Bulk and Surface Dielectric Dispersion of Water Ice

by

Robert K. Svec

Independent Study Report

Submitted in partial fulfillment of the requirements for the
Master of Science degree in Geophysics.

Geoscience Department
New Mexico Institute of Mining and Technology
Socorro, New Mexico 87801

May 15, 1993

Advisor: Dr. Gerardo Wolfgang Gross

Abstract

The dielectric response of ice is of interest to researchers in the fields of atmospheric physics (thunderstorm electrification) and polar studies (dielectric ice core logging). An automated measurement system, based on the lock-in amplifier, was developed in order to expedite the dielectric measurement process. A frequency domain interpretation procedure was developed for the lock-in data which avoids some of the model assumptions common to prior methods of interpreting dielectric data.

Lock-in measurements were made on pure ice and ice doped with ammonium chloride or hydrochloric acid over a wide range of concentration. The frequency range of the measurement spanned 1 Hz to 100 kHz at 31 frequencies about equally spaced in log-frequency space. Each ice sample was measured at temperatures ranging from -1°C to -80°C.

Dielectric relaxation times in the ice were found to be most depressed in the samples with the highest impurity content. The dc conductivity was found to be nearly an order of magnitude greater in chloride doped samples than in ammonium chloride doped samples of similar concentration. Dielectric conductivities were most elevated in those samples with the highest impurity content. The polarization strength was generally found to be most depressed in samples with the highest impurity content.

The automated lock-in measurement system and the associated frequency domain interpretation method were found to give reliable estimates of several ice dielectric parameters. Of these parameters, the relaxation time and dielectric conductivity were most diagnostic of impurity content. The lower limit of detectability for the impurities studied lies in the range of 10^{-7} to 10^{-8} *N*.

Table of Contents

List of Figures

List of Tables

Acknowledgements

Special thanks are due to several individuals who offered assistance during the course of this research. Dr. Gerardo Gross served as my academic advisor and directed my research efforts. I had the pleasure of working closely with Dr. Gross on a daily basis. Mr. Bruce Hervey of Aztec Instruments arranged for the trial of several instruments during the time when I was developing the measurement technique. Mr. Steve Hunyady lent his assistance on several occasions when I encountered problems with software and system configuration. Mr. Jim McLemore was helpful in machining various fixtures in support of this work. Stanford Research Systems and Princeton Applied Research Company both sent lock-in amplifiers for extended trials.

Introduction

Measurement

This research was performed as an extension of work previously done by Dr. Gerardo Gross using capacitance bridge measurements of ice samples in the blocking electrode configuration (Gross et al., 1980). Capacitance bridge measurements have several disadvantages however. The balancing procedure can be very time consuming, especially at low frequencies. The balance is also highly sensitive to electromagnetic noise.

The lock-in amplifier measurements developed for this research offer several advantages over the bridge method. Perhaps most importantly, the lock-in measurements are designed to be automated. With the measurement under computer control a typical measurement sequence of 31 frequencies requires only 35 minutes to complete. The lock-in method also offers virtual immunity from noise interference because of the ability of the instrument to "lock" onto the measurement frequency (SRS, 1989). Another benefit of the automated measurement is the simplification of data storage. Rather than recording data in notebooks each measurement run is stored on disk as a separate ASCII file. To date this research has generated nearly 900 measurement files totalling close to 1.6 Megabytes.

In this report, acquaintance is assumed with elementary dielectric theory and practice (particularly, see Jonscher, 1983), as well as with relationships developed in previous work by Gross and co-workers. The important references are: Gross et al., 1978; Gross et al., 1980; Gross and Johnson, 1983; Gross and McGehee, 1988.

Interpretation

Interpretation of the bridge measurements was primarily based on fitting the measured response to a model circuit response (Gross and McGehee, 1988). This necessarily involves making assumptions about the physical mechanisms. The interpretation method developed for the lock-in data is a more generalized approach avoiding most of these assumptions. The only major assumption involved is that the dispersion ranges are of the Debye type. This has been observed to be correct, with only minor deviations, for the beta dispersion in all of the samples measured.

A series of procedures has been developed for interpretation of the lock-in data. These procedures are performed on the data in both the XY (blocking capacitor) domain and the pq (ice) domain.

Methods

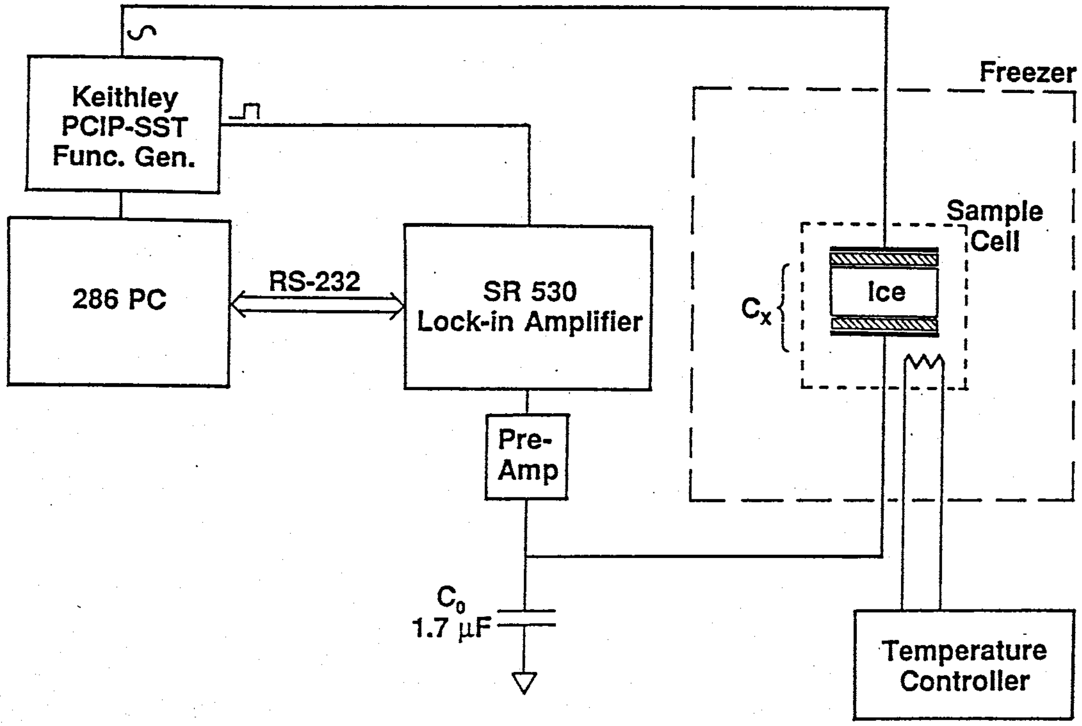
The elements of the lock-in measurement system are pictured in Figure 1.

Temperature Control

The freezer is a So-Low Model PR120-5 with a temperature range of -20°C to -90°C. The temperature controller is an Omega 4202-PC2 resistance thermometer type which provides control to within ±0.1°C. Four rod heaters are inserted into the outer sample cell wall and a ring heater is located beneath the inner cell. The heaters are operated at 40 V by a Variac and the normal current draw is approximately 3.5 A.

Sample Cell

The sample cell is a double shielded design. The inner shield serves as the signal ground and the outer shield is held at earth ground by a grounding lug. Teflon foils of 0.005" (0.13mm) thickness are used to prevent direct contact between the sample and the electrodes. To facilitate the placement of the foils the lower foil is cut 0.005" oversize in diameter so that it must be press-fit into the recess which houses the Low and Guard electrodes. Similarly, the high foil is also cut oversize in diameter. However it is fastened to the High electrode by a pin arrangement. Two steel pins are held in Teflon clamps at 180° from each other. The pins project below the surface of the High electrode and the foil is cut with ears to coincide with these pins. The foil is pushed down over the pins and is held in place by two small rubber holders. This operation is best performed with the High electrode out of the cell, to be reinstalled after completion and final cleaning. A schematic diagram and description of the sample cell is given in Appendix E.



Measurement System Block Diagram

Figure 1. Measurement system block diagram.

Instrumentation

The PC 286 serves to control the measurement sequence via instructions in the FORTRAN program MEASURE.FOR (See Appendix C). The PC 286 also houses the Keithley PCIP-SST function generator card. This instrument is controlled by the MEASURE program to supply a 20.00 V sine wave and a 5 V TTL square wave reference signal. The PCIP-SST sets the frequency as directed by the program and the sine wave serves as the excitation for the High electrode in the sample cell. The TTL square wave is fed to the reference input of the SR530 Lock-in amplifier.

The SR530 Lock-in amplifier is also controlled by the program via an RS232 serial interface. The RS232 serial interface serves to transmit instructions to the lock-in and to receive data from the lock-in. It should be noted that the lock-in uses a 19.2 kbaud rate on the RS232 interface.

The lock-in is able to measure the signal strength at one frequency by virtue of the reference signal which is supplied by the PCIP-SST function generator. The reference signal is fed to phase-lock loop circuits in the lock-in which track the signal-input at the reference frequency. This allows the lock-in to measure very small signals, even when obscured by noise (SRS, 1989). The lock-in detects any phase difference between the input signal and the reference and then displays the components of the input which are in phase and 90° out of phase with the reference. The effective phase resolution is 0.1°.

Measurement Circuit

The measurement circuit is based on the voltage division principle. The sample C_x is supplied with the 20.00 V excitation sinusoid by the PCIP-SST. This signal is then divided on the fixed capacitor C_0 according to the expression $V_o=V_i(C_x/(C_0+C_x))$. And since C_0 is a 1.7 μF polystyrene low loss capacitor with a very flat frequency response and C_x is always less than 36 pF, then $C_0 \gg C_x$ and the expression becomes $V_o=V_i(C_x/C_0)$. But this is an over-simplification because the sample is actually a complex capacitance with a non-negligible conductance G_x. G_x/ω is always less than 1/2 $C_{x\,max}$, therefore $C_0 \gg G_x/\omega$. Now the complete expression for the voltage division can be written as $V_o=V_i((C_x-jG_x/\omega)/C_0)$. The lock-in amplifier measures the two quadrature components of the complex capacitance C_x. They are specifically $V_o'=V_i(C_x/C_0)$ and $V_o''=V_i(G_x/\omega C_0)$ (Malchow, no date).

Calibration

The lock-in measurement system is calibrated using a General Radio 1422-CB precision capacitor. This capacitor is characterized by extremely low loss and a dial precision of 0.1 pF. The low loss characteristic is essential since we wish to calibrate the system in the simplest way possible, i.e. a purely capacitive response. In the calibration procedure data is obtained which characterizes the many components of the measurement system. The frequency response of the system depends on cable capacitance, PCIP-SST output impedance, non-zero loss in C_0, and the input impedance of the SR530 lock-in. It must also be remembered that most of these factors will also show some variation with temperature and humidity.

Calibration procedure

1. The GR 1422-CB capacitor is placed in the circuit as the sample C_x. The actual measurement cables must be used. The dial is set to give 100.0 pF, which satisfies the condition that the calibration be performed on a capacitance that is equal to or larger than the greatest expected sample capacitance C_x.

2. The PCIP-SST and SR530 lock-in are both set to accept manual inputs. Both instruments should be configured as for a normal measurement run (see Appendix D).

3. The frequency is adjusted through the measurement range manually, and for each frequency the lock-in R(X display) and ϕ(Y display) are examined. The reference phase angle ϕ_{REF} is manually adjusted for each frequency until the ϕ(Y display) reading is -90.0°, allowing ample time to approach steady state at frequencies less than 10 Hz.

4. Record the R(X display) and ϕ_{REF} for each frequency in the calibration notebook.

5. Calculate the correction coefficients K. K is an amplitude adjustment factor which assures a flat response over the entire frequency range. K=100.0 pF/R. If K (or R) varies more than 1% from the previous calibration then it should be updated in the CAL.DAT file. If K does not exceed this limit do not update the cal.dat file. Minor adjustments are not justified since the dial accuracy of the GR 1422-CB is only ±0.1 pF.

Sample Preparation

Ice columns 1.5" (38mm) in diameter are grown in Lucite tubes from carefully prepared solutions. The tubes are suspended from a rack above a freezer and slowly (2mm/hour) lowered through a thermistor-controlled heater ring into a silicone oil bath at -20°C. This procedure yields slightly poly-crystalline ice columns about 25 cm long with crystallographic c-axes aligned approximately perpendicular to the axis of the tube.

The ice columns are either melted or sawed into fractions for chemical analysis and a slice 1.5 cm thick is sawed off for dielectric analysis. This slice is then ground down to a final thickness between 14 mm and 6 mm thick. Smooth planar surfaces are obtained by using progressively finer grits of silicon carbide paper.

Pre-measurement Procedures

After grinding is completed the sample is placed into the sample cell, which has been previously cleaned with acetone, between the two Teflon foils. The foils are examined to assure that there is no direct contact between the stainless steel electrodes and the sample. The high electrode is pressed down onto the sample to maximize contact and minimize air gaps. The inner cell is closed and inserted into the outer cell and all electrical connections are applied. For measurements made since November, 1992, a special "defrosting" sequence is performed by lowering the freezer temperature to -30°C and raising the sample temperature to -2.0°C. The sample is generally left over night in this state.

Two measurement configurations are used. The bulk configuration is used to obtain data about the bulk properties of the sample. This configuration is illustrated in Figure 1. The high electrode is connected to the PCIP-SST, the low electrode is connected to the SR530 pre-amp at the C_0 capacitor, and the guard electrode is connected to signal ground via a shorting BNC cap. The surface configuration is not illustrated. In the surface configuration the low electrode is connected to the PCIP-SST, the guard electrode is connected to the SR530 pre-amp at the C_0 capacitor, and the high electrode is floated via a floating BNC cap. The surface configuration is no longer used.

Measurement Sequence

Each sample is measured over a range of temperatures. The general sequence is: -2, -5,-10, -15, -20, -30, -40, -50, -60, -70, -80, -5, -2, -1°C. If examination of the data sets indicates an interesting transition, the sequence may be expanded to intermediate temperatures. At all measurement temperatures a gradient of 20°C is maintained between the sample and the freezer to discourage migration of frost to the sample.

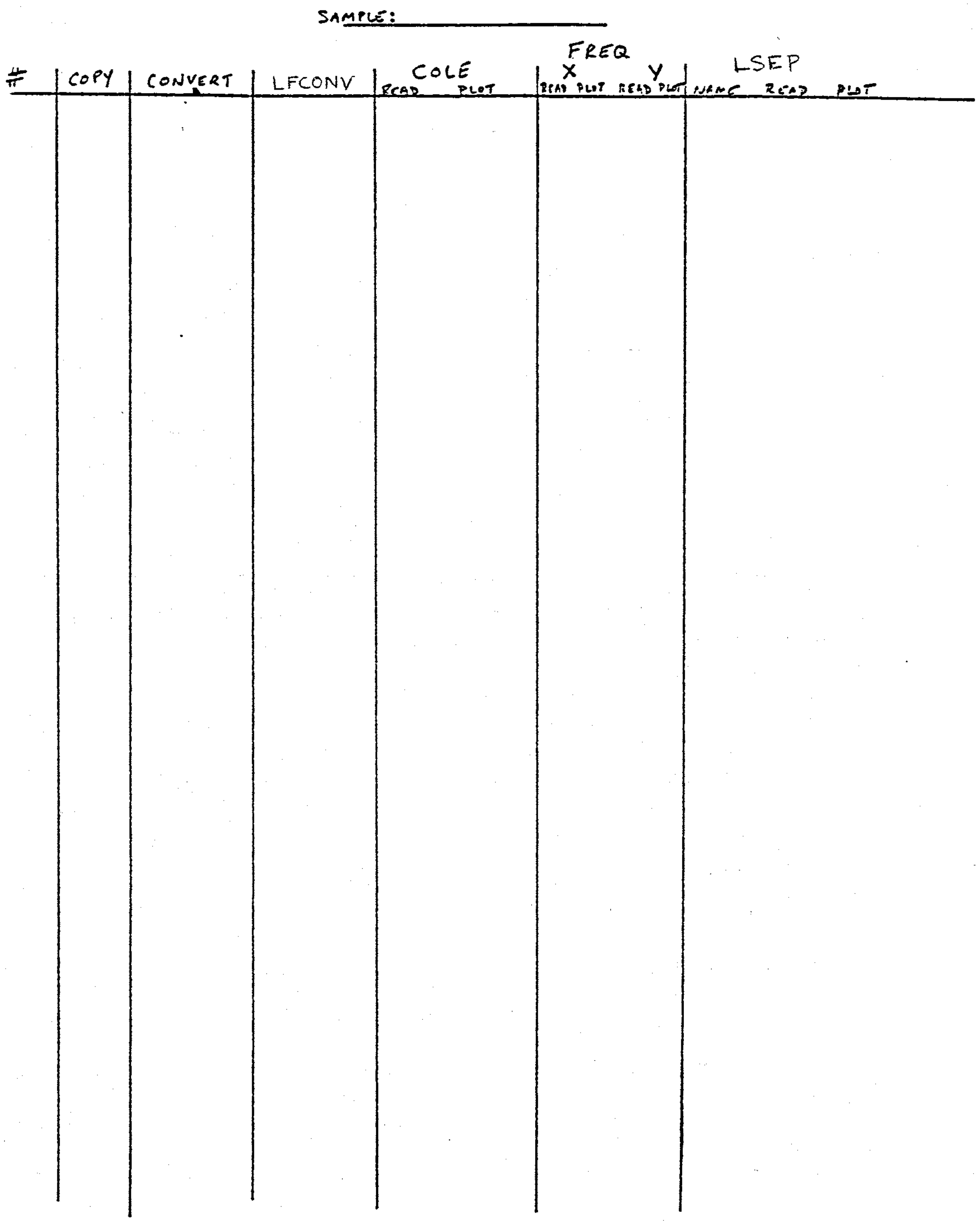
Each dielectric measurement is performed after the sample has reached temperature equilibrium. The measurement sequence lasts 35 minutes and covers the frequency range from 1 Hz to 100 kHz at 31 frequencies about equally spaced in log frequency space.

The actual measurement is controlled by the FORTRAN program MEASURE.FOR which is found on the measurement disk as the executable MEASURE.EXE. The functions performed by the program are described in a flow diagram in the Appendix. A brief description follows:

1. PCIP-SST and SR530 are initialized and set to computer control. Manual inputs are locked out.
2. PCIP-SST performs an auto-calibration.
3. PCIP-SST adjusts to measurement frequency.
4. SR530 receives ϕ_{REF} data and seeks a phase-lock.
5. SR530 searches for optimum sensitivity level.
6. Computer waits for an additional 5 time constants.
7. Computer reads C' and C'' (the real and quadrature capacitive response components) from the SR530.
8. Repeat steps 3 to 7 for remaining frequencies.
9. Computer writes frequency, $X \equiv C'$, $Y \equiv C''$ to output file.

Data Analysis

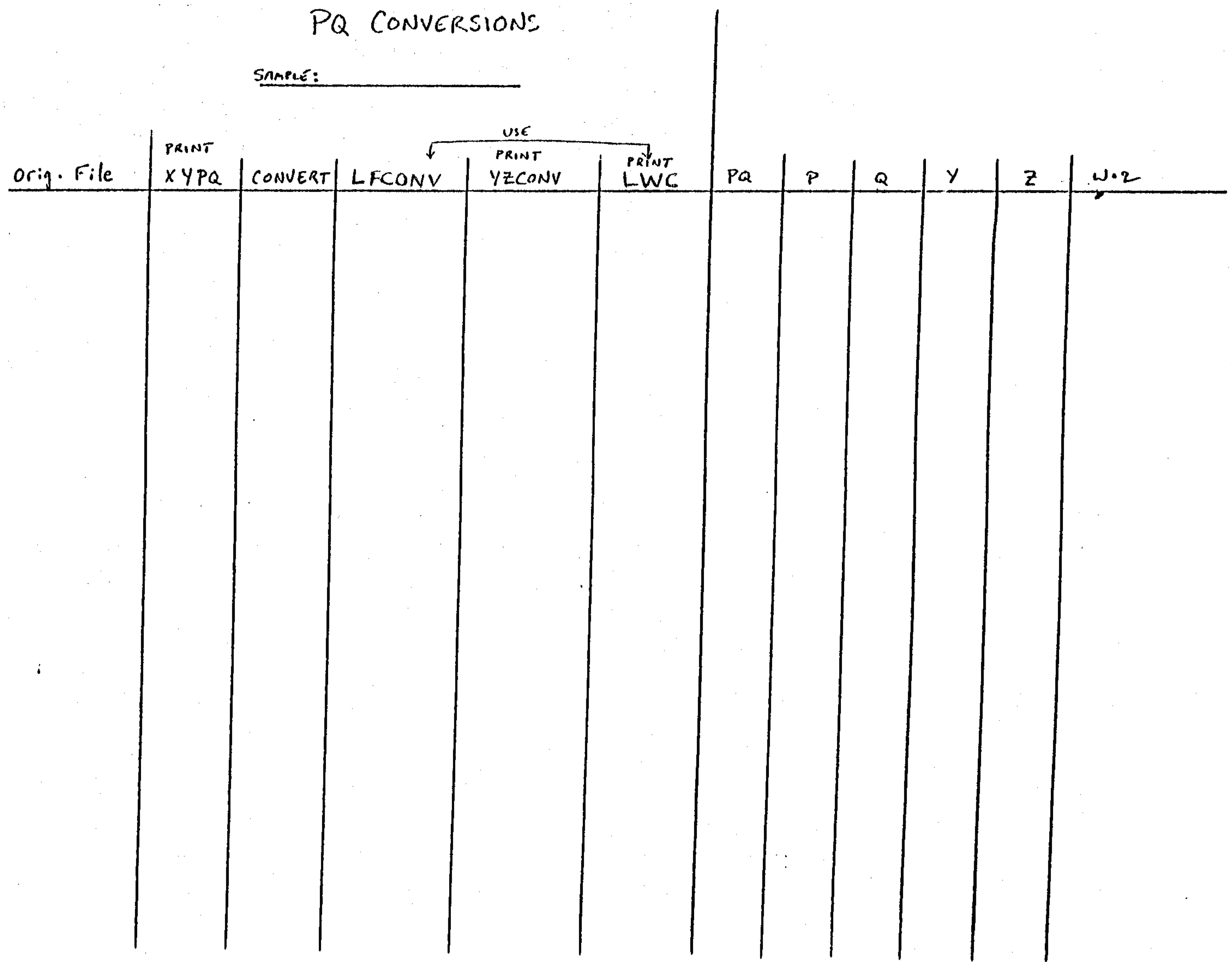
The analysis of the data collected with the lock-in measurement system requires several steps which are described below. All of these steps are described in reference to the samples supplied as figures. The XY (X/Y= real/imaginary components of the blocking capacitor response) and pq (p/q= real/imaginary components of the ice response) tally sheets, Figures 2 and 3 respectively, are used to tabulate the many steps in the interpretation procedure. Some of the steps described below will not correspond to any entry on the sheets because they are seldom used. All



SAMPLE: ____________________

#	COPY	CONVERT	LFCONV	COLE		FREQ				LSEP		
						X		Y				
				READ	PLOT	READ	PLOT	READ	PLOT	NAME	READ	PLOT

Figure 2. Computer XY tally sheet.



PQ CONVERSIONS

SAMPLE: ____________________

Orig. File	PRINT XYPQ	CONVERT	LFCONV	USE PRINT YZCONV	PRINT LWC	PQ	P	Q	Y	Z	W.2

Figure 3. Computer pq tally sheet.

the plots are generated from within Mathematica by importing the plot files into Mathematica (Wolfram, 1991).

Figure 4 is the lock-in measurement file for sample 186156.02. The designation 02 indicates the chronological order in which the measurement was taken. A hard copy of this file is kept in the measurement folder. This file is the basis for all subsequent analysis steps.

Figure 5 is the Cole-Cole plot for sample 186156.02 (Cole and Cole, 1941). The data file for this plot is generated by running the lock-in file 186156.02 through the FORTRAN program CONVERT (Microsoft Corp., 1991). CONVERT generates a plottable output file which contains two columns of X and Y data and no header. The Cole-Cole plot is primarily used to monitor the behavior of the sample and to obtain estimates of C_1, the zero frequency capacitance at closure of the complex arc.

Figure 6 is the X and Y Response plot for sample 186156.02. The data file for this plot is generated by running the lock-in file 186156.02 through the FORTRAN program LFCONV. LFCONV generates two plottable output files which each contain a column of log frequencies and a column of corresponding log X or log Y values. The X and Y Response plot is used to identify the β-dispersion and obtain estimates of the peak frequency f_β and amplitude C_β. This is performed on a light table using a Debye type-curve to visually fit the dispersion.

Typically, the response shows two major components or relaxation ranges, designated as α and β, respectively, in this paper. The α- or low frequency range is related to the dc or static conductivity. The β-range is the principal dipole relaxation range of ice.

Figure 7 is the Separated Y Response Plot for sample 186156.02. The data file for this plot is generated by running the Y Response file through the program LSEP. The user must supply to the program the f_β and C_β values picked from the X and Y Response plot. The LSEP program generates a plottable output file which contains a column of log frequencies, a column of corresponding log Y values for the calculated β-dispersion, and the residual at each measurement frequency. The Separated Y Response plot is used to identify the α-dispersion, and any additional dispersions, and to obtain an estimate of the peak frequency f_α. The f_α determination is also performed on a light table using a visual fit to the Debye type-curve.

Once the steps documented above have been performed for all the measurements in a given series, then the C_2 and τ_2 calculation sheet, shown in Figure 8, is begun. The measurement number, temperature T [°C], and 1000/T [K^{-1}] are tabulated. Also tabulated are the dispersion frequency

```
3/20/93; 14:50
186156.02: 6E-6N NaOH 8mm Cell 2 (0.25mmTFL) BULK -10.0 C
      1.0          30.87          .17
      1.5          30.95          .18
      2.0          30.91          .10
      3.0          30.92          .16
      5.0          30.90          .18
      7.0          30.91          .17
     10.0          30.91          .25
     15.0          30.87          .34
     20.0          30.84          .48
     30.0          30.80          .78
     50.0          30.66         1.26
     70.0          30.48         1.71
    100.0          30.07         2.51
    150.0          29.37         3.27
    200.0          28.67         3.87
    300.0          27.28         4.37
    500.0          25.36         4.65
    750.0          24.01         4.47
   1000.0          23.33         4.43
   1500.0          22.65         4.65
   2000.0          22.15         5.15
   3000.0          21.15         6.33
   5000.0          18.73         8.46
   7000.0          16.20         9.66
  10000.0          12.72        10.16
  15000.0           8.79         9.32
  20000.0           6.61         8.04
  30000.0           4.60         6.03
  50000.0           3.35         3.87
  70000.0           2.93         2.80
 100000.0           2.70         1.95
```

Figure 4. 186156.02 lock-in measurement file.

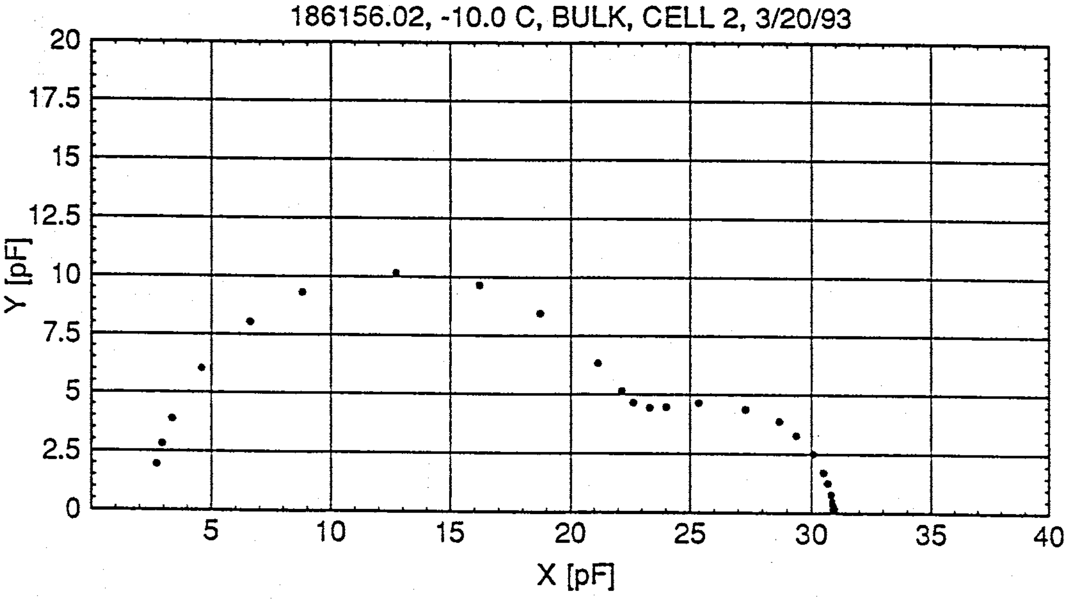


Figure 5. 186156.02 Cole-Cole plot.

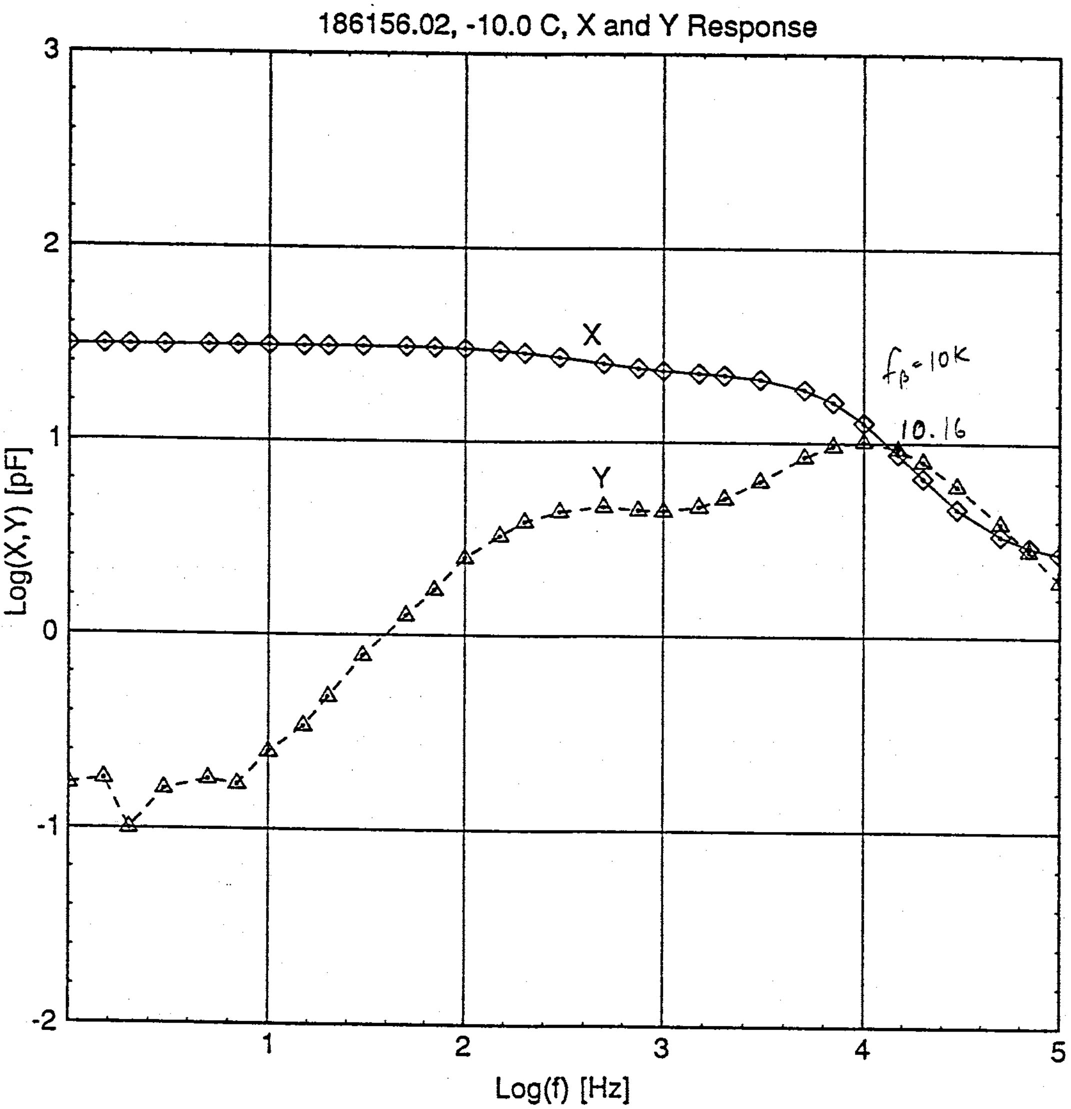


Figure 6. 186156.02 X and Y Response.

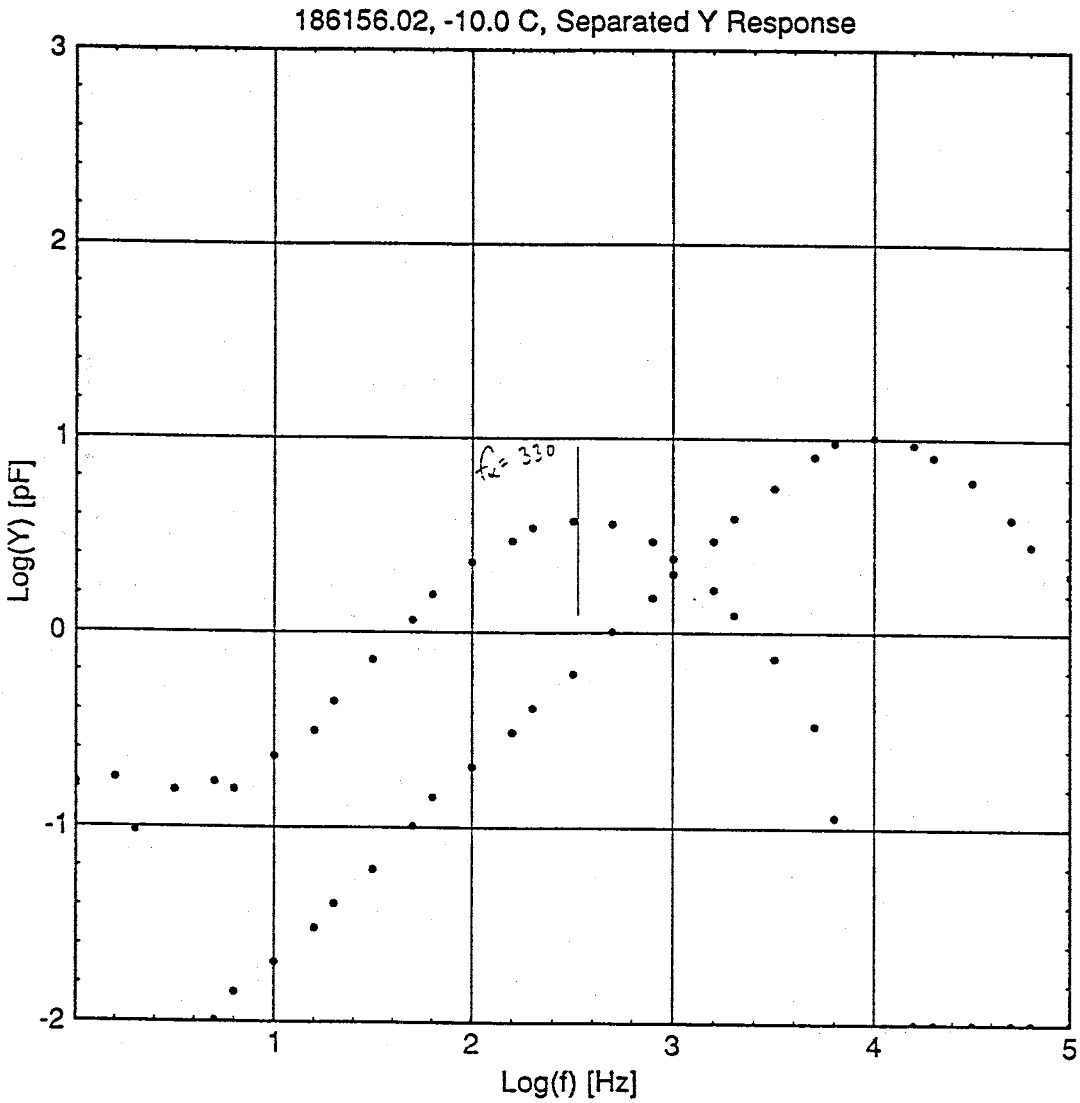
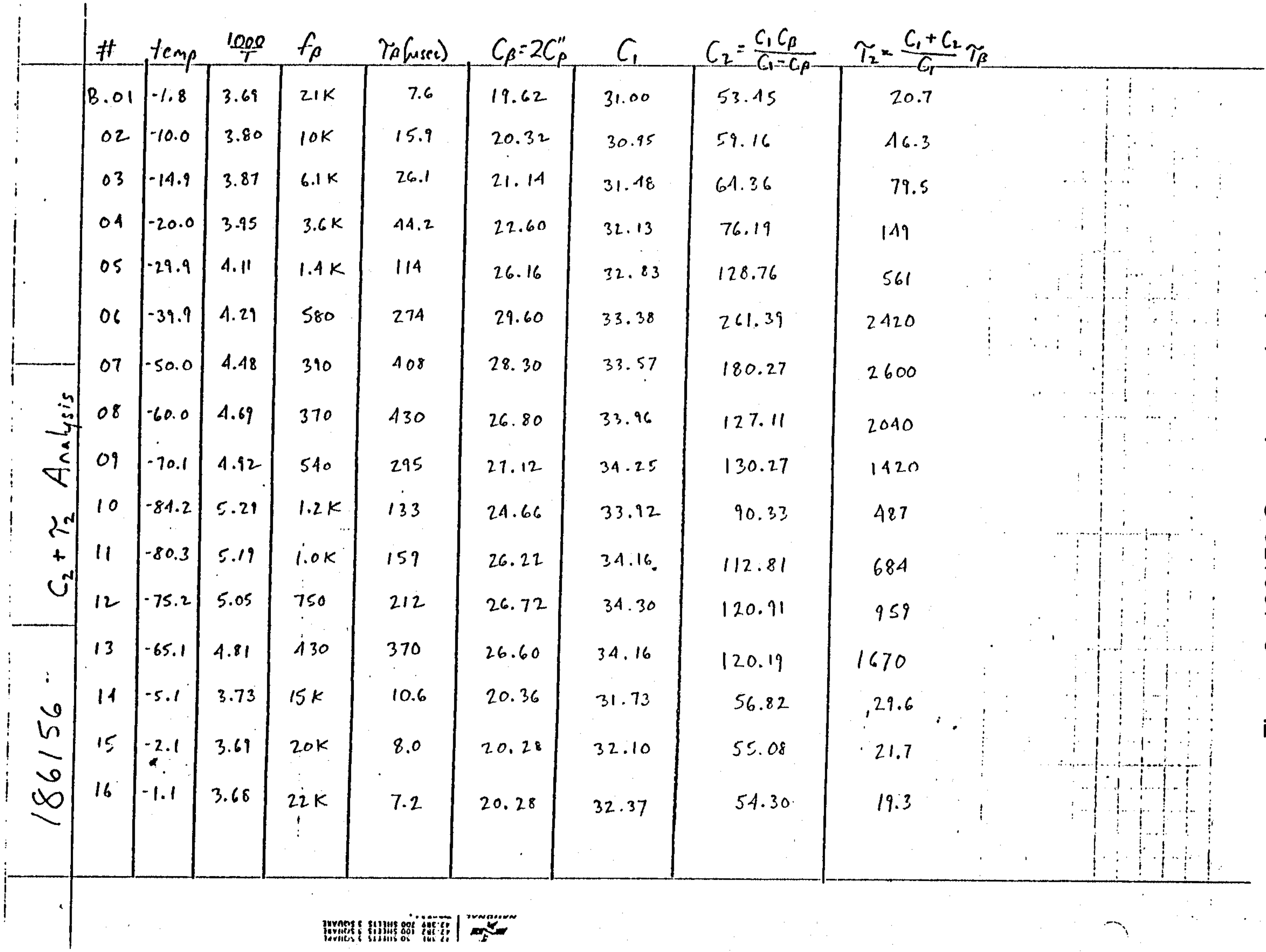


Figure 7. 186156.02 Separated Y Response.



186156

$C_2 + \tau_2$ Analysis

#	temp	$\frac{1000}{T}$	f_p	τ_p(μsec)	$C_p = 2C_p''$	C_1	$C_2 = \frac{C_1 C_p}{C_1 - C_p}$	$\tau_2 = \frac{C_1 + C_2}{C_1}\tau_p$
B.01	-1.8	3.69	21K	7.6	19.62	31.00	53.45	20.7
02	-10.0	3.80	10K	15.9	20.32	30.95	59.16	46.3
03	-14.9	3.87	6.1K	26.1	21.14	31.48	64.36	79.5
04	-20.0	3.95	3.6K	44.2	22.60	32.13	76.19	149
05	-29.9	4.11	1.4K	114	26.16	32.83	128.76	561
06	-39.9	4.29	580	274	29.60	33.38	261.39	2420
07	-50.0	4.48	310	408	28.30	33.57	180.27	2600
08	-60.0	4.69	370	430	26.80	33.96	127.11	2040
09	-70.1	4.92	540	295	27.12	34.25	130.27	1420
10	-84.2	5.29	1.2K	133	24.66	33.92	90.33	487
11	-80.3	5.19	1.0K	159	26.22	34.16	112.81	684
12	-75.2	5.05	750	212	26.72	34.30	120.91	959
13	-65.1	4.81	430	370	26.60	34.16	120.19	1670
14	-5.1	3.73	15K	10.6	20.36	31.73	56.82	29.6
15	-2.1	3.69	20K	8.0	20.28	32.10	55.08	21.7
16	-1.1	3.66	22K	7.2	20.28	32.37	54.30	19.3

Figure 8. 186156 C_2 and τ_2 analysis sheet.

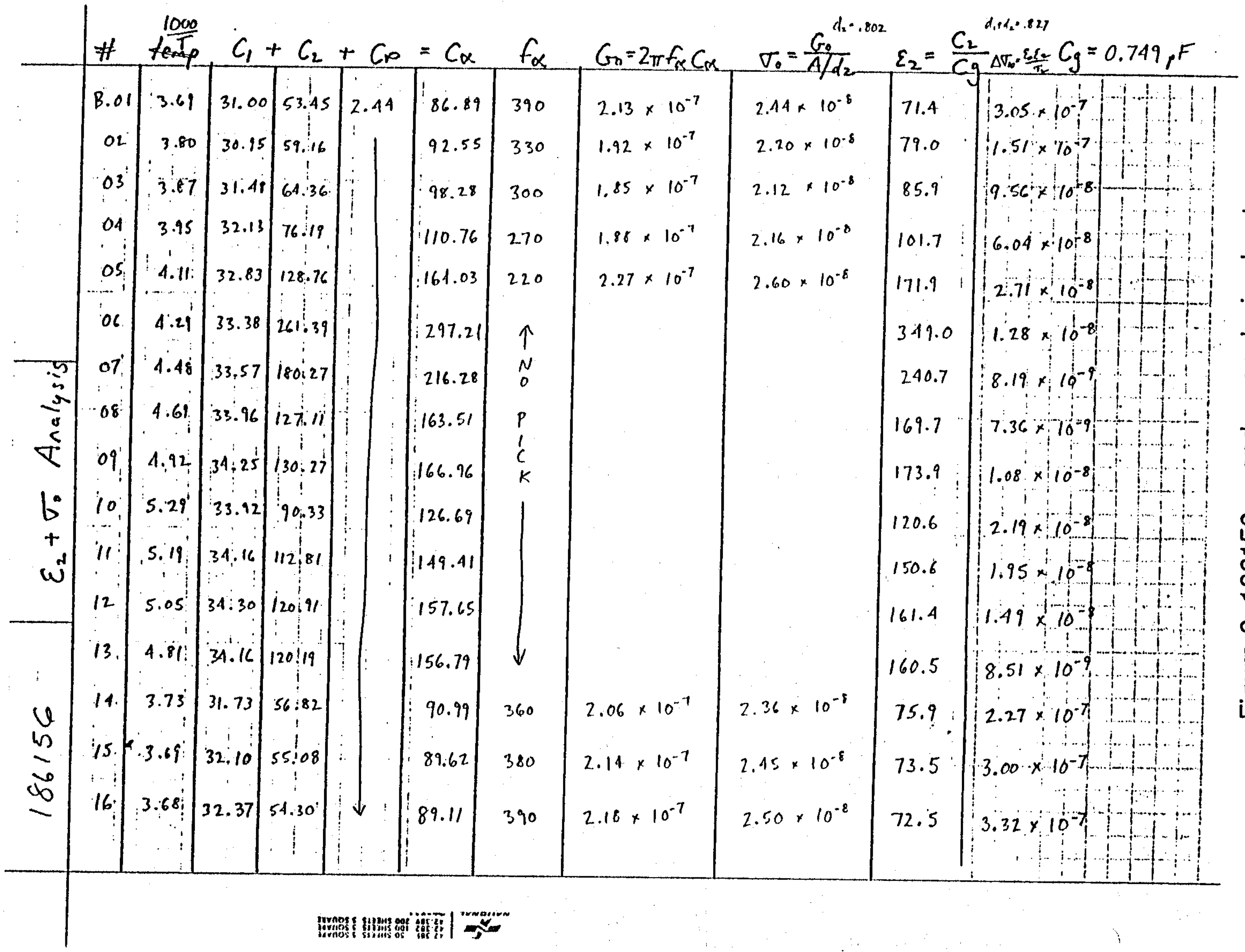
f_β [Hz], the principal relaxation time in the blocking capacitor $\tau_\beta=(2\pi f_\beta)^{-1}$ [μsec], the principal dispersion capacitance $C_\beta=2Y_{\beta peak}$ [pF], the low-frequency limiting capacitance C_1 [pF], the principal ice capacitance $C_2=(C_1C_\beta)/(C_1-C_\beta)$ [pF], and the principal relaxation time in the ice $\tau_2=\tau_\beta((C_1+C_2)/C_1)$ [μsec]. For a discussion of these parameters, refer to papers by Gross and co-workers (see References).

The ε_2 and σ_0 calculation sheet is shown in Figure 9. The following quantities are tabulated, several previously described: the measurement number, 1000/T, C_1, C_2, the high frequency limiting capacitance C_∞ [pF], the α-range capacitance $C_\alpha=C_1+C_2+C_\infty$ [pF], the α-dispersion peak frequency f_α [Hz], the dc conductance $G_0=2\pi f_\alpha C_\alpha$ [Ω^{-1}], the dc conductivity $\sigma_0=G_0/(A/d_2)$ [Ω^{-1}cm^{-1}], the geometric capacitance $C_g=\varepsilon_0A/(d_1+d_2)$ [pF], the ice principal polarization strength $\varepsilon_2=C_2/C_g$, and the dielectric conductivity $\Delta\sigma_D=\varepsilon_0\varepsilon_2/\tau_2$ [Ω^{-1}cm^{-1}].

An Arrhenius plot of τ_β and τ_2 versus 1000/T for sample 186156 is shown in Figure 10. Plotted for reference is a solid line representing the data measured by Auty and Cole for pure ice (Auty and Cole, 1952). The τ plots are useful in identifying departures from the pure ice response. Other quantities such as σ_0, $\Delta\sigma_D$, and ε_2 are also plotted against 1000/T, but not generally for every sample.

Figure 11 is the pq data set for the XY lock-in measurement 186156.02. It is generated by the program XYPQ which performs the transformation from the XY (blocking capacitor) domain to the pq (ice) domain. The pq output file has the same format as a normal lock-in measurement file so that the pq data can also be run through the various analysis programs and plotted.

The pq Cole-Cole plot for 186156.02 is shown in Figure 12. The data file for this plot is generated by running the pq data file through the CONVERT program. This plot is on a logarithmic scale because of the large range of data values. The pq Cole-Cole plot is used to observe low frequency trends which may indicate the presence of a conductivity. But it is surpassed in this role by the q and ωxq plots. The p and q Response plot for 186156.02, shown in Figure 13, is more useful for observing conductivity trends and the behavior of the dispersions. The data files for the p and q Response plot are generated by running the pq data file through the LFCONV program. The ωxq plot for 186156.02, shown in Figure 14, represents the total ice conductance over the frequency range 1 Hz to 100 kHz. The ωxq plot file is generated by running the q response data file through the LWC program. The horizontal plateau between frequencies 10



186156

$\varepsilon_2 + \sigma_0$ Analysis

$C_g = 0.749$ pF

#	$\frac{1000}{T}$ ~~temp~~	C_1 +	C_2 +	C_p =	C_α	f_α	$G_0 = 2\pi f_\alpha C_\alpha$	$\sigma_0 = \frac{G_0}{A/d_2}$ $d_2 = .802$	$\varepsilon_2 = \frac{C_2}{C_g}$ $d_1+d_2 = .827$	$\Delta\sigma_0 \cdot \frac{\varepsilon_0\varepsilon_2}{\tau_\varepsilon}$
B.01	3.69	31.00	53.45	2.44	86.89	390	2.13×10^{-7}	2.44×10^{-8}	71.4	3.05×10^{-7}
02	3.80	30.15	59.16		92.55	330	1.92×10^{-7}	2.20×10^{-8}	79.0	1.51×10^{-7}
03	3.87	31.48	64.36		98.28	300	1.85×10^{-7}	2.12×10^{-8}	85.9	9.56×10^{-8}
04	3.95	32.13	76.19		110.76	270	1.88×10^{-7}	2.16×10^{-8}	101.7	6.04×10^{-8}
05	4.11	32.83	128.76		161.03	220	2.27×10^{-7}	2.60×10^{-8}	171.9	2.71×10^{-8}
06	4.29	33.38	261.39		297.21	↑			349.0	1.28×10^{-8}
07	4.48	33.57	180.27		216.28	NO			240.7	8.19×10^{-9}
08	4.61	33.96	127.11		163.51	PICK			169.7	7.36×10^{-9}
09	4.92	34.25	130.27		166.96				173.9	1.08×10^{-8}
10	5.29	33.92	90.33		126.69				120.6	2.19×10^{-8}
11	5.19	34.16	112.81		149.41				150.6	1.95×10^{-8}
12	5.05	34.30	120.91		157.65				161.4	1.49×10^{-8}
13.	4.81	34.16	120.19		156.79	↓			160.5	8.51×10^{-9}
14.	3.73	31.73	56.82		90.99	360	2.06×10^{-7}	2.36×10^{-8}	75.9	2.27×10^{-7}
15.	3.69	32.10	55.08		89.62	380	2.14×10^{-7}	2.45×10^{-8}	73.5	3.00×10^{-7}
16.	3.68	32.37	54.30	↓	89.11	390	2.18×10^{-7}	2.50×10^{-8}	72.5	3.32×10^{-7}

Figure 9. 186156 ε_2 and σ_0 analysis sheet.

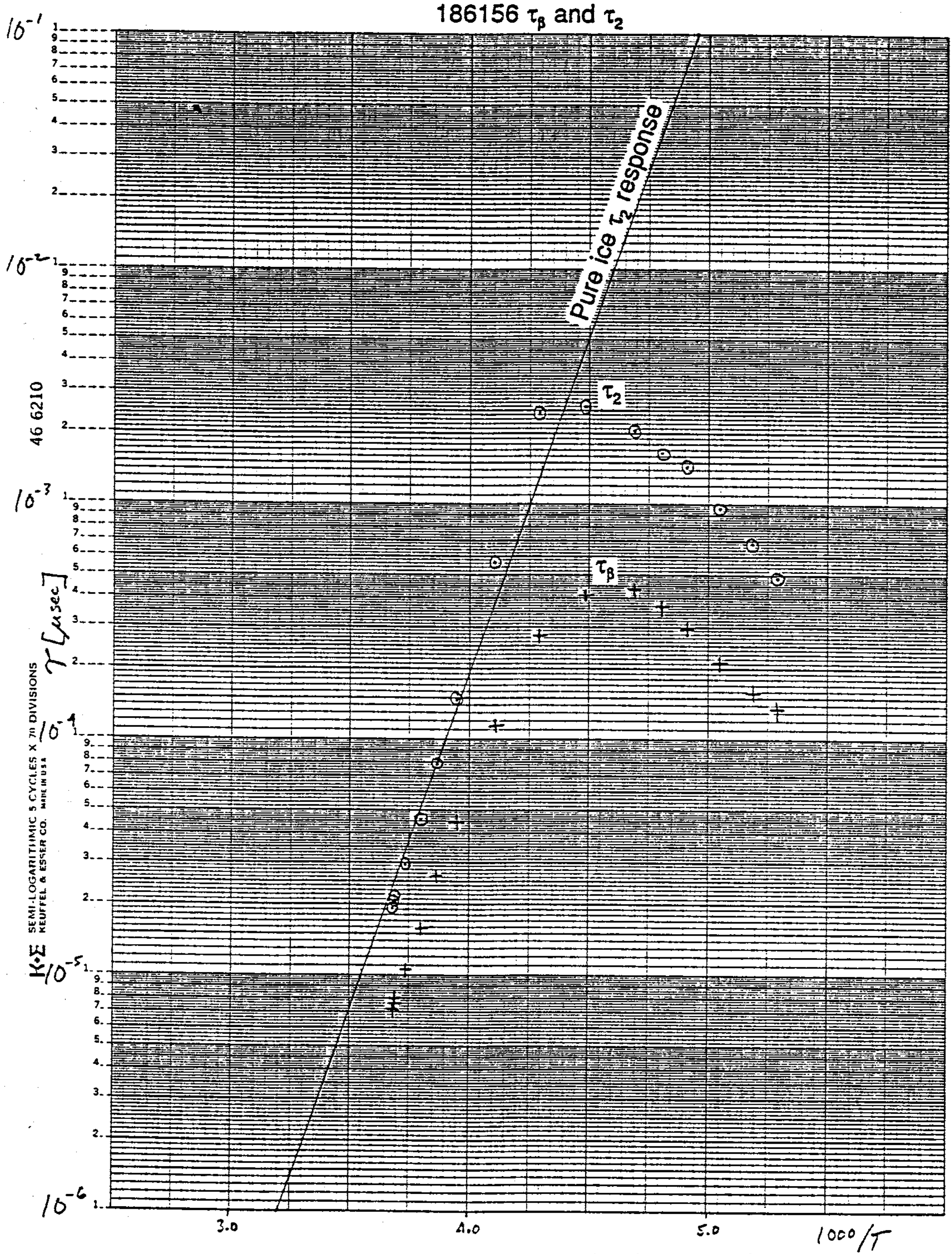


Figure 10. 186156 Arrhenius plot for τ_β and τ_2.

```
 dummy date
 PQ converted 186156.02
     1.0          2799.92          2673.72
     1.5          2242.76          4092.92
     2.0          4528.90          3257.12
     3.0          2917.97          3629.58
     5.0          2603.11          3161.00
     7.0          2751.92          3379.34
    10.0          1612.97          2935.76
    15.0          1141.50          2214.84
    20.0           706.51          1685.86
    30.0           328.21          1120.88
    50.0           185.08           698.26
    70.0           138.09           507.42
   100.0            99.08           333.30
   150.0            88.79           233.26
   200.0            80.11           180.76
   300.0            78.07           126.48
   500.0            70.54            83.02
   750.0            66.55            61.97
  1000.0            62.90            53.91
  1500.0            56.80            48.63
  2000.0            50.10            46.96
  3000.0            38.07            44.20
  5000.0            22.13            36.52
  7000.0            14.57            29.68
 10000.0             9.19            22.30
 15000.0             5.80            15.43
 20000.0             4.55            11.71
 30000.0             3.60             7.90
 50000.0             3.09             4.77
 70000.0             2.90             3.38
100000.0             2.80             2.33
```

Figure 11. 186156.02 pq data.

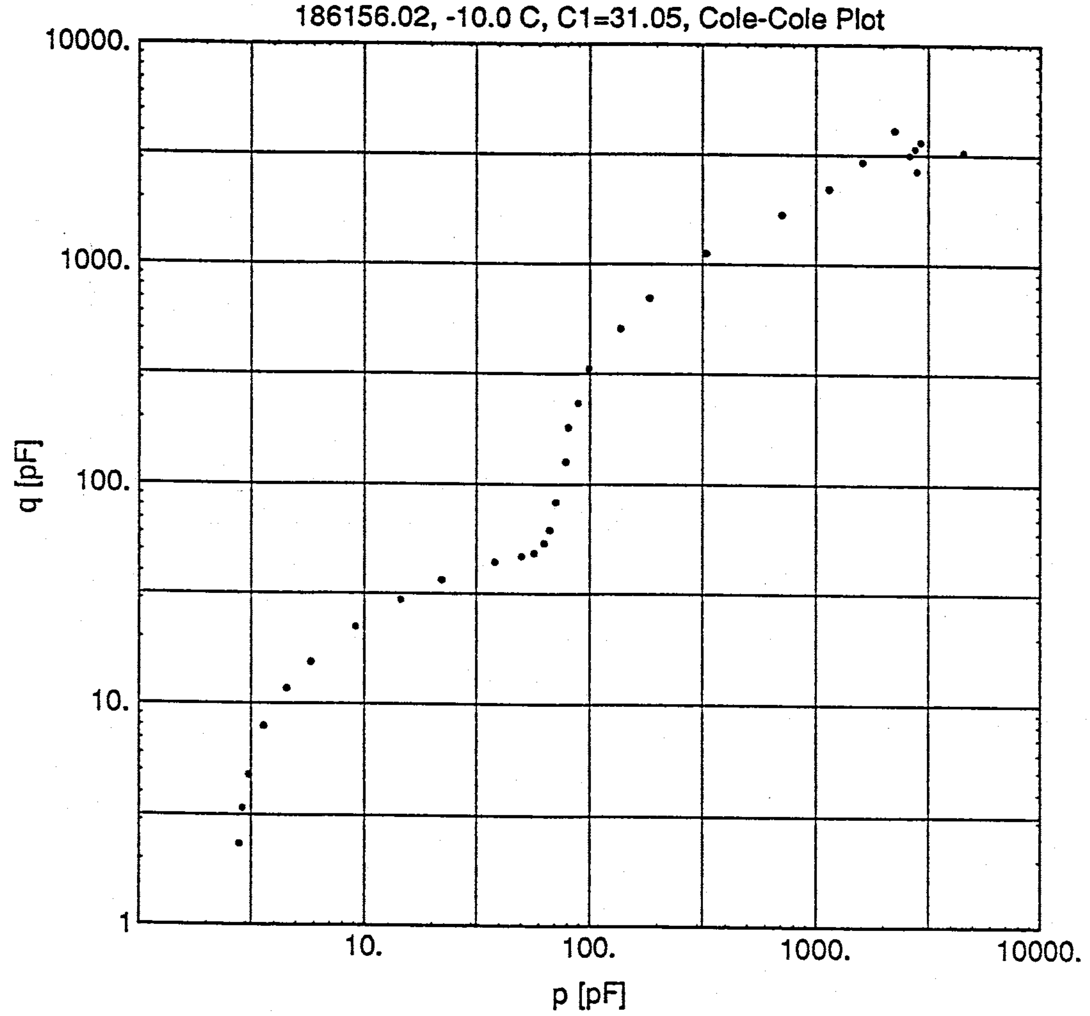


Figure 12. 186156 pq Cole-Cole plot.

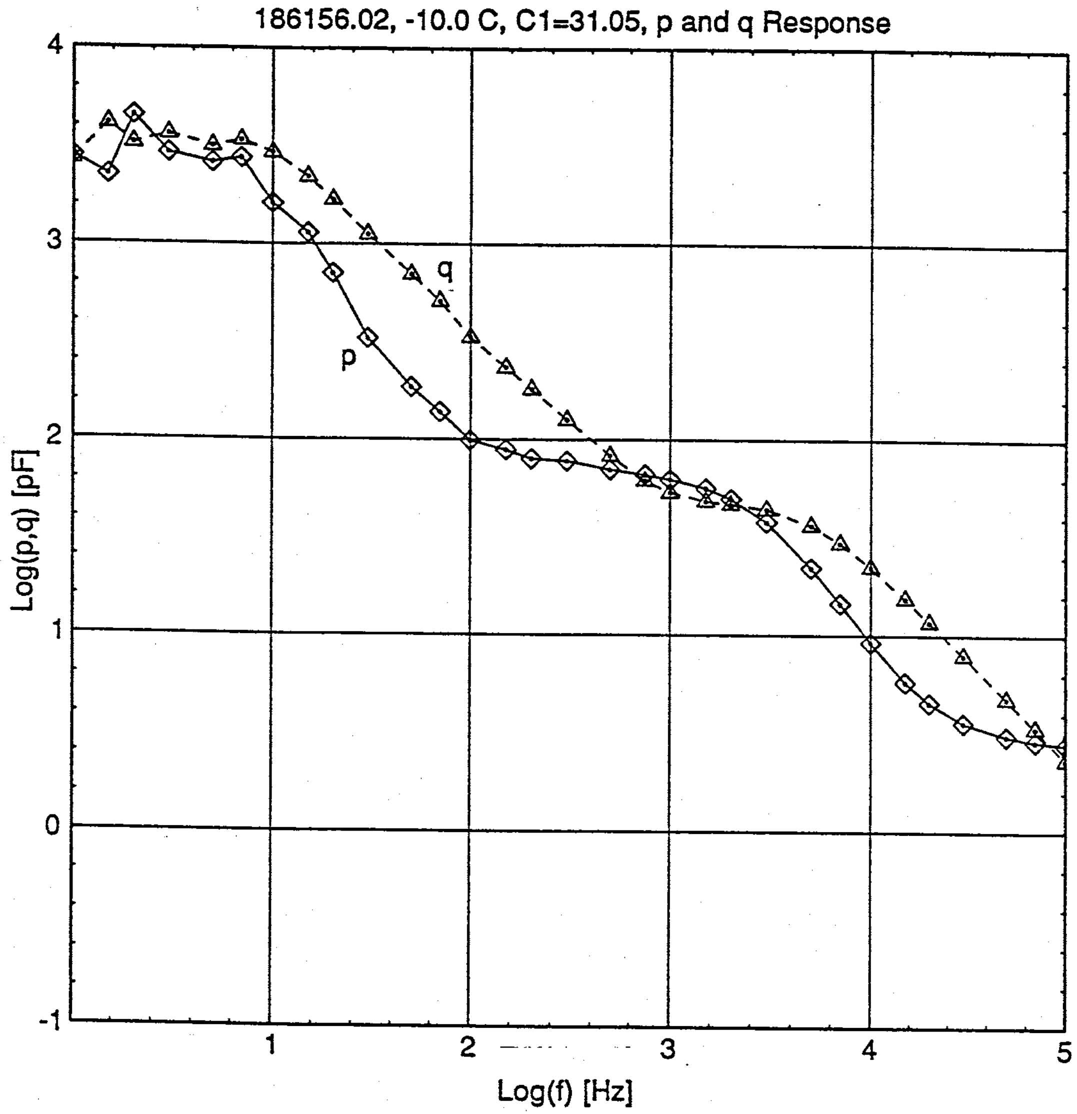


Figure 13. 186156.02 p and q response.

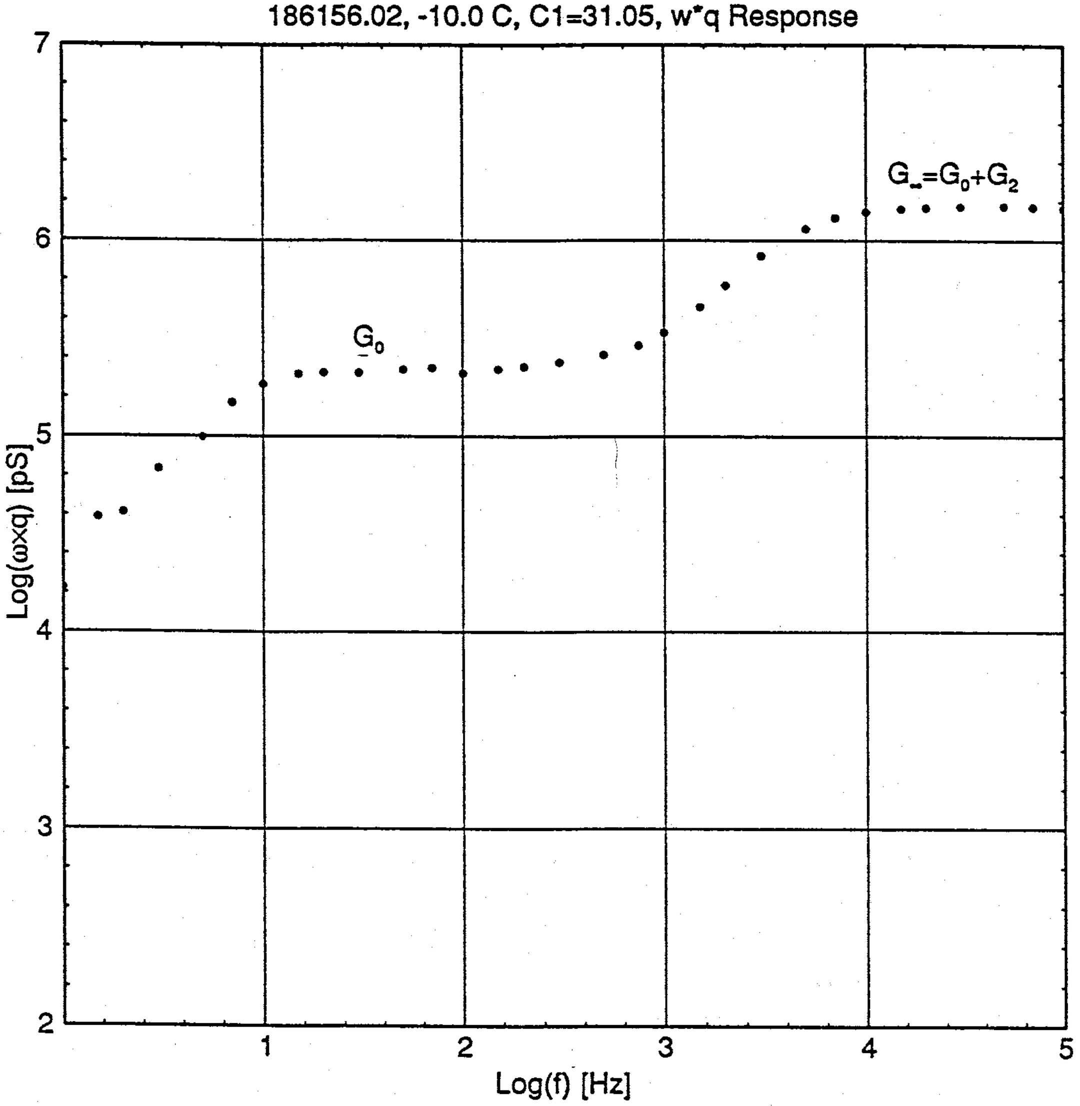


Figure 14. 186156.02 ω×q response.

Hz and 100 Hz is the dc conductance, G_0, whereas the plateau at the high frequency end of the plot is the sum $G_\infty=G_0+G_2$.

Other pq analysis tools are the XYp and XYq plots shown in Figures 15 and 16, respectively. These plots are only used to verify the location of the XY data points on the theoretical p and q surfaces. This helps establish criteria for determining if a pq data point has fallen into a highly non-linear zone during the XY to pq transformation. The XY to pq transformation equations (Gross and McGehee, 1988, eqs. 9 and 10) are discontinuous in the region where X approaches C_1 (C_1 is C_0 in that paper).

Several additional procedures which are available, but rarely used, are transformations to the complex Y (admittance) and complex Z (impedance) domains from the XY (capacitance) domain, cumulative plotting of several X or Y Response curves, and subtraction of C_∞ from the X Response curve. Y and Z transformations are performed by running the XY lock-in data through the YZCONV program which generates plottable files of Y pairs and Z pairs. The cumulative plots are generated by running several X or Y Response data files through the CUMULAT program. The C_∞ subtraction operation is accomplished by running the X Response data file through the LCINF program.

Results

The lock-in measurement method was tested before data collection on ice samples began. Measurements made on fixed capacitors verified that the calibration data was correct. Model circuits based on an ice equivalent circuit model (Gross and McGehee, 1988) were measured by the lock-in and the data compared to the bridge measurements. In all cases the data sets generally agreed to within 1%, with occasional larger deviations at the highest and lowest frequencies.

After the testing was completed the lock-in measurement method was used to obtain 900 measurements in 42 sample runs. Some runs were duplicates, made with different foil thicknesses, or samples reground to reduced thickness. An average sample run lasted about four days and required at least three hours between temperatures. A second sample cell was constructed and brought into use to reduce down-time between samples. Presently only one sample cell is routinely used, having the 0.005″ (0.13mm) Teflon foils mounted on pins.

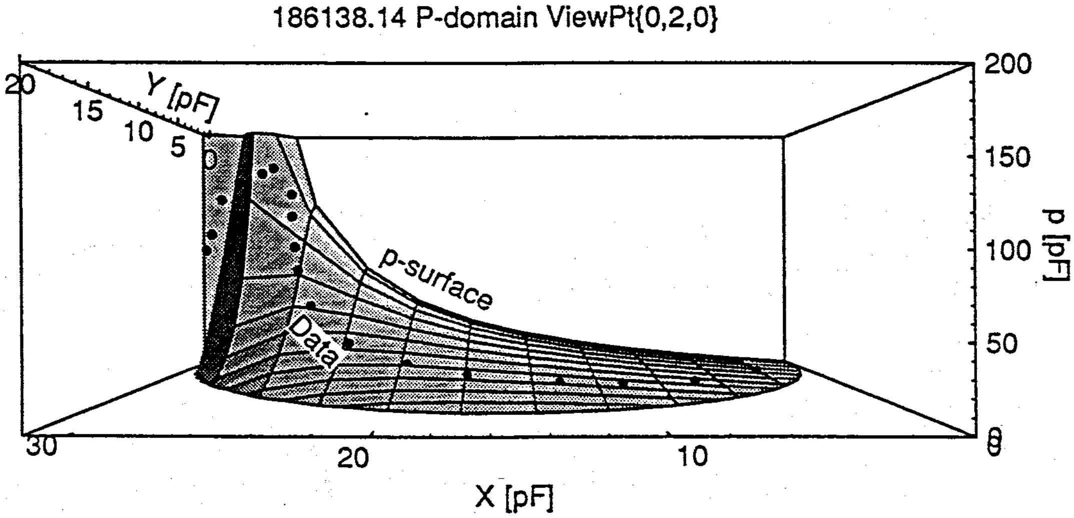


Figure 15. 186138.14 XYp 3-dimensional plot.

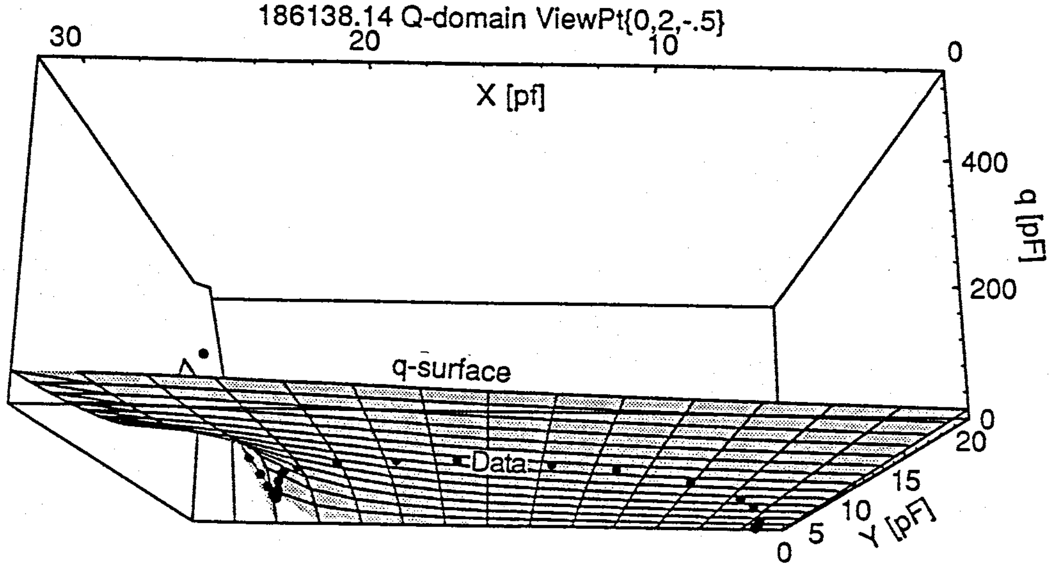


Figure 16. 186138.14 XYq 3-dimensional plot.

Table 1 contains information on the samples cited in this paper, including sample number, dopant concentration in the ice, and dopant concentration in the mother solution. A pure ice sample was chosen as a comparison standard. The remaining ice samples (except two) fall into two categories: alkali chlorides and ammonium chlorides.

The alkali chloride samples were grown from either hydrochloric acid or sodium chloride solution. In both cases the chloride ion enters the ice lattice relatively easily and is electrically compensated by a hydrogen ion from the solution. The sodium ion is not incorporated into the ice lattice. Therefore, in both cases the chloride enters the ice lattice as H^+Cl^-. The addition of hydrogen ions to the ice is expected to increase the dc conductivity of these samples.

The ammonium chloride samples were grown from ammonium chloride solutions with ammonium hydroxide sometimes added. The ammonium ion is polar, and an ammonium salt is incorporated into the ice matrix more easily than alkaline salts of the same anion. Ammonium hydroxide was added to the mother solution to increase the uptake of chloride by the ice. The incorporation of ammonium into the ice has a proton-suppressing effect since an excess of hydrogen ions is not present. This should cause a decrease in the dc conductivity of the ice. The presence of the polar ammonium ions should also cause an increase in the dielectric conductivity of the ice.

Surface Measurements

A typical surface measurement Cole-Cole plot is shown in Figure 17. Almost all the surface measurement curves are characterized by some combination of small normal and retrograde arcs. However the size and distribution were not constant from sample to sample and even varied considerably within sample runs. This type of retrograde arc could not be correlated to any known phenomenon and therefore surface measurements were discontinued early in the study.

Sample	Type	Conc. in Ice	Conc. of Mother
186122	Cl^-	2.2×10^{-8} *N* Cl^-	5×10^{-6} *N* HCl
186040	Cl^-	2.3×10^{-8} *N* Cl^-	5×10^{-6} *N* NaCl
186046	Cl^-	6.1×10^{-6} *N* Cl^-	1.2×10^{-3} *N* NaCl
186118	Cl^-	1.1×10^{-5} *N* Cl^-	1×10^{-2} *N* NaCl
186062	Cl^-	1.3×10^{-5} *N* Cl^-	1×10^{-2} *N* NaCl
186100	NH_4Cl	2.5×10^{-7} *N* NH_4Cl	1×10^{-5} *N* NH_4Cl and $(NH_4)_2SO_4$
186134	NH_4Cl	2.0×10^{-6} *N* NH_4Cl	1×10^{-4} *N* NH_4Cl
186114	NH_4Cl	1.9×10^{-6} *N* NH_4Cl	1×10^{-4} *N* NH_4Cl and 100% NH_4OH
186110	NH_4Cl	1.7×10^{-5} *N* NH_4Cl	1×10^{-3} *N* NH_4Cl and 25% NH_4OH
186106	NH_4Cl	1.1×10^{-4} *N* NH_4Cl	1×10^{-2} *N* NH_4Cl and 25% NH_4OH
186102	NH_4Cl	2.1×10^{-4} *N* NH_4Cl	1×10^{-2} *N* NH_4Cl and 25% NH_4OH
186050	MISC	PURE	PURE
186076	MISC	1×10^{-8} *N* MSA	MSA
186092	MISC	1.7×10^{-4} *N* $(NH_4)_2SO_4$	2×10^{-2} *N* $(NH_4)_2SO_4$

Table 1. Ice sample data.

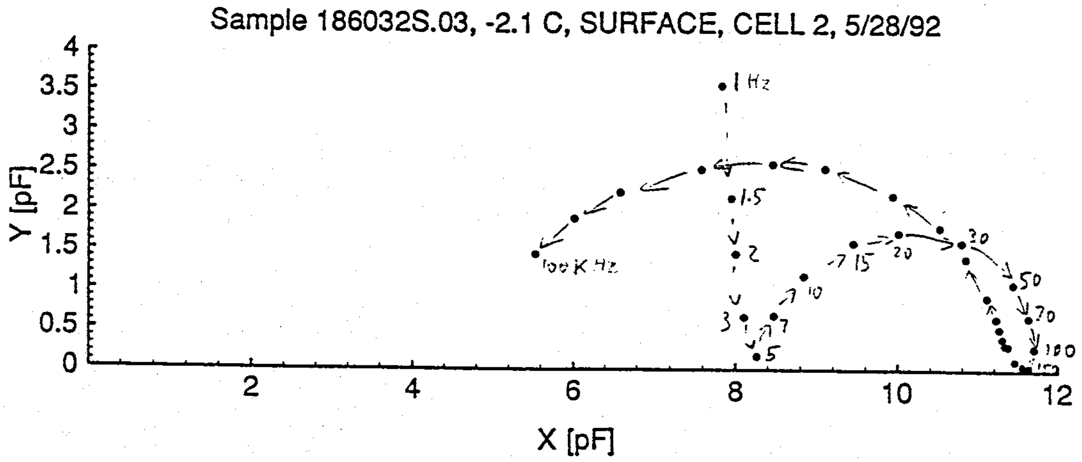


Figure 17. 186032S.03 surface measurement Cole-Cole plot.

Bulk Measurements

The bulk parameters derived from the lock-in measurements are the principal relaxation time, τ_β, in the blocking capacitor, the principal relaxation time, τ_2, in the ice, the dc conductivity, σ_0, the dielectric conductivity, $\Delta\sigma_D$, and the principal polarization strength, ε_2. All of these parameters are plotted as Arrhenius plots for the samples in this study. For clarity the samples are plotted in three groups (chloride, ammonium chloride, and miscellaneous) for each parameter.

τ_β

The principal relaxation time in the blocking capacitor reflects the dielectric relaxation behavior of the ice in series with the Teflon blocking foils. In Figure 18 the chloride samples show a regular sequence with concentration. The sample with the highest concentration (1.3×10^{-5} *N*) of chloride deviates most from the Auty-Cole line (Auty and Cole, 1952). The effect of the blocking capacitor is a vertical offset of τ toward shorter relaxation times in relation to ice values. The 2.2×10^{-8} *N* chloride sample shows a response very similar to the pure ice sample in Figure 20.

The ammonium chloride sample data for τ_β is illustrated in Figure 19. The ammonium chloride samples also show a well defined concentration sequence with 2.5×10^{-7} *N* close to the pure ice response and 2.1×10^{-4} *N* being the most depressed from the Auty-Cole line. The ammonium chloride samples of 2.0×10^{-6} *N* and 1.9×10^{-6} *N* both show very similar behavior, including the change in slope of the response.

One of the miscellaneous samples illustrated in Figure 20 shows the pure ice response. The 1×10^{-8} *N* MSA sample also shows a response very close to that of pure ice. The ammonium sulfate sample is depressed with respect to the pure ice response, but not as much as the ammonium chloride samples of similar concentration.

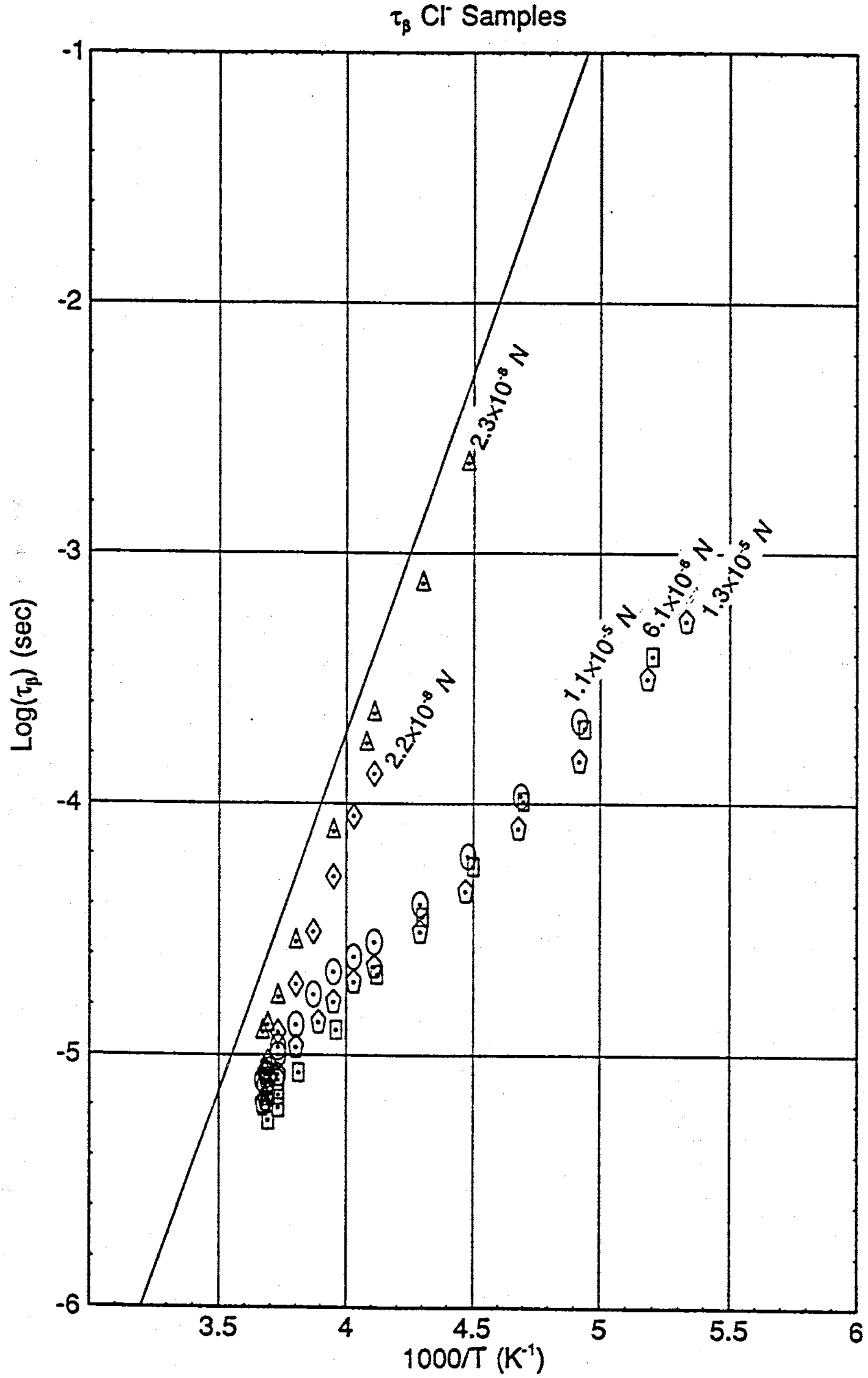


Figure 18. τ_β - chloride samples.

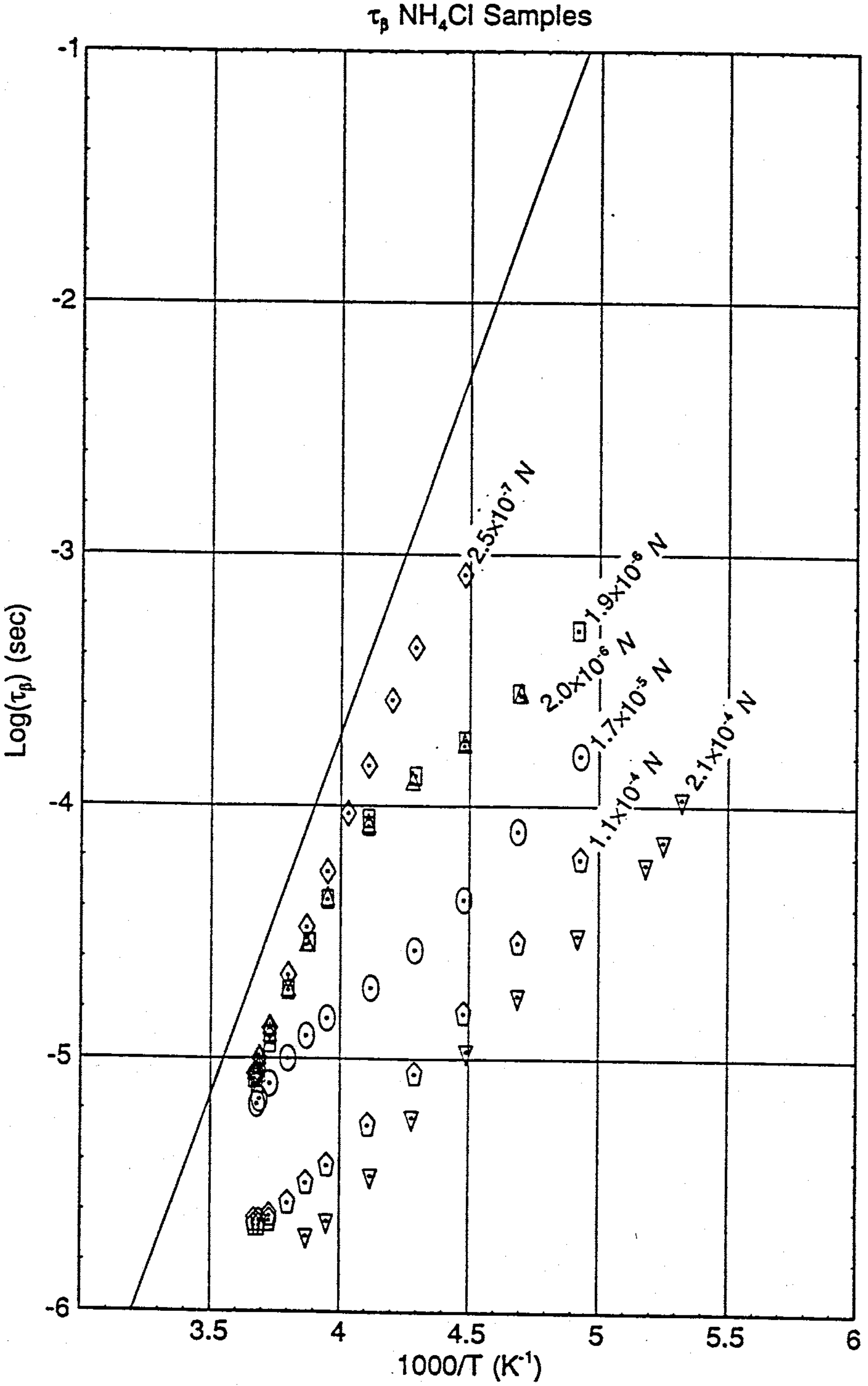


Figure 19. τ_β - ammonium chloride samples.

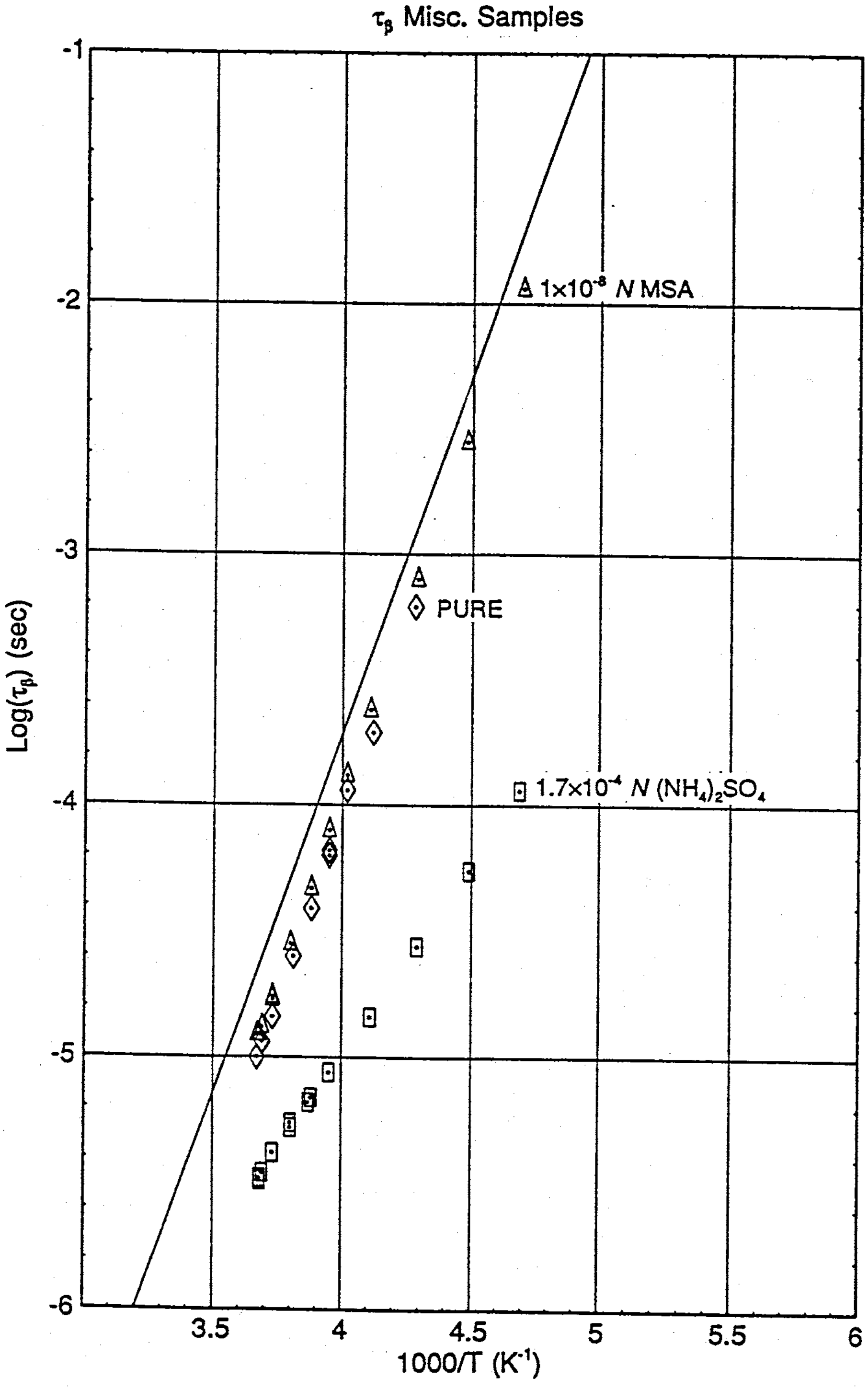


Figure 20. τ_β - miscellaneous samples.

τ_2

The principal relaxation time in the ice is obtained by inversion of the blocking capacitor data to ice parameters. The chloride samples illustrated in Figure 21 show similar trends as in τ_β. The samples show the predicted concentration sequence with both 10^{-8} *N* samples falling nearly on the Auty-Cole line.

The ammonium chloride samples are shown in Figure 22. The ammonium chloride samples also show the predicted concentration sequence. The 2.5×10^{-7} *N* sample falls close to the Auty-Cole line. And again the 2.0×10^{-6} *N* and 1.9×10^{-6} *N* samples are in excellent agreement and simultaneously show a well defined change in slope.

The pure ice response is illustrated in the miscellaneous sample data in Figure 23. The pure ice response lies almost perfectly on the Auty-Cole line. The 10^{-8} *N* MSA response is slightly elevated above the Auty-Cole line. The ammonium sulfate response is again depressed with respect to pure ice, but not so much as for ammonium chloride samples of similar concentration.

σ_0

The dc conductivity is derived from the peak frequency of the α-dispersion and represents a measure of the abundance and mobility of free charge carriers in the ice. Figure 24 illustrates the dc conductivity response of the chloride samples. The 6.1×10^{-6} *N* sample shows a dc conductivity two orders of magnitude higher than the other samples and appears to deviate from the expected concentration sequence. The 1.1×10^{-5} *N* sample has not been plotted due to difficulty in distinguishing the α-dispersion peak.

The ammonium chloride samples are shown in Figure 25. The ammonium chloride samples show no identifiable concentration sequence. All of the samples show similar behavior with a very steep drop in conductivity from -1.0 to -10.0 C. Then the response tends to level off from -10.0 to -80.0 C. The ammonium chlorides show much lower dc conductivities than the chloride samples by approximately an order of magnitude.

The miscellaneous samples in Figure 26 show behavior similar to the ammonium chloride samples. The pure ice response is a well defined steep slope which levels off. The 1×10^{-8} *N* MSA sample nearly matches the pure

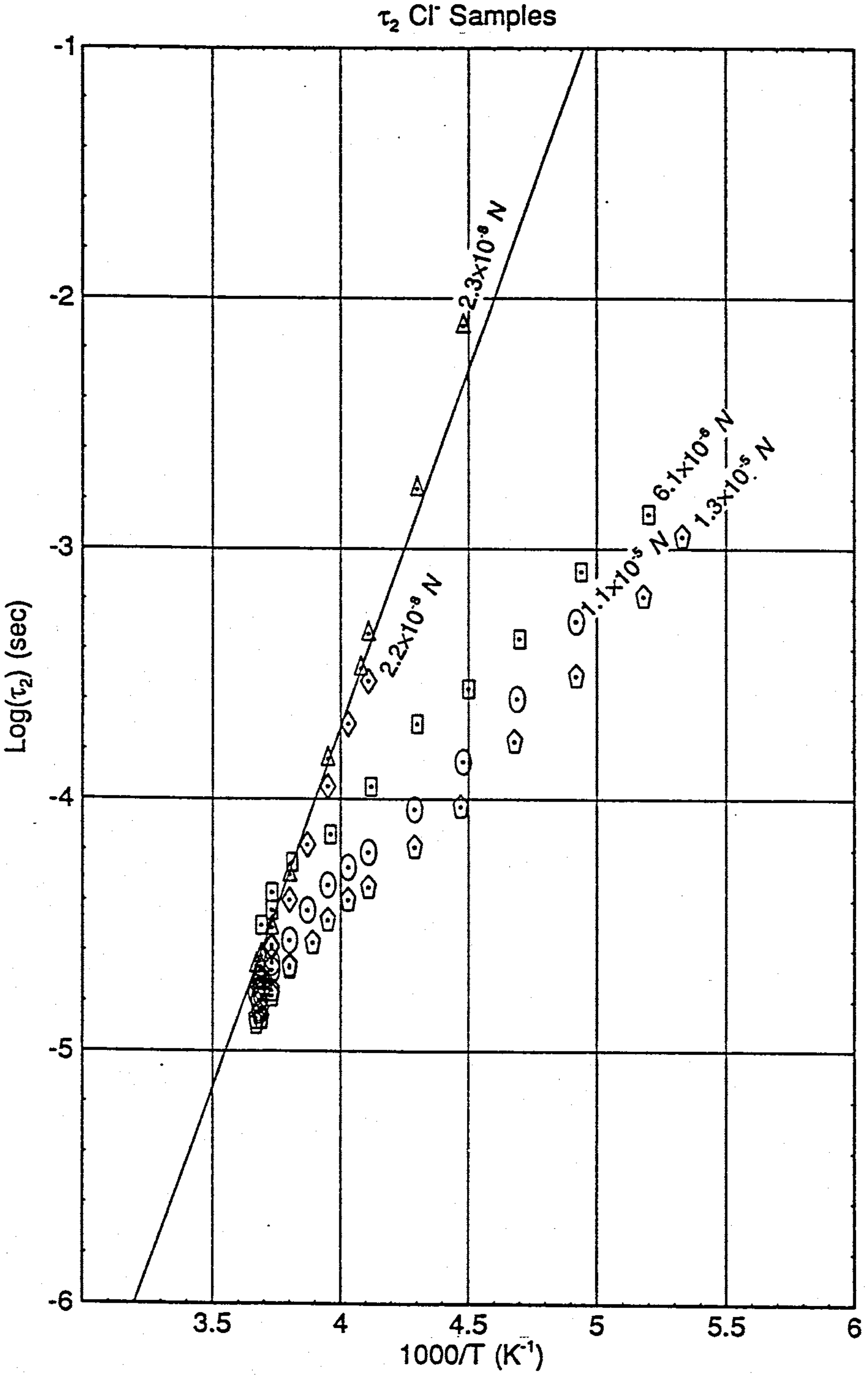


Figure 21. τ_2 - chloride samples.

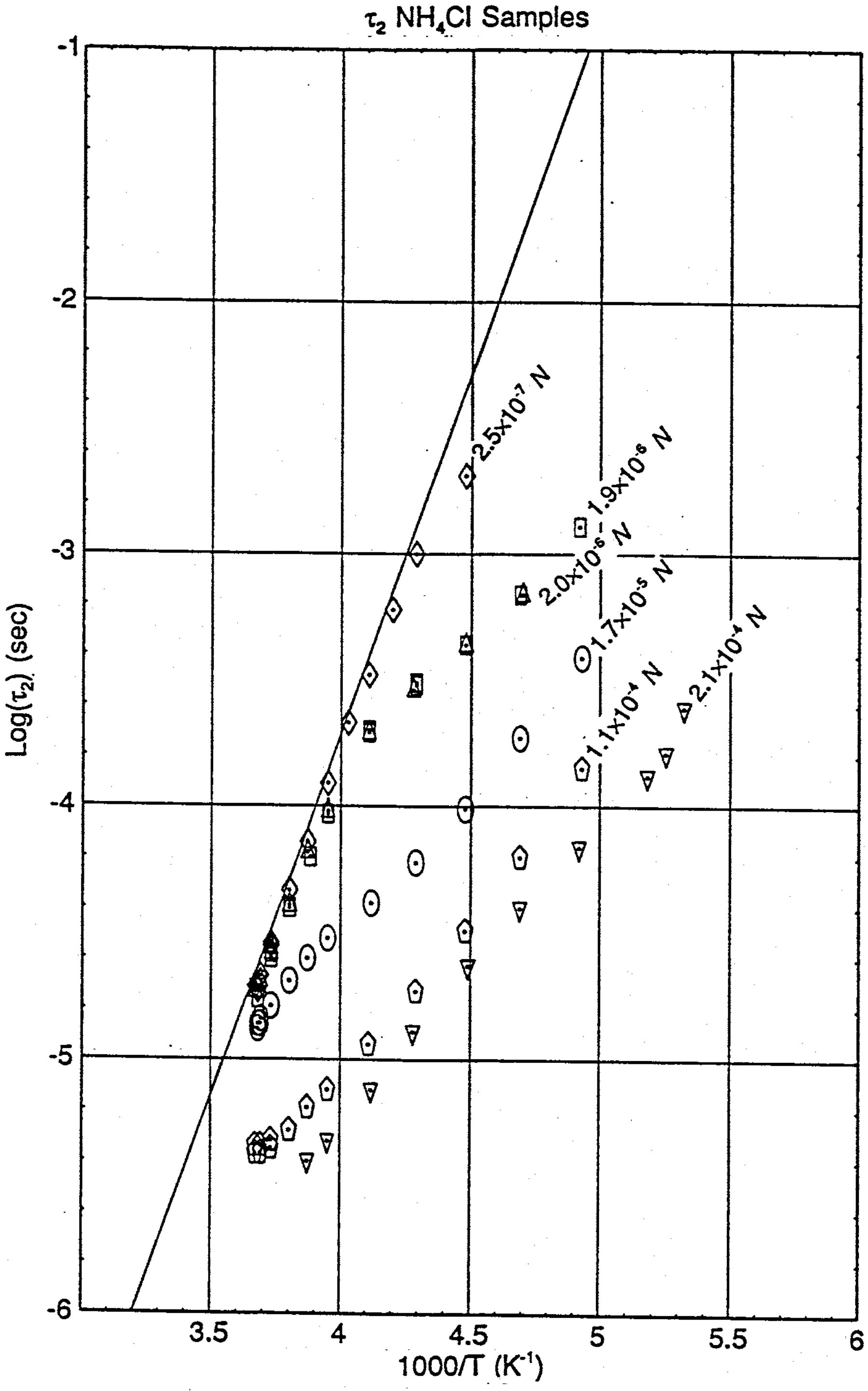


Figure 22. τ_2 - ammonium chloride samples.

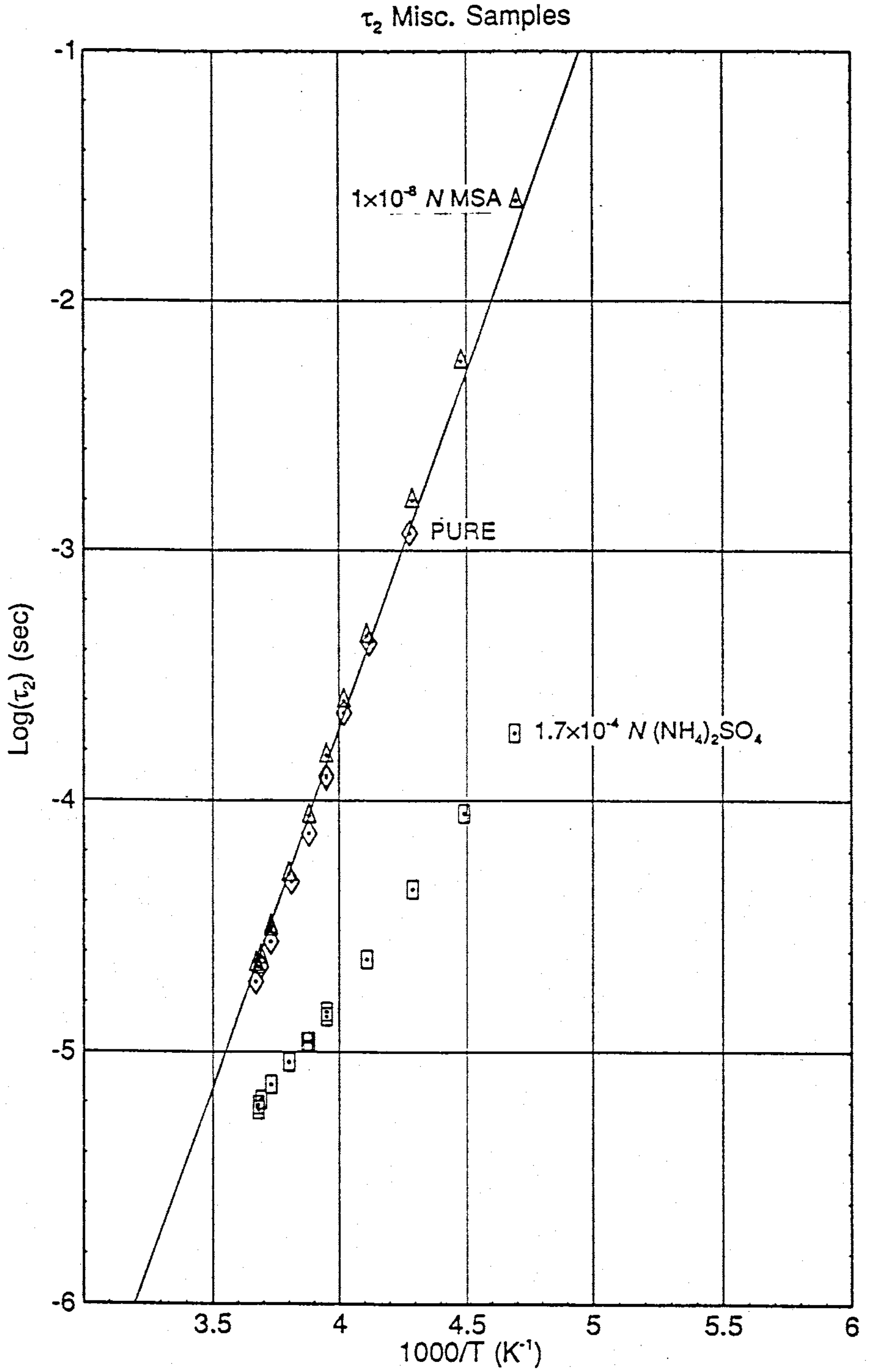


Figure 23. τ_2 - miscellaneous samples.

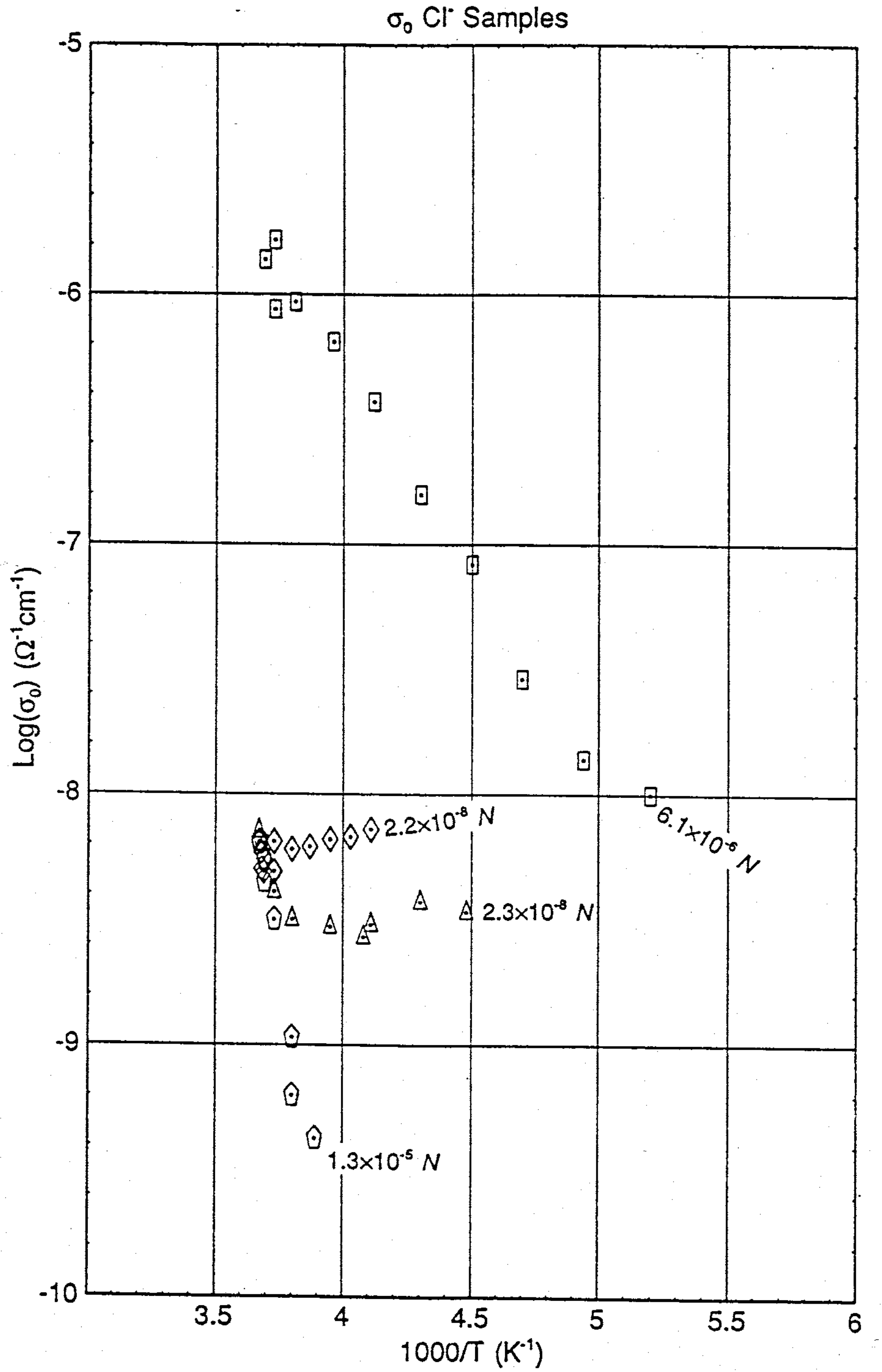


Figure 24. σ_0 - chloride samples.

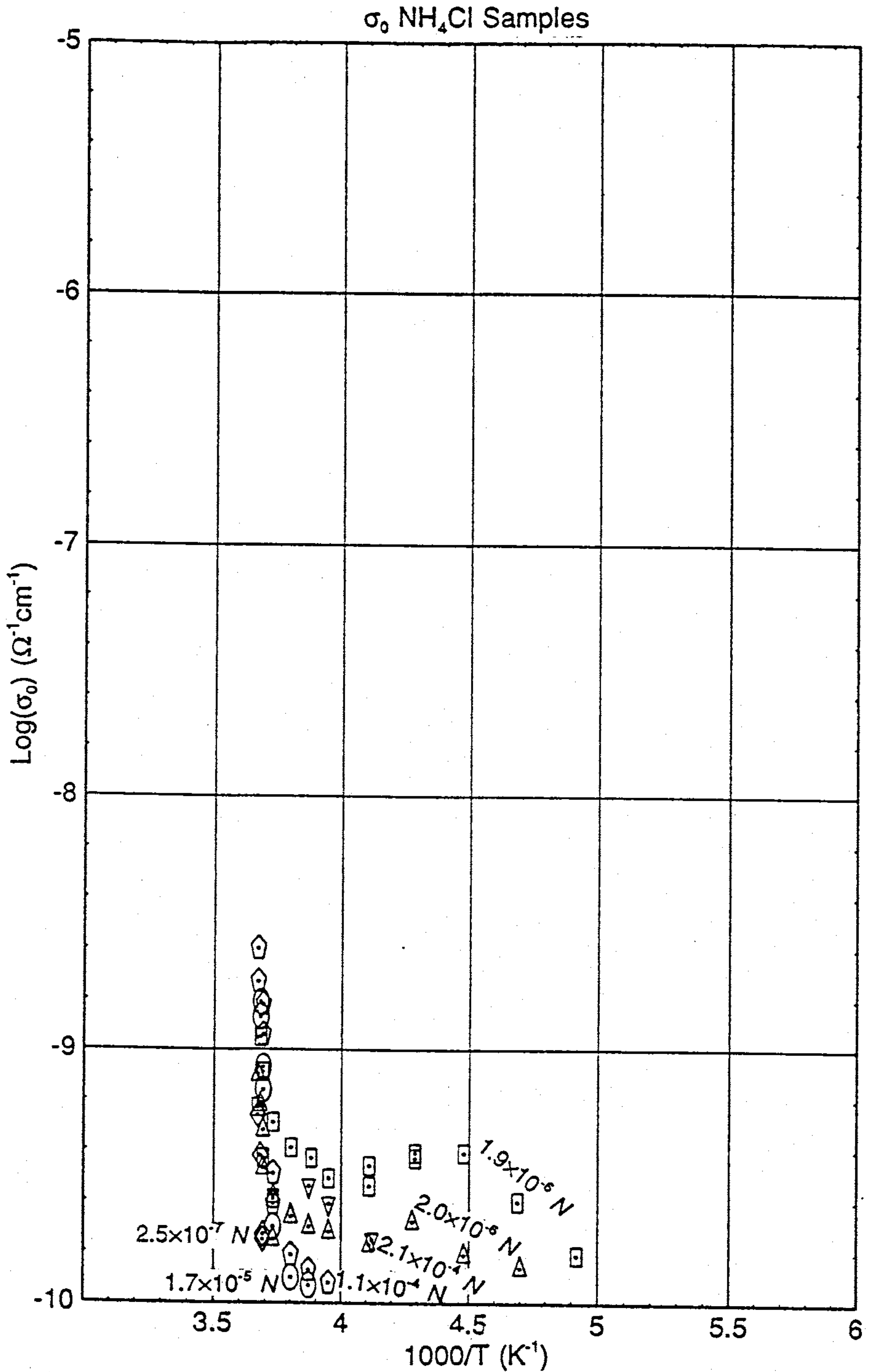


Figure 25. σ_0 - ammonium chloride samples.

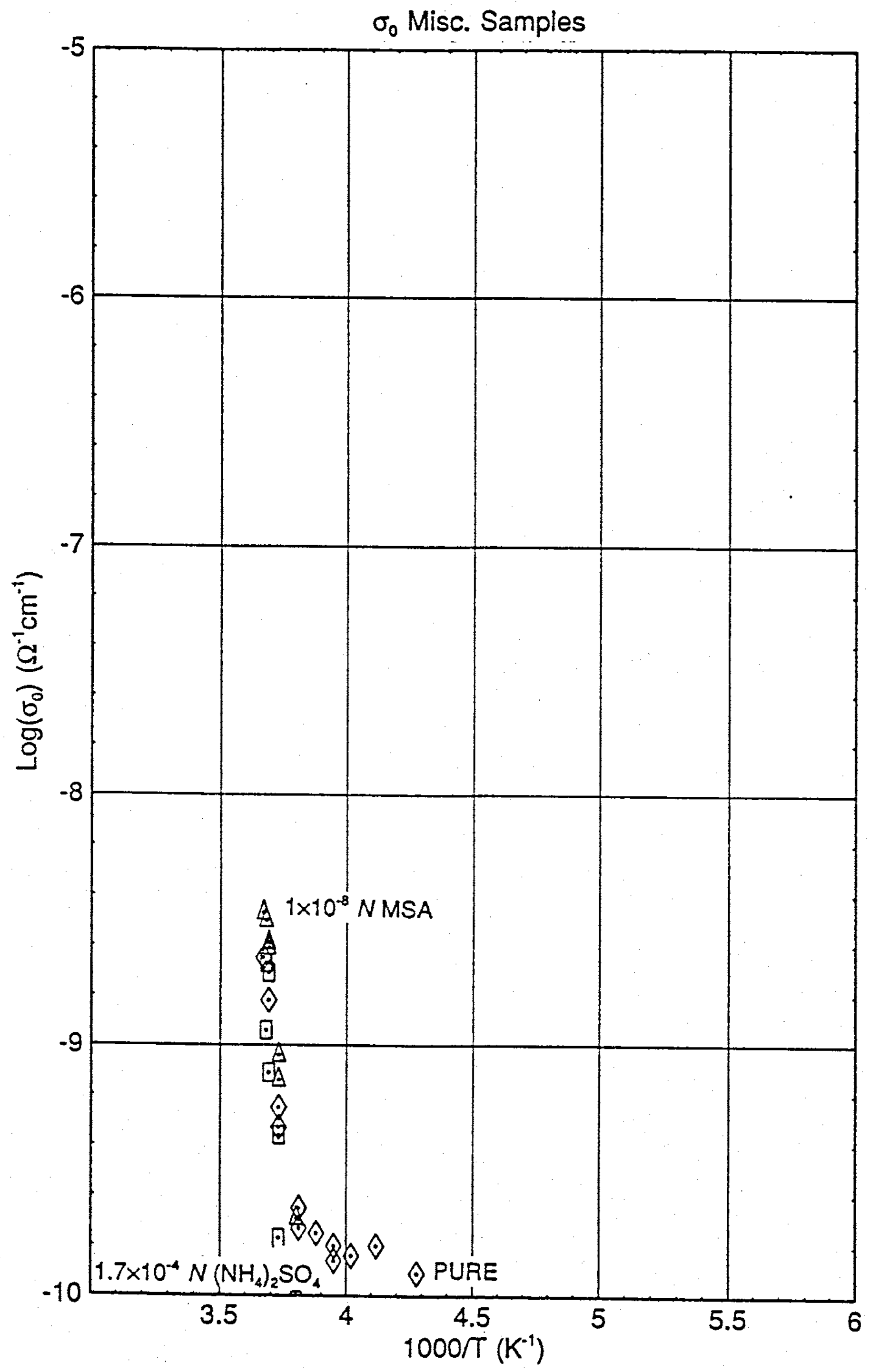


Figure 26. σ_0 - miscellaneous samples.

ice response. The ammonium sulfate response appears to continue to decline steeply.

$\Delta\sigma_D$

The dielectric conductivity is not a conductivity in the sense of mobile charge migration. The dielectric conductivity is an apparent conductivity which arises as the water dipoles dissipate energy by relaxing in the electric field of the blocking capacitor. The dielectric conductivity is derived from the peak frequency of the principal dipolar dispersion.

The response of the chloride samples is illustrated in Figure 27. The 2.2×10^{-8} *N* and 2.3×10^{-8} *N* samples show excellent agreement with both describing virtually the same steeply descending line. This agrees well with the behavior observed for the pure ice sample. The remaining samples merge at high temperatures. Only the 6.1×10^{-6} *N* sample plots above the concentration of data points at high temperature.

Figure 28 shows the response of the ammonium chloride samples. A concentration sequence is very clearly demonstrated in these samples, with the most dilute samples showing the most depressed response. the 2.5×10^{-7} *N* sample shows a response which is close to that of the pure ice sample. And again the 1.9×10^{-6} *N* and the 2.0×10^{-6} *N* samples show very good agreement, including duplication of the change in slope at about -30 C (1000/T=4.11).

The miscellaneous sample responses are shown in Figure 29. The pure ice response declines steeply and is followed very closely by the 1×10^{-8} *N* MSA sample. The ammonium sulfate sample is elevated above the pure ice response by nearly an order of magnitude.

ε_2

The principal polarization strength (or dielectric susceptibility of the principal dispersion range) is an indication of the degree to which the ice sample polarizes in an electric field. Figure 30 shows the response of the chloride samples. There is no concentration sequence evident. The response of the 2.3×10^{-8} *N* sample increases very abruptly at -40 C. The 6.1×10^{-6} *N* sample exhibits a very puzzling response. The high temperature data indicates an extremely high polarization strength that decreases

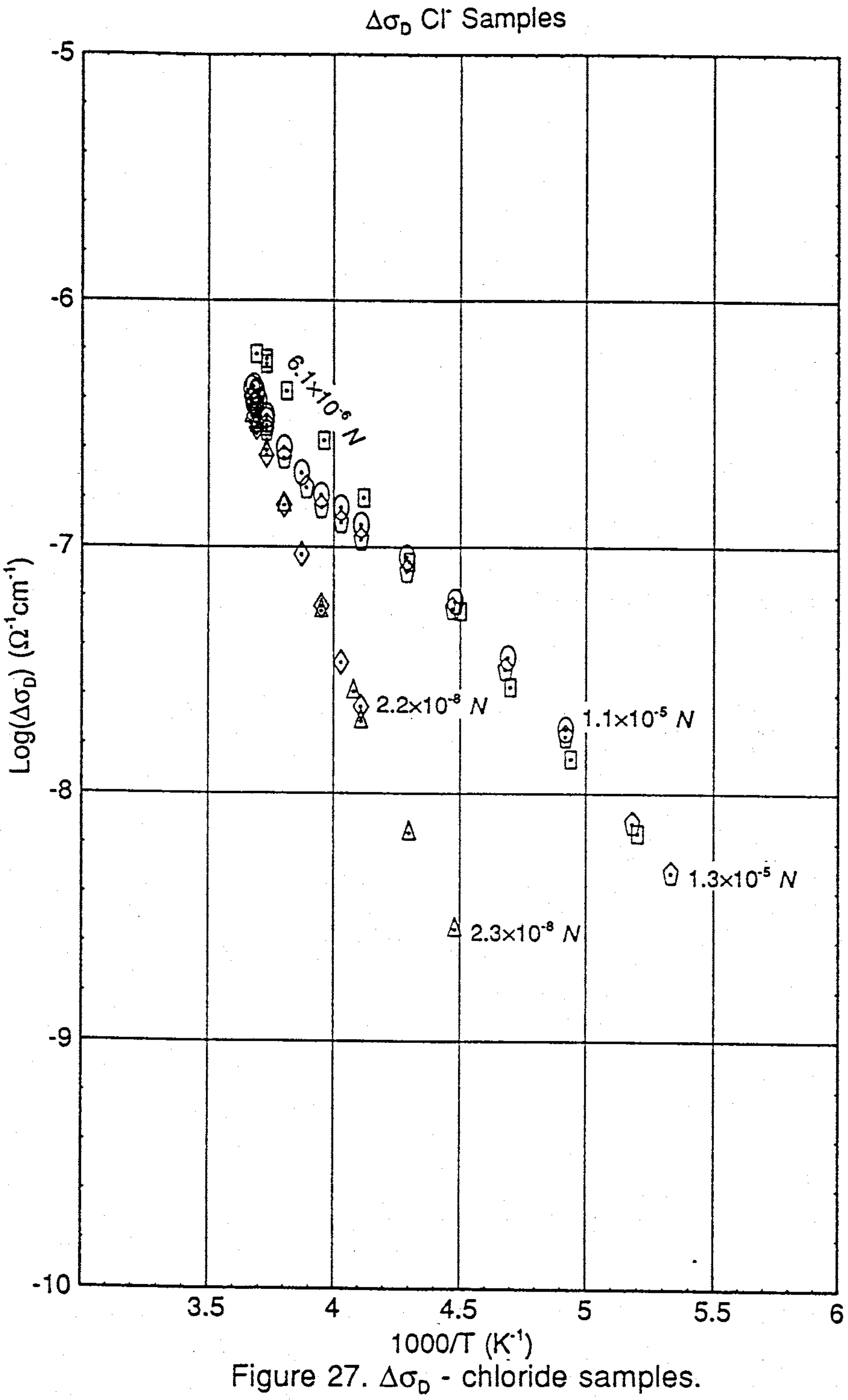
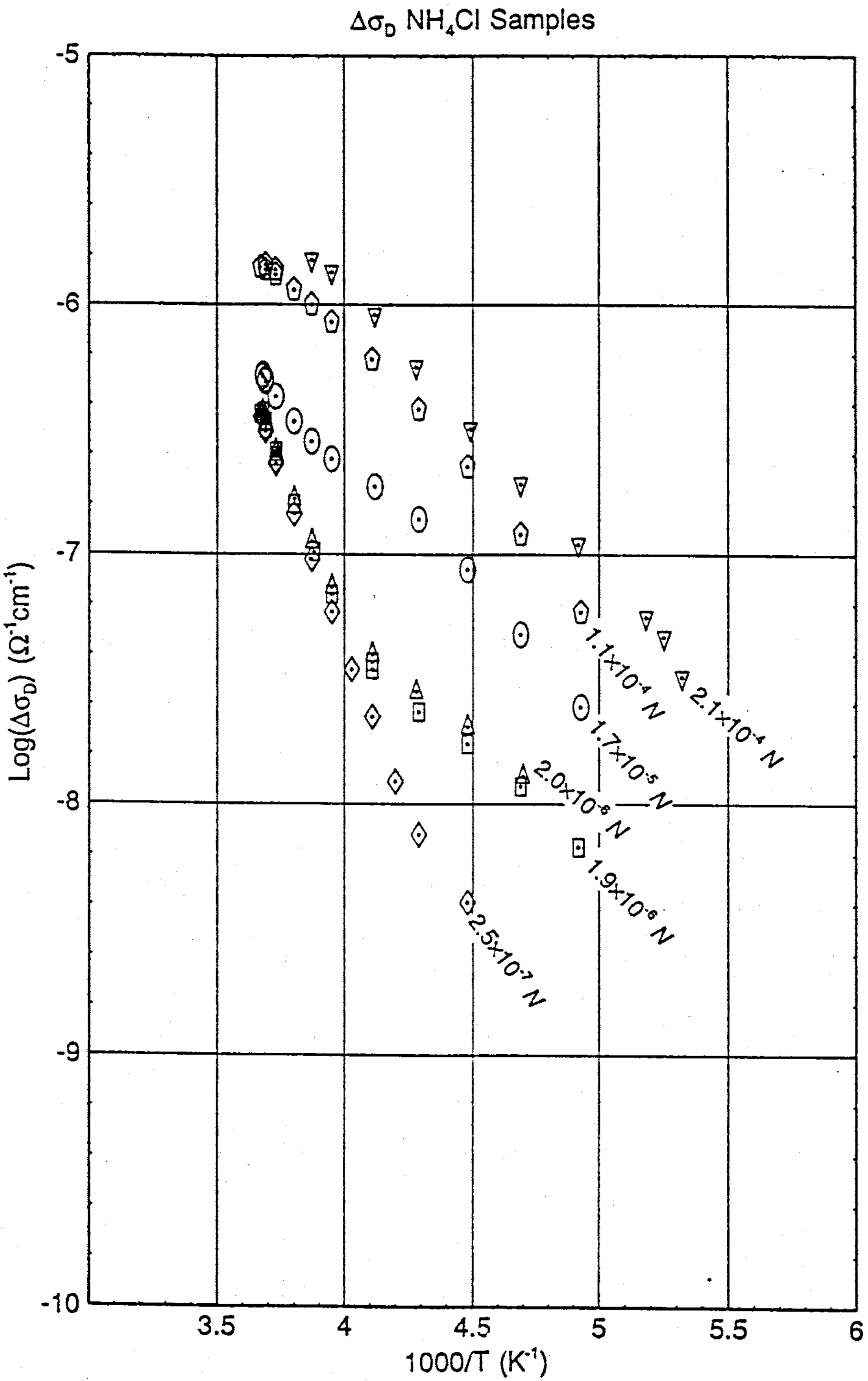


Figure 27. $\Delta\sigma_D$ - chloride samples.



$\Delta\sigma_D$ NH_4Cl Samples

Figure 28. $\Delta\sigma_D$ - ammonium chloride samples.

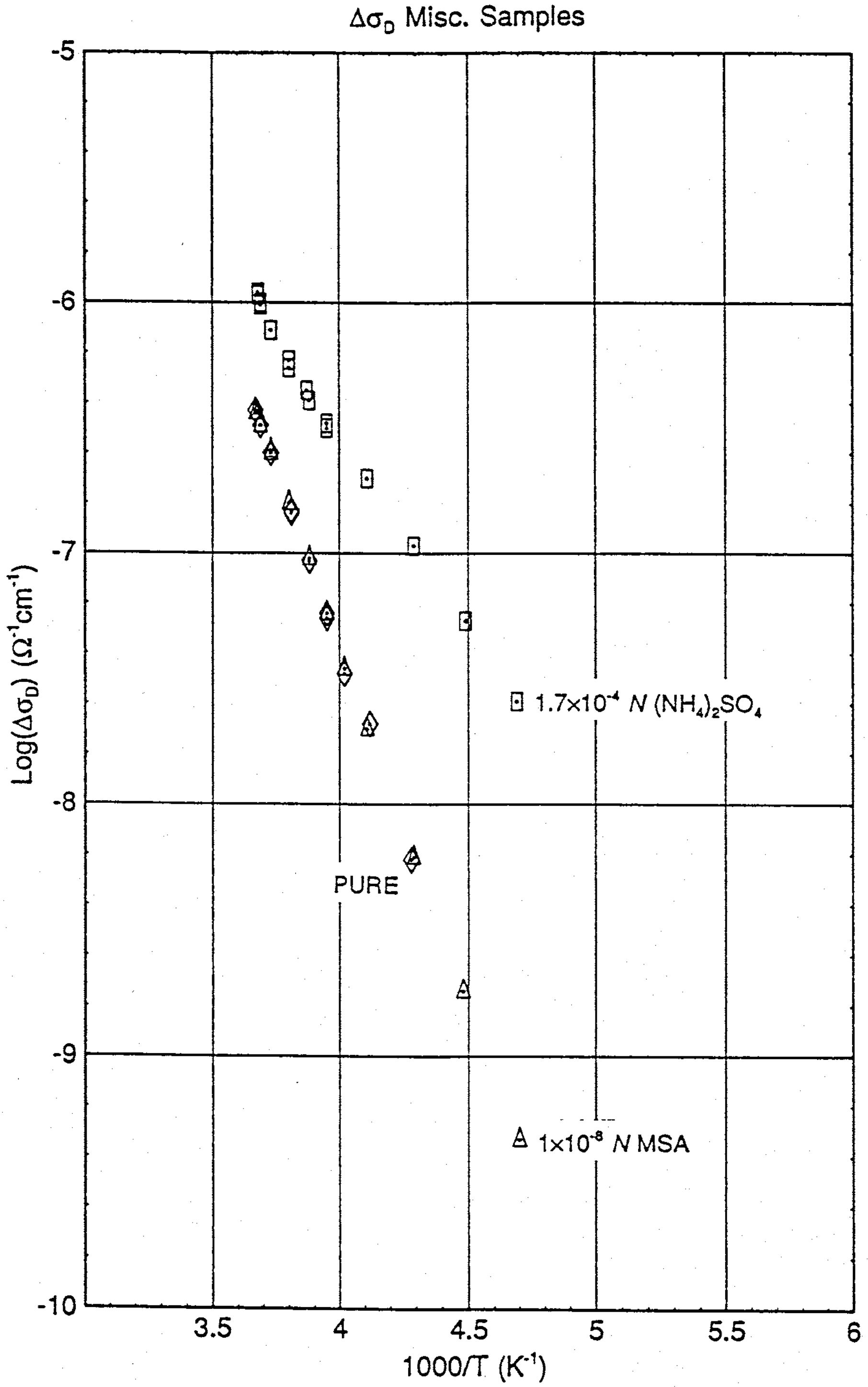


Figure 29. $\Delta\sigma_D$ - miscellaneous samples.

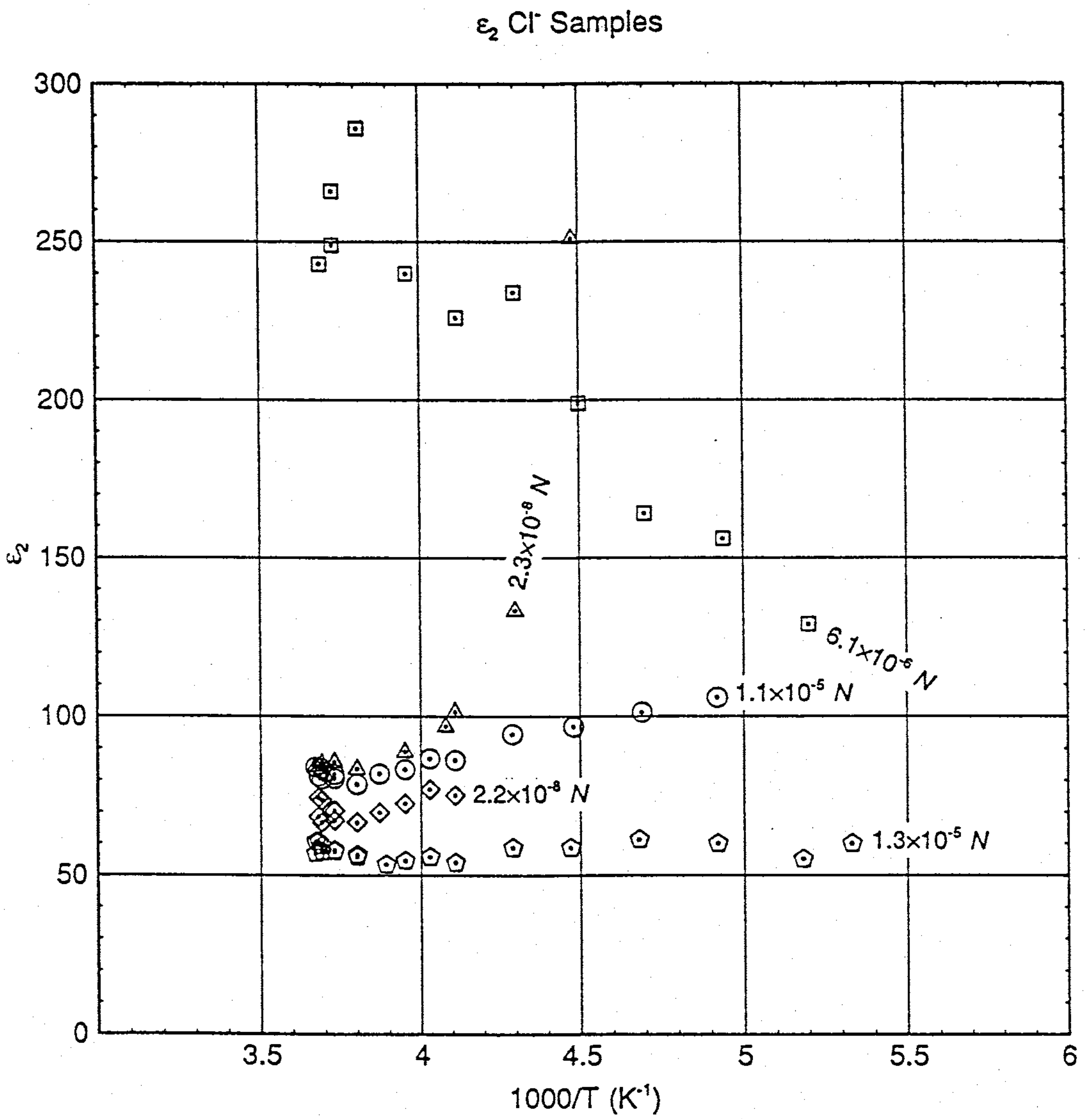


Figure 30. ε_2 - chloride samples.

sharply with decreasing temperature.

Figure 31 shows the response of the ammonium chloride samples. The samples cluster together at high temperature. Some samples fall out of the concentration sequence, however the most concentrated samples do show the lowest values of polarization strength.

The miscellaneous samples are shown in Figure 32. The pure ice response is nearly flat. It is interesting that in the polarization strength the 10^{-8} *N* MSA sample deviates from the pure ice response. Even at high temperatures the MSA sample has an elevated polarization strength. And at low temperatures the response is seen to increase significantly while the pure ice response remains flat. The ammonium sulfate sample has values of polarization strength similar to pure ice at the highest temperatures only. The response then quickly drops to a substantially lower value and then levels off.

Discussion

Nature of the Dielectric Response

The response of the layered capacitor is generally characterized by two loss peaks when Y vs X is plotted. These losses result from two different mechanisms. The β-dispersion shows a loss peak at high frequency. The β-dispersion is a true dielectric loss, in that it results from the orientation of water dipoles in response to the applied electric field. As temperature decreases and randomizing forces due to thermal motion also decrease, the principal relaxation time associated with the loss peak is seen to increase. This is due to the reduction of thermal motion which tends to randomize (or depolarize) the water dipoles.

The α-dispersion is observed at lower frequency than the β-dispersion. The α-dispersion is not a dielectric loss in that it does not result from the polarization of dipoles. Free charge carriers in the ice migrate under the influence of the applied electric field and accumulate at the blocking electrodes. This space charge accumulation is primarily due to protons, which are thought to be the majority charge carriers in ice (Hobbs, 1974). The motion of the protons through the ice lattice is limited by the abundance and position of defects in the lattice. The protons are thought to move along these defects by quantum mechanical tunnelling from one

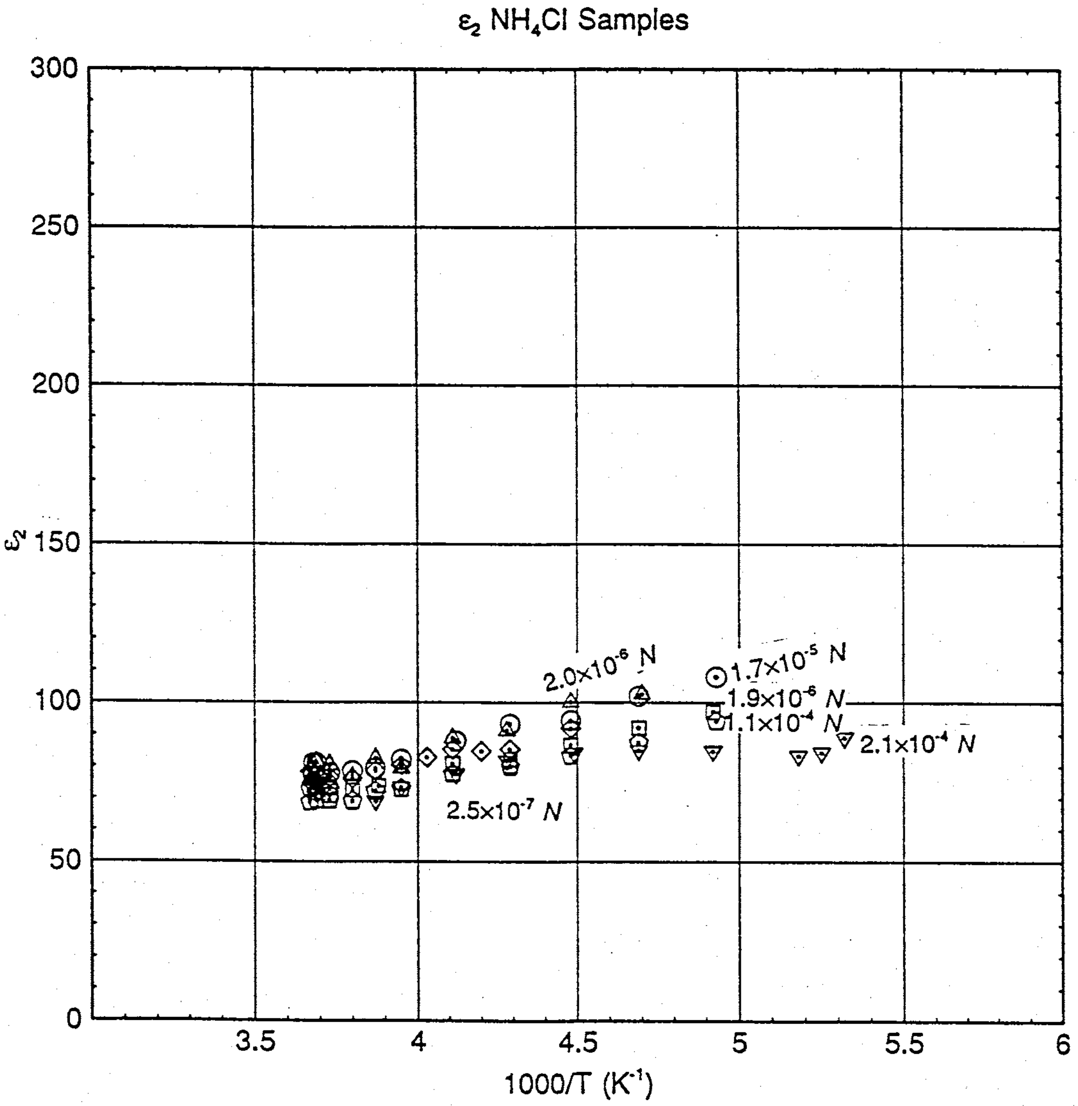


Figure 31. ε_2 - ammonium chloride samples.

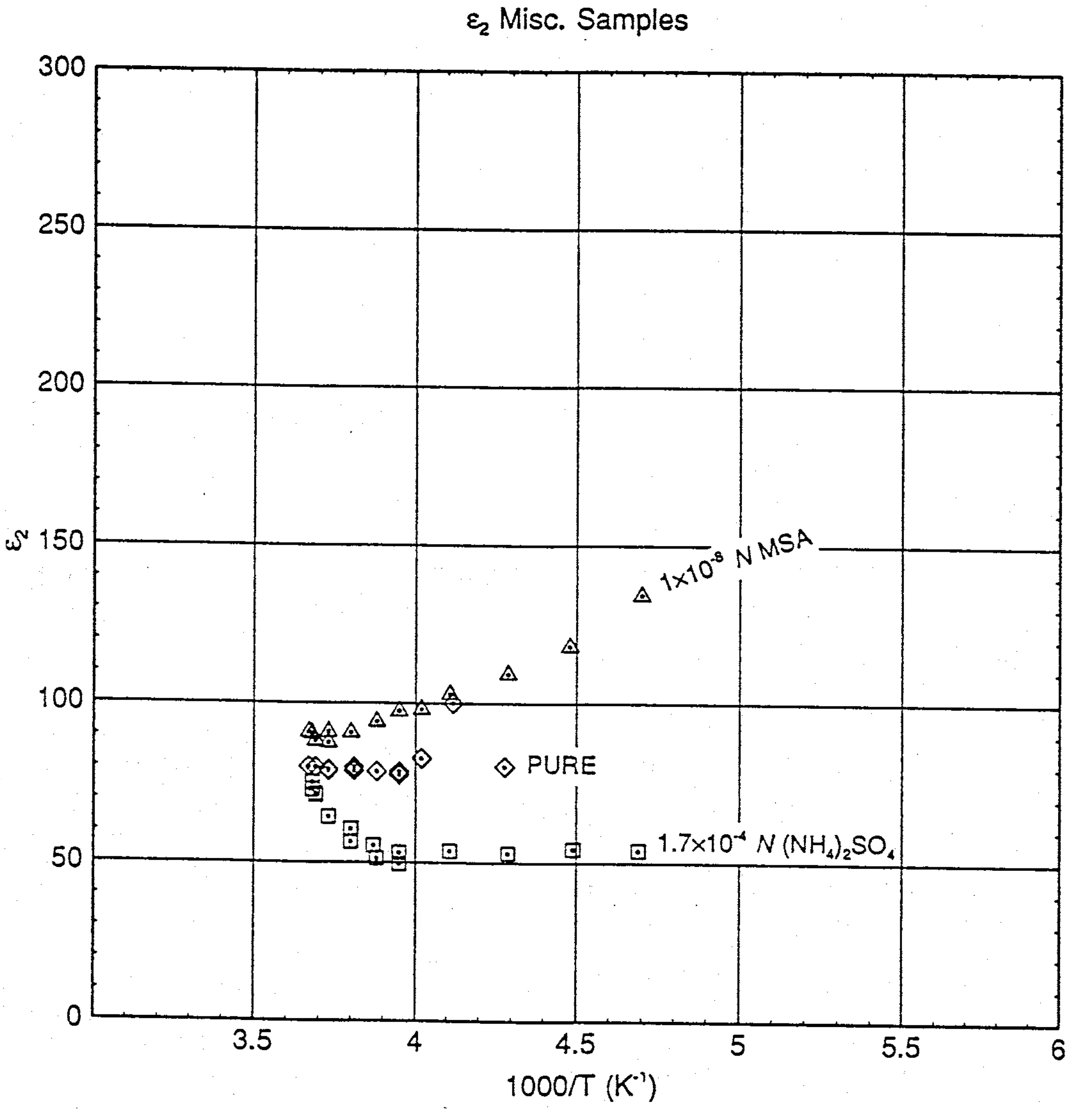


Figure 32. ε_2 - miscellaneous samples.

water molecule to another, passing through the hydrogen bond energy barrier (Hobbs, 1974).

The blocking capacitor method is most useful because it prevents reactions from occurring which can obscure the ice response. Chemical reactions may occur at the ice-electrode interface which create ionic polarization that completely masks the true polarization of the ice. This is eliminated by inserting a blocking (Teflon) layer between the ice and electrode. The result is a greatly increased resolution of the ice response at low frequencies.

Surface Measurements

The surface measurement technique failed to provide any useful data about the surface properties of the ice samples. The Cole-Cole plots of the surface measurement data sets show highly irregular, inconsistent, and retrograde arcs. The retrograde arcs were the most bizarre aspect of these measurements. Scrutiny of these retrograde arcs yielded no clue as to their meaning or origin. Only upon observing the lock-in during one retrograde measurement sequence was a plausible explanation for this behavior developed.

During a normal non-retrograde measurement the phase angle on the lock-in amplifier is observed to range between -90.0° (pure capacitance) and -180.0° (pure conductance), illustrated in Figure 33. However, during the acquisition of retrograde data the phase angle was seen to range between -90.0° and 0.0°. It must be remembered that during calibration the purely capacitive response is assigned a phase angle of -90.0° in what is essentially a two-dimensional plane of complex capacitance. So during normal measurements all the data fell into the third quadrant, which is the domain of positive $Re[C_X]$ and positive $Im[C_X]$, by definition. But during retrograde measurements the data fell into the fourth quadrant, which is the domain of positive $Re[C_X]$ and negative $Im[C_X]$. The $Im[C_X]$ component represents the conductance divided by the angular frequency, G_p/ω. Clearly the conductance must be negative for this component to have a negative value, because a negative frequency is non-physical.

This negative conductance begs an explanation and I offer the following hypothesis. The guard and low electrodes both contact the under surface of the low foil. During the surface measurement these two electrodes become the high and low measurement electrodes. The

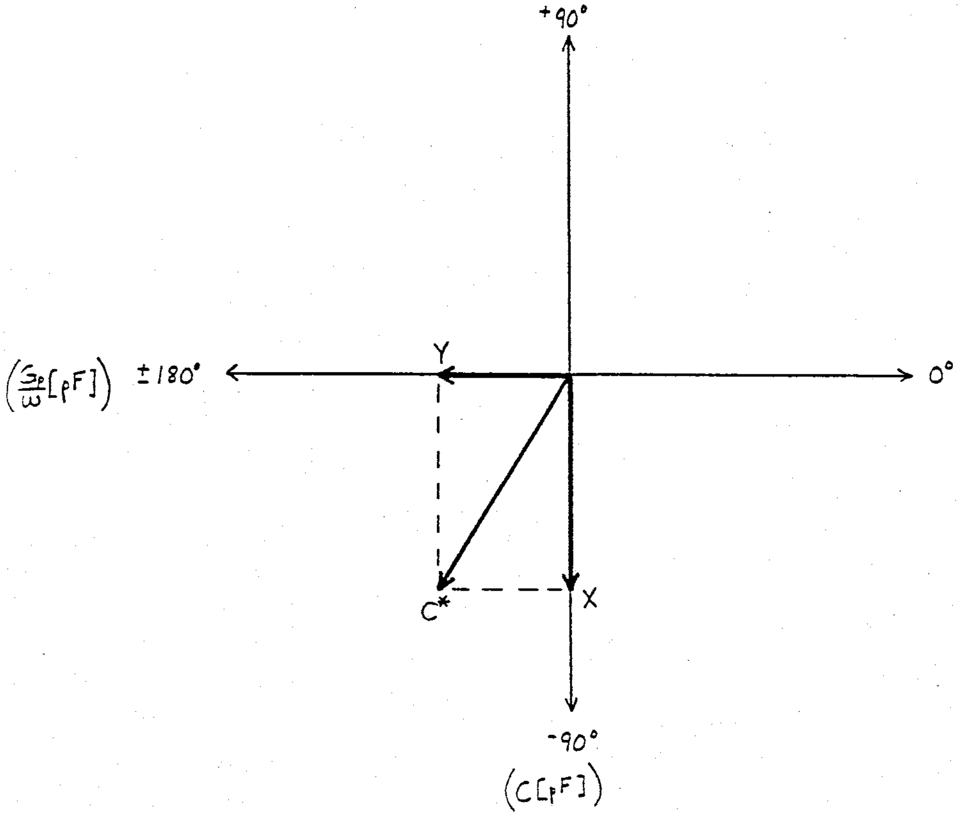


Figure 33. Measurement phasor diagram.

separation between the two is less than 0.1″. It is likely that, unless special precautions are taken, small accumulations of frost may form on the foil between the two electrodes. This would cause a conductive path to bridge between the two electrodes. The bridging path could appear as a negative conductance if the metal-ice-metal contact generated an electrical potential due to some chemical reaction (hydrolysis?).

There is one other fatal flaw to the surface measurement technique. Because the Teflon blocking foil is continuous across the surface of the sample, it is likely that the surface measurements are dominated by the response of the blocking foil surface and reflect very little of the intrinsic ice response. It is clear that the existing surface measurement technique is inadequate and needs to be redesigned.

Bulk Measurements

The bulk measurements were very successful, with only minor incidents of unusual behavior. Measurement abnormalities did periodically occur during the early part of the study. It was thought that this might be due to frost accumulating on the sample and foils. Silicone vacuum grease was applied to the sample and foils in an effort to minimize frosting. The problem persisted or worsened. A new procedure was developed in which the sample temperature was raised to -2.0°C and the freezer temperature lowered to -30°C. The sample was kept in this state overnight, allowing the high vapor pressure of the ice at -2.0°C and the large temperature gradient to cause migration of the frost away from the sample and toward the freezer. This procedure worked very well and is regularly used at the start of each sample run. The use of silicone grease was discontinued when the defrosting procedure was discovered.

Teflon foils of 0.0025″ (0.07mm) thickness were initially used in these measurements. However these foils are easily damaged during cleaning and installation into the cell. Foils of 0.005″ (0.13mm) thickness were used almost exclusively for the last half of the study. These foils are much more resilient and withstand cleaning and installation very well. It is interesting to note that upon substitution of the thicker foils there was only a very small change in the magnitude of the dielectric response. This is contrary to the Q ratio relationship expounded by Mounier and Sixou (Mounier and Sixou, 1969). This is probably due to the fact that the 0.0025″ foil suffered from air gaps resulting from its lack of rigidity. This would explain why the thin foil measurements showed C1 values which were frequently 20-40% lower than the theoretical value. The more rigid 0.005″ foil appears to fill more nearly the space between the ice and the electrode, and therefore, shows C1 values which usually agree to within 15% of the theoretical value.

Because the foils show such sensitivity to air gaps, a better way to control the Q ratio is by varying the sample thickness. Sample thicknesses used in this study ranged from 14mm to 8mm. Increasing the sample thickness, and therefore the Q ratio, has been shown by our measurements to be effective in attaining slightly better closure of the low frequency dispersion. However, the dramatic gain in amplitude predicted by Mounier and Sixou has not been observed.

τ_β

The principal relaxation time in the blocking capacitor is derived from the peak frequency of the β-dispersion on the plot of Y versus frequency. In all cases where the β-and α-dispersions are well separated in frequency, the shape of the β-dispersion is observed to be of the Debye type. The shape of the β-dispersion is distorted as the two dispersions merge at lower temperatures. The effect of this superposition can be negated by subtracting off a Debye response centered on the β-dispersion from the Y response. This procedure yields a separated Y response which more clearly shows the α-dispersion.

The principal dispersion time in the blocking capacitor is the simplest parameter to obtain because it is derived from the peak frequency without calculation of inversion parameters. This makes it less sensitive to the effect of superposition of the α-dispersion range, which tends to cause the inversion parameters to increase too rapidly. The principal dispersion time in the blocking capacitor is always depressed below the principal dispersion time in the ice. However, the two parallel each other with deviations only when strong superposition of ranges occurs. This feature makes the principal dispersion time in the blocking capacitor a useful diagnostic tool for polar ice core logging as developed by Paren and Moore of the British Antarctic Survey (Moore et al., 1989).

The τ_β plots shown in Figures 18, 19, and 20 illustrate the effects of the various impurities. The chloride samples show a regular sequence with concentration, however the samples bunch up into two groups. The samples with 10^{-8} *N* chloride agree well with the pure ice response. The remaining samples all fall close together and show a distinctly different slope from the

10^{-8} *N* samples. This change in slope indicates a transition from an intrinsic to extrinsic mechanism at higher chloride concentrations.

The ammonium chloride samples show a much clearer example of concentration dependance. The sequence is very well defined. The 2.5×10^{-7} *N* response is very close to the pure water response. The transition of mechanisms is documented by the two 10^{-6} *N* samples. The responses agree remarkably well, in spite of the fact that sample 186114 was prepared with 100% excess ammonium hydroxide. Comparison with the ammonium sulfate sample indicates that, at equal concentrations, ammonium chloride causes about an order of magnitude greater depression of τ_β than ammonium sulfate.

The 10^{-8} *N* MSA response is again very close to the pure water response. This would indicate that, for the impurities investigated, the range 10^{-7} to 10^{-8} *N* is the lower limit at which the τ_β response of doped ice is indistinguishable from the pure ice response.

τ_2

The principal dispersion time in the ice is calculated from τ_β by use of inversion parameters. Ideally the pure ice response should fall on the solid line which represents the trend of the data obtained by Auty and Cole. However, the inversion parameters can be artificially increased by the superposition of the α-dispersion with the β-dispersion. Then the data are observed to fall above the Auty-Cole line. Generally the elevation is not so large as to compromise the quality of the data.

The τ_2 plots in Figures 21, 22, and 23 show trends which parallel those in the τ_β domain. The only notable exception is in the chloride samples where the concentration sequence is better separated in τ_2.

σ_0

The dc conductivity is derived from the peak frequency of the α-dispersion and the inversion parameter C_2. The dc conductivity is difficult to interpret because of the sensitivity of the C_2 parameter to superposition of dispersion ranges. Another difficulty with the dc conductivity is the assignment of the peak frequency when a third dispersion range appears. This is most often seen in ammonium hydroxide samples, however it forces the question of which dispersion is actually that due to conductivity? And when only two dispersion ranges are visible, which is the case for the samples in this study, is a third range lurking at frequencies below 1 Hz?

In an attempt to determine the true dc conductivity a series of inversions were performed from the blocking capacitor (XY) domain to the ice (pq) domain. The true dc conductivity in ice should be apparent as a plateau in p and a 45° slope in q at low frequency (log log plot). Also, a plot of total ice conductivity (w×q) should indicate a minimum plateau at low frequency if the dc conductivity has been reached. Unfortunately the XY to pq inversion maps the low frequency data points into a highly non-linear region in pq space. This means that the low frequency information content of the data is often reduced and the pq data is inconclusive about the presence of a true dc conductivity.

Increased resolution of the low frequency behavior of the samples is necessary to reach the region where a true dc conductivity should be apparent. There are several methods to increase the resolution of low frequency behavior, however each has associated difficulties. The Q ratio of the sample may be adjusted to higher values by using thinner foils or by increasing the sample thickness. Any foil thickness less than 0.005″ is impractical however. Foils of 0.0025″ were used with unsatisfactory results due to damage in handling which caused holes to form bridging paths for frost. It is also possible that these foils may contain manufacturing defects, such as minute pinholes or thin spots which could fail due to temperature cycling. Also the thin foils suffer more greatly from the effect of air gaps which effectively increase the apparent foil thickness. The use of thicker samples showed no dramatic gain in low frequency resolution. At best the response was shifted by only a few frequency steps. Then the use of experimental frequencies below 1 Hz was considered as a method to increase resolution. But examination of data sets showed that in several cases a lower limiting value (on the order of 0.1 pF) had already been reached in the Y component. We interpret this to indicate that the properties of the sample cell become dominant in this region and the lower limit of Y is the contribution of stray conductive paths within the cell around the extremely high impedance sample. It is therefore highly unlikely that increased low frequency resolution of the dc conductivity can be obtained with the present method of measurement.

All of the X and Y response plots in this study revealed α-dispersions which deviated from the Debye characteristic. The α-dispersion is modelled by a Debye element consisting of the blocking foil capacitance and the dc conductance of the ice. This model can only be correct if the ice behaves as an ohmic conductor. For protons in ice this is clearly not the case. The term "free charge carrier" is not quite correct when referring to protons in ice because they are not actually free to respond instantaneously to an applied electric field. The protons are thought to tunnel through energy barriers and move along point defects in the ice lattice. When a proton moves along a bond it causes the vacated molecule to seek an equilibrium orientation within the lattice. This effectively blocks the proton from moving back, at least temporarily. Therefore the protons in the ice are hindered in their motion, both by their own effects and by those of other protons.

Suppose that when an ac voltage cycle ends we find the protons near the blocking foil as a space charge accumulation. When the field changes direction the protons will again migrate in the direction of the other blocking foil. However their motion will be hindered, but not uniformly. The path of each proton will have a degree of hindering associated with it according to how many defects must reorient, etc. This would cause the α-dispersion to behave as the superposition of several smaller dispersions corresponding to the degree of hindering in the path. This is a plausible explanation of why the α-dispersion, which represents the dc conductivity, does not exhibit the characteristic Debye half-width but a broadened one.

Examination of Figures 24, 25, and 26 shows the scatter found in the dc conductivity data. All samples show a high temperature spike in conductivity which is due to the intrinsic water response. The dc conductivity is observed to increase dramatically as the temperature approaches the discontinuity at 0°C. However the low temperature trends are not so predictable. This is best demonstrated in Figure 25 for the ammonium chloride samples. No clear trend for concentration is visible. Even more puzzling is the relationship between the two 10^{-6} *N* samples. 1.9×10^{-6} *N* shows a higher conductivity than 2.0×10^{-6} *N*, even though 100% excess ammonium hydroxide was present in the mother solution which should have a proton-suppressing effect.

It is unclear if a detectability limit can be established from this dc conductivity data. 10^{-8} *N* MSA and 2.5×10^{-7} *N* ammonium chloride showed conductivity trends similar to pure ice. But the 2.2×10^{-8} *N* chloride sample showed greatly elevated conductivity compared to pure ice.

The dc conductivity in ice may be similar to that in semiconductors, in that the dc conductivity is very sensitive to minute impurity levels. These impurities are unintentionally incorporated into the ice and are very difficult to control.

$\Delta\sigma_D$

The dielectric conductivity is derived from the principal relaxation time in the ice and the principal polarization strength. The dielectric conductivity appears to be less sensitive to the superposition of dispersion ranges. The dielectric conductivity is, therefore, expected to be a more reliable indicator of impurity content in ice.

All the samples illustrated in Figures 27, 28, and 29 show regular sequences in impurity concentration. It is interesting to note that the two 10^{-6} *N* ammonium chloride samples are distinguished by dielectric conductivity. The 1.9×10^{-6} *N* + 100% excess ammonium hydroxide sample shows a depressed conductivity compared to the 2.0×10^{-6} *N* sample. This feature is present in both the intrinsic and extrinsic portions of the response, but is more pronounced in the extrinsic region.

A lower limit for impurity detection with dielectric conductivity is suggested by the data. 10^{-8} *N* MSA, 2×10^{-8} *N* chloride, and 2.5×10^{-7} *N* ammonium chloride all show responses virtually identical to the pure ice response.

ε_2

The principal dielectric polarization strength (susceptibility of the principal range) is derived from the inversion parameter C_2. The principal polarization strength is often observed to rise steeply when the α-dispersion begins to merge with the β-dispersion. This tendency is clearly demonstrated in Figures 30 and 32 for the chloride and miscellaneous samples, respectively. The chloride sample with 2.3×10^{-8} *N* is a perfect worst case example, showing clearly the strong tendency of the principal polarization strength to rise as the relaxation ranges merge. An example of the inconsistency of polarization strength data is seen when the previously mentioned response is compared against the 2.2×10^{-8} *N* chloride response. The latter response is depressed by approximately 25% in the temperature range where the two overlap.

The ammonium chloride samples in Figure 31 exhibit polarization strength responses which show less than 20% variation over the entire concentration range. Examination of the MSA response reveals a steep increase of polarization strength at low temperature. It is clear from comparison of the dilute samples with the pure ice response that the principal polarization strength is not a diagnostic parameter for predicting impurity content in ice.

Error Analysis

The lock-in measurement technique is subject to instrumental errors. Accuracy and stability data for the SR530 lock-in amplifier are given below in Table 2.

Component	Parameter	Specification
Signal Channel	Gain Accuracy	1% (2 Hz - 100 kHz)
	Gain Stability	200 ppm/°C
Reference Channel	Phase Drift	0.1°/°C
	Phase Error	<1° for f>10 Hz
Demodulator	Stability	5 ppm/°C (LOW D.R.)
Pre-amplifier	Gain Accuracy	1% (2 Hz - 100 kHz)
	Gain Stability	100 ppm/°C

Table 2. SR530 Lock-in Amplifier specifications

The measurement is also subject to a calibration error of ±0.1° and ±0.1pF/100.0pF. In addition, the sample cell shows a limiting capacitance in the imaginary component of capacitance during measurements. This is due to stray conductive paths that bypass the high impedance sample at low frequencies. This limiting value is estimated at 0.08 pF for Cell 2 and is assumed to be the same in Cell 1. The PCIP-SST function generator card has a frequency accuracy of ±1.0% and frequency stability of 20 ppm/°C. The effect of these errors is cumulative with changes in temperature and humidity. Therefore the calibration should be periodically checked, especially during the change of seasons.

Analysis of the lock-in data requires the visual fitting of a Debye type-curve to the X and Y response plot. The error in determination of the peak frequency and amplitude is estimated at 3 to 6%, depending on location in the log cycle. This error can increase significantly when the β-and α-dispersions superpose strongly. It is essentially useless to make calculations with inversion parameters derived from the Y response if two distinct peaks are not visible. Even with some correction applied, the error in cases where the dispersions have merged into a single peak will likely exceed 10 to 20%.

The calculation to determine the dc conductivity assumes that the α-dispersion is of the Debye type. This is not the case, to varying degree, for all the samples in this study. The α-dispersion is always broadened with respect to the Debye type-curve. However the α-dispersion is usually quasi-symmetrical. Therefore the peak frequency is adequately determined by the curve matching procedure. However, in certain samples the α-dispersion is so flattened that no peak could be determined. In these cases an alternative calculation method was used to estimate the conductivity. The parameters σ_0, τ_2, and ε_2 are all subject to apparent anomalous behavior due to their sensitivity to the inversion parameter C_2. They tend to be overestimated, sometimes greatly, when the β- and α-dispersions merge. A correction can be applied to the inversion parameter by recalculation with adjusted frequency and amplitude from the Y response plot, but errors of 10% or more should be expected in the ice parameters.

Analysis of the data in the pq domain is also prone to difficulties. The inversion from XY to pq is highly non-linear and is especially sensitive as X approaches C1. This corresponds to the low-frequency data where $f<10$ Hz. Unfortunately this is exactly the data which is most diagnostic in pq. It is helpful to add 0.10 pF to the measured value of C1 during the inversion to avoid the mathematical singularity. The pq analysis is useful in the effort to identify the dc conductivity in ice, however the discontinuous character of the inversion must be borne in mind when comparing small magnitude trends in pq plots.

Summary of Conclusions

1. The lock-in measurement method allows rapid data acquisition via a computer controlled measurement sequence.

2. The analysis procedure developed for this study gives reliable estimates of several ice parameters.

3. The surface measurements failed to give any useful data, due to inadequacies in the present measurement technique. An improved surface measurement technique is suggested.

4. The bulk measurements indicate several interesting trends in the impurities investigated. The parameters τ_β, τ_2, and $\Delta\sigma_D$ show well defined concentration responses. The parameters σ_0 and ε_2 are more difficult to interpret because of sensitivity of the inversion parameter C_2 to the superposition of dispersion ranges.

5. In both the ammonium chloride and chloride data sets a transition from an intrinsic to extrinsic mechanism is evidenced by a change in slope in τ_β, τ_2, and $\Delta\sigma_D$.

6. Ammonium chloride causes greater depression in τ and greater elevation in $\Delta\sigma_D$ than an equivalent concentration of ammonium sulfate.

7. At some concentration the response of a sample containing an impurity will become indistinguishable from the response of pure ice. For the impurities investigated in this study (chloride, ammonium chloride, ammonium sulfate, MSA) this lower limit of detectability lies in the range of 10^{-7} to 10^{-8} *N*.

Recommendations for Future Work

A need for total redesign of the surface measurement electrodes is indicated by the failure to obtain any meaningful results with the method as previously described. A split electrode arrangement is proposed to improve the measurement technique. Figures 34 through 37 illustrate the components necessary to operate the upgraded surface measurements. These components are designed to utilize one of the existing sample cells, to be installed as a dedicated surface cell.

The proposed surface measurement system features a split upper electrode, the halves of which serve as HIGH and LOW electrodes. The gap between the electrodes is adjustable and may be set with a feeler gauge. The Teflon foil is discontinuous across the electrodes to discourage frost bridging and enhance measurement of ice properties. The gap also serves to allow ultraviolet radiation to be directed onto the sample via a fiber-optic cable. The Teflon foils are held on the electrodes by two semi-circular clamps, which also serve to confine the sample. The lower electrode may be connected to serve either as a ground (signal or earth) or to float the sample. An elevation of the assembled system is shown in Figure 37.

The defrosting sequence developed during the course of this study will be of value for the proposed surface measurements as well. During placement of the sample into the cell there is a tendency to accumulate frost on the electrodes. It is essential that this frost be removed from the surface electrodes to prevent bridging.

An additional method of data analysis could be performed in the XY domain. This would entail creating three-dimensional data sets such as (X,Y,1000/T) for an entire sample run. A three-dimensional plot can be performed in Mathematica to show the temperature dependence of the dispersions and the migration of frequencies. The same type of plot could be created for the X and Y responses using data sets of (f,X,1000/T) and (f,Y,1000/T), respectively.

In response to the recent interest in electrical logging of polar ice cores, a continuation of this dielectric study of ice should be considered. The purpose would be to amass data from a systematic investigation of other impurities commonly found in polar ice, such as nitrate, carbonate, and sulfate.

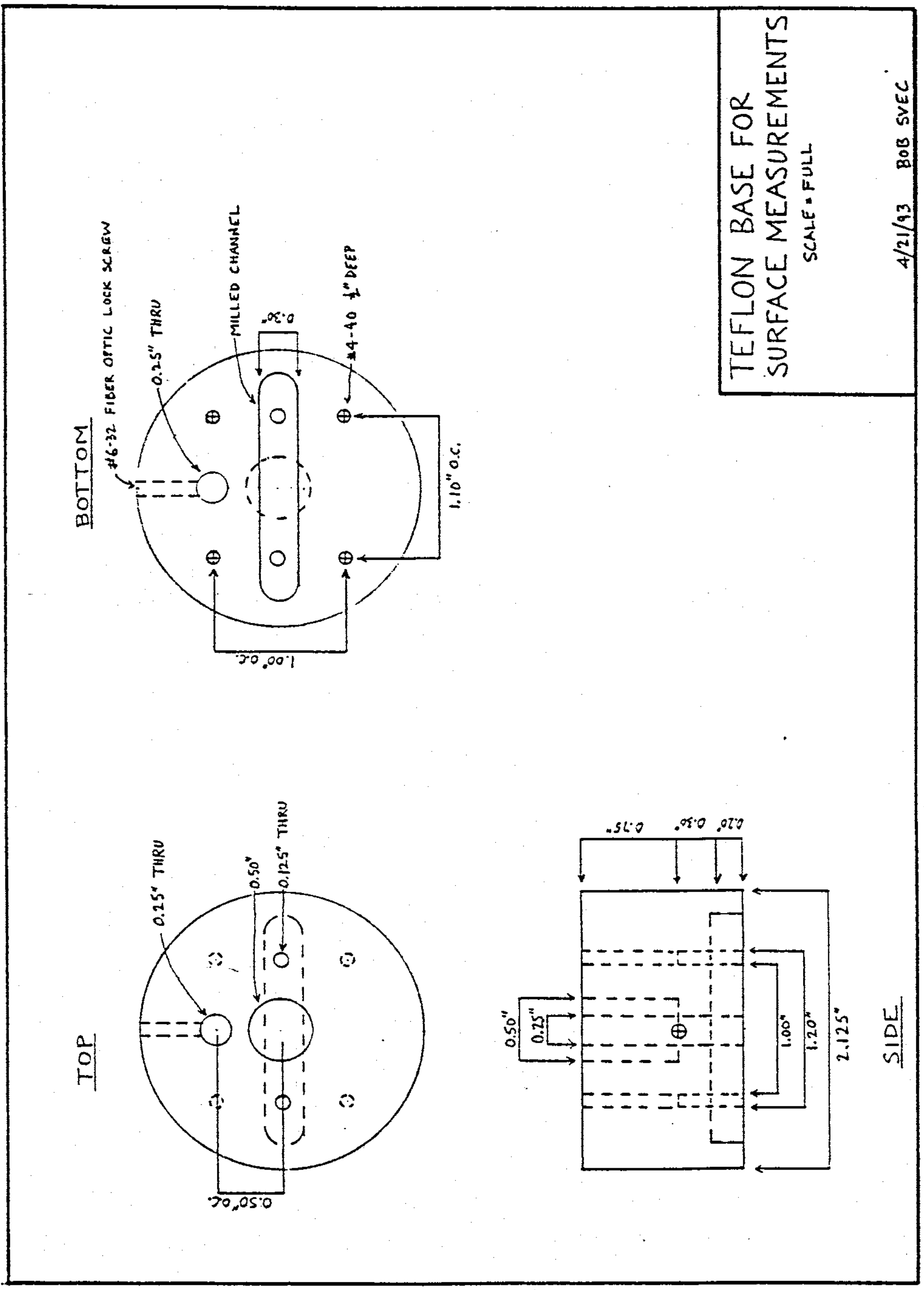


Figure 34. Surface cell: Teflon upper base.

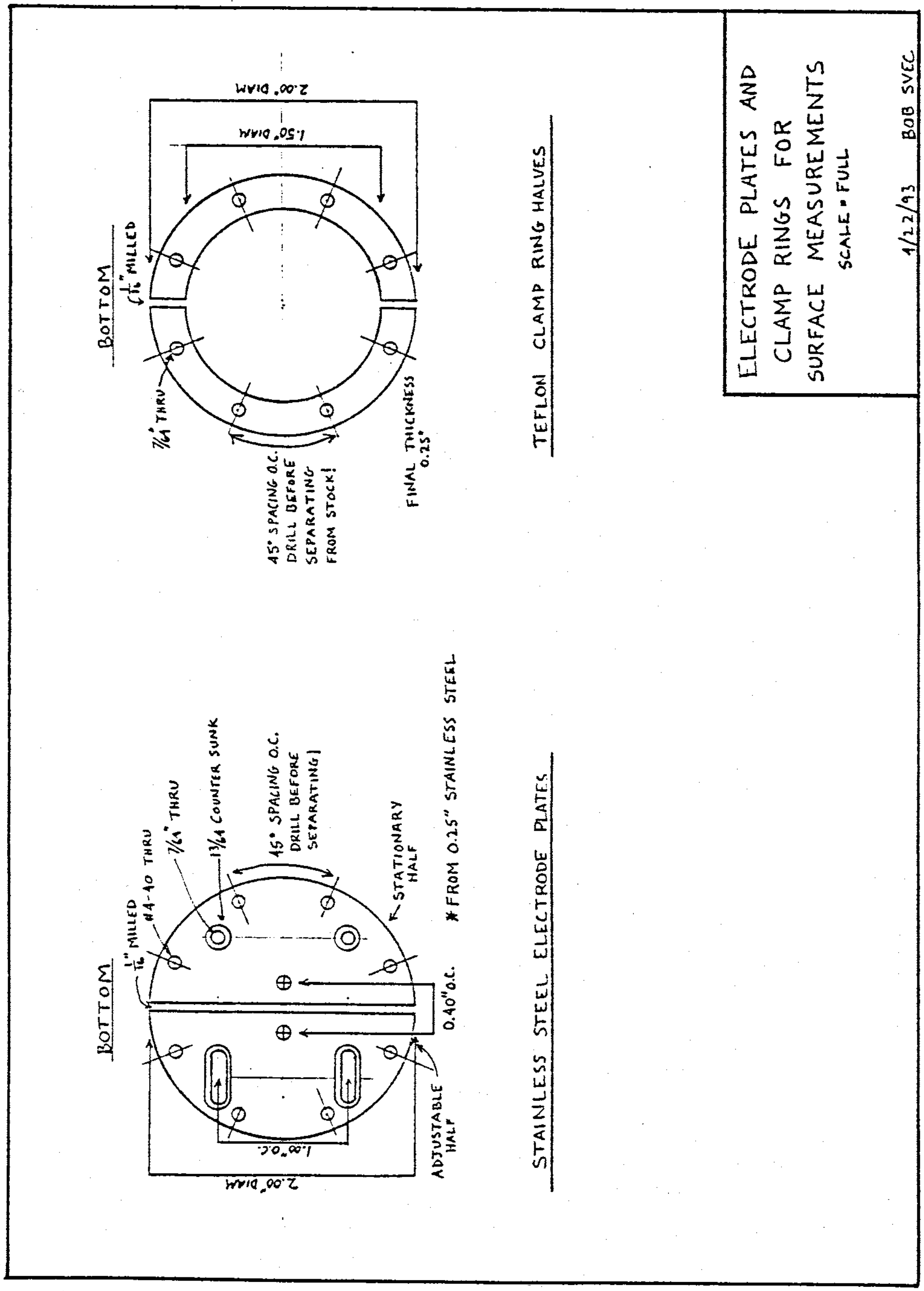


Figure 35. Surface cell: electrode plates.

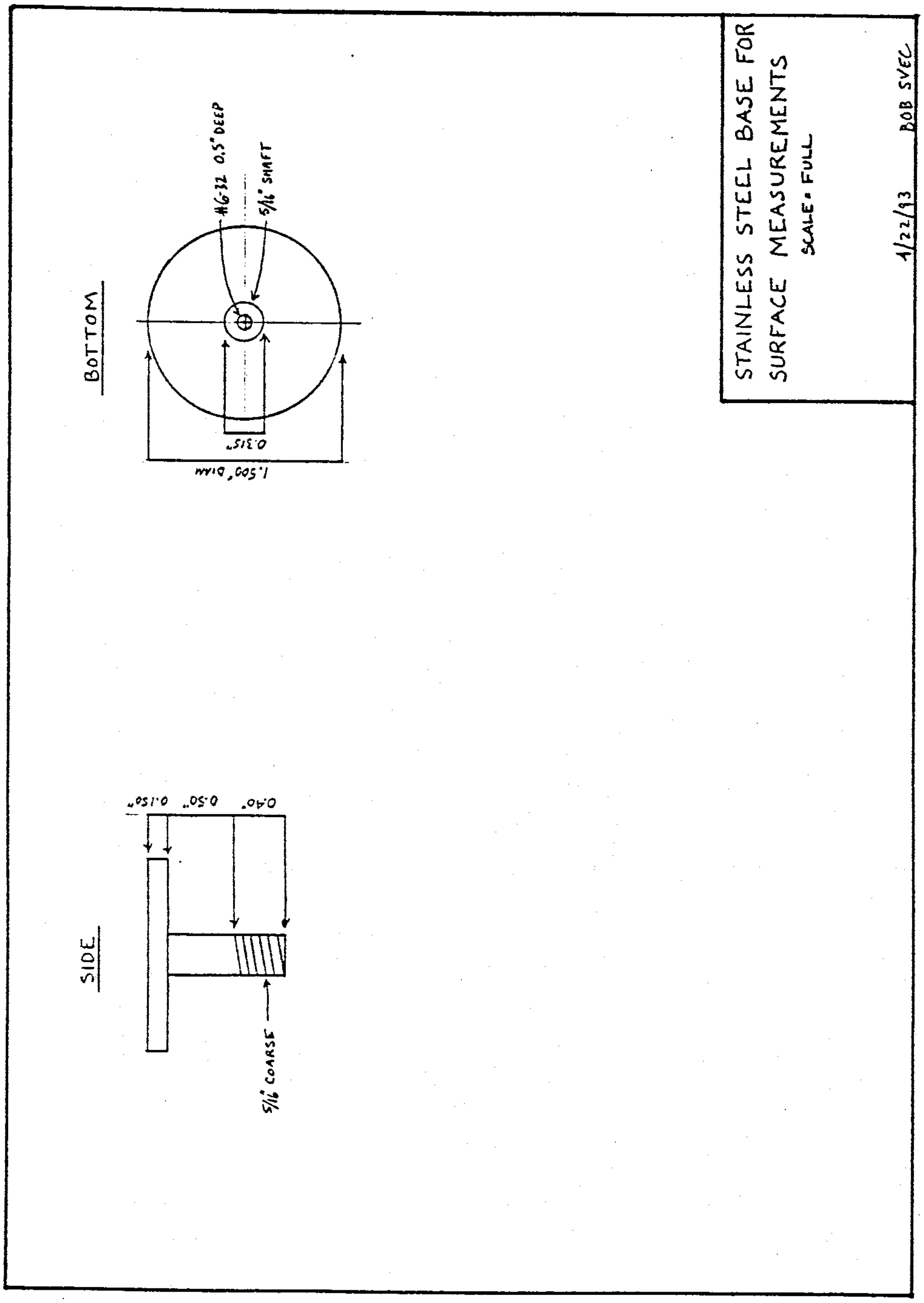


Figure 36. Surface cell: steel lower electrode.

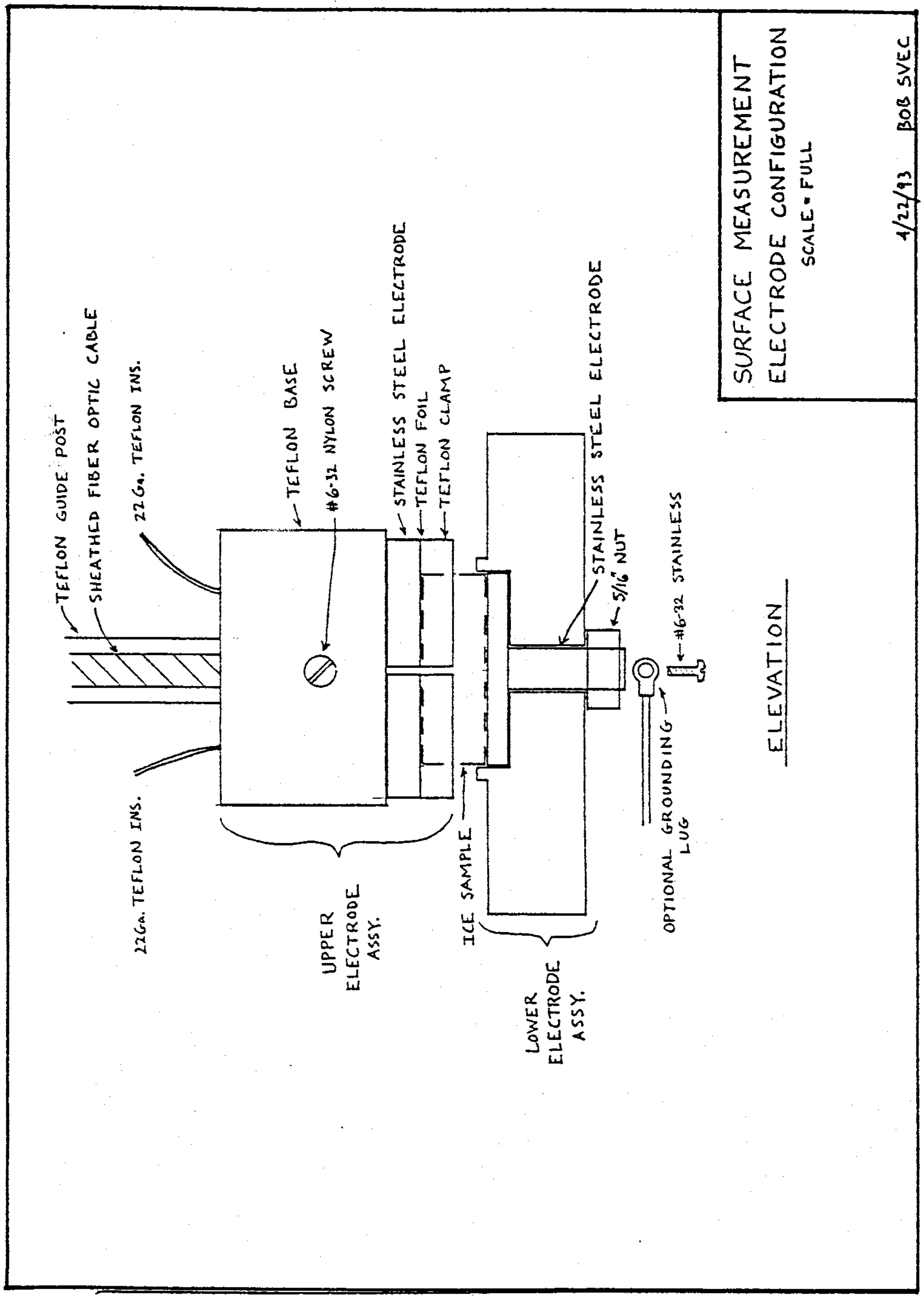


Figure 37. Surface cell: assembly elevation.

References

Auty, R.P., and Cole, R.H., Dielectric properties of ice and solid D_2O, *J. Chem. Phys.*, 21, 372-373, 1952.

Cole, K.S., and Cole, R.H., Dispersion and absorption in dielectrics 1: Alternating current characteristics, *Jour. Chem. Phys.*, 9, 341-350, 1941.

Gross, G.W., Hayslip, I.C., and Hoy, R.N., Electrical conductivity and relaxation in ice crystals with known impurity content, *Jour. Glaciology*, 21, 143-160, 1978.

Gross, G.W., Hayslip, I.C., and Hoy, R.N., Dielectric relaxation spectrum of ice measured with linear blocking layers, *Geophysics*, 45, 914-927, 1980.

Gross, G.W., and Johnson, J., The layered capacitor method for dielectric bridge measurements, data analysis and interpretation of fluoride doped ice, *IEEE Trans. Elec. Ins.*, EI-18, 485-497, 1983.

Gross, G.W., and McGehee, R.M., The layered-capacitor method for bridge measurements of conductive dielectrics, *IEEE Trans. Elec. Ins.*, 23, 387-396, 1988.

Hobbs, P.V., *Ice Physics*, p. 111,166, Clarendon Press, Oxford, 1974.

Jonscher, A.K., *Dielectric Relaxation in Solids*, Chelsea Dielectrics Press, London, 1983.

Malchow, D.(ed.), *Lock-in applications anthology*, LIA Note 13: Measurement of semiconductor device capacitance, EG&G Princeton Applied Research, Princeton, New Jersey, No date.

Microsoft Corporation, *Microsoft FORTRAN version 5.1*, 1991.

Moore, J.C., Mulvaney, R., and Paren, J.G., Dielectric stratigraphy of ice: a new technique for determining total ionic concentrations in polar ice cores, *Geophys. Res. Lett.*, 16, 1177-1180, 1989.

Mounier, S., and Sixou, P., A contribution to the study of conductivity and dipolar relaxation in doped ice crystals, in *Physics of Ice*, p. 562-570, Plenum Press, New York, 1969.

SRS (Stanford Research Systems, Inc.), *Model SR530 lock-in amplifier* (manual), p. 29, SRS, Inc., Sunnyvale, CA., 1989.

von Hippel, A.R., Knoll, D.B., and Westphal, W.B., Transfer of protons through "pure" ice I_h single crystals. 1. Polarization spectra of ice I_h, *J. Chem. Phys.*, 54, 134-144, 1971.

Wolfram Research, Inc., *Mathematica 386/7 version 2.0*, 1991.

Appendix A - Symbols and Definitions

Symbol	**Definition**
X/Y	Real/Imaginary part of capacitance in the blocking capacitor.
p/q	Real/Imaginary part of capacitance in the ice.
C_x	Complex capacitance of the blocking capacitor.
C_0	1.7 µF polystyrene reference capacitor.
G_x	Conductance of the blocking capacitor.
V_i	Input voltage to the blocking capacitor.
V_o	Voltage division output voltage.
V_o'/V_o''	Real/Imaginary part of the output voltage.
ϕ_{REF}	Lock-in reference signal phase angle.
R	Lock-in R output, magnitude of output signal.
C_1	Low frequency closure capacitance, theoretically the capacitance of the Teflon blocking foils. This parameter is designated C_0 in Gross and McGehee, 1988.
β-dispersion	Dielectric dispersion in the blocking capacitor due to the relaxation of water dipoles in the electric field (principal dispersion).
α-dispersion	Dielectric dispersion in the blocking capacitor due to the accumulation of space charge at the Teflon blocking foils.
f_β	Peak frequency of the β-dispersion.
C_β	Amplitude of the β-dispersion.
τ_β	Principal relaxation time in the blocking capacitor.
C_2	Principal ice capacitance.
ε_2	Ice principal polarization strength or susceptibility (cf. Jonscher, 1983, eq. 2.48, p. 46).
G_2	Dielectric conductance.
τ_2	Principal relaxation time in the ice.
C_∞	High frequency limiting capacitance.
C_α	α-dispersion capacitance.
f_α	Peak frequency of the α-dispersion.
G_0	dc conductance of the ice.
σ_0	dc conductivity of the ice.
C_g	Geometric capacitance of the sample.
$\Delta\sigma_D$	Dielectric conductivity. $\Delta\sigma_D = G_2/C_g$
ε_0	Permittivity of free space.

Appendix B - Mathematica Plot Procedures

XY Cole-Cole plots:

```
ListPlot[c01,
PlotRange->{{0,40},{0,20}},
PlotLabel->"186150.01, -1.0 C, BULK, CELL 2, 3/4/93",
AspectRatio->Automatic,
GridLines->Automatic,
Frame->True,
DefaultFont->{"Helvetica",15}]
```

X and Y (frequency) Response plots:

```
MultipleListPlot[x01,y01,
PlotRange->{{0,5},{-2,3}},
AxesOrigin->{0,-2},
Prolog->{Thickness[0.001],PointSize[0.005]},
PlotJoined->True,
PlotLabel->"186150.01, -1.0 C, X and Y Response",
AspectRatio->Automatic,
GridLines->Automatic,
Frame->True,
DefaultFont->{"Helvetica",15}]
```

Separated Y Response plots

```
ListPlot[sy01,
PlotRange->{{0,5},{-2,3}},
AxesOrigin->{0,-2},
PlotLabel->"186150.01, -1.0 C, Separated Y Response",
AspectRatio->Automatic,
GridLines->Automatic,
Frame->True,
DefaultFont->{"Helvetica",15}]
```

pq Cole-Cole plots:

```
LogLogListPlot[pq01,
PlotRange->{{-2,4},{-2,4}},
AxesOrigin->{-2,-2},
```

```
PlotLabel->"186150.01, -1.0 C, C1=35.00, pq Cole Plot",
AspectRatio->Automatic,
GridLines->Automatic,
Frame->True,
DefaultFont->{"Helvetica",15}]
```

p and q Response plots:

```
MultipleListPlot[p01,q01,
PlotRange->{{0,5},{-1,4}},
AxesOrigin->{0,-1},
Prolog->{Thickness[0.001],PointSize[0.005]},
PlotJoined->True,
PlotLabel->"186150.01, -1.0 C, C1=35.00, p and q Response",
AspectRatio->Automatic,
GridLines->Automatic,
Frame->True,
DefaultFont->{"Helvetica",15}]
```

w*q plots:

```
ListPlot[wq01,
PlotRange->{{0,5},{2,7}},
PlotLabel->"186150.01, -1.0 C, C1=35.00, w*q Response",
AspectRatio->Automatic,
GridLines->Automatic,
Frame->True,
DefaultFont->{"Helvetica",15}]
```

Arrhenius plots:

```
MultipleListPlot[tb050,tb076,tb087,
PlotRange->{{3,6},{-6,-1}},
AxesOrigin->{3,-6},
Prolog->{Thickness[0.001],PointSize[0.005]},
PlotJoined->True,
PlotLabel->"Tau Beta, Chloride Samples",
AspectRatio->Automatic,
GridLines->Automatic,
Frame->True,
DefaultFont->{"Helvetica",15}]
```

Appendix C - FORTRAN Programs

Program	**Function**
ALTCOND.FOR	Performs the alternative dc conductivity calculation. Reads the lock-in data file, outputs a plot file and a hardcopy file.
CONVERT.FOR	Converts lock-in data files to Cole-Cole plottable data files.
CUMULAT.FOR	Creates a cumulative plot data file from several frequency response data files. The data sets are normalized to the parameters of the first data file the user enters.
LCINF.FOR	Subtracts the value of C_∞ from the X frequency response file.
LFCONV.FOR	Makes frequency response files from lock-in measurement files.
LSEP.FOR	Separates the α- and β-dispersion ranges in a Y frequency response plot. The separation is based on a Debye model.
LWC.FOR	Calculates total conductivity from a Y response plot.
MEASURE.FOR	The measurement program which controls the PCIP-SST and the SRS 530 lock-in. This program creates the lock-in measurement files. A full description is in the comment section of the program. A flowchart follows the program listing.
T3PLOT.FOR	Creates 3-dimensional data files for plotting data versus temperature (1000/T).

XYPQ.FOR	Conversion program which transforms XY data to pq. Yields a pq output file which is in the lock-in standard format so that the pq data can be processed with the previously mentioned programs.
YZCONV.FOR	Conversion program for taking lock-in XY data to Y^* (admittance) or Z^* (impedance) domains.

```
c   Bob Svec
c   ALTCOND.FOR
c   This is the program to perform the conductivity calculation by the
c   alternate method. This program reads in the lockin data file, asks
c   for sample parameters ( C1, TAU2, etc. ), and then writes two output
c   files, one for hardcopy, and another for plotting G0 vs freq.
c   *******************************************************************

       real c1,c2,tau2,geom,x,y,freq,temp,wc,gdiel,go,w,sigma
       character*12 infile,hardcopy,plotfile
       character*60 date,header

c   get names for files
       write(*,*) 'Enter the name of the input file (186124.02): ->'
       read(6,1000) infile
1000   format(A12)
       write(*,*) 'Enter the name of the conductivity hardcopy file->'
       read(6,1000) hardcopy
       write(*,*) 'Enter the name of the conductivity plot file ->'
       read(6,1000) plotfile

c   open the files
       open(unit=1,file=infile,status='old')
       open(unit=2,file=hardcopy,status='new')
       open(unit=3,file=plotfile,status='new')

c   get sample parameters
       write(*,*) 'Enter the value of C1 (31.08) pF ->'
       read(6,1001) temp
       c1=temp*1.0e-12
1001   format(F6.2)
       write(*,*) 'Enter the value of C2 (22.79) pF ->'
       read(6,1001) temp
       c2=temp*1.0e-12
       write(*,*) 'Enter the value of TAU2 (12.7) microsec ->'
       read(6,1002) temp
       tau2=temp*1.0e-6
1002   format(F8.1)
       write(*,*) 'Enter the value of the A/d2 cm factor (5.234) ->'
       read(6,1003) geom
1003   format(F6.3)

c   write header to hardcopy file
       write(2,*) infile,' Alternate Method Conductivity'
       write(*,*)' '
       write(2,*)'     Freq(Hz)   Gdiel(S)     G0(S)     Sigma0(S/cm)'
       write(2,*)'     -----------------------------------------------'

c   dummy read
       read(1,999) date,header
999    format(A60,/,A60)

c   loop on 31 frequencies
       do 100 i=1,31
            read(1,*) freq,x,y
            if (y.eq.0.00) y=0.01
            x=x*1.0e-12
            y=y*1.0e-12
            w=2*3.14159*freq
            wc=(c1**2*w*y)/((c1-x)**2+y**2)
            gdiel=(c2*w**2*tau2)/(1+w**2*tau2**2)
            go=wc-gdiel
            sigma=go/geom
            write(2,1004) freq,gdiel,go,sigma
1004        format(5X,F8.1,5X,E8.2,5X,E8.2,5X,E8.2)
            if (sigma.le.0) sigma=1.0e-12
            write(3,1005) log10(freq),log10(sigma)
1005        format(F8.6,5X,F10.6)
100    continue
       end
```

```
c    Bob Svec 7/10/92
c    CONVERT.FOR
c    This is the converter program which is intended to take lockin data
c    files and convert them to C* (Cole-Cole), Y*, Z* formats for Mathematica
c    input. The user is prompted for names of the input file and names for
c    the output files. Please follow a logical format. For instance:
c           input file = 186040.02
c           C* file    = c02
c           Y* file    = y02
c           Z* file    = z02
c     *************************************************************************

      real freq,c1,c2,y1,y2,z1,z2,w
      character*12 infile,cfile,yfile,zfile
      character*70 header
      character*10 date

c     get names for input and output files
      write(*,*) 'Enter the name of the file to convert(186040.02): ->'
      write(*,*) 'WARNING:this must be a standard lock-in output file!'
      read(6,1000) infile
1000  format(A12)
      write(*,*) 'Enter the name of the C* output file (c02): ->'
      read(6,1000) cfile
c      write(*,*) 'Enter the name of the Y* output file (y02): ->'
c      read(6,1000) yfile
c      write(*,*) 'Enter the name of the Z* output file (z02): ->'
c      read(6,1000) zfile

c     open the files
      open(unit=1,file=infile,status='old')
      open(unit=2,file=cfile,status='new')
c      open(unit=3,file=yfile,status='new')
c      open(unit=4,file=zfile,status='new')

c     display info from input data file
c      write(*,1001) infile
1001  format(/,'You have selected the file',A12,'for conversion')
      read(1,1002) date,header
1002  format(A10,/,A70)
c      write(*,1003) infile,date,header
1003  format(/,A12,'was created on',A10,'and has the following header:'
     + ,/,A70)

c     loop on 31 frequencies
      do 8000 i=1,31

c          get the raw data from input file
           read(1,*) freq,c1,c2

c          write to the C* file
           write(2,1004) c1,c2
1004       format(F9.2,4X,F9.2)

c          calcs for Y*
c          w=2*3.14159*freq
c          y1=w*c2
c          y2=w*c1
c          write to the Y* file
c          write(3,1005) y1,y2
```

```
c1005       format(E9.4,10X,E9.4)

c           calcs for Z*
c           denom=Y1**2+Y2**2
c           z1=y1/denom
c           z2=y2/denom
c           write to the Z* file
c           write(4,1006) z1,z2
c1006       format(E9.4,10X,E9.4)

8000   continue

       write(*,*) char(27)
       write(*,1007) infile
1007   format(/,/,'Conversion completed for ',A12)
       end
```

```
c       Bob Svec 12/21/92
c       CUMULAT.FOR
c       This program creates a cumulative curve data file from several
c       frequency response files. Subsequent data sets are all normalized
c       to the first data set you input.
c       ****************************************************************
c
        real pfreq(40),pc(40),rawfreq(40),rawc(40)
        real normfreq(40),normc(40)
        integer i,j,filenum
        character*12 file(20),outfile

        write(*,*) "Ready to prepare cummulative plot data file!"
c       prompt user for information
        write(*,*) "Enter the number of files you will use"
        read(6,1000) filenum
1000    format(I2)
        write(*,*) "Enter data to normalize on:"
        do 100 i=1,filenum
            write(*,*)"Enter data for file",i
            write(*,*)"Im file name (i03) ->"
            read(6,1001) file(i)
1001        format(A12)
            write(*,*)"peak frequency (15000.0) ->"
            read(6,1002) pfreq(i)
1002        format(F8.1)
            write(*,*)"peak amplitude (12.67) ->"
            read(6,1003) pc(i)
1003        format(F6.2)
100     continue

c       output file
        write(*,*) "Enter name of cummulative plot data file"
        read(6,1005) outfile
1005    format(A12)
c       open output file
        open(unit=99,file=outfile,status='new')

c       normalization routine
c       all files log normalized to freq and amp of first file
c       loop on files
        do 300 i=1,filenum
            open(unit=i,file=file(i),status='old')
            do 200 j=1,31
                read(i,*) rawfreq(j),rawc(j)
                normfreq(j)=log10(rawfreq(j)/pfreq(i))
                normc(j)=log10(rawc(j)/pc(i))
                write(99,*) normfreq(j),normc(j)
200         continue
300     continue
        end
```

```
c   Bob Svec 1/6/93
c   LCINF.FOR
c   This program takes the real response file created by freqconv.for
c   and subtracts the value of cinfinity from each entry. This is
c   performed as a separate step in this program because the value of
c   cinfinity is usually not known until after the frequency response
c   files are created.
c   *******************************************************************

       real freq,creal,adjcreal,cinf,logc
       character*12 infile,outfile

c   get names for files
       write(*,*)'Enter the name of the real response file (r02): ->'
       read(6,1000) infile
1000   format(A12)
       write(*,*)'Enter the name of the adj. real output file: ->'
       read(6,1000) outfile

c   open the files
       open(unit=1,file=infile,status='old')
       open(unit=2,file=outfile,status='new')

c   get value of cinfinity from user
       write(*,*)'Enter the value you determined for cinf (2.34): ->'
       read(6,1001) cinf
1001   format(F4.2)

c   loop on 31 frequencies
       do 8000 i=1,31

c           get data from input file
            read(1,*) freq,logc
            creal=10.0**logc
c           subtract away cinfinity
            adjcreal=creal-cinf
c           write new value to output file
            write(2,1002) freq,log10(adjcreal)
1002        format(F9.6,5X,F9.6)

8000   continue
       end
```

```
c       Bob Svec 7/16/92
c       LFCONV.FOR
c       This is the converter program which makes frequency response files
c       from lock-in measurement files.
c       *******************************************************************

        real freq,c1,c2
        character*12 infile,realfile,imagfile
        character*70 header
        character*10 date

c       get names for input and output files
        write(*,*) 'Enter the name of the file to convert(186040.02):->'
        write(*,*) 'WARNING:This must be a standard lock-in output file'
        read(6,1000) infile
1000    format(A12)
        write(*,*) 'Enter the name of the real response output file:->'
        read(6,1000) realfile
        write(*,*) 'Enter the name of the imag. response output file:->'
        read(6,1000) imagfile

c       open the files
        open(unit=1,file=infile,status='old')
        open(unit=2,file=realfile,status='unknown')
        open(unit=3,file=imagfile,status='unknown')

c       read the header
        read(1,1001) date,header
1001    format(A10,/,A70)

c       loop on 31 frequencies
        do 8000 i=1,31

c           get the data from the input file
            read(1,*) freq,c1,c2
c           check c2 for zeros - avoid log(0)!!!!
            if (c2.lt.0.01) c2=0.01

c           write to the real file
            write(2,1002) log10(freq),log10(c1)
1002        format(F9.6,4X,F9.6)

c           write to the imag file
            write(3,1002) log10(freq),log10(c2)

8000    continue

        write(*,*)'Conversion completed.'
        end
```

```
c       Bob Svec  8/10/92
c       LSEP.FOR
c       This program takes the imaginary response file derived from a lockin
c       measurement file and performs a separation of the dispersion ranges
c       based on the theoretical Debye model. The parameters fbeta and cpeak
c       are obtained by the user from curve matching the Debye curve to the
c       imaginary response plots.
c       ***************************************************************

        real freq(31),cdprime(31),fbeta,cpeak,f1,thdebye(31),cresid(31)
        real func,logf,logc
        integer i
        character*12 irfile,sepfile

c       get file names
        write(*,*) "Please enter the Imaginary Response file name ->"
        read(6,1000) irfile
        write(*,*) "Please enter the Separated Response file name ->"
        read(6,1000) sepfile
1000    format(A12)

c       open the files
        open(unit=1,file=irfile,status='old')
        open(unit=2,file=sepfile,status='new')

c       read the imaginary response data
        do 10 i=1,31
             read(1,*) logf,logc
             freq(i)=10.0**logf
             cdprime(i)=10.0**logc
10      continue

c       begin seperation procedure, ask for parameters
        write(*,*) "Please enter the values of the following parameters"
        write(*,*) "fbeta (eg. 487.0) -->"
        read(6,1001) fbeta
        write(*,*) "cpeak (eg. 11.47) -->"
        read(6,1002) cpeak
1001    format(F8.1)
1002    format(F6.2)

c       seperation calculation loop
30      do 40 i=1,31
c            calculate the coefficient f1
             func=cosh(log(freq(i)/fbeta))
             f1=(func)**(-1)
c            obtain theoretical debye contribution (HF dispersion)
             thdebye(i)=f1*cpeak
c            obtain residual (LF dispersion)
             cresid(i)=cdprime(i)-thdebye(i)
             if (cresid(i).le.0.0) cresid(i)=0.01
40         continue

c       write the seperated dispersions to sepfile
1003    format(F8.1,4X,F9.6)
        do 50 i=1,31
c                HF dispersion
                 write(2,1003) log10(freq(i)),log10(thdebye(i))
c                LF dispersion
                 write(2,1003) log10(freq(i)),log10(cresid(i))

50      continue
        end
```

```
c    Bob Svec 1/8/93
c    LWC.FOR
c    takes an imaginary response file and multiplies the imaginary part
c    by 2*pi*freq to obtain total conductivity.
c    *****************************************************************

       real freq,cdprime,wcdprime,w,logf,logc
       character*12 infile,outfile

c      get the file names
       write(*,*)'Enter the name of the Im file to convert (i02) ->'
       read(6,1000) infile
1000   format(A12)
       write(*,*)'Enter the name of the sigma infinity file (sig02)->'
       read(6,1000) outfile
c      open the files
       open(unit=1,file=infile,status='old')
       open(unit=2,file=outfile,status='new')

c      read in data and do calculation
       do 8000 i=1,31
            read(1,*) logf,logc
            freq=10.0**logf
            cdprime=10.0**logc
            w=2*3.14159*freq
            wcdprime=w*cdprime
            write(2,1001) log10(freq),log10(wcdprime)
1001        format(8X,F9.6,5X,F9.6)
8000   continue
       end
```

```
$INCLUDE:'for232.inc'
c       Bob Svec 6/10/91
c       MEASURE.FOR
c       must link with rs232.obj for SR530 subroutines. for232.inc and rs232.obj
c       must be in working directory to compile.
c       compile command: fl /FPc measure.for rs232.obj
c       you must be sure that Microsoft Fortran has been installed with the
c       emulator math option for this program to execute on the 286 machine
c
c       ************PROGRAM DESCRIPTION***************************
c       This program "measure.for" allows the user to make complex
c       capacitance measurements with an SRS 530 lock-in amplifier
c       and a Keithley PCIP-SST function generator card.
c
c       The program assumes that you have already provided a file called
c       "freq.dat" which contains the frequencies to be used. The program
c       also assumes that you have a file called "cal.dat" which
c       contains information from the calibration of the voltage division
c       circuit using the GR 1422 capacitor set at 100pF (this can be
c       changed by the user during his calibration, but it is strongly
c       recommended that the calibration value be as close to the
c       maximum expected sample capacitance as possible). Look at the
c       data files in the directory with "measure.exe" to observe the
c       correct format.
c
c       During the measurement the computer will verify that
c       the "freq.dat" and "cal.dat" files have the same frequency information.
c       All calibrations and subsequent measurements should
c       be made with an input voltage of 20V.
c
c       The program will continously update the user on the
c       status of the measurement. Due to time constant cosiderations, the
c       first third of the total frequency span will take five times longer
c       to measure than each of the next two thirds.The program will initialize
c       all SR530 front panel settings before the measurement sequence begins.
c       The SR530 will be locked against manual inputs to preserve the correct
c       settings during the measurement.
c
c       The PCIP-SST function generator card provides a sinusoid to drive
c       the measurement and a TTL signal to drive the SR530 reference channel.
c       The PCIP-SST drivers "vi.sys" and "sst.sys" must be installed in order
c       for the program to sucessfully control the SST card. These should be
c       automatically installed at initial computer boot. If the SST card seems
c       to be unresponsive you should make sure that the .sys files are
c       included in the "config.sys" in the root directory. The SST instrument
c       will be displayed on the screen during the measurement and will be
c       locked against manual input until the measurement is finished.
c       The frequency on the SST display should be assumed to be correct,
c       not the frequency displayed on the SR530 reference(it will be 1-2% off).
c       You may notice that there is a trick in the program to control the
c       SST card. It is necessary to OPEN $SST, send commands, then CLOSE $SST
c       before they will actually be sent to the card. This is because of the
c       way Microsoft FORTRAN sends commands to its buffer. If $SST is not closed
c       and the measurement continues, the card will not receive the commands
c       and the measurement integrity will be seriously compromised.
c
c       All timing of measurements is done with respect to the computer's
c       on board clock so multi-tasking should not interfere with the
c       measurements.
```

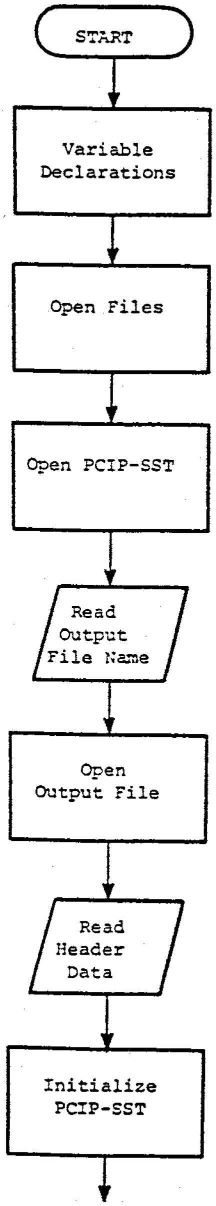
```
c     *****************************************************
c                 INITIALIZATION
c     *****************************************************
      character*20 str1,str2,outname,str,date
      character*70 header
      real FREQ,PHIREF,X,Y,K,KX,KY,OLOAD,TC,DELAY
      integer FNUM
      open(unit=1,file=’freq.dat’,status=’old’)
      open(unit=2,file=’cal.dat’,status=’old’)
      open(unit=8,file=’$SST’,status=’old’)

c     prompt user for name of output file
      write(*,*) ’enter name of output file ---->’
      read(6,1000) outname
1000  format(A20)
      open(unit=3,file=outname,status=’unknown’)
c     prompt for output file setup
      write(*,*) ’enter the date (mo/da/yr) ---->’
      read(6,1001) date
1001  format(A20)
      write(3,*) date
      write(*,*) ’enter a header for the output file ---->’
      read(6,1002) header
1002  format(A70)
      write(3,*) header

c     SST initialization
c     clear input string buffer of SST
      write(8,*)’CLear’
c     lock SST against manual input
      write(8,*)’LOck’
c     activate SST virtual instrument display
      write(8,*)’SHow’
c     send calibration command to SST
      write(8,*)’CAlibrate’
      write(*,*)’PCIP-SST performing self-calibration...’
c     activate meter display
      write(8,*)’MEter On’
c     set waveform to sinusoid
      write(8,*)’SIne’
c     set offset to zero
      write(8,*)’OFFset 0.00’
c     set signal amplitude to 20.00V
      write(8,*)’Set Amplitude 20.00’
      close(8)

c     SR530 initialization
c      call init
c     lock sr530 against manual control
      call txstr(’i2$’)
c     take out filters (FLAT)
      call txstr(’b0$’)
      call txstr(’l1,0$’)
      call txstr(’l2,0$’)
c     select LOW DYN RES
      call txstr(’d0$’)
c     set REF to 1f
      call txstr(’m0$’)
c     turn off offsets
      call txstr(’ox0$’)
```

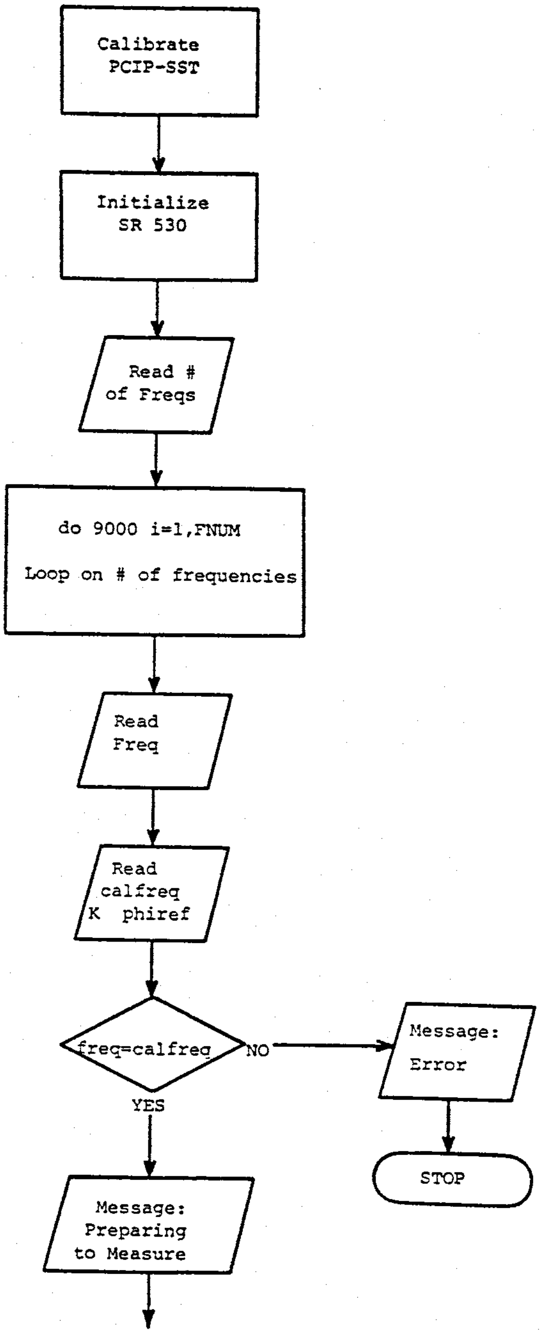
```
      call txstr('oy0$')
      call txstr('or0$')
c     set REF TRIG to rising edge
      call txstr('r0$')
c     select R,PHI display (*needed for correct sensitivity)
      call txstr('s2$')
c     set character wait interval to 4ms
      call txstr('w0$')
c     set post time constant
      call txstr('t2,2$')
c     set delay to four time constants
      DELAY=5

c     *******************************************************
c                 MEASUREMENT
c     *******************************************************

c     read # of freqs from data file and begin loop
      read(1,*) FNUM
      do 9000 i=1,FNUM
          read(1,*) FREQ
          read(2,*) CALFREQ,K,PHIREF
c         verify that freqs are same
          if(FREQ.eq.CALFREQ) then
             write(*,1008) FREQ
1008         format(/,' Preparing to measure at',f8.1,' Hz')
          else
             write(*,*) 'The frequencies in the FREQ and CAL data'
             write(*,*) 'files do not agree and this measurement is'
             write(*,*) 'terminated. Correct the error and restart.'
             stop
          end if

c         adjust TC to 10sec for low freq
          if(FREQ.lt.11) then
              TC=10
              call txstr('t1,9$')
          else
              TC=2
              call txstr('t1,7$')
          end if

c         reopen $SST to set frequency
          open(unit=8,file='$SST',status='old')
c         make freq string to send to card
          write(str,1009) FREQ
1009      format('Set Freq ',f9.1)
          write(8,*) str
c         activate SST frequency tracking for maximum freq stability
          write(8,*)'TRack'
          close(8)

c         send new PHIREF to lock-in
c         make string to send to P
          write(str,1010) PHIREF
1010      format('p',f7.3,'$')
          call txstr(str)


c         routine to detect overload and nonoptimum sensitivity
```

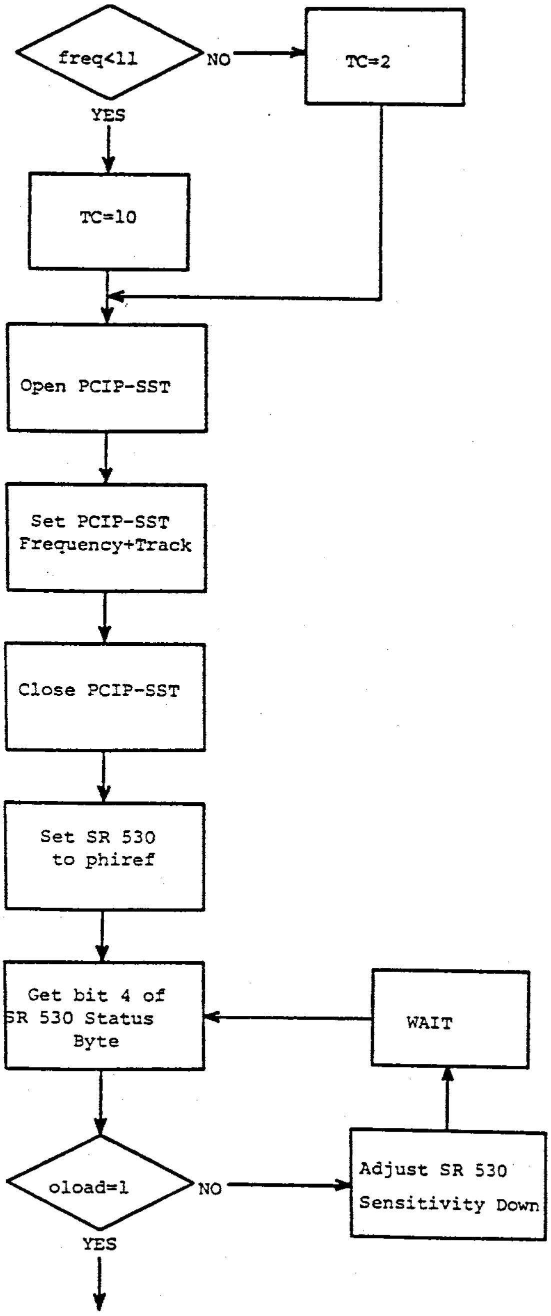
```
c          will increase sensitivity until overload is detected
c          and then backoff one step
c          gets bit 4(overload) of the status byte
           OLOAD=0.0
1050       call txstr('y4$')
           call rxstr(str)
           read(str,1051) OLOAD
1051       format(bn,f10.0)
c          test for overload
           if(OLOAD.eq.1) goto 1100
c             no overload so decrease sensitivity
              call txstr('k28$')
              write(*,*)'      Adjusting sensitivity down...'
c             wait
              call wait(TC,DELAY)
c             retest for overload
              goto 1050
c          overload detected so increase sensitivity
1100       call txstr('k27$')
           write(*,*)'      Adjusting sensitivity up...'
c          wait
           call wait(TC,DELAY)
c          retest for overload (bit 4 checked twice)
           call txstr('y4$')
           call rxstr(str)
           call txstr('y4$')
           call rxstr(str)
           read(str,1051) OLOAD
           if(OLOAD.eq.1) goto 1100

c          wait 4 TC to take reading
           write(*,*)'      Waiting for reading...'
           call wait(TC,DELAY)

c          take reading of X and Y
           call txstr('qx$')
           call rxstr(str1)
           call txstr('qy$')
           call rxstr(str2)
           read(str1,1051) X
           read(str2,1051) Y
c          multiply measured value by correction factor K
           KX=abs(K*X)/1.0e-12
           KY=abs(K*Y)/1.0e-12
c          write results to output file
           write(3,1105) FREQ,KY,KX
1105       format(f9.1,4x,f9.2,4x,f9.2)
           write(*,1107) FREQ
1107       format(' Measurement at',f8.1,' Hz completed.')

9000   continue

       write(*,*) 'MEASUREMENT SEQUENCE FOR ',outname,'COMPLETED'
c      unlock SST and SR530
       open(unit=8,file='$SST',status='old')
       write(8,*)'Set Amplitude 0.00'
       write(8,*)'UNlock'
       write(8,*)'HIde'
       close(8)
       call txstr('i0$')
```

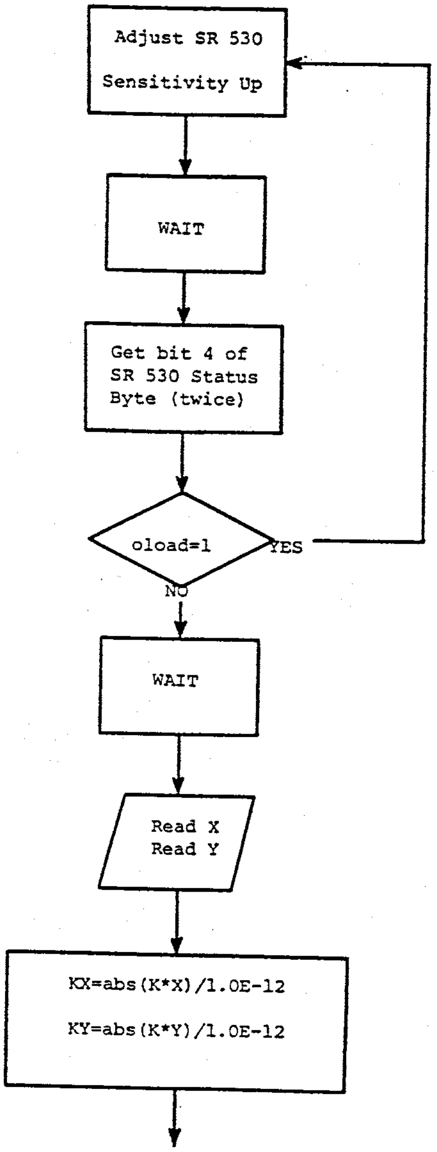
```
      end

      subroutine nocom
      write(*,*) char(7)
      write(*,*) 'RS-232 TIMEOUT ERROR!!!!!'
      write(*,*) 'CAN NOT COMMUNICATE WITH SRS 530 LOCK-IN'
      write(*,*) 'TERMINATING MEASUREMENT.'
      stop
      end

      subroutine wait(TC,DELAY)
c     a subroutine to provide a variable delay
c     will delay for TC*DELAY sec
          call gettim(ihr,imin,isec,i100th)
          TIME=ihr*3600+imin*60+isec+i100th/100
9020      call gettim(ixhr,ixmin,ixsec,ix100th)
          NEWTIME=ixhr*3600+ixmin*60+ixsec+ix100th/100
          if(NEWTIME.lt.TIME+TC*DELAY) goto 9020
      end
```

MEASURE.FOR Program Flow-chart

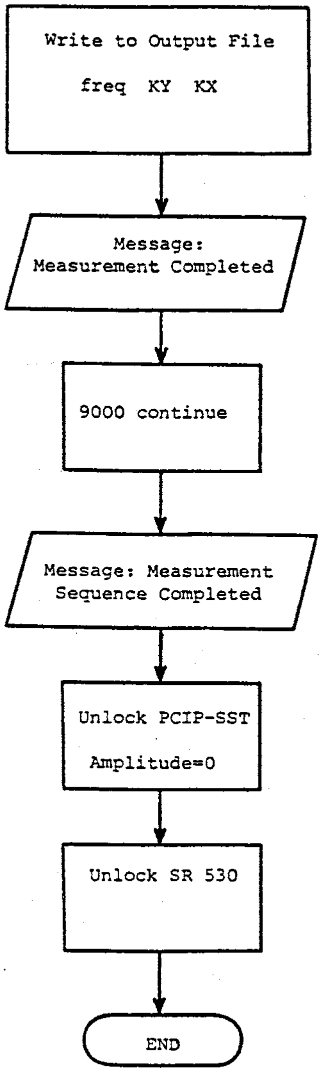



Calibrate
PCIP-SST
Initialize
SR 530
Read #
of Freqs
do 9000 i=1,FNUM
Loop on # of frequencies
Read
Freq
Read
calfreq
K phiref
freq=calfreq
NO
YES
Message:
Error
STOP
Message:
Preparing
to Measure


freq<11
NO
TC=2
YES
TC=10
Open PCIP-SST
Set PCIP-SST Frequency+Track
Close PCIP-SST
Set SR 530 to phiref
Get bit 4 of SR 530 Status Byte
WAIT
oload=1
NO
Adjust SR 530 Sensitivity Down
YES



Adjust SR 530
Sensitivity Up
WAIT
Get bit 4 of
SR 530 Status
Byte (twice)
oload=1
YES
NO
WAIT
Read X
Read Y
KX=abs(K*X)/1.0E-12
KY=abs(K*Y)/1.0E-12


Write to Output File
freq KY KX
Message:
Measurement Completed
9000 continue
Message: Measurement
Sequence Completed
Unlock PCIP-SST
Amplitude=0
Unlock SR 530
END

```
c       Bob Svec 5/26/93
c       T3PLOT.FOR
c       This program makes data files for 3-dimensional temperature
c       plots. Can be used for X,Y,p,q vs 1000/T and log freq.
c       Cole-Cole data file should be converted to logs before running
c       through this program to obtain a better scale in the plot.
c       ***************************************************************

        real logfreq(40),logc(40),t1000(20)
        integer i,j,filenum
        character*12 file(20),outfile

        write(*,*) "Ready to prepare T 3-plot data file!"
        write(*,*) "Have the analysis sheet ready."
c       prompt user for information
        write(*,*) "Enter the number of files you will use"
        read(6,1000) filenum
1000    format(I2)
        write(*,*)"   "
        do 100 i=1,filenum
            write(*,*)"   "
            write(*,*)"Enter data for file ",i
            write(*,*)"  File name (x01) ->"
            read(6,1001) file(i)
1001        format(A12)
            write(*,*)"  1000/T (3.67) ->"
            read(6,1002) t1000(i)
1002        format(F4.2)
100     continue

c       output file
        write(*,*) "Enter name of T 3-plot data file:"
        read(6,1005) outfile
1005    format(A12)
c       open output file
        open(unit=99,file=outfile,status='new')

c       Build T 3-plot data file
c       all files in log format by LFCONV
c       loop on files
        do 300 i=1,filenum
            open(unit=i,file=file(i),status='old')
            do 200 j=1,31
                read(i,*) logfreq(j),logc(j)
                write(99,*) logfreq(j),t1000(i),logc(j)
200         continue
300     continue
        end
```

```
c     Bob Svec
c     XYPQ.FOR
c     Converts xy lockin data files to cole-cole plottable
c     pq data files for Mathematica input. pq files must be run
c     through CONVERT.FOR before plotting.
c     ***************************************************************

      real x,y,p,q,czero,freq,denom
      integer i
      character*10 date
      character*70 header
      character*12 xyfile,pqfile

c     get file information
      write(*,*)'Enter the name of the XY Lockin file (186040.02): ->'
      write(*,*)'WARNING:this must be a standard lockin output file!'
      read(6,1000) xyfile
1000  format(A12)
      write(*,*)'Enter the name of the PQ file (ex. pq02): ->'
      read(6,1000) pqfile

c     open the files
      open(unit=1,file=xyfile,status='old')
      open(unit=2,file=pqfile,status='new')

c     get C0 estimate
      write(*,*)'An estimate of C0 is necessary to invert XY -> PQ !'
      write(*,*)'Enter the estimate of C0 (43.60): ->'
      read(6,1001) czero
1001  format(F6.2)

      write(2,*)'dummy date'
      write(2,*)'PQ converted ',xyfile

c     read from xyfile
      read(1,1002) date,header
1002  format(A12,/,A70)

c     loop on 31 frequencies
      do 10 i=1,31

c          read data from xyfile
           read(1,*) freq,x,y

c          do calculations
           denom=(czero-x)**2+y**2
           p=(czero*((czero-x)*x-y**2))/denom
           q=(czero**2*y)/denom

c          write to pqfile
           write(2,1003) freq,p,q
1003       format(5X,F8.1,8X,F9.2,8X,F9.2)

10    continue

      write(*,*)' XY -> PQ inversion completed.'
      end
```

```
c    Bob Svec 7/10/92
c    YZCONV.FOR
c    This is the converter program which is intended to take lockin data
c    files and convert them to Y* and Z* formats for mathematica
c    input. The user is prompted for names of the input file and names for
c    the output files. Please follow a logical format. For instance:
c           input file = 186040.02
c           C* file    = c02
c           Y* file    = y02
c           Z* file    = z02
c     ************************************************************************

       real freq,c1,c2,y1,y2,z1,z2,w
       character*12 infile,cfile,yfile,zfile
       character*70 header
       character*10 date

c      get names for input and output files
       write(*,*) 'Enter the name of the file to convert(186040.02): ->'
       write(*,*) 'WARNING:this must be a standard lock-in output file!'
       read(6,1000) infile
1000   format(A12)
c       write(*,*) 'Enter the name of the C* output file (c02): ->'
c       read(6,1000) cfile
        write(*,*) 'Enter the name of the Y* output file (y02): ->'
        read(6,1000) yfile
        write(*,*) 'Enter the name of the Z* output file (z02): ->'
        read(6,1000) zfile

c      open the files
       open(unit=1,file=infile,status='old')
c       open(unit=2,file=cfile,status='new')
        open(unit=3,file=yfile,status='new')
        open(unit=4,file=zfile,status='new')

c      display info from input data file
       write(*,1001) infile
1001   format(/,'You have selected the file',A12,'for conversion')
       read(1,1002) date,header
1002   format(A10,/,A70)
       write(*,1003) infile,date,header
1003   format(/,A12,'was created on',A10,'and has the following header:'
     + ,/,A70)

c      loop on 31 frequencies
       do 8000 i=1,31

c           get the raw data from input file
            read(1,*) freq,c1,c2

c           write to the C* file
c           write(2,1004) c1,c2
1004        format(F9.2,4X,F9.2)

c           calcs for Y*
            w=2*3.14159*freq
            y1=w*c2
            y2=w*c1
c           write to the Y* file
            write(3,1005) y1,y2
```

```
1005        format(E10.4,10X,E10.4)

c           calcs for Z*
            denom=Y1**2+Y2**2
            z1=y1/denom
            z2=y2/denom
c           write to the Z* file
            write(4,1006) z1,z2
1006        format(8X,E10.4,10X,E10.4)

8000    continue

        write(*,*) char(27)
        write(*,1007) infile
1007    format(/,/,'Conversion completed for ',A12)
        end
```

Appendix D - Measurement System Notes

Files that need to be on the STARTUP+MEASURE disk.

FILE	FUNCTION
command.com	DOS
more.com	"
config.sys	"
autoexec.bat	"
for232.inc	SR530 communications
rs232.obj	"
ser19200.exe	Initialize COM1 port to 19.2 kbaud
vi.sys	SST device driver
sst.sys	"
driver.def	SST definitions file
ls.com	Utility to install SST device drivers
us.com	Utility to uninstall SST device drivers
measure.exe	The measurement executable program
cal.dat	Calibration data file
freq.dat	Frequency data file

General use of the PC 286 and the measurement system

The disk labeled STARTUP+MEASUREMENT must be in the drive for the system to boot. The first attempt to run the measurement program usually fails. Don't panic. This is due to a glitch in MS FORTRAN. Retry the measurement program and it will function correctly. It will continue to function correctly until the system is rebooted.

No measurement or calibration should be attempted unless the entire system has warmed up for at least 3 hours. It is good practice to measure the calibration capacitor at least monthly to verify that the calibration is valid. It is normal for the calibration to change slightly as weather conditions change (temperature, humidity, etc.).

Measurement procedure

1. At the DOS prompt type: measure
2. Name the measurement file. Use this format:
   (book)(page).(number)
   187034.01
   This indicates that the sample is 187034 and this is the first measurement of this sample.
3. Enter the date.
4. Give a descriptive header for the file:
   187034.01, -1.0 C, BULK, CELL 2, 16:00 (etc.)
5. The PCIP-SST will auto-calibrate then the measurement will cycle through the frequencies 1Hz to 100kHz.
6. Repeat 1-5 at each temperature of interest.
7. You may view the measurement file in DOS after the measurement is completed by typing: type 187034.01|more

Manual adjustment of the PCIP-SST function generator

1. Type CTRL-ESC to show the instrument.
2. Type ALT-M to activate manual entry mode.
3. Use the arrow keys and ENTER to select parameters.
4. Select KEYBOARD ENTRY from the menu.
5. Modify the instrument settings as needed.
6. Type ESC to end manual entry (go to menu).
7. Type ESC again to deactivate manual entry mode.
8. Type CTRL-ESC to hide the instrument.

Calibration Procedure

If a test measurement of the calibration capacitor reveals the need for recalibration then follow the procedure outlined below.

1. Be sure that the PC 286 and the SR530 lock-in have warmed up for at least 3 hours.
2. Remove the freezer extension cables from the freezer feed-through and allow the extension cables to come to room temperature (wait a few hours).
3. Connect the freezer extension cables to the GR1422-CB precision capacitor so that it is in the measurement circuit in place of the unknown.
4. Set the dial on the GR1422-CB to obtain a capacitance of 100.0 pF.
5. Activate the PCIP-SST function generator for manual input.
6. Set the PCIP-SST output voltage to 20.00 V, offset to 0.0 V, and select the sinusoid waveform.
7. Do not add any filters to the SR530 lock-in input. Leave the front panel settings alone unless specifically told to change them. The last measurement will have left the front panel in the correct configuration for you.
8. Set the SR530 PRE time constant to 10 for 1Hz-10Hz or 1 for 15Hz-100kHz.
9. Set the SR530 sensitivity to 500 microvolts.
10. Use the previous calibration data as a starting point for the present calibration. Use the calibration sheet in the notebook as a guide to set up a new calibration sheet.
11. Set the PCIP-SST to the desired frequency.
12. Set the SR530 REFERENCE PHASE angle to that specified in the previous calibration.
13. Allow the lock-in to come to equilibrium. If the PHI display does not read -90.0 ±0.1 then you must change the reference phase in order to bring the PHI display to -90.0.
14. Record the frequency, R (modulus), and REFERENCE PHASE angle on the calibration sheet.
15. Repeat 11 through 14 for each measurement frequency. Pay particular attention to the end frequencies because these tend to drift the most.

16. Calculate the K coefficients from your R values.
    K = (100.0 pF) / (R microvolts).
17. Update the calibration data in the CAL.DAT file on the STARTUP+MEASURE disk. First copy the old CAL.DAT to CAL.OLD then modify the CAL.DAT file with the new calibration data.
18. Lastly, make a measurement of the GR1422-CB capacitor to verify your new calibration.

Appendix E - Sample Cell Description

The three-terminal sample cell (see illustration) represents an improved design of the one used by the M.I.T. group (von Hippel, et al., 1971). Numbers between "[ ]" in the following text correspond to those in the illustration.

Insertion of blocking layers between measuring electrodes and sample creates a high-impedance "microphonic" system; *i.e.*, measurements are extremely susceptible to degradation by noise and instability. The new design takes this into account by using two separate shields. The thick-walled outer shield, or cavity [1], contains rod heaters. It is connected to earth ground. An inner shield [2] completely surrounds the sample holder proper. It is electrically insulated from the outer shield by a Teflon spacer [3] and is connected to the signal ground. The inner shield has a removable section, about 120°, for sample insertion and for access to the electrodes. Excellent stability and noise reduction are achieved with this design. The inner and outer shields can be grounded together with an adjustable metal screw [4] normally used to ground the cavity.

The electrode guard ring is normally connected to signal ground but the cell is constructed in such a way that any electrode element may be connected either to earth ground, signal ground, or kept floating. Thus, surface measurements are possible.

The sample cell is housed in a low-temperature freezer (not in a circulating coolant bath as in von Hippel et al. (1971)). Therefore, to insure temperature stability as well as slow cooling and heating, the cavity is machined of thick-walled aluminum stock.

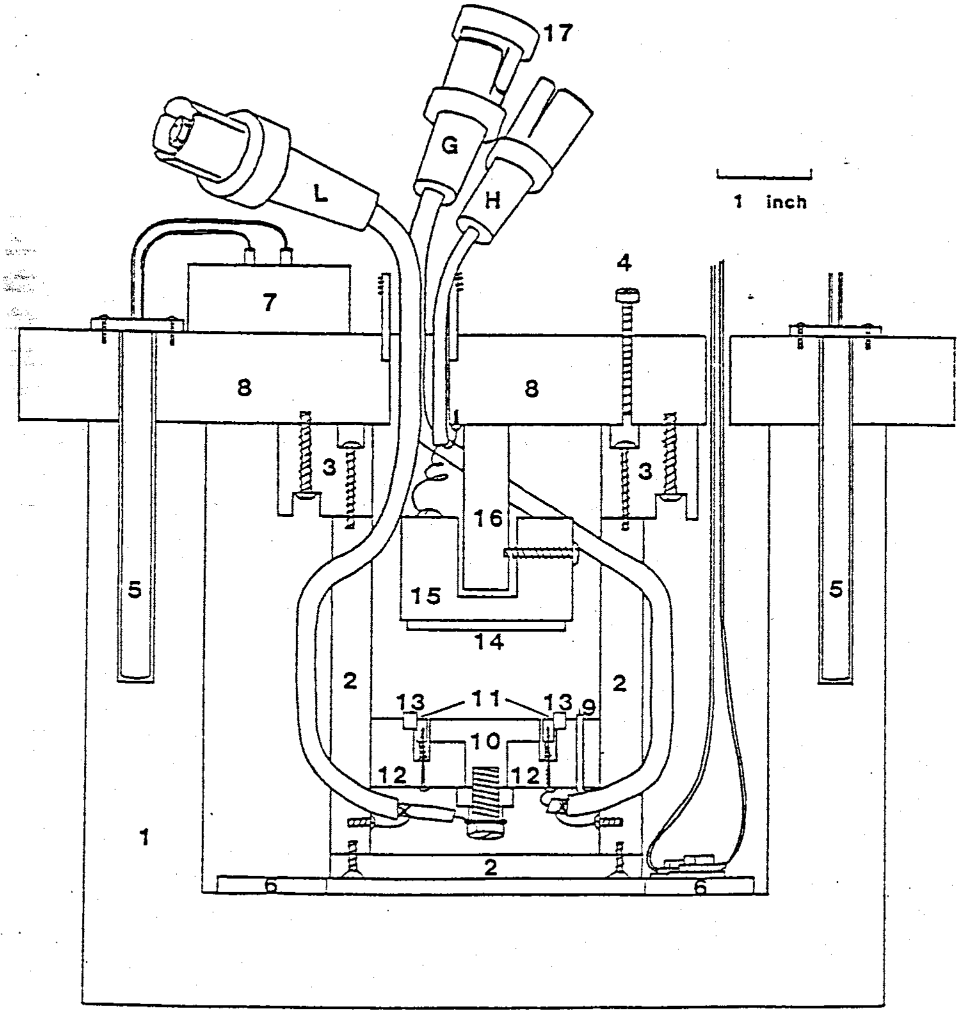
Temperature control and measurement are accomplished with a platinum resistance thermometer (RTD Omega Type PR-13) housed in the inner shield wall, and a controller (Omega model 4201PC2). Even heating is achieved by distributed heating elements: four rod heaters (Chromalox type CIR-2040) [5] are housed in wells in the cavity wall. A heat tape (not shown) is wound on the outside of the cavity and covered with insulation. A ring heater (Chromalox type A-40) [6] rests on the cavity bottom between the two shields. All heaters are connected in parallel by means of a terminal strip [7] mounted on the sample cell cover [8], from where they are connected to a Variac through the controller. To check on temperature gradients, thermocouples are housed in the wall of the inner shield and in the space between the inner shield and guard ring adjacent to the sample

[9]. The maximum aggregate heater output is 2100 Watts, and they are actually operated at from 25% to 30% of capacity. With temperature fluctuations in the freezer chamber of about 2°C, the sample temperature is held constant to about 0.1°C, which is the smallest significant figure of the controller's digital readout.

The electrodes are made of stainless steel. The low electrode [10] is guarded and has the following dimensions: electrode diameter - 29.85mm; gap width - 3.18mm; guard ring - 38.10mm O.D., 33.02mm I.D. The guard ring [11] is mounted on springs to insure proper contact with the sample. The low electrode/guard ring assemblage is mounted on a Teflon support [12] fastened by screws to the inner shield. A Teflon ring [13] insures proper positioning of the sample. The high electrode (38.10mm diameter) [14] has a weight of 239g to 354g in order to insure an adequate and temperature independent pressure on the sample. It is insulated with a thin Teflon sleeve [15]. It is connected to the lead-in cable by a coiled Teflon insulated wire, and it slides on a guiding rod of Teflon [16], where it can be suspended with a set screw.

To minimize error due to lead capacitance, all lead-in wires and patch cables are made of RG-59/U Type 75 ohm cable.

Lead-in wires enter the cavity through a short duct threaded at the top, where they are held in place with an Amphenol #8 cable clamp (not shown in illustration). Guard connection to signal ground is achieved with a General Radio 874-WN Short-Circuit Termination [17]. The connectors for high, low, and guard electrode are labeled [H], [L], and [G], respectively, in the illustration.



Sample cell illustration.