	1.3
623.15	28.28	0.6383	1389.4 \pm 1.1	1.08 \pm 0.4	1.4
643.15	27.74	0.5642	1396.3 \pm 1.5	1.29 \pm 0.3	1.8
653.15	27.19	0.5002	1403.1 \pm 62.4	2.01 \pm 0.3	2.6
663.15	28.18	0.422	1414.5 \pm 6.6	2.11 \pm 0.1	1
678.15	31.31	0.348	1476.5 \pm 1.5	2.85 \pm 0.1	1.2

these three hydroxides were calculated based on values for the chlorides. The deviations between Λ_{expt} and Λ_{calcd} using the best fit of each data set with eq 1 are in most cases less than 0.2%. Figure 1 illustrates an example of percentage average relative errors $\alpha\Lambda$ of LiOH at 380 °C and 29.85 MPa as a function of the molar concentration. The results, especially at densities < 0.6 g·cm $^{-3}$, show an improvement by at least 2 orders of magnitude in precision compared to those measured by the static cell and show values as low as 3 orders of magnitude in terms of the lowest solute concentration that can be measured.^{1–3}

In previous studies,^{1–3} it was realized that in dilute aqueous alkali hydroxide solutions, the solvent plays a more important role in determining the ionic conductivities of hydroxide ions compared to their salt solutions. Thus, at lower temperatures the ionic conductances of OH $^{-}$ ions are abnormally higher than anions such as Cl $^{-}$ (aq). This is due to hydrogen jumping along the interlinked hydrogen-bond network connecting the bulk water molecules, which produces excess ionic conductivity of OH $^{-}$ ions in addition to the intrinsic conductivity arising from hydrodynamic mobility. The value of the limiting excess ionic conductance of OH $^{-}$ ions ($\lambda_0^E(\text{OH}^{-})$) approximately equals the difference between an alkali hydroxide and its corresponding chloride analogues at corresponding conditions. In dilute aqueous solutions, the excess ionic conductivity decreases with increasing temperature and decreasing density due to the drastic weakening of the hydrogen-bonding network and added ion–dipole/solvent interactions. The latter effect results in a larger reduction in the mobility of the anions in solution, increasing tendencies for ionic association. Values of $\lambda_0^E(\text{OH}^{-})$ obtained from the Λ_0 of LiOH, NaOH, and KOH solutions in this study and those of LiCl, NaCl, and KCl⁵ at temperatures 380–405

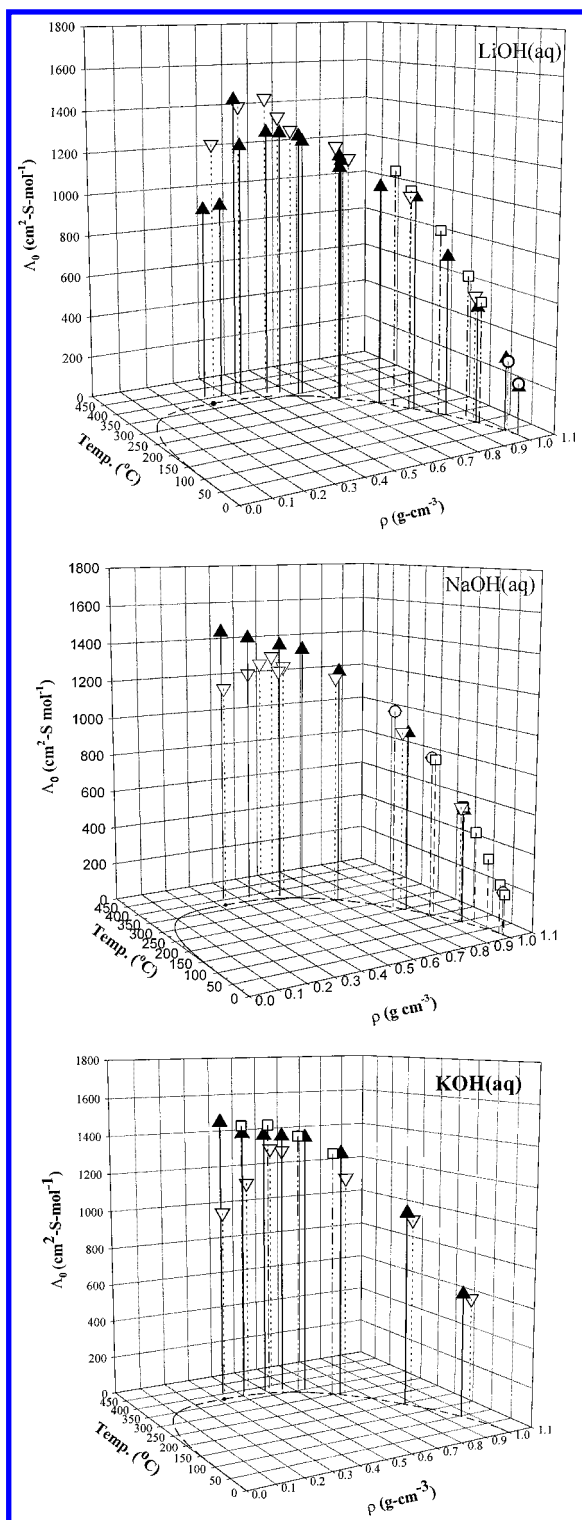


Figure 2. (a) Comparison of Λ_0 values of LiOH as a function of temperature and density with those reported by Ho and Palmer² (∇), by Corti et al.¹⁹ (\circ), by Wright et al.²⁰ (\square), and this study (\blacktriangle) at corresponding conditions. (b) Comparison of Λ_0 values of NaOH as a function of temperature and density with those reported by Ho and Palmer¹ (∇), by Bianchi et al.²¹ (\square), by Lukashov et al.²² (\circ), by Noyes²³ (\diamond) and this study (\blacktriangle) at corresponding conditions. (c) Comparison of Λ_0 values of KOH as a function of temperature and density with those reported by Ho and Palmer³ (∇), by Lukashov et al.²² (\square) and this study (\blacktriangle) at corresponding conditions.

$^{\circ}\text{C}$, show that the $\lambda_0^{\text{E}}(\text{OH}^-)$ value indeed decreases with decreasing density and is nearly temperature independent in this temperature range, approaching zero at a density of ca. 0.45

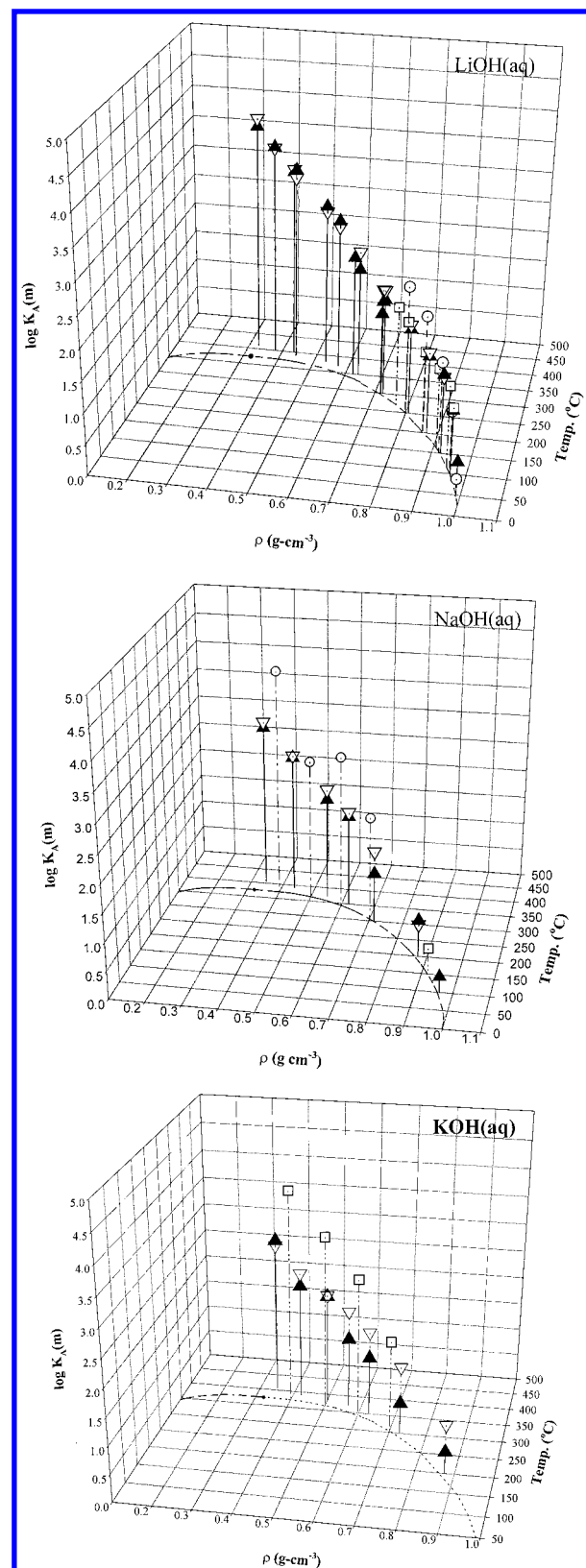


Figure 3. (a) Comparison of $\log K_A(m)$ of LiOH as a function of temperature and density with those reported by Ho and Palmer² (∇), by Corti et al.¹⁹ (\circ), and by Wright et al.²⁰ (\square) and this study (\blacktriangle) at corresponding conditions. (b) Comparison of $\log K_A(m)$ of NaOH as a function of temperature and density with those reported by Ho and Palmer¹ (∇), by Bianchi et al.²¹ (\square), by Lukashov et al.²² (\circ), and this study (\blacktriangle) at corresponding conditions. (c) Comparison of $\log K_A(m)$ of KOH as a function of temperature and density with those reported by Ho and Palmer³ (∇), by Lukashov et al.²² (\square), and this study (\blacktriangle) at corresponding conditions.

$\text{g}\cdot\text{cm}^{-3}$. This is in agreement with our previous results 1, 2 that $\lambda_0^E(\text{OH}^-)$ values become relatively small at temperatures $\geq 400^\circ\text{C}$ and densities $< 0.5 \text{ g}\cdot\text{cm}^{-3}$.

Table 3 gives the calculated values of Λ_0 and $K_A(m)$ of LiOH, NaOH, and KOH. Figures 2a–c and 3a–c show the comparisons and the trends of Λ_0 and $K_A(m)$ as functions of temperatures and densities with reported values^{1–3,19–23} at or close to the analogous conditions of this study. At densities $> 0.5 \text{ g}\cdot\text{cm}^{-3}$, the agreements between the present data and the reported values are well within experimental errors. Below $0.5 \text{ g}\cdot\text{cm}^{-3}$ only our former results^{1–3} and those from Lukashov et al.²² are available. At temperatures near the critical temperature of water (374°C) and $\rho < 0.5 \text{ g}\cdot\text{cm}^{-3}$, Λ_0 values of all three hydroxides are slightly higher and less scattered than our previous values in refs 1 to 3 (see Figs. 2a–c). In the case of KOH, the new Λ_0 values are found to be closer to the values reported by Lukashov et al.²² at $305\text{--}373^\circ\text{C}$ and $0.6\text{--}0.4 \text{ g}\cdot\text{cm}^{-3}$, although their $K_A(m)$ values in this range are nearly one log unit higher than this study (see Figures 2c and 3c). Note that the values of Λ_0 in refs 1–3 were obtained using the Shedlovsky equation at $\rho \geq 0.6 \text{ g}\cdot\text{cm}^{-3}$ and eq 1 below $0.6 \text{ g}\cdot\text{cm}^{-3}$, although data obtained with the static cell is not precise enough to fit with eq 1. The discrepancies between the new results and those measured with the static cell^{1–3} are probably attributed to the accuracy of the previous data, because the physical limitations of the static cell restricted our ability to obtain trustworthy Λ measurement at low densities.

Compared to Λ_0 , it is apparent that $K_A(m)$ is less sensitive than Λ_0 to systematic uncertainties in the experimental data. Thus values of $K_A(m)$ of LiOH, NaOH, and KOH are in excellent agreement with our previous data^{1–3} (see Figures 3a–c) within experimental uncertainties. Note that the equation used to calculate the ion association constants from refs 1 to 3 was developed exclusively for temperatures $\geq 400^\circ\text{C}$ and densities $\geq 0.4 \text{ g}\cdot\text{cm}^{-3}$.

Combining $K_A(m)$ values for LiOH,² NaOH,¹ and KOH³, at temperatures $\geq 400^\circ\text{C}$ and $\rho \geq 0.4 \text{ g}\cdot\text{cm}^{-3}$, where the measurements with the static cell are most precise, with the values from this study at lower temperatures and densities, allows the equations of $\log K_A(m)$ as functions of temperature (T , Kelvin) and the logarithm of density (ρ , $\text{g}\cdot\text{cm}^{-3}$) in refs 1 to 3 to be modified to

$$\log K_A(m)(\text{LiOH}) = 2.094 - 793.65/T - (8.192 - 1385.2/T)\log \rho \quad (50\text{--}600^\circ\text{C}) \quad (4)$$

$$\log K_A(m)(\text{NaOH}) = 2.068 - 656.61/T - (12.432 - 5876.9/T)\log \rho \quad (100\text{--}600^\circ\text{C}) \quad (5)$$

and

$$\log K_A(m)(\text{KOH}) = 2.302 - 954.72/T - (9.862 - 3993.5/T)\log \rho \quad (100\text{--}600^\circ\text{C}) \quad (6)$$

IV. Conclusion

The Λ_0 values presented in this study show that the new results are in agreement with the values measured using the

static cell for LiOH, NaOH, and KOH at $\rho \geq 0.5 \text{ g}\cdot\text{cm}^{-3}$ but are slightly higher and less scattered below $0.5 \text{ g}\cdot\text{cm}^{-3}$, especially in the cases of NaOH and KOH. Within experimental uncertainties, values of $K_A(m)$ of all three hydroxides are in good agreement with the former results. Second, the modified eqs 4 to 6 can be used to calculate ion association constants for LiOH, NaOH, and KOH over a wide range of temperatures and densities.

Finally, we plan to extend accurate conductance measurements of LiOH, NaOH, and KOH at temperatures up to 600°C and pressures up to 300 MPa after modification of the flow-through apparatus as discussed previously.⁵

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