

# A New Flow Instrument for Conductance Measurements at Elevated Temperatures and Pressures: Measurements on NaCl(aq) to 458 K and 1.4 MPa

G.H. Zimmerman · Philip W. Scott · Wendy Greynolds

Received: 16 October 2006 / Accepted: 7 December 2006 /

Published online: 5 May 2007

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**Abstract** A new flow electrical conductance instrument was constructed and tested on dilute NaCl solutions up to 458 K, and on more concentrated solutions (maximum  $0.436 \text{ mol}\cdot\text{kg}^{-1}$ ) at 373 K. The results of the new instrument agreed with those of previous authors within the estimated experimental errors. The model of Bernard et al. (*J. Phys. Chem.* **96**, 3833–3840 (1992), MSA) was found to represent the high-temperature results without introducing an ion-pairing equilibrium constant. The Fuoss–Hsia conductance equation as given by Fernandez-Prini was found to represent the dilute concentrations with  $\Lambda^\circ$  (NaCl) as the only adjustable parameter. It was found that  $\Lambda^\circ$  (NaCl) could be expressed as a function of solvent viscosity and density by using three parameters found by regression of literature results between 278.15 and 523 K. This equation along with the FHP theory permits the equivalent conductivity of dilute sodium chloride solutions to be calculated within the accuracy of the existing experimental measurements.

**Keywords** Conductivity · Flow-instrument · Aqueous solutions · High temperature · High pressure · Sodium chloride · Mean spherical approximation · Transport properties · Limiting equivalent conductances · Electrolytes

## 1 Introduction

There are many equilibrium constants at elevated temperatures and pressures for reactions that change the number of ions in solution that have yet to be determined [1]. The flow electrical conductance technique has been proven to accurately determine equilibrium constants for systems such as these [1–11]. These facts motivated us to build a new high-temperature ( $\sim 458 \text{ K}$ ) elevated pressure ( $\sim 1.8 \text{ MPa}$ ) flow-conductance instrument. Reported herein are

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G.H. Zimmerman (✉)

Department of Chemistry, Bloomsburg University, Bloomsburg, PA 17815, USA  
e-mail: gzimmerm@bloomu.edu

P.W. Scott · W. Greynolds

Department of Chemistry, Tennessee State University, Nashville, TN 37209, USA

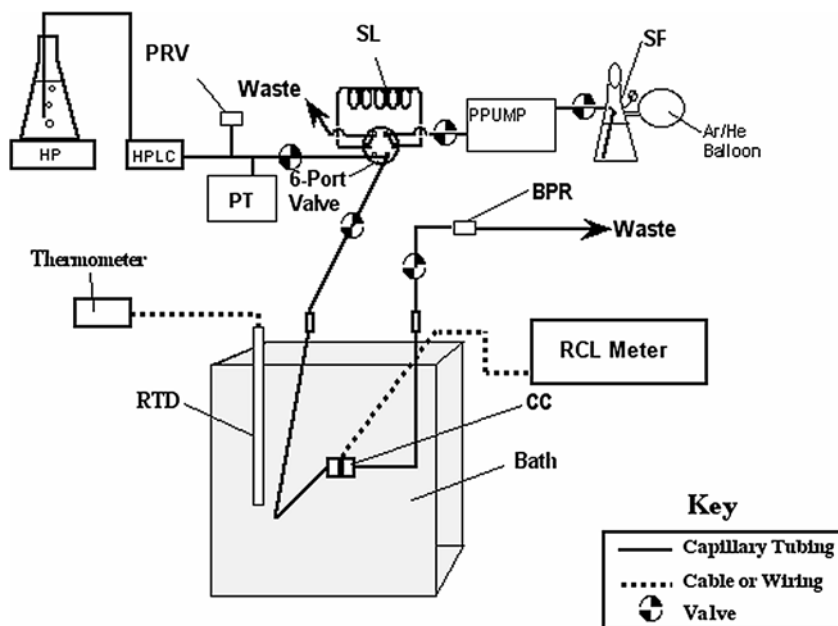
the details of the construction and operation of this instrument and conductance measurements on sodium chloride that by their good agreement with the results of others validate the accuracy of the new instrument. It was found that the MSA conductance model [12–14] was able to successfully model our results without the introduction of ion pairing. However, for more accurate room temperature measurements [15, 16], this model showed systematic errors unless ion pairing was introduced into the model. It was also found that the Fuoss–Hsia conductance equation as given by Fernandez-Prini (FHFP) [17, 18], was able to describe our dilute measurements with a single adjustable parameter. Finally, a three-parameter equation that expresses the equivalent conductance at infinite dilution,  $\Lambda^\circ(\text{NaCl})$ , as a simple function of the solvent viscosity and density is given that describes the existing results to 523 K.

## 2 Experimental

### 2.1 Instrument

There were two instruments built at two different places that were essentially identical. One of these was built at Tennessee State University (TSU) and the most recent at Bloomsburg University (BU). The schematic diagram shown in Fig. 1 is the instrument built at BU. Because it is similar to the flow instruments described in earlier work [5, 10, 19], the method of operation of the instrument was also similar.

Pure water (18 M $\Omega$ -cm from an Elga Ultra Pure Water system), which was boiled on a hot plate HP to remove gases, was continuously pumped with an HPLC pump (Constametric I)



**Fig. 1** Schematic of the flow-conductance instrument. *HP*, hot plate; *PRV*, pressure-relief valve; *HPLC*, high performance liquid chromatography pump; *PT*, pressure transducer; *SL*, sample loop; *PPUMP*, peristaltic pump; *SF*, solution flask; *RTD*, platinum resistance probe; *CC*, conductance cell; *BPR*, back-pressure regulator. Modified figure reprinted with permission from Ref. [10]. Copyright 1995, American Chemical Society

though the instrument. The water passed through a six-port HPLC valve (Rheodyne, 9010), through a series of tubing into the conductance cell CC in the temperature-controlled oil bath and finally through a back-pressure regulator BPR (250 psi, Upchurch P-788). All tubing connections to the six-port valve were short (about one inch) and made with PEEK tubing (polyether ether ketone, 0.063 in. o.d., 0.020 in. i.d.) with the exception of a two-foot section connecting the HPLC valve to Teflon-lined stainless steel (TFSS) tubing. The tubing before, after and in the hot zone was TFSS tubing (10 ft., 0.062 in. i.d., 0.125 in. o.d., Alltech), with the exception of a short piece of Pt/Rh tubing (80% Pt, 0.040 in. o.d., 0.020 in. i.d.) that was a part of the cell. The TFSS tubing was connected to the Pt/Rh tubing by placing a short Teflon tube that fit snugly over the Pt/Rh tubing and telescoped inside the TFSS-tubing. Tightening a stainless steel Swagelok nut with SS ferrules over the TFSS tubing, Teflon tubing and Pt/Rh tubing provided the high temperature seal. For the outflow tube, a Swagelok SS fitting was connected to the Pt/Rh outflow tube with a Vespel ferrule. The solution then came into contact with stainless steel, but the measuring electrodes were never exposed to contamination from this source.

The sample loop SL was constructed with two 50-foot sections of NO-OX tubing (Alltech). A pressure transducer PT (Heise DXD,  $\pm 0.02$  percent of full scale, 0–5000 psi) was used to measure the pressure continuously with a computer. A lower accuracy pressure gauge (not shown, Alltech,  $\pm 0.1$  percent of full scale, 0–1000 psi) was used as well to monitor the pressure when the computer was not turned on. A pressure-relief valve PRV was included and set between 350 and 750 psi to prevent damage to the instrument should a plug occur in the system.

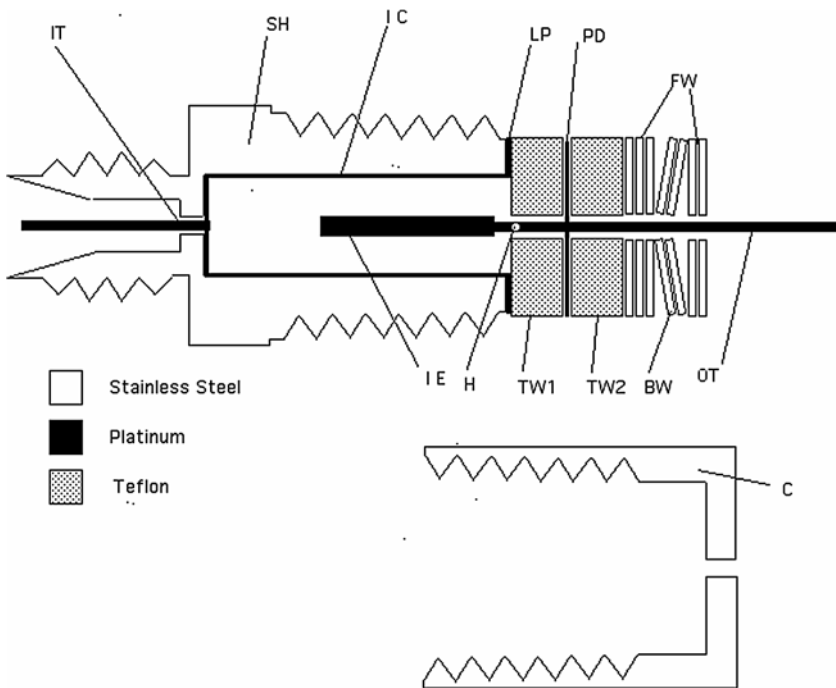
The conductance cell CC was immersed in a NESLAB Model EX-250 constant temperature bath. The manufacturer's stated constant temperature stability was  $\pm 0.01$  at 333 K and  $\pm 0.02$  at 523 K. This bath was filled with Dow Corning 710 fluid. This fluid was later replaced with Dynalene SF oil for measurements at 378 K.

The temperature was measured with a Hart 1502 thermometer with a Hart 5612 platinum resistance probe RTD. The Hart 1502 thermometer was calibrated with standards traceable to the National Institute of Standards and Technology (NIST) in accordance with ITS-90. When considering all of the estimated errors in the temperature measurements (resistance measurement, probe stability and calibration, and bath stability) it is estimated that the overall temperature uncertainty was  $\pm 0.025$  at 273 K and  $\pm 0.04$  at 473 K.

The resistance measurements were measured with a programmable automatic RCL meter (Fluke Model PM 6304C). This instrument has an overall accuracy of 0.05 percent as given by the manufacturer.

The solution flasks SF were similar to those described Zimmerman [19] except that the graded glass to metal seal was replaced with a glass arm. The connection of the PEEK tubing to the flask was done with Swagelok fittings (stainless steel) using Teflon ferrules. The peristaltic pump PPUMP (MasterFlex with drive 7520-60 LS and pump head 07014-20) with Viton tubing was used to fill the sample-loop with the solution to be measured.

The differences between the instrument at TSU and BU were as follows. The pressure gauge used (Omega) had an accuracy given from the manufacturer as  $\pm 0.1$  MPa. The RTD used to measure the temperature of the CC (concentric cylinder) cell was a Burns Platinum Resistance Probe (model 12001). Its expanded uncertainty was  $\pm 0.006$  K and it was calibrated to the International Temperature Scale of 1990 (ITS-90). A peristaltic pump was not used to fill the sample loop. Instead the sample loop was filled by withdrawing the solution with a syringe [10].



**Fig. 2** Schematic of the concentric cylinder conductance cell and cap, *C*. *SH*, stainless steel housing; *IC*, inner cup; *LP*, inner cup lip; *IT*, in-flow tube; *IE*, inner electrode; *H*, holes for out-flow; *PD*, platinum disk; *TW1* and *TW2*, Teflon washers; *FW*, flat washers; *BW*, Belleville washer springs

## 2.2 Conductance Cell

Figure 2 shows a schematic diagram of the conductance cell. The SS housing (*SH*) was made from a Swagelok fitting (part number SS-200-1-4), in which the male 1/4 in. NPT pipe-fitting was drilled out to a diameter of 0.250 in. to a depth of 11/16 in. with the bottom of the hole made flat. The inner cup (*IC*), which served as one electrode, was made from pure platinum sheet (11/16 long, 0.850 in. wide, 0.005 in. thick). The sheet was first annealed by heating to a cherry-red color with a torch. This sheet was shaped around a drill bit (15/64 in.) with a short overlap and then slid into the SS housing (*SH*) to insure a snug fit. A strip of pure gold (about 2 mm wide, 0.5 mm thick) was then laid in the seam and heated with a small torch to seal the walls of what now was a Pt tube. A pure Pt ring (3/8 in. o.d. and 1/4 in. i.d., 0.020 in. thick) made with a punch from a Pt disk (3/8 in. o.d.) was gold soldered to one end of the Pt tube to form a lip (*LP*) that would rest on the SS housing. The center punched out from the Pt disk (1/4 in. o.d.) was used to make the other end of the cup. A center hole (0.040 in.) was drilled in this disk to which a short piece of tubing (80% Pt, 20% Rh by mass, 1.0 mm o.d., 0.5 mm i.d.) was gold soldered. This disk was gold soldered to form the end of the cup by laying a gold ring (o.d. 1/4 in., i.d. 3/16 in., 0.5 mm thick) on the end and heating strongly with a torch. To prevent undoing the gold seam during this last gold weld, a drill bit (11/32 in.) was pushed about 3/4 of the way inside the cup to act as a heat sink. The SS housing *SH* had six holes drilled into the center on the hexagonal flats to relieve any pressure build-up should water become trapped between the inner cup and the stainless steel housing when going over 373 K. This idea was taken from the design of Noyes [20]. One

of these holes was larger (3/32 in.) and was the conduit for a short single electrical lead (24 gauge pure silver wire, not shown) that was melted on to the Pt/Rh in-flow tube. The length of this lead was 1.5 in., to which two pure silver wire leads were melted together and then covered with Teflon tubing.

The inner electrode IE was formed by tightly wrapping pure 0.005 in. thick Pt sheet with a width of 3/8 in. around the 0.040 in. o.d. Pt/Rh tubing that was about 2 in. long. The resulting diameter of this electrode was about 1/8 in. Both ends were gold-soldered. The tubing had two holes H on opposite sides about 1/16 in. from the inner electrode to allow the solution to flow out of the cell. The holes were not directly across from each other to retain strength of this section of tubing. A center hole of 0.040 in. was drilled into a disk of pure platinum (0.020 in. thick, 3/8 in. o.d.). This disk PD was gold-soldered perpendicular to the 0.040 in. o.d. Pt/Rh outlet tubing. Two Teflon washers TW1 and TW2 were used to seal the cell. These were 1/16 in. thick with an o.d. of 3/8 in. and i.d. of 3/16 in. Most recently, TW1 was only 0.030 in. thick, due to ease of fabrication with a Precision Brand punch. To close the cell, a SS cap C with 1/4 in. NPT threads (Swagelok part number SS-4-CP) was screwed on to the SS housing. This cap had a center hole of 3/32 in. drilled into the end to allow the outlet tube to pass through. To compress the Teflon seals, flat washers FW and two Belleville washer springs BW (Small Parts Inc. WSX-375/15, 3/16 in. i.d., 3/8 in. o.d.) were used as spacers. It was found that about a 3/4 turn past finger-tight was usually sufficient to seal the cell, although occasionally one of the Teflon washers got moved off-center when tightening, resulting in a leak. Conventional wisdom dictates that a “good” seal was attained when there were no detectable leaks when flowing water through the cell at 500 psi at room temperature. A Teflon sleeve (not shown) was slid over the Pt/Rh tubing between the flat and Belleville washers to electrically insulate the inner electrode should one of the washers become off-center during assembly. Two leads made from 24-gauge pure silver wire were welded on to the outlet Pt/Rh tubing. This along with the other dual lead connection permitted a four-lead resistance measurement. A lead correction for both short single-lead connections (0.0107  $\Omega$  at room temperature) was applied to the measurements and was negligible for all except the very highest solution concentrations. The change of resistance with temperature was calculated from known temperature coefficients. This total lead correction was at most one percent of the measured resistance in the worst case. All leads were covered with Teflon tubing to prevent any electrical contact with each other or the SS bath walls. There was some concern that putting the cell into the bath oil might somehow introduce an error into the measurements. To check this, some solutions were measured at room temperature with the cell in the bath. Immediately after this measurement, the cell was removed from the bath and another measurement made with the cell in air on the same solution. The only differences seen in the measurements were attributable to the temperature differences between the bath and the air. Additionally, the agreement between our results in this paper with those of other authors is further proof that the bath oil did not introduce significant error.

### 2.3 Methods

The method used was largely that of Zimmerman et al. [10, 19] with a few modifications. Pure water (18 M $\Omega$ ·cm) was first introduced into the flask that was previously filled with helium or argon and then weighed. The flask was then connected to the peristaltic pump that was used to pump pure water into the sample loop. A volume equal to three times the sample loop volume was found to sufficiently rinse the sample loop of the previous solution. To bring the filled sample loop to the pressure in the conductance cell, a valve

between the HPLC valve and conductance cell was closed and the HPLC valve immediately switched to the inject position. This temporarily resulted in pumping on a closed system that included the sample loop. The operator then waited for the pressure to rise to the pressure in the cell, at which time the valve was opened allowing the sample to flow into the cell. A stable impedance was observed for pure water after 45 minutes whereupon resistance of the solvent was measured. During this waiting period, the next solution was prepared in the solution flask in the solvent just measured. To do this, the solvent flask was disconnected from the peristaltic pump and weighed to the nearest 0.1 g. A stock solution of known molality was injected into the solution flask using a polyethylene syringe as a weight burette weighed to the nearest 0.0001 g. After stirring well with a magnetic stirrer, the solution flask was reconnected to the system. After the impedance was measured, the HPLC valve was returned to the load position and the new solution was loaded into the sample loop and the pre-pressurization and injection process repeated. For each subsequent solution, the time required for constant impedance became shorter with the most concentrated solutions requiring only 28 minutes. Generally, up to six solutions were prepared and measured in a day. A few measurements were made on the stock solutions themselves. In these cases, the solutions were loaded directly from a flask open to the atmosphere.

There were short-term periodic fluctuations in the impedance measurements due to pressure changes that occurred during the experiments. The pressure dropped up to 0.4 MPa each time the back-pressure regulator opened. There were also instances of pressure fluctuations of  $\pm 0.2$  MPa when only one side of the dual piston HPLC pump was working. The average impedance was used, because of these fluctuations. For pure water, the deviation of this average within a five-minute period was usually less than 0.5%. For a given solution, the deviation of this average over a five-minute period was only 0.1% in the worst case. Very dilute solutions had larger deviations than the more concentrated solutions.

The flow rate was  $0.5 \text{ mL}\cdot\text{min}^{-1}$  for all experiments, except for some temperature equilibration experiments. In these experiments the flow rate was increased to  $0.75 \text{ mL}\cdot\text{min}^{-1}$  and impedance measurements were made. The results at the faster flow rate agreed with those at the slower flow rate to 0.1% or less at all temperatures, indicating that the solutions were reaching thermal equilibrium. During the course of a series of experiments (about eight hours) the temperature generally did not change more than a few hundredths Kelvin.

For each solution, measurements were usually made at 10, 8, 5, 4, 2, 1, 0.5, 0.2 and 0.1 kHz, but the lowest three frequencies were not used in the extrapolation.

## 2.4 Cell Constants

The solutions used to determine the cell constants at BU were prepared using certified ACS grade KCl (Fisher Scientific) which was recrystallized three times from pure water and dried for four days at 523 K. The molalities of these solutions prepared by mass were 0.04134 and  $1.411 \text{ mol}\cdot\text{kg}^{-1}$ . The solutions used at TSU were prepared from KCl (Baker Analyzed reagent) which was recrystallized three times from pure water and then dried for two days at 573 K. The molalities of these solutions prepared by mass were 0.03912 and  $1.480 \text{ mol}\cdot\text{kg}^{-1}$ . All masses were corrected for buoyancy. The water used was first purified by reverse osmosis and then passed through two ion-exchange columns and one activated carbon cartridge. This water had a resistivity of  $18 \text{ M}\Omega\cdot\text{cm}$ . Since better temperature control was possible at 308 K, and this temperature is above a solid phase transition of Teflon at 298 K [21], the cell constant was usually determined at this temperature. The equation used at 308 K, obtained from regression of the KCl results at 308.15 K of Gunning and Gordon

[22] with the corrections given by Benson and Gordon [23], was found to be

$$\Lambda = 180.52 - 117.76c^{1/2} + 328.44c - 653.56c^{3/2} + 31.950c \ln c \quad (1)$$

where the units are in  $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ . The standard deviation of the fit was 0.016. This equation gives a value to within 0.08% of the conductance of a 0.01 Demal KCl solution reported by Wu and Koch [24] without applying any of the small corrections such as different temperature scales. The densities required for the conversion between the molality and molarity were calculated from Sohnel and Novotny [25]. The equation given by Justice [26] as reported by Juhasz and Marsh [27] at 298.15 K was used to calculate temperature derivatives to correct for small differences between 308.15 K and the experimental temperatures. The equation given in Zimmerman and Wood [4] for the high-pressure results of Fisher and Fox [28] were used to calculate corrections when making measurements at higher pressures (up to about 1.8 MPa). This assumes that the pressure derivative at 308 K is the same as that at 298 K. The results of Gancy and Brummer [29] show that this approximation introduces negligible error in comparison with the other uncertainties. In all cases, the cell constant at high pressures agreed with those at room pressure within 0.1%. The precision of the cell constants determined using solutions of different concentrations agreed to within 0.1%, indicating that there was no significant Parker effect. The cell constant actually used was the room temperature value (nominally  $0.1 \text{ cm}^{-1}$ ) corrected for thermal expansion of the cell. This correction was at most 0.15% at the highest temperature. In one case KCl measurements were used to determine the cell constant at 298.15 K for the CC cell where the equation given by Justice [26] as reported by Juhasz and Marsh [27] was used. This cell constant was in general agreement with those determined at 308.15 K.

It was found in one case that after temperature cycling from 308 to 373 to 308 K in a period of two weeks, that the cell constant increased by about 1%. There was one more indication of changes in cell constant with time. A series of NaCl solutions at 378 K (reported herein) was compared to another series of NaCl solutions (not reported) measured about one year later at 378 K. The cell had been maintained at 378 K for the entire year with no change in temperature. The new measurements on NaCl(aq) contained a 2% systematic error across the entire concentration range in comparison with the measurements done a year earlier. This was attributed to a change in cell constant. A new cell constant was calculated at 378 K from the older measurements. This assumes that the first set of measurements was the most accurate. Immediately after this, the measurements at 429 and 458 K were performed, using this new cell constant. Changes in cell constants after temperature cycling with the concentric cylinder design have been seen before [1, 9, 10, 19], but this was the first time that the cell constant increased. Undetected changes in the cell constant are probably the largest source of error in these measurements.

## 2.5 Solutions

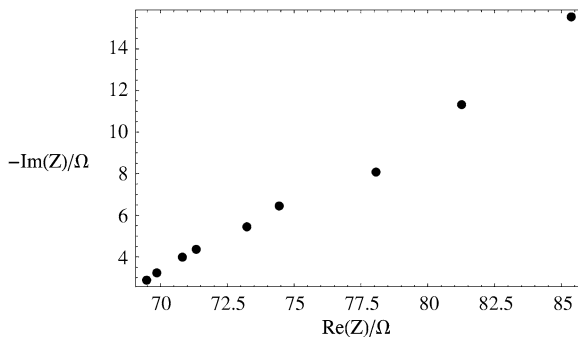
The solutions were prepared by mass from NaCl (Alfa Aesar, Purotronic, 99.999% pure, metals basis, Stock 10862, Lot # 22999) that was dried for two days at 623 K. The molalities of the solutions were 0.02915 and 0.7663 at BU and 0.03178 and  $1.341 \text{ mol}\cdot\text{kg}^{-1}$  (TSU). These were believed to be accurate to 0.1%.

## 2.6 Extrapolations to Determine the True Ohmic Resistance

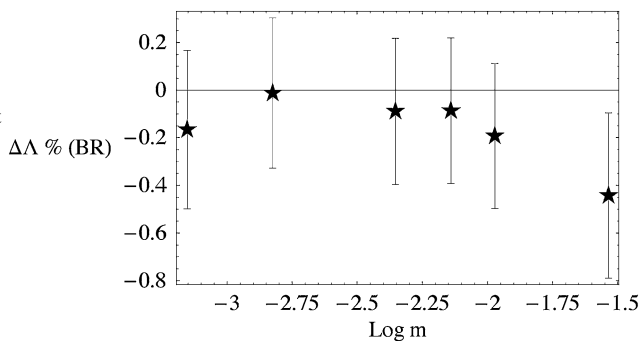
The recent work of Hnedkovsky et al. [3] used a different method than the traditional resistance versus  $f^{-1/2}$  extrapolation to find the true ohmic resistance of the solution ( $f$  is



**Fig. 3** Nyquist plot following [3]. The point farthest to the right is 100 Hz and that to the left is 10 kHz



**Fig. 4** Percent difference of the present experimental results ( $\Lambda_{\text{exp}}$ ) from the MSA conductance theory fitted to the results of [15] and [16],  $\Lambda_{\text{MSA}}$  at 308 K;  $\Delta\Lambda\%(\text{BR}) = 100(\Lambda_{\text{exp}} - \Lambda_{\text{MSA}})/\Lambda_{\text{MSA}}$



frequency). They used the linear portion of a Nyquist plot ( $-\text{Im}(Z)$  versus Real ( $Z$ ) where  $Z$  is the impedance). Figure 3 shows a Nyquist plot for one of our solutions at room temperature. The point on the lower left is at 10 kHz and that on the upper right is at 100 Hz. It is believed that the nonlinearity at low frequencies seen in Fig. 3 is because the lower frequency measurements (100, 200 and 500 Hz) for the higher concentrations were not constant with time. When changing the RCL meter to 100 Hz for one of these solutions, the measured resistance and capacitance (in parallel) immediately decreased with time. The instrument operator recorded these measurements as quickly as possible, but error was introduced. This effect was greater for the more concentrated solution, except it was not seen for the most concentrated solutions, ruling out self-heating as a possible reason for this increase. It was not detected at any frequency in the more dilute solutions. If we were to acquire our measurements quickly via computer (as did Hnedkovsky et al.) before this interfering process took place to an appreciable extent, it may be true that the new extrapolation method may be equal or better than the traditional method.

To check the accuracy of the traditional extrapolation method, the conductance equation (described later) based on the MSA [14] with the parameters  $\Lambda_0$  and  $K_A$  was fit to the highly accurate results at 308.15 K of Bester-Rogac et al. [15, 16] up to  $1.04 \text{ mol}\cdot\text{dm}^{-3}$ . The resulting equation reproduced their results to within 0.32%. The resulting equation was then used to calculate the molar conductivity  $\Lambda_{\text{MSA}}$  at the experimental molalities of the present results at 308 K. The quantity  $\% \Delta \Lambda (\text{BR})$  is the difference between our experimental results,  $\Lambda_{\text{exp}}$ , and that calculated from the fit equation based on the results of Bester-Rogac et al. in percent at the same molality:

$$\% \Delta \Lambda = 100(\Lambda_{\text{exp}} - \Lambda_{\text{MSA}})/\Lambda_{\text{MSA}}. \quad (2)$$



The fact that our experimental temperature differed slightly from that use in the fit equation based on the measurements of Bester-Rogac et al. is very small and was not taken into consideration. Figure 4 is a plot of  $\% \Delta \Lambda$  versus the log of molality. Clearly, for our results, the traditional extrapolation method gives good agreement with Bester-Rogac et al. within our expected experimental errors. Therefore, all of our reported  $\Lambda$  values were found by extrapolation of resistance versus  $f^{-1/2}$  using the frequencies between 1 and 10 kHz except for the concentrated solutions greater than  $0.011 \text{ mol} \cdot \text{kg}^{-1}$ , which had a stronger frequency dependency. For these solutions, the frequencies between 4 and 10 kHz were used.

### 3 Results

The specific conductivities,  $\kappa$ , ( $\text{S} \cdot \text{cm}^{-1}$ ) of the NaCl solutions are given in Table 1. The extrapolated resistance was corrected for lead resistance as well as the measured solvent conductance,  $\kappa_s$  (meas.), used to prepare each solution. The solvent corrections are given in Table 2. The series given in Tables 1 and 2 correspond to measurements made in the same solvent. Table 1 contains some measurements of stock solutions that were directly injected into the instrument (series b and m). These have no solvent correction applied because it was never measured. Since these were concentrated solutions, this introduces negligible error. The measured temperature, pressure and molality given in Table 1 were used to calculate the density of the solution,  $\rho_{\text{soln}}$ , from the equation of state of Archer [30] for aqueous sodium chloride. From the solution density, the concentration in  $\text{mol} \cdot \text{dm}^{-3}$  was calculated from the molality.

Table 1 also gives the total estimated error of  $\kappa$  in percent for each measurement. It is the sum of 5% of the measured solvent conductance correction, 20% of the measured lead correction and 0.3% of the measured specific conductance of the solution for solutions of less than or equal to about  $0.011 \text{ mol} \cdot \text{dm}^{-3}$ . For the more concentrated solutions another error estimate was added to account for the fact that the extrapolation of the resistance measured at the different frequencies became more uncertain because the measured resistance was lower. The total error estimates range between 0.31 and 1.4% for all of our measurements. Additionally, after the measurements were made at 429 and 458 K, it was discovered that the secondary component as measured by the RCL meter was an inductor, not a capacitor. This was unprecedented in our experience. This puzzle was not solved until several years later when one of us (GHZ) discovered that if an electrically uninsulated portion of the Teflon-lined stainless steel tubing touched the side of the stainless steel oil bath, an inductive component was introduced. This error was estimated to be about 0.10% at the lowest concentration measured and 1% at the highest concentration for a worst case scenario. The estimated errors given in Table 1 account for this. Earlier it was mentioned that the largest error in our measurements is likely due to an undetected change in the cell constant. Based on long-term cell constant changes with time that were found, it is believed that the maximum error introduced by a changed cell constant would be at most about two percent at 429 and 458 K, which is greater than the estimated errors from this unwanted inductor.

The precision of the instrument is dependent upon the concentration of the solution as well as the skill of the operator. Duplicate measurements for a very dilute concentration (series j,  $0.0001490 \text{ mol} \cdot \text{dm}^{-3}$ ) have a difference of 0.27%. Duplicate measurements for a concentrated solution (series h,  $0.2361 \text{ mol} \cdot \text{dm}^{-3}$ ) have a difference of 0.18%. Regressions of sets of these measurements (series g, j, k, o) with the FHPF equation indicate that when the instrument is used by a careful operator, the precision between 0.001 and  $0.008 \text{ mol} \cdot \text{dm}^{-3}$  is 0.15% or better. Many of the results at 373 K were done by BU undergraduate

**Table 1** Measured specific conductivities of sodium chloride solutions<sup>a</sup>

Series	Place	<i>T</i>	<i>p</i>	$\rho_{\text{soln}}$	$10^4 \times m$	$10^4 \times c$	$10^4 \times \kappa$	Est. error
a	BU	308.07	0.13	994.09	7.021	6.980	1.057	0.33
a	BU	308.07	0.13	994.12	14.96	14.88	2.230	0.32
a	BU	308.08	0.13	994.24	44.34	44.07	6.470	0.31
a	BU	308.05	0.13	994.36	72.40	71.96	10.44	0.31
a	BU	308.06	0.13	994.50	106.5	105.8	15.16	0.31
b	BU	308.07	0.12	995.24	291.5	289.6	39.83	0.35
c	BU	373.12	1.82	959.21	3.145	3.017	1.086	0.38
d	BU	373.11	1.85	994.05	4.323	4.147	1.480	0.34
d	BU	373.11	1.79	994.09	8.983	8.616	3.031	0.32
d	BU	373.10	1.78	994.12	20.79	19.94	6.944	0.31
e	BU	373.12	1.79	986.56	11.97	11.81	4.024	0.33
e	BU	373.12	1.79	986.61	24.97	24.63	8.281	0.32
f	BU	373.12	1.79	959.22	8.719	8.363	2.944	0.32
f	BU	373.13	1.79	959.26	22.80	21.87	7.578	0.31
f	BU	373.12	1.79	959.36	44.92	43.08	14.78	0.31
g	BU	373.11	1.78	959.20	3.957	3.795	1.355	0.35
g	BU	373.12	1.78	959.21	8.953	8.588	3.018	0.32
g	BU	373.12	1.78	959.26	19.71	18.90	6.566	0.31
h	TSU	373.91	1.45	958.68	57.80	55.40	18.84	0.31
h	TSU	373.91	1.45	958.93	118.8	113.8	37.87	0.31
h	TSU	373.91	1.45	960.72	571.8	547.5	169.2	0.47
h	TSU	373.91	1.45	962.86	1117	1068	312.4	0.62
h	TSU	373.91	1.45	968.12	2474	2361	656.8	0.97
h	TSU	373.91	1.45	968.12	2474	2361	655.6	0.97
h	TSU	373.91	1.45	975.33	4364	4151	1103	1.42
i	BU	378.00	1.84	955.66	3.279	3.134	1.161	0.37
i	BU	378.00	1.84	955.68	6.782	6.481	2.373	0.33
i	BU	378.01	1.84	955.70	13.93	13.32	4.834	0.32
i	BU	377.99	1.85	955.86	48.07	45.93	16.37	0.31
j	TSU	378.18	1.45	955.34	1.560	1.490	0.5651	0.40
j	TSU	378.18	1.45	955.34	1.560	1.490	0.5669	0.40
j	TSU	378.18	1.45	955.36	7.230	6.907	2.548	0.32
j	TSU	378.21	1.45	955.31	28.72	27.44	9.862	0.31
j	TSU	378.19	1.45	955.57	60.38	57.68	20.39	0.31
j	TSU	378.18	1.45	955.68	87.31	83.40	29.11	0.31
k	TSU	378.19	1.45	955.51	44.41	42.43	15.10	0.31
k	TSU	378.18	1.45	955.77	109.2	104.3	35.95	0.31
k	TSU	378.18	1.45	958.25	735.1	701.4	221.5	0.53
k	TSU	378.19	1.45	963.69	2128	2026	601.2	0.91
k	TSU	378.18	1.45	967.49	3114	2959	863.2	1.18
m	TSU	378.18	1.45	956.61	317.8	303.5	101.4	0.40
n	TSU	429.29	1.38	911.72	1.867	1.704	0.951	0.54
n	TSU	429.29	1.38	911.73	3.845	3.505	1.924	0.57

**Table 1** (Continued)

Series	Place	$T$	$p$	$\rho_{\text{soln}}$	$10^4 \times m$	$10^4 \times c$	$10^4 \times \kappa$	Est. error
n	TSU	429.30	1.38	912.00	6.580	6.000	3.260	0.64
n	TSU	429.30	1.38	911.97	61.48	56.05	29.15	0.91
n	TSU	429.30	1.38	912.24	123.1	112.1	57.09	1.31
o	TSU	458.20	1.38	881.81	1.904	1.679	1.112	0.71
o	TSU	458.19	1.38	881.82	3.946	3.480	2.259	0.50
o	TSU	458.20	1.38	881.82	6.092	5.372	3.455	0.50
o	TSU	458.19	1.38	881.94	29.19	25.74	16.00	0.44
o	TSU	458.20	1.38	882.19	82.57	72.81	43.97	0.72

<sup>a</sup>Units:  $T$ , K according to IPTS-90;  $p$ , MPa;  $m$ , mol·kg<sup>-1</sup>;  $\rho_{\text{soln}}$ , kg·m<sup>-3</sup>, the density of the solution as calculated from Archer [30];  $c$ , mol·dm<sup>-3</sup>;  $\kappa$ , S·cm<sup>-1</sup>, corrected for the solvent and leads; Est. error is the estimated error of  $\kappa$  in percentage

**Table 2** Solvent conductivity at the average temperature and pressure in the present results<sup>a</sup>

Series	Place	$T$	$p$	$\rho_s$	$10^6 \times \kappa_s$ (meas.)	$10^6 \times \kappa_s$ (pure)
a	BU	308.06	0.13	994.06	0.69	0.090
b	BU	308.07	0.12	994.06	–	0.090
c	BU	373.12	1.82	959.20	1.76	0.767
d	BU	373.11	1.85	959.22	1.25	0.766
e	BU	373.12	1.79	959.18	2.43	0.766
f	BU	373.12	1.79	959.18	1.25	0.766
g	BU	373.11	1.78	959.18	1.27	0.766
h	TSU	373.91	1.45	958.45	2.25	0.777
i	BU	378.00	1.84	955.65	1.57	0.863
j	TSU	378.18	1.45	955.33	1.15	0.865
k	TSU	378.19	1.45	955.33	1.17	0.865
m	TSU	378.18	1.45	955.33	–	0.865
n	TSU	429.29	1.38	911.72	2.59	1.81
o	TSU	458.20	1.38	881.80	3.41	2.32

<sup>a</sup>Units as in Table 1. In addition,  $\rho_s$  is in kg·m<sup>-3</sup> and was calculated according to Hill [36];  $\kappa_s$  (meas.) is the measured solvent conductance and  $\kappa_s$  (pure) is that calculated from Eq. 3. The solvent was not measured for Series b and m because these were stock solutions

students as a part of the physical chemistry lab course (series c, d, e and f). There is usually more scatter ( $\pm 0.3\%$ ) in these measurements, using the FHFP regressions as a precision estimator.

There are some measurements that are not reported in Table 1 because of leaks. Small leaks at high temperatures were not easy to detect because the bath oil becomes full of air bubbles prohibiting vision of the cell. However, in the course of gaining experience with the instrument, three indicators of a leak at high temperatures were found: (1) absurdly low values of the resistance of the solvent if the temperature of the instrument was dropped just below 373 K (1 k $\Omega$  when it should be around 60 k $\Omega$ ); (2) an increased frequency dependence for a given solution when a leak was present; and (3) increased short-term fluctuations of

the measured resistance. If the leak was very small, it was found that accurate measurements could still be made of dilute solutions, presumably because the solvent evaporates away, and the residual salt does not conduct.

The measured solvent conductance given in Table 2 also contain the conductance of pure water if there was no contamination as calculated by the following equation

$$\kappa_s(\text{pure}) = \sqrt{K_w} \rho_s [\lambda^\circ(\text{H}^+) + \lambda^\circ(\text{OH}^-)] \quad (3)$$

where  $K_w$  is the ion product of water. The equation of Harned and Robinson as given by Robinson and Stokes [31] was used to calculate  $K_w$  at all temperatures. The values for the molar conductance at infinite dilution were taken or estimated from Robinson and Stokes [31] at temperatures of 378 K and lower. At the higher temperatures, the reduced density relationship of Marshall was used [32]. The  $\kappa_s$  (meas) values of the new instrument are comparable with those of previous flow instruments [3, 4].

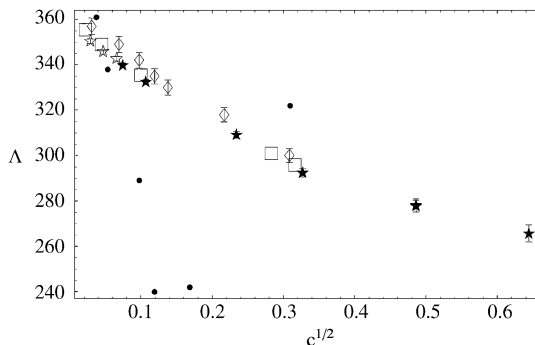
## 4 Discussion

### 4.1 Comparison with other Authors

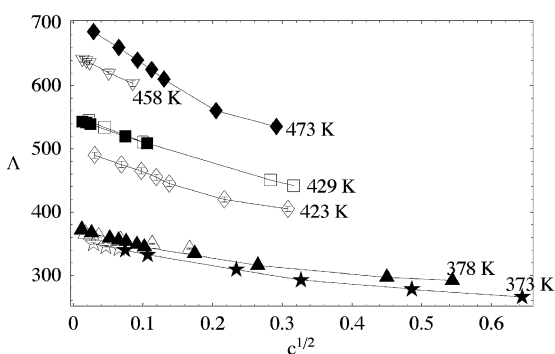
Figure 5 shows selected results (series f at BU and series h at TSU) at 373 K along with those of other authors. The measurements in Table 1 not on the graph differ from those plotted by at most 0.3% and are omitted for clarity. The present results of the two different instruments (BU and TSU) blend together. The agreement with the remarkable time-tested measurements of Noyes [20] is excellent. There is also very good agreement with the measurements of Quist and Marshall [33]. The results of Ho et al. [34] have obvious errors of unknown origin. The strange concentration dependence shown in Fig. 5 also exists in the reported NaCl results of Ho et al. at the other densities at 373 K, 473 K as well as some anomalies at 573 K. Perhaps there are typographical errors in the reported measurements. Measurements reported from this laboratory with a newer flow instrument show the expected concentration dependence at the lowest reported temperature of 523 K.

Figure 6 shows selected results at high temperatures with the points connected to aid the eye. For comparison, the results of Noyes [20] at 429 K are also reported. There is agreement with our results and Noyes within our estimated errors. This graph also shows the results of Quist and Marshall [33] at 423 and 473 K. When comparing all of these results, it is seen that as the temperature increases, the slope of the curves in the dilute region also increase.

**Fig. 5** Molar conductivity of NaCl solutions at 373 K versus  $c^{1/2}$ . ☆, Series f; ★, Series h; □, Ref. [20]; ◇, Ref. [33]; ●, Ref. [34]



**Fig. 6** Equivalent conductivity of NaCl solutions at several temperatures versus  $c^{1/2}$  either at or close to the saturation vapor pressure. ☆, Series f; ★, Series h; △, Series i; ▲, Series j, k, m; ◇, Ref. [33]; □, Ref. [20]; ■, Series n; ▽, Series o; ◆, Ref. [33]



## 4.2 Data Analysis

Two models (FHFP and MSA) were fit to the present results using a weighted least-squares regression program. The weights used in the regression, given as a percent in Table 1, were  $1/\sigma^2$  where  $\sigma$  was the estimated absolute error. To correct for small temperature and pressure fluctuations, derivatives of  $\lambda^\circ$  with respect to temperature at constant density and with density at constant temperature were used as done previously [4, 10]. These derivatives were calculated from the reduced density relationship given by Marshall [32]. An initial screening by preliminary fits indicated that measurements in series i were discordant with the other measurements by greater than 1%. The slope of a graph of  $\Lambda$  versus  $c^{1/2}$  for this series also was noticeably different in comparison with the other measurements. This series was therefore not included in any of the final reported fits.

Properties of water were required for these calculations. For the dielectric constant of water, the equations given by Archer and Wang [35] were used that are built on the equation of state for water given by Hill [36]. For the viscosity of water, the equations given by Sengers and Kamgar-Parsi were used [37].

The FHFP model expresses the concentration dependence of the specific conductivity for a strong electrolyte as:

$$\kappa = c\Lambda = c(\Lambda^\circ - Sc^{1/2} + Ec \ln c + J_1c + J_2c^{3/2}) \quad (4)$$

where  $c$  is the concentration,  $\Lambda^\circ$  is the equivalent conductance of the electrolyte at infinite dilution, and  $S$ ,  $E$ ,  $J_1$  and  $J_2$  are calculated using the equations following Fernandez-Prini [17, 18]. For the present low-concentration results ( $c_{\max} \sim 0.011 \text{ mol}\cdot\text{dm}^{-3}$ ),  $\Lambda^\circ$  was the only adjustable parameter required. No advantage was found by adjusting  $J_1$  or  $J_2$  or adding an equilibrium reaction involving ion-pair formation,  $K_A$ . The analytical expressions [18] for  $J_1$  and  $J_2$  with the distance of closest approach set equal to the Bjerrum distance  $q$  following Justice [26] successfully model the present low-concentration results. This can be seen by comparing the AAD (average absolute deviation in percent) of the regressions given in Table 3 with the estimated errors given in Table 1.

Figure 7 shows a graph of  $\% \Delta \Lambda$  (res)

$$\% \Delta \Lambda(\text{res}) = 100(\Lambda_{\text{exp}} - \Lambda_{\text{fit}})/\Lambda_{\text{exp}} \quad (5)$$

for the FHFP model versus the log of the concentration for our results at 429.3 and 458.2 K. In our experience, the FHFP equations successfully model high-temperature conductivity measurements at low concentrations without systematic residuals. It is therefore concluded

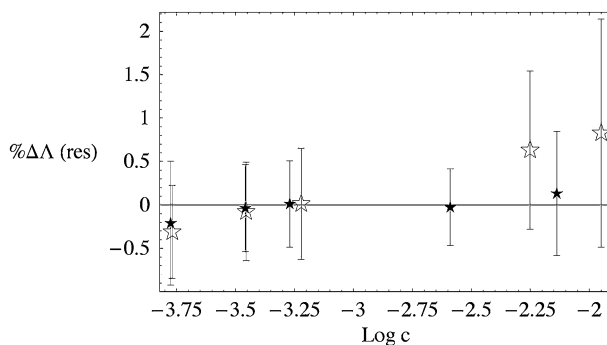
**Table 3** Fit parameters for sodium chloride<sup>a</sup>

<i>T</i>	<i>p</i>	$\rho_s$	$c_{\max}$	Theory	$\Lambda^\circ$ (NaCl)	<i>d</i>	<i>AAD</i>	$K_A$
308.07	0.13	994.1	0.01058	FHFP	153.54 ± 0.14	0.362	0.06	
308.07	0.13	994.1	0.02896	TBBK	153.19 ± 0.36	0.279	0.17	
308.07	0.13	994.1	0.02896	TBBK	153.52 ± 0.19	0.279	0.05	0.35 ± 0.15
308.15 <sup>b</sup>	0.12	994.0	1.044	TBBK	153.64 ± 0.07	0.279	0.12	0.18 ± 0.03
373.23	1.75	959.1	0.01138	FHFP	360.57 ± 0.52	0.404	0.18	
373.41	1.67	958.9	0.4151	TBBK	360.22 ± 0.55	0.279	0.28	
378.19	1.45	955.3	0.01043	FHFP	374.91 ± 0.83	0.407	0.18	
378.19	1.45	955.3	0.01043	TBBK	374.43 ± 0.98	0.279	0.23	
378.19	1.45	955.3	0.2959	TBBK	374.86 ± 1.20	0.279	0.64	
378.19	1.45	955.3	0.2959	TBBK	373.85 ± 1.06	0.391	0.42	
429.30	1.38	911.7	0.01122	FHFP	551.65 ± 2.54	0.454	0.37	
458.20	1.38	881.8	0.007281	FHFP	651.92 ± 0.97	0.489	0.08	

<sup>a</sup>Units as in Tables 1 and 2. In addition, *d* is the Bjerrum distance (*q*) for the FHFP equation and the sum of the hard sphere radii ( $\sigma_{\text{HS}}$ ) for TBBK in nm. *AAD* is the average absolute deviation from the fit in percent. The errors for  $\Lambda^\circ$  and  $K_A$  are the 95% confidence level estimate

<sup>b</sup>The results of Bester-Rogac et al. [15, 16]

**Fig. 7** Percent deviation of the measured conductivities from the FHFP fit % $\Delta\Lambda$ (res) versus the log of the concentration. The error bars are the estimated experimental errors from Table 1. ☆, Series m at 429.3 K; ★, Series o at 458.2 K



that while there is good agreement with Noyes at 429.3 K, the systematic error in our measurements was due to the effect of the inductor discussed earlier. The fit is much better at 458.2 K where the residuals are somewhat more random and not larger than 0.22%.

One limitation of the FHFP theory is that it is accurate only to about 0.01 mol·dm<sup>-3</sup> at room temperature and some of our concentrations are as high as 0.4 mol·dm<sup>-3</sup>. The model put forth by Bernard et al. was therefore chosen because it has been shown to fit conductance measurements to much higher concentrations [12–14, 16]. The equivalent conductivity for an ion  $\lambda_i$  is given by

$$\lambda_i = \lambda_i^\circ \left( 1 + \frac{\delta v_i^{\text{el}}}{v_i} \right) \left( 1 + \frac{\delta X}{X} \right) \quad (6)$$

where  $\lambda_i^\circ$  is the equivalent conductivity at infinite dilution for an ion,  $\delta v_i^{\text{el}}/v_i$  is the electrophoretic term and  $\delta X/X$  is the relaxation term. This is the same starting point as in the Fuoss–Hsia conductivity equation, but the derived expressions for these terms are based on

the mean spherical approximation (MSA). The specific expressions for these two terms can be found in the original papers [12], with important misprints given in Sharygin et al. [1] and Bianchi et al. [38]. The essence of this equation is that the relaxation and electrophoretic terms can be calculated by supplying ionic radii,  $\lambda_i^o$  and the dielectric constant and temperature of the solvent. In the treatment of conductivity measurements,  $\lambda_i^o$  is a fit parameter. For sodium chloride, Kohlrausch's additivity law is applied:

$$\Lambda^o(\text{NaCl}) = \lambda^o(\text{Na}^+) + \lambda^o(\text{Cl}^-) \quad (7)$$

so that the fit parameter reported is for the salt NaCl.

When association is included in the model, the thermodynamic equilibrium constant  $K_A$  (1 mol·kg<sup>-1</sup> standard state) is given by

$$K_A/\rho_s = \frac{c(\text{NaCl})}{c(\text{Na}^+)\gamma(\text{Na}^+)c(\text{Cl}^-)\gamma(\text{Cl}^-)}. \quad (8)$$

The activity coefficient model required according to the MSA is

$$\ln \gamma_i = \ln \gamma_i^{\text{el}} + \ln \gamma_i^{\text{hs}} \quad (9)$$

where  $\gamma_i^{\text{el}}$  is the Coulombic contribution and  $\gamma_i^{\text{hs}}$  is the hard-sphere contribution. The Bjerrum distance was used in the Coulombic contribution for the MSA activity coefficient model as was done by Sharygin [1]. The expressions for each of these terms can be found in Turq et al. [14].

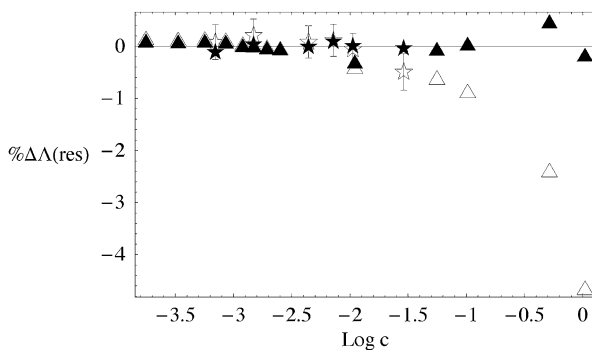
Some observations from preliminary fits with the MSA model were: (1) the sum of the hard-sphere radii,  $\sigma_{\text{HS}}$ , giving the best fit was sometimes smaller than the sum of crystallographic radii (sodium ion, 0.098 nm; chloride ion, 0.181 nm taken from Bernard et al. [12]); (2) the hard-sphere radii giving the best fit increased as the highest concentration included increased; and (3) at the higher temperatures if  $K_A$  was included in the model, its converged value was somewhat correlated with the choice of the value of the hard-sphere radius. These first two observations are in agreement with Bianchi et al. [38]. It was also found that when assuming the solutions were completely dissociated and choosing the crystallographic radii, about 70% of our results were modeled within the estimated errors of the measurements. The fit parameters for these regressions with no  $K_A$  using the crystallographic radii are given in Table 3.

Table 3 also contains some calculated results for regressions with a  $K_A$  as well as using radii larger than the crystallographic one. At 308 K, the introduction of  $K_A$  into the model resulted in a better fit as shown in Table 3. The reason for this increase becomes apparent when examining the residuals. These are shown in Fig. 8 as a percent deviation  $\% \Delta \Lambda$  (res) versus the log of the concentration. This plot also contains the same calculation for the highly accurate results of Rogac-Bester et al. [15, 16]. All the open symbols are the residuals with no  $K_A$  in the model that systematically increase with concentration. Adding a  $K_A$  improves the fit dramatically. Clearly, the MSA model begins to have a systematic error at the higher concentrations when no  $K_A$  is included.

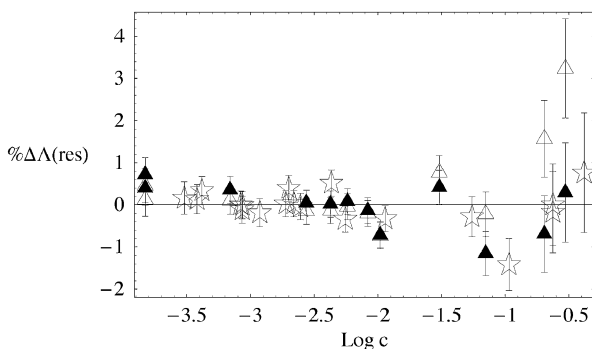
Figure 9 shows a graph of  $\% \Delta \Lambda$  (res) for the MSA model versus the log of the concentration for our 373 and 378 K results. The MSA model does fit our experimental results within our estimated error for most of our measurements with most of the exceptions occurring at the higher concentrations. All of the open symbols are the residuals when using the crystallographic radii. By increasing the value of the sum of the radii to 0.391 nm, a better fit was obtained at 378 K. This had a similar effect in the fit as adding  $K_A$  at 308 K. At



**Fig. 8** Percent deviation of the measured conductivities from the MSA fit,  $\% \Delta \Lambda(\text{res})$  versus the log of the concentration at 308 K using the crystallographic radii sum (0.279 nm). The error bars are the estimated experimental errors from Table 1. ☆, Series a and b no  $K_A$ ; ★, Series a and b with  $K_A$ ; △, Ref. [15] and [16], no  $K_A$ ; ▲, Ref. [15] and [16] with  $K_A$



**Fig. 9** Percent deviation of the measured conductivities from the MSA fit,  $\% \Delta \Lambda(\text{res})$  versus the log of the concentration at 373 and 378 K. The error bars are the estimated experimental errors from Table 1. ☆, Series c through h at 373 K using crystallographic radii; △, Series j, k and m at 378 K using crystallographic radii (0.279 nm); ▲, Series j, k and m at 378 K using radii sum = 0.391 nm



373 K, however, the fit was essentially insensitive to changes in the value of the sum of the radii. It was disappointing that adding  $K_A$  to the model did not significantly improve the fits at 373 and 378 K like it did at 308 K, and is curious because one would expect to have more association at the higher temperature. This is attributed to lower accuracy of the results at the higher temperatures and concentrations over those reported at 308 K.

#### 4.3 Calculating $\Lambda^\circ$ (NaCl) to Elevated Temperatures and Pressures

The result that the FHFP equation successfully models  $\Lambda$  as a function of concentration at elevated temperatures by using the theoretical expressions for  $J_1$  and  $J_2$  with the Bjerrum distance has an important ramification: if an equation for  $\Lambda^\circ$  (NaCl) as a function of state variables or water properties were available, fairly accurate molar conductances for dilute sodium chloride solutions could be calculated rather easily at elevated temperatures and pressures. There are at least two equations capable of this [32, 39]. These formulations are designed to predict  $\Lambda^\circ$  to very high temperatures and pressures (1073 K and 1000 MPa), but do not usually reproduce the lower temperature results to within the estimated errors. They also have many parameters. Our goal was to cover a smaller range that would predict  $\Lambda^\circ$  (NaCl) to within the estimated accuracy of the existing sodium chloride results.

It was found that by making one modification to an equation that described  $\Lambda^\circ$  (NaOH) between 288.15 and 348 K [21], a simple three-parameter equation fulfilled this goal. Equation 10 successfully describes the existing reported results between 278 and 523 K, and 0.1 and 50 MPa.

$$\Lambda^\circ = 1.6473\eta^{(-0.87390-0.045992d_s)} \quad (10)$$

**Table 4**  $\Lambda^\circ$  (NaCl) data regressed to determine the parameters of Eq. 10<sup>a</sup>

Reference	$T_{\min}$	$T_{\max}$	$p_{\min}$	$P_{\max}$	Est. error	$n$	AAD	AAD Ref. [39]	AAD Ref. [32]
[41]	288.15	308.15	0.1	0.1	0.10	5	0.06	3.53	3.33
[42]	298.15	298.15	0.1	0.1	0.10	1	0.04	3.43	0.12
[15]	278.15	308.15	0.1	0.1	0.10	7	0.10	4.45	3.12
[43]	298.15	298.15	25.33	50.66	0.20	2	0.06	3.22	3.07
[29]	278.15	328.15	0.1	40.53	0.20	24	0.12	3.46	5.56
This work	308.07	458.20	0.13	1.75	0.86 <sup>b</sup>	5	0.40	2.08	2.31
[20]	373.15	491.15	0.102	2.24	1.67 <sup>c</sup>	3	0.84	2.30	1.54
[33]	373.15	523.15	0.102	100.6	5.0	5	2.16	2.69	1.59
[7]	523.15	523.15	10.05	10.05	3.0	2	1.90	1.80	1.48

<sup>a</sup>Units as in Table 1. In addition, Est. error is the average error assigned to each point in the set in percent;  $n$  is the number of data points; AAD is the average absolute deviation from the fit in percent

<sup>b</sup>The estimated errors assigned were 0.3, 1.0, 1.0, 1.0, 1.0 at temperatures of 308, 373, 378, 429, 458 K, respectively

<sup>c</sup>The estimated errors assigned were 1.0, 1.0, and 3.0 at 373, 429 and 491 K, respectively

In this equation,  $\eta$  is the viscosity of the solvent as calculated by Sengers and Kamgar-Parsi [37] in Poise,  $d_s$  is the density of the solvent as calculated by Hill [36] in  $\text{g}\cdot\text{cm}^{-3}$  and  $\Lambda^\circ$  (NaCl) is in units of  $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ . The constants in Eq. 10 were found by applying a weighted least-squares fit to the data summarized in Table 4. The weights assigned in the fit are given in Table 4 as “Est. error”.

We should note that Gancy and Brummer [29] reported polynomials as a function of pressure to calculate the ratio of specific conductivities,  $\kappa_p/\kappa_1$ , where the subscripts are the pressures in atmospheres. To calculate  $\Lambda^\circ$  (NaCl) at pressure  $p$  requires densities at the pressure  $p$ , and  $\Lambda^\circ$  (NaCl) at 1 atmosphere [40]. The results of Gordon and coworkers [22, 23] as reported by Robinson and Stokes [31] were used for  $\Lambda^\circ$  (NaCl) at the temperatures of Gancy and Brummer, and the Hill equation of state was used for the densities [36]. The results of Gordon and coworkers, while not directly listed in Table 4, were therefore included in the fit.

It can be seen in Table 4 that the absolute average deviation in percent of the fit is less than the assigned weights for all data sets. The few points that had deviations larger than the assigned weights were at the extremes of the data sets (for example, Gancy and Brummer at 278.15 and 328.15 K and 40.53 MPa). It was not possible to include the results of Gancy and Brummer with pressures greater than 40 MPa without adding more parameters, so for pressures greater than 40 MPa between 278 and 328 K, their polynomials should be used rather than Eq. 10. The maximum pressures at 373 K and higher temperatures were usually between 50 and 65 MPa with the exception of one point at 100 MPa at 373 K. It is therefore recommended that Eq. 10 not be used for pressures greater than 50 MPa.

For comparison purposes, Table 4 also includes the average absolute deviation in percent between the values of  $\Lambda^\circ$  (NaCl) used and those calculated from the equations given by Oelkers and Helgeson and that of Marshall. Equation 10 reproduces the data much better than either of these equations for the low temperatures. The ability of Eq. 10 to reproduce the data decreases as the temperature increases, whereas both the Oelkers and Helgeson and the Marshall equations improve as the temperature increases. At around 523 K, Eq. 10 is no

**Table 5**  $\Lambda^\circ$  (NaCl) calculated from Eq. 10<sup>a</sup>

<i>T</i>	<i>p</i>	<i>d<sub>s</sub></i>	$\eta$	$\Lambda^\circ$ (NaCl)
283.15	0.10	0.99970	0.013066	89.06
283.15	40.0	1.01798	0.012728	91.57
298.15	0.10	0.99704	0.0089050	126.65
298.15	40.0	1.01431	0.0088507	127.84
323.15	0.10	0.98803	0.0054704	197.84
323.15	40.00	1.00471	0.0055503	196.00
373.15	10.00	0.96295	0.0028447	358.46
373.15	40.00	0.97612	0.0029249	350.67
423.15	10.00	0.92236	0.0018490	526.18
423.15	40.00	0.93788	0.0019221	510.08
473.15	10.00	0.87102	0.0013644	684.39
473.15	40.00	0.89097	0.0014342	657.86
523.15	10.00	0.80585	0.0010782	831.54
523.15	40.00	0.83436	0.0011521	789.74

<sup>a</sup>Units as in Table 1. In addition,  $d_s$  is the density of water in  $\text{g}\cdot\text{cm}^{-3}$  calculated from Ref. [36];  $\eta$  is the viscosity of the solvent in Poise calculated from [37]

longer superior to the other equations, so either the Oelkers and Helgeson or the Marshall equation should be used at temperatures greater than 523 K rather than Eq. 10. Table 5 contains some test cases for those who wish to use Eq. 10.

## 5 Conclusions

A new flow-conductance instrument has been built that is capable of accurate, electrical conductivity measurements up to 458 K, 1.8 MPa and high concentrations ( $0.4 \text{ mol}\cdot\text{dm}^{-3}$  in one case). The conductance model based on the MSA was able to fit our measurements in most cases without introducing an ion-pairing equilibrium constant. The FHPF conductance equation was able to describe our dilute sodium chloride solutions with only one adjustable parameter,  $\Lambda^\circ$  (NaCl). This fact along with a simple three-parameter equation derived from the regression of existing  $\Lambda^\circ$  (NaCl) data, provides a relatively easy method to calculate the equivalent conductivities of dilute solutions (less than  $0.01 \text{ mol}\cdot\text{dm}^{-3}$ ) at elevated temperatures and pressures.

**Acknowledgements** We thank R.H. Wood for helpful comments on the initial draft of this manuscript. We thank Mr. Abram C. Campbell (Chemical Research 1 & 2, BU), and Ms. Nazila Pourmoghadan, Mr. Timothy Brockman and Mr. Adam Detweiler (Physical Chemistry 1, BU) for making some of the measurements. Acknowledgment is also made to the donors of The Petroleum Research Fund, administered by the ACS, for support of this research by GHZ at TSU (PRF# 32015-GB2) and funding from Bloomsburg University through a Research and Disciplinary Project Grant.

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