

Conductance of Aqueous Electrolyte Solutions at High Pressures

Data for Eleven 1,1 Electrolyte Systems

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Electrical conductivity measurements accurate to 0.1% were made as a function of temperature, pressure, and solution concentration for the following dilute aqueous electrolyte systems: LiCl, NH₄Cl, KCl, NaCl, RbCl, CsCl, (Et)₄NCl, KF, KBr, KI, and KNO₃. Studies were made with solutions of concentrations from 3–15 mM, pressures from 1–2300 atm, and temperatures from 3–55°C. Concentration-dependent pressure ratios of conductance (κ_p/κ_1) were extrapolated to infinite dilution with the aid of the Debye-Hückel-Onsager conductance equation, modified for variation of pressure. The infinite dilution ratios, internally consistent to 0.05% and accurate to <0.2%, are fitted to a third-order polynomial in pressure. These polynomial coefficients are presented, as well as representative original electrical resistance data.

The earliest measurements on the pressure coefficient of electrical conductance of aqueous solutions were concerned more with the magnitude and direction of the pressure effect than with its theoretical significance. Zisman (31) applied the Debye-Hückel equation to his dilute aqueous solution data and purported to show that a large compressibility of the ions was necessary to account for the results. Other investigators studied the chemical effects of pressure on weak electrolyte ionization (4–6, 11, 12, 29). Horne et al. (14–22) made a number of investigations of the pressure coefficient of the conductance of dilute as well as seawater concentrations of aqueous solutions.

Impetus for accurate and systematic determination of conductivities under pressure was provided by the work of Jobling and Lawrence (25) who showed the importance of the density in helping to determine the viscosities of liquids. Following this line, Brummer and Hills (3, 4) determined pressure coefficients of electrolytic conductance in the context of the Stearn and Eyring model for ion conduction (28) and derived certain activation parameters of interest. Ovenden (27) was the first to attempt careful extrapolation of dilute aqueous solution data to zero concentration to eliminate ion-ion interactions from consideration.

None of the prior studies was either sufficiently detailed in scope or experimentally well characterized for the purposes of a detailed analysis of the conduction process. Consequently, we conducted a systematic investigation of several aqueous 1,1 electrolyte systems over ranges of temperature and pressure. This work differs from previous investigations in terms of its higher accuracy, extrapolation to infinite dilution, and the scope of both the temperature and the pressure variable. Literally hundreds of experimental measurements were made over a two-year period. In some cases reproducibility was tested with a year's time intervening and was better than 0.1%.

EXPERIMENTAL

Brief Review of Earlier Methods. A detailed review of the experimental methods of previous investigators was made in an earlier paper (8). Early workers (10) used Pt-in-glass cells for which corrections were not made for the variation

of cell constant with pressure. The high precision required for extrapolation to infinite dilution was not required for those higher concentration studies. Only one investigator appeared to have considered the criticality of the Pt-in-glass electrode seal (26). In some cases mercury was used to isolate the study solution from the pressure-transmitting fluid. In other cases an organic liquid was used (7, 14–22).

At pressures above 3000 atm the Pt-in-glass seal was no longer reliable, and a Teflon-bodied cell employing a tight-fitting Teflon piston was employed (24). Because of reports of several phase changes in Teflon occurring over the temperature and pressure ranges of interest (30), a Teflon-bodied cell with an internally supported electrode system was devised. The cell constant in this case varies as the pressure coefficient of the borosilicate glass support (7).

The first careful investigation of dilute solutions employed slightly modified conventional Pt-in-glass cells satisfactory to about 2000 atm (27). The rod-ring electrode configuration used in this work was later used to show the unsatisfactory nature of the parallel plate design with respect to the pressure coefficient of its cell constant (23).

In the present investigation Pt-in-glass cells were satisfactory but only after considerable modification of the electrode-to-glass seal. Close attention was also paid to the effect of mercury as an isolation medium, the effect of weak electrolyte impurities, and the pressure coefficient of the cell constant (8).

The Pt electrode connection to the borosilicate glass pressure cell electrode, for example, is effected through a graded glass seal formed around a thin Pt ribbon. This seal was reliable over the entire range of temperature and pressure employed here. Mercury was the preferred medium for solution isolation. To obviate mercury corrosion reactions, solutions were carefully deaerated. The high-pressure conductance cells were filled by manipulating the solutions with helium gas in a closed glass apparatus (8). Weak electrolyte contamination from all sources was negligible in our "clean" experiments simply by deliberately doping test solutions with known amounts of weak electrolyte impurity.

To obtain suitable values of the measured cell resistance, two types of electrode configuration were used: the rod-ring design for dilute solutions and a capillary design for the more concentrated ones. The interrelationship between pressure coefficients of cell constants for the two were exhaustively studied by employing both types simultaneously in one and the same cell. All results were converted to the rod-ring equivalent. The pressure coefficient of the cell constant for the latter was

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Table I. Scope of Independent Variables

Concentration dependent data	
Temperatures, °C	
3, 5, 10, 15, 20, 25, 35, 45, 55	
Pressures, atm (typical, NaCl at 15°C)	
1, 207, 410, 621, 814, 1000, 1264, 1475, 1748, 1994, 2240	
Solution concentrations, mM	
LiCl	3.60 6.42 10.00 14.40
NH ₄ Cl	3.59 6.43 9.98 14.41 19.63
NaCl	3.61 6.41 9.99 14.43 19.57
KCl	1.62 3.62 6.42 10.00 19.61
RbCl	3.61 6.41 9.99 14.42 19.59
(Et) ₄ NCl	3.61 6.40 10.00 14.40
3 mM data	
Temperatures, °C	
3, 5, 10, 15, 20, 25, 35, 45, 55	
Pressures, atm (all salts)	
1, 200, 400, 600, 1000, 1250, 1500, 1750, 2000, 2250	

close to the compressibility of the Pt metal and involved a correction at 2000 atm, just small enough to be ignored.

The data were taken at rounded temperatures (Table I) measured with Hg-in-glass thermometers accurate to within 0.05°C (NBS). Pressures were measured with a Bourdon tube gauge (Heise Co., Newton, Conn.), and are accurate to 0.1% of full scale (3 atm). Other details of the apparatus and techniques used were described elsewhere (1, 2, 4, 8, 9).

After all of the factors already mentioned were taken into account, the accuracy attained in the high pressure coefficients of conductance of dilute aqueous solutions (≥ 2 mM) of strong electrolytes is about 0.1% which is believed to be the most reliable information obtained to date.

Scope of Data Investigation. Six strong 1,1 electrolytes, LiCl, NH₄Cl, NaCl, KCl, RbCl, and (Et)₄NCl, were studied over the range 3–55°C, and the approximate ranges 1–2250 atm and 3–15 mM. The actual way in which the ranges were covered is shown in Table I. This investigation, with the exception of the (Et)₄NCl data, established the reproducibility of the data and the appropriate applicability of the pressure-dependent Debye-Hückel-Onsager limiting conductance equation

$$\kappa_p/\kappa_1 = (\kappa_p/\kappa_1)^\circ \left[1 + \left\{ \frac{S_1}{\Lambda_1^\circ} - \frac{S_p}{\Lambda_p^\circ} \left(\frac{\rho_p}{\rho_1} \right)^{1/2} \right\} (c_1)^{1/2} \right] \quad (1)$$

$S \equiv \alpha\Lambda^\circ + \beta$, where α and β are the usual constants (13). ρ is, strictly speaking, the density of the solution; water densities were used and are sufficiently accurate.

A full description of the applicability of this equation was given elsewhere (9). κ_p/κ_1 data increased linearly with $(c_1)^{1/2}$ up to ~ 20 mM, to within 0.1% in κ_p/κ_1 . Without benefit of the equation, somewhat lower slopes were usually drawn through the data points owing to what are now recognized as negative deviations from limiting law (0.1% at 2000 atm and 20 mM).

Thereafter, it was sufficient to study only one appropriate solution concentration (~ 3 mM) for each salt, and to determine infinite dilution values using the theoretical limiting slopes. This practice greatly accelerates the acquisition of data. The five strong 1,1 electrolytes studied at ~ 3 mM only were CsCl, KF, KBr, KI, and KNO₃. The temperature and pressure ranges were essentially the same as those mentioned earlier. All five salts were studied simultaneously in the same pressure vessel. Thus, the actual temperatures and pressures shown in Table I apply to all five systems.

The measured cell resistances corresponding to the above

Table II. Representative Original Data of LiCl System at 25°C

P, atm	Cell resistance, ohms			
	c, mM			
	3.60	6.42	10.0	14.4
1	1474.1 ^a	8646.5	5595.1	3935.1
200	1446.0	8483.7	5489.3	3860.2
400	1421.6	8340.8	5306.2	3794.4
800	1384.2	8122.0	5253.8	3693.3
1000	1369.4	8037.2	5198.7	3654.0
1500	1344.6	7890.8	5102.9	3585.8
1750	1336.4	7842.6	5071.4	3563.4
2000	1330.8	7809.0	5049.4	3547.5
2250	1327.8	7792.8	5038.7	3539.6
1287	1354.4	7944.0	5138.0	3610.4
600	1403.7	8224.6	5322.1	3740.2
1	1476.9	8650.8	5599.3	3935.9

^a Rod-ring electrode design, requiring no correction for the pressure coefficient of the cell constant. All others are capillary cells, where corrections have been made, approximately equal to the compressibility of borosilicate glass.

variety of conditions comprise some 2700 data points (2) too numerous to be included here. For illustration typical original data for the LiCl system are given in Table II.

Treatment of Data. The first step in data reduction is the division of each measured resistance at pressure P into the corresponding value at 1 atm which gives the ratio R_1/R_p ($\equiv \kappa_p/\kappa_1$ after correction for cell constant variation with P). The κ_p/κ_1 ratio is then plotted against $c^{1/2}$, and extrapolation to infinite dilution is made with the help of the theoretical limiting law (Equation 1) adapted for variation in pressures (9).

For the LiCl, NH₄Cl, KCl, NaCl, and RbCl systems, where data were collected as a function of salt concentration, $(\kappa_p/\kappa_1)^\circ$ was found by direct graphical extrapolation with the aid of the theoretical limiting slope. This treatment, applied to the (Et)₄NCl data, was not entirely satisfactory. Tentatively, only the raw data for this system are reported (2). For the five remaining salt systems, Equation 1 was solved explicitly for $(\kappa_p/\kappa_1)^\circ$ (this ratio is implicit in the slope term), and the latter was then calculated directly from the 3 mM data.

$(\kappa_p/\kappa_1)^\circ$ values were fitted to the third-order polynomial expression

$$\ln (\kappa_p/\kappa_1)^\circ = \sum_{N=0}^3 D(N)P^N \quad (2)$$

by the method of least squares. P designates the gauge pressure in the experiment. At each temperature, pressure ratios are adequately represented by four entries per salt system— $D(0)$, $D(1)$, $D(2)$, and $D(3)$. These coefficients are given in Table III.

That the polynomial expression accurately represents the data is illustrated in Table IV. Typical differences between measured 3 mM data in conjunction with the theoretical slope) and calculated values of $(\kappa_p/\kappa_1)^\circ$, shown for the CsCl system, are well within the 0.1% experimental accuracy. Also given are similar results for the KI system, the least satisfactory of the entire series and whose fit is still within experimental error.

Reliability of Infinite Dilution Data. The accuracy of the conductance ratios at infinite dilution is influenced by the accuracy of the concentration-dependent data points as well as their degree of scatter.

Important factors are the constancy of temperature over the pressure cycles which start and end at 1 atm and attainment of thermal equilibrium after each pressure increment. The accuracy of the pressure coefficient is not a strong function of the absolute temperature as long as the temperature is

Table III. Polynomial Coefficients in Expression $\ln(\kappa_p/\kappa_1)^\circ = \sum_{N=0}^3 D(N)P^N$

LiCl	Temperatures, °C								
	3	5	10	15	20	25	35	45	55
D(0) × 10 ⁴	3.215	-1.657	-1.376	-1.741	-1.027	-0.6098	-0.1705	-0.4221	0.1116
D(1) × 10 ⁴	1.958	1.851	1.592	1.363	1.159	1.018	0.7664	0.5796	0.4430
D(2) × 10 ⁸	-6.755	-6.406	-5.538	-4.591	-3.670	-3.354	-2.465	-1.903	-1.519
D(3) × 10 ¹²	7.979	7.631	6.896	5.285	3.635	3.731	2.444	1.737	1.262
NH ₄ Cl									
D(0) × 10 ⁴	0.7839	0.3419	-2.503	-0.2943	0.3560	-0.7373	0.5812	-1.221	-1.581
D(1) × 10 ⁴	1.775	1.656	1.417	1.205	1.049	0.8977	0.6736	0.5258	0.3864
D(2) × 10 ⁸	-6.965	-6.281	-5.394	-4.541	-3.970	-3.314	-2.473	-2.223	-1.647
D(3) × 10 ¹²	9.099	7.624	6.543	5.346	4.630	3.491	2.215	2.505	1.416
NaCl									
D(0) × 10 ⁴	-0.2432	2.946	-1.463	-1.513	-2.031	-0.9871	-2.715	0.2682	-0.3163
D(1) × 10 ⁴	1.663	1.532	1.321	1.140	0.9589	0.8182	0.6113	0.4326	0.3305
D(2) × 10 ⁸	-6.412	-5.719	-4.927	-4.329	-3.481	-2.959	-2.354	-1.622	-1.520
D(3) × 10 ¹²	8.166	6.653	5.708	5.143	3.728	2.881	2.260	1.232	1.681
KCl									
D(0) × 10 ⁴	8.019	-1.855	-0.3459	-1.707	-1.382	-0.0859	-0.8493	-1.237	3.864
D(1) × 10 ⁴	1.655	1.536	1.318	1.125	0.9751	0.8293	0.6314	0.4739	0.3012
D(2) × 10 ⁸	-6.312	-5.513	-4.811	-4.038	-3.496	-2.945	-2.338	-1.813	-0.7245
D(3) × 10 ¹²	8.261	6.147	5.661	4.450	3.759	2.930	2.313	1.583	-1.499
RbCl									
D(0) × 10 ⁴	-1.560	-3.063	-0.1641	-1.564	-0.1306	-1.837	-0.9944	-0.3806	0.2574
D(1) × 10 ⁴	1.609	1.482	1.265	1.071	0.9195	0.7893	0.5729	0.4060	0.2953
D(2) × 10 ⁸	-6.440	-5.695	-4.938	-4.105	-3.499	-3.048	-2.109	-1.645	-1.398
D(3) × 10 ¹²	8.622	6.795	6.168	4.827	3.838	3.240	1.490	1.309	1.445
CsCl									
D(0) × 10 ⁴	0.8316	-2.164	-1.274	-1.107	-1.185	-1.234	-0.0944	-0.8013	0.2515
D(1) × 10 ⁴	1.502	1.391	1.169	0.9742	0.8283	0.7107	0.5097	0.3491	0.2429
D(2) × 10 ⁸	-6.317	-5.685	-4.725	-3.931	-3.368	-2.947	-2.359	-1.718	-1.603
D(3) × 10 ¹²	8.524	7.097	5.576	4.473	3.604	3.210	2.679	1.594	2.224
KF									
D(0) × 10 ⁴	2.209	-0.0308	-0.4858	0.7505	0.0156	-1.172	0.8747	-3.262	1.282
D(1) × 10 ⁴	1.618	1.496	1.289	1.107	0.9507	0.8162	0.6186	0.4859	0.3401
D(2) × 10 ⁸	-6.059	-5.300	-4.541	-3.965	-3.228	-2.676	-2.086	-2.096	-1.211
D(3) × 10 ¹²	8.575	6.692	5.748	5.350	3.807	2.865	2.251	3.735	1.203
KBr									
D(0) × 10 ⁴	3.747	-0.9306	-1.028	-0.5682	-2.021	-2.844	-0.0347	-2.888	-3.684
D(1) × 10 ⁴	1.543	1.446	1.224	1.028	0.8814	0.7534	0.5494	0.3867	0.3339
D(2) × 10 ⁸	-6.411	-5.933	-4.990	-4.184	-3.566	-3.142	-2.445	-1.744	-2.204
D(3) × 10 ¹²	8.515	7.531	6.055	4.977	3.884	3.559	2.770	1.419	3.117
KI									
D(0) × 10 ⁴	0.5503	-1.186	-1.122	-1.137	-1.286	-4.549	-1.758	-7.638	-3.225
D(1) × 10 ⁴	1.341	1.240	1.023	0.8372	0.7016	0.5811	0.3850	0.2461	0.1388
D(2) × 10 ⁸	-6.269	-5.788	-4.731	-3.915	-3.416	-2.992	-2.230	-1.912	-1.513
D(3) × 10 ¹²	8.581	7.700	5.759	4.540	3.943	3.569	2.465	2.463	2.060
KNO ₃									
D(0) × 10 ⁴	0.3480	-1.275	-0.4411	-1.160	-1.593	-0.3279	-0.1232	-2.900	-1.369
D(1) × 10 ⁴	1.233	1.139	0.9449	0.7688	0.6411	0.5348	0.3664	0.2183	0.1286
D(2) × 10 ⁸	-5.747	-5.306	-4.424	-3.608	-3.163	-2.735	-2.254	-1.545	-1.544
D(3) × 10 ¹²	7.771	6.959	5.454	4.172	3.772	3.096	2.911	1.379	2.492

Table IV. Adequacy of Equation 2 in Representing $(\kappa_p/\kappa_1)^\circ$

Pressure, atm	Temperature, 25°C			
	CsCl		KI	
	Measured	Calcd	Measured	Calcd
200	1.0127	1.0123	1.0092	1.0100
800	1.0398	1.0396	1.0299	1.0291
1500	1.0506	1.0509	1.0315	1.0319
2000	1.0490	1.0492	1.0247	1.0249

constant. Our constancy of better than 0.01°C and absolute certainty of 0.05°C are sufficient to ensure an accuracy of 0.1% in the conductance ratios. To ensure thermal equilibration after each incremental change of pressure, readings were always taken as a function of time; the final resistance reading was not recorded unless constancy had been apparent for about 30 min.

Even when intrinsic point-by-point accuracy and reproducibility are good, and scatter is kept to a minimum by observing the mentioned precautions, errors may exist in the process of extrapolation to infinite dilution. Without the aid of the theoretical limiting slopes, the tendency is to draw the best

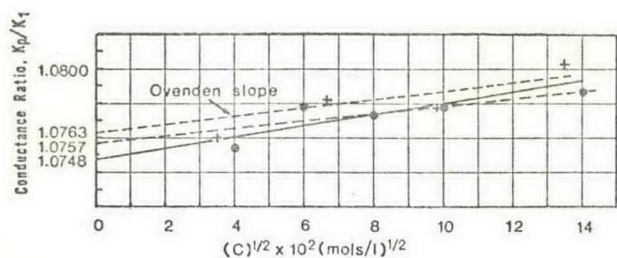


Figure 1. Extrapolation of conductance ratios to infinite dilution for KCl at 25°C

+ Ovenden, 210 atm (27) ● Present work, 1925 atm
 — Theoretical limiting slope - - - Hand-drawn slopes

straight line through the data points. This generally leads to slopes too low and an extrapolant too high because the deviations from the limiting slope are negative at the higher concentrations (9). With this in mind, the extrapolation through the concentration-dependent data can be carried out more confidently (Figure 1).

Figure 1 shows that a single experimental point appropriately placed can yield an accurate infinite dilution value when used in conjunction with the theoretical limiting slope. This practice assumes that measurements can be made with enough confidence to rely upon a single data point at each temperature for a given salt system. In this regard, we carried out many hundreds of individual measurements prior to our point-slope program. The uncertainty in the single point is no greater than that introduced in extrapolating from a typically scattered set; thus, the procedure is justified by the saving of time.

Previous workers have variously treated the concentration dependence of κ_p/κ_1 . Körber found that for KCl solutions κ_p/κ_1 decreased monotonically in the range 10^{-4} – $3N$ —i.e., the concentration dependence was in the wrong direction (26). Ellis (7) reported that in the range 10^{-3} – $10^{-1}N$ for KCl and HCl the effect of concentration was negligible. One practice

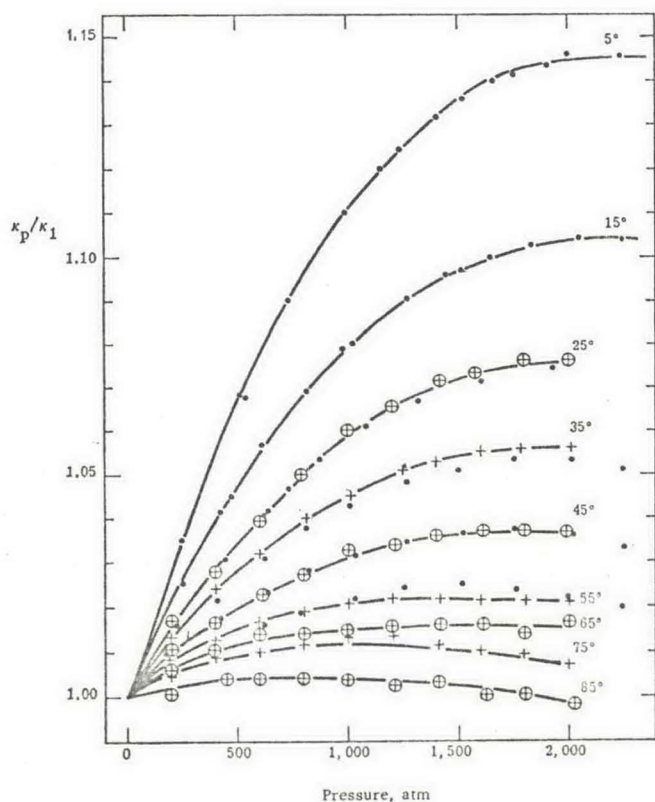


Figure 2. Conductance of KCl solutions at infinite dilution as function of pressure

⊕, + Ovenden (27) ● Present work

is to disregard the relatively small concentration dependence and to take results at one concentration, say 10 mM (22). This procedure introduces a systematic pressure- and temperature-dependent error at infinite dilution (0.35% at 25°C and 2000 atm for NaCl) (9).

The most careful work to date is that of Ovenden (27). Figure 2 compares our infinite dilution data with those of Ovenden for KCl. Agreement is excellent—typically 0.1% and never worse than 0.2%—contrasted with previous disagreements in the literature, even at high concentrations as discussed by Ellis (7), Hamann (10), and Horne et al. (22).

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