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Determination of Ion Association in Dilute Aqueous Lithium Chloride and Lithium Hydroxide Solutions to 600 °C and 300 MPa by Electrical Conductance Measurements†

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The limiting molar conductances (Λ_0) and ion association constants of dilute aqueous lithium chloride and lithium hydroxide solutions (<0.01 mol·kg^{-1}) were determined by electrical conductance measurements at temperatures from 100 to 600 °C and pressures up to 300 MPa. The values of Λ_0(LiCl) and Λ_0(LiOH) obtained from with Shedlovsky (at densities ≥0.6 g·cm^{-3}) and Fuoss−Hsia−Fernandez-Prini (FHFP) equations (at densities <0.6 g·cm^{-3}) increase with increasing temperature up to 300 °C and decreasing density. Above 300 °C and densities between 0.8 and 0.5 g·cm^{-3} for $LiCl_{(aq)}$ and 0.8 to 0.6 g·cm^{-3} for $LiOH_{(aq)}$, Λ_0 is nearly temperature-independent but does increase linearly with decreasing density. The molal association constants, K_A(m) for both electrolytes were computed exclusively from the data ≥400 °C (at densities 0.8−0.3 for LiCl and 0.8−0.5 g·cm^{-3} for LiOH) by the Shedlovsky equation and can be represented as functions of temperature (Kelvin) and the logarithm of water density (ρ_w) as follows: $\log K_A(\mathrm{m})(\mathrm{LiCl}) = 0.724 - 8.980/(T/\mathrm{K}) - (12.796 - 5431.2/(T/\mathrm{K})) \log \rho_W/(\mathrm{g{\cdot}cm^{-3}})$ and $\log K_A(\mathrm{m})(\mathrm{LiOH}) = 0.856 + 135.60/(T/\mathrm{K}) - (11.998 - 4226.3/(T/\mathrm{K})) \log \rho_W/(\mathrm{g{\cdot}cm^{-3}})$. At corresponding conditions and within experimental error, the degree of ion association of $LiCl_{(aq)}$ is comparable with $NaCl_{(aq)}$ and $KCl_{(aq)}$, whereas ion association for $LiOH_{(aq)}$ is significantly stronger than for $NaOH_{(aq)}$ and $KOH_{(aq)}$. Moreover, the same values of K_A(m) were obtained for each electrolyte irrespective of the whether the Shedlovsky or FHFP equations were employed. This point is exemplified by a comparison of the K_A(m) value for LiCl obtained from the present study with those of a recent investigation that utilized an advanced design for moderately high temperature conductance measurements.

Introduction

LiCl and LiOH behave similarly to other electrolytes, which in dilute aqueous solutions tend to associate at high temperatures and low solution densities. Electrical conductance measurements of dilute aqueous LiCl and LiOH solutions at high temperatures and pressures provide a convenient, and perhaps unique, means of determining the extent of the association of $Li^+_{(aq)}$ ion with $Cl^-_{(aq)}$ and $OH^-_{(aq)}$ ions. Knowledge of the association constants of $LiCl_{(aq)}$ and $LiOH_{(aq)}$ is not only important in interpreting the thermodynamics of ion−ion and ion−water interactions but also provides 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, LiCl, and LiOH to the vapor phase. Such quantitative information is invaluable in evaluating chemical processes that occur in steam generators in power plants, nuclear waste disposal, and natural hydrothermal systems.

In past decades, the electrical conductivities of dilute aqueous LiCl have been studied as a function of concentration by Lukashov et al. (1975) at 305 to 373 °C at saturation vapor pressures. Other studies were conducted by Mangold and Franck (1969) to 1000 °C and 1200 MPa and Zimmerman et al. (1995) at 308 to 400 °C and 28 MPa. On the other hand, ion association of LiOH in dilute aqueous solutions was studied only at saturation vapor pressures by Darken and Meier (1942) at 25 °C, Corti et al. (1979) at 15−45 °C, and Wright et al. (1961) at 37.8−271.1 °C.

In two previous papers in this series (Ho and Palmer, 1996, 1997) ion association constants of dilute aqueous NaOH and KOH solutions were reported to 600 °C at pressures up to 300 MPa by electrical conductance measurements. In the present study, ion association constants of dilute aqueous LiCl and LiOH solutions (<0.01 mol·kg^{-1}) are presented at temperatures from 100 to 600 °C at pressures up to 300 MPa by the same method.

Experimental Section

1. Solutions. A concentrated stock solution of LiCl was prepared from pure crystalline material (ultrapure, Alfa) and conductivity water. The dilute solutions (concentration ranging from 0.001 to 0.01 mol·kg^{-1}) were obtained by diluting the stock LiCl solution with conductivity water on a mass basis. A ca. 0.955 mol·kg^{-1} LiOH solution prepared from $LiOH{\cdot}H_2O$ (Fluka, 99.5%(T)), and conductivity water was first mixed with barium hydroxide under argon to precipitate any carbonate present. After filtration (twice with 0.2-μm filters), the clear supernatant liquid, which still contained 110 ppm carbonate (elemental analysis) (standardized at 0.9597 mol·kg^{-1} LiOH), was diluted with conductivity water to achieve the desired concentrations. The concentrations of each stock solution were redeter-

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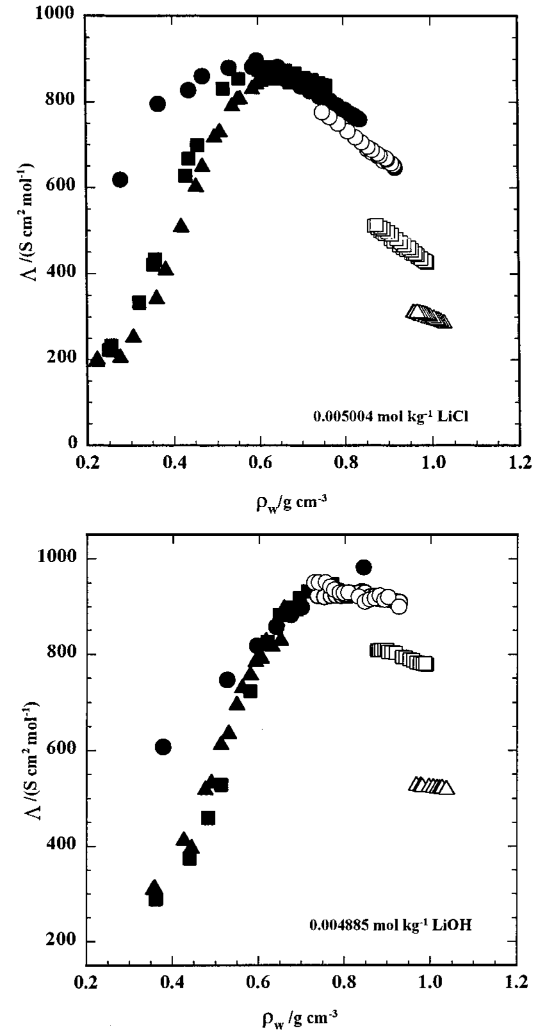

Figure 1. Molar conductance of (a) a 0.005 004 mol·kg^{-1} LiCl solution and (b) a 0.004 885 mol·kg^{-1} LiOH solution as a function of the density of water at constant temperature (100−600 °C). *t*/°C = 100 (△), 200 (□), 300 (○), 400 (●), 500 (■), 600 (▲).

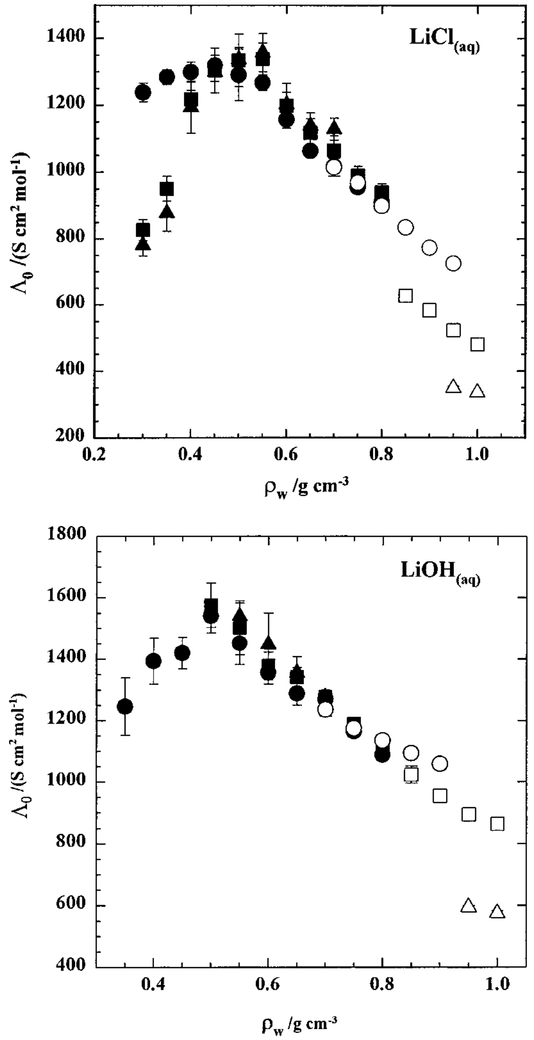

Figure 2. Limiting molar conductance of (a) LiCl and (b) LiOH solutions as a function of the density of water at constant temperature (100−600 °C). *t*/°C = 100 (△), 200 (□), 300 (○), 400 (●), 500 (■), 600 (▲).

mined by titration with standardized HCl solutions using weight burets. The isotopic ratio of the lithium in LiCl and LiOH is presumably equivalent to its natural abundance. The conductivity water used was obtained by bubbling argon through distilled, deionized water for at least 2 h and had a specific conductance of ca. 4 × 10^{-7} S·cm^{-1}.

2. Experimental Procedures. The experimental procedures and design of the conductance apparatus, including the configuration of the Al_2O_3/ZrO_2-insulated inner electrode of the Udimet cell, are similar to those described in detail in previous papers (Ho and Palmer, 1996, 1997; Ho et al., 1994).

The conductance measurements were carried out in the following manner. The clean conductance cell and the separator vessel (Ho et al., 1994) were first flushed with argon and rinsed three times with the sample solution. The cell was then filled with solution and sealed under argon, before heating at pressures adjusted to maintain an initial density >0.5 g·cm^{-3}. Subsequent measurement procedures were conducted in a similar fashion as reported earlier (Ho and Palmer, 1996, 1997; Ho et al., 1994).

The cell constants of the high-pressure cell ranged from 0.09 to 0.16 cm^{-1} and were determined by measuring the conductances of 0.001, 0.002, 0.005, and 0.01 demal (mol/(kg of solution)) KCl solutions at (25.0 ± 0.1) °C. The mean values of the cell constants were computed on the basis of the specific conductances of KCl solutions reported from 0 to 50 °C (Wu et al., 1987; Wu and Koch, 1991).

3. Calculation of Specific and Molar Conductance. The specific conductance, k_0, was corrected for the conductivity of water (Ho and Palmer, 1996), which has significant impact on the measured specific conductance of $LiCl_{(aq)}$ and $LiOH_{(aq)}$ below 0.005 and 0.002 mol·kg^{-1}, respectively. For example, at a concentration of 0.001 mol·kg^{-1} and temperatures from 300 to 400 °C, the specific conductance of water accounts for about 3% and 2% of the k_0 values of $LiCl_{(aq)}$ and $LiOH_{(aq)}$, respectively. k_0 increases with increasing temperature, reaching a maximum between 300 and 400 °C and increases initially with pressure, becoming independent at high pressures.

The molar conductances (Λ) of $LiCl_{(aq)}$ and $LiOH_{(aq)}$ were calculated by least-squares analysis at each experimental condition from the equation:

$$\Lambda = \{1000 + mM\}k_0/m\rho_w \qquad (1)$$

where m is the molality of LiCl or LiOH, M is the molecular weight of these solutes, and ρ_w is the density of water. The densities of the dilute solutions were assumed to be the same as for pure water as obtained from Hill (1990). The differences between the densities of the dilute solutions and

Table 1. Molar Conductance (Λ/(S·cm^2·mol^{-1})) of Aqueous LiCl Solutions

	t/°C							*t*/°C				
ρ/g·cm^{-3}	100	200	300	400	500	600	ρ/g·cm^{-3}	200	300	400	500	600
0.000 805/(mol·kg^{-1})												
1.00	312	459					0.60			1083	1179	1120
0.95	326	507	704				0.55			1120	1118	1124
0.90		565	727				0.50			1150	1090	1069
0.85		604	800				0.45			1120	1025	959
0.80			856	914	936		0.40			1080	877	731
0.75			909	945	979		0.35			997	700	556
0.70			958	960	1069	1070	0.30			910	532	455
0.65				984	1120	1089						
0.002 541/(mol·kg^{-1})												
1.00	281	440					0.60			949	905	941
0.95	284	470	631				0.55			964	900	921
0.90		503	692				0.50			910	846	843
0.85		546	714				0.45			937	779	724
0.80			758	792	821		0.40			902	676	569
0.75			813	846	853		0.35			841	554	419
0.70			836	890	870	910	0.30			770	415	330
0.65				941	885	930						
0.005 004/(mol·kg^{-1})												
1.00	252	425					0.60			880	871	851
0.95	258	451	590				0.55			892	840	796
0.90		476	657				0.50			881	781	707
0.85		516	679				0.45			840	694	593
0.80			737	782	797		0.40			796	570	455
0.75			778	812	826		0.35			703	455	318
0.70			821	840	863	870	0.30			630	318	262
0.65				872	880	857						
0.007 553/(mol·kg^{-1})												
1.00	235	396					0.60			839	836	826
0.95	239	437	572				0.55			842	792	765
0.90		464	610				0.50			832	716	635
0.85		504	638				0.45			776	574	509
0.80			667	772	794		0.40			726	483	370
0.75			697	780	811		0.35			628	349	259
0.70			733	790	835	830	0.30			544	275	204
0.65				816	847	847						
0.009 973/(mol·kg^{-1})												
1.00							0.60			797	803	758
0.95			547				0.55			790	757	688
0.90			580				0.50			743	678	542
0.85			612				0.45			694	528	432
0.80			646	759	771		0.40			630	444	315
0.75			678	765	789		0.35			548	311	228
0.70			709	767	811	754	0.30			460	220	180
0.65				792	819	785						

water are less than 4% (Zimmerman et al., 1995), which is within the experimental uncertainties of this study. The estimated uncertainties of the specific conductances are about 3 to 5% and 6 to 10% at and below 300 °C, respectively, whereas at temperatures above 300 °C, the uncertainties increase from 1 to 12% as densities decrease from 0.75 to 0.4 g·cm^{-3}.

Results and Discussion

Due to the large amount of experimental data acquired in this study, only the Λ values at integral densities as shown in Table 1 (LiCl $_{(aq)}$) and Table 2 (LiOH$_{(aq)}$), as obtained from polynomial fits [$\Lambda = a_0 + a_1\rho_w + \cdots + a_n(\rho_w)^n$, $n = 2$ to 4]. At densities ≥ 0.45 g·cm^{-3}, the precision of the fit to the experimental data was usually better than 0.1%. Figure 1a,b presents examples of experimental Λ values at one concentration of LiCl$_{(aq)}$ (0.005 004 mol·kg^{-1}) and LiOH$_{(aq)}$ (0.004 885 mol·kg^{-1}) as a function of water density (ρ_w) at temperatures from 100 to 600 °C, respectively. Below 300 °C, Λ(LiCl) and Λ(LiOH) increase near linearly with increasing temperature and decreasing density. Above 300 °C, Λ(LiCl) and Λ(LiOH) increase linearly at first with decreasing density, reaching a maximum from 0.5 to 0.75 g·cm^{-3} as the concentration increases from 0.001 to 0.01 mol·kg^{-1}. The increases in Λ(LiCl) and Λ(LiOH) at temperatures below 300 °C, and above 300 °C for densities >0.6 g·cm^{-3}, are due principally to the increase in ionic mobility caused by the decrease in viscosity (η) and dielectric constant (ϵ) of water. Above 300 °C at densities <0.6 g·cm^{-3}, the decrease in Λ(LiCl) and Λ(LiOH) with decreasing density reflects the onset of ion association plus a rapid decrease of the excess ionic conductance of the OH$^-_{(aq)}$ ions in LiOH$_{(aq)}$. In the case of LiCl$_{(aq)}$ the ionic conductances, λ(Li$^+$) and λ(Cl$^-$), arise mainly from the hydrodynamic ionic mobilities of the ions. However, for LiOH solutions, in addition to the intrinsic hydrodynamic ionic mobilities of Li$^+_{(aq)}$ and OH$^-_{(aq)}$ ions, excess ionic conductances of OH$^-_{(aq)}$ ions [λ^E(OH$^-$)] is obtained through hydrogen transfer along the interlinked hydrogen-bonded network connecting the bulk water molecules (Ho and Palmer, 1996, 1997). Hydrodynamic mobility is a function of temperature, pressure, dielectric constant, and viscosity of the solvent, whereas the excess ionic mobility of the OH$^-_{(aq)}$ ion varies with temperature, pressure, and concentration (Eigen and de Maeyer, 1958; Tödheide, 1972; Lengyel and Conway, 1983; Erde-Grúz and Lengyel, 1977;

Table 2. Molar Conductance (Λ/(S·cm^2·mol^{-1})) of Aqueous LiOH Solutions

	t/°C							t/°C					
ρ/g·cm^{-3}	100	200	300	400	500	600	ρ/g·cm^{-3}	100	200	300	400	500	600
0.001 011/(mol·kg^{-1})													
1.00	545	830					0.80			1047			
0.95	565	879					0.75			1097			
0.90		930	985				0.70			1140			
0.85		981	1015										
0.001 002/(mol·kg^{-1})													
1.00	547	845					0.60				1156	1185	1188
0.95	570	879					0.55				1142	1120	1090
0.90		935	990				0.50				1124	1078	1032
0.85		995	1020				0.45				1028	987	938
0.80			1055	1040	1040		0.40				977	929	815
0.75			1102	1084	1120		0.35				898	815	799
0.70			1146	1160	1166	1168	0.30				856	815	760
0.65				1184	1180	1200							
0.001 460/(mol·kg^{-1})													
0.80				1006	993		0.50				1047	982	930
0.75				1037	1063		0.45				983	843	819
0.70				1068	1088	1100	0.40				908	835	768
0.65				1069	1078	1120	0.35				830	733	702
0.60				1076	1059	1043	0.30				800	713	696
0.55				1065	1031	1010							
0.001 963/(mol·kg^{-1})													
0.80				974	981		0.50				982	926	851
0.75				1007	1012		0.45				913	772	757
0.70				1029	1024	1073	0.40				809	720	652
0.65				1027	1035	1078	0.35				772	654	597
0.60				1033	995	994	0.30				770	604	601
0.55				1019	949	947							
0.002 453/(mol·kg^{-1})													
0.80				952	963		0.50				952	852	776
0.75				991	984		0.45				873	751	674
0.70				998	1018	1028	0.40				797	686	596
0.65				974	1007	1011	0.35				697	602	526
0.60				977	975	976	0.30				662	569	505
0.55				959	897	896							
0.003 137/(mol·kg^{-1})													
1.00	537	798					0.60				919	928	909
0.95	540	805					0.55				874	827	820
0.90		827	962				0.50				856	780	703
0.85		857	971				0.45				803	668	595
0.80			977	943	939		0.40				719	609	528
0.75			984	952	956		0.35				670	535	439
0.70			989	972	984	980	0.30				631	407	366
0.65				956	981	947							
0.004 885/(mol·kg^{-1})													
1.00	521	778					0.70			957	911	924	927
0.95	529	778								940[a]			
0.90		815	926				0.65				897	864	853
			916[a]				0.60				845	823	792
0.85		839	930				0.55				845	772	708
			923[a]				0.50				769	669	595
0.80			930	876	904		0.45				697	524	457
			924[a]				0.40				670	465	359
0.75			938	908	913		0.35				636	394	319
			923[a]				0.30				474	349	295
0.007 568/(mol·kg^{-1})													
1.00	490	757					0.60				765	766	760
0.95	493	759					0.55				687	634	621
0.90		808	849				0.50				652	594	495
0.85		824	852				0.45				591	425	343
0.80			856	839	830		0.40				546	331	276
0.75			871	836	835		0.35				479	255	218
0.70			878	824	878	835	0.30				343	233	186
0.65				826	806	813							
0.009 885/(mol·kg^{-1})													
1.00	466	738					0.60				734	718	635
0.95	480	743					0.55				638	587	555
0.90		773	818				0.50				617	499	465
0.85		775	825				0.45				552	412	317
0.80			835	823	811		0.40				493	297	233
0.75			846	815	809		0.35				431	211	198
0.70			841	770	778	805	0.30				240	195	108
0.65				785	742	764							

[a] 0.004 905 mol·kg^{-1}.

Table 3. Limiting Molar Conductance (Λ_0/(S·cm^2·mol^{-1})) of Aqueous LiCl Solutions[a]

	t/°C					
ρ/g·cm^{-3}	100	200	300	400	500	600
1.00	335 ± 3	480 ± 5				
0.95	349 ± 5	523 ± 5	725 ± 12			
0.90		583 ± 13	773 ± 8			
0.85		626 ± 11	834 ± 11			
0.80			899 ± 18	910 ± 28	939 ± 26	
0.75			968 ± 18	955 ± 16	990 ± 27	
0.70			1014 ± 37	1017 ± 5	1064 ± 44	1128 ± 33
0.65				1063 ± 10	1117 ± 60	1138 ± 21
0.60				1157 ± 17	1198 ± 67	1202 ± 36
0.55				1267 ± 23	1338 ± 48	1357 ± 42
				(1222 ± 21)	(1197 ± 48)	(1286 ± 43)
0.50				1290 ± 77	1334 ± 79	1337 ± 35
				(1246 ± 63)	(1339 ± 81)	(1453 ± 90)
0.45				1319 ± 30	1304 ± 67	1299 ± 28
				(1331 ± 37)	(1410 ± 109)	(1568 ± 182)
0.40				1299 ± 30	1217 ± 27	1193 ± 78
				(1372 ± 71)	(1324 ± 76)	(1623 ± 262)
0.35				1284 ± 22	950 ± 37	877 ±38
				(1437 ± 115)	(1409 ± 441)	(1445 ± 447)
0.30				1238 ± 28	826 ± 32	781 ± 33
				(1555 ± 289)	(1513 ± 755)	(1357 ± 604)

[a] At $\rho < 0.6$ values in parentheses are from eq 2.

Lown and Thirsk, 1971; Eberz and Franck, 1995), reaching a maximum with increasing temperature and then decreasing due to the breakdown of hydrogen-bonding networks. Consequently, at constant temperature in dilute solutions, $\lambda^E(OH^-)$ values increase with increasing pressure due to the enhancement of the structure of water. Moreover, at constant temperature and pressure, $\lambda^E(OH^-)$ increases initially with increasing concentration, only to decrease at higher concentrations as the hydrogen-bonded network is destroyed.

Limiting Molar Conductance and Association Constant. The values of molar conductance at infinite dilution (Λ_0) and the association constants of $LiCl_{(aq)}$ and $LiOH_{(aq)}$ on the molarity scale (K_A(M)) were calculated primarily by the Shedlovsky equation (eq 2), which is a combination of the Onsager equation (eq 3) and the mass action law equation (eq 4) with the mean ionic activity coefficient being estimated according to eq 5. However, as ion association becomes more significant the corresponding Λ values become very concentration dependent and consequently the Λ_0 values of free ions obtained by the Shedlovsky equation have greater uncertainty. Hence, the values of Λ_0 and K_A(M) at temperatures ≥ 400 °C and $\rho_w < 0.6$ g·cm^{-3} were also computed by the Fuoss, Hsia, Fernandez-Prini equation (FHFP, eq 6) along with the mass action law equation by setting the closest approach distance of ions (*a*-parameter) equal to the Bjerrum distance (Fuoss and Hsia, 1967; Fernández-Prini, 1973; Justice, 1983). In eqs 2−6, *c* is the molar concentration

$$1/\Lambda F(z) = 1/\Lambda_0 + c\Lambda F(z) f_\pm^{\,2} K_A(M)/\Lambda_0^{\,2} \qquad (2)$$

$$\Lambda = \theta[\Lambda_0 - (\Lambda/\Lambda_0) S (c\theta)^{1/2}] \qquad (3)$$

$$K_A(M) = (1 - \theta)/\theta^2 c f_\pm^{\,2} \qquad (4)$$

$$\ln f_\pm = -\kappa q \theta^{1/2}/(1 + \kappa a \theta^{1/2}) \qquad (5)$$

$$\Lambda = \Lambda_0 - S(c\theta)^{1/2} + E(c\theta)\ln(c\theta) + J_1 c\theta + J_2 (c\theta)^{3/2} - K_A(M)\Lambda f_\pm^{\,2}(c\theta) \qquad (6)$$

(mol·dm^{-3}); *F*(*z*) is a function of *c*, Λ_0, and the limiting Onsager slope; θ is the degree of dissociation so that $c\theta$ is the concentration of the free ions; $f_\pm$ is the mean ionic molar activity coefficient of the constituent ions (based on the Debye−Hückel law in eq 5); κ is the reciprocal radius of the ionic atmosphere; *q* is the Bjerrum distance; *a* is the closest approach distance of the ions; and the constants *S* (the theoretical Debye−Hückel limiting slope) and *E* are functions of Λ_0, temperature, ϵ (dielectric constant), and η (viscosity), whereas J_1 and J_2 are functions of the *a*-parameter. The values of η and ϵ used in this study were obtained from Dudziak and Franck (1966), Quist and Marshall (1965), and Uematsu and Franck (1980) (for 100 to 300 MPa), and from the NBS/NRC Steam Tables (Haar et al., 1984) (for 10 to 100 MPa).

Tables 3 and 4 present the least-squares fit values of Λ_0(LiCl) and Λ_0(LiOH) at integral temperatures and densities according to eq 2 at 100 to 600 °C, for $\rho_w \geq 0.6$ g·cm^{-3} and eq 6 at temperatures ≥ 400 °C and $\rho_w < 0.6$ g·cm^{-3}. The propagated uncertainties in Λ_0 presented in Tables 3 and 4 were derived from standard deviations in the fitting of the conductance data by eqs 2 and 6, and uncertainties in conductance, temperature, and pressure readings. The uncertainty in conductance is the most significant source of the overall uncertainty, particularly at low densities.

Figure 2a,b shows the values of Λ_0(LiCl) and Λ_0(LiOH) (≤300 °C and ≥400 °C, $\rho_w > 0.6$ g·cm^{-3} obtained from eq 2; $\rho_w < 0.6$ g·cm^{-3} from eq 6, respectively) as a function of ρ_w. At constant density, Λ_0(LiCl) and Λ_0(LiOH) increase with increasing temperature to 300 °C and increase almost linearly with decreasing density. Above 300 °C, Λ_0(LiCl) and Λ_0(LiOH) are virtually independent of temperature but increase linearly with decreasing density between 0.5 and 0.8 g·cm^{-3} for the $LiCl_{(aq)}$ and 0.6 to 0.8 g·cm^{-3} for the $LiOH_{(aq)}$.

Tables 5a and 5b give the logarithms of the molar ion association constants, K_A(M), for $LiCl_{(aq)}$ and $LiOH_{(aq)}$, respectively, at integral temperatures 400−600 °C calculated from eq 2 at densities 0.8 to 0.3 g·cm^{-3} and eq 6 at densities <0.6 g·cm^{-3} (given in parentheses). The uncertainties in log K_A(M) given in Tables 5a and 5b were accumulated from the effects of temperature, pressure, molar and limiting molar conductances, and the standard deviations incurred in the fits of the experimental data. The uncertainty in conductance is again the most significant source of the total uncertainty. Within experimental uncertainty, K_A(M) values for both $LiCl_{(aq)}$ and $LiOH_{(aq)}$

Table 4. Limiting Molar Conductance (Λ_0/(S·cm^2·mol^{-1}) of Aqueous LiOH Solutions at High Temperature[a]

	t/°C					
ρ/g·cm^{-3}	100	200	300	400	500	600
1.00	574 ± 8	863 ± 10				
0.95	594 ± 5	894 ± 14				
0.90		954 ± 22	1058 ± 18			
0.85		1023 ± 28	1093 ± 15			
0.80			1134 ± 11	1088 ± 16	1109 ±16	
0.75			1174 ± 16	1164 ± 17	1189 ± 21	
0.70			1235 ± 21	1270 ± 28	1276 ± 33	1276 ± 24
0.65				1287 ± 37	1344 ± 30	1355 ± 52
0.60				1355 ± 36	1377 ± 45	1447 ± 102
0.55				1450 ± 69	1501 ± 88	1539 ± 43
				(1576 ± 70)	(1587 ± 82)	(1664 ± 48)
0.50				1539 ± 56	1574 ± 72	
				(1621 ± 48)	(1905 ± 176)	
0.45				1418± 51	1664 ± 335	
				(1622 ± 77)	(2915 ± 1000)	
0.40				1392 ± 75		
				(1636 ± 134)		
0.35				1245 ± 94		
				(1768 ± 302)		

[a] At ρ < 0.6, values in parentheses are from eq 2.

Table 5. Logarithm of Molar Association Constants of Aqueous LiCl and LiOH Solutions[a]

	t/°C		
ρ/g·cm^{-3}	400	500	600
	(a) LiCl Solutions		
0.80	1.34 ± 0.32	1.37 ± 0.25	
0.75	1.49 ± 0.25	1.57 ± 0.31	
0.70	1.54 ± 0.16	1.76 ± 0.26	1.9 ±0.26
0.65	1.83 ± 0.08	1.93 ± 0.17	2.18 ± 0.04
0.60	2.0 ± 0.07	2.23 ± 0.1	2.35 ± 0.04
0.55	2.2 ± 0.08	2.47 ± 0.2	2.59 ± 0.33
	(2.22 ± 0.21)	(2.66 ± 0.27)	(2.67 ± 0.40)
0.50	2.38 ± 0.08	2.65 ±0.19	3.03 ± 0.07
	(2.47 ± 0.22)	(2.78 ± 0.22)	(2.86 ± 0.09)
0.45	2.61 ± 0.16	3.03 ± 0.2	3.34 ± 0.19
	(3.04 ± 0.37)	(3.12 ± 0.44)	(3.03 ± 0.25)
0.40	3.01 ± 0.08	3.48 ± 0.2	3.74 ± 0.27
	(2.95 ± 0.13)	(3.21 ± 0.56)	(3.05 ± 0.42)
0.35	3.33 ± 0.21	3.86 ± 0.38	4.19 ± 0.36
	(3.09 ± 0.32)	(3.21 ± 0.50)	(3.54 ± 0.62)
0.30	3.72 ± 0.23	4.36 ± 0.44	4.61 ± 0.48
	(3.32 ± 0.33)	(3.66 ± 0.54)	(3.76 ± 0.55)
	(b) LiOH Solutions		
0.80	1.73 ± 0.12	1.75 ± 0.14	
0.75	1.94 ± 0.12	2.01 ± 0.10	
0.70	1.98 ± 0.14	2.22 ± 0.10	2.28 ± 0.13
0.65	2.32 ± 0.11	2.44 ± 0.10	2.50 ± 0.10
0.60	2.54 ± 0.10	2.65 ± 0.13	2.82 ± 0.09
0.55	2.77 ± 0.16	3.07 ± 0.15	3.20 ± 0.16
	(2.74 ± 0.89)	(2.96 ± 0.63)	(3.00 ± 0.45)
0.50	3.11 ± 0.12	3.45 ± 0.15	3.65 ± 0.20
	(3.02 ± 0.44)	(3.16 ± 0.45)	(3.63 ± 0.62)
0.45	3.30 ± 0.07		
	(3.05 ± 0.46)		
0.40	3.53 ± 0.14		
	(3.22 ± 0.61)		

[a] At ρ < 0.6, values in parentheses are from eq 6.

Table 6. Logarithm of Molal Association Constants of Aqueous LiCl and LiOH Solutions

	t/°C				*t*/°C		
ρ/g·cm^{-3}	400	500	600	ρ/g·cm^{-3}	400	500	600
		(a) LiCl Solutions					
0.80	1.18	1.27		0.50	2.13	2.35	2.69
0.75	1.31	1.45		0.45	2.35	2.68	2.99
0.70	1.45	1.59	1.75	0.40	2.58	3.08	3.34
0.65	1.60	1.74	1.99	0.35	2.86	3.40	3.73
0.60	1.76	2.01	2.13	0.30	3.17	3.84	4.09
0.55	1.94	2.21	2.39				
		(b) LiOH Solutions					
0.80	1.63	1.65		0.55	2.51	2.81	2.94
0.75	1.82	1.89		0.50	2.81	3.15	
0.70	1.83	2.07	2.13	0.45	2.95		
0.65	2.13	2.25	2.31	0.40	3.14		
0.60	2.32	2.43	2.6				

systems calculated by either the Shedlovsky, eq 2, or the FHFP equations, eq 6, are in close agreement.

Tables 6a and 6b give the logarithm for the molal ion association constants, K_A(m), for $LiCl_{(aq)}$ and $LiOH_{(aq)}$, respectively, converted from K_A(M) in Tables 5a and 5b from eq 2 and the density of pure water. Equations 8 and 9 present the weighted-least-squares fits of K_A(m) data derived in this study exclusively at temperatures ≥400 °C for $LiCl_{(aq)}$ and $LiOH_{(aq)}$ as functions of temperature (kelvin) and density (with data in the range of 0.8−0.3 g·cm^{-3} for LiCl and 0.8−0.5 g·cm^{-3} for LiOH, respectively) based on the best weighted-least-squares fits at temperatures ≥400 °C.

$$\log K_A(\mathrm{m})(\mathrm{LiCl}) = 0.724 - 8.980/(T/\mathrm{K}) - (12.796 - 5431.2/(T/\mathrm{K}))\log \rho_w/(\mathrm{g{\cdot}cm^{-3}}) \quad (8)$$

$$\log K_A(\mathrm{m})(\mathrm{LiOH}) = 0.856 + 135.60/(T/\mathrm{K}) - (11.998 - 4226.4/(T/\mathrm{K}))\log \rho_w/(\mathrm{g{\cdot}cm^{-3}}) \quad (9)$$

Parts a and b of Figure 3 present log K_A(m) values for $LiCl_{(aq)}$ and $LiOH_{(aq)}$, respectively, as functions of temperature (kelvin), where the dotted lines were obtained from eqs 8 and 9. Ion-pair formation for $LiCl_{(aq)}$ and $LiOH_{(aq)}$ increases with increasing temperature and decreasing density of the solvent. The degree of ion association in dilute (<0.01 mol·kg^{-1}) LiCl solutions is similar in magnitude to those reported for NaCl and KCl solutions (Ho and Palmer, 1997; Ho et al., 1994). On the other hand, LiOH $_{(aq)}$ is substantially more associated than either $NaOH_{(aq)}$ or $KOH_{(aq)}$ at corresponding conditions (Ho and Palmer, 1996, 1997), as illustrated by the example at 500 °C in Figure 4a,b.

Figure 5a compares fitted values of log K_A(m)(LiCl) from eq 8 at temperatures 328.54 to 399.74 °C and 28 MPa with the values reported by Zimmerman et al. (1995) at these conditions. The log K_A(m) values of Lukashov et al. (1975) at 343, 365, and 373 °C and densities at 0.6, 0.5, and 0.4

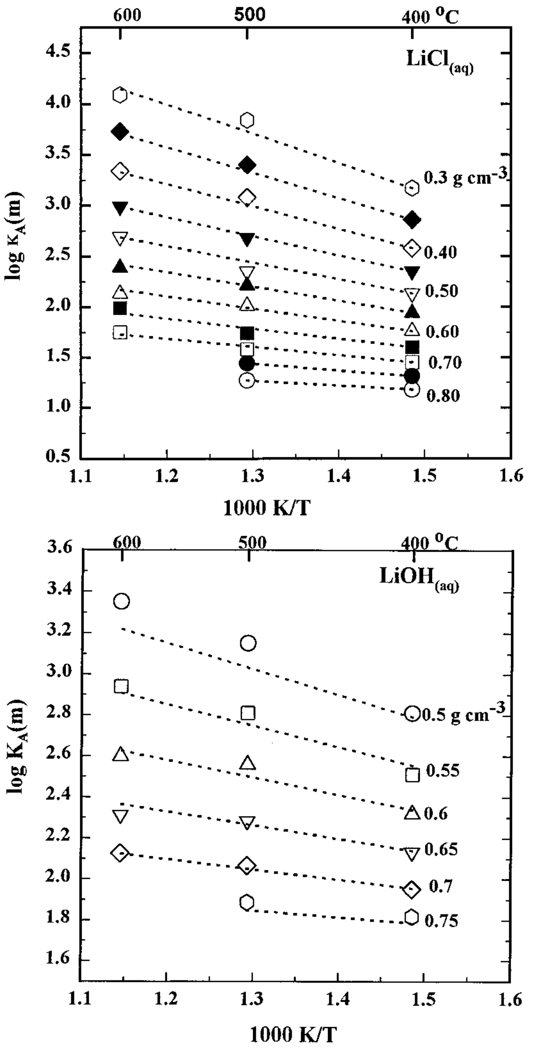

Figure 3. (a) Log K_A(m) for $LiCl_{(aq)}$ at 400−600 °C as a function of the reciprocal temperature (kelvin) at constant densities (dotted lines are from the model in eq 8). (b) Log K_A(m) for $LiOH_{(aq)}$ at 400−600 °C as a function of the reciprocal temperature (kelvin) at constant densities (dotted lines are from the model in eq 9).

g·cm^{-3} are also included in Figure 5a. It can be seen that log K_A(m)(LiCl) values of the present study are generally in good agreement with those of Zimmerman et al. (1995), except at lower densities and higher temperatures (i.e., 396.4 °C, ~ 0.32 g·cm^{-3} and 399.7 °C, ~0.26 g·cm^{-3}). This trend demonstrates the limitations of present apparatus at low densities, presumably due to poorer temperature control than is obtained in the improved cell configuration of Zimmerman et al. (1995). On the other hand, the K_A (m)(LiCl) values of Lukashov et al. (1975) are about 0.3−1.0 log unit higher than in either of the above studies. Figure 5b illustrates the temperature dependence of log K_A(m) values for $LiOH_{(aq)}$ from eq 9 at temperatures 50 to 271 °C at saturation vapor pressures, which are the conditions specified by Wright et al. (1961). The results from the present study are in good agreement with those of Wright et al. (1961) above 50 °C. However, the values of K_A from extrapolation of eq 9 may only be reliable down to 100 °C, so that these results cannot be compared with those from Corti et al. (1979) in the range 15 to 45 °C. On the other hand, the K_A(m)(LiOH) values reported at 150 to 250 °C by Corti and Svaro (1995) based on density measurements are 0.5 to 1.0 log units higher than either those of Wright et al. (1961) or the extrapolated values of this study.

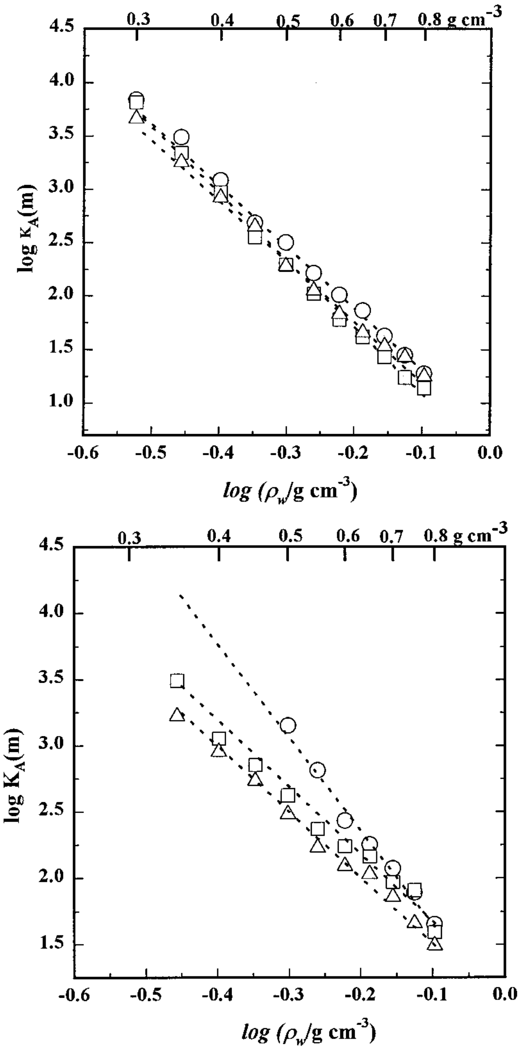

Figure 4. (a) Comparison of log K_A(m) values of $LiCl_{(aq)}$ (○), $NaCl_{(aq)}$ (□) (Ho et al. 1994), and $KCl_{(aq)}$ (△) (Ho and Palmer, 1997) as a function of log(ρ_w/g·cm^{-3}) at 500 °C. (b) Comparison of log K_A(m) values of $LiOH_{(aq)}$ (○), $NaOH_{(aq)}$ (□) (Ho and Palmer, 1996), and $KOH_{(aq)}$ (△) (Ho and Palmer, 1997) as a function of log(ρ_w/g·cm^{-3}) at 500 °C.

As discussed in a previous study (Ho and Palmer, 1997), ion association constants can be used to compute the pH values of chloride-containing salt solutions from the known equilibrium constants and charge and mass balances equations:

$$Li^+_{(aq)} + Cl^-_{(aq)} \rightleftarrows LiCl_{(aq)} \qquad K_A(LiCl) \qquad (10)$$

$$Li^+_{(aq)} + OH^-_{(aq)} \rightleftarrows LiOH_{(aq)} \qquad K_A(LiOH) \qquad (11)$$

$$H^+_{(aq)} + Cl^-_{(aq)} \rightleftarrows HCl_{(aq)} \qquad K_A(HCl) \qquad (12)$$

$$H_2O \rightleftarrows H^+_{(aq)} + OH^-_{(aq)} \qquad K_w \qquad (13)$$

$$H^+_{(aq)} + Li^+_{(aq)} \rightleftarrows OH^-_{(aq)} + Cl^-_{(aq)} \qquad (14)$$

$$\sum Li^+ = Li^+_{(aq)} + LiCl_{(aq)} + LiOH_{(aq)} \qquad (15)$$

$$\sum Cl^- = Cl^-_{(aq)} + LiCl_{(aq)} + HCl_{(aq)} \qquad (16)$$

Figure 6 presents pH values of a 0.01 mol·kg^{-1} LiCl solution at temperatures 300 to 600 °C and at densities

0.3, 0.4, 0.5, 0.6, and 0.75 g·cm^{-3} as a function of temperature (kelvin) using ion association constants of LiCl and LiOH from this study and HCl from Franck (1956) compared to the pH values of water (i.e., $^1/_2$pK_w) (Marshall and Franck, 1981), 0.01 mol·kg^{-1} NaCl and KCl. Above 400 °C and densities <0.75 g·cm^{-3}, the pH of $LiCl_{(aq)}$ is slightly more basic than water but lower than the pH values of $NaCl_{(aq)}$ and $KCl_{(aq)}$, because K_A(HCl) > K_A(LiOH) and K_A(LiOH) > K_A(NaOH) > K_A(KOH). At constant temperature the pH values of water and chloride salts increase with decreasing density and decrease with increasing temperature at constant density.

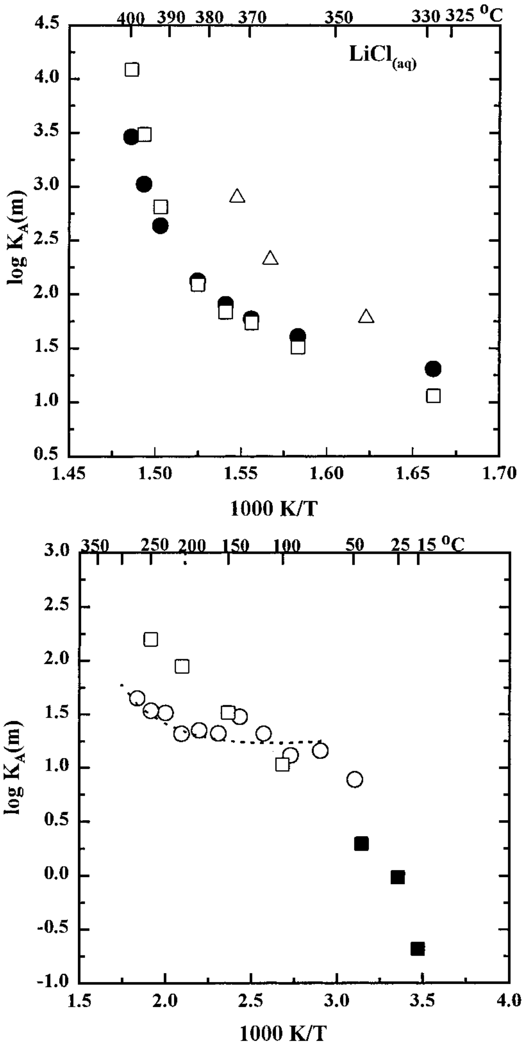

Figure 5. (a) Comparison of log K_A(m)(LiCl) values with those reported by Zimmerman et al. (1995) (□), the extrapolated values from eq 8 (●), and the data reported by Lukashov et al. (1975) (△) (28 MPa; 343 °C, 0.6 g·cm^{-3}; 365 °C, 0.5 g·cm^{-3}; 373 °C, 0.4 g·cm^{-3}). (b) Comparison of log K_A(m)(LiOH) values with those reported by Wright et al. (1961) (○), Corti et al. (1979) (■), Corti and Svaro (1995) (□), and the extrapolated values from eq 9 (···).

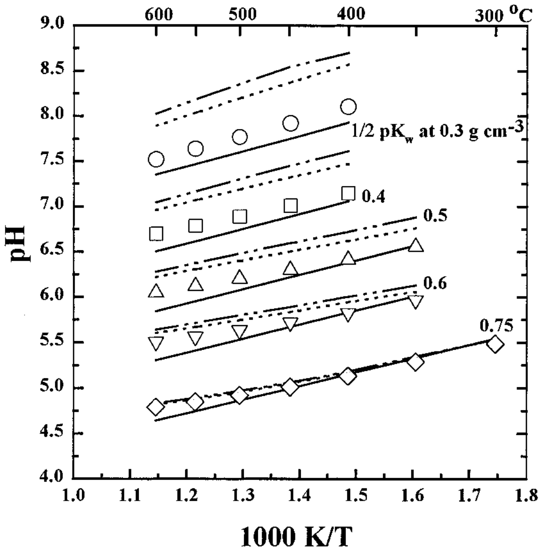

Figure 6. Comparison of the pH values for 0.01 mol·kg^{-1} LiCl (symbols), NaCl (— - -), and KCl (···) solutions with $^1/_2$pK_w (in solid line) (Marshall and Franck, 1981) at 300 to 600 °C and 0.3 to 0.75 g·cm^{-3}.

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