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DIFFERENTIAL SCANNING CALORIMETRIC STUDY OF LOW MELTING ORGANIC CHLOROGALLATE SYSTEMS

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ABSTRACT

The thermal stabilities of mixtures of Ga_2Cl_6 with 1-butylpyridinium chloride (BPC) and 1-methyl-3-ethylimidazolium chloride (MEIC) have been investigated in the temperature range -65 to $+125\,^\circ$C. Solid-liquid transition temperatures along with enthalpies of fusion or glass transition data, determined by differential scanning calorimetry, are reported. MEIC based chlorogallate melts are found to possess lower phase transition temperatures than the corresponding BPC based melts. The liquidus range at room temperature for the MEIC based chlorogallate system extends from mole fraction $GaCl_3$, $N = 0.3$ to 0.8.

INTRODUCTION

Low melting chloroaluminate electrolytes have been investigated extensively for battery applications; see, for example, refs. 1 and 2. The major acid-base equilibria in Al_2Cl_6 and organic chloride mixtures, established by potentiometric, spectroscopic (Raman and IR) and thermal methods, can be represented by

$$2\ RCl + Al_2Cl_6 \rightleftharpoons 2\ R^+ + 2\ AlCl_4^- \qquad (1)$$

$$2\ AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad (2)$$

Gallium ($z = 31$), which lies directly below Al in Group III of the Periodic Table, might be expected to have a nonaqueous halide complex ion chemistry analogous to the haloaluminates, but relatively little is known concerning the molten salt physical and chemical properties of chlorogallates.

A general discussion of the application of thermal methods to molten salts has been given by Franzosini and Sanesi [3]. In this study, the melting points and thermal stabilities of mixtures of Ga_2Cl_6 with 1-butylpyridinium chloride (BPC) and 1-methyl-3-ethylimidazolium chloride (MEIC) are measured and compared to the known solid-liquid phase data for low melting organic chloroaluminate systems. Our interest in low melting chlorogallates relates to prospects for using these media for the electrodeposition of GaAs [4], an important III–V semiconductor for photocell or other electronic devices.

EXPERIMENTAL

The organic halides were prepared following published procedures [5,6]. Crystalline anhydrous gallium trichloride of 99.999% purity was obtained from Aesar in sealed ampoules. It was stored until use in a glovebox, in glass weighing bottles with ground glass stoppers and sealed with Parafilm. Various mixtures of Ga_2Cl_6 and BPC, or MEIC, have been found to be liquids at room temperature [7]. When Ga_2Cl_6 is mixed with BPC, or MEIC, an exothermic reaction occurs and slow gradual addition of Ga_2Cl_6 to either BPC or MEIC is required to control the exothermic reaction which results and to avoid melt decomposition. The chlorogallate melts when properly prepared are clear, colorless liquids. The compositions of these melts may be expressed as the mole fraction, N, of $GaCl_3$.

Melting points or glass transitions, along with overall thermal stability, were determined for the chlorogallate melts using a Perkin Elmer series 7 thermal analysis system. This system consisted of a Perkin Elmer (DSC-7) differential scanning calorimeter, a Perkin Elmer (7500) professional computer, a Perkin Elmer (TAC 7) instrument controller and a Perkin Elmer graphics plotter. Samples were contained in stainless-steel pans which were loaded in a glovebox with 10–40 mg of melt. After sealing the sample pans, they were stored in the glovebox until required for analyses. Each sample was scanned from $-65\,^\circ C$ to $125\,^\circ C$ at a fixed rate between 2 and $10\,^\circ C$ min^{-1}. (Samples usually were cooled at $-65\,^\circ C$ for 10–20 min before analysis). Unfortunately, the lowest temperature accessible experimentally ($-65\,^\circ C$) was too high to permit the determination of solid–liquid phase transition data for all the samples which were analyzed.

Differential scanning calorimetry studies were performed on samples from the two chlorogallate melt systems and the results are presented below. Each sample was analyzed at least twice (usually at different scan rates) to determine transition temperatures and overall thermal stability. All samples exhibited good thermal stability to $125\,^\circ C$ without any signs of decomposition.

RESULTS

DSC studies of BPC based melts

Chlorogallate melts based on BPC were investigated in the 0.3–0.68 mole fraction composition range. Table 1 contains a summary of DSC data for

TABLE 1

Summary of DSC data for acidic $GaCl_3$: BPC melts

Mole fraction	M.P. (° C)	ΔH ($J g^{-1}$)	Comments [a]
0.50	47	53.2	5 ° C min^{-1}
0.51	46	40.9	5 ° C min^{-1}
0.54	39	34.9	5 ° C min^{-1}
0.57	31	27.1	10 ° C min^{-1}
0.59	−2	23.9	CR, 5 ° C min^{-1}
0.62	12	8.8	CR, 5 ° C min^{-1}
0.65	Unknown	–	Inconclusive
0.68	6	–	Possible Tg

[a] Crystalline rearrangement (CR) or glass transition (Tg) occurs where indicated.

the acidic chlorogallate melts. For these melts, the melting points decrease with increased acidity and then rise slightly. Though no samples of mole fraction greater than 0.68 were analyzed by DSC, visual examination of such melts showed an abrupt rise in transition temperatures. In fact, the transition temperatures for very acidic melts quickly rose to over 40 ° C. Thus, the liquidus range for acidic melts at 40 ° C appears to extend from $N = 0.53$ to $N = 0.7$. Figure 1 depicts a typical DSC scan of a neutral $GaCl_3$: BPC melt. Of particular interest, the neutral melt ($N = 0.5$) exhibits the highest melting point for the range of these mixtures analyzed by DSC, and it yielded typical endothermic behavior for a melting point. Additionally, it is noted that a trend of decreasing enthalpies of fusion exists with increasing melt acidity in the acidic composition range. Though only one sample was analyzed between mole fractions 0.62 and 0.68, it is quite probable that the transition temperatures are well below room temperature and involve glass transitions.

Table 2 contains a summary of DSC data for basic $GaCl_3$: BPC melts. With increased basicity, the melting points decrease gradually. At 35 ° C, the liquidus range of this molten salt system extends from mole fraction 0.47 to 0.29. Visual observation of melts of composition less than $N = 0.30$ revealed

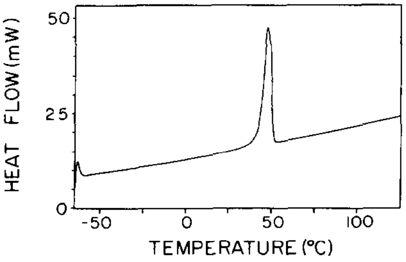

Fig. 1. DSC analysis of 30 mg $GaCl_3$: BPC ($N = 0.50$) at 5 ° C min^{-1}.

TABLE 2

Summary of DSC data for basic $GaCl_3$: BPC melts

Mole fraction	M.P. (° C)	ΔH (J g^{-1})	Comments [a]
0.49	46	47.5	5 ° C min^{-1}
0.46	34	62.8	10 ° C min^{-1}
0.43	32	67.1	DCR, 5 ° C min^{-1}
0.40	31	64.6	DCR, 5 ° C min^{-1}
0.37	32	57.1	DCR, 5 ° C min^{-1}
0.34	32	52.4	CR, 5 ° C min^{-1}
0.30	31	45.9	5 ° C min^{-1}

[a] Crystalline rearrangement (CR), double crystalline rearrangement (DCR).

that an abrupt increase occurs in transition temperatures. Of particular interest is the tendency of the basic melts to exhibit one or two exotherms, prior to the endothermic peaks that correspond to the solid–liquid phase transition. Figure 2 contains a DSC scan for a basic melt which exhibited two exotherms at −8 ° C and −30 ° C, which may involve crystalline/plastic rearrangements. This phenomenon is of interest because similar behavior does not appear to have been reported for the corresponding chloroaluminate systems. These apparent mesomorphic rearrangements exhibit typical exothermic behavior and, in general, they had a greater tendency to occur in the scans of basic than those of acidic chlorogallate melts (BPC and MEIC).

DSC studies of MEIC based melts

As anticipated, similar to BPC, MEIC when mixed with $GaCl_3$ also formed a molten salt. Chlorogallate melts based on MEIC were investigated in the mole fraction composition range 0.28–0.84. Table 3 contains a summary of DSC data for the acidic $GaCl_3$: MEIC melts. All chlorogallate melts in this system, from the neutral melt to $N = 0.81$, are liquids below room temperature. Comparison of the data in Tables 1 and 3 reveals that the

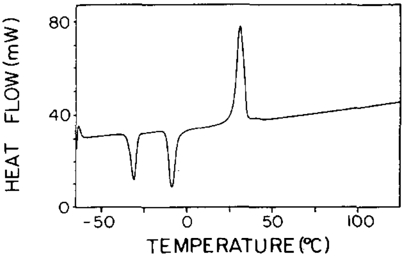

Fig. 2. DSC analysis of 41 mg $GaCl_3$: BCP ($N = 0.40$) at 5 ° C min^{-1}.

TABLE 3

Summary of DSC data for acidic $GaCl_3$:MEIC melts

Mole fraction	M.P. (°C) [a]	ΔH ($J\,g^{-1}$) [b]	Comments [c]
0.51	15	37.3	7°C min^{-1}
0.53	9	22.7	5°C min^{-1}
0.56	1	11.6	2°C min^{-1}
0.58	−3	12.4	5°C min^{-1}
0.60	−16	−0.87	Tg, 5°C min^{-1}
0.63–0.73	Unknown Tg (below −25)	– –	Inconclusive results
0.79	11		Tg, 5°C min^{-1}
0.81	21	−0.31	Tg, 7°C min^{-1}
0.84	49	−0.24	Tg, 5°C min^{-1}

[a] Glass transition temperatures provided when indicated. [b] For glass transitions Cp ($J\,g^{-1}$ $°C^{-1}$) provided. [c] Glass transition (Tg) occurs.

MEIC based acidic chlorogallate melts possess significantly lower transition temperatures (melting points or glass transitions) than corresponding BPC chlorogallate melts. This behavior is consistent with transition temperatures exhibited by MEIC based versus BPC based chloroaluminate melts [8]. Another interesting result is that all melts of $GaCl_3$ mole fraction greater than $N = 0.59$ exhibited glass transitions. Figure 3 illustrates a DSC analysis of an $N = 0.60$ melt. The glass transition at −16°C is a typical example of the endothermic behavior exhibited in the transitions of the higher acidity melts. Inconclusive results were obtained on analyses of melts between mole fractions $N = 0.62 - 0.74$. Most likely these melts exhibit glass transitions, but these could not be detected owing to the experimental constraint of not being able to cool the samples to below −65°C and/or insufficient cooling periods which precluded the liquids from glassing or freezing.

Of further interest, the acidic liquidus range at room temperature is significantly greater for this chlorogallate molten salt system than for the MEIC chloroaluminate system [8]. The melting point for a chloroaluminate

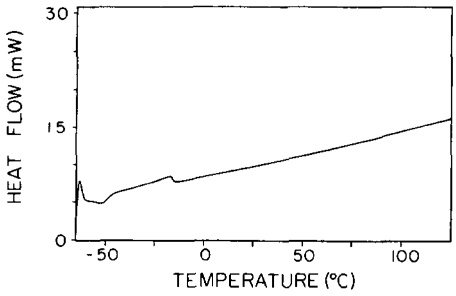

Fig. 3. DSC analysis of 18 mg $GaCl_3$:MEIC ($N = 0.60$) at 5°C min^{-1}.

TABLE 4

Summary of DSC data for basic $GaCl_3$: MEIC melts

Mole fraction	M.P. (°C)	ΔH (J g^{-1})	Comments [a]
0.50	15	40.9	5°C min^{-1}
0.47	11	25.6	5°C min^{-1}
0.45	7	14.9	5°C min^{-1}
0.44	4	41.3	CR, 5°C min^{-1}
0.42	3	40.1	CR, 5°C min^{-1}
0.41	1	40.7	CR, 4°C min^{-1}
0.39	6	39.4	CR, 5°C min^{-1}
0.36	1	1.4	10°C min^{-1}
0.34	Unknown		Inconclusive
0.32	15	3.1	4°C min^{-1}
0.28	39	20.6	CR, 5°C min^{-1}

[a] Crystalline rearrangement (CR) occurs prior to M.P.

melt (MEIC) at $N = 0.70$ is 79°C, while the corresponding chlorogallate melt is a liquid below room temperature and, even with further $GaCl_3$ addition, remains a liquid until $N = 0.80$. This greater acidic liquidus range, quite possibly, may allow the determination of gallium chlorocomplexes previously undetected in the liquid phase, e.g. $Ga_3Cl_{10}^-$ ion.

A summary of DSC data for basic $GaCl_3$: MEIC melts is contained in Table 4. Once again, the MEIC based chlorogallate melts in the basic regime possess significantly lower melting points than their BPC counterparts. Approximately one-half of the basic samples experienced exothermic transition behavior, believed to be due to some type of crystalline rearrangement. From the neutral regime to $N = 0.30$ the melts remained liquids at room temperature. With the exception of the most basic limit of the liquidus range, the highest melting points occurs for a neutral melt. Figure 4 contains a DSC analysis of a neutral melt. A sharp peak, indicating a melting point at 15.3°C, demonstrates typical endothermic behavior for the neutral melt. As the melt basicity is increased from the neutral regime, the melting points

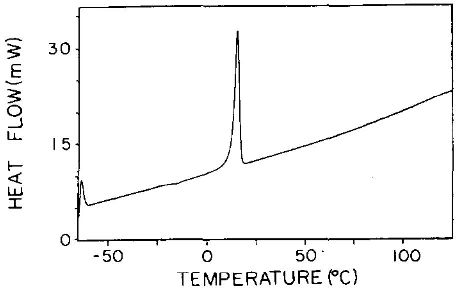

Fig. 4. DSC analysis of 20 mg $GaCl_3$: MEIC ($N = 0.50$) at 5°C min^{-1}.

gradually decrease until approximately mole fraction $N = 0.34$. The region from $N = 0.36$ to $N = 0.32$ quite possibly involves glass transitions. Unfortunately, these transitions could not be detected because of experimental difficulties in attaining the low temperatures required. At mole fractions lower than $N = 0.32$, the melting points begin to increase sharply with increase of basicity and the melts are no longer liquids at room temperature.

DISCUSSION

To develop a better overall view of the phase transitions involved in the chloroaluminate versus chlorogallate system, selected phase transition data for the MEIC based systems have been plotted in Fig. 5. The available phase transition data are plotted for mole fractions $N = 0.28$–0.84 and $N = 0.25$–0.73 for the $GaCl_3$: MEIC and $AlCl_3$: MEIC systems, respectively. Qualitatively, the solid–liquid phase diagrams are similar. In addition, these phase diagrams are similar to that reported for $AlCl_3$: 1-ethylpyridinium bromide and $AlCl_3$: 1-butylpyridinium chloride binaries [9]. Examination of the phase transition data for these room temperature molten salts reveals that these systems exhibit eutectic points near the $N = 0.33$ and $N = 0.66$ mole fraction compositions. In addition, within the $N = 0.33$ and $N = 0.66$ composition range there exists an apex of the liquid–solid phase diagrams at $N = 0.50$, the neutral melt composition. The apex (called the dystectic point) indicates compound formation. The composition corresponds to the com-

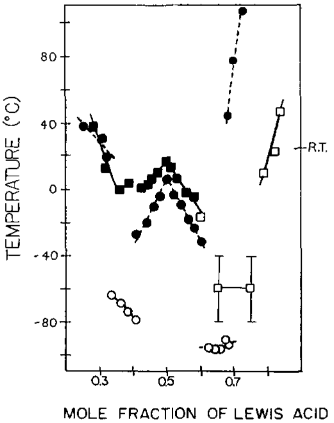

Fig. 5. Phase transition data for $AlCl_3$: MEIC (●), mp; (○), Tg and $GaCl_3$: MEIC; (■), mp; (□), Tg.

pound $RGaCl_4$, which is in accord with the changes in the major anionic species present in these melts, represented by the primary equilibria

$$2\ RCl + Ga_2Cl_6 \rightleftharpoons 2\ R^+ + 2\ GaCl_4^- \tag{3}$$

$$2\ GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^- \tag{4}$$

If the dystectic point (i.e. a maximum with congruent melting) is rounded, dissociation with melting is indicated. On the other hand, if the peak is "pointed" then the system remains largely associated when it melts. This phenomenon is well discussed in ref. 10. Additional support for the presence of two major anionic species, $GaCl_4^-$ and $Ga_2Cl_7^-$, has been obtained by Raman vibrational spectroscopy [4].

In conclusion, from the eutectic points that occur in the DSC study of these chlorogallates, similar acid–base complex chemistry to that of the chloroaluminates is inferred. The presence of exotherms, presumably due to crystalline rearrangements, found in basic chlorogallate melts is not well understood at present. Lower melting temperatures for the very acidic Ga_2Cl_6 melts over those for Al_2Cl_6 based systems may reflect in part the lower melting point of the former (Ga_2Cl_6 m.p. = 77.9 ° C; Al_2Cl_6 m.p. = 190 ° C at 2.5 atm).

Metal chlorides in Groups other than III also form room temperature liquids, e.g. chlorocuprates [11], chloroborates [12]. DSC measurements are of value to assess both complex chemistry and phase properties of these interesting room temperature ionic solvent systems.

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REFERENCES

1 H. Li Chum and R.A. Osteryoung, in D. Inman and D.G. Lovering (Eds.), Ionic Liquids, Plenum Press, New York, 1981, p. 407.
2 C.L. Hussey, in G. Mamantov and C.B. Mamantov (Eds.), Advances in Molten Salt Chemistry, Elsevier, New York, 1983, Vol. 5, p.185.
3 P. Franzosini and M. Sanesi, in D.G. Lovering and R.J. Gale (Eds.), Molten Salt Techniques, Vol. 1, Plenum Press, New York, 1983, p. 177.
4 S.P. Wicelinski, Ph.D. Thesis, Louisiana State University, 1987.
5 R.J. Gale, B. Gilbert and R.A. Osteryoung, Inorg. Chem., 17 (1978) 2728.
6 J.S. Wilkes, J.A. Levisky, R.A. Wilson and C.L. Hussey, Inorg. Chem., 21 (1982) 1263.
7 S.P. Wicelinski, R.J. Gale and J.S. Wilkes, J. Electrochem. Soc., 134 (1987) 262.
8 A.A. Fannin, D.A. Floreani, L.A. King, J.S. Landers, B.J. Piersma, D.J. Stetch, R.L. Vaughn, J.S. Wilkes and J.L. Williams, J. Phys. Chem., 88 (1984) 2614.

9 F.H. Hurley and T.P. Wier, J. Electrochem. Soc., 98 (1951) 203; C.D. Desjardins, R.S. Salter, T.G. Cadger and E.J. Casey, in M. Blander, D.S. Newman, G. Mamantov, M.-L. Saboungi and K. Johnson (Eds.), Proc. Fourth Int. Symp. Molten Salts, The Electrochemical Society, Pennington, NJ, 1984, Vol. 84-2, p. 146.
10 A. Findlay, in A.N. Campbell and N.O. Smith (Eds.), The Phase Rule and its Applications, Ninth Edn., Dover Publications, 1951, p. 144.
11 J.R. Silkey and J.T. Yoke, J. Electrochem. Soc., 127 (1980) 1092.
12 S.D. Williams, J.P. Schoebrechts, J.C. Selkirk and G. Mamantov, J. Am. Chem. Soc., 109 (1987) 2218.