Electrical Resistivity of Geothermal Brines

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ABSTRACT

The electrical resistivities at a frequency of
1 kHz of aqueous solutions of the chlorides of sodium,
calcium, and potassium have been measured under 30 MPa
hydrostatic pressure over a concentration range of
roughly 0.2 to 4 molar (or approximately 3 to 26
weight percent) while varying the temperature from 22
to 375°C. The observed behavior of the electrical
resistivity between 200 and 375°C is markedly diff-
erent from that predicted by the extrapolation of
lower temperature data. Considerable errors on the
order of 25 percent or greater in log interpretation
will result from the use of existing formulas for high
temperature resistivity of brines. A new formula is
given from three-dimensional regression analysis of
these measurements with an order of magnitude increase
in accuracy over the existing formulas.

INTRODUCTION

The electrical resistivity of dilute aqueous salt
solutions has been studied for a number of years[1] but
very little data exists above concentrations of 0.1
molar[2] (recently reviewed[3]). Normal groundwaters are
commonly near 0.1 molar[4] while most geothermal and oil
field fluids are at least several molar (see Table 1).
Thus, the interpretation of electrical measurements in
geothermal areas[7] at present are mainly based upon
extrapolations of lower temperature and lower concen-
tration data[3]. Such extrapolation may introduce
serious errors into the interpretation of geothermal
reservoir characteristics determined from electrical
measurements[9].

This paper presents new experimental data and an
improved descriptive model of the electrical properties
of brines as a function of temperature from 22 to 375°C
and concentration from roughly 3 to 26 weight percent
while under 30 MPa hydrostatic pressure. Data and
models are given for brines composed of the chlorides
of sodium, calcium, and potassium and their mixtures.
Comparison of the older log interpretation formulas[10]
to the new models illustrates an order of magnitude
improvement in accuracy with an overall fit to within
12 percent.

RESISTIVITY DEPENDENCE UPON TEMPERATURE

The electrical resistivity of fluid saturated
rocks has been postulated to follow the temperature
dependence of the saturating fluid in the absence of
conducting minerals or significant surficial conduc-
tion along altered pore walls[11][12][13]. This has
occurred due to the success of a simple empirical
formula relating the resistivity of a rock to the
resistivity of the fluid filling the pores of the
rock[14]:

$$\rho_r = F \rho_w$$

where ρ_r = resistivity of clay-free, non-shale
material that is 100 percent saturated

ρ_w = resistivity of saturating solution

and F = formation resistivity factor.
A number of investigators have derived formulas to fit
this which add the temperature of the saturating
fluids[15][16].

Experimental observations have shown that some
rocks obey these formulas while others do not[19][20][21].
Part of the problem is the inadequate knowledge of the
resistivity dependence upon temperature for the
solution that fills the rock pores.

We have empirically found the best fit of the
resistivity data to temperature to be

$$\rho_w = b_0 + b_1 T^{-1} + b_2 T + b_3 T^2 + b_4 T^3$$

where T is temperature and the coefficients, b, are
empirically found.

RESISTIVITY DEPENDENCE UPON CONCENTRATION

The concentration dependence of the electrical
resistivity of aqueous solutions has been extensively
studied and is best represented by the formula

$$\rho_w = 10/(\Lambda c)$$

where Λ is the equivalent conductivity according to[22]

$$\Lambda = B_0 - B_1 c^{1/2} + B_2 c \ln c + \text{higher order terms}$$

where c is the molar concentration and the coeffic-
ients, B, are dependent upon the solution chemistry[23].
Further discussion may be found in nearly any text
on electrochemistry[2].

EXPERIMENTAL

The measurement of the electrical resistivity of concentrated salt solutions at elevated temperatures is very difficult due to the corrosive nature of the solution chemistries. A special sample holder (Figures 1 and 2) and pressure vessel assembly was manufactured from mullite ceramic, platinum, inconel, stainless steel, and teflon components. The salt solution contacted only mullite and platinum. A four electrode configuration at a measurement frequency of 1 kHz was chosen to eliminate electrode polarization problems. Measurements at frequencies from 0.1 to 10 kHz were performed to confirm the lack of polarization at the electrodes. Two electrode measurements were found to have polarization errors on the order of an order of magnitude.

Cumulative experimental errors due to thermal expansion, errors in determining cell constants, instrument errors, and so forth did not exceed ±1 percent in the final resistivity determination. The temperature of the solution was measured with a type S, Pt-10%Rh thermocouple in the solution with an accuracy of ±1°C. The system was hydrostatically pressurized with argon gas through a series of snubbers and pressure regulators as illustrated in Figure 3. Pressure was measured and monitored with two strain gauge pressure transducers as well as a manual Bourdon tube gauge. The electrical resistance of the sample cell was measured with a Hewlett-Packard 4262A automatic digital LCR meter. A computer was used to control the environmental parameters and to perform the electrical measurements as schematically illustrated in Figure 3.

Each experiment began with the cleaning in distilled water and assembly of the sample cell and pressure vessel. A teflon calibration cell of precisely known geometry was used with standard potassium chloride solutions[24] to calibrate the pressure vessel sample cell.

Salt solutions were prepared from reagent grade crystals (anhydrous $CaCl_2$) which were gravimetrically measured into 150,000 ohm-m water. Resultant room temperature (22°C) resistivities were checked against reference table values[24].

All measurements reported here were performed at hydrostatic pressures of 30 MPa as the resistivities of the studied solutions were found to be independent of pressure in agreement with earlier studies[1]. Pressure dependence only becomes significant well above the critical region or as the solution nears and passes below its vapor pressure.

RESULTS

Isobaric resistivities of NaCl, KCl, and $CaCl_2$ solutions versus temperature at several salt concentrations are shown in Figures 4, 5, and 6. In general, the electrical resistivity decreases with increasing temperature and with increasing salt concentration. However, as the critical temperature of the solutions is approached at the higher temperatures studied, the resistivity reaches a minimum and then begins to increase with increasing temperature.

Quist and Marshall[1] have given the best explanation for the behavior of the physical properties of aqueous salt solutions. The electrical resistivity is controlled by a variety of parameters including viscosity, density, and the dielectric permittivity of the solution. As temperature or concentration increases, these properties of water begin to change very rapidly. The rapid decrease of viscosity with increasing temperature results in a rapid increase in ionic mobilities with a resultant decrease in electrical resistivity. Above roughly 300°C as the critical point is approached, the rate of decrease in viscosity with increasing temperature diminishes and the change in ionic mobility becomes less. As the temperature continues to increase, the changes in density overtake the effects of viscosity. The decreasing density results in a lowering of the dielectric permittivity and in the number of ions per unit volume. This results in the increased association among ion pairs and an increase in the electrical resistivity. Thus when the increase in ionic mobility is offset by the decrease in permittivity and in ionic concentration, the electrical resistivity reaches a minimum versus temperature. As the concentration of the salt solution increases significantly above 0.1 molar, the minimum in the resistivity shifts to higher temperatures due to the effects of the increasing salt concentration upon the critical properties of water.

The solid lines in Figures 4, 5, and 6 are formula fits to the data points by three-dimensional regression analysis[25]. The coefficient matrices and computer program to generate the resistivity at a given temperature and concentration is given in the appendix.

Figure 7 illustrates a comparison of the experimental data with the formula from three-dimensional regression and with Arp's approximation[16]. Both formulas are in reasonable agreement with the data up to about 200°C. Beyond 200°C, Arp's approximation encounters serious difficulties.

Figures 8, 9, and 10 illustrate the concentration dependence of NaCl, KCl, and $CaCl_2$ at three temperatures. Note that the curves of resistivity versus concentration crossover each other. These crossovers are a direct result of the differences in the salt solution viscosities versus temperature and concentration. These crossovers also illustrate the need for great caution when reducing a solution of mixed salts to an equivalent solution of NaCl.

Commonly, this is performed by the use of multipliers which convert a given ionic concentration of salt to an equivalent amount of NaCl:

$$k_K K^+ + k_{Cl} Cl^- = \text{measured equivalent NaCl}$$
$$\text{concentration in weight percent}$$

$$k_{Ca} Ca^{++} + k_{Cl} Cl^- = \text{measured equivalent NaCl}$$
$$\text{concentration}$$

where the k's are multipliers and it is assumed that $k_{Na} = k_{Cl} = 1$. The k_K and k_{Ca} multipliers are then empirically determined (usually from electrical resistivity measurements). Desai and Moore[18] report that the multipliers are fairly constant and independent of temperature up to 71°C with errors less than 5 percent for concentrations below 1 weight percent. As illustrated in Figures 11 and 12, we have found this no longer to be the case at higher temperatures and concentrations.

To illustrate the errors involved in the extrapolation of lower temperature and lower concentration data to higher values, a mixed salt of 3 weight percent total salt concentration composed of 1.5 wt% NaCl, 0.75 wt% KCl, and 0.75 wt% $CaCl_2$ was measured. Figure 13 illustrates the results with a 3 wt% NaCl solution for comparison. Table 2 gives the resulting measured resistivities compared with values calculated by our three-dimensional regression formula and values using Desai and Moore's multipliers in Arp's equation. Our newer formula is an order of magnitude better.

CONCLUSIONS

The use of low temperature and low concentration data to extrapolate electrical resistivities to high salt concentrations at geothermal temperatures must be treated with extreme caution. Errors as high or higher than 25 percent in the estimation of electrical resistivity may result. Further, different salts have widely varying temperature and concentration dependencies in the normal geothermal range which greatly complicate the reduction of a mixed salt solution to an equivalent NaCl solution.

A new set of measurements to 375°C and 25 weight percent salt concentration has been fitted by three-dimensional regression analysis to an accuracy of ± 2 percent to model the electrical resistivities of aqueous solutions of the chlorides of sodium, potassium, and calcium. New temperature and concentration dependent NaCl equivalent multipliers have been generated for potassium and calcium. For convenience, Figure 14 gives the formula generated curves for the electrical resistivity of NaCl aqueous solutions as a function of temperature and concentration. This graph should replace existing graphs for high temperature applications in liquid dominated geothermal systems.

NOMENCLATURE

ρ_r = resistivity of clay-free, non-shale material that is 100% solution saturated, ohm-m

ρ_w = solution resistivity, ohm-m

F = formation factor

T = temperature, °C

b = resistivity temperature coefficients

B = resistivity concentration coefficients

c = concentration, molar

Λ = equivalent conductance, $ohm^{-1}cm^2eq^{-1}$

k = equivalent NaCl multiplier

TDS = total dissolved solids

ACKNOWLEDGEMENT

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APPENDIX

Using the coefficients for B that are listed in

Table 3, the following short BASIC program will
generate electrical resistivity in ohm-m at a given
temperature in °C and salt concentration (molar).

```
10   DIM B(3,5),O(1,1),C(1,3),T(5,1),D(1,5)
20   FOR I = 1 to 5
30   INPUT B(1,I),B(2,I),B(3,I)
40   NEXT I
50   DISP"Enter molar concentration and Celcius temp";
60   INPUT C,T
70   C(1,1)=C
80   C(1,2)=C*SQR(C)
90   C(1,3)=C*C*LOG(C)
100  T(1,1)=1
110  T(2,1)=1/T
120  T(3,1)=T
130  T(4,1)=T*T
140  T(5,1)=T*T*T
150  MAT D =C*B
160  MAT O =D*T
170  PRINT T,C,1/O(1,1)
180  END
```

Line 10 sets up the matrix dimensions.
Lines 20-40 enter the B matrix coefficients from
    Table 3 for the appropriate salt.
Lines 50-60 enter the desired concentration and
    temperature.
Lines 70-140 compute the concentration and temperature
    matrices.
Lines 150-160 compute the electrical conductivity (due
    to the form of the concentration dependence)
Line 170 prints out the temperature (°C), molar
    concentration, and electrical resistivity (ohm-m).

To compute the molar concentration of the solution,
multiply the solution concentration in weight percent
by the density of the solution, multiply that product
by ten, and divide by the molecular weight of the
solute. See any standard chemistry textbook.

TABLE 1

Examples of typical water chemistries in weight percent.

Ion	Normal ground water	Seawater	Salton Sea Brine	East Mesa Brine	Cerro Prieto Brine
Na^+	0.061	1.5	5.04	0.7	0.6
K^+	0.061	0.038	1.75	0.089	0.17
Ca^{++}	0.0037	0.04	2.8	0.077	0.034
Cl^-	0.0082	1.9	15.5	1.4	1.1
Mg^{++}	0.00024	0.135	0.0054	0.0016	0.0016
SO_4^{--}	0.1	0.27	-	0.02	-
$(HCO_3)^-$	0.0429	0.014	0.01	0.03	0.0011
TDS	0.198	3.45	25.8	2.5	2.0
molarity	0.03	0.56	3.6	0.36	0.3
T°C			340	138	290
Reference	6	6	5	25	25

TABLE 2

Comparison of actual measured resistivities with various derived parameters

Temperature (°C)	Measured Resistivity (ohm-m)	Resistivity from Desai and Moore's method	Multipliers in this study from Fig. 12 & 13		Equivalent NaCl Concentration (weight percent)	Formula Resistivity from this study
			K^+	Ca^{++}		
25	0.22	0.22	0.592	0.723	2.77*	0.22
100	0.078	0.070	0.331	0.160	2.51	0.0765
300	0.043	0.0345	0.203	-0.385	2.31	0.0430

Chemical composition of solution: TS 3 wt%, 0.5901 wt% Na^+, 0.3933 K^+, 0.2711 Ca^{++}, 1.7462 Cl^-

*Example calculation:
   Equivalent NaCl = 0.5901 x 1 + 1.7462 x 1 + 0.3933 x 0.592 + 0.2711 x 0.723 = 2.77 wt%

TABLE 3

Coefficient matrices for B for the three-dimensional regression
analysis of the data in the text:

$CaCl_2$:

$$B = \begin{matrix} -34.62 & 24.64 & -3.907 \\ 780.3 & -492.3 & 64.59 \\ 1.050 & -0.5922 & 0.06735 \\ -0.002459 & 0.001461 & -1.216 \times 10^{-4} \\ 9.986 \times 10^{-7} & -7.109 \times 10^{-7} & -4.731 \times 10^{-9} \end{matrix}$$

KCl:

$$B = \begin{matrix} 5.783 & -6.607 & 1.665 \\ -59.23 & 149.7 & -31.21 \\ 0.2051 & 0.1064 & -0.03418 \\ 1.815 \times 10^{-4} & -7.037 \times 10^{-4} & 1.539 \times 10^{-4} \\ -1.094 \times 10^{-6} & 1.080 \times 10^{-6} & -1.945 \times 10^{-7} \end{matrix}$$

NaCl:

$$B = \begin{matrix} 3.470 & -6.650 & 2.633 \\ -59.21 & 198.1 & -64.80 \\ 0.4551 & -0.2058 & 0.005799 \\ -9.346 \times 10^{-5} & 7.368 \times 10^{-5} & 6.741 \times 10^{-5} \\ -1.766 \times 10^{-6} & 8.768 \times 10^{-7} & -2.136 \times 10^{-7} \end{matrix}$$
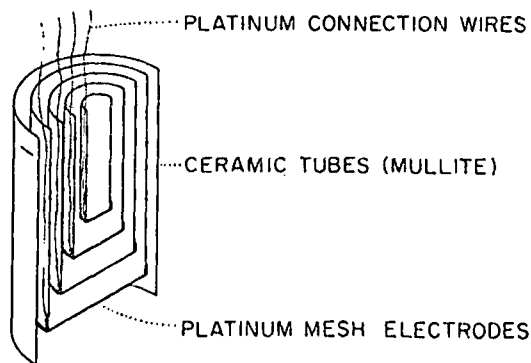
FIG. 1 – RESISTIVITY SAMPLE CELL MADE FROM MULLITE CERAMIC WITH FOUR PLATINUM ELECTRODES

PLATINUM CONNECTION WIRES

CERAMIC TUBES (MULLITE)

PLATINUM MESH ELECTRODES

FIG. 2 – PRESSURE VESSEL ARRANGEMENT

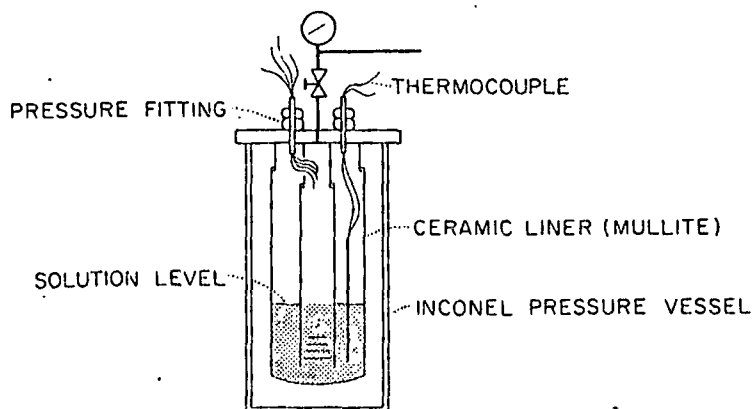PRESSURE FITTING

THERMOCOUPLE

CERAMIC LINER (MULLITE)

SOLUTION LEVEL
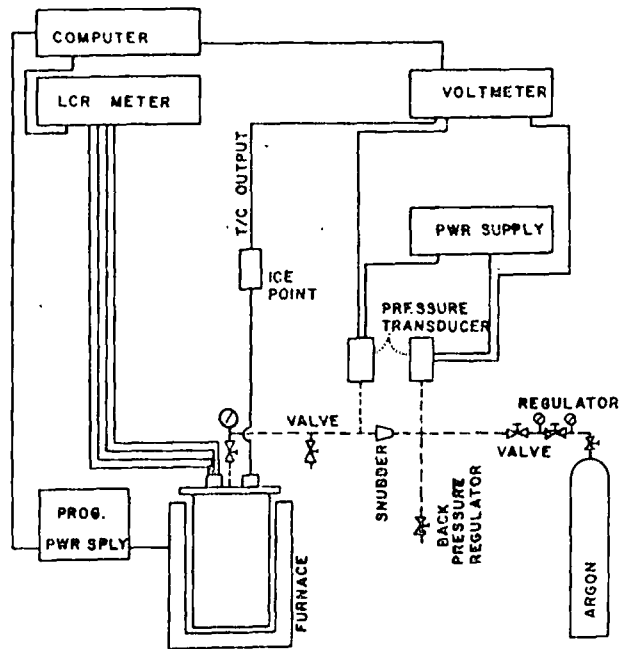
INCONEL PRESSURE VESSEL

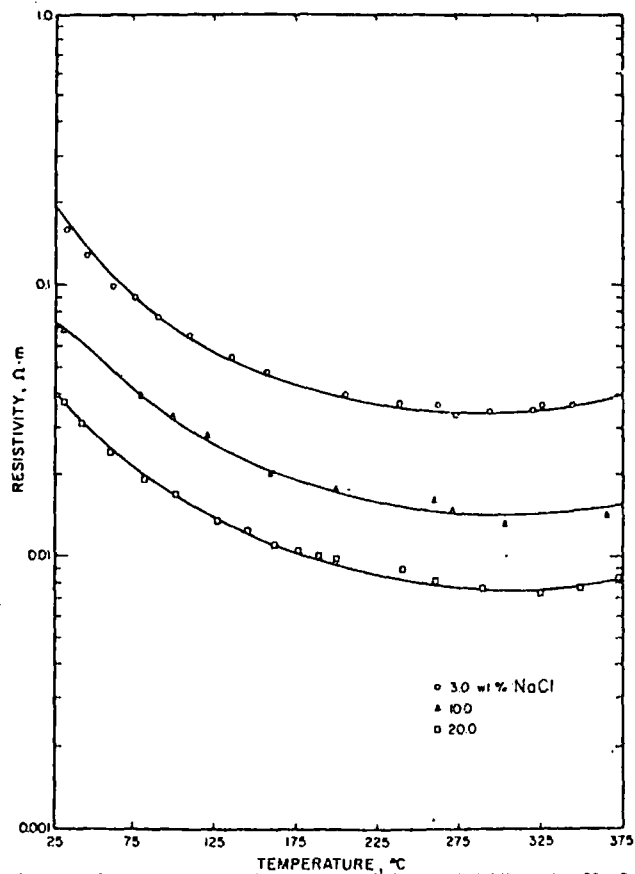Fig. 3 - Experimental equipment and plumbing

Fig. 4 - Resistivity of NaCl aqueous solutions at 1 kHz under 30 MPa
hydrostatic pressure. Solid lines are formula fitted by three-
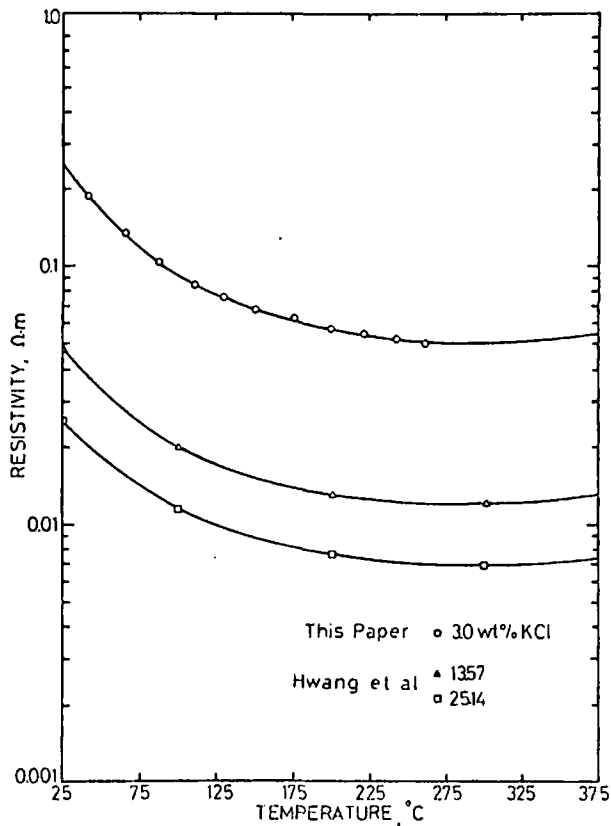dimensional regression analysis.
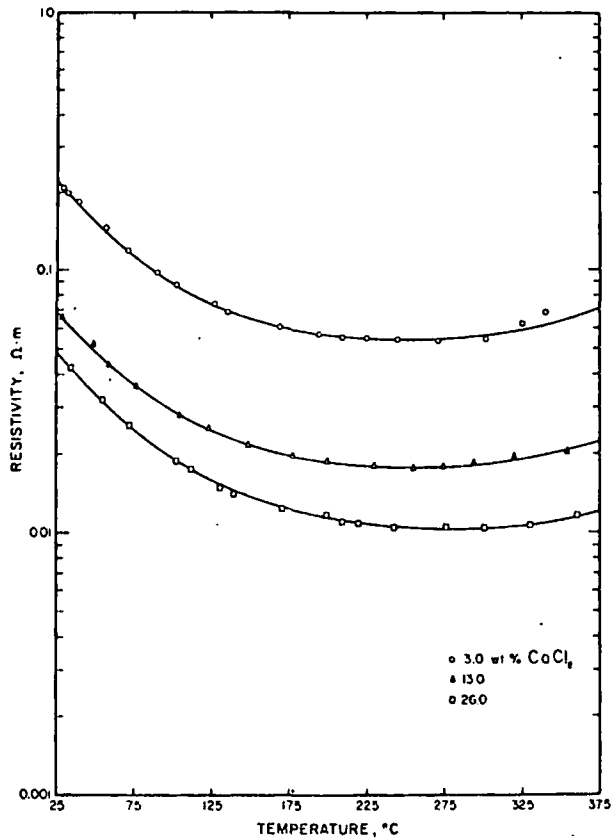
Fig. 5 - Resistivity of KC1 solutions as for figure 4

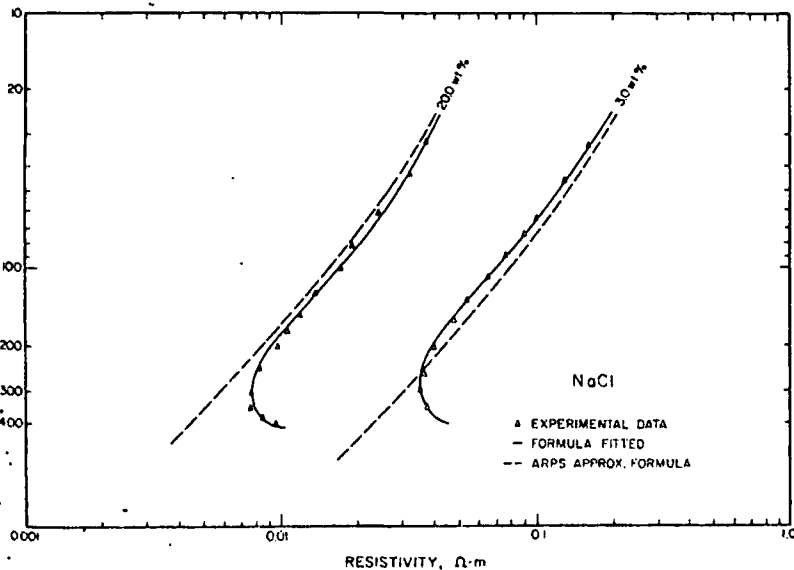
Fig. 6 - Resistivity of CaCl$_2$ solutions as for figure 4

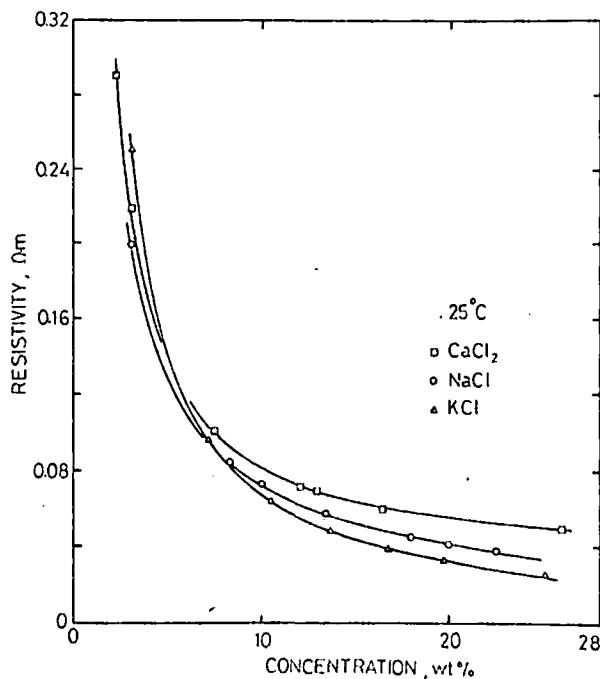Fig. 7 - Resistivity of NaC1 solution showing fit of Arp's approximation and our new formula to the data

Fig. 8 - Resistivity variations of NaC1, KC1, and CaCl$_2$ solutions with concentration at 1 kHz under 30 MPa hydrostatic pressure at 25°C
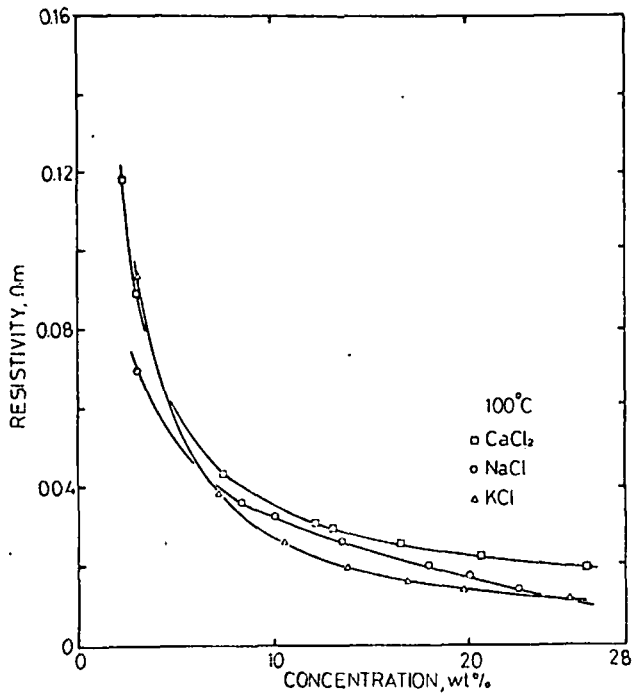
Fig. 9 - Resistivity variations at 100°C as for figure 8
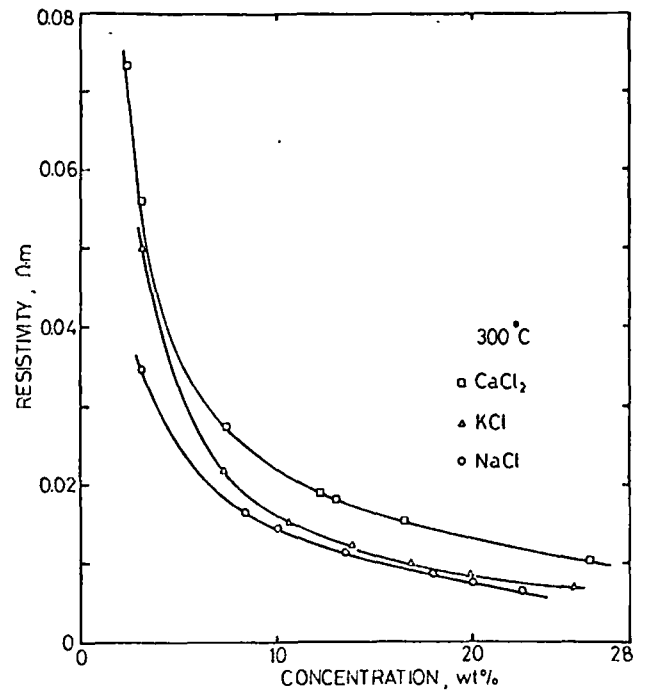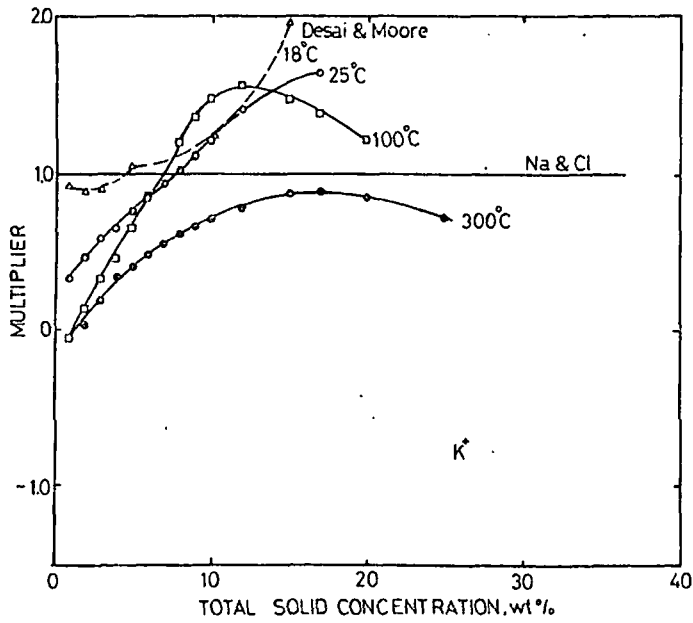

Fig. 10 - Resistivity variations at 300°C as for figure 8

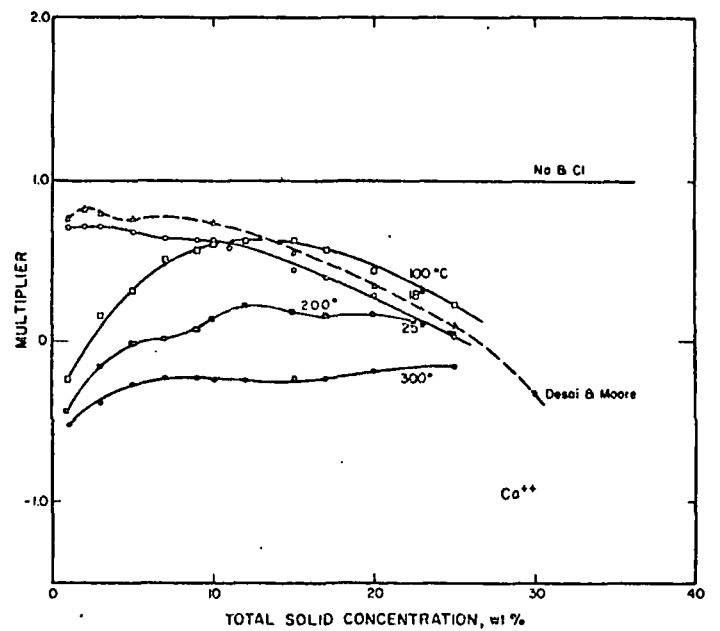Fig. 11 - NaCl equivalent multipliers for K⁺ ion versus total solid concentration at several temperatures

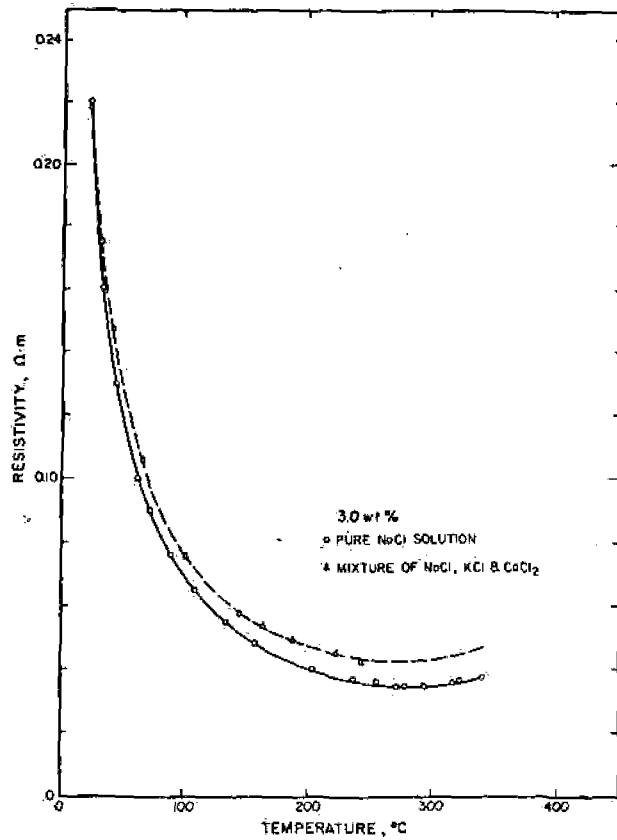Fig. 12 - Multipliers for Ca⁺⁺ ion as for figure 11

Fig. 13 - Resistivity versus temperature for a 3 weight percent solution of NaCl and a 3 weight percent solution of 2:1:1 NaCl: KCl:CaCl$_2$.
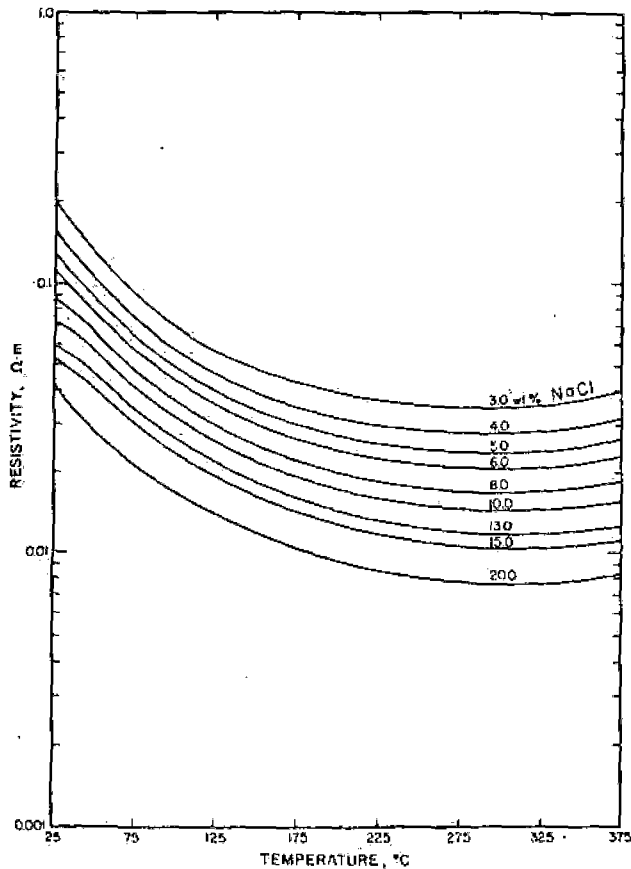

Fig. 14 - Resistivity of NaCl solution versus temperature and concentration calculated from the regression analysis formula