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Received for review January 24, 1978. Accepted June 26, 1978.

Conductance of Lithium Tetrafluoroborate Solutions in Tetrahydrofuran

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Conductivities are presented for 19 solutions of lithium tetrafluoroborate in tetrahydrofuran at 25 °C between 0.0015 and 3.2 mol kg^{-1} (0.0013–2.6 mol dm^{-3}). Solution conductance is unaffected by small amounts of water. Equivalent conductances are quite low and display a distinct minimum at about 0.03 mol kg^{-1}.

In connection with the study of an experimental battery, we needed to select as electrolyte a suitably conducting solution of $LiBF_4$ in tetrahydrofuran (THF). However, a literature search failed to reveal any account of conductance vs. concentration for this couple. Thus, we undertook the following short study.

Experimental Section

Tetrahydrofuran was secured from Fisher Scientific Co. "Cat. No. T-397, Water Content 0.01%". One batch of this THF was used as received; a second batch was dried over pellets of Linde molecular sieve, Type X. Lithium fluoroborate from two sources was used: Cat. No. LX342 from Matheson Coleman and Bell and lot no. 101-1 from Foote Mineral Co. Both of the chemicals were nominally 98% pure so a factor of 0.98 was used in converting mass of salt to mass of $LiBF_4$. The Matheson Coleman Bell salt was used as received whereas the Foote material was first dried to constant weight over magnesium perchlorate.

The conductivity cell vessel was a 140 × 41 mm Pyrex test tube closed by a silicone rubber stopper. Through holes in this stopper were pushed a mercury thermometer and the conductivity cell, a Beckman, dip-type cell, Model CEL-KO1. The Pt electrodes of this cell were platinized, and its cell constant was determined as 0.0985 cm^{-1}. A Teflon-covered stirring bar provided magnetic stirring. Solution resistance was measured with a General Radio, Type 1650-A, impedance bridge at 1000 Hz. Capacitative balance was provided to ensure sharp null points at all measured resistances. This bridge measures resistance with an accuracy of ±1.0%.

Table I. Conductance of $LiBF_4$ Solutions in THF at 25.0 °C

		Conductance	
molal concn m, mol kg^{-1}	molar concn C, mol dm^{-3}	specific Ω^{-1} cm^{-1} × 10^3 κ	equivalent, Ω^{-1} cm^2 $equiv^{-1}$ λ
	Dried Solutions		
0.00153	0.00134	0.000370	0.275
0.00353	0.00310	0.000604	0.195
0.00995	0.00874	0.00122	0.140
0.0310	0.0272	0.00353	0.130
0.0916	0.0803	0.0157	0.195
0.345	0.301	0.198	0.659
	Undried Solutions		
0.00155	0.00136	0.000390	0.287
0.344	0.300	0.200	0.667
0.460	0.400	0.353	0.883
0.574	0.497	0.544	1.095
0.689	0.595	0.770	1.29
0.809	0.696	1.027	1.48
1.050	0.898	1.57	1.74
1.292	1.097	2.16	1.96
1.534	1.294	2.67	2.06
1.895	1.583	3.27	2.07
2.257	1.867	3.69	1.98
2.736	2.234	3.97	1.78
3.218	2.595	3.89	1.50

Solution preparation (by weight) and bridge measurements were done in a dry room at 2–3% relative humidity. We measured resistance over a range of about 5 °C around ambient temperature. This enabled us to correct figures to 25 °C for tabulation. The procedure was to begin with a weighed amount of THF (about 60 cm^3) in the test tube. A weighed amount of salt was added and stirred to effect dissolution and the resistance measured (while adding salt the dip cell was inserted in a dummy test tube containing a little anhydrous calcium sulfate to minimize evaporation and humidification of solution clinging to it). This

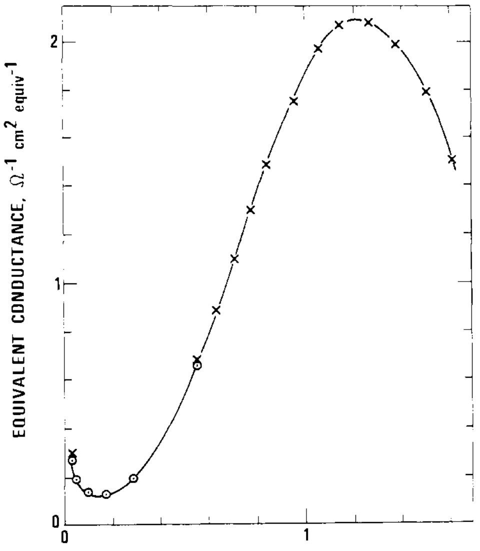

Figure 1. Equivalent conductance of $LiBF_4$-THF solutions at 25 °C: O, dried solutions; ×, undried solutions.

procedure was then successively repeated adding increments of salt to cover the concentration range.

Results and discussion

In arriving at the volume concentrations, *C*, listed in Table I, use was made of the fact that the ratio m/C changes quite slowly and linearly with concentration. Thus we measured solution densities of 1.138, 1.147, and 1.240 g cm^{-3} at 25 °C and m = 0, 0.344, and 3.218, respectively, enabling us to calculate C and m/C at these three values. Then from the linear plot of m vs. m/C the other m/C and hence C values were interpolated. We estimate a maximum error of ±1% in C due to this interpolation. The total uncertainties in m, c, κ, and λ are estimated as ±1, 2, 2, and 4%, respectively. Sharply rising dissolution times at the higher concentrations indicated that the solubility of $LiBF_4$ in THF is within a few tenths molar of 2.6 mol dm^{-3}. The resistivity of the pure solvent THF (both dried and undried) was too great to be measured with our bridge which means that its conductivity was below 9×10^{-9} Ω^{-1} cm^{-1}. Other workers (*1*) have reported a value of 0.4×10^{-9} for pure THF.

In Figure 1 the smooth merging of the curves for dried and undried solutions shows that, within experimental error, water traces do not affect conductivity. This is true even in the most dilute solution where the undried THF's nominal water content of 0.01% or 0.006 mol dm^{-3} is four times that of the salt. Thus there is no large, specific effect of water on the conductance (as opposed to a small, general effect operating via changes in solution fluidity). This accords with data on alkali metal salts in a variety of solvents reviewed by Fernandez-Prini (*2*). The low values of λ, 0.2–2.0, reported here point to extensive ion association. Minima in λ at low concentration such as appears in Figure 1 have commonly been observed (*2*) in solvents of dielectric constant below 10–15 (THF, 7.39 at 25 °C) and attributed to the conversion of nonconducting ion pairs to conductive ion triplets (*3*). The maximum in λ at high concentrations may be associated with the sharply increasing solution viscosity that we qualitatively observed in this region. Such maxima are frequently observed in aprotic solvents and have also been described as due to "activity effects" (*4*). The highest conductance, 4×10^{-3} Ω^{-1} cm^{-1}, in our data at about 2.2 mol dm^{-3} is quite respectable and must qualify a statement (*5*) to the effect that polarography in THF is difficult due to poorly conducting solutions. In fact, conductivity as high as 11×10^{-3} Ω^{-1} cm^{-1} has been attained in THF-propylene carbonate mixtures used as battery electrolytes (*6*).

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Received for review February 7, 1978. Accepted June 5, 1978. This work was supported by the Independent Research Program of the U.S. Naval Surface Weapons Center, White Oak, Md.

Activity Coefficients of Hydrochloric Acid in $HCl–KCl–H_2O$ Mixtures at Ionic Strengths up to 1.5 mol kg^{-1} and Temperatures from 5 to 45 °C

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Electromotive-force measurements of the cell $Pt;H_2(g,\ 1\ atm)|HCl(m_A),KCl(m_B)|AgCl;Ag$ have been made at five ionic strengths from 0.1 to 1.5 mol kg^{-1} and over the temperature range 5–45 °C. The results are interpreted in terms of Harned's rule for the activity coefficient of hydrochloric acid. Up to 1.5 mol kg^{-1}, log γ_{HCl} varies linearly with solution composition at constant ionic strength. It is also demonstrated that the partial molal enthalpy of $HCl–KCl–H_2O$ solutions follows an expression analogous to Harned's rule up to ionic strengths at least as high as 1.5 mol kg^{-1}.

Introduction

We have recently reported (*10*) measurements of the activity coefficient of hydrochloric acid in HCl/NaCl mixtures at several ionic strengths from 0.1000 to 0.8720 mol kg^{-1} and over the temperature range 5–45 °C. These measurements focused on our interest in developing a scale of pH for seawater systems (*3*), and the temperature range and choice of ionic strengths reflected this interest. In a similar manner we now report measurements of γ_{HCl} in HCl/KCl mixtures over the same temperature range for values of the ionic strength from 0.1 to 1.5 mol kg^{-1}. The present work is a more comprehensive study

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