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Rechargeable Lithium-Inorganic Electrolyte Cell

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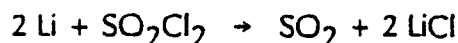
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INTRODUCTION

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/SO₂Cl₂ cells in 1.5M LiAlCl₄ electrolyte using different carbon cathodes and established the following reactions:

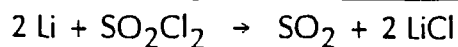
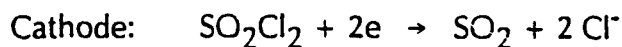
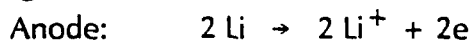


Based on cyclic voltammetry results and the work of Gilman and Wade (3), Behl (4) concluded that the mechanism of cathodic reduction involved first the reduction of free chlorine resulting from the homogeneous and/or heterogeneous dissociation of sulfuryl chloride (5) followed by the reduction of undissociated sulfuryl chloride. Klinedinst and Gary (2) examined primary Li/SO₂Cl₂ system with LiGaCl₄ electrolyte and observed relatively insignificant anode corrosion.

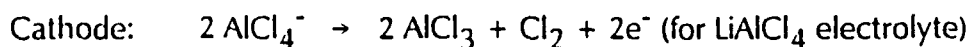
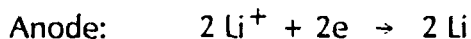
One of the advantages of Li/SO₂Cl₂ system over Li/SOCl₂ is its safety characteristics which are probably related to the fact that no elemental sulfur is produced during discharge and that sulfur is believed to be involved actively in the process of cell venting and/or explosion.

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/SO₂Cl₂ systems. Razzini et al (6), while investigating the characteristics of primary Li/SO₂Cl₂ cells, observed some potential rechargeability of the system. Later, Smith and co-workers (7) confirmed the observation and proposed the following discharge-charge reactions:

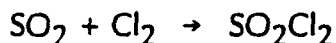
Discharge Reactions:



Charge Reactions:



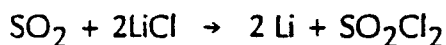
Chemical recombination of sulfur dioxide formed on discharge and chlorine formed on charge regenerate the original solvent:



While AlCl_3 combines with 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/cm². The authors also examined the effect of addition of SO_2 and 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 LiAlCl_4 and LiGaCl_4 in sulfuryl 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 LiAlCl_4 and LiGaCl_4 electrolytes.

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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 LiAlCl_4 and LiGaCl_4 were prepared by dissolving the required amount of the individual salts, LiCl (Baker Analytical Reagent, 99.3%), anhydrous AlCl_3 (Kings Mountain) and anhydrous GaCl_3 (Eagle pitcher, 99.999%). LiCl was dried at 120°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°C warming $10\text{-}15^\circ\text{C}$ at a time to the maximum temperature of 55°C .

RESULTS AND DISCUSSION

Figures 2 and 3 show the frequency dependance of conductivity of LiAlCl_4 and LiGaCl_4 in SO_2Cl_2 at 25°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 LiAlCl_4 and 1.5M 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°C) but is less pronounced at lower temperature (see Figures 6 and 7 for -30°C) probably due to predominant viscosity effect. The threshold frequency also decreases with decreasing temperature.

The conductivity of LiAlCl_4 and LiGaCl_4 at 25°C as a function of concentration is shown in Figure 8. LiGaCl_4 salt conductivities are slightly lower than those for LiAlCl_4 , particularly at higher concentrations. This difference in conductivities is probably related to the difference in size of GaCl_4^- and AlCl_4^- anions. Conductivity of 1.5M LiAlCl_4 at 25°C in SO_2Cl_2 is half that in SOCl_2 . This may be related to the fact that the Li^+ coordination of SO_2Cl_2 is stronger than that of SOCl_2 .

Conductivity was also measured as a function of temperature for each of three concentrations for both LiAlCl_4 and LiGaCl_4 . Figures 9 and 10 show the variation of conductivity with temperature for LiAlCl_4 and 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.

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8. C. W. Walker, Jr. and M. Binder, *J. Electrochem. Soc.*, 135, 1060 (1988).

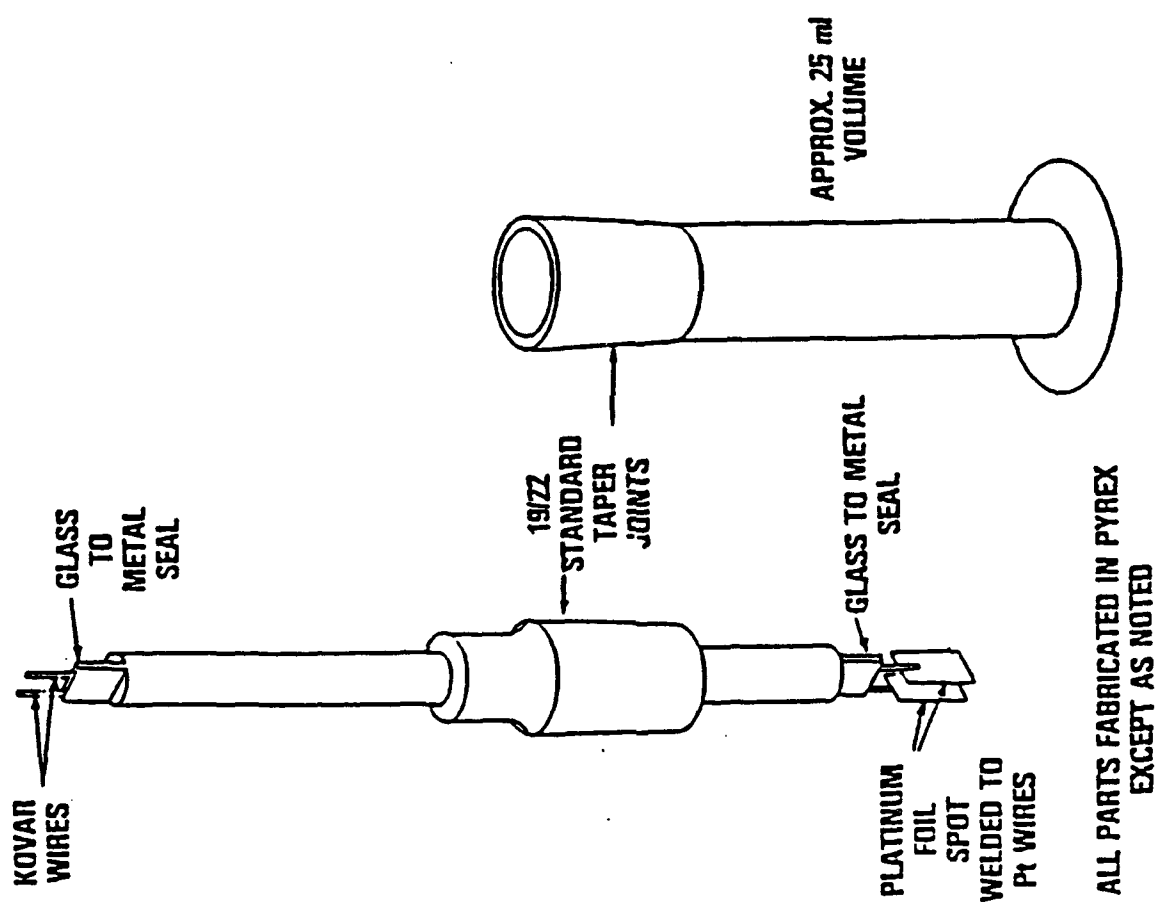


Figure 1. Conductivity Cell

FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiAlCl₄/SO₂Cl₂ AT 25 DEG C

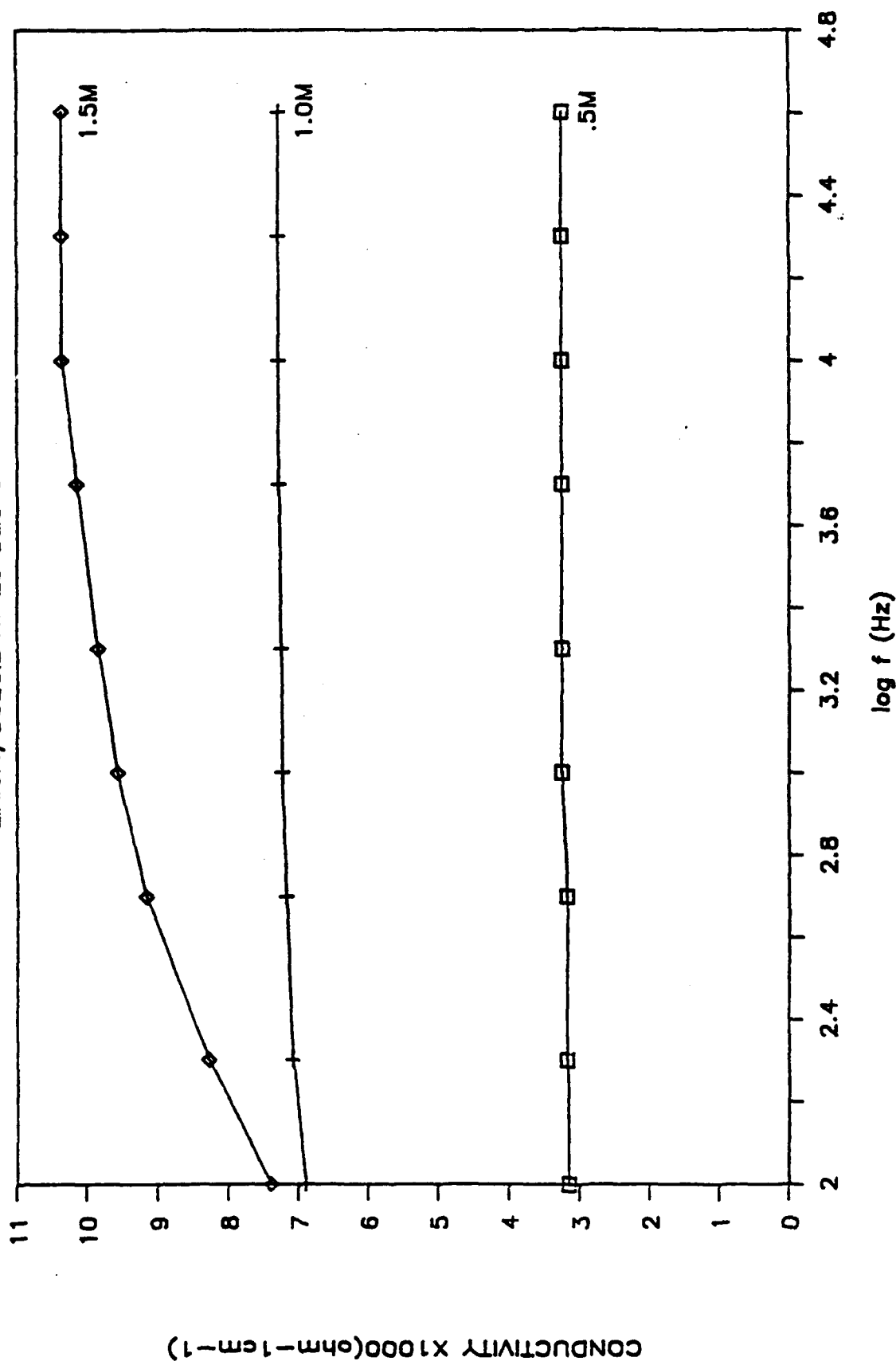


Figure 2. Frequency-Dependence of Conductivity of LiAlCl₄/Cl₂ at 25°C

FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiGaCl₄/SO₂Cl₂ AT 25 DEG C

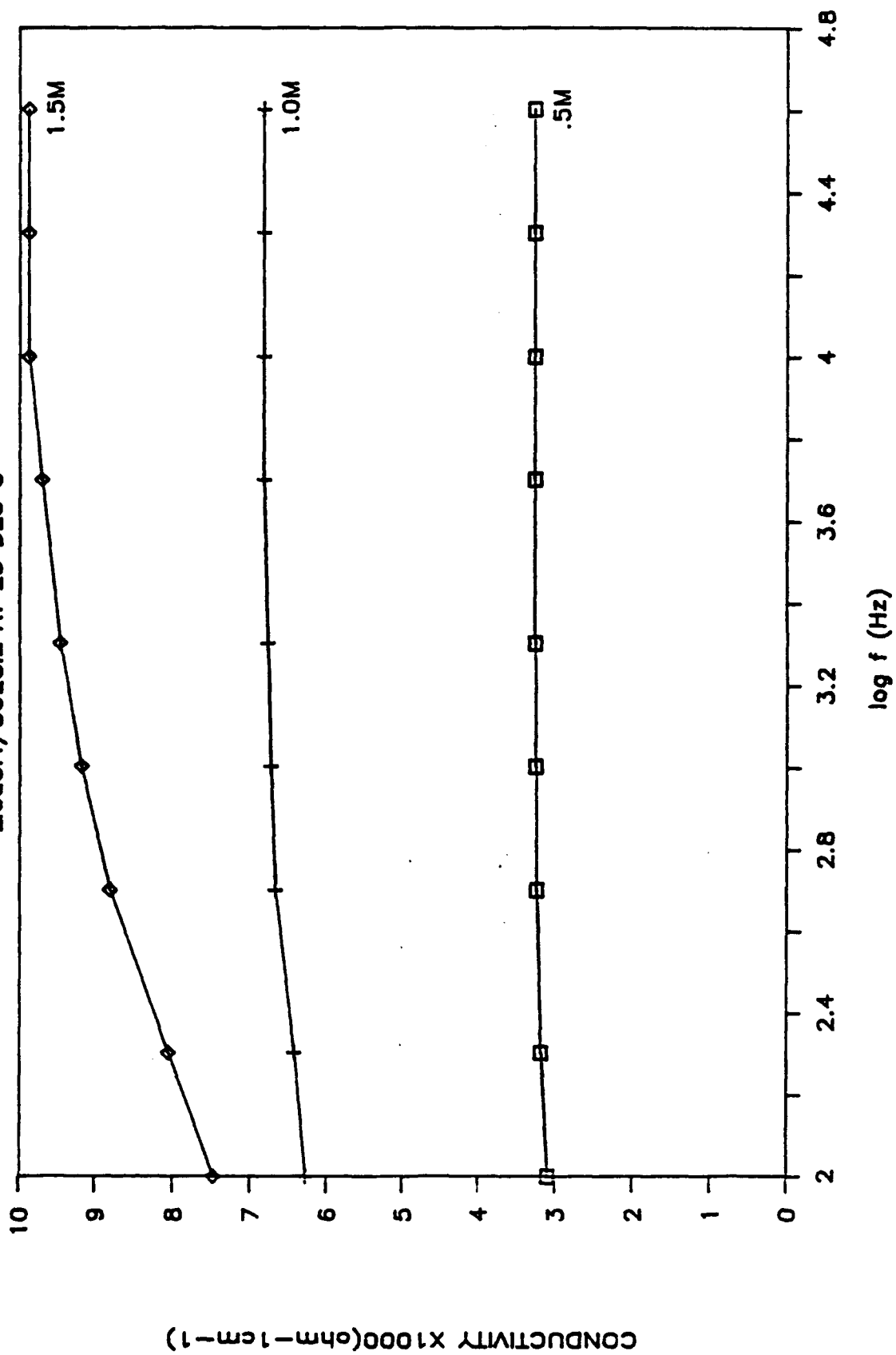


Figure 3. Frequency-Dependence of Conductivity of LiGaCl₄/SO₂Cl₂ at 25°C

FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiAlCl₄/SO₂Cl₂ AT 55 DEG C

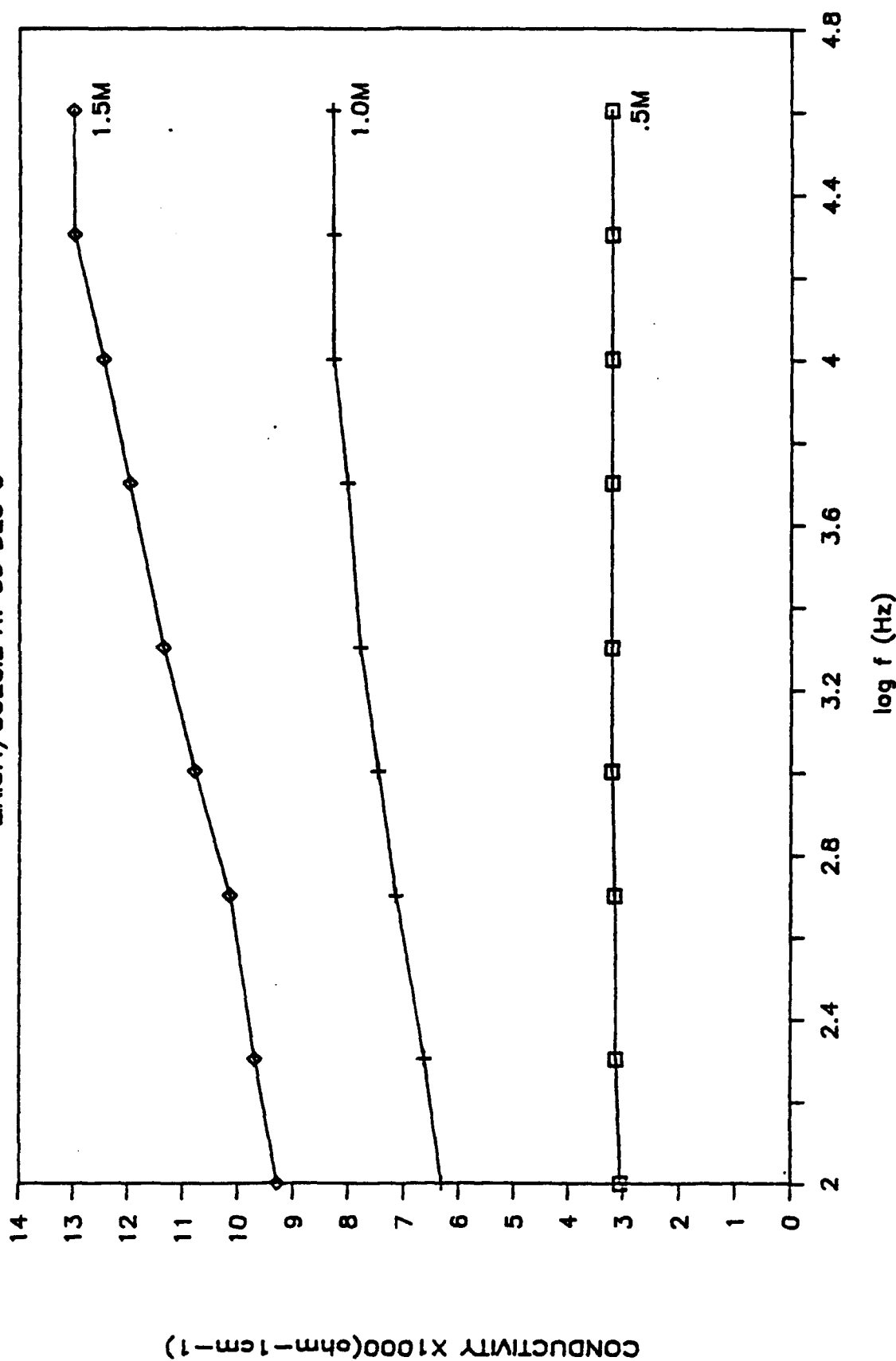


Figure 4. Frequency-Dependence of Conductivity of LiAlCl₄/SO₂Cl₂ at 55°C

FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiGaCl₄/SO₂Cl₂ AT 55 DEG C

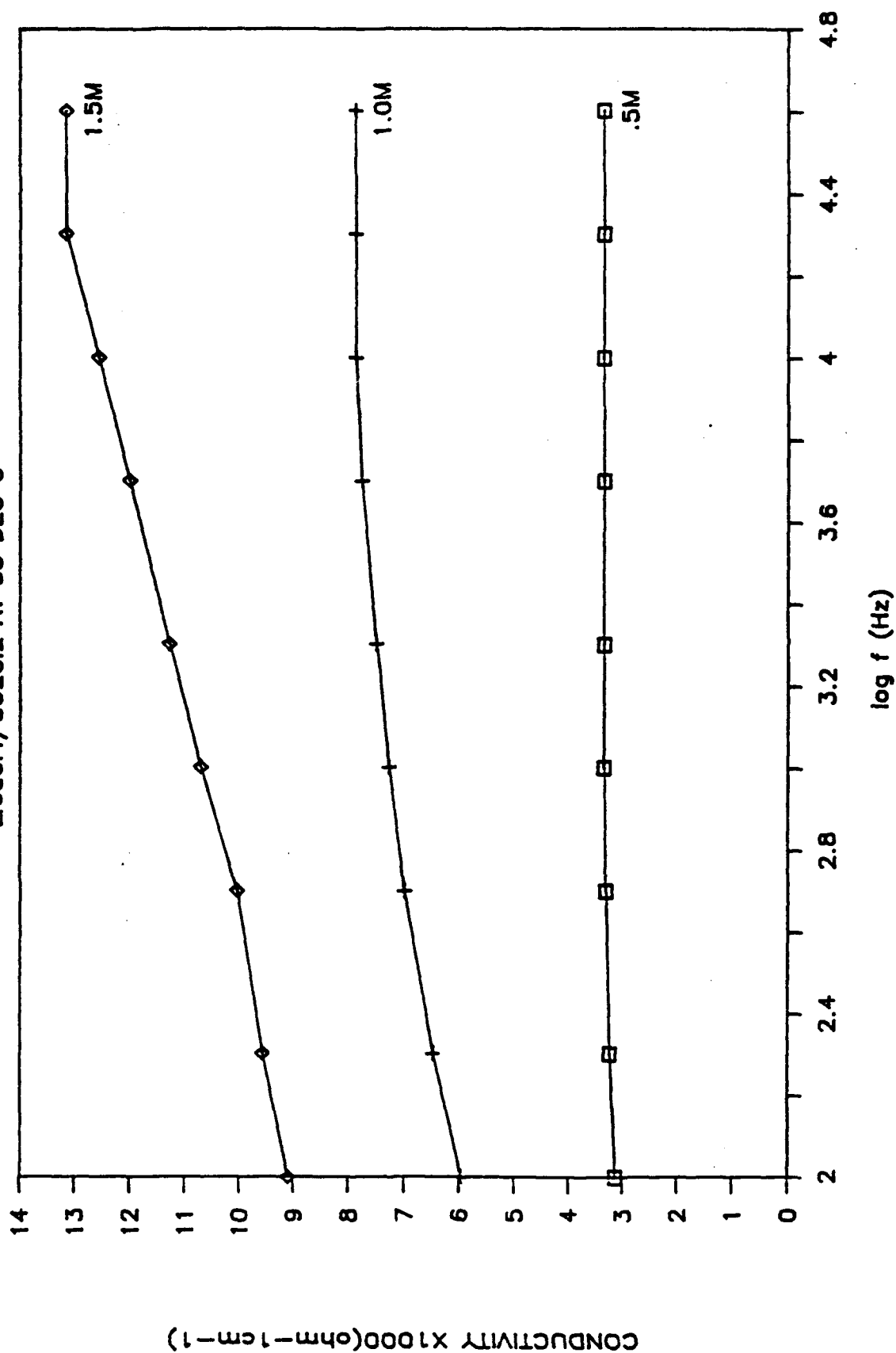


Figure 5. Frequency-Dependence of Conductivity of LiGaCl₄ in SO₂Cl₂ at 55°C

FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiAlCl₄/SO₂Cl₂ AT -30 DEG C

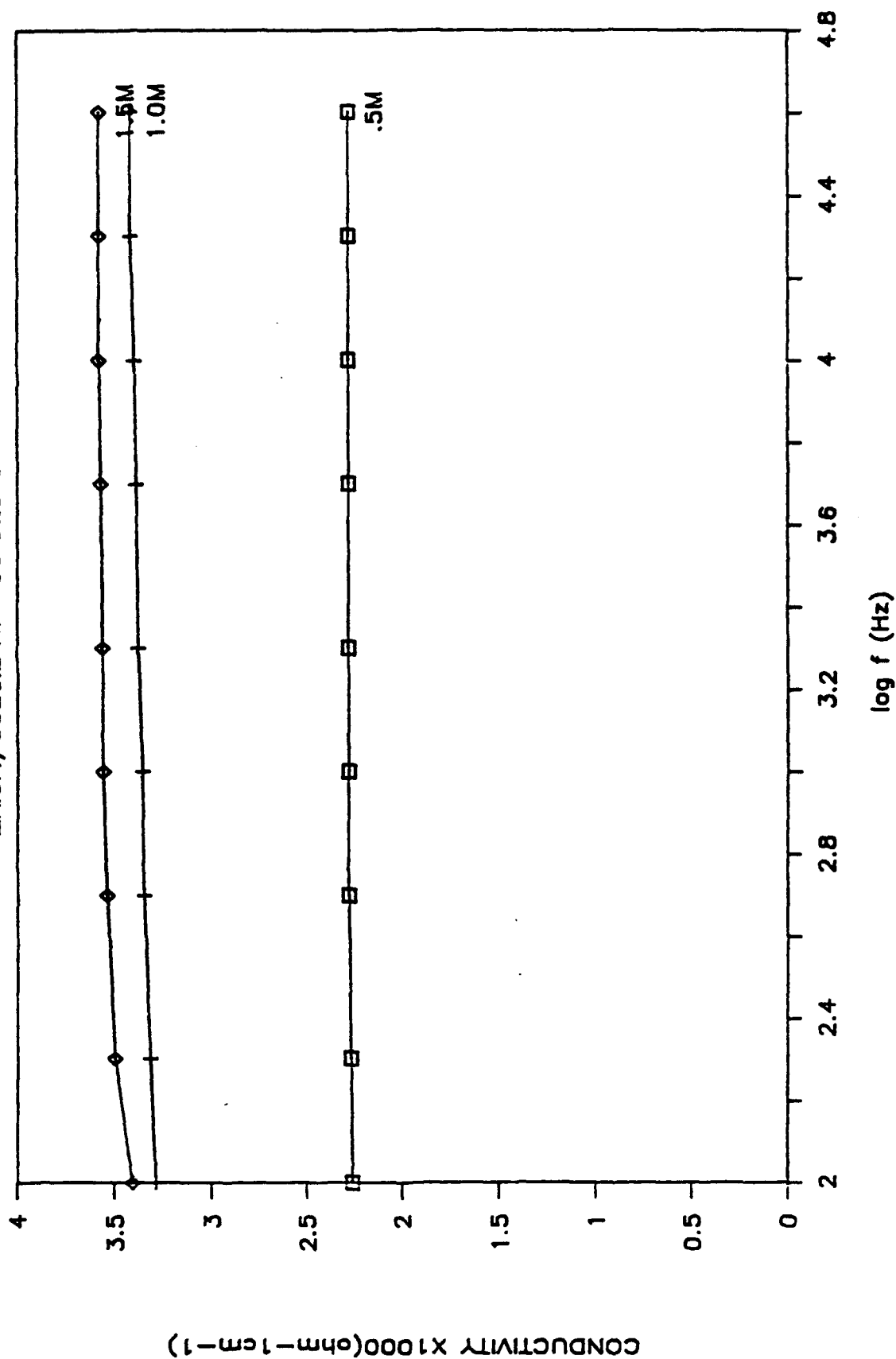


Figure 6. Frequency-Dependence of Conductivity of LiAlCl₄/SO₂Cl₂ at -30°C

FREQUENCY-DEPENDENCE OF CONDUCTIVITY

LiGaCl₄/SO₂Cl₂ AT -30 DEG C

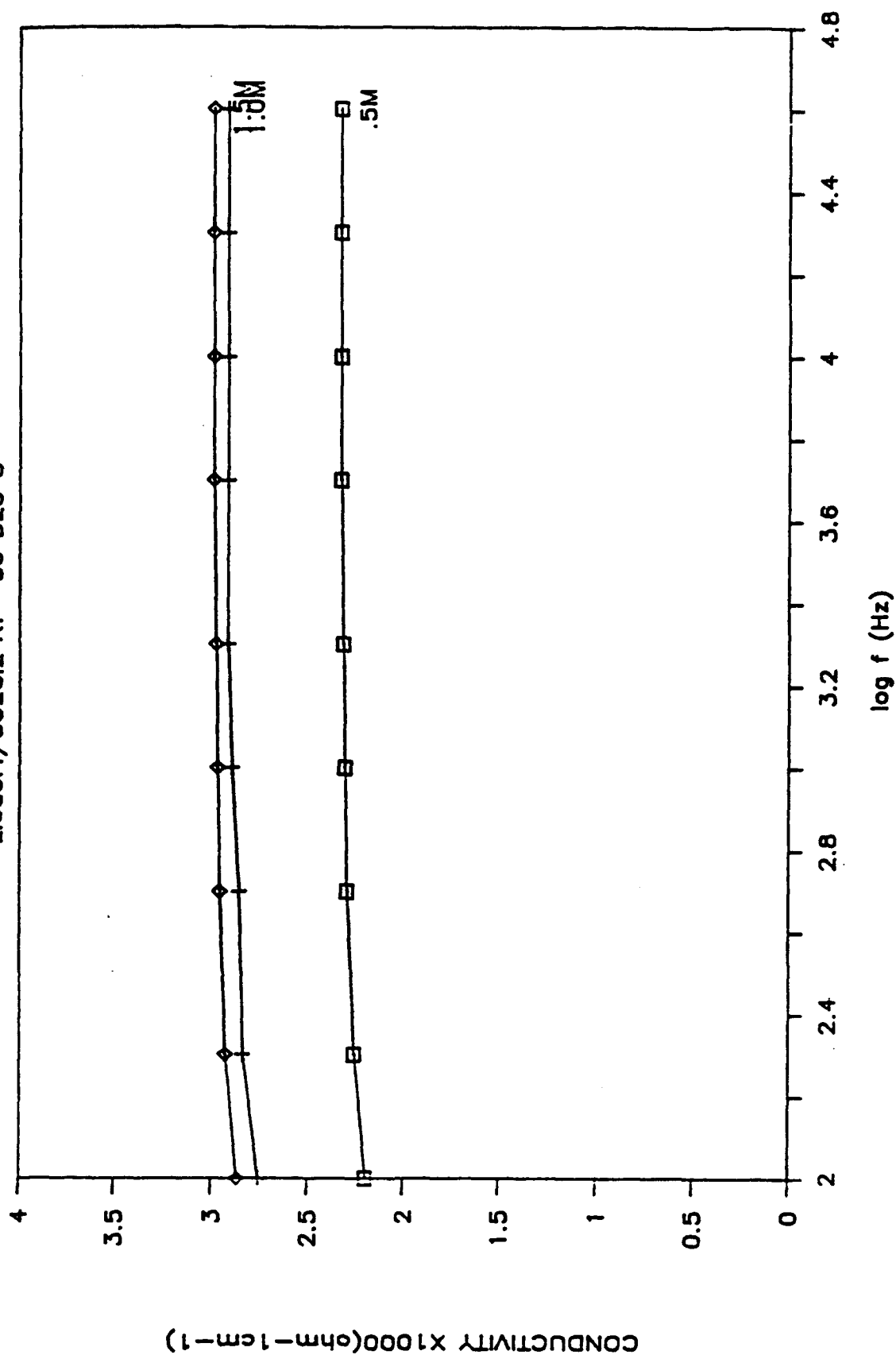


Figure 7. Frequency-Dependence of Conductivity of LiGaCl₄/SO₂Cl₂ at -30°C

CONC.-DEPENDENCE OF CONDUCTIVITY

LiAlCl₄, LiGaCl₄/SO₂Cl₂ AT 25 DEG C

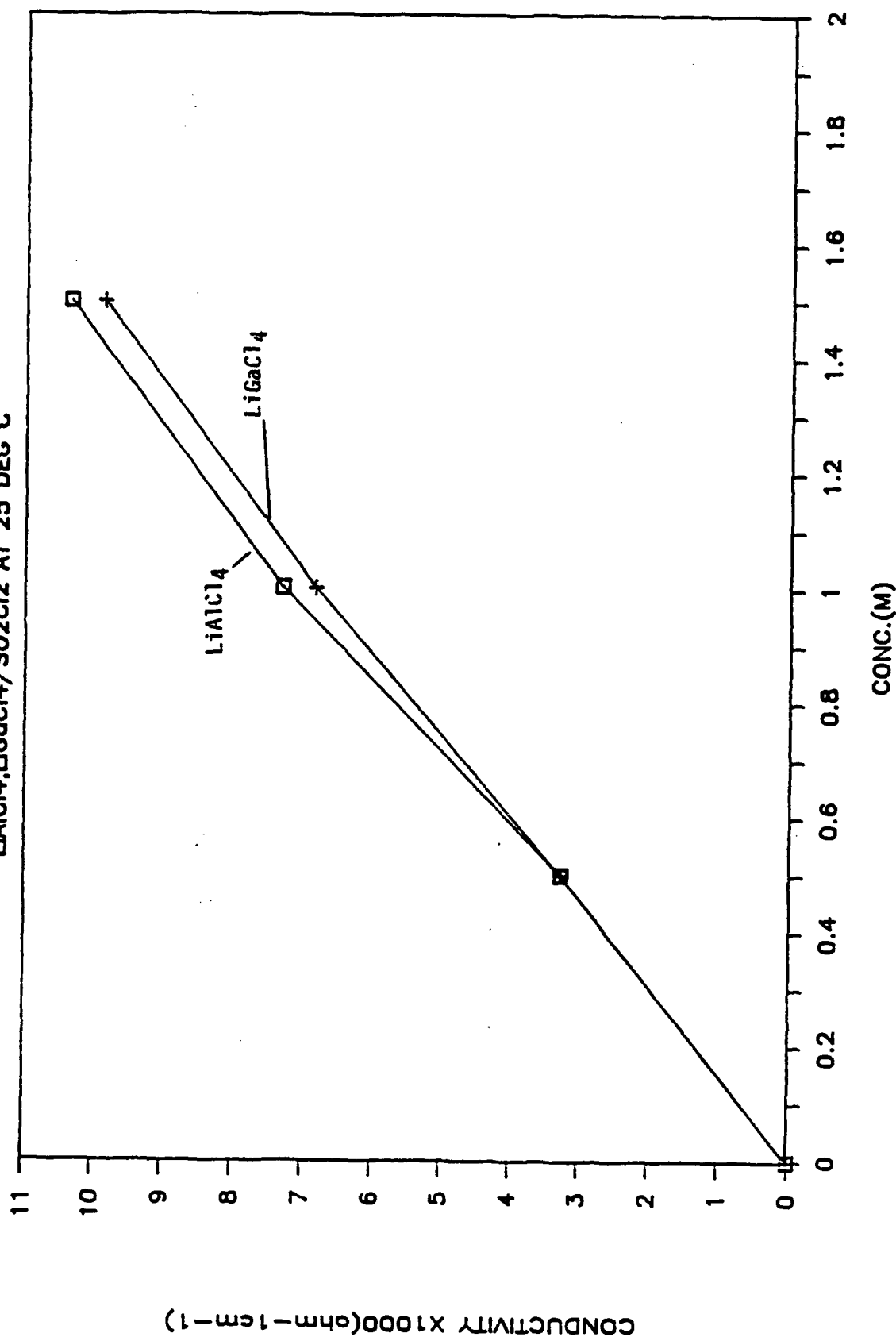


Figure 8. Conductivity of LiGaCl₄ and LiAlCl₄ at 25°C as a Function of Concentration

TEMPERATURE--DEPENDENCE OF CONDUCTIVITY

LiAlCl₄/SO₂Cl₂

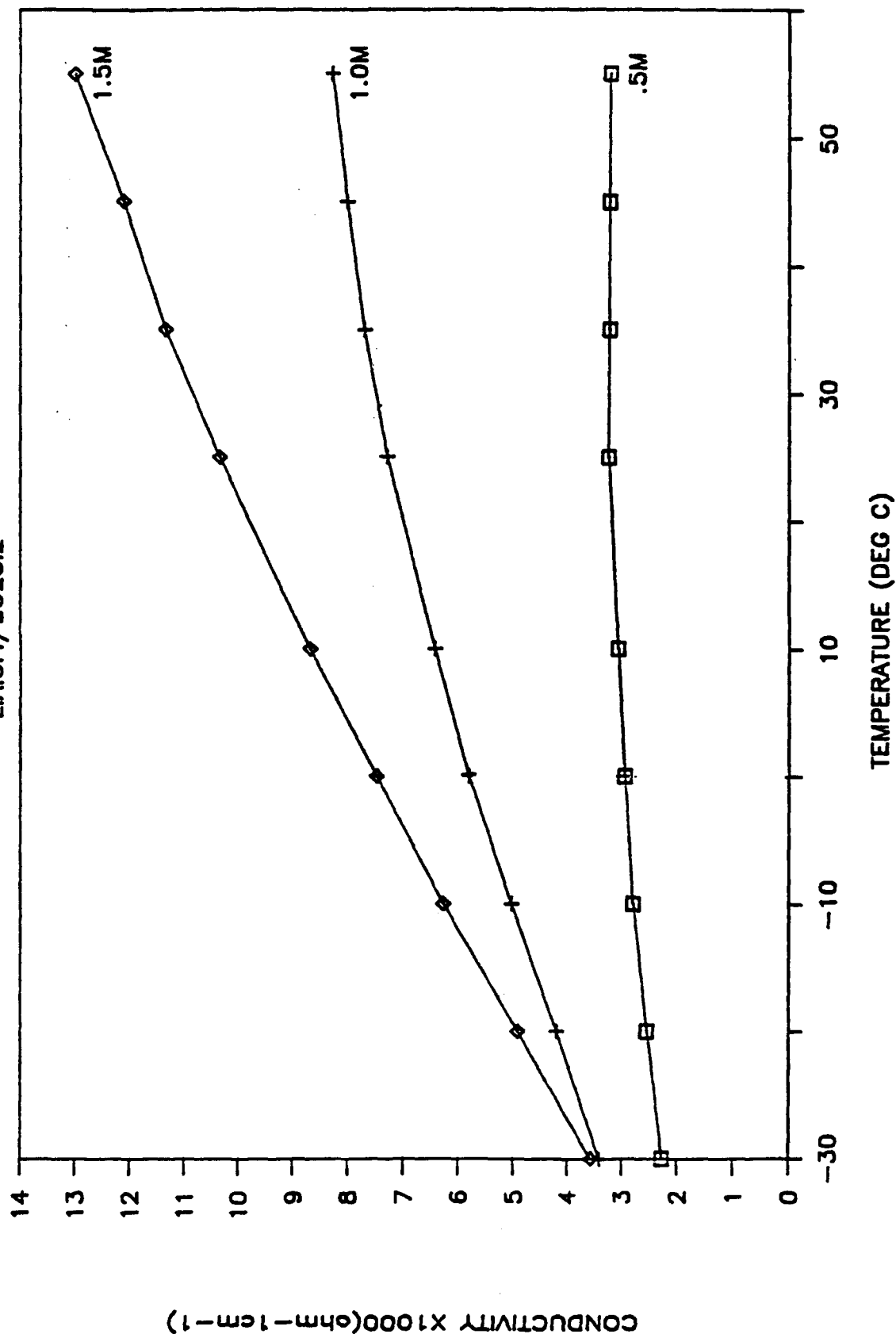


Figure 9. Variation of Conductivity with Temperature for LiAlCl₄ in SO₂Cl₂ at Threshold Frequency

TEMPERATURE--DEPENDENCE OF CONDUCTIVITY

LiGaCl₄/SO₂Cl₂

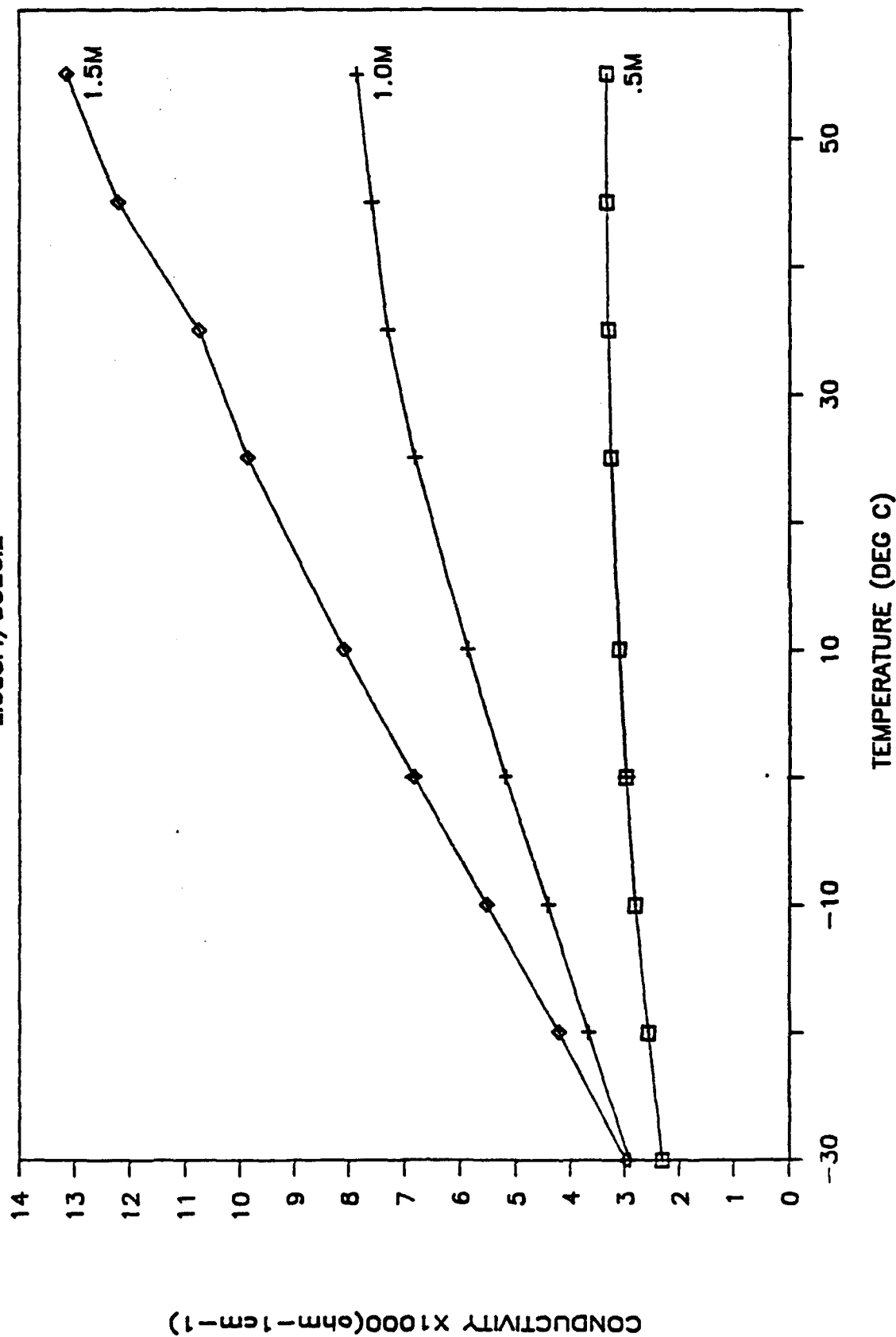


Figure 10. Conductivity vs. Temperature Plots for LiGaCl₄ in SO₂Cl₂ at Threshold Frequency