

Electrical Conductivity of Electrolytes Found In Natural Waters from (5 to 90) °C

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The electrical conductivities of 34 electrolyte solutions found in natural waters ranging from (10^{-4} to 1) $\text{mol}\cdot\text{kg}^{-1}$ in concentration and from (5 to 90) °C have been determined. High-quality electrical conductivity data for numerous electrolytes exist in the scientific literature, but the data do not span the concentration or temperature ranges of many electrolytes in natural waters. Methods for calculating the electrical conductivities of natural waters have incorporated these data from the literature, and as a result these methods cannot be used to reliably calculate the electrical conductivity over a large enough range of temperature and concentration. For the single-electrolyte solutions, empirical equations were developed that relate electrical conductivity to temperature and molality. For the 942 molar conductivity determinations for single electrolytes from this study, the mean relative difference between the calculated and measured values was 0.1 %. The calculated molar conductivity was compared to literature data, and the mean relative difference for 1978 measurements was 0.2 %. These data provide an improved basis for calculating electrical conductivity for most natural waters.

Introduction

Electrical conductivity is a water-quality property often measured when environmental water samples are collected. It is a simple and highly accurate measurement and is used in many environmental and industrial applications. In solutions, the electrical conductivity is the sum of the conductivities of all the conducting constituents. Electrical conductivity measurements have been used to predict the salinity,^{1–3} ionic strength,^{4–7} major solute concentrations,^{8,9} and total dissolved solids concentrations^{10–13} of natural waters. Apart from relating electrical conductivity to these general chemical properties, more specific chemical interpretations of electrical conductivity measurements are typically lacking for natural waters.

Accurate measurements and calculations of electrical conductivities for natural waters will provide a greater understanding of the relative contributions of individual ions to the electrical conductivity. In addition, when coupled with charge balance, electrical conductivity can be used to identify erroneous chemical analyses.^{14–17} Several methods have been developed to calculate electrical conductivities of natural waters from their chemical compositions.^{14–20} However, the reliability of these electrical conductivity methods is limited by the lack of available electrical conductivity data for electrolytes found in natural waters. Numerous high-quality conductivity data for many electrolytes exist in the scientific literature, and conveniently, a large amount of these data have been compiled into a few books.^{21–24} However, for many electrolytes the electrical conductivity data do not span the concentration or temperature range necessary for reliably calculating the electrical conductivity of a wide range of natural waters. The lack of data has resulted in methods that can only accurately predict the electrical conductivities of waters that are either dilute or have a major-ion composition similar to that of seawater and temperatures near 25 °C. Reliable calculations of electrical conductivity for acidic waters, geothermal waters, or wastewaters are not possible using existing methods.

In this study, the electrical conductivities of 34 electrolytes found in natural waters at temperatures ranging from (5 to 90) °C were measured. Although for some electrolytes (e.g., NaCl and KCl) the data in the literature are highly accurate and span the necessary temperature and concentration ranges, measurements of these electrolytes were repeated to evaluate the uncertainty of the methods used here. Furthermore, unlike the existing data in the literature, all the data reported here were produced using the same equipment and techniques. In addition, measurements were made at the same temperatures, (5, 10, 25, 35, 45, 70, and 90) °C, for each electrolyte, which simplifies the interpretations and calculations of ionic conductivities.

Experimental Details

The goal of this study was to provide electrical conductivity data that would be useful for interpreting the electrical conductivities of natural waters. To ensure that the electrical conductivity data reported in this study encompass a large range of natural waters, a water quality database with nearly 1800 water samples including acid mine waters, geothermal waters, seawater, dilute mountain waters, and river water impacted by municipal wastewater was compiled, and the range of electrical conductivity, pH, temperature, and the maximum solute molality were determined (Table 1). The majority of the water quality data can be found in a series of reports on Yellowstone National Park,^{25–28} the Questa Baseline and Pre-Mining Ground Water Quality investigation,^{29–32} the Boulder Creek Watershed,³³ and the Leviathan Mine drainage basin.³⁴ Additional, unpublished water quality data generated by our laboratory for samples from Summitville Mine, CO, Upper Animas River, CO, and San Diego Bay, CA, are included in the database.

The electrical conductivity (κ) of a solution can be determined by using a commercially available conductivity meter and probe and the following equation

$$\kappa = K_{\text{cell}}G \quad (1)$$

Table 1. Ranges of Electrical Conductivity (κ), pH, and Temperature and the Maximum Solute Molality Found in a Wide Range of Natural Waters

field-measured properties	
$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	33 to 70 000
pH	1.02 to 12.4
$t/^\circ\text{C}$	0 to 93
maximum solute, $m/\text{mmol}\cdot\text{kg}^{-1}$	
Ca	18
Mg	52
Na	470
K	11
HCO_3	14
SO_4	570
Cl	500
F	2.9
Br	0.8
NO_3	4.5
SiO_2	13
NH_4	49
Al	35
Cu	3.5
Fe(II)	156
Fe(III)	104
Li	1.6
Mn	9.1
Sr	0.2
Zn	19

where the K_{cell} is the conductivity cell constant (cm^{-1}) and G is the conductance (S). The K_{cell} is the ratio of the distance between two plates (d) and their area (A). The electrical conductivity of an electrolyte solution depends on the type and concentration of the ions in solution and also the solution temperature. Hence, the sources of uncertainties are measuring G and temperature, determining K_{cell} , and preparing the electrolyte solutions.

Several different conductivity meters and cells were considered. Elaborate, custom-built conductivity cells have been used to measure the electrical conductance of electrolyte solutions.^{35,36} These devices have produced highly precise measurements, with uncertainties as low as 0.01 %. Most field electrical conductivity measurements are reliable to only three significant figures. Consequently, the five-figure accuracy that can be produced using custom-built conductivity cells is not warranted. The variation of electrical conductivity with the type of electrolyte, concentration, and temperature with an uncertainty that exceeds or is comparable to that obtained using field meters is of interest in this study. Therefore, a relatively simple procedure was used to measure the electrical conductivities of single electrolyte solutions over a range of temperatures from (5 to 90) $^\circ\text{C}$. The experimental apparatus consisted of a constant-temperature water bath, conductivity meter, digital thermometer, measurement vessel, and two conductivity cells to measure the conductances of electrolyte solutions.

Conductance measurements were made with a commercially available conductivity meter (YSI, Inc., model 3200). The meter makes ratio-metric resistance measurements by placing an unknown resistor and a known resistor in a series circuit with an alternating current voltage source. Because the current is constant across the circuit, the voltage across each resistor can be measured and the conductance of the unknown solution computed by an internal microprocessor. The optimal conductance range of the conductivity meter is (0.05 to 500) mS.

To estimate the uncertainty associated with the conductance (G) measurement, seven resistors with known conductances (1.000 μS to 1000 mS by decades, YSI, Inc., model 3166, National Institute of Standards and Technology (NIST) trace-

Table 2. Measured Conductance (G_m) and Relative Difference (δ) of Standard Resistors (G_s)

G_s/mS	G_m/mS	$\delta\cdot 100$
1000	999.8 ± 0.04	-0.02
100.0	100.0 ± 0.04	0.02
10.00	10.00 ± 0.004	0.02
1.000	0.9994 ± 0.00004	-0.06
0.1000	0.1000 ± 0.000004	-0.002
0.01000	0.01002 ± 0.00001	0.20
0.001000	0.001001 ± 0.000001	0.12

able) were each measured 6 times over the duration of the study. The results revealed that the conductance measurements were precise (< 0.1 % relative standard deviation) and accurate (< 0.2 % relative difference) over the entire range of conductance (Table 2). The relative difference (δ) was determined using the following equation

$$\delta = \frac{G_m - G_s}{G_s} \quad (2)$$

where G_m is the measured conductance of the conductance standard (G_s). The largest relative differences were observed for the 0.001 mS and 0.01 mS conductance standards (0.12 % and 0.20 %, respectively), which are below the optimal range of the conductivity meter. Except for conductance measurements of purified water, all conductance measurements were at least 0.05 mS. On the basis of the measurements of the standard resistors, the relative uncertainties in the conductance measurement were estimated to be less than 0.1 %.

Depending on the chemical composition, the electrical conductivity of an aqueous solution increases between (1 and 3) % per $^\circ\text{C}$ increase in temperature;³⁷ therefore, accurate temperature measurements are important. A digital thermometer (VWR International, LLC) with a resolution of 0.001 $^\circ\text{C}$ and an uncertainty of ± 0.01 $^\circ\text{C}$ between (0 and 100) $^\circ\text{C}$ was used for all temperature measurements. The thermometer conforms to the International Temperature Standard (ITS-90) and was calibrated by the manufacturer to standards provided by NIST. The 16 cm stainless steel temperature probe was positioned within 1 cm of the conductivity cells for all temperature measurements. To check the uncertainty of the thermometer, temperature readings were compared to those made with another digital thermometer (ERTCO-Eutechnics), which had been certified at eight temperatures from (-20 to 120) $^\circ\text{C}$ by the manufacturer. The temperature readings for the two digital thermometers were within 0.04 $^\circ\text{C}$ of each other for all temperatures tested. A refrigerating/heating water bath circulator (Thermo Scientific NESLAB, model RTE-7) was used to control the temperature of the electrolyte solutions. The temperature stability of the water bath, reported by the manufacturer, was ± 0.01 $^\circ\text{C}$. The water bath was set to the same temperature, (5, 10, 25, 35, 45, 70, or 90) $^\circ\text{C}$, and the electrolyte solution was allowed to thermally equilibrate with the water bath before its conductance was measured.

Two dip-style conductivity cells with cell constants of 0.1 cm^{-1} (YSI, Inc., model 3256) and 1.0 cm^{-1} (YSI, Inc., model 3253) were used. Both conductivity cells were placed in the same measurement vessel within 1 cm of each other. The K_{cell} for each conductivity cell was determined using eq 1 and KCl solutions of known conductivity.^{35,38-43} When the conductances from both conductivity cells were within the optimal range of the conductivity meter, the electrical conductivities derived from the two cells were averaged. For dilute solutions (< 0.001

Table 3. Electrical Conductivities of Single Electrolytes from (5 to 90) °C

m mol·kg ⁻¹	$t/^\circ\text{C}$						
	5.0	10.0	25.0	35.0	45.0	70.0	90.0
$\kappa(\text{KCl})/\text{mS}\cdot\text{cm}^{-1}$							
0.000100	0.009464	0.01074	0.01487	0.01786	0.02105	0.02969	0.03716
0.001000	0.09198	0.1050	0.1471	0.1773	0.2070	0.2897	0.3587
0.01000	0.8910	1.014	1.408	1.688	1.977	2.761	3.426
0.10000	8.184	9.292	12.83	15.32	17.88	24.71	30.86
0.5000	38.75	43.75	59.20	69.81	81.07	112.3	134.8
1.000	72.03	80.84	108.6	128.0	147.7	202.5	245.8
$\kappa(\text{NaCl})/\text{mS}\cdot\text{cm}^{-1}$							
0.000104	0.008271	0.009431	0.01295	0.01610	0.01893	0.02693	0.03358
0.000990	0.07531	0.08619	0.1224	0.1478	0.1747	0.2497	0.3126
0.01000	0.7349	0.8395	1.185	1.425	1.694	2.418	3.029
0.10000	6.588	7.505	10.60	12.77	15.05	21.48	26.91
0.5000	29.48	33.48	46.52	56.25	66.24	93.50	116.8
0.9999	54.44	61.23	84.30	101.9	119.4	168.0	209.4
$\kappa(\text{HCl})/\text{mS}\cdot\text{cm}^{-1}$							
0.000110	0.03313	0.03683	0.04665	0.05310	0.05973	0.07487	0.08461
0.000958	0.2800	0.3088	0.3978	0.4565	0.5121	0.6414	0.7325
0.00937	2.714	3.001	3.869	4.408	4.932	6.227	7.132
0.09398	26.04	28.72	36.84	41.90	46.73	58.72	67.22
0.4603	119.8	131.4	166.9	189.7	210.9	262.3	298.7
0.8500	202.0	220.6	279.0	315.3	349.5	434.5	482.4
$\kappa(\text{LiCl})/\text{mS}\cdot\text{cm}^{-1}$							
0.000085	0.005986	0.006826	0.009588	0.01170	0.01388	0.01978	0.02483
0.000952	0.06496	0.07487	0.1069	0.1311	0.1528	0.2191	0.2774
0.00845	0.5562	0.6414	0.9167	1.123	1.315	1.886	2.366
0.09523	5.516	6.326	9.019	10.99	12.76	18.09	22.57
0.9613	43.17	49.86	71.30	83.50	97.94	126.4	155.7
$\kappa(\text{CsCl})/\text{mS}\cdot\text{cm}^{-1}$							
0.000106	0.01018	0.01151	0.01597	0.01917	0.02242	0.03135	0.04007
0.00101	0.09529	0.1089	0.1510	0.1817	0.2103	0.2930	0.3658
0.01058	0.9738	1.107	1.539	1.850	2.142	2.972	3.702
0.1009	8.548	9.735	13.46	16.14	18.59	26.04	31.07
0.4763	37.54	42.56	57.62	68.16	79.17	110.1	132.3
1.090	83.03	93.55	122.9	142.5	165.5	229.8	268.7
$\kappa(\text{NH}_4\text{Cl})/\text{mS}\cdot\text{cm}^{-1}$							
0.000977	0.08892	0.1017	0.1441	0.1738	0.2024	0.2870	0.3591
0.00965	0.8560	0.9786	1.381	1.671	1.938	2.731	3.363
0.09765	7.999	9.148	12.76	15.45	18.01	25.35	31.42
0.4735	35.42	40.27	55.25	65.77	76.91	107.5	132.6
1.034	73.01	82.93	111.2	131.3	153.6	215.5	253.5
$\kappa(\text{CaCl}_2)/\text{mS}\cdot\text{cm}^{-1}$							
0.000076	0.01256	0.01432	0.01998	0.02384	0.02814	0.04073	0.0517
0.000755	0.1195	0.1369	0.1945	0.2351	0.2784	0.3992	0.5001
0.00755	1.103	1.263	1.792	2.160	2.547	3.636	4.547
0.07550	9.331	10.62	14.96	17.93	21.10	29.82	36.94
0.3773	41.79	47.30	65.31	77.92	90.92	126.6	155.8
$\kappa(\text{MgCl}_2)/\text{mS}\cdot\text{cm}^{-1}$							
0.000119	0.01861	0.02134	0.02989	0.03553	0.04209	0.06086	0.07640
0.000984	0.1481	0.1700	0.2432	0.2937	0.3478	0.5010	0.6265
0.01137	1.537	1.760	2.503	3.020	3.534	5.068	6.347
0.09942	11.00	12.56	17.72	21.37	25.15	35.75	44.24
0.3609	34.49	39.27	54.91	66.06	77.53	109.4	136.0
$\kappa(\text{BaCl}_2)/\text{mS}\cdot\text{cm}^{-1}$							
0.000092	0.01632	0.01880	0.02597	0.03085	0.03626	0.05187	0.06436
0.00110	0.1799	0.2060	0.2897	0.3508	0.4141	0.5911	0.7372
0.00896	1.386	1.585	2.229	2.681	3.161	4.493	5.593
0.1029	13.66	15.53	21.67	25.88	30.34	42.47	48.14
0.3100	36.57	41.27	55.89	67.94	78.59	103.2	125.1
$\kappa(\text{SrCl}_2)/\text{mS}\cdot\text{cm}^{-1}$							
0.000125	0.02084	0.02384	0.03331	0.03972	0.04689	0.06780	0.08422
0.00141	0.2222	0.2538	0.3603	0.4353	0.5151	0.7369	0.9235
0.01200	1.807	2.072	2.926	3.531	4.164	5.927	7.383
0.1313	16.63	18.92	26.46	31.74	37.19	52.29	61.84
0.3891	41.94	47.51	64.57	77.97	90.74	125.1	153.8
$\kappa(\text{Na}_2\text{SO}_4)/\text{mS}\cdot\text{cm}^{-1}$							
0.000100	0.01565	0.01807	0.02576	0.03181	0.03786	0.05401	0.06763
0.00100	0.1463	0.1680	0.2415	0.2920	0.3475	0.5015	0.6330
0.01000	1.296	1.488	2.128	2.575	3.049	4.381	5.474
0.1001	10.00	11.48	16.39	19.86	23.47	33.47	41.70
0.1989	17.56	20.22	28.82	35.08	41.53	59.46	74.30
0.4999	33.83	38.54	54.70	67.08	79.54	113.9	137.0

Table 3a. Continued

m mol·kg ⁻¹	$t/^\circ\text{C}$						
	5.0	10.0	25.0	35.0	45.0	70.0	90.0
$\kappa(\text{K}_2\text{SO}_4)/\text{mS}\cdot\text{cm}^{-1}$							
0.000102	0.01969	0.02257	0.03175	0.03884	0.04575	0.06401	0.08
0.00105	0.1881	0.2141	0.3006	0.3611	0.4268	0.6018	0.7466
0.01061	1.685	1.919	2.675	3.216	3.765	5.269	6.441
0.1048	13.41	15.23	21.10	25.16	29.40	40.64	49.57
0.2029	23.62	26.72	37.05	44.09	51.38	70.99	87.22
0.4783	51.51	57.80	78.01	92.98	108.0	149.1	179.7
$\kappa(\text{CaSO}_4)/\text{mS}\cdot\text{cm}^{-1}$							
0.000076	0.01230	0.01409	0.01963	0.02529	0.03011	0.04223	0.05363
0.00102	0.1397	0.1601	0.2275	0.2808	0.325	0.4537	0.5546
0.01245	1.154	1.331	1.850	2.255	2.573	3.419	3.973
$\kappa(\text{H}_2\text{SO}_4)/\text{mS}\cdot\text{cm}^{-1}$							
0.000094	0.05493	0.06105	0.07827	0.08931	0.09949	0.1221	0.1367
0.000936	0.5201	0.5749	0.7292	0.8174	0.9001	1.026	1.058
0.00944	4.321	4.729	5.772	6.319	6.759	7.372	7.698
0.09223	31.20	34.44	41.30	45.25	48.85	55.75	61.59
0.4664	134.6	145.0	173.7	193.4	209.6	256.2	280.5
$\kappa(\text{Cs}_2\text{SO}_4)/\text{mS}\cdot\text{cm}^{-1}$							
0.000101	0.01962	0.02237	0.03069	0.03625	0.04233	0.06348	0.07804
0.00105	0.1932	0.2195	0.3060	0.3666	0.4304	0.6181	0.7641
0.01021	1.676	1.906	2.654	3.173	3.716	5.216	6.438
0.1047	13.58	15.39	21.24	25.29	29.58	40.94	50.22
0.1836	22.40	25.28	34.68	41.19	47.92	65.90	80.00
0.3588	40.83	45.80	62.04	73.20	84.63	115.8	137.3
$\kappa(\text{KHSO}_4)/\text{mS}\cdot\text{cm}^{-1}$							
0.000161	0.06027	0.06684	0.08772	0.1017	0.1154	0.1478	0.1675
0.000981	0.3588	0.3981	0.5156	0.5895	0.6564	0.7958	0.8540
0.01608	4.635	5.067	6.230	6.784	7.238	7.958	8.195
0.09815	21.41	23.18	27.91	29.98	31.57	34.69	36.65
0.2291	43.79	47.28	57.10	61.37	64.56	71.59	76.99
$\kappa(\text{KHCO}_3)/\text{mS}\cdot\text{cm}^{-1}$							
0.001000	0.07403	0.08340	0.1179	0.1416	0.1673	0.2401	0.3038
0.00992	0.6870	0.7877	1.107	1.335	1.573	2.237	2.794
0.09998	6.141	7.003	9.852	11.76	13.83	19.63	24.46
0.5001	26.64	30.31	42.06	50.66	59.40	83.91	104.9
0.9999	47.48	53.58	73.65	88.02	103.1	143.0	179.3
$\kappa(\text{K}_2\text{CO}_3)/\text{mS}\cdot\text{cm}^{-1}$							
0.00132	0.2129	0.2471	0.3642	0.4390	0.5331	0.7921	0.9755
0.01048	1.568	1.809	2.575	3.146	3.758	5.522	6.987
0.1319	15.89	18.15	25.42	30.54	35.90	50.98	63.45
0.3525	38.00	43.05	59.42	71.15	83.19	116.0	143.1
$\kappa(\text{NaHCO}_3)/\text{mS}\cdot\text{cm}^{-1}$							
0.00121	0.06911	0.08034	0.1162	0.1437	0.1703	0.2506	0.3284
0.01187	0.6467	0.7485	1.086	1.346	1.589	2.340	3.056
0.1223	5.728	6.641	9.60	11.77	13.95	20.44	24.57
0.7226	26.34	30.55	43.83	53.46	64.10	94.04	113.9
$\kappa(\text{Na}_2\text{CO}_3)/\text{mS}\cdot\text{cm}^{-1}$							
0.000912	0.1348	0.1603	0.2439	0.2888	0.3495	0.5196	0.6513
0.01031	1.285	1.491	2.182	2.684	3.237	4.867	6.187
0.09334	8.860	10.24	14.86	18.22	21.82	32.22	41.17
0.3041	23.24	26.85	38.93	47.81	57.13	83.62	106.4
$\kappa(\text{NaOH})/\text{mS}\cdot\text{cm}^{-1}$							
0.00100	0.1671	0.1919	0.2459	0.2833	0.3327	0.4401	0.5213
0.01000	1.596	1.793	2.414	2.784	3.201	4.294	5.115
0.1000	14.98	16.77	22.51	26.35	30.26	40.62	48.61
0.5000	66.39	74.17	98.75	115.9	132.5	177.2	206.3
1.000	121.3	135.0	180.1	211.9	243.8	327.4	366.6
$\kappa(\text{NaF})/\text{mS}\cdot\text{cm}^{-1}$							
0.000088	0.005802	0.006955	0.009523	0.01220	0.01433	0.02014	0.02517
0.000920	0.06016	0.06909	0.09683	0.1152	0.1398	0.2009	0.2474
0.00878	0.5214	0.5994	0.8551	1.038	1.234	1.798	2.270
0.09060	4.638	5.338	7.669	9.341	11.12	16.21	20.42
0.4176	19.17	22.01	31.51	38.24	45.47	65.70	81.37
0.8404	34.32	39.15	55.79	67.91	74.78	113.7	145.4

Table 3b. Continued

m $\text{mol} \cdot \text{kg}^{-1}$	$t/^\circ\text{C}$						
	5.0	10.0	25.0	35.0	45.0	70.0	90.0
$\kappa(\text{KF})/\text{mS} \cdot \text{cm}^{-1}$							
0.000325	0.02576	0.02933	0.04125	0.05036	0.05965	0.08448	0.1046
0.00109	0.08262	0.09509	0.1357	0.1642	0.1929	0.2734	0.3426
0.03500	2.417	2.829	3.939	4.778	5.576	7.954	9.964
0.1100	7.375	8.455	11.95	14.45	16.92	24.09	30.04
0.5200	30.23	34.35	48.04	57.71	68.01	96.83	118.6
0.9900	52.72	60.34	82.75	99.07	117.5	168.5	201.3
$\kappa(\text{KBr})/\text{mS} \cdot \text{cm}^{-1}$							
0.000099	0.009344	0.01066	0.01469	0.0175	0.02072	0.02896	0.03522
0.000975	0.09114	0.1037	0.1441	0.1716	0.2007	0.2802	0.3430
0.00987	0.8994	1.022	1.417	1.689	1.974	2.761	3.376
0.09755	8.252	9.355	12.90	15.35	17.87	24.91	29.52
1.210	84.09	93.63	124.5	145.4	167.2	224.6	262.8
$\kappa(\text{KNO}_3)/\text{mS} \cdot \text{cm}^{-1}$							
0.000103	0.009389	0.01073	0.01486	0.01798	0.02048	0.0283	0.03480
0.000997	0.08901	0.1015	0.1411	0.1701	0.1956	0.2717	0.3380
0.01026	0.8740	0.9971	1.385	1.664	1.919	2.666	3.287
0.09972	7.601	8.658	12.01	14.40	16.69	23.42	28.75
0.4093	28.15	32.11	44.07	52.64	61.62	85.90	104.5
0.7941	48.06	54.74	74.28	88.31	103.8	146.3	169.7
$\kappa(\text{Zn}(\text{NO}_3)_2)/\text{mS} \cdot \text{cm}^{-1}$							
0.000087	0.01368	0.01579	0.02248	0.02744	0.03188	0.04549	0.05750
0.00127	0.1814	0.2081	0.2942	0.3606	0.4205	0.6014	0.7615
0.00874	1.162	1.334	1.891	2.299	2.687	3.830	4.824
0.1275	13.91	15.92	22.17	26.58	31.18	44.02	54.42
0.3325	31.11	36.53	49.31	59.06	69.86	99.37	118.3

$\text{mol} \cdot \text{kg}^{-1}$), only the conductances measured with the 0.1 cm^{-1} conductivity cell were used. For concentrated solutions ($> 0.5 \text{ mol} \cdot \text{kg}^{-1}$), only the conductances measured with the 1.0 cm^{-1} conductivity cell were used. When the conductances for both cells were in the optimum range, the relative difference (δ) for each of these determinations was computed using the following equation

$$\delta = \frac{|\kappa_{0.1} - \kappa_{1.0}|}{\frac{(\kappa_{0.1} + \kappa_{1.0})}{2}} \quad (3)$$

where $\kappa_{0.1}$ and $\kappa_{1.0}$ are the electrical conductivities determined with the 0.1 cm^{-1} and 1.0 cm^{-1} conductivity cells, respectively. The relative differences determined using eq 3 are depicted in box plots showing the mean, median, first standard deviation, 95th percentile, 99th percentile, and maximum value for each temperature in Figure S1 (Supporting Information). For temperatures below 25°C , 95 % of the electrical conductivity measurements were within 1 % of each other. For the (35 and 45) $^\circ\text{C}$ measurements, 95 % of the electrical conductivities were within 1.2 % of each other. The difference was the largest for the (70 and 90) $^\circ\text{C}$ measurements, for which thermal expansion of the conductivity cells is expected to be the greatest. For all data, the mean difference was 0.6 %; thus, four significant figures are reported for the electrical conductivity determinations.

Electrolyte solutions were placed in 500 mL high-density polyethylene (HDPE) measurement vessels containing two conductivity probes and a temperature probe. The measurement vessels and the conductivity probes were cleaned by soaking in HCl ($\phi = 0.05$ in water) for at least 24 h and rinsing three times with deionized water ($18 \text{ M}\Omega \cdot \text{cm}$). The lid containing the probes was tightly sealed to minimize evaporation.

The electrical conductivities of 34 electrolyte solutions, of which 26 were single electrolyte solutions and 8 were single

electrolyte + acid mixtures, were determined for molalities of (10^{-4} to 1) $\text{mol} \cdot \text{kg}^{-1}$. The single electrolyte solutions measured in this study were: KCl, NaCl, HCl, LiCl, CsCl, NH_4Cl , CaCl_2 , MgCl_2 , BaCl_2 , SrCl_2 , H_2SO_4 , Na_2SO_4 , K_2SO_4 , Cs_2SO_4 , CaSO_4 , KHSO_4 , KHCO_3 , K_2CO_3 , NaHCO_3 , Na_2CO_3 , NaOH, NaF, KF, KBr, KNO_3 , and $\text{Zn}(\text{NO}_3)_2$. The single electrolyte + acid solution mixtures measured in this study were: $\text{Al}(\text{NO}_3)_3 + \text{HNO}_3$, $\text{Cu}(\text{NO}_3)_2 + \text{HNO}_3$, $\text{FeCl}_2 + \text{HCl}$, $\text{FeSO}_4 + \text{H}_2\text{SO}_4$, $\text{Fe}(\text{NO}_3)_3 + \text{HNO}_3$, $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$, $\text{Mg}(\text{NO}_3)_2 + \text{HNO}_3$, and $\text{Mn}(\text{NO}_3)_2 + \text{HNO}_3$. Most of the chemicals used to prepare the electrolytes were of high purity ($> 99.9\%$ min., GFS chemicals). Trace-metal grade HCl and HNO_3 (Fisher Scientific) were distilled using a sub-boiling purification technique⁴⁴ and assayed by titration to determine their molalities.⁴⁵ Magnesium nitrate and ferrous sulfate were purchased as $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, respectively, and were of high purity ($> 99\%$ min., Fisher Scientific). The reagents were stored in desiccators and dried in an oven at 55°C for a minimum of 48 h prior to solution preparation.

Electrolyte solutions were gravimetrically prepared (Sartorius R160P analytical and GP5202 5 kg top-loading balances), and all compositions are reported in molality ($\text{mol} \cdot \text{kg}^{-1}$). The resolutions of the analytical and top-loading balances were (0.00001 and 0.01) g, respectively. The accuracy of the balances was checked with certified weights. The relative uncertainties in the gravimetric preparation of electrolyte solutions are less than 0.1 %. The water used in all preparations was passed through a deionizing system prior to being distilled twice (DI–DD). The DI–DD water used in all preparations was allowed to equilibrate with atmospheric CO_2 for several days before use. Similar to the method described by Pratt et al.,³⁵ the conductance of the CO_2 -equilibrated DI–DD water was measured 30 different times at each temperature of interest from (5 to 90) $^\circ\text{C}$, and the median conductance was subtracted from the conductance of the electrolyte solution. Electrolytes that hydrolyze or precipitate at circumneutral pH (Al, Cu, Fe(II),

Table 4. Electrical Conductivities of Electrolytes + Acid Solutions from (5 to 90) °C

m^a	$t/^{\circ}\text{C}$							comments ^b
$\text{mol}\cdot\text{kg}^{-1}$	5.0	10.0	25.0	35.0	45.0	70.0	90.0	
$\kappa(\text{Al}(\text{NO}_3)_3)/\text{mS}\cdot\text{cm}^{-1}$								
0.000088	0.3869	0.4302	0.5552	0.6334	0.7101	0.9049	1.042	+ HNO ₃ , pH 2.92
0.000883	0.5671	0.6384	0.8484	0.9898	1.135	1.533	1.872	+ HNO ₃ , pH 2.91
0.00871	2.168	2.457	3.424	4.110	4.827	6.932	8.941	+ HNO ₃ , pH 2.90
0.0881	15.51	17.06	23.78	28.73	33.87	48.67	59.23	+ HNO ₃ , pH 2.67
0.1580	25.11	28.26	39.13	47.88	55.95	76.89	96.98	+ HNO ₃ , pH 2.62
$\kappa(\text{Cu}(\text{NO}_3)_2)/\text{mS}\cdot\text{cm}^{-1}$								
0.000100	0.1101	0.1227	0.1613	0.1870	0.2080	0.2684	0.3180	+ HNO ₃ , pH 3.53
0.00110	0.2486	0.2823	0.3880	0.4633	0.5303	0.7303	0.8992	+ HNO ₃ , pH 3.53
0.01032	1.433	1.641	2.308	2.795	3.256	4.628	5.792	+ HNO ₃ , pH 3.51
0.1108	12.07	13.82	19.35	23.33	27.46	39.18	48.38	+ HNO ₃ , pH 3.48
0.3459	32.19	36.80	50.93	60.92	72.35	103.4	125.7	+ HNO ₃ , pH 3.18
$\kappa(\text{FeCl}_2)/\text{mS}\cdot\text{cm}^{-1}$								
0.000090	3.365	3.724	4.835	5.486	6.142	7.702	8.954	+ HCl, pH 1.99
0.000726	3.437	3.802	4.940	5.646	6.350	8.025	9.282	+ HCl, pH 1.99
0.00908	4.397	4.997	6.568	7.661	8.715	11.48	13.54	+ HCl, pH 1.99
0.1169	16.00	18.07	24.94	30.03	35.16	48.89	59.66	+ HCl, pH 1.99
$\kappa(\text{FeSO}_4)/\text{mS}\cdot\text{cm}^{-1}$								
0.001120	0.6212	0.6791	0.8697	0.9771	1.075	1.235	1.274	+ H ₂ SO ₄ , pH 2.75
0.00212	0.6435	0.7287	0.9366	1.063	1.165	1.409	1.543	+ H ₂ SO ₄ , pH 2.76
0.01287	1.183	1.326	1.784	2.092	2.419	3.214	3.988	+ H ₂ SO ₄ , pH 2.87
0.1121	2.469	2.690	3.516	3.913	4.714	—	—	+ H ₂ SO ₄ , pH 3.07
0.2576	12.38	14.15	19.80	23.03	26.92	36.31	41.10	+ H ₂ SO ₄ , pH 3.10
$\kappa(\text{Fe}(\text{NO}_3)_3)/\text{mS}\cdot\text{cm}^{-1}$								
0.000099	40.31	44.78	57.30	65.32	72.45	90.86	102.7	+ HNO ₃ , pH 0.92
0.000984	40.37	44.86	57.39	65.47	72.59	91.06	103.3	+ HNO ₃ , pH 0.92
0.00985	41.40	45.97	59.15	67.60	75.32	95.53	109.1	+ HNO ₃ , pH 0.92
0.09618	51.43	57.77	75.76	87.88	101.5	138.5	165.2	+ HNO ₃ , pH 0.92
0.2534	66.56	75.23	100	118.3	140.2	203.2	—	+ HNO ₃ , pH 0.92
$\kappa(\text{Fe}_2(\text{SO}_4)_3)/\text{mS}\cdot\text{cm}^{-1}$								
0.000104	3.946	4.306	5.228	5.695	6.051	6.590	6.888	+ H ₂ SO ₄ , pH 1.93
0.000829	4.036	4.402	5.350	5.829	6.204	6.810	7.180	+ H ₂ SO ₄ , pH 1.93
$\kappa(\text{Mg}(\text{NO}_3)_2)/\text{mS}\cdot\text{cm}^{-1}$								
0.000098	0.07334	0.08166	0.1072	0.1244	0.1407	0.1831	0.2164	+ HNO ₃ , pH 3.71
0.000976	0.1971	0.2238	0.3083	0.3667	0.4272	0.5910	0.7277	+ HNO ₃ , pH 3.71
0.00937	1.291	1.472	2.073	2.488	2.927	4.146	5.165	+ HNO ₃ , pH 3.71
0.09844	10.79	12.28	17.24	20.78	24.42	34.71	42.61	+ HNO ₃ , pH 3.89
0.3271	31.29	35.38	49.26	59.22	69.68	98.61	116.2	+ HNO ₃ , pH 3.92
$\kappa(\text{Mn}(\text{NO}_3)_2)/\text{mS}\cdot\text{cm}^{-1}$								
0.000917	0.5151	0.5774	0.7688	0.8959	1.015	1.307	1.550	+ HNO ₃ , pH 2.90
0.01047	1.786	2.033	2.820	3.382	3.934	5.380	6.651	+ HNO ₃ , pH 2.82
0.08600	10.40	11.79	16.30	19.58	22.95	31.25	36.92	+ HNO ₃ , pH 2.40
0.8521	70.64	79.73	106.9	125.4	144.1	194.1	—	+ HNO ₃ , pH 1.29

^a m is molality of electrolyte. ^b Reported pH was determined at 22 °C.

Fe(III), Mg, and Mn) were prepared in dilute acid solutions. The pH of the acid solutions was adjusted such that the molalities of the main hydrolysis species were at least 2 orders of magnitude lower than the molalities of the unhydrolyzed free ions. Chemical-speciation calculations were performed with the geochemical computer program PHREEQCI.^{46,47} Care was taken to keep the pH as high as possible given the hydrolysis constraints because the H⁺ ion transport number is so large that accurate determination of ionic conductivities of other solutes is difficult at low pH.

All solutions were checked for major and trace cations (Al, Ca, Cu, K, Mg, Mn, Na, Sr, and Zn) by inductively coupled plasma atomic emission spectroscopy (ICP–AES, Leeman Labs, DRE), for Fe by the FerroZine method,^{48–50} and for carbonate species by alkalinity titration.⁴⁵

Results

The electrical conductivities of 26 single electrolyte and 8 electrolyte + acid solutions from (5 to 90) °C are shown in Tables 3 and 4, respectively. The electrical conductivities

reported for KCl were used to determine K_{cell} using eq 1. Following the procedure of Pratt et al.,³⁵ the values in Tables 3 and 4 were corrected for the electrical conductivity of the water (solvent) in equilibrium with atmospheric CO₂ at the temperature of measurement. The median electrical conductivity of the solvent water at each temperature and the median absolute

Table 5. Electrical Conductivity of the Solvent Water in Equilibrium with Atmospheric CO₂ for This Study and from Pratt et al.^{35a}

$t/^\circ\text{C}$	$\kappa_{\text{H}_2\text{O}}/\mu\text{S}\cdot\text{cm}^{-1}$		
	this study	MAD	Pratt et al. ²⁵
5.0	0.67	0.07	0.68
10.0	0.77	0.09	0.79
25.0	1.10	0.10	1.10
35.0	1.33	0.16	1.30
45.0	1.59	0.15	1.51
70.0	1.88	0.19	
90.0	2.37	0.29	

^a MAD, median absolute deviation.

Table 6. Source of Molar Conductivity Data Taken from the Literature for This Investigation

electrolyte	reference
BaCl ₂	54, 58–62
CaCl ₂	58, 61–65
CaSO ₄	66
Cs ₂ SO ₄	67
CsCl	61, 68–71
H ₂ SO ₄	61, 72, 73
HCl	61, 65, 74–80
K ₂ CO ₃	81
K ₂ SO ₄	58, 61, 67, 82–84
KBr	61, 71, 85–93
KCl	35, 38, 61, 65, 78, 85, 87, 91, 92, 94–105
KF	71, 106
KHCO ₃	81
KHSO ₄	61
KNO ₃	61, 68, 78, 107, 108
LiCl	61, 68, 74, 78, 87, 92, 93, 104, 109–111
MgCl ₂	58, 60–62, 112–114
Na ₂ CO ₃	61
Na ₂ SO ₄	58, 61, 67, 84, 115, 116
NaCl	61, 65, 71, 78, 87, 92, 94, 96, 101, 117, 118
NaF	119
NaHCO ₃	61
NaOH	61, 120–123
NH ₄ Cl	61, 92, 124, 125
SrCl ₂	58, 61, 81
Zn(NO ₃) ₂	61

deviation (MAD)⁵¹ for 30 replicate measurements obtained from this study along with the values reported by Pratt et al.³⁵ are shown in Table 5. Use of the median and MAD provides trustworthy results in the presence of outliers.⁵¹ The good agreement between the results of this study and those of Pratt et al.³⁵ for the electrolytic conductivity of water in equilibrium with atmospheric CO₂ demonstrates that the DI–DD water used as a solvent in this study was of high quality and that the low-level conductance measurements were sufficiently accurate.

Discussion

The molar conductivities (Λ) for 26 single electrolytes determined in this study were compared to values reported in

the literature (Figures S2–S8, Supporting Information). The molar conductivity is calculated using the following equation

$$\Lambda = \frac{\kappa}{C} \quad (4)$$

where Λ is the molar conductivity ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$); κ is the electrical conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$); and C is the electrolyte concentration ($\text{mol}\cdot\text{dm}^{-3}$). The molar conductivities for the electrolyte + acid mixtures were not compared because either the data were not available in the literature or the acid concentrations were not the same. Molar concentrations were determined using density data reported by Söhnel and Novotný.⁵² A tabulation of all sources of conductivity data taken from the literature for this comparison is in Table 6. There is excellent agreement between the molar conductivity data taken from the literature and data determined in this study for KCl, NaCl, HCl, LiCl (Figure S2, Supporting Information), CaCl₂, MgCl₂, BaCl₂, SrCl₂ (Figure S3, Supporting Information), H₂SO₄, K₂SO₄, Na₂SO₄, Cs₂SO₄ (Figure S4, Supporting Information), KHCO₃, K₂CO₃, NaHCO₃, Na₂CO₃ (Figure S5, Supporting Information), NaOH, NaF, KF, KBr (Figure S6, Supporting Information), KNO₃, CsCl, NH₄Cl, Zn(NO₃)₂ (Figure S7, Supporting Information), and CaSO₄ and KHSO₄ (Figure S8, Supporting Information). The most discrepant measurements are for H₂SO₄ (Figure S4A, Supporting Information) and for KHSO₄ (Figure S8B, Supporting Information) at higher temperatures, (70 and 90) °C, although literature values are sparse.

Several options are possible for fitting the electrical conductivity data to empirical functions of concentration and temperature. Harned and Owen⁵³ and Jones and Dole⁵⁴ did a thorough review of numerous empirical equations, many of which have been used to calculate the electrical conductivities of natural waters.^{14,19} An empirical equation in the form suggested by Lattey⁵⁵ can predict the molar conductivity of the ions used in this study

Table 7. Parameters Used to Calculate the Molar Conductivities ($\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) of Single Electrolyte Solutions

electrolyte	Λ^0	A	B	comment
KCl	$0.009385t^2 + 2.533t + 81.17$	$0.01390t^2 + 1.886t + 44.11$	1.7	
NaCl	$0.008967t^2 + 2.196t + 67.03$	$0.00726t^2 + 1.762t + 44.55$	1.3	
HCl	$-0.006766t^2 + 6.614t + 262.4$	$0.000090t^2 + 1.776t + 48.53$	0.01	
LiCl	$0.008784t^2 + 1.996t + 59.90$	$0.01656t^2 + 1.198t + 42.79$	1.0	
CsCl	$0.01008t^2 + 2.479t + 83.79$	$0.01733t^2 + 1.176t + 41.29$	1.4	
NH ₄ Cl	$0.006575t^2 + 2.684t + 78.03$	$0.006133t^2 + 1.423t + 30.00$	0.7	
1/2CaCl ₂	$0.01124t^2 + 2.224t + 72.36$	$0.03918t^2 + 3.905t + 137.7$	3.8	
1/2MgCl ₂	$0.009534t^2 + 2.247t + 68.19$	$0.02469t^2 + 4.374t + 129.8$	3.1	
1/2BaCl ₂	$0.01038t^2 + 2.346t + 75.51$	$0.04427t^2 + 2.237t + 111.8$	2.4	
1/2SrCl ₂	$0.009597t^2 + 2.279t + 70.76$	$0.01668t^2 + 1.833t + 60.18$	0.8	
1/2H ₂ SO ₄	$-0.01985t^2 + 7.421t + 283.3$	$0.09194t^2 + 63.37t + 1869$	11.5	(0 to 45) °C
1/2Na ₂ SO ₄	$0.009501t^2 + 2.317t + 66.58$	$0.02388t^2 + 4.509t + 135.5$	2.2	
1/2K ₂ SO ₄	$0.008819t^2 + 2.872t + 83.72$	$0.03799t^2 + 9.784t + 247.1$	5.3	
1/2Cs ₂ SO ₄	$0.01273t^2 + 2.457t + 85.97$	$0.05456t^2 + 4.561t + 187.4$	3.3	
1/2CaSO ₄	$0.01192t^2 + 2.564t + 73.30$	$0.2402t^2 + 19.78t + 644.4$	9.6	
KHSO ₄	$-0.003092t^2 + 9.759t + 360.2$	$0.3102t^2 + 63.75t + 1776$	8.2	(0 to 45) °C
KHCO ₃	$0.007807t^2 + 2.040t + 63.03$	$0.00661t^2 + 1.577t + 38.58$	0.9	
1/2K ₂ CO ₃	$0.01145t^2 + 2.726t + 68.62$	$0.02438t^2 + 5.180t + 81.12$	2.1	
NaHCO ₃	$0.01260t^2 + 1.543t + 52.09$	$0.02793t^2 + 0.4556t + 52.94$	1.1	
1/2Na ₂ CO ₃	$0.02296t^2 + 5.211t + 147.0$	$0.05707t^2 + 22.22t + 455.8$	4.8	
NaOH	$0.006936t^2 + 3.872t + 148.3$	$0.01018t^2 + 0.6742t + 56.76$	0.2	
NaF	$0.007346t^2 + 2.032t + 56.36$	$0.004903t^2 + 3.101t + 69.99$	2.3	
KF	$0.007451t^2 + 2.294t + 66.42$	$0.005788t^2 + 1.501t + 39.40$	0.9	
KBr	$0.007076t^2 + 2.612t + 80.86$	$0.009019t^2 + 1.200t + 29.49$	0.6	
KNO ₃	$0.009117t^2 + 2.309t + 80.33$	$0.009090t^2 + 1.099t + 49.12$	0.7	
1/2Zn(NO ₃) ₂	$0.01526t^2 + 4.519t + 134.5$	$0.05938t^2 + 10.15t + 302.9$	4.0	

$$\Lambda = \Lambda^0(t) - A(t) \frac{m^{1/2}}{1 + Bm^{1/2}} \quad (5)$$

where Λ^0 and A are functions of temperature ($^{\circ}\text{C}$) and B is an empirical constant. Equation 6 is in accord with Debye and Hückel's thesis⁵⁶ for very dilute solutions, and Robinson and Stokes^{37,57} describe a similar theoretical equation where they modified Onsager's original limiting law. For molalities up to $0.1 \text{ mol}\cdot\text{kg}^{-1}$, A can be estimated by theory, and B can be estimated by the ion size parameter.³⁷ The parameters (Λ^0 , A , and B) reported in Table 7 were determined using the following procedure. The molar conductivity for each electrolyte was plotted against $(m^{1/2})(1 + Bm^{1/2})^{-1}$, and a linear regression was fitted to the data at each temperature. Next, B was optimized so that the mean of the square of the Pearson product-moment correlation coefficient, R^2 , for all of the linear regressions was maximized. With only a few exceptions, this optimization procedure generated data that correlates well ($R^2 = 0.993 \pm 0.005$) with linear equations, suggesting that eq 5 can be used to predict the molar conductivity from (0 to 90) $^{\circ}\text{C}$ and molalities of up to $1 \text{ mol}\cdot\text{kg}^{-1}$. An equation for the limiting molar conductivity (Λ^0) was then determined by plotting the intercept from eq 5 (Λ^0) against temperature ($^{\circ}\text{C}$). A second-order polynomial equation was used to fit this relationship. Similarly, the slope for each linear regression (A) was plotted against temperature, and a second-order polynomial equation was used to fit this relationship. To confirm the reliability of the Λ^0 , A , and B parameters used in eq 5, the molar conductivities and the calculated values are plotted (dashed lines in Figure S2–S8, Supporting Information).

The uncertainty of the parameters reported in Table 7 was estimated by computing the relative difference between the calculated and measured molar conductivities for data from this study and the literature for temperatures (5 to 90) $^{\circ}\text{C}$ (Figure 1). The equation used to calculate the relative difference was

$$\delta = \frac{\Lambda_c - \Lambda_m}{\Lambda_m} \quad (6)$$

where Λ_m is the measured molar conductivity and Λ_c is the calculated molar conductivity. The parameters reported in Table 7 are only valid for molalities of up to $1 \text{ mol}\cdot\text{kg}^{-1}$. For the 942 molar conductivity determinations of single electrolytes from

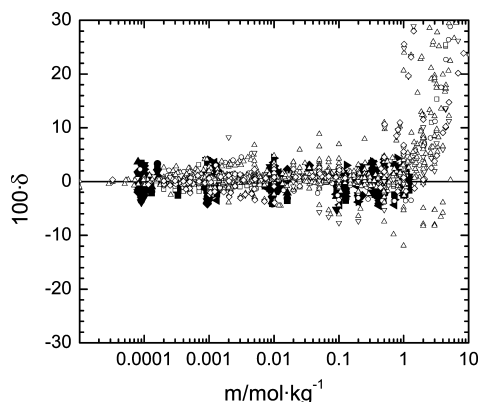


Figure 1. Relative difference (δ) between the calculated (using parameters in Table 7) and measured molar conductivities for data from this study and the literature. Solid symbols, this study; open symbols, published data: ■, 5 $^{\circ}\text{C}$; ●, 10 $^{\circ}\text{C}$; ▲, 25 $^{\circ}\text{C}$; ▼, 35 $^{\circ}\text{C}$; ◆, 45 $^{\circ}\text{C}$; triangle pointing left, 70 $^{\circ}\text{C}$; triangle pointing right, 90 $^{\circ}\text{C}$.

this study, the mean relative difference between the calculated and measured values was 0.1 % with a standard deviation of 1.6 %. The calculated molar conductivity also was compared to the literature data, and the mean relative difference for 1978 measurements up to $1 \text{ mol}\cdot\text{kg}^{-1}$ was 0.2 % with a standard deviation of 2.3 %.

Conclusions

Electrical conductivity determinations for 26 single electrolyte solutions and 8 electrolyte + acid solutions ranging in molality from (10^{-4} to 1) $\text{mol}\cdot\text{kg}^{-1}$ and in temperature from (5 to 90) $^{\circ}\text{C}$ are reported. This is the first study in which the electrical conductivities of electrolytes found in a wide variety of natural waters have been determined using the same equipment and procedure, over the necessary temperature and concentration ranges to provide basic data for calculating the electrical conductivities of natural waters. A series of equations are presented that can be used to calculate the molar conductivities of single electrolytes from (0 to 90) $^{\circ}\text{C}$ and up to $1 \text{ mol}\cdot\text{kg}^{-1}$.

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Supporting Information Available:

Figures showing the relative difference (δ) between the electrical conductivity determined using the 0.1 cm^{-1} and 1.0 cm^{-1} conductivity cells (Figure S1) and the molar conductivities (Λ) determined in this study and in the scientific literature for the single electrolyte solutions (Figures S2 to S8). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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