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FRANK J. SEILER RESEARCH LABORATORY

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HEAT CAPACITIES OF 1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE-ALUMINUM CHLORIDE MOLTEN SALTS

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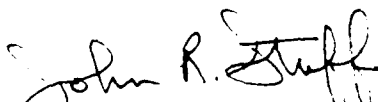89 9 25 074

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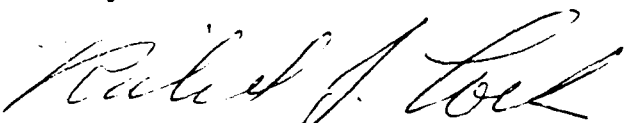
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Directorate of Chemical Sciences
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SUMMARY

A standard method for the determination of heat capacities using differential scanning calorimetry is described. The heat capacities for the molten salt system aluminum chloride/ 1–methyl–3–ethylimidazolium chloride ($AlCl_3$/MEIC) were determined over the composition range $0.30 < N < 0.65$, where N is the apparent mole fraction of aluminum chloride.

INTRODUCTION

The addition of aluminum chloride to 1—methyl—3—ethylimidazolium chloride results in the formation of a room temperature molten salt. (1) This ionic liquid has shown to be a useful electrolyte for battery applications. (2) In practical situations, batteries are often subjected to extremes in temperatures, knowledge of the electrolytes' basic thermal properties, such as melting point, decomposition temperature and heat capacity, may help to predict how a battery containing the electrolyte of interest will behave under such conditions. The molar heat capacity, C_p, is defined as the amount of heat needed to raise the temperature of one mole of a substance by one kelvin. It is a measure of a systems ability to store heat through the vibrational and rotational motion of chemical bonds and through the translational motion of atoms and molecules in the system. The use of a differential scanning calorimeter makes the measurement of heat capacities an easy task. In differential scanning calorimetry, a sample is subjected to a linear temperature program and the heat flow between the sample and a reference is recorded as a function of temperature. The heat flow into the sample is directly proportional to the samples' specific heat at that temperature. The displacement between the sample curve and the baseline is then proportional to the heat capacity. The displacement is given by the equation;

$$d = KC_pm(dT/dt) \qquad \text{Equation 1}$$

where K is a calibration constant, C_p is the heat capacity of the sample, m is the mass of the sample and dT/dt is the heating rate. (3,4) The calibration constant is determined by using a suitable standard.

EXPERIMENTAL

A typical run consists of two experiments. In the first a crimped sample pan is placed in the reference chamber and an uncrimped sample bottom and top are placed in the sample chamber. The baseline is scanned through a set temperature program. The temperature program contains an isothermal portion at the start of the run and at the end in order to establish the baseline. The sample top and bottom are then removed from the sample chamber and a known amount of sample placed into the pan which is then crimped under an inert atmosphere. The sample is then run through the same temperature program and the displacement at any point in the program is calculated by subtraction of the two curves. A suitable standard is run in the same way and the calibration constant calculated from Equation 1 using the known heat capacity of the standard.

The heat capacities of the ionic liquid $AlCl_3$/MEIC were measured at 25 °C over the composition range 0.30<N<0.65. The temperature program was isothermal for two minutes at 20 °C, 5 °C/min to 30 °C and hold at 30 °C for two minutes. Sample sizes ranged from 50 to 80 milligrams. A Perkin–Elmer DSC–7 differential scanning calorimeter with 7500 series computer was used for all experiments. Stainless steel sample pans were used for all runs. Glycerol was chosen as a standard material because of its low vapor pressure and known heat capacity at the temperatures of interest. Ethylene glycol was used as an "unknown" to check the accuracy of the method. Experimental values were within 1.00% of the literature value for ethylene glycol. The molecular weights of the melts were calculated from Equation 2;

$$M_b = M_m + M_a (N/1-N) \qquad \text{Equation 2}$$

where M_b is the molecular weight of the melt, M_m is the molecular weight of MEIC, M_a is the molecular weight of $AlCl_3$ and N is the apparent mole fraction of $AlCl_3$.

RESULTS AND DISCUSSION

Glycerol standards were run each morning of the study in order to calculate a calibration constant. A typical run with corresponding baseline is shown in Figure 1. The average value for 23 runs was 70.67 ± 1.87 (standard deviation). The average value of the heat capacity for three runs vs mole fraction aluminum chloride are given in Table 1. The data is graphed in Figure 2, where the error bars represent one standard deviation for the composition $N = 0.602$. Three samples of this melt were made and three runs made on each sample. The graph shows that for the basic compositions the heat capacities remain essentially constant. In the acidic range, the heat capacities increase with increasing acidity. This may be caused by the increase in the concentration of the $Al_2Cl_7^-$ which increases the degrees of freedom in the rotational and vibrational modes in the melt.
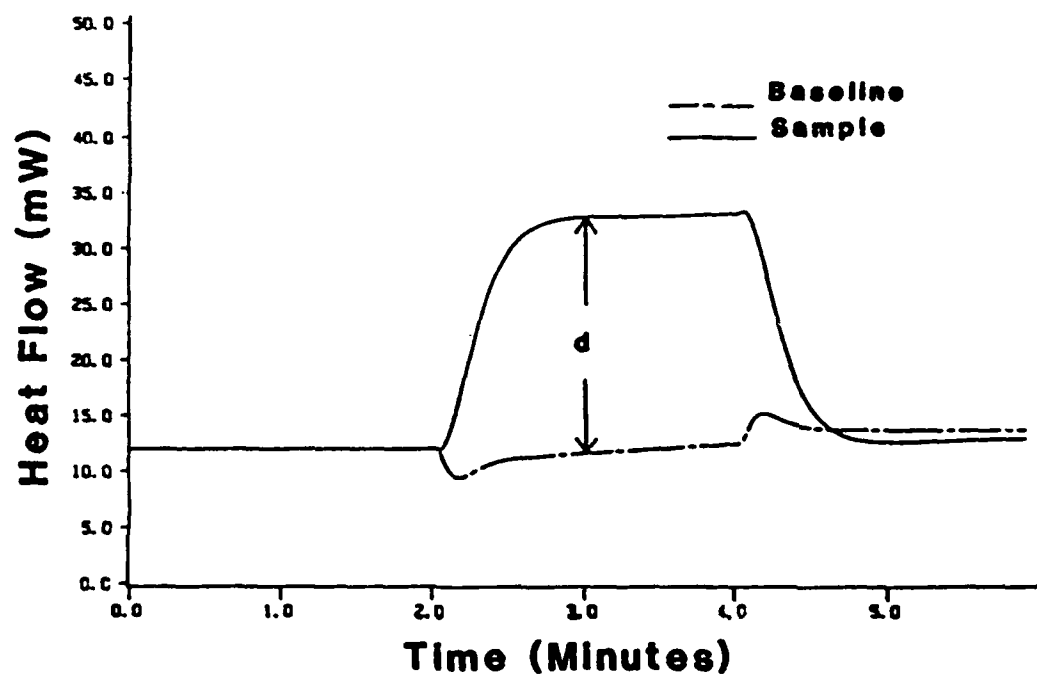
Figure 1: DSC Curve of Glycerol with Baseline

Table 1: Mole Fraction vs Heat Capacity

N	C_p (cal/mol/K)
0.3124	94.28
0.3438	95.26
0.3755	93.45
0.3973	96.86
0.4548	97.99
0.5000	102.19
0.5902	115.48
0.6016	119.40
0.6469	128.61
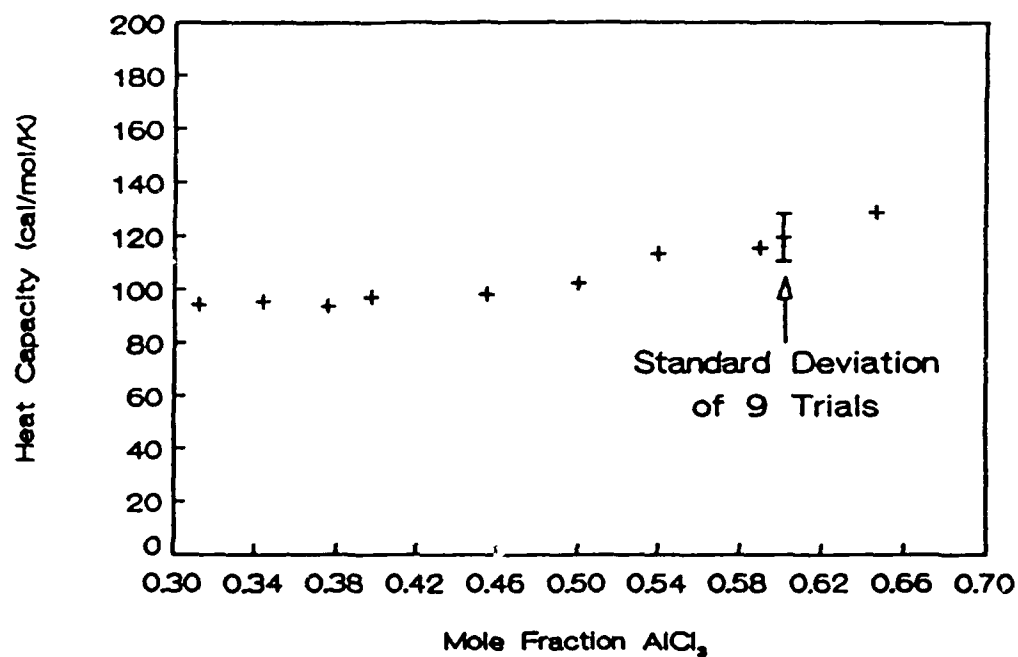
Figure 2: Heat Capacity vs Composition

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