Resistivity of NaI-Glycerol Solutions

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Introduction

Fluid resistivity is an important parameter in the experimental development of charged droplet sources and colloid microthrusters.[1] In these systems droplet beams are charged and accelerated by feeding an electrically conducting fluid through a hypodermic needle held at high potential (typically 6kv) opposite an aperture in a ground plane. Although fluid pressure and needle voltage influence the charge to mass ratio of the droplets, a more effective parameter is fluid resistivity, which can be varied by doping the working fluid, usually glycerol, with agents such as NaI or $FeCl_3$. Resistivity has proven to be a reliable indicator of the presence of contaminants in the fluid which in turn affect beam stability and electrical breakdown at the needle tip.[2] Also, theories attempting to explain the droplet formation process use resistivity as a parameter.[3]

Table 1 shows some values of NaI-glycerol solution resistivities found in the literature.[4–7] Details of solution preparation, outgas history, and measurement techniques are generally omitted from the literature. Inconsistencies may be noted, in particular for the 20 g NaI/100 ml glycerol solutions.

The importance of the resistivity values, the variation in quoted values, and the scarcity of experimental information prompted the current investigation into the resistivity of NaI-glycerol solutions. The effects of measurement frequency, temperature, outgas procedure, glycerol purity, and doping level have been determined.

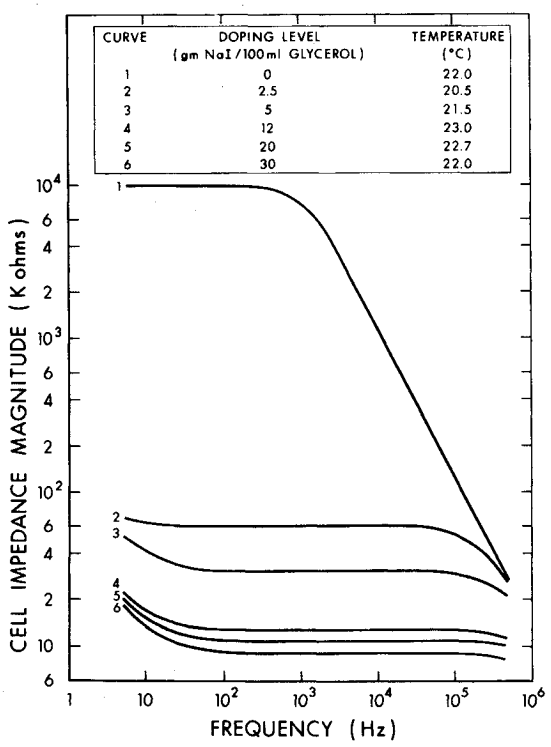

Fig. 1 Cell impedance magnitude vs frequency for outgassed NaI-glycerol solutions.

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Table 1 Values of resistivity for NaI-glycerol solutions, as quoted in the literature

Solution concentration, g NaI/100 ml glycerol	Resistivity, kohm-cm	Measurement temperature, °C
0	2000.0[4]	25
5	68.0[5]	...
10	30.0[5]	...
15	7.28[6]	25
20	20.1[5]	...
20	2.5[7]	...
30	4.65[4]	25

Measurements

The resistivity was obtained from the measured resistance of a cell of fluid. The resistance cell was a glass tube, 3.93 cm long and 1.88 cm in diameter, with aluminum end plates.

The cell impedance was measured for frequencies from 5 Hz–500 kHz with a Hewlett Packard Model 4800A Vector Impedance Meter. Figure 1 shows impedance magnitude vs frequency for six outgassed solutions of varying doping level. At high frequencies the impedance decreased due to cell and test lead shunt capacitance, which was measured to be about 10 pf. On the other hand, the cell impedance increase at low frequencies was attributed to polarization of the ionic solution within the cell.[8,9] At frequencies below 300 Hz it is impossible to unambiguously define the resistivity of the doped glycerol solutions, because of this frequency dependence. When cell impedance is independent of frequency, fluid resistivity is given by

$$\rho = RA/L \tag{1}$$

where ρ is the resistivity, R is the cell resistance, A is the cell area, and L is the cell length. Values of resistivity given below have been computed from Eq. (1) using measurements at a reference frequency of 1 kHz.

Fluid resistivity was found to be extremely temperature dependent. Figure 2 shows measurements of resistivity versus fluid temperature for outgassed 5 g and 30 g NaI/100 ml glycerol solutions. From approximately 10°–35°C both curves satisfy the empirical relationship

$$\rho = \rho_0 \, 10^{-0.0364(T-T_0)} \tag{2}$$

where ρ is the resistivity in kohm-cm and T is the temperature in degrees Centigrade. Thus the resistivity decreases approximately one decade for each 27.5°C increase in temperature. This result is consistent with an approximate value of 30°C/decade estimated from data given by Kidd.[1]

Table 2 Measured resistivities of NaI-glycerol solutions at 25°C[a]

Doping level, g NaI/100 ml glycerol	Glycerol, grade	Resistivity of original solution, kohm-cm	Resistivity of outgassed solution, kohm-cm
0	USP	2,300	5,500
0	reagent	10,900	...
2.5	reagent	18	29
5	reagent	9.8	17
12	reagent	4.6	7.8
12	USP	3.5	7.5
20	USP	2.3	5.5
30	USP	1.9	4.9
30	reagent	2.6	4.5

[a] Resistivity values given here have been normalized to 25°C from ambient temperatures ranging from 20°–23°C using Eq. (2).

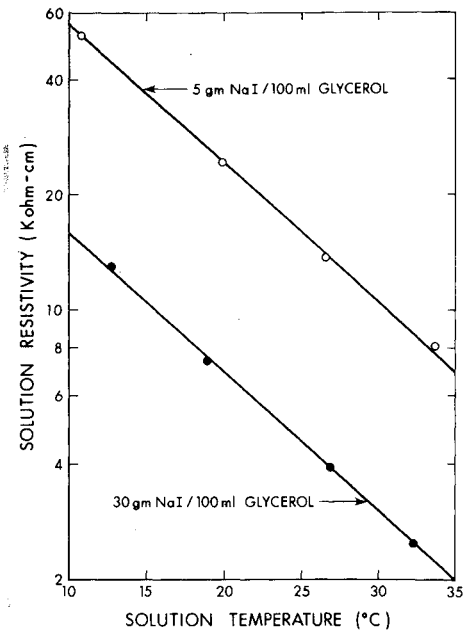

Fig. 2 Solution resistivity at 1 kHz vs temperature for outgassed 5 g and 30 g NaI/100 ml glycerol solutions.

Solutions were outgassed by liquid nitrogen trapped pumping on about 50 ml of solution in a 250 ml Erlenmeyer flask immersed in a 65°C bath. The resistivity of a 30 g NaI/100 ml glycerol solution rose from 2.6 kohm-cm initially to 4.5 kohm-cm after two hours of outgassing, and rose only 15% more in a further sixteen hours of outgassing. The characteristic yellow color of the NaI-glycerol solutions disappeared after about four hours of outgassing. A standard time of five hours of outgassing at 65°C was used for solution preparation.

The resistivities of various NaI-glycerol solutions are shown in Table 2. Two different glycerol grades were tested at doping levels of 12 g and 30 g/100 ml glycerol. The resistivity of USP grade glycerol solutions was initially lower than that of the reagent grade glycerol solutions, but outgassing essentially removed the difference. A total of six doping levels were measured ranging from pure glycerol to 30 g NaI/100 ml glycerol, in both original and outgassed form. It was found that solutions with a particular resistivity value could be reproduced within ±5%.

The measured resistivity values show general agreement with the values from the literature (Table 1). The values of Makin and Bright[5] are inexplicably high.

Some recommendations on solution resistivity measurement procedure can be made from the observed dependence of resistivity on the experimental conditions. The frequency dependence of cell impedance must be examined to find a range in which the impedance is independent of frequency, thus allowing an unambiguous determination of resistivity. The strong temperature dependence of resistivity makes temperature control essential. This can be done by using a controlled environment or applying an empirical temperature normalization, but the cell must be allowed to completely stabilize before measurement in either case. Solutions should be outgassed before measurement. Once outgassed, solution resistivity depends only on doping level, and is stable under vacuum. If these precautions are observed the resistivities of NaI-glycerol solutions are clearly defined, stable, and reproducible.

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Use of Polynomial Approximations to Calculate Suboptimal Controls

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Introduction

MANY methods have been developed to calculate optimal and suboptimal control laws for control problems.[1] The purpose of this Note is to present a new method for calculating suboptimal controls. The method is based on assuming a functional form such as a polynomial for the control. The functional form will contain several arbitrary constants. These constants are then selected to produce a control which causes the trajectory to meet terminal conditions and extremize the performance index in some sense.

Problem Statement and Method of Solution

The problem to be considered may be stated in the following manner: minimize

$$I = G(\mathbf{x}_f, t_f) \tag{1}$$

subject to

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, \mathbf{u}, t) \tag{2}$$

and

$$\mathbf{x}_o = \mathbf{x}_{os} \qquad \mathbf{M}(\mathbf{x}_f, t_f) = 0 \tag{3}$$

where $\mathbf{x}$ is an n vector of state variables, $\mathbf{u}$ is an m vector of control variables, t is time, $\mathbf{x}_{os}$ is the specified initial state vector, G is a scalar performance index, and $\mathbf{M}$ is a p vector of terminal conditions.

The control $\mathbf{u}$ is now chosen as some arbitrary function, such as a polynomial in time, with arbitrary constant coefficients. Thus

$$\mathbf{u} = U(\mathbf{a}, t) \tag{4}$$

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