

**AD-A274 937**



①

## Rechargeable Lithium-Inorganic Electrolyte Cell

LABCOM Contract DAAL01-89-C-0939

First Quarterly Report

1 September 1989 to 30 November 1989

**S** DTIC  
ELECTE  
JAN 26 1994  
**A**

S. Hossain, P. Harris, R. McDonald, C. Todino, W. Ragsdale  
Whittaker-Yardney Power Systems  
520 Winter Street  
Waltham, Massachusetts 02154-1275

This document has been approved  
for public release and sale; its  
distribution is unlimited.

Prepared for:  
Dr. Michael Binder  
U. S. Army Laboratory Command  
Fort Monmouth, New Jersey 07703-5000

**94-02306**



94 1 25 108

## INTRODUCTION

Because of its high energy density (225 Wh/lb), the lithium-sulfuryl chloride system has been studied extensively (1,2) as an alternate of primary lithium-thionyl chloride electrochemical cells. Gilman and Wade (3) examined the discharge characteristics of primary Li/SO<sub>2</sub>Cl<sub>2</sub> cells in 1.5M LiAlCl<sub>4</sub> electrolyte using different carbon cathodes and established the following reactions:

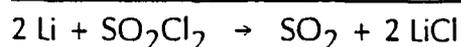
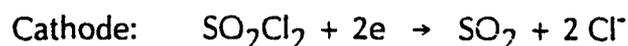


Based on cyclic voltammetry results and the work of Gilman and Wade (3), Behl (4) concluded that the mechanism of cathodic reduction involved first the reduction of free chlorine resulting from the homogeneous and/or heterogeneous dissociation of sulfuryl chloride (5) followed by the reduction of undissociated sulfuryl chloride. Klinedinst and Gary (2) examined primary Li/SO<sub>2</sub>Cl<sub>2</sub> system with LiGaCl<sub>4</sub> electrolyte and observed relatively insignificant anode corrosion.

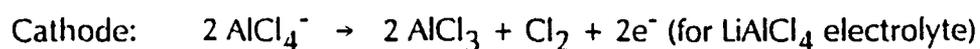
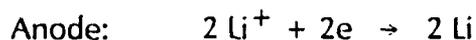
One of the advantages of Li/SO<sub>2</sub>Cl<sub>2</sub> system over Li/SOCl<sub>2</sub> is its safety characteristics which are probably related to the fact that no elemental sulfur is produced during discharge and that sulfur is believed to be involved actively in the process of cell venting and/or explosion.

The nature of the discharge reaction and the fact that sulfuryl chloride can be prepared by the reaction of sulfur dioxide and chlorine on carbon have encouraged researchers (6,7) to examine the rechargeability of Li/SO<sub>2</sub>Cl<sub>2</sub> systems. Razzini et al (6), while investigating the characteristics of primary Li/SO<sub>2</sub>Cl<sub>2</sub> cells, observed some potential rechargeability of the system. Later, Smith and co-workers (7) confirmed the observation and proposed the following discharge-charge reactions:

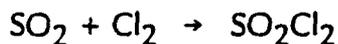
Discharge Reactions:



Charge Reactions:



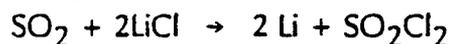
Chemical recombination of sulfur dioxide formed on discharge and chlorine formed on charge regenerate the original solvent:



While  $\text{AlCl}_3$  combines with  $\text{LiCl}$  formed during discharge to regenerate the electrolyte salt:



The sum of the charge and regeneration reactions gives



the reverse of the discharge reaction.

The Li cycling efficiencies in  $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$  were examined by Walker and Binder (8) at different rates and observed >80 percent efficiency at current density >5 mA/cm<sup>2</sup>. The authors also examined the effect of addition of  $\text{SO}_2$  and  $\text{Cl}_2$  to the electrolyte on Li cycling efficiency.

The overall objective of the present contract research is to develop and improve performance of  $\text{Li}/\text{SO}_2\text{Cl}_2$  rechargeable cells with particular emphasis on:

- i) Safety
- ii) discharge capacity, and
- iii) cycle life.

In order to achieve these objectives our approach is to investigate the chemistry of  $\text{Li}/\text{SO}_2\text{Cl}_2$  system with different carbon cathode materials, to optimize the cathode structure, to minimize the anode corrosion problem and to examine the effects of electrochemical parameters on cycle performance.

The conductivity of  $\text{LiAlCl}_4$  and  $\text{LiGaCl}_4$  in suluryl chloride have not, so far as we know, been previously reported. The conductivity values were determined as a function of temperature for each of several concentrations for both  $\text{LiAlCl}_4$  and  $\text{LiGaCl}_4$  electrolytes.

DTIC QUALITY INSPECTED 5

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By <i>Perltz</i>	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

## EXPERIMENTAL

Sulfuryl chloride obtained from Alfa Products (claimed purity 99%) was stored under Li chips at least 72 hours prior to use. Three different concentrations (0.5M, 1.0M and 1.5M) of the electrolytes  $\text{LiAlCl}_4$  and  $\text{LiGaCl}_4$  were prepared by dissolving the required amount of the individual salts, LiCl (Baker Analytical Reagent, 99.3%), anhydrous  $\text{AlCl}_3$  (Kings Mountain) and anhydrous  $\text{GaCl}_3$  (Eagle pitcher, 99.999%). LiCl was dried at  $120^\circ\text{C}$  under vacuum for at least 24 hours. The concentrations of the electrolyte solutions were checked by Direct Current Plasma (DCP) spectroscopy.

The conductivity cell is shown in Figure 1. The capacity of the barrel, with the electrodes in place, was about 25 ml. The electrodes of the cell were platinized in platinic chloride solution by applying 4.0 V for 30 seconds each time with changed polarity. The cell constant was determined using 0.1N and 0.01N potassium chloride solutions. Conductance measurements were carried out using a General Radio Type 1608-A impedance bridge in the frequency range of 0.1-40 KHz. The conductivity cell with the electrolyte solutions was placed in a temperature bath, equilibrated with the experimental temperature and then readings were taken at  $-30^\circ\text{C}$  warming  $10\text{-}15^\circ\text{C}$  at a time to the maximum temperature of  $55^\circ\text{C}$ .

## RESULTS AND DISCUSSION

Figures 2 and 3 show the frequency dependence of conductivity of  $\text{LiAlCl}_4$  and  $\text{LiGaCl}_4$  in  $\text{SO}_2\text{Cl}_2$  at  $25^\circ\text{C}$  for 0.5M, 1.0M and 1.5M solutions. The conductivity varies significantly at lower frequencies particularly with more concentrated solutions. For example, the conductivity of 1.5M  $\text{LiAlCl}_4$  and 1.5M  $\text{LiGaCl}_4$  changes with applied frequency until at 10 KHz (threshold frequency) after which no change in conductivity was observed. The effect is almost the same at higher temperature (see Figures 4 and 5 for  $55^\circ\text{C}$ ) but is less pronounced at lower temperature (see Figures 6 and 7 for  $-30^\circ\text{C}$ ) probably due to predominant viscosity effect. The threshold frequency also decreases with decreasing temperature.

The conductivity of  $\text{LiAlCl}_4$  and  $\text{LiGaCl}_4$  at  $25^\circ\text{C}$  as a function of concentration is shown in Figure 8.  $\text{LiGaCl}_4$  salt conductivities are slightly lower than those for  $\text{LiAlCl}_4$ , particularly at higher concentrations. This difference in conductivities is probably related to the difference in size of  $\text{GaCl}_4^-$  and  $\text{AlCl}_4^-$  anions. Conductivity of 1.5M  $\text{LiAlCl}_4$  at  $25^\circ\text{C}$  in  $\text{SO}_2\text{Cl}_2$  is half that in  $\text{SOCl}_2$ . This may be related to the fact that the  $\text{Li}^+$  coordination of  $\text{SO}_2\text{Cl}_2$  is stronger than that of  $\text{SOCl}_2$ .

Conductivity was also measured as a function of temperature for each of three concentrations for both  $\text{LiAlCl}_4$  and  $\text{LiGaCl}_4$ . Figures 9 and 10 show the variation of conductivity with temperature for  $\text{LiAlCl}_4$  and  $\text{LiGaCl}_4$  solutions, respectively.

### FUTURE WORK

Several hermetically sealed experimental cells will be fabricated using Ketjen Black and mixed carbon cathodes, 1.5M  $\text{LiAlCl}_4/\text{SO}_2\text{Cl}_2$  and 1.5M  $\text{LiGaCl}_4/\text{SO}_2\text{Cl}_2$  electrolytes. The cycling performance of these cells will be evaluated at different discharge and charge rates.

### REFERENCES

1. C. R. Schlaikjer, in *Lithium Batteries*, ed. by J. P. Gabano, Academic Press (1983).
2. K. A. Klinedinst and R. A. Garry, GTE Final Report, Contract No. DAAK20-83-C-0404, December 1985.
3. S. Gilman and W. Wade, Jr., *J. Electrochem. Soc.*, 127, 1427 (1980)
4. W. K. Behl, *J. Electrochem. Soc.*, 127, 1444 (1980).
5. K. A. Klinedinst, *J. Electrochem. Soc.*, 131, 342 (1984).
6. G. Razzini, S. Rovellini, F. Alessandrini, B. Di Pietro, and B. Scrosati, *J. Power Sources*, 5, 263 (1980).
7. P. H. Smith, A. A. Papanicolaou, M. H. Wilson and S. D. James, ECS Fall Meeting, San Diego, CA, 19-24 October 1986, Abstract No. 15, P. 23.
8. C. W. Walker, Jr. and M. Binder, *J. Electrochem. Soc.*, 135, 1060 (1988).

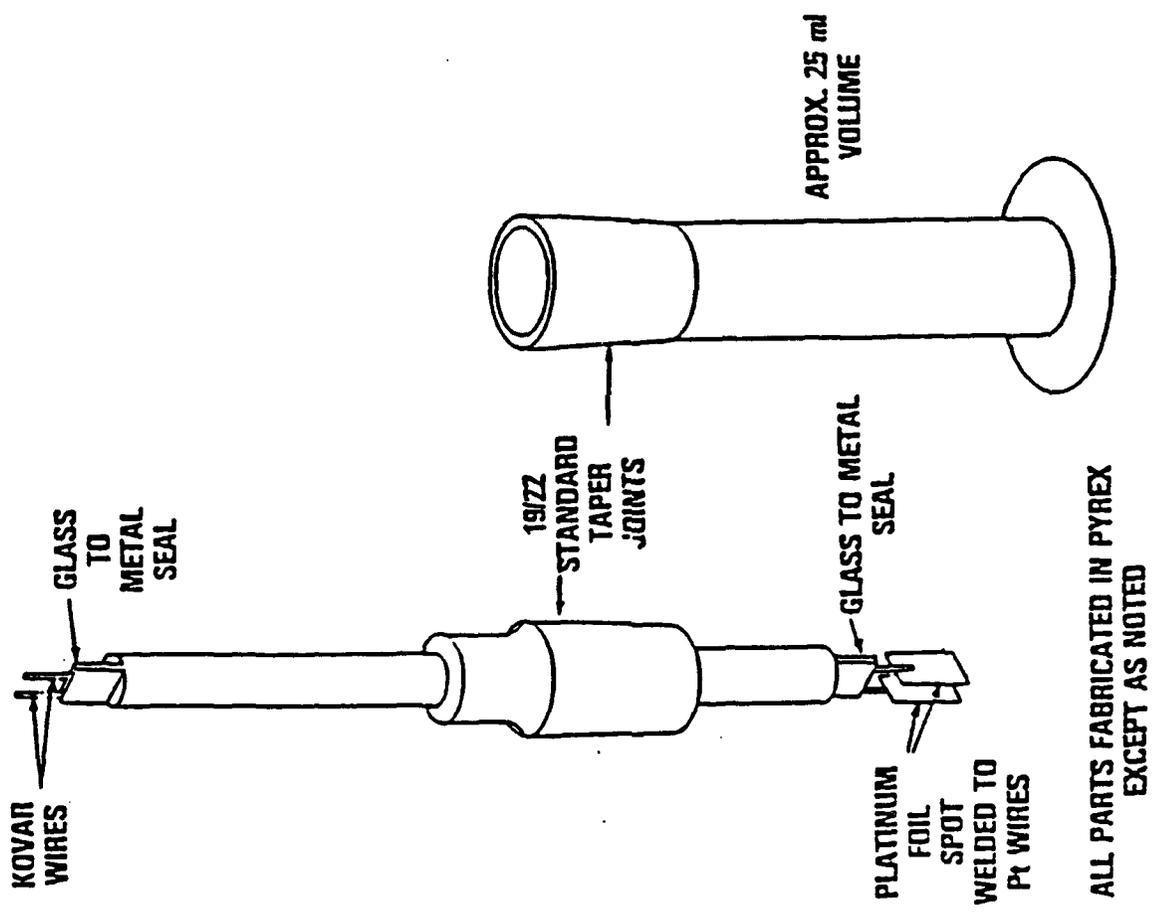


Figure 1. Conductivity Cell

# FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiAlCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> AT 25 DEG C

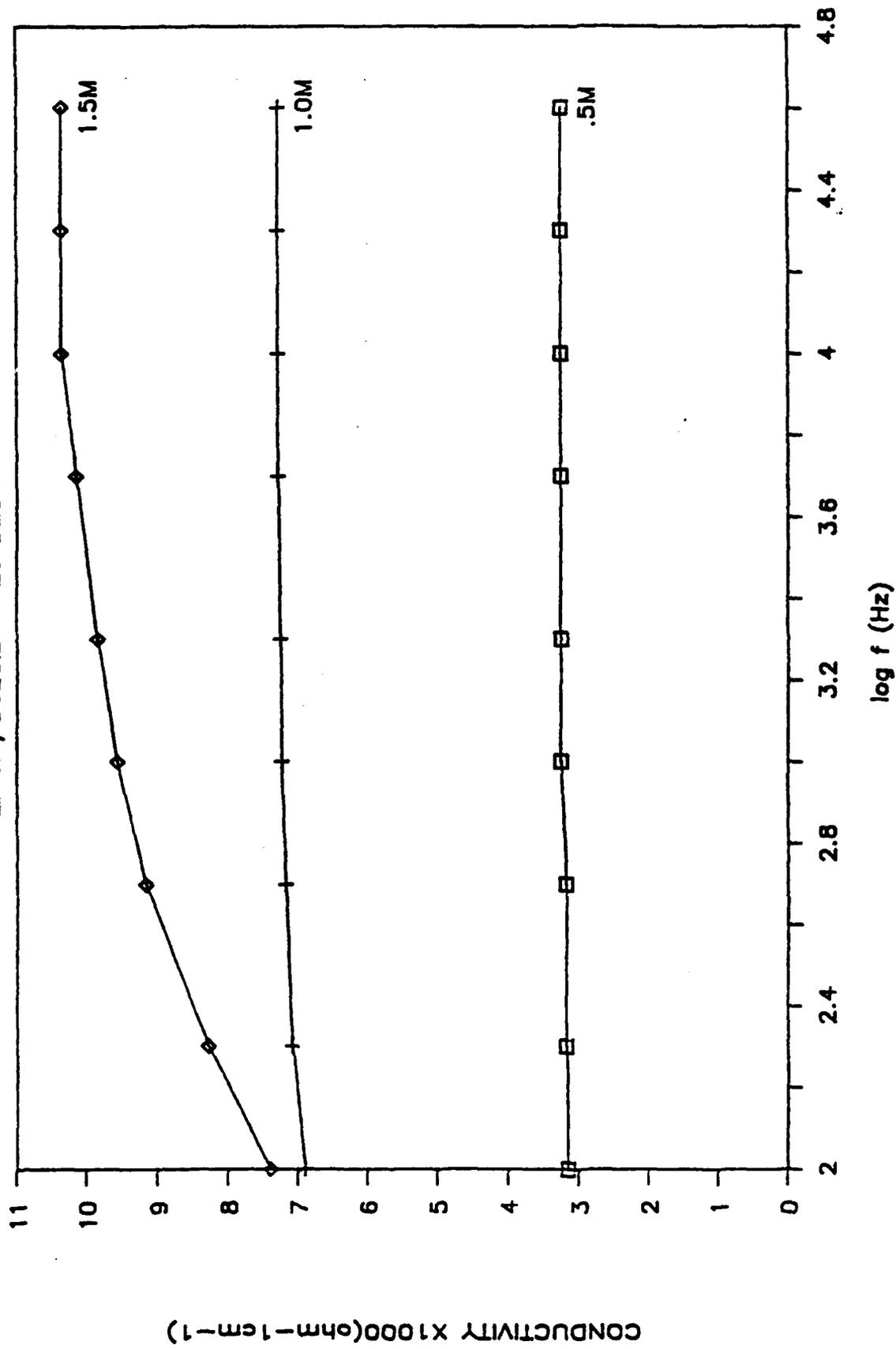


Figure 2. Frequency-Dependence of Conductivity of LiAlCl<sub>4</sub>/Cl<sub>2</sub> at 25°C

# FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiGaCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> AT 25 DEG C

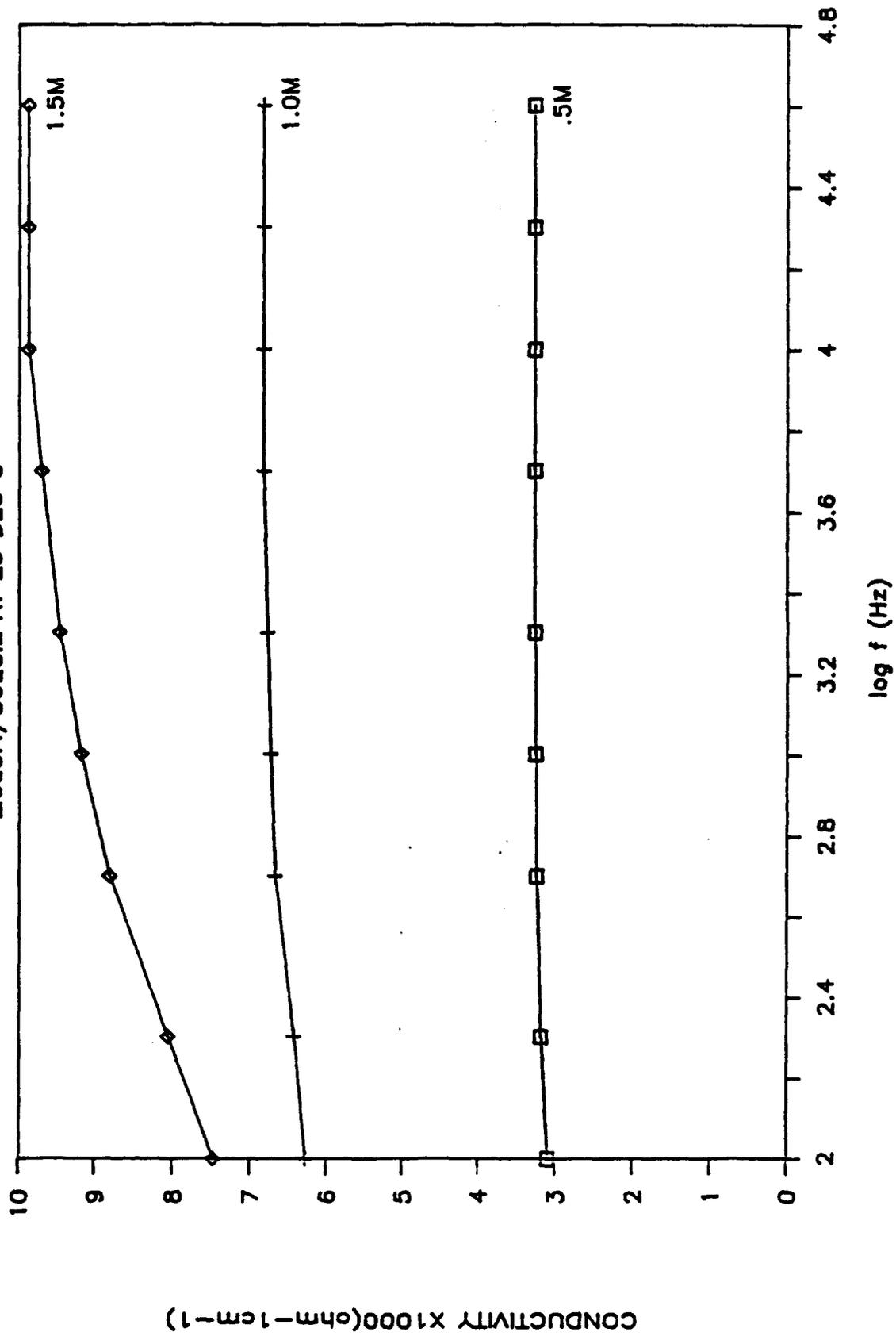


Figure 3. Frequency-Dependence of Conductivity of LiGaCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> at 25°C

# FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiAlCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> AT 55 DEG C

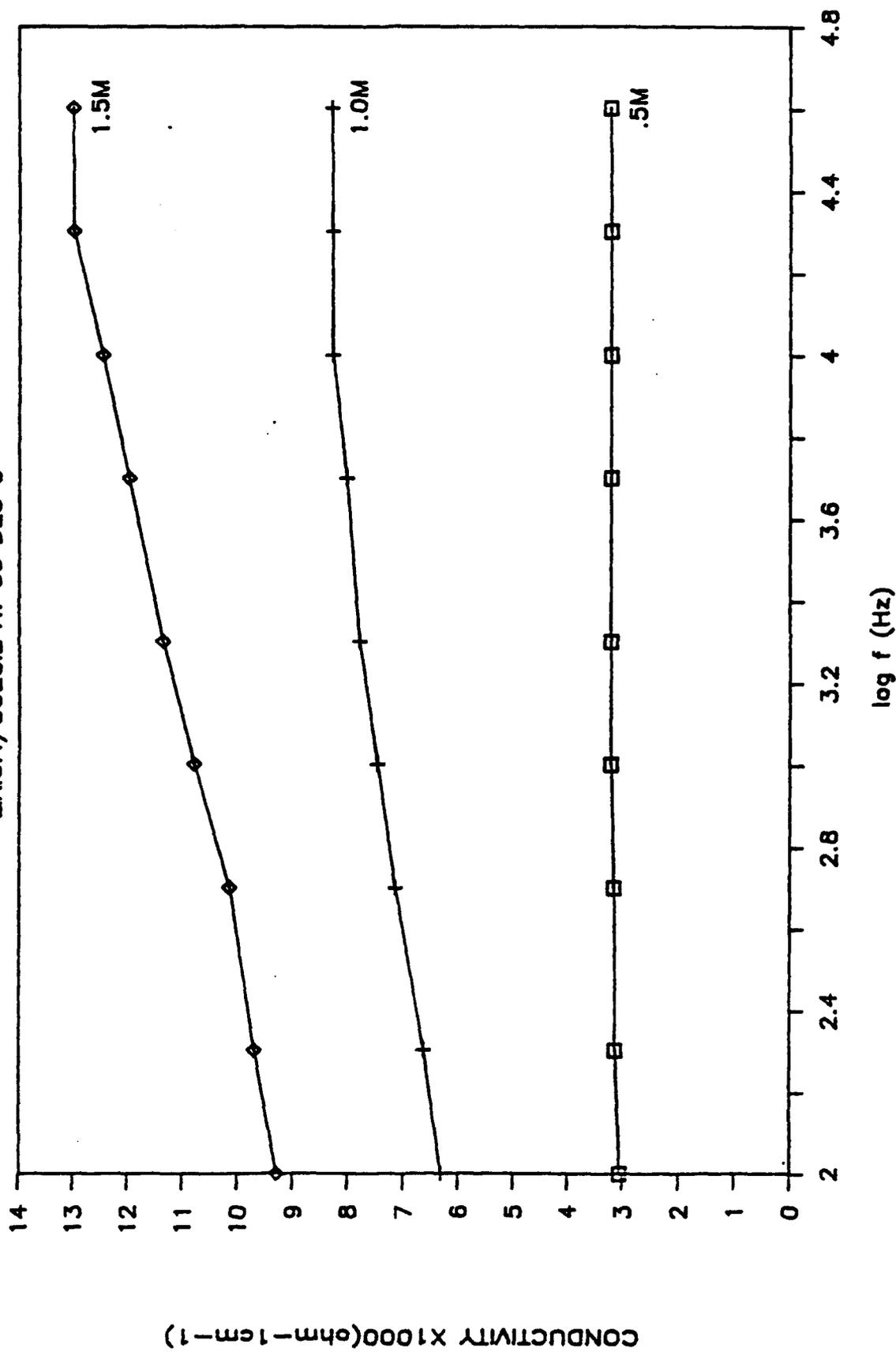


Figure 4. Frequency-Dependence of Conductivity of LiAlCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> at 55°C

# FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiGaCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> AT 55 DEG C

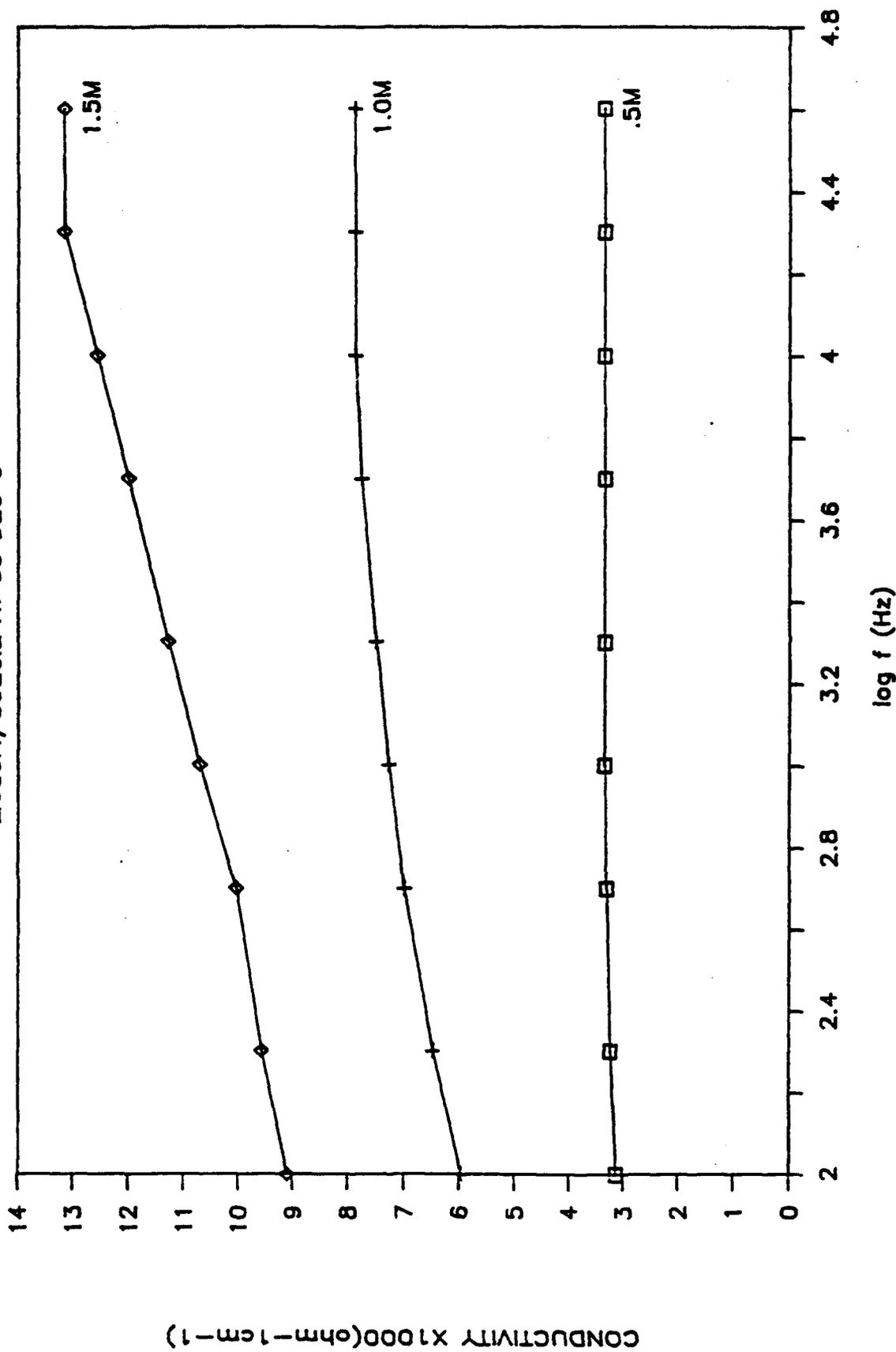


Figure 5. Frequency-Dependence of Conductivity of LiGaCl<sub>4</sub> in SO<sub>2</sub>Cl<sub>2</sub> at 55°C

# FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiAlCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> AT -30 DEG C

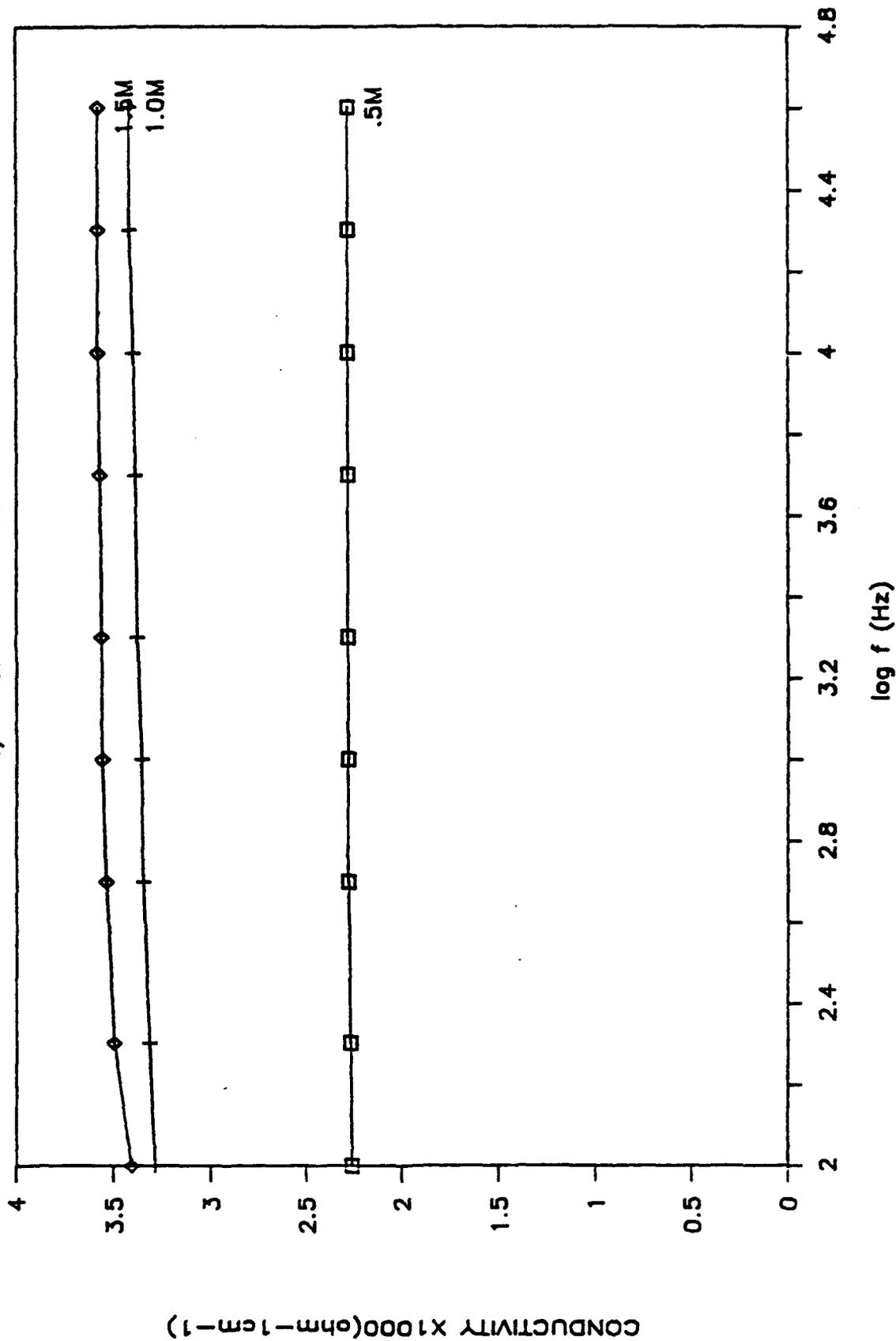


Figure 6. Frequency-Dependence of Conductivity of LiAlCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> at -30°C

# FREQUENCY--DEPENDENCE OF CONDUCTIVITY

LiGaCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> AT -30 DEG C

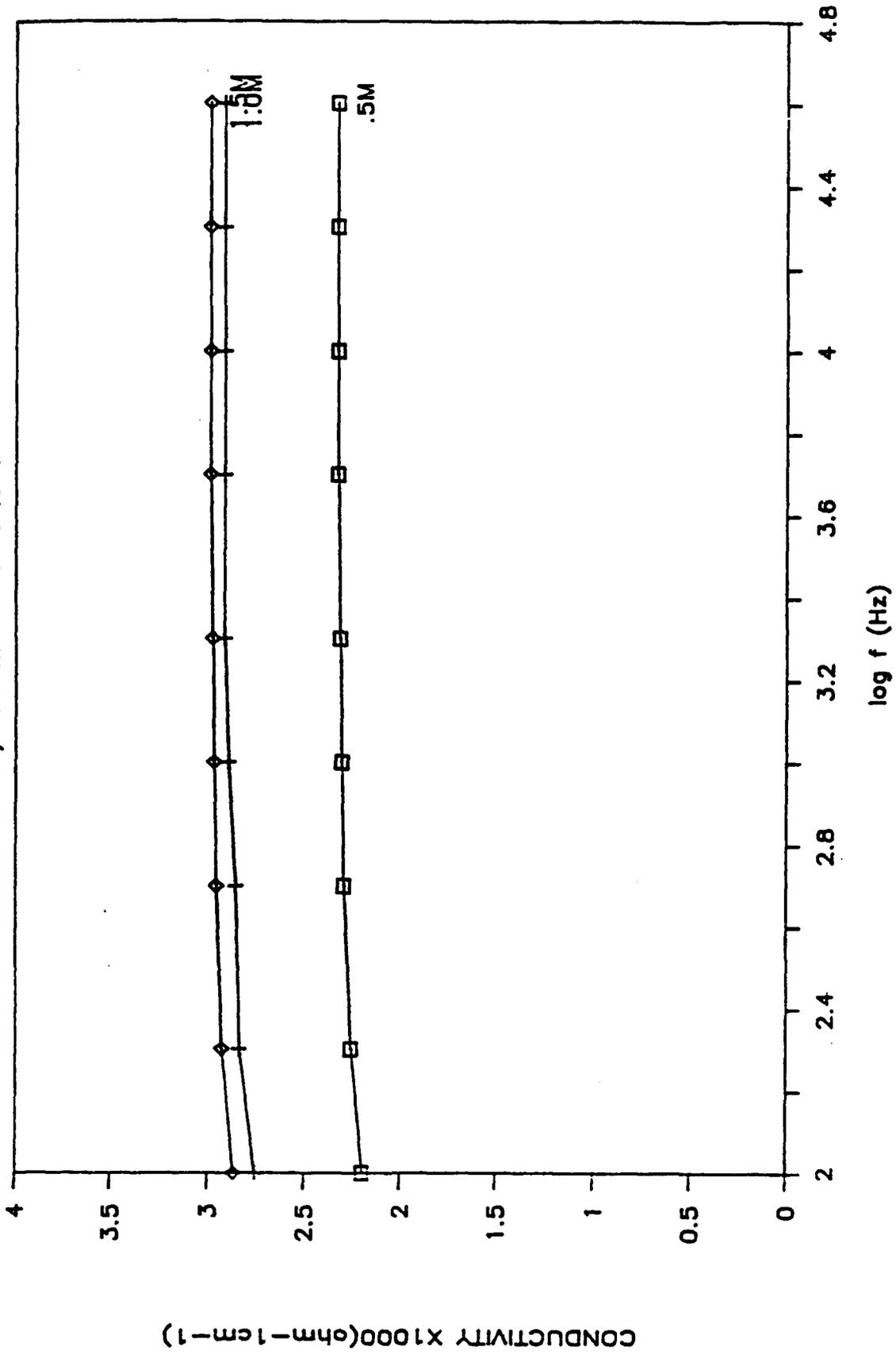


Figure 7. Frequency-Dependence of Conductivity of LiGaCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> at -30°C

# CONC.-DEPENDENCE OF CONDUCTIVITY

LiAlCl<sub>4</sub>, LiGaCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub> AT 25 DEG C

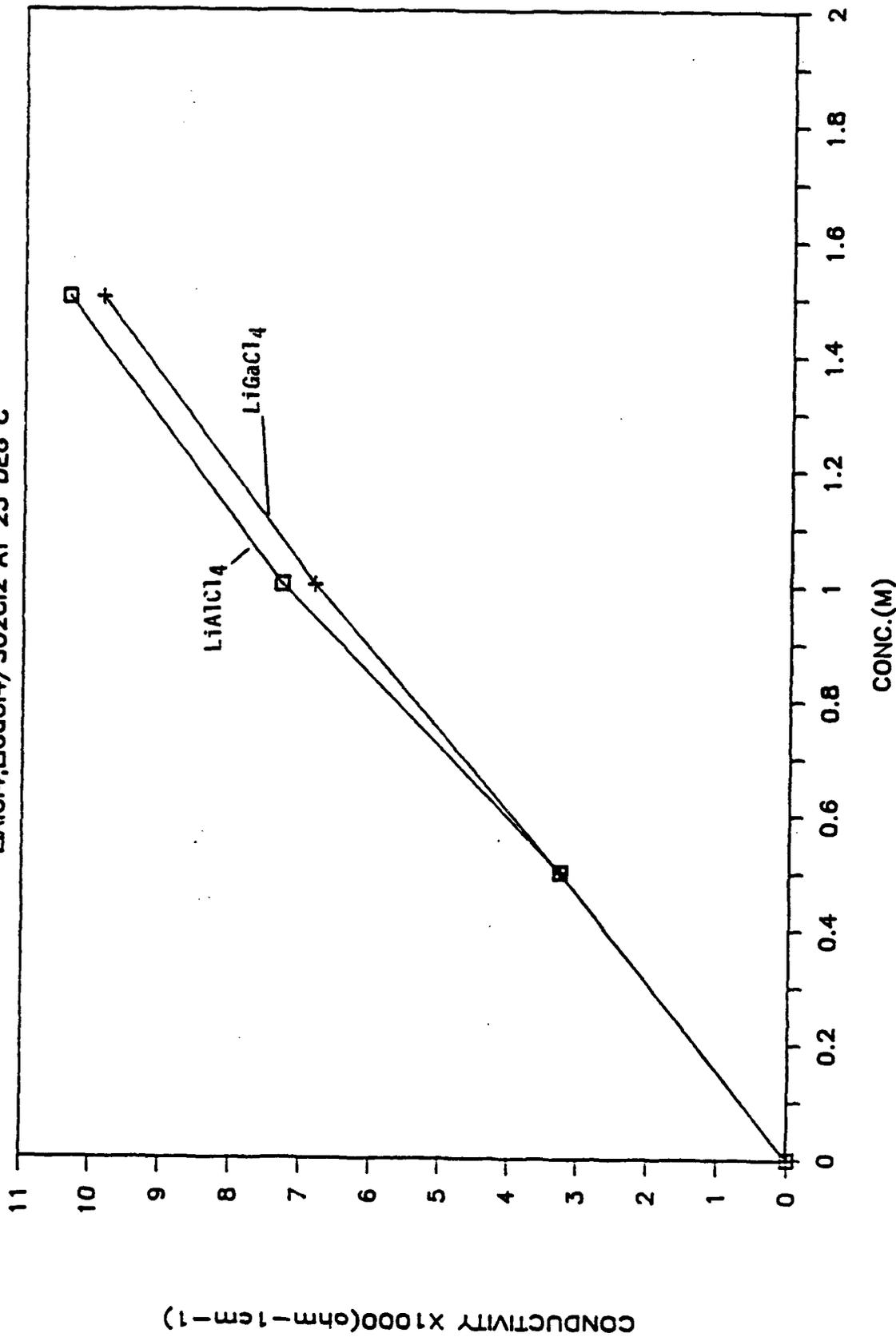


Figure 8. Conductivity of LiGaCl<sub>4</sub> and LiAlCl<sub>4</sub> at 25°C as a Function of Concentration

# TEMPERATURE--DEPENDENCE OF CONDUCTIVITY

LiAlCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub>

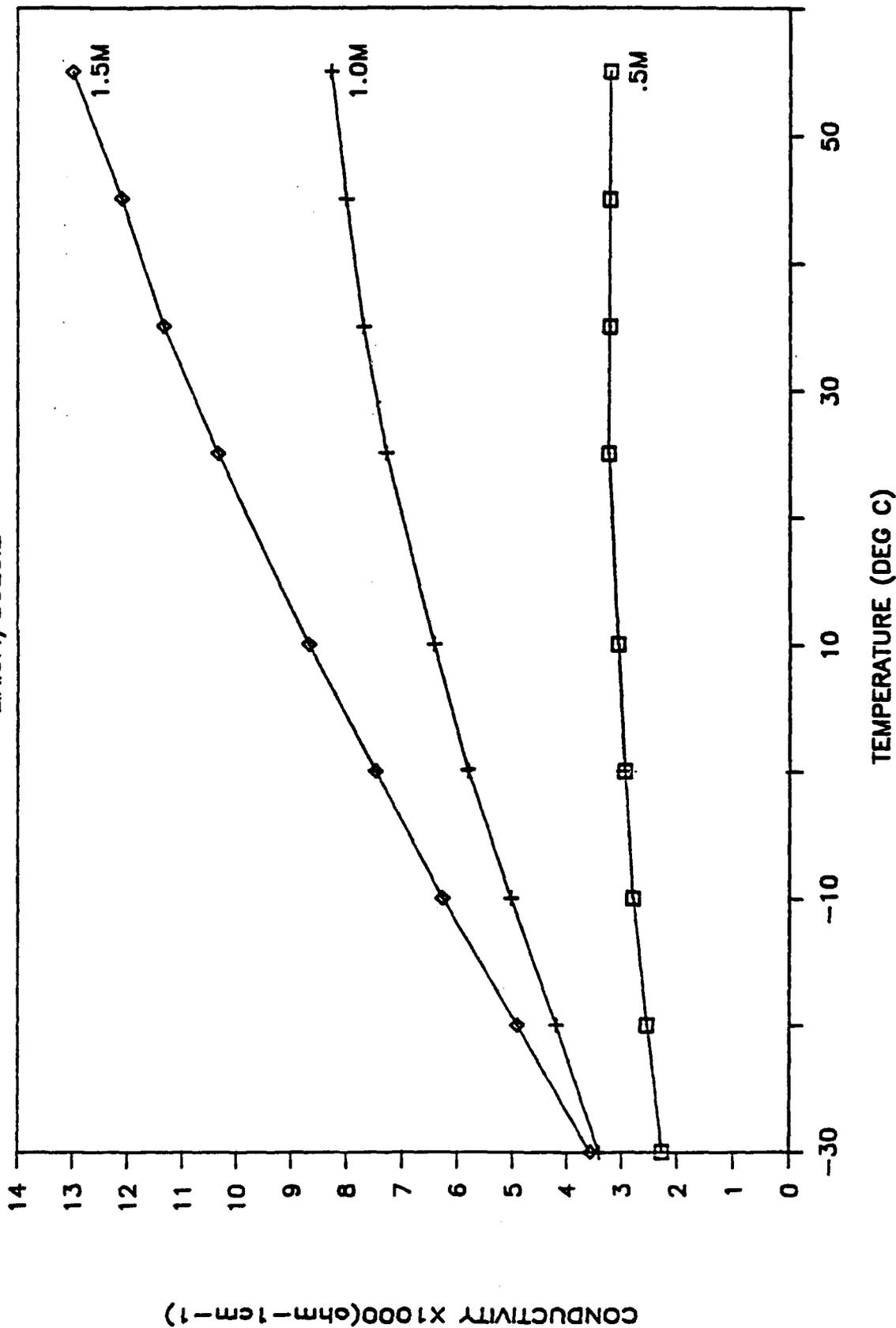


Figure 9. Variation of Conductivity with Temperature for  $\text{LiAlCl}_4$  in  $\text{SO}_2\text{Cl}_2$  at Threshold Frequency

# TEMPERATURE--DEPENDENCE OF CONDUCTIVITY

LiGaCl<sub>4</sub>/SO<sub>2</sub>Cl<sub>2</sub>

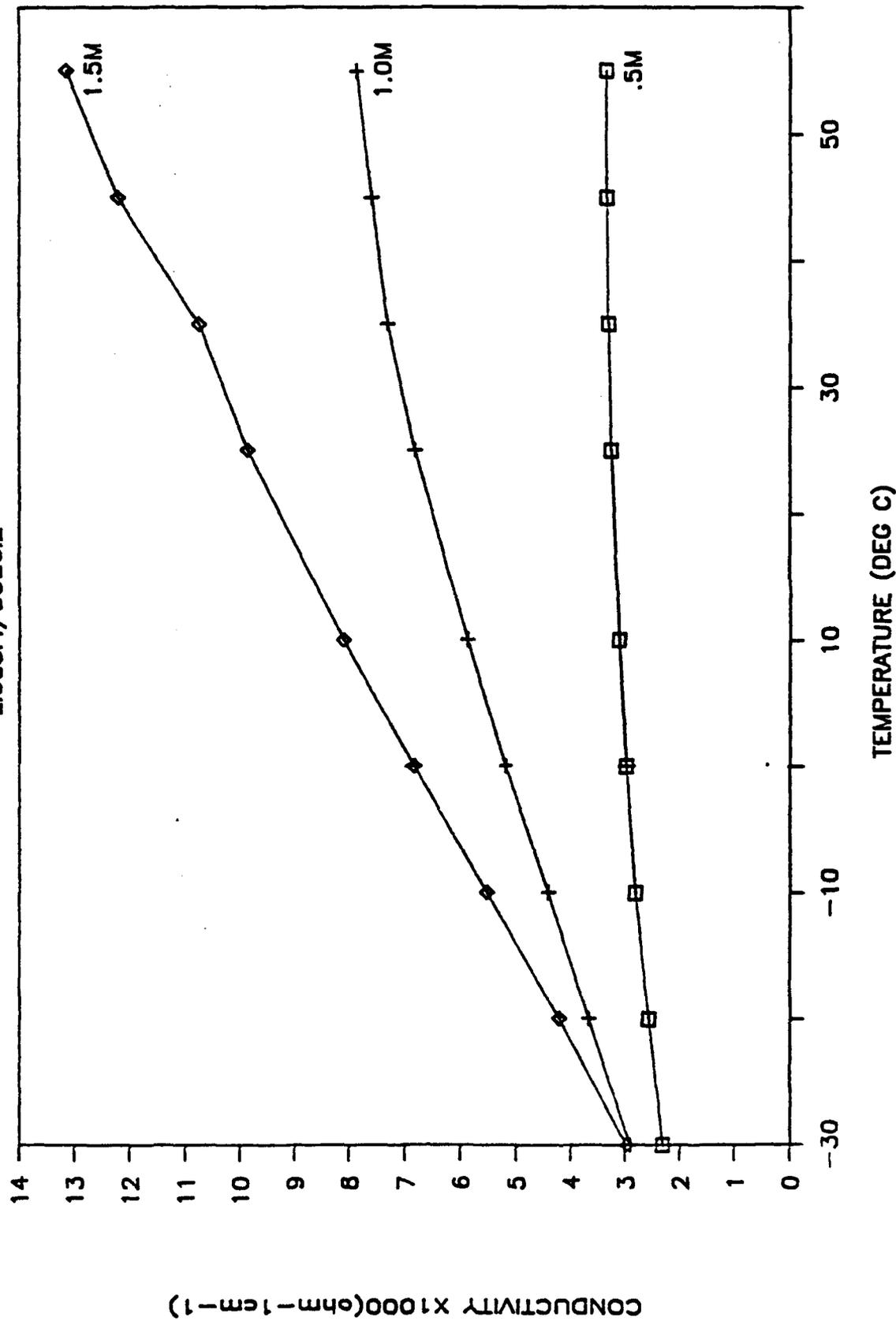


Figure 10. Conductivity vs. Temperature Plots for LiGaCl<sub>4</sub> in SO<sub>2</sub>Cl<sub>2</sub> at Threshold Frequency