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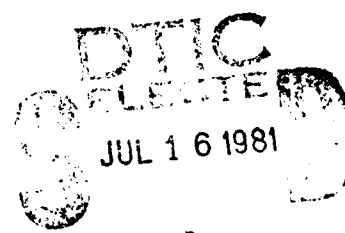
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EVALUATION OF LOW MELTING HALIDE SYSTEMS FOR BATTERY APPLICATIONS

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MARCH 1981

TECHNICAL REPORT AFWAL-TR-81-2003  
Interim Report for Period September 1979 - September 1980



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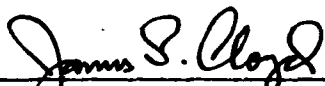
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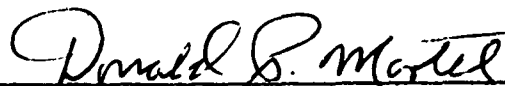
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>This three year program involves evaluation of selected low temperature molten salt solvent systems containing inorganic and/or organic chlorides and bromides for battery applications. The research involves determination of the liquidus temperatures, the specific electrical conductivity, and the electrochemical span of selected halide systems. Characterization of the solvent species by Raman spectroscopy, vapor pressure measurements, and the electrochemical study of a few cathode and anode systems will be undertaken for the most promising solvent systems. |                                      |                                                                                       |

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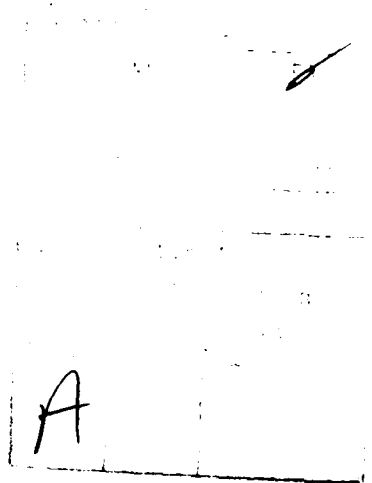
The research during the second year of this project involved the determination of liquidus temperatures and/or specific electrical conductivities for a number of binary and ternary molten salt systems containing  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{SbCl}_3$ ,  $\text{FeCl}_3$ , and  $\text{GaCl}_3$ .

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## FOREWORD

This report describes the work performed during the second year of a three-year program dealing with the experimental evaluation of some low melting halide systems for battery applications. This work was performed at the Department of Chemistry, The University of Tennessee, Knoxville, under Contract No. F33615-78-C-2075 with the Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. The principal investigator is Professor Gleb Mamantov. The Air Force Project officer is Mr. J. S. Cloyd, AFWAL/POOC, Wright-Patterson Air Force Base, Ohio.

The personnel working on the project consisted of Dr. Cedomir Petrovic, postdoctoral research associate, Jeff Cobb, Douglas Goff, and Robert Walton, undergraduate research assistants.



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## I. INTRODUCTION

The purpose of this three year project is to critically evaluate a wide range of binary and ternary low temperature molten salt systems for battery applications. These systems include chlorides and/or bromides of aluminum, antimony, iron and gallium as one component, and various alkali, alkaline earth, quaternary ammonium, n-butyl pyridinium and antimony chlorides and/or bromides as the other(s). Measurements of the liquidus range and the specific electrical conductivity are being performed on a number of the above systems. Vapor pressure, background voltammograms and Raman spectra will be studied for a few selected systems. Electrochemistry of selected cathode and anode materials will also be examined. The results of the first year of the work on this project have been presented in the Technical Report AFAPL-TR-79-2124 (1). This report covers the second year of the project.

During this period the liquidus range and/or electrical conductivity measurements have been performed on the following molten salt systems:  $\text{AlCl}_3\text{-LiCl-NaCl}$ ,  $\text{AlCl}_3\text{-NaBr}$ ,  $\text{AlBr}_3\text{-NaCl}$ ,  $\text{AlBr}_3\text{-Bu}_4\text{NBr}$ ,  $\text{AlBr}_3\text{-Me}_4\text{NBr}$ ,  $\text{AlCl}_3\text{-SbCl}_3$ ,  $\text{AlCl}_3\text{-SbCl}_3\text{-n-BuPyCl}$ ,  $\text{FeCl}_3\text{-NaCl}$ ,  $\text{FeCl}_3\text{-LiCl-NaCl}$ , and  $\text{GaCl}_3\text{-NaCl}$ .

Four molten salt systems have been selected for further work:  $\text{AlCl}_3\text{-LiCl-NaCl}$ ,  $\text{AlCl}_3\text{-SbCl}_3\text{-x}$  (where x is a third chloride to be chosen),  $\text{FeCl}_3\text{-LiCl-NaCl}$ , and  $\text{AlCl}_3\text{-Bu}_4\text{NCl}$ . These salt systems will be studied in the third and last year of this project.

## II. EXPERIMENTAL

The experimental aspects of the present work have been discussed in our Technical Report AFAPL-TR-79-2124 (1). The only changes in the equipment were the upgrading of the temperature stability of the furnace used for the electrical conductivity measurements by the addition of a Bayley Model 124 proportional temperature controller, and a recent change over from a chromel-alumel to a copper-constantan thermocouple, which has a superior reproducibility, for the temperature measurements.

Purified antimony chloride (Mallinckrodt, anhydrous, digested with antimony and distilled under vacuum) was obtained from the laboratory of Dr. G. P. Smith, Oak Ridge National Laboratory. Ferric chloride (Alfa-Ventron, anhydrous) was distilled under vacuum. Gallium chloride (Alfa-Ventron, 99.999%) was used as received.

### III. $\text{AlCl}_3$ -LiCl-NaCl SYSTEM

The  $\text{AlCl}_3$ -LiCl-NaCl system has been discussed in our Technical Report AFAPL-TR-79-2124 (1). Its low liquidus temperatures ( $\geq 86^\circ\text{C}$ ), high specific conductivity (0.1 to  $0.7 \text{ ohm}^{-1} \text{ cm}^{-1}$  in the temperature range to  $300^\circ\text{C}$ ); and a wide electrochemical span ( $>2.0\text{V}$ ) make this molten salt system a very promising solvent for battery use. Our specific conductivity measurements on this system have been reported previously (1). Independent high precision conductivity measurements on the same system have been performed at the F. J. Seiler Research Laboratory (2).

Our phase diagram data for the two pseudobinary sections of the  $\text{AlCl}_3$ -LiCl-NaCl phase diagram (with the LiCl to NaCl mole ratios of 3:1 and 1:1) have also been reported (1). The new phase diagram data for the third pseudobinary section with the LiCl to NaCl mole ratio of 1:3 are listed in Table 1. This table also includes the additional data for the 3:1 and 1:1 sections. These data conclude our liquidus range measurements on the  $\text{AlCl}_3$ -LiCl-NaCl system. Figure 1 shows our combined data for the three pseudobinary sections of this system. The minimum in the liquidus curve of the 1:3 section is shifted by less than 2 mole % from the minimum in the 1:1 section. The solidus temperature in all three sections is the same ( $86^\circ\text{C}$ ). The only new feature of the data for the 1:3 section, which does not appear in the 1:1 section, is an intermediate phase transition at  $97^\circ\text{C}$  in the melts with less than 58 mole %  $\text{AlCl}_3$ , and at  $103^\circ\text{C}$  in the melts in which  $\text{AlCl}_3$  is over 58 mole %. The nature of this transition is not clear.

### IV. $\text{AlCl}_3$ -NaBr SYSTEM

The addition of LiCl to the  $\text{AlCl}_3$ -NaCl system lowers its solidus temperature by  $29^\circ\text{C}$  without a significant change of the specific conductivity of this melt (1). In order to determine the effect of added bromide anion on the properties of the chloroaluminate melts we have studied the  $\text{AlCl}_3$ -NaBr system.

The phase diagram data for the  $\text{AlCl}_3$ -NaBr system have been presented previously (1). It was shown that the liquidus curve for the  $\text{AlCl}_3$ -NaBr system strongly resembles the liquidus curve for the  $\text{AlCl}_3$ -NaCl system, that the liquidus temperatures of the  $\text{AlCl}_3$ -NaBr system were lowered by as much as  $32^\circ\text{C}$ , and that the solidus temperatures (ranging from  $72$  to  $86^\circ$ ) were a function of the mole fraction of the bromide ion.

Table 1

Phase Diagram Data for  $\text{AlCl}_3$ -LiCl-NaCl System

| Composition<br>(Mole %) |      |      | Solidus<br>Temperature<br>(°C) | Intermediate<br>Transition<br>(°C) | Liquidus<br>Temperature<br>(°C) |
|-------------------------|------|------|--------------------------------|------------------------------------|---------------------------------|
| $\text{AlCl}_3$         | LiCl | NaCl |                                |                                    |                                 |
| 52.0                    | 12.0 | 36.0 | 86                             | 98*                                | 128                             |
| 54.0                    | 11.5 | 34.5 | 86                             | ?                                  | 120                             |
| 56.0                    | 11.0 | 33.0 | 86                             | 96*                                | 110                             |
| 59.0                    | 10.2 | 30.8 | 86                             | ?                                  | 103#                            |
| 60.0                    | 10.0 | 30.0 | 86                             | 103                                | 113                             |
| 62.0                    | 9.5  | 28.5 | 86                             | 103                                | 130#                            |
| 64.0                    | 9.0  | 27.0 | 86                             | 102                                | 139                             |
| 68.0                    | 8.0  | 24.0 | 86                             | 103                                | 162                             |
| 62.0                    | 28.5 | 9.5  | 86                             |                                    | 132                             |
| 64.0                    | 27.0 | 9.0  | 86                             |                                    | 150                             |
| 64.0                    | 18.0 | 18.0 | 86                             |                                    | 151                             |

---

\* Not reported previously

# Supercedes previously reported data

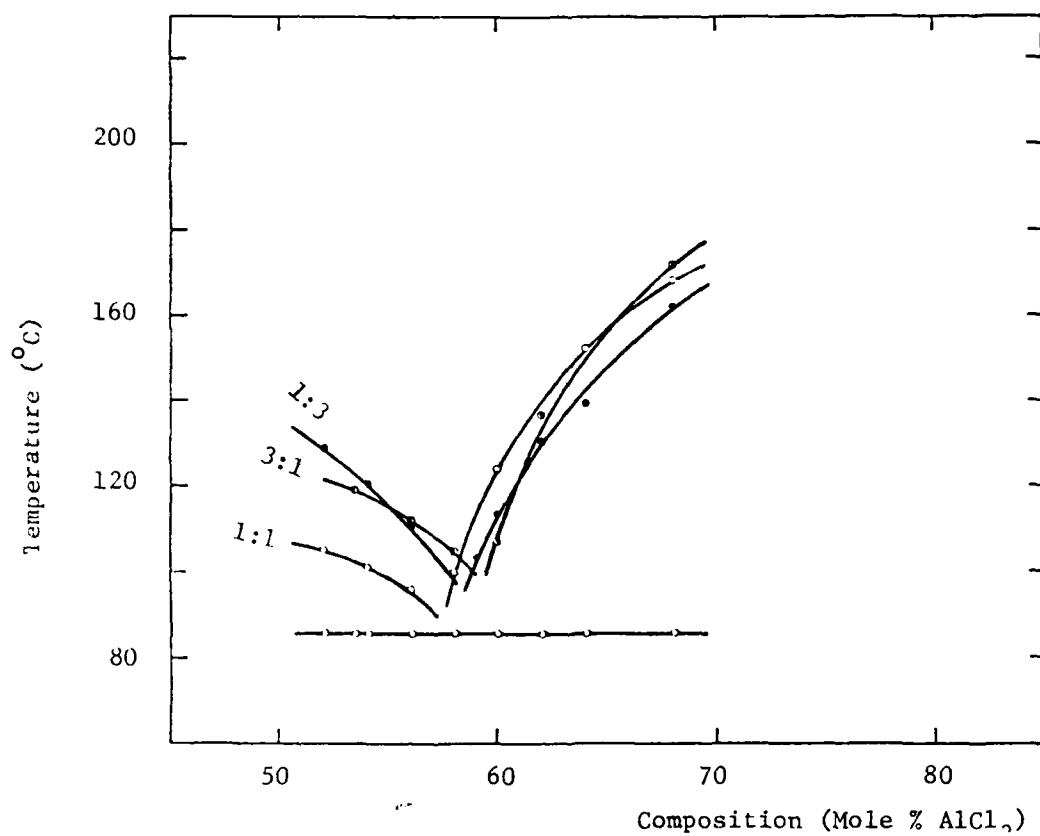


Figure 1. Phase Diagram Data for the  $\text{AlCl}_3$ - $\text{LiCl}$ - $\text{NaCl}$  System.  
 $\text{LiCl}$  to  $\text{NaCl}$  mole ratios are indicated on the liquidus curves.

Our specific conductivity data for this system are listed in Tables 2 to 5, and shown in Figure 2. These conductivity vs. temperature plots are quite similar to the conductivity plots for the  $\text{AlCl}_3$ -LiCl-NaCl system which are also shown in the same figure. The difference in the specific conductivities of the two systems is within 7% for the 52.0 mole %  $\text{AlCl}_3$  melts, and within 3% for the others. The specific conductivity of the pure bromide system,  $\text{AlBr}_3$ -NaBr, however, is lower than the conductivity of the  $\text{AlCl}_3$ -NaCl system by nearly an order of magnitude (3).

Based on the liquidus temperature and specific conductivity data, the system  $\text{AlCl}_3$ -NaBr is quite comparable to the  $\text{AlCl}_3$ -LiCl-NaCl system. However, literature data (4) indicate that the electrochemical span in the  $\text{AlCl}_3$ -NaBr system is 0.4 to 0.5V smaller than in the  $\text{AlCl}_3$ -NaCl system. From the battery use standpoint, this loss in the electrochemical span is not justified. About the same lowering of the liquidus temperatures of the  $\text{AlCl}_3$ -NaCl system can be accomplished by introducing LiCl as a third component, without paying any penalty in the electrochemical span.

#### V. $\text{AlBr}_3$ -NaCl SYSTEM

Our phase diagram data for the  $\text{AlBr}_3$ -NaCl system, the second subsystem of the  $\text{AlCl}_3$ - $\text{AlBr}_3$ -NaCl-NaBr system, are listed in Table 6 and shown in Figure 3. The similarity of our phase diagram data with the phase diagram of the corresponding pure bromide system  $\text{AlBr}_3$ -NaBr, which is also shown in Figure 3, is obvious. The lowering of the liquidus temperature of the pure bromide system by the addition of NaCl is only 7 to 10°C in the  $\text{AlBr}_3$ -rich composition region, and as much as 25°C in the region with less than 60 mole %  $\text{AlBr}_3$ . In that region, however, the liquidus temperatures of the  $\text{AlBr}_3$ -NaCl system are still above the liquidus temperatures of the  $\text{AlCl}_3$ -NaCl system. The bromide species, being in large excess, determines the shape of the phase diagram of this mixed chloride-bromide system. The measured liquidus temperatures in this system are as low as 94°C, but the eutectic temperature is outside the studied composition region ( $\geq 72$  mole %  $\text{AlBr}_3$ ).

Our specific conductivity data for the  $\text{AlBr}_3$ -NaCl system are listed in Tables 7 to 10 and shown in Figure 4. The conductivity vs. temperature plots are nearly linear and qualitatively similar to the conductivity plots for the  $\text{AlCl}_3$ -LiCl-NaCl system, which are also shown in Figure 4. The values of the specific conductivity of the  $\text{AlBr}_3$ -NaCl melts, however, are

Table 2

Specific Conductivity Data for  $\text{AlCl}_3$ -NaBr System at 1.0 KHz

Composition: 52.0 - 48.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 130.0               | 0.2386*                                                      |
| 140.0               | 0.2654*                                                      |
| 150.0               | 0.2919*                                                      |
| 158.4               | 0.3147                                                       |
| 169.3               | 0.3423                                                       |
| 180.4               | 0.3703                                                       |
| 190.8               | 0.3963                                                       |
| 200.6               | 0.4207                                                       |
| 210.1               | 0.4442                                                       |
| 220.4               | 0.4698                                                       |
| 229.4               | 0.4919                                                       |
| 240.8               | 0.5186                                                       |
| 250.9               | 0.5425                                                       |
| 260.6               | 0.5660                                                       |
| 269.4               | 0.5861                                                       |
| 279.9               | 0.6095                                                       |
| 290.2               | 0.6318                                                       |
| 300.2               | 0.6530                                                       |

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\* Calculated from Eqn. 1 (Ref. 1)

Table 3

Specific Conductivity Data for  $\text{AlCl}_3\text{-NaBr}$  System at 1.0 KHz

Composition: 60.0 - 40.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 110.3               | 0.1275                                                         |
| 120.2               | 0.1440                                                         |
| 131.5               | 0.1634                                                         |
| 141.0               | 0.1797                                                         |
| 150.0               | 0.1955*                                                        |
| 160.4               | 0.2134                                                         |
| 171.4               | 0.2325                                                         |
| 181.2               | 0.2499                                                         |
| 190.0               | 0.2652                                                         |
| 200.3               | 0.2834                                                         |
| 210.2               | 0.3009                                                         |
| 220.1               | 0.3183                                                         |
| 230.4               | 0.3363                                                         |
| 240.7               | 0.3544                                                         |
| 250.3               | 0.3712                                                         |

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\* Calculated from Eqn. 1 (Ref. 1)

Table 4

Specific Conductivity Data for  $\text{AlCl}_3$ -NaBr System at 1.0 KHz

Composition: 64.0 - 36.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 120.0               | 0.1206*                                                        |
| 130.4               | 0.1364                                                         |
| 139.6               | 0.1498                                                         |
| 150.9               | 0.1665                                                         |
| 160.3               | 0.1808                                                         |
| 170.0               | 0.1954                                                         |
| 179.9               | 0.2104                                                         |
| 189.9               | 0.2254                                                         |
| 200.0               | 0.2410                                                         |
| 209.6               | 0.2560                                                         |
| 220.2               | 0.2722                                                         |
| 230.0               | 0.2868                                                         |
| 240.0               | 0.3024                                                         |
| 249.8               | 0.3172                                                         |

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\* Calculated from Eqn. 1

Table 5

Specific Conductivity Data for  $\text{AlCl}_3$ -NaBr System at 1.0 KHz

Composition: 68.0 - 32.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 169.7               | 0.1624                                                         |
| 177.8               | 0.1727                                                         |
| 188.8               | 0.1868                                                         |
| 198.1               | 0.1988                                                         |
| 208.5               | 0.2124                                                         |
| 217.7               | 0.2250                                                         |
| 229.4               | 0.2400                                                         |
| 239.1               | 0.2532                                                         |
| 250.6               | 0.2686                                                         |

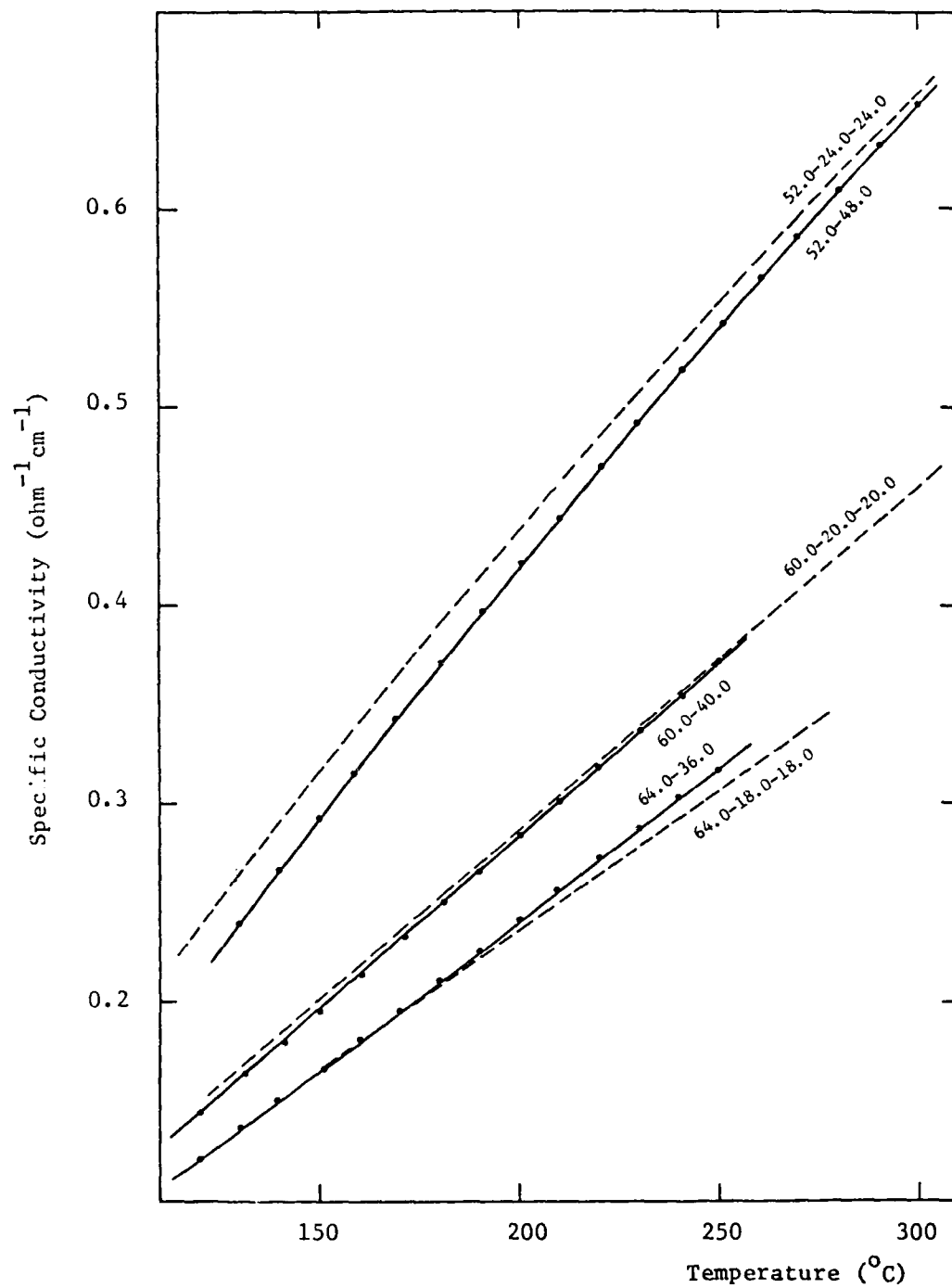


Figure 2. Specific Conductivity of  $\text{AlCl}_3\text{-NaBr}$  System (Full Line) and  $\text{AlCl}_3\text{-LiCl-NaCl}$  System (Dashed Line). Composition in mole % is indicated on the curves.

Table 6

Phase Diagram Data for  $\text{AlBr}_3$ -NaCl System

| Composition<br>(Mole %) |      | Solidus<br>Temperature<br>(°C) | Liquidus<br>Temperature<br>(°C) |
|-------------------------|------|--------------------------------|---------------------------------|
| $\text{AlBr}_3$         | NaCl |                                |                                 |
| 52.0                    | 48.0 | 83                             | 168                             |
| 56.0                    | 44.0 | 89                             | 155                             |
| 60.0                    | 40.0 | 95                             | 138                             |
| 64.0                    | 36.0 | ?                              | -114                            |
| 68.0                    | 32.0 | 81                             | 97                              |
| 72.0                    | 28.0 | 82                             | 94                              |

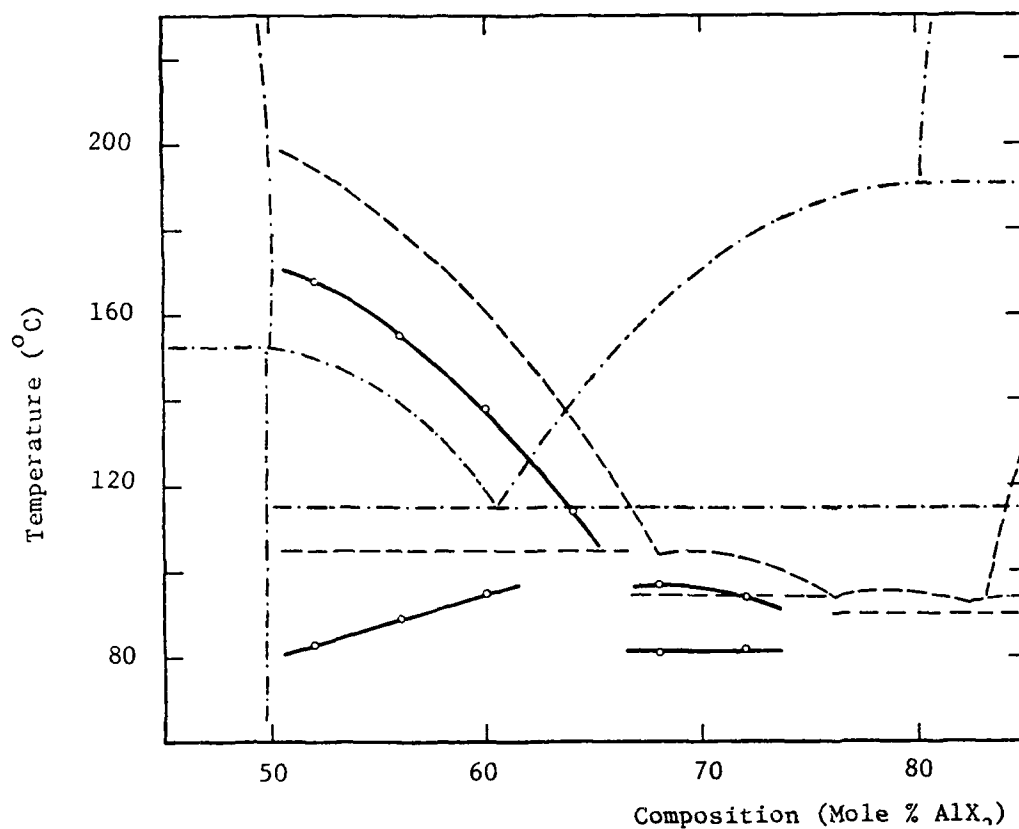


Figure 3. Phase Diagram Data for the AlBr<sub>3</sub>-NaCl System. The phase diagrams of AlBr<sub>3</sub>-NaBr system (dashed line) and AlCl<sub>3</sub>-NaCl system (dot-dash line) are shown for reference.

Table 7

Specific Conductivity Data for  $\text{AlBr}_3$ -NaCl System at 1.0 KHz

Composition: 52.0 - 48.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 188.6               | 0.3189                                                       |
| 198.4               | 0.3408                                                       |
| 209.4               | 0.3637                                                       |
| 218.9               | 0.3848                                                       |
| 228.9               | 0.4065                                                       |
| 238.9               | 0.4281                                                       |
| 249.5               | 0.4507                                                       |
| 259.6               | 0.4718                                                       |
| 270.7               | 0.4947                                                       |
| 280.2               | 0.5141                                                       |
| 290.6               | 0.5346                                                       |
| 299.5               | 0.5521                                                       |

Table 8

Specific Conductivity Data for  $\text{AlBr}_3$ -NaCl System at 1.0 KHz

Composition: 56.0 - 44.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 177.6               | 0.2318                                                         |
| 189.2               | 0.2532                                                         |
| 199.8               | 0.2729                                                         |
| 208.5               | 0.2887                                                         |
| 219.0               | 0.3079                                                         |
| 229.8               | 0.3277                                                         |
| 239.6               | 0.3456                                                         |
| 249.6               | 0.3634                                                         |

Table 9

Specific Conductivity Data for  $\text{AlBr}_3$ -NaCl System at 1.0 KHz

Composition: 64.0 - 36.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 137.7               | 0.09986                                                      |
| 147.4               | 0.1115                                                       |
| 158.8               | 0.1256                                                       |
| 169.5               | 0.1389                                                       |
| 178.9               | 0.1508                                                       |
| 188.2               | 0.1626                                                       |
| 198.7               | 0.1760                                                       |
| 208.2               | 0.1882                                                       |
| 219.7               | 0.2029                                                       |
| 229.3               | 0.2157                                                       |
| 238.7               | 0.2278                                                       |
| 249.7               | 0.2421                                                       |

Table 10

Specific Conductivity Data for  $\text{AlBr}_3$ -NaCl System at 1.0 KHz

Composition: 68.0 - 32.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 119.1               | 0.06191                                                        |
| 130.9               | 0.07299                                                        |
| 138.8               | 0.08052                                                        |
| 149.5               | 0.09121                                                        |
| 159.6               | 0.1014                                                         |
| 171.0               | 0.1132                                                         |
| 180.9               | 0.1234                                                         |
| 189.7               | 0.1325                                                         |
| 199.6               | 0.1428                                                         |
| 209.9               | 0.1535                                                         |
| 220.8               | 0.1653                                                         |
| 229.8               | 0.1748                                                         |
| 240.4               | 0.1862                                                         |
| 250.3               | 0.1971                                                         |

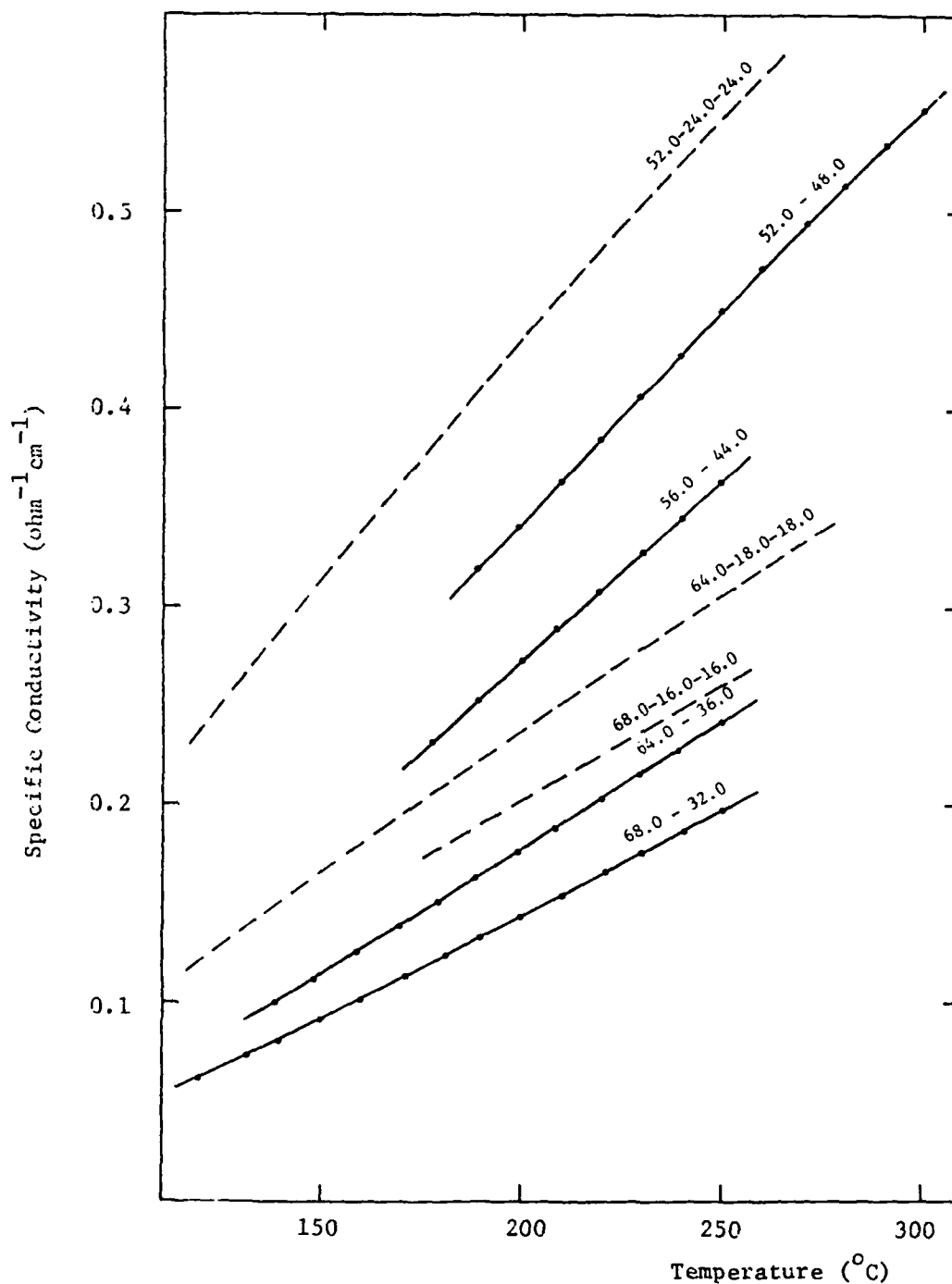


Figure 4. Specific Conductivity of  $\text{AlBr}_3$ - $\text{NaCl}$  System (Full Line) and  $\text{AlCl}_3$ - $\text{LiCl}$ - $\text{NaCl}$  System (Dashed Line). Composition in mole % is indicated on the curves.

considerably lower ( $\sim 20\%$  for the 52.0-48.0 mole % melt, and up to 30% at 68.0 mole %  $\text{AlBr}_3$ ).

In summary, the low melting region of the  $\text{AlBr}_3$ -NaCl system is shifted towards highly acidic compositions, so that the liquidus temperatures below 62 mole %  $\text{AlBr}_3$  are actually higher than in the  $\text{AlCl}_3$ -NaCl system. The specific conductivity of the  $\text{AlBr}_3$ -NaCl system is 20 to 30% lower than in the  $\text{AlCl}_3$ -LiCl-NaCl system. Based on these data, the  $\text{AlBr}_3$ -NaCl system does not seem to offer much promise for the battery use.

#### VI. $\text{AlBr}_3$ - $\text{Bu}_4\text{NBr}$ SYSTEM

The  $\text{AlBr}_3$ - $\text{Bu}_4\text{NBr}$  system has been discussed previously (1). Based on the low melting point of the pure  $\text{Bu}_4\text{NBr}$  ( $\geq 101^\circ\text{C}$ ) (5), the  $\text{AlBr}_3$ - $\text{Bu}_4\text{NBr}$  system was expected to be a very low melting system. Our preliminary experiments indicated that the liquidus temperatures of the melts with more than 50 mole %  $\text{Bu}_4\text{NBr}$  were indeed below room temperature (1). Subsequent experiments have shown, however, that these melts were merely supercooled for unusually long periods of time ( $\sim 9$  months for the 40.0-60.0 mole % melt, and  $\sim 1$  year for the 30.0-70.0 mole % melt). The true liquidus temperature of these two melts, determined by the visual method, was  $111^\circ\text{C}$  for the 40.0-60.0 mole % melt, and  $89^\circ\text{C}$  for the 30.0-70.0 mole % melt. The solidus temperature in the  $\text{Bu}_4\text{NBr}$ -rich composition region is  $62^\circ\text{C}$ . Therefore, our statement in Technical Report AFAPL-TR-79-2124 (1) about the room temperature melts of the  $\text{AlBr}_3$ - $\text{Bu}_4\text{NBr}$  system is being withdrawn.

Our specific conductivity data for the  $\text{AlBr}_3$ - $\text{Bu}_4\text{NBr}$  system are listed in Tables 11 to 16 and shown in Figure 5. The conductivity of these melts, less than  $0.03 \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $220^\circ\text{C}$ , is quite low. In view of the high viscosity of these melts, however, and of the large size of the  $\text{Bu}_4\text{N}^+$  cation, which is presumably the conducting species in these melts, such low specific conductivity seems to be reasonable. The conductivity vs. temperature plots exhibit a very pronounced curvature. The conductivity at a given temperature has little dependence on the composition of the melt, with the exception of the 30.0-70.0 mole % melt. This may be a result of the increase in the molar volume with the increasing mole fraction of  $\text{Bu}_4\text{NBr}$ .

In summary, even though the liquidus temperatures in the  $\text{AlBr}_3$ - $\text{Bu}_4\text{NBr}$  melts are quite low ( $\geq 62^\circ\text{C}$ ), their very low specific conductivity, as well as their electrochemical span, smaller by 0.4 to 0.5V than in the chloride

Table 11

Specific Conductivity Data for  $\text{AlBr}_3\text{-Bu}_4\text{NBr}$  System at 1.0 KHz

Composition 30.0 - 70.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 95.4                | 0.001238                                                     |
| 105.1               | 0.001736                                                     |
| 114.3               | 0.002328                                                     |
| 125.2               | 0.003190                                                     |
| 135.5               | 0.004159                                                     |
| 144.8               | 0.005252                                                     |
| 154.2               | 0.006587                                                     |
| 164.8               | 0.008356                                                     |
| 172.8               | 0.010221                                                     |
| 182.9               | 0.012342                                                     |
| 195.0               | 0.015118                                                     |
| 205.3               | 0.017712                                                     |
| 214.9               | 0.020414                                                     |

Table 12

Specific Conductivity Data for  $\text{AlBr}_3\text{-Bu}_4\text{NBr}$  System at 1.0 KHz

Composition 40.0 - 60.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 127.1               | 0.006026                                                     |
| 137.9               | 0.007592                                                     |
| 147.2               | 0.009165                                                     |
| 157.6               | 0.011114                                                     |
| 167.6               | 0.013130                                                     |
| 176.5               | 0.015143                                                     |
| 186.8               | 0.017667                                                     |
| 196.0               | 0.020560                                                     |

Table 13

Specific Conductivity Data for  $\text{AlBr}_3\text{-Bu}_4\text{NBr}$  System at 1.0 KHz

Composition: 50.0 - 50.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 152.1               | 0.01049                                                        |
| 161.2               | 0.01235                                                        |
| 171.2               | 0.01448                                                        |
| 180.4               | 0.01669                                                        |
| 189.2               | 0.01883                                                        |
| 198.6               | 0.02136                                                        |
| 209.1               | 0.02427                                                        |
| 218.6               | 0.02696                                                        |

Table 14

Specific Conductivity Data for  $\text{AlBr}_3\text{-Bu}_4\text{NBr}$  System at 1.0 KHz

Composition: 60.0 - 40.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 113.9               | 0.004614                                                     |
| 118.6               | 0.005142                                                     |
| 122.7               | 0.005609                                                     |
| 128.4               | 0.006297                                                     |
| 135.2               | 0.007195                                                     |
| 145.2               | 0.008585                                                     |
| 154.2               | 0.009871                                                     |
| 163.3               | 0.01152                                                      |
| 172.4               | 0.01312                                                      |

Table 15

Specific Conductivity Data for  $\text{AlBr}_3\text{-Bu}_4\text{NBr}$  System at 1.0 KHz

Composition: 64.0 - 36.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 99.2                | 0.003440                                                     |
| 110.5               | 0.004499                                                     |
| 118.6               | 0.005361                                                     |
| 129.3               | 0.006654                                                     |
| 139.4               | 0.007970                                                     |
| 150.0               | 0.009484                                                     |
| 160.4               | 0.01112                                                      |
| 171.1               | 0.01291                                                      |
| 181.6               | 0.01478                                                      |
| 193.5               | 0.01704                                                      |
| 200.6               | 0.01843                                                      |
| 209.4               | 0.02022                                                      |
| 219.0               | 0.02223                                                      |

Table 16

Specific Conductivity Data for  $\text{AlBr}_3\text{-Bu}_4\text{NBr}$  System at 1.0 KHz

Composition: 68.0 - 32.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 85.0                | 0.002423                                                     |
| 92.5                | 0.002966                                                     |
| 102.2               | 0.003758                                                     |
| 112.3               | 0.004685                                                     |
| 122.5               | 0.005743                                                     |
| 133.8               | 0.007053                                                     |
| 144.8               | 0.008438                                                     |
| 157.7               | 0.01024                                                      |
| 169.5               | 0.01206                                                      |
| 178.5               | 0.01351                                                      |
| 192.2               | 0.01585                                                      |
| 203.9               | 0.01796                                                      |
| 212.6               | 0.01958                                                      |
| 219.6               | 0.02092                                                      |

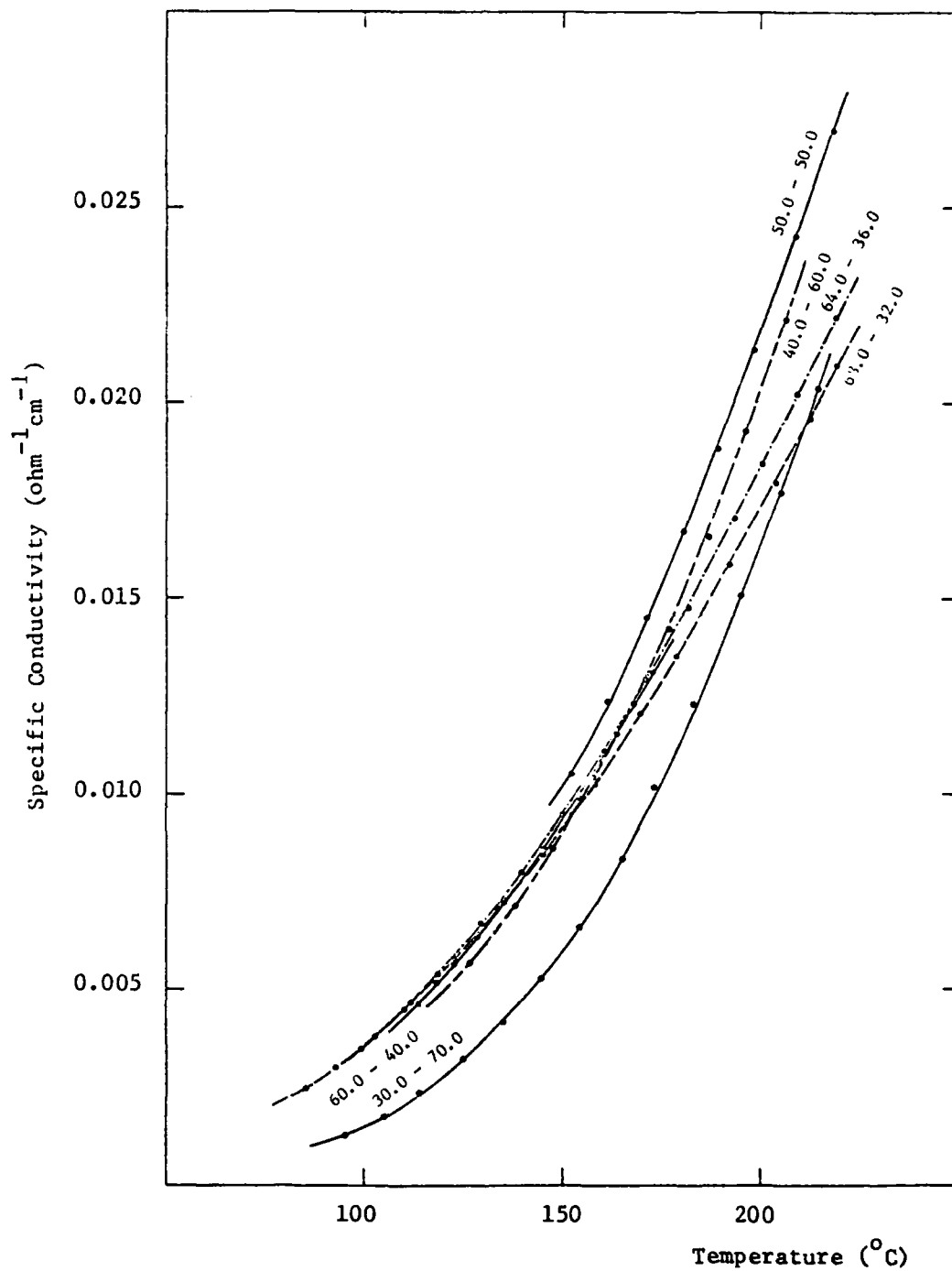


Figure 5. Specific Conductivity of AlBr<sub>3</sub>-Bu<sub>4</sub>NBr System. Composition in mole % is indicated on the curves.

melts, severely limit the potential usefulness of these melts for battery applications.

#### VII. $\text{AlBr}_3\text{-Me}_4\text{NBr}$ SYSTEM

The  $\text{AlBr}_3\text{-Me}_4\text{NBr}$  system has also been discussed previously (1). The pure  $\text{Me}_4\text{NBr}$  decomposes without melting at  $\sim 230^\circ\text{C}$  (6), and its mixtures with less than 50 mole %  $\text{AlBr}_3$  decompose before reaching the liquidus temperature. The solidus temperature in the  $\text{AlBr}_3$ -rich composition region is in the  $70\text{--}80^\circ\text{C}$  range. Our specific conductivity data for the 70.0-30.0 mole %  $\text{AlBr}_3\text{-Me}_4\text{NBr}$  melt are listed in Table 17 and shown in Figure 6. These conductivity data are  $\sim 70\%$  higher than the values for the 68.0-32.0 mole %  $\text{AlBr}_3\text{-Bu}_4\text{NBr}$  melt at the same temperature. This higher conductivity is presumably due to the smaller size and consequently higher mobility of the  $\text{Me}_4\text{N}^+$  cation compared to the  $\text{Bu}_4\text{N}^+$  cation. The conductivity of the  $\text{AlCl}_3\text{-Me}_4\text{NBr}$  melt, however, is still too low to justify a further study of this system.

#### VIII. $\text{AlCl}_3\text{-SbCl}_3$ SYSTEM

The phase diagram of the  $\text{AlCl}_3\text{-SbCl}_3$  system, based on the data of Kendall *et al.*, (7) and Niselson *et al.*, (8) is shown in Figure 7. The eutectic temperature in this system is  $70^\circ\text{C}$ , and the eutectic composition is  $\sim 10$  mole %  $\text{AlCl}_3$ . Since  $\text{SbCl}_3$  is a weaker acid than  $\text{AlCl}_3$ , an acid-base equilibrium is expected to take place in their binary melts:



However, the phase diagram of this system (Figure 7), gives no indication of the formation of a compound in the solid phase. Moreover, the Raman studies show no evidence for the presence of the  $\text{AlCl}_4^-$  or  $\text{Al}_2\text{Cl}_7^-$  ions in these melts (9). Since the molten pure  $\text{AlCl}_3$  and  $\text{SbCl}_3$  are both nonconducting molecular liquids, the electrical conductivity of the  $\text{AlCl}_3\text{-SbCl}_3$  melts is expected to be very low.

Our specific conductivity data for the  $\text{AlCl}_3\text{-SbCl}_3$  system are listed in Tables 18 to 28, and shown in Figures 8 and 9. The observed relatively high specific conductivity of the order of  $0.05$  to  $0.09 \text{ ohm}^{-1}\text{cm}^{-1}$ , ( $\sim 20\%$  of the conductivity of the  $\text{AlCl}_3\text{-LiCl-NaCl}$  melts) is quite surprising. The conductivity *vs.* temperature plots exhibit a pronounced curvature, particularly at

Table 17

Specific Conductivity Data for  $\text{AlBr}_3\text{-Me}_4\text{NBr}$  System at 1.0 KHz

Composition: 70.0 - 30.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 108.4               | 0.00728                                                        |
| 118.3               | 0.00887                                                        |
| 129.8               | 0.0110                                                         |
| 144.8               | 0.0141                                                         |
| 148.4               | 0.0150                                                         |
| 167.3               | 0.0196                                                         |
| 188.2               | 0.0254                                                         |
| 208.0               | 0.0314                                                         |
| 224.2               | 0.0367                                                         |

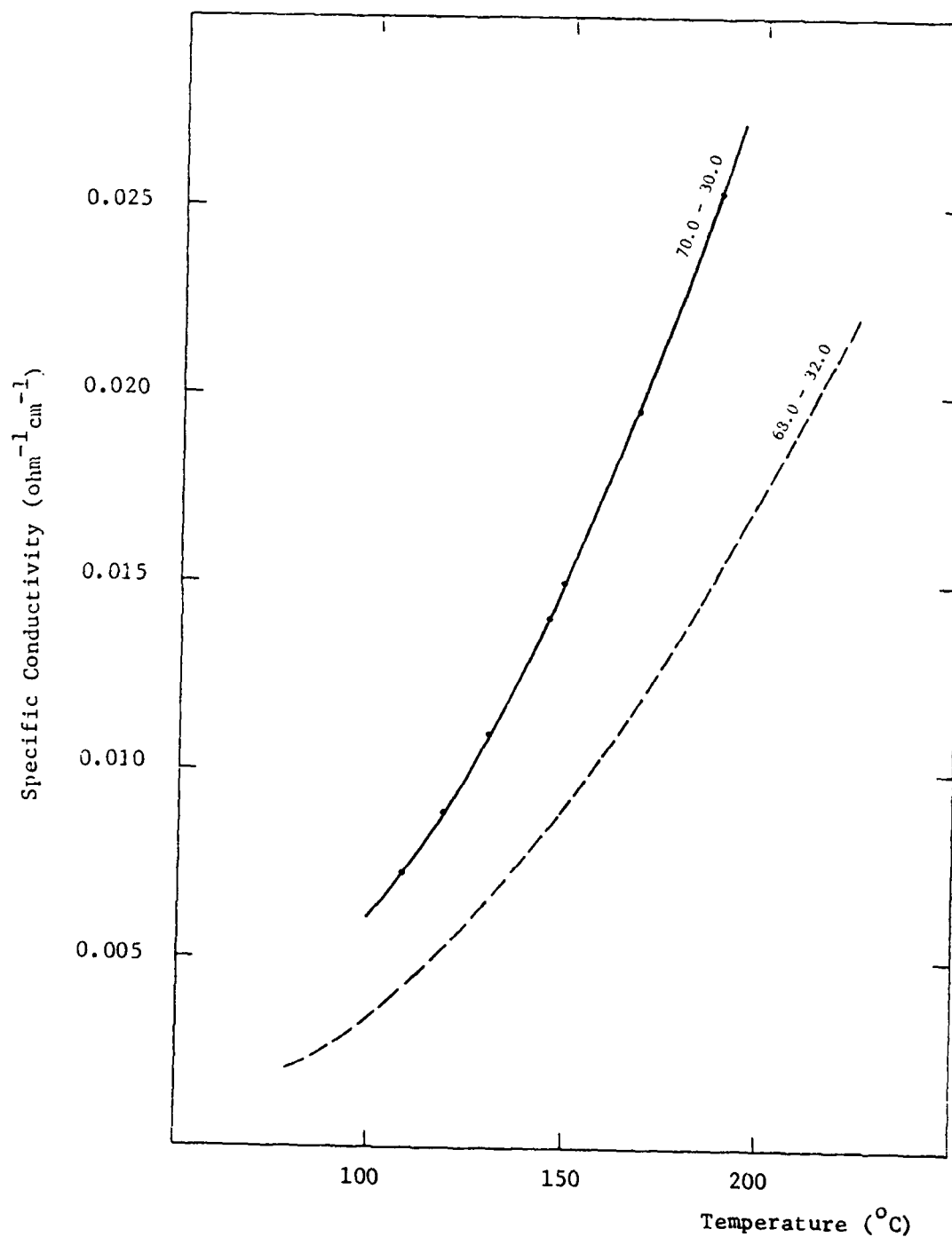


Figure 6. Specific Conductivity of  $\text{AlBr}_3\text{-Me}_4\text{NBr}$  70.0-30.0 Mole % Melt (Full Line) and  $\text{AlBr}_3\text{-Bu}_4\text{NBr}$  68.0-32.0 Mole % Melt (Dashed Line). Composition in mole % is indicated on the curves.

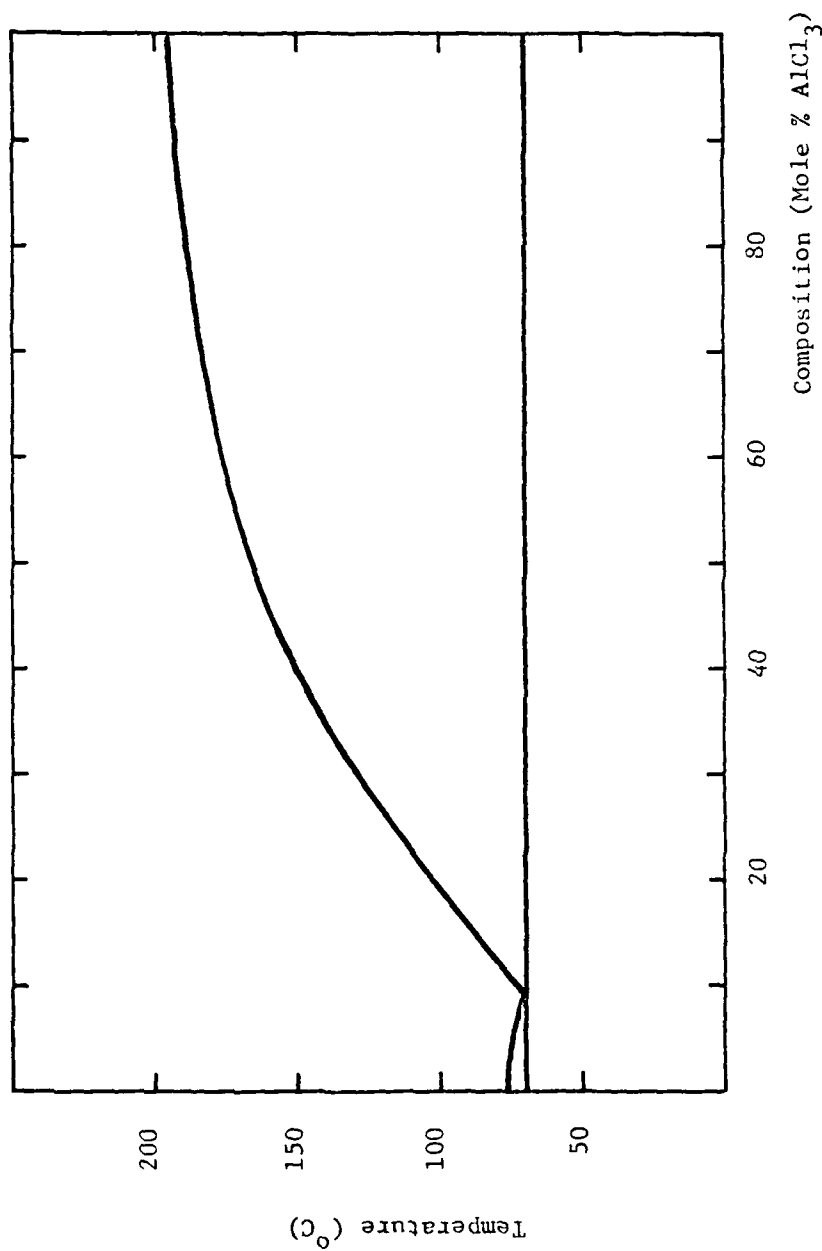


Figure 7. Phase Diagram of the  $\text{AlCl}_3$ - $\text{SbCl}_3$  System.

Table 18

Specific Conductivity Data for  $\text{AlCl}_3\text{-SbCl}_3$  System at 1.0 KHz.

Composition: 2.5 - 97.5 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 86.7                | 0.007845                                                     |
| 95.6                | 0.008355                                                     |
| 106.6               | 0.008919                                                     |
| 116.6               | 0.009367                                                     |
| 126.8               | 0.009750                                                     |
| 134.9               | 0.010010                                                     |
| 144.3               | 0.010255                                                     |
| 154.6               | 0.010469                                                     |
| 167.8               | 0.010638                                                     |
| 178.0               | 0.010699                                                     |
| 187.0               | 0.010708                                                     |
| 200.2               | 0.010652                                                     |
| 204.4               | 0.010601                                                     |
| 212.9               | 0.010511                                                     |
| 222.5               | 0.010364                                                     |
| 231.3               | 0.010197                                                     |

Table 19

Specific Conductivity Data for  $\text{AlCl}_3$ - $\text{SbCl}_3$  System at 1.0 KHz

Composition: 5.0 - 95.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 83.8                | 0.01399                                                      |
| 93.1                | 0.01514                                                      |
| 102.8               | 0.01623                                                      |
| 113.2               | 0.01735                                                      |
| 123.3               | 0.01825                                                      |
| 134.0               | 0.01908                                                      |
| 144.2               | 0.01974                                                      |
| 154.1               | 0.02027                                                      |
| 164.0               | 0.02071                                                      |
| 173.8               | 0.02101                                                      |
| 185.4               | 0.02122                                                      |
| 193.3               | 0.02129                                                      |
| 201.2               | 0.02133                                                      |
| 206.5               | 0.02126                                                      |
| 211.6               | 0.02120                                                      |
| 217.6               | 0.02110                                                      |
| 226.0               | 0.02089                                                      |
| 232.0               | 0.02070                                                      |

Table 20

Specific Conductivity Data for  $\text{AlCl}_3\text{-SbCl}_3$  System at 1.0 KHz

Composition: 10.0 - 90.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 80.2                | 0.02326                                                        |
| 90.0                | 0.02610                                                        |
| 101.2               | 0.02864                                                        |
| 109.9               | 0.03070                                                        |
| 119.4               | 0.03276                                                        |
| 129.2               | 0.03473                                                        |
| 138.9               | 0.03646                                                        |
| 148.7               | 0.03802                                                        |
| 158.3               | 0.03938                                                        |
| 167.6               | 0.04048                                                        |
| 170.8               | 0.04090                                                        |
| 180.1               | 0.04176                                                        |
| 190.8               | 0.04252                                                        |
| 199.8               | 0.04294                                                        |
| 208.7               | 0.04320                                                        |
| 218.9               | 0.04331                                                        |
| 229.6               | 0.04320                                                        |

Table 21

Specific Conductivity Data for  $\text{AlCl}_3\text{-SbCl}_3$  System at 1.0 KHz

Composition: 15.0 - 85.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 108.8               | 0.03951                                                      |
| 119.2               | 0.04306                                                      |
| 128.8               | 0.04613                                                      |
| 138.3               | 0.04891                                                      |
| 147.8               | 0.05152                                                      |
| 150.1               | 0.05214                                                      |
| 157.0               | 0.05385                                                      |
| 158.5               | 0.05415                                                      |
| 170.2               | 0.05673                                                      |
| 178.8               | 0.05837                                                      |
| 190.0               | 0.06018                                                      |
| 191.8               | 0.06051                                                      |
| 200.0               | 0.06150                                                      |
| 201.4               | 0.06171                                                      |
| 210.8               | 0.06262                                                      |
| 221.1               | 0.06329                                                      |
| 230.2               | 0.06363                                                      |
| 239.8               | 0.06370                                                      |

Table 22

Specific Conductivity Data for  $\text{AlCl}_3$ - $\text{SbCl}_3$  System at 1.0 KHz

Composition: 20.0 - 80.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 123.0               | 0.05071                                                      |
| 128.0               | 0.05285                                                      |
| 132.2               | 0.05447                                                      |
| 132.7               | 0.05480                                                      |
| 140.5               | 0.05787                                                      |
| 144.4               | 0.05942                                                      |
| 150.8               | 0.06171                                                      |
| 158.0               | 0.06430                                                      |
| 162.0               | 0.06563                                                      |
| 169.3               | 0.06801                                                      |
| 172.1               | 0.06886                                                      |
| 183.6               | 0.07223                                                      |
| 197.4               | 0.07551                                                      |
| 209.0               | 0.07771                                                      |
| 217.3               | 0.07897                                                      |
| 226.0               | 0.07998                                                      |

Table 23

Specific Conductivity Data for  $\text{AlCl}_3\text{-SbCl}_3$  System at 1.0 KHz

Composition: 25.0 - 75.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 125.5               | 0.05378                                                        |
| 128.4               | 0.05527                                                        |
| 137.5               | 0.05961                                                        |
| 148.2               | 0.06461                                                        |
| 160.4               | 0.07001                                                        |
| 170.2               | 0.07407                                                        |
| 182.4               | 0.07869                                                        |
| 193.6               | 0.08242                                                        |
| 204.6               | 0.08561                                                        |
| 215.0               | 0.08815                                                        |
| 225.1               | 0.09016                                                        |

Table 24

Specific Conductivity Data for  $\text{AlCl}_3$ - $\text{SbCl}_3$  System at 1.0 KHz

Composition: 30.0 - 70.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 160.8               | 0.07205                                                        |
| 168.2               | 0.07566                                                        |
| 171.7               | 0.07728                                                        |
| 172.4               | 0.07767                                                        |
| 179.0               | 0.08067                                                        |
| 184.8               | 0.08320                                                        |
| 191.1               | 0.08579                                                        |
| 197.1               | 0.08811                                                        |
| 203.9               | 0.09058                                                        |
| 209.2               | 0.09243                                                        |
| 213.6               | 0.09382                                                        |
| 217.0               | 0.09484                                                        |
| 220.2               | 0.09575                                                        |

Table 25

Specific Conductivity Data for  $\text{AlCl}_3\text{-SbCl}_3$  System at 1.0 KHz

Composition: 40.0 - 60.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 173.6               | 0.07461                                                      |
| 177.3               | 0.07661                                                      |
| 179.3               | 0.07835                                                      |
| 185.5               | 0.08083                                                      |
| 191.1               | 0.08400                                                      |
| 197.4               | 0.08674                                                      |
| 201.4               | 0.08891                                                      |
| 204.9               | 0.09037                                                      |
| 211.4               | 0.09311                                                      |
| 214.0               | 0.09428                                                      |
| 217.8               | 0.09575                                                      |

Table 26

Specific Conductivity Data for  $\text{AlCl}_3$ - $\text{SbCl}_3$  System at 1.0 KHz

Composition: 50.0 - 50.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 181.7               | 0.06879                                                        |
| 191.9               | 0.07444                                                        |
| 192.2               | 0.07455                                                        |
| 197.2               | 0.07704                                                        |
| 201.2               | 0.07904                                                        |
| 202.0               | 0.07933                                                        |
| 210.3               | 0.08282                                                        |

Table 27

Specific Conductivity Data for  $\text{AlCl}_3\text{-SbCl}_3$  System at 1.0 KHz

Composition: 55.0 - 45.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 183.1               | 0.06313                                                      |
| 186.3               | 0.06486                                                      |
| 189.4               | 0.06637                                                      |
| 194.4               | 0.06854                                                      |
| 198.3               | 0.07012                                                      |
| 200.6               | 0.07156                                                      |
| 203.4               | 0.07242                                                      |
| 205.2               | 0.07351                                                      |
| 208.4               | 0.07470                                                      |
| 212.8               | 0.07666                                                      |
| 218.0               | 0.07880                                                      |

Table 28

Specific Conductivity Data for  $\text{AlCl}_3$ - $\text{SbCl}_3$  System at 1.0 KHz

Composition: 60.0 - 40.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 193.3               | 0.06271                                                        |
| 195.0               | 0.06344                                                        |
| 202.0               | 0.06620                                                        |
| 206.6               | 0.06747                                                        |
| 211.6               | 0.06941                                                        |
| 216.7               | 0.07125                                                        |

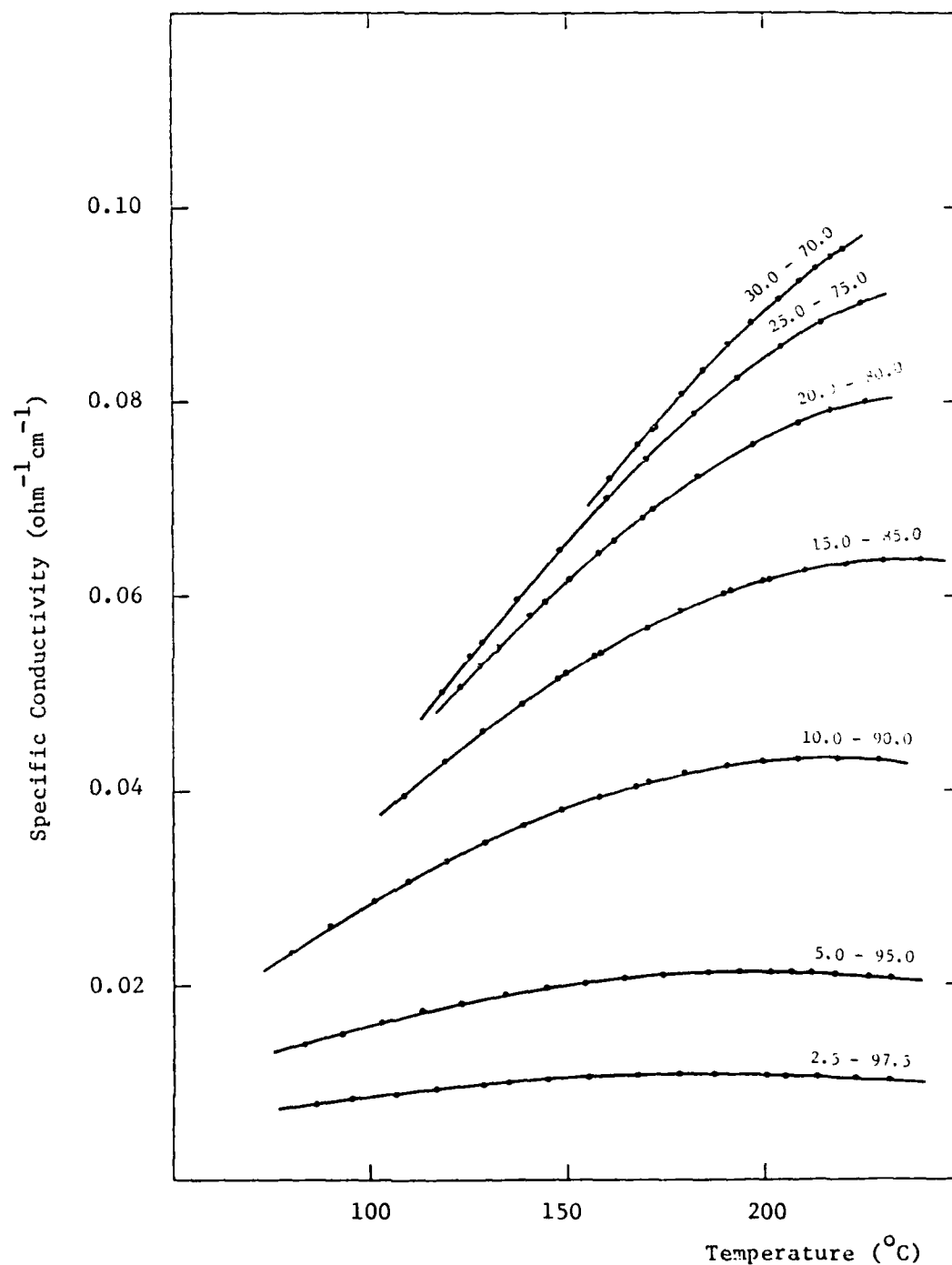


Figure 8. Specific Conductivity of  $\text{AlCl}_3$ - $\text{SbCl}_3$  System (Part 1). Composition in mole % is indicated on the curves.

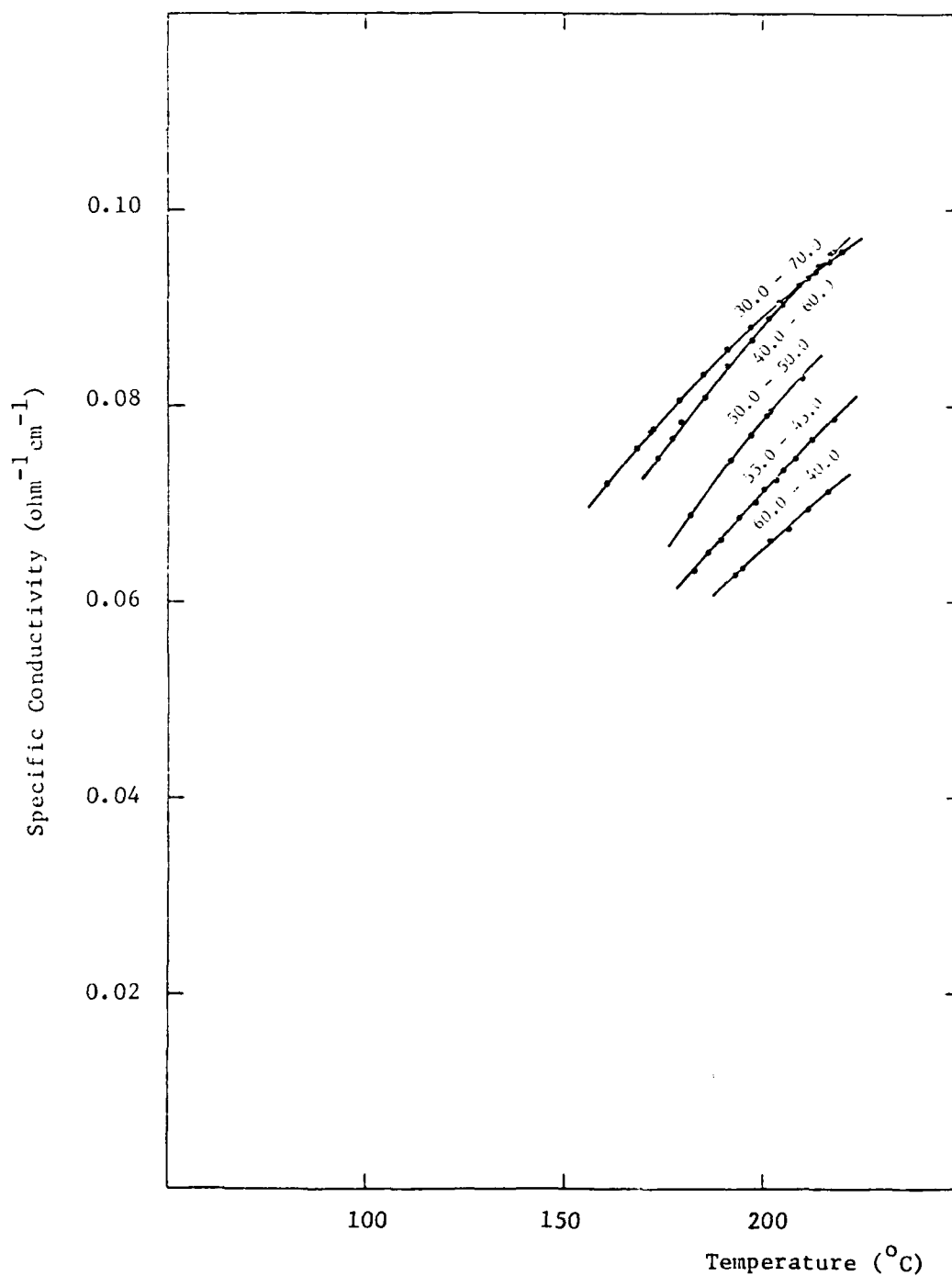


Figure 9. Specific Conductivity of  $\text{AlCl}_3\text{-SbCl}_3$  System (Part 2). Composition in mole % is indicated on the curves.

low mole fractions of  $\text{AlCl}_3$ . The plots for the melts with 10 mole %  $\text{AlCl}_3$  or less exhibit a maximum. The specific conductivity at constant temperature reaches a maximum at a composition between 30 and 35 mole %  $\text{AlCl}_3$ . A detailed evaluation of the experimental results obtained on this system is currently in progress.

Our conductivity measurements on the 60.0-40.0 mole % melt are not very reproducible. This appears to be due to the high volatility of this melt even at temperatures close to its liquidus point. Therefore, no conductivity measurements were performed on the melts with more than 60 mole %  $\text{AlCl}_3$ .

In summary, the  $\text{AlCl}_3$ - $\text{SbCl}_3$  melts have very low liquidus temperatures, and unexpectedly high specific conductivity. The melts with less than 50 mole %  $\text{AlCl}_3$  seem to be promising for use in batteries in which  $\text{SbCl}_3$  is used as a cathode material.

#### IX. $\text{AlCl}_3$ - $\text{SbCl}_3$ -n-BuPyCl SYSTEM

Samples of the  $\text{AlCl}_3$ - $\text{SbCl}_3$ -n-BuPyCl melts were obtained from the laboratory of Dr. G. P. Smith at Oak Ridge National Laboratory. Since the liquidus temperature of the two compositions studied, 19.0-60.0-21.0 and 21.0-60.0-19.0 mole %, is below 25°C, we have performed no phase diagram measurements. The results of our specific conductivity measurements are listed in Tables 29 and 30, and shown in Figure 10. The conductivity data for the 25.0-75.0 mole %  $\text{AlCl}_3$ - $\text{SbCl}_3$ , which has approximately the same  $\text{AlCl}_3$  to  $\text{SbCl}_3$  mole ratio as the two ternary n-BuPyCl melts, are shown for comparison in the same figure.

The addition of n-BuPyCl to the  $\text{AlCl}_3$ - $\text{SbCl}_3$  melt has a very pronounced effect on its specific conductivity. In the low temperature region, below  $\sim 100^\circ\text{C}$ , the conductivity vs. temperature plots become increasingly nonlinear. Also, the specific conductivity of the  $\text{AlCl}_3$ - $\text{SbCl}_3$ -n-BuPyCl ternary melts is  $\sim 40\%$  lower than the conductivity of the corresponding 25.0-75.0 mole %  $\text{AlCl}_3$ - $\text{SbCl}_3$  binary melt at the same temperature. The factors responsible for this significant decrease in conductivity are currently under study at Oak Ridge National Laboratory.

From the practical point of view, however, the lowering of the liquidus temperatures in the  $\text{AlCl}_3$ - $\text{SbCl}_3$ -n-BuPyCl melts is offset by the large decrease in the specific conductivity of the  $\text{AlCl}_3$ - $\text{SbCl}_3$  melts. Therefore, no more additional work is planned on the  $\text{AlCl}_3$ - $\text{SbCl}_3$ -n-BuPyCl system during the coming year.

Table 29

Specific Conductivity Data for  $\text{AlCl}_3$ - $\text{SbCl}_3$ -n-BuPyCl System  
at 1.0 KHz

Composition: 19.0 - 60.0 - 21.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 24.4                | 0.003947                                                       |
| 36.5                | 0.006524                                                       |
| 44.3                | 0.008438                                                       |
| 49.2                | 0.009756                                                       |
| 59.3                | 0.01275                                                        |
| 68.2                | 0.01570                                                        |
| 79.1                | 0.01954                                                        |
| 89.7                | 0.02357                                                        |
| 99.8                | 0.02759                                                        |
| 107.8               | 0.03087                                                        |
| 119.8               | 0.03595                                                        |
| 129.8               | 0.04024                                                        |
| 139.9               | 0.04470                                                        |
| 149.9               | 0.04922                                                        |
| 160.8               | 0.05422                                                        |

Table 30

Specific Conductivity Data for  $\text{AlCl}_3$ - $\text{SbCl}_3$ -n-BuPyCl System  
at 1.0 KHz

Composition: 21.0 - 60.0 - 19.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 24.4                | 0.003979                                                       |
| 36.8                | 0.006289                                                       |
| 44.2                | 0.007912                                                       |
| 49.3                | 0.009099                                                       |
| 59.3                | 0.01163                                                        |
| 68.2                | 0.01413                                                        |
| 79.0                | 0.01732                                                        |
| 89.7                | 0.02071                                                        |
| 99.8                | 0.02408                                                        |
| 107.4               | 0.02665                                                        |
| 119.9               | 0.03103                                                        |
| 129.7               | 0.03455                                                        |
| 139.9               | 0.03828                                                        |
| 149.8               | 0.04203                                                        |
| 160.8               | 0.04624                                                        |

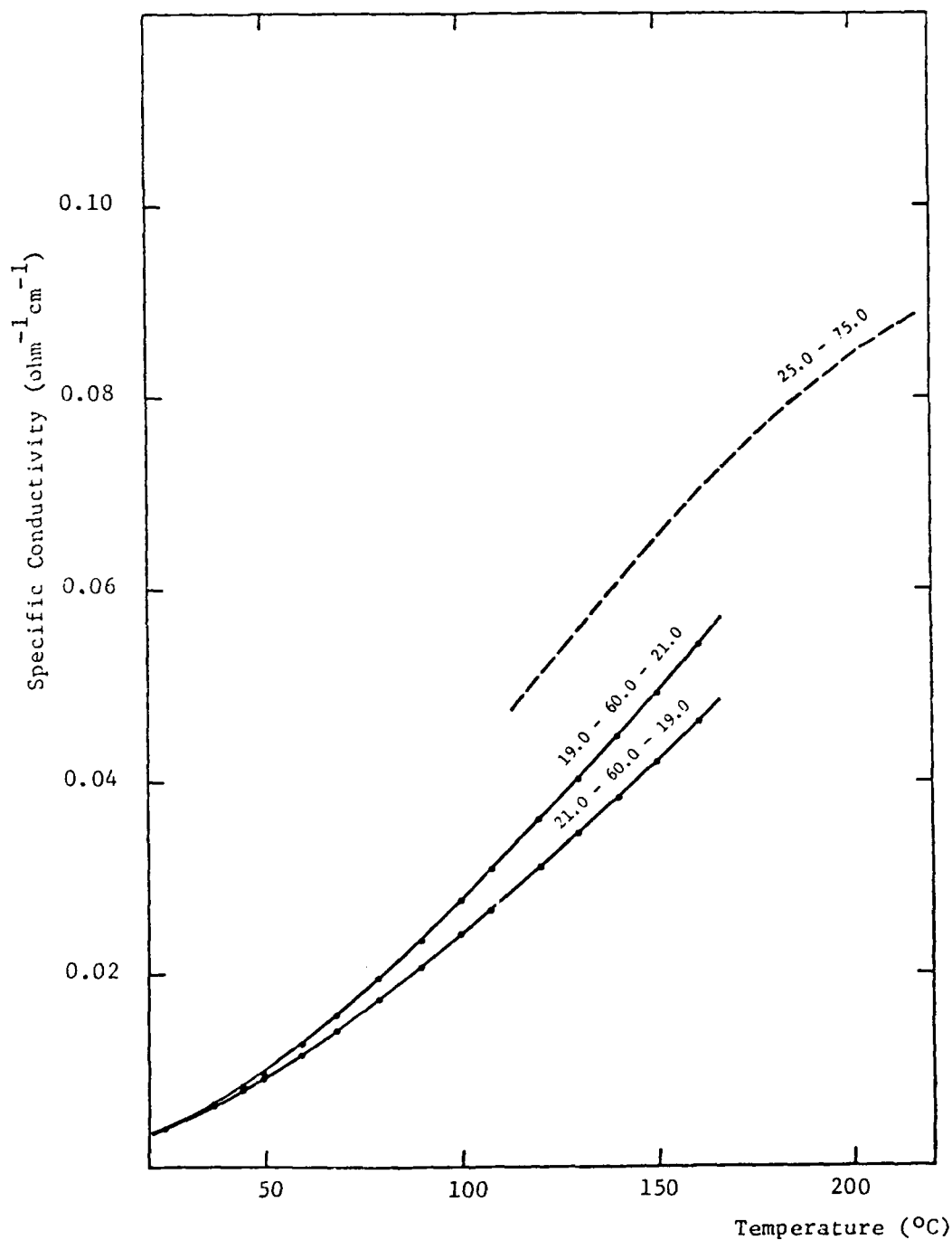


Figure 10. Specific Conductivity of  $\text{AlCl}_3\text{-SbCl}_3\text{-n-BuPyCl}$  System (Full Line) and  $\text{AlCl}_3\text{-SbCl}_3$  (Dashed Line). Composition in mole % is indicated on the curves.

## X. $\text{FeCl}_3$ -NaCl SYSTEM

The phase diagram of the  $\text{FeCl}_3$ -NaCl system, based on the data of Morozov et al., (10), is shown in Figure 11. It is qualitatively similar to the phase diagram of the  $\text{AlCl}_3$ -NaCl system, shown for comparison in the same figure. In both systems a compound with 1:1 stoichiometry is formed in the solid phase,  $\text{NaFeCl}_4$  and  $\text{NaAlCl}_4$ , respectively, and only one eutectic point exists in the acidic composition region in each case. However, the eutectic composition in the  $\text{FeCl}_3$ -NaCl system is close to 51 mole %  $\text{FeCl}_3$ , i.e., it is shifted by about 10 mole % from the eutectic composition in the  $\text{AlCl}_3$ -NaCl system. Also, the eutectic temperature in the  $\text{FeCl}_3$ -NaCl system is relatively high ( $156^\circ\text{C}$ ) compared to that of  $115^\circ\text{C}$  in the  $\text{AlCl}_3$ -NaCl system. As a result of these two differences, the liquidus temperature in the  $\text{FeCl}_3$ -NaCl melts is about  $80^\circ\text{C}$  higher than the liquidus temperature of the corresponding  $\text{AlCl}_3$ -NaCl melts in the 60 to 80 mole % region.

Our conductivity data for the  $\text{FeCl}_3$ -NaCl system are listed in Tables 31 to 34, and shown in Figure 12. The specific conductivity vs. temperature plots are linear and qualitatively similar to the conductivity plots for the  $\text{AlCl}_3$ -LiCl-NaCl melts. However, the specific conductivity of the  $\text{FeCl}_3$ -NaCl melts is higher than the specific conductivity of the corresponding  $\text{AlCl}_3$ -LiCl-NaCl melts, which is shown for comparison in Figure 12. Thus, the conductivity of the 52.0-48.0 mole %  $\text{FeCl}_3$ -NaCl melt is  $\sim 10\%$  higher than the conductivity of the 52.0-24.0-24.0 mole %  $\text{AlCl}_3$ -LiCl-NaCl melt at the same temperature. This difference increases to  $\sim 16\%$  for the 56.0-44.0 mole % melt, and becomes as high as  $\sim 25\%$  for the 64.0-36.0 mole %  $\text{FeCl}_3$ -NaCl melt when its conductivity is extrapolated to lower temperatures.

The reproducibility of our conductivity measurements on the  $\text{FeCl}_3$ -NaCl melts was not very good. The platinum electrodes in the conductivity cells were attacked by the melt. The cause of this problem is not clear. The  $\text{FeCl}_3$  used to prepare our melts (Alfa-Ventron, anhydrous) was distilled in vacuum before use, but some residual oxychloride or  $\text{FeCl}_2$  may have been still present in the purified product.

The  $\text{FeCl}_3$ -NaCl melts appear to be promising only for batteries in which  $\text{FeCl}_3$  is used as a cathode material. The important drawback of these melts is their high liquidus temperature. It is expected, however, that this drawback can be minimized by introducing a third component, such as another alkali chloride, into the  $\text{FeCl}_3$ -NaCl system.

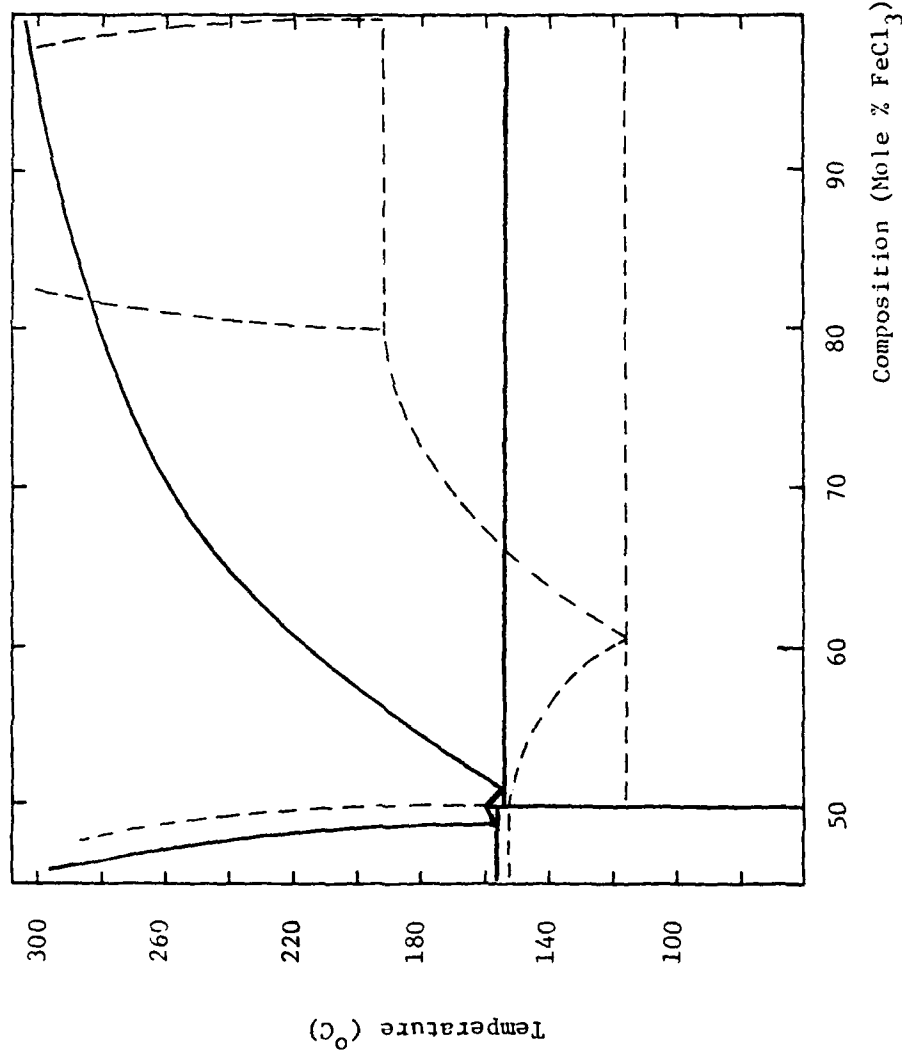


Figure 11. Phase Diagrams of the FeCl<sub>3</sub>-NaCl System (Full Line) and AlCl<sub>3</sub>-NaCl System (Dashed Line).

Table 31

Specific Conductivity Data for  $\text{FeCl}_3$ -NaCl System at 1.0 KHz

Composition: 52.0 - 48.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 182.8               | 0.4318                                                         |
| 193.6               | 0.4611                                                         |
| 204.2               | 0.4901                                                         |
| 213.4               | 0.5157                                                         |
| 223.2               | 0.5420                                                         |
| 233.6               | 0.5682                                                         |
| 244.0               | 0.5953                                                         |
| 253.6               | 0.6196                                                         |
| 263.7               | 0.6477                                                         |
| 273.2               | 0.6686                                                         |
| 286.0               | 0.6997                                                         |
| 298.2               | 0.7290                                                         |
| 310.4               | 0.7579                                                         |
| 320.2               | 0.7794                                                         |
| 330.1               | 0.7986                                                         |
| 337.1               | 0.8148                                                         |
| 348.2               | 0.8389                                                         |

Table 32

Specific Conductivity Data for  $\text{FeCl}_3$ -NaCl System at 1.0 KHz

Composition: 54.0 - 46.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 236.7               | 0.5462                                                       |
| 247.1               | 0.5715                                                       |
| 258.3               | 0.5984                                                       |
| 267.4               | 0.6201                                                       |
| 277.2               | 0.6428                                                       |
| 286.4               | 0.6635                                                       |
| 297.7               | 0.6895                                                       |
| 305.7               | 0.7072                                                       |
| 315.8               | 0.7309                                                       |
| 325.0               | 0.7524                                                       |
| 331.7               | 0.7654                                                       |
| 342.7               | 0.7869                                                       |

Table 33

Specific Conductivity Data for  $\text{FeCl}_3$ -NaCl System at 1.0 KHz

Composition: 56.0 - 44.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 232.0               | 0.4789                                                         |
| 249.0               | 0.5184                                                         |
| 260.2               | 0.5428                                                         |
| 276.4               | 0.5786                                                         |
| 289.2               | 0.6015                                                         |
| 302.4               | 0.6277                                                         |
| 308.7               | 0.6406                                                         |
| 316.2               | 0.6551                                                         |
| 326.2               | 0.6746                                                         |
| 333.1               | 0.6879                                                         |
| 341.5               | 0.7070                                                         |
| 346.8               | 0.7156                                                         |
| 350.8               | 0.7261                                                         |

Table 34

Specific Conductivity Data for  $\text{FeCl}_3$ -NaCl System at 1.0 KHz

Composition: 64.0 - 36.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 286.8               | 0.4443                                                         |
| 297.0               | 0.4612                                                         |
| 307.4               | 0.4779                                                         |
| 320.2               | 0.4986                                                         |
| 331.6               | 0.5177                                                         |
| 341.9               | 0.5311                                                         |
| 350.0               | 0.5436                                                         |

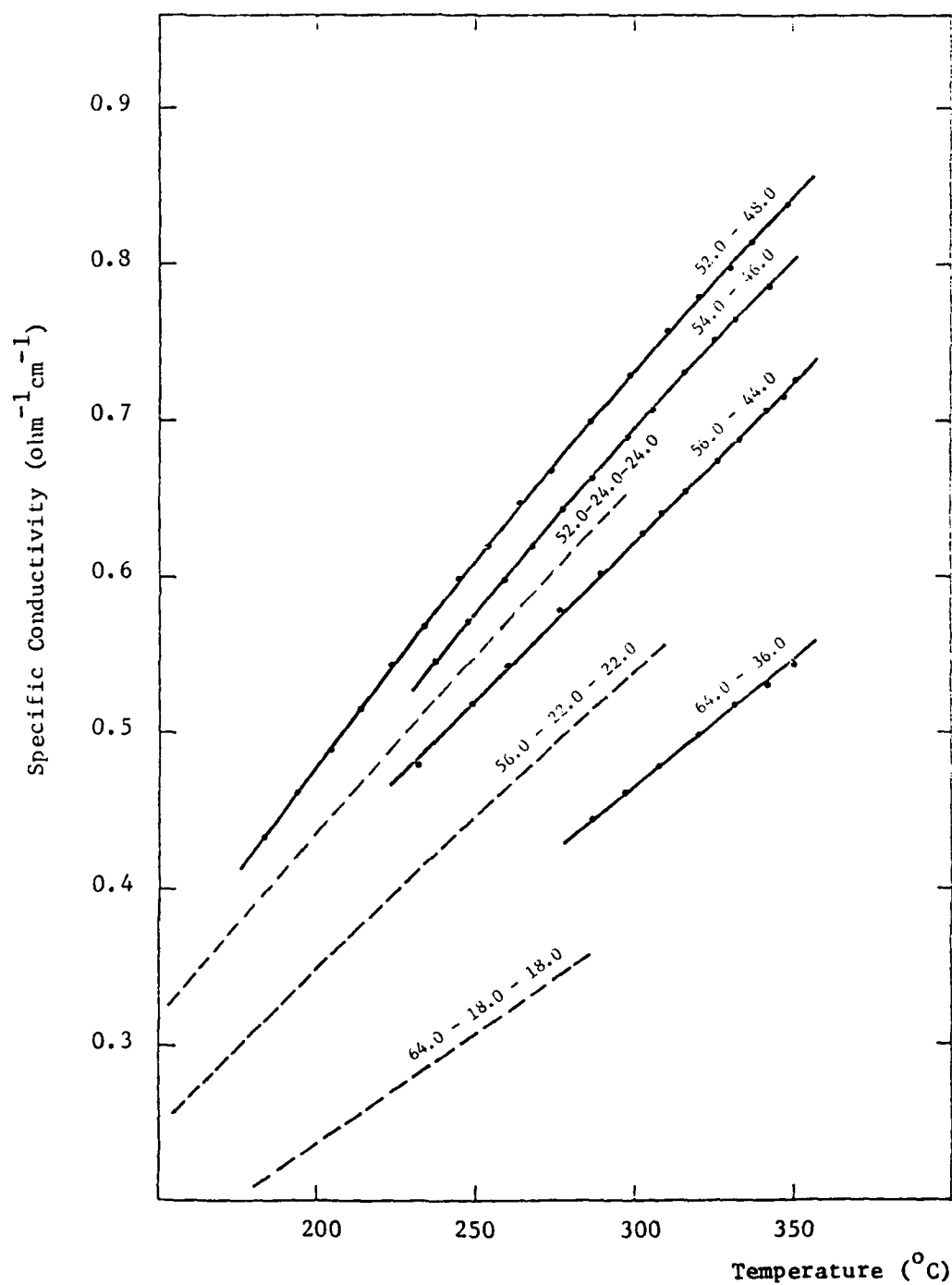


Figure 12. Specific Conductivity of FeCl<sub>3</sub>-NaCl System (Full Line) and AlCl<sub>3</sub>-LiCl-NaCl System (Dashed Line). Composition in mole % is indicated on the curves.

## XI. $\text{FeCl}_3$ -LiCl-NaCl SYSTEM

Our specific conductivity data for the  $\text{FeCl}_3$ -LiCl-NaCl system are listed in Table 35 and shown in Figure 13. The specific conductivity vs. temperature plot for the 56.0-22.0-22.0 mole % melt is virtually identical to the conductivity plot for the 56.0-44.0 mole %  $\text{FeCl}_3$ -NaCl melt, which is also shown in the same figure. The specific conductivity of the  $\text{FeCl}_3$ -LiCl-NaCl melt is, therefore,  $\sim 10\%$  higher than the conductivity of the 56.0-22.0-22.0 mole %  $\text{AlCl}_3$ -LiCl-NaCl melt at the same temperature (Figure 13).

The problem with impurities in the ferric chloride, discussed in the previous section, was even more evident during the present measurements. Since the conductivity measurements were extended to lower temperatures than in the case of  $\text{FeCl}_3$ -NaCl melts, the freezing out of the impurities in the conductivity cells was considerably more pronounced. As a consequence, not only the composition of the melt was changed, but the deposition of the solid phase in the conductivity cell was effectively changing the cell constant during the measurement. Therefore, the data obtained below  $220^\circ\text{C}$  were not reproducible and were discarded. Conductivity measurements on the other compositions of the  $\text{FeCl}_3$ -LiCl-NaCl melts were postponed until ferric chloride of better purity becomes available.

Liquidus temperatures in the  $\text{FeCl}_3$ -LiCl-NaCl system are visually estimated to be  $40$  to  $50^\circ\text{C}$  lower than in the  $\text{FeCl}_3$ -NaCl system at the equivalent compositions. The literature value for the eutectic temperature of the  $\text{FeCl}_3$ -LiCl-KCl system is as low as  $109$ - $110^\circ\text{C}$  (11, 12). The differential scanning calorimetry measurements on this system will be performed on the melts prepared with a better quality ferric chloride.

In summary, the liquidus temperatures of the  $\text{FeCl}_3$ -LiCl-NaCl system appear to be in approximately the same range as the liquidus temperatures of the  $\text{AlCl}_3$ -NaCl system. The specific conductivity of the  $\text{FeCl}_3$ -LiCl-NaCl system competes favorably with the conductivity of the  $\text{AlCl}_3$ -NaCl system. Moreover, ferric chloride is relatively inexpensive. Based on our preliminary results, therefore, the  $\text{FeCl}_3$ -LiCl-NaCl system is quite promising for batteries in which  $\text{FeCl}_3$  is used as a cathode material. However, this system clearly requires more study.

Table 35

Specific Conductivity Data for  $\text{FeCl}_3$ -LiCl-NaCl System at 1.0 KHz

Composition: 56.0 - 22.0 - 22.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 226.6               | 0.4681                                                       |
| 236.4               | 0.4911                                                       |
| 246.2               | 0.5126                                                       |
| 256.0               | 0.5363                                                       |
| 265.9               | 0.5569                                                       |
| 275.6               | 0.5754                                                       |
| 302.8               | 0.6380                                                       |
| 312.0               | 0.6572                                                       |
| 322.8               | 0.6766                                                       |

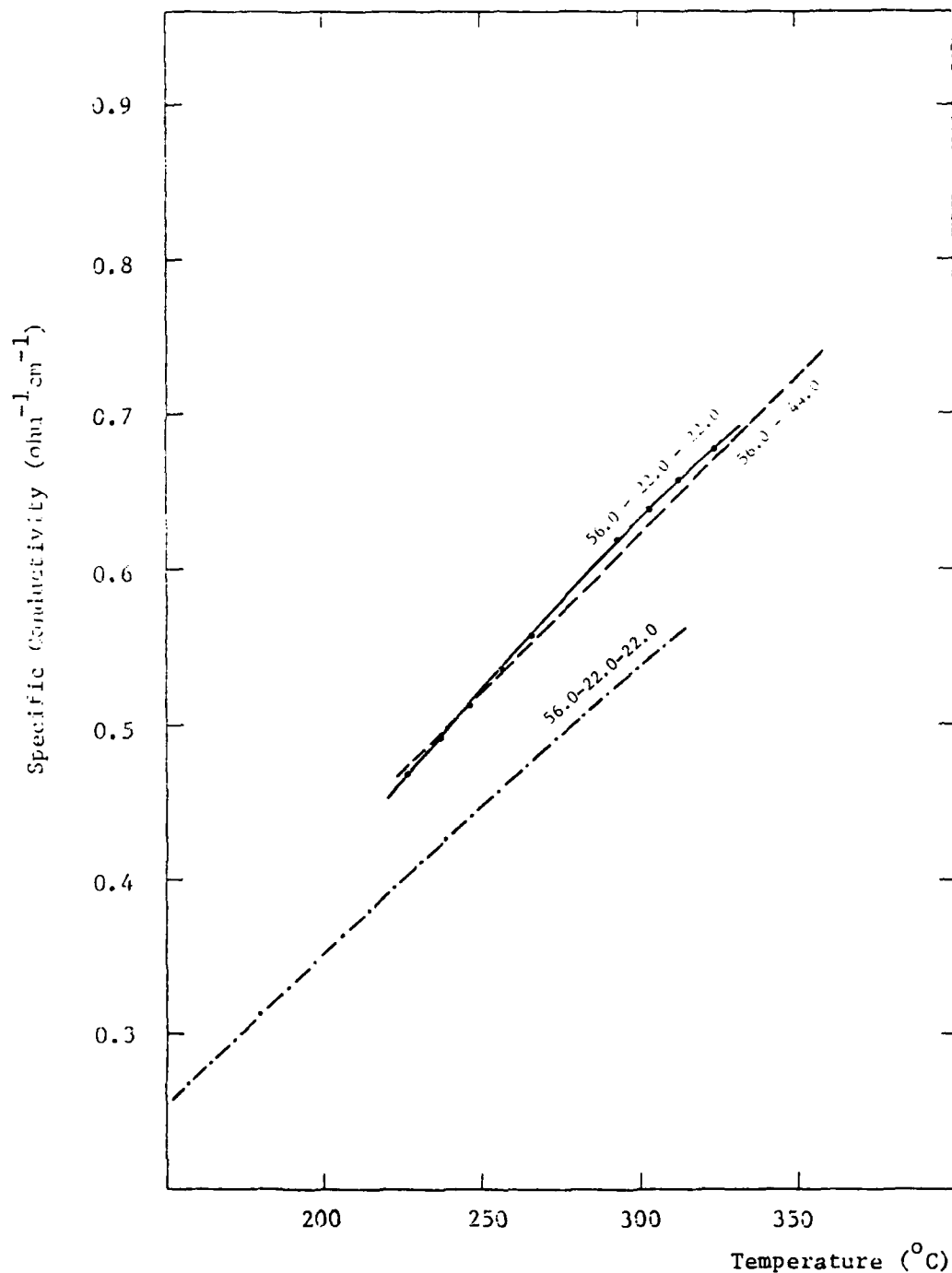


Figure 13. Specific Conductivity of  $\text{FeCl}_3$ - $\text{LiCl}$ - $\text{NaCl}$  56.0-22.0-22.0 Mole % Melt,  $\text{FeCl}_3$ - $\text{NaCl}$  56.0-44.0 Mole % Melt (Dashed Line) and  $\text{AlCl}_3$ - $\text{LiCl}$ - $\text{NaCl}$  56.0-22.0-22.0 Mole % Melt (Dot-dash Line). Composition in mole % is indicated on the curves.

## XII. $\text{GaCl}_3$ -NaCl SYSTEM

The phase diagram of the  $\text{GaCl}_3$ -NaCl system, based on the data of Fedorov *et al.*, (13) is shown in Figure 14. The most conspicuous difference between this phase diagram and the phase diagram of the  $\text{AlCl}_3$ -NaCl system, shown in the same figure, is that the 1:1 compound,  $\text{NaGaCl}_4$ , melts incongruently (solidus temperature  $238^\circ\text{C}$ , liquidus temperature  $\sim 450^\circ\text{C}$ ). The other important difference is the very low eutectic temperature of  $62^\circ\text{C}$  in the  $\text{GaCl}_3$ -NaCl system. However, due to the very low melting point of pure  $\text{GaCl}_3$  compared to  $\text{NaGaCl}_4$ , the eutectic composition is displaced to 95 mole %  $\text{GaCl}_3$ . As a consequence, the liquidus temperatures in this system are higher than in the  $\text{AlCl}_3$ -NaCl system in the melts with less than  $\sim 74$  mole %  $\text{GaCl}_3$ . In the 50 to 65 mole %  $\text{GaCl}_3$  region this difference is as high as  $70^\circ\text{C}$  or more. The low melting compositions of the  $\text{GaCl}_3$ -NaCl melts are between 90 and 100 mole %  $\text{GaCl}_3$ , *i.e.*, in the region where the volatility, as well as the acidity of the melts, is quite high.

Our specific conductivity data for the  $\text{GaCl}_3$ -NaCl system are listed in Tables 36 to 38 and shown in Figure 15. The conductivity *vs.* temperature plots are linear. The specific conductivity of the 70.0-30.0 mole %  $\text{GaCl}_3$ -NaCl melt is 15 to 20% higher than the conductivity of the 68.0-24.0-8.0 mole %  $\text{AlCl}_3$ -LiCl-NaCl melt, which has a comparable content of the acidic component. The conductivities for the  $\text{GaCl}_3$ -KCl,  $\text{GaCl}_3$ -RbCl and  $\text{GaCl}_3$ -CsCl systems, which are available in literature (14), are slightly lower. The substantial decrease of the conductivity in the melts with 80.0 and 90.0 mole %  $\text{GaCl}_3$  reflects a drop in the concentration of  $\text{Na}^+$  ions, which are presumably charge carriers in these melts.

Only high purity  $\text{GaCl}_3$  is commercially readily available at present and its cost is high. Perhaps the more important drawback, however, is the fact that the low melting ( $< 100^\circ\text{C}$ ) region of  $\text{GaCl}_3$ -NaCl melts is the narrow region above  $\sim 90$  mole %  $\text{GaCl}_3$ . This is the region of low specific conductivity as well as of high volatility, both undesirable melt properties from the battery use standpoint.

## XIII. CONCLUSIONS

On the basis of the phase diagram and specific conductivity data presented in this Report, four molten salt systems emerge as the most promising for battery applications:  $\text{AlCl}_3$ -LiCl-NaCl,  $\text{AlCl}_3$ - $\text{SbCl}_3$ -MCl

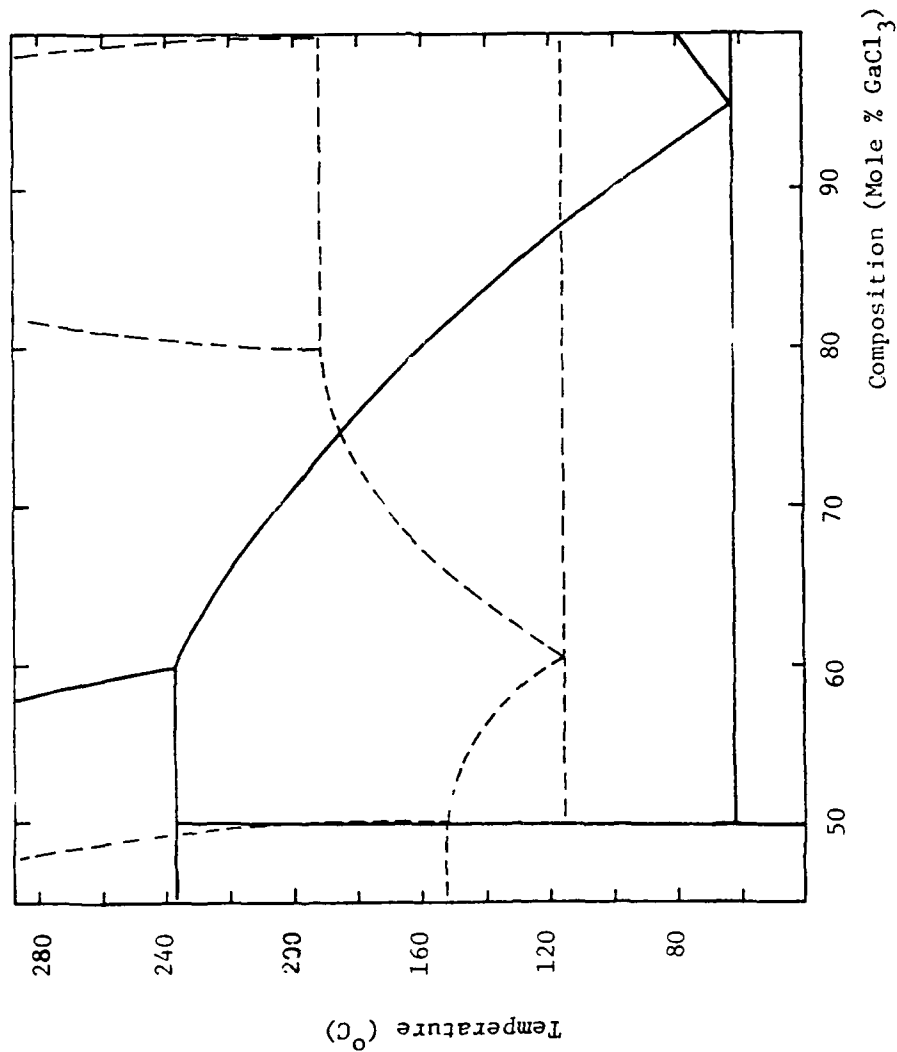


Figure 14. Phase Diagrams of the GaCl<sub>3</sub>-NaCl System (Full Line) and AlCl<sub>3</sub>-NaCl System (Dashed Line).

Table 36

Specific Conductivity Data for  $\text{GaCl}_3$ -NaCl System at 1.0 KHz

Composition: 70.0 - 30.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>(ohm <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------------|----------------------------------------------------------------|
| 158.1               | 0.1626                                                         |
| 165.3               | 0.1730                                                         |
| 172.0               | 0.1824                                                         |
| 179.5               | 0.1933                                                         |
| 186.1               | 0.2029                                                         |
| 193.7               | 0.2134                                                         |
| 200.5               | 0.2239                                                         |
| 211.5               | 0.2397                                                         |
| 219.2               | 0.2514                                                         |
| 227.6               | 0.2647                                                         |
| 237.0               | 0.2790                                                         |

Table 37

Specific Conductivity Data for  $\text{GaCl}_3$ -NaCl System at 1.0 KHz

Composition: 79.6 - 20.4 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 145.9               | 0.0946                                                       |
| 153.0               | 0.1009                                                       |
| 160.6               | 0.1075                                                       |
| 166.8               | 0.1130                                                       |
| 175.4               | 0.1206                                                       |
| 182.2               | 0.1265                                                       |
| 189.9               | 0.1332                                                       |
| 201.4               | 0.1428                                                       |
| 209.0               | 0.1503                                                       |
| 217.5               | 0.1584                                                       |
| 225.7               | 0.1668                                                       |

Table 38

Specific Conductivity Data for  $\text{GaCl}_3$ -NaCl System at 1.0 KHz

Composition: 90.0-10.0 (Mole %)

| Temperature<br>(°C) | Specific Conductivity<br>( $\text{ohm}^{-1}\text{cm}^{-1}$ ) |
|---------------------|--------------------------------------------------------------|
| 110.8               | 0.02618                                                      |
| 118.6               | 0.02859                                                      |
| 125.3               | 0.03075                                                      |
| 132.2               | 0.03292                                                      |
| 138.7               | 0.03498                                                      |
| 145.4               | 0.03706                                                      |
| 151.5               | 0.03902                                                      |
| 163.7               | 0.04174                                                      |
| 170.1               | 0.04368                                                      |
| 175.0               | 0.04533                                                      |
| 182.3               | 0.04789                                                      |
| 190.4               | 0.05063                                                      |
| 197.7               | 0.05326                                                      |
| 206.1               | 0.05689                                                      |
| 211.1               | 0.05886                                                      |
| 220.9               | 0.06328                                                      |

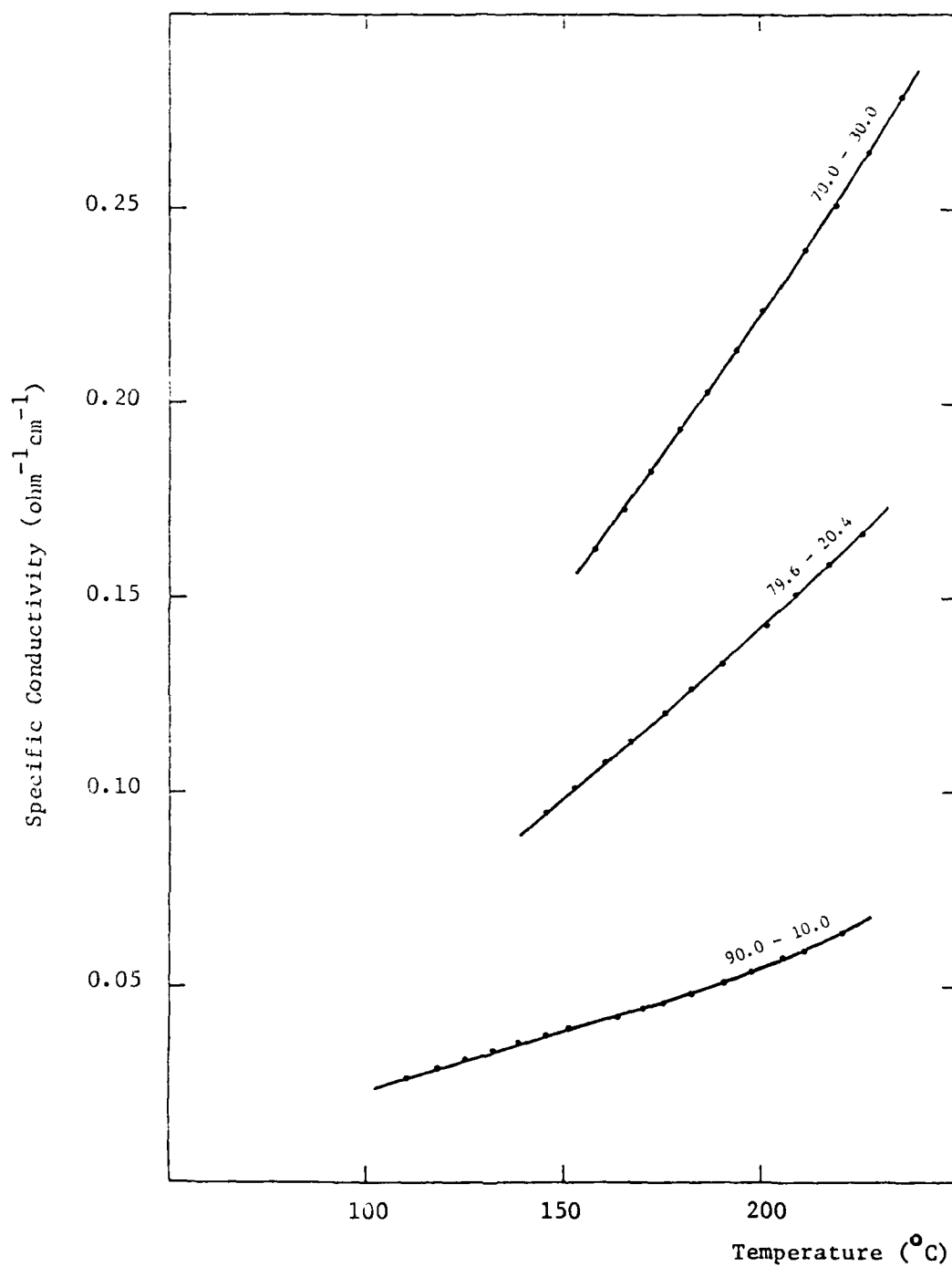


Figure 15. Specific Conductivity of  $\text{GaCl}_3$ - $\text{NaCl}$  System.  
Composition in mole % is indicated on the curves.

(where MCl stands for an alkali chloride),  $\text{FeCl}_3\text{-LiCl-NaCl}$  and, possibly,  $\text{AlCl}_3\text{-Bu}_4\text{NCl}$ .

The addition of LiCl to the binary  $\text{AlCl}_3\text{-NaCl}$  melts, the most widely used of the chloroaluminate melts, significantly lowers the liquidus temperature of these melts. The specific conductivity of the  $\text{AlCl}_3\text{-LiCl-NaCl}$  melts is not substantially lower than the conductivity of the  $\text{AlCl}_3\text{-NaCl}$  melts. Therefore, the  $\text{AlCl}_3\text{-LiCl-NaCl}$  system remains one of the most promising low melting molten salt systems for further study.

The  $\text{AlCl}_3\text{-SbCl}_3$  system is promising for use in batteries which employ  $\text{SbCl}_3$  as a cathode material. The liquidus temperatures in this system are low, and, considering the molecular character of the melt constituents,  $\text{AlCl}_3$  and  $\text{SbCl}_3$ , the specific conductivity of the  $\text{AlCl}_3\text{-SbCl}_3$  melts is relatively high. Compared to the conductivity of the  $\text{AlCl}_3\text{-LiCl-NaCl}$  melts in the same temperature range, however, the conductivity of the  $\text{AlCl}_3\text{-SbCl}_3$  melts is lower by a factor of five. Therefore, it is desirable to attempt to improve the specific conductivity of the  $\text{AlCl}_3\text{-SbCl}_3$  melts by adding another ionic component to these melts. The most promising  $\text{SbCl}_3$ -containing molten salt system for further study is probably  $\text{AlCl}_3\text{-SbCl}_3\text{-MCl}$ , where MCl is an alkali chloride.

The specific conductivity of the two  $\text{FeCl}_3$ -based molten salt systems is higher than the conductivity of the  $\text{AlCl}_3\text{-LiCl-NaCl}$  system. The liquidus temperatures in the  $\text{FeCl}_3\text{-LiCl-NaCl}$  system, the lower melting of the two  $\text{FeCl}_3$ -containing systems, appear to be in the same range as the liquidus temperatures in the  $\text{AlCl}_3\text{-NaCl}$  melts. The  $\text{FeCl}_3\text{-LiCl-NaCl}$  system, therefore, is quite promising for batteries which employ  $\text{FeCl}_3$  as a cathode material.

No data are presented in this report for the  $\text{AlCl}_3\text{-Bu}_4\text{NCl}$  system. In view of the low melting point of the pure  $\text{Bu}_4\text{NCl}$  salt and its strongly ionic character, as well as our experience with the  $\text{AlBr}_3\text{-R}_4\text{NBr}$  systems, the  $\text{AlCl}_3\text{-Bu}_4\text{NCl}$  system is probably the most promising system of the  $\text{AlCl}_3\text{-R}_4\text{NCl}$  type.

Further work on the present project will concentrate on the four molten salt systems singled out in this section.

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