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THERMAL STUDIES ON LITHIUM, SODIUM, POTASSIUM AND AMMONIUM MONOMETHYL VIOLURATES

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ABSTRACT

A study of the ammonium and some alkaline salts of monomethyl violuric acid by TG and DSC is described. These salts form hydrates in all cases and are, with some exceptions, very soluble in water.

INTRODUCTION

Monomethyl violuric acid (HAMV) is an excellent bidentate ligand capable of bonding through the 5-nitroso and 6-oxo groups in its transition metal complexes [1]; although, with the ammonium ions and alkaline metal ions, HMVA gives highly coloured salts. The study of these salts by TG and DSC is the aim of the present work.

EXPERIMENTAL

Monomethyl violuric acid (2,4-dioxo-6-hydroxy-1-methyl-5-nitrosol,2,3,4-tetrahydro-pyrimidine) was synthesized using the method described previously [2]. It was recrystallized in water and had a melting point of 202–203°C (dec.).

Lithium monomethyl violurate (LiAMV) was prepared by mixing an

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TABLE 1

Analytical and reflectance spectra data for some monomethyl violurate salts

Compound	Colour	Analysis (%)						Reflectance bands (cm^{-1})		
		Found			Calcd.					
		C	H	N	C	H	N			
HAMV	White	31.75	3.61	22.20	31.76	3.70	22.22	31.950	39.525	
LiAMV·H_2O	Pink	30.82	2.85	21.50	30.78	3.08	21.55	19.300	31.950	39.525
NaAMV·2 H_2O	Violet-red	26.71	3.50	18.59	26.20	3.49	18.34	18.100	31.950	39.525
KAMV·H_2O	blue	26.42	2.59	18.23	26.43	2.64	18.50			
NH_4AMV·0.5 H_2O	Violet-red	31.08	4.50	28.75	30.45	4.56	28.42	18.400	32.400	40.300

aqueous solution of lithium acetate with an aqueous solution of HAMV. The pink precipitate was collected on a filter and washed with ethanol. This procedure of preparation, filtration and washing was used for each of the salts.

Thermogravimetric analysis was carried out on a Mettler thermobalance Model TG 50 at a heating rate of 10°C min^{-1}, whereas the DSC runs were carried out on a Mettler differential scanning calorimeter Model DSC 20 at a heating rate of 5°C min^{-1}. The thermolytic reactions in air were run with samples varying in weight from 3.466 to 9.030 mg. The monomethyl violurates prepared, along with their elemental analysis and reflectance spectra data, are presented in Table 1.

RESULTS AND DISCUSSION

The TG and DSC plots of some monomethyl violurates are given in Figs. 1 and 2, respectively. The thermogravimetric results indicate that decomposition of these salts occurs in two steps: in the first, complete dehydration of the salts occurs; in the second, the anhydrous salts are completely decomposed to the metal oxide or metal carbonate.

Dehydration occurs in the temperature range 100–200°C. The observed weight losses in this temperature range are indicative of the hemihydrate (NH_4AMV), monohydrate (LiAMV and KAMV) and dihydrate (NaAMV) nature of these compounds. The expected endothermic behaviour for the dehydration process associated with these salts has been observed from DSC curves in the same temperature range.

The TG curve of monomethyl violuric acid (Fig. 1) shows that dehydration of the acid starts at 75°C and finishes at 130°C, yielding the stable anhydrous acid from 130 to 200°C. The experimental value for the weight loss (9.44%) agrees very well with the theoretical value (9.52%). The necessary energy for the elimination of this molecule of water (calculated by DSC) is 13.4 kcal mole^{-1}. Finally pyrolitic destruction of the pyrimidinic ring starts at 200°C and finishes above 600°C.

Lithium monomethyl violurate monohydrate becomes completely dehydrated in the temperature range 175–230°C. The observed weight loss along this temperature range (9.15%) corresponds to one molecule of water. The theoretical value calculated from this elimination (9.23%) is in good agreement with the experimental value. Elimination of this molecule of water requires 18.5 kcal mole^{-1}; this high value suggests that the water molecule is strongly linked to LiAMV. The anhydrous salt is very unstable and decomposes rapidly. At 700°C, the end of the determination, the residual weight is 15.5% of the original, which corresponds narrowly with the theoretical value required for Li_2O (15.24%).

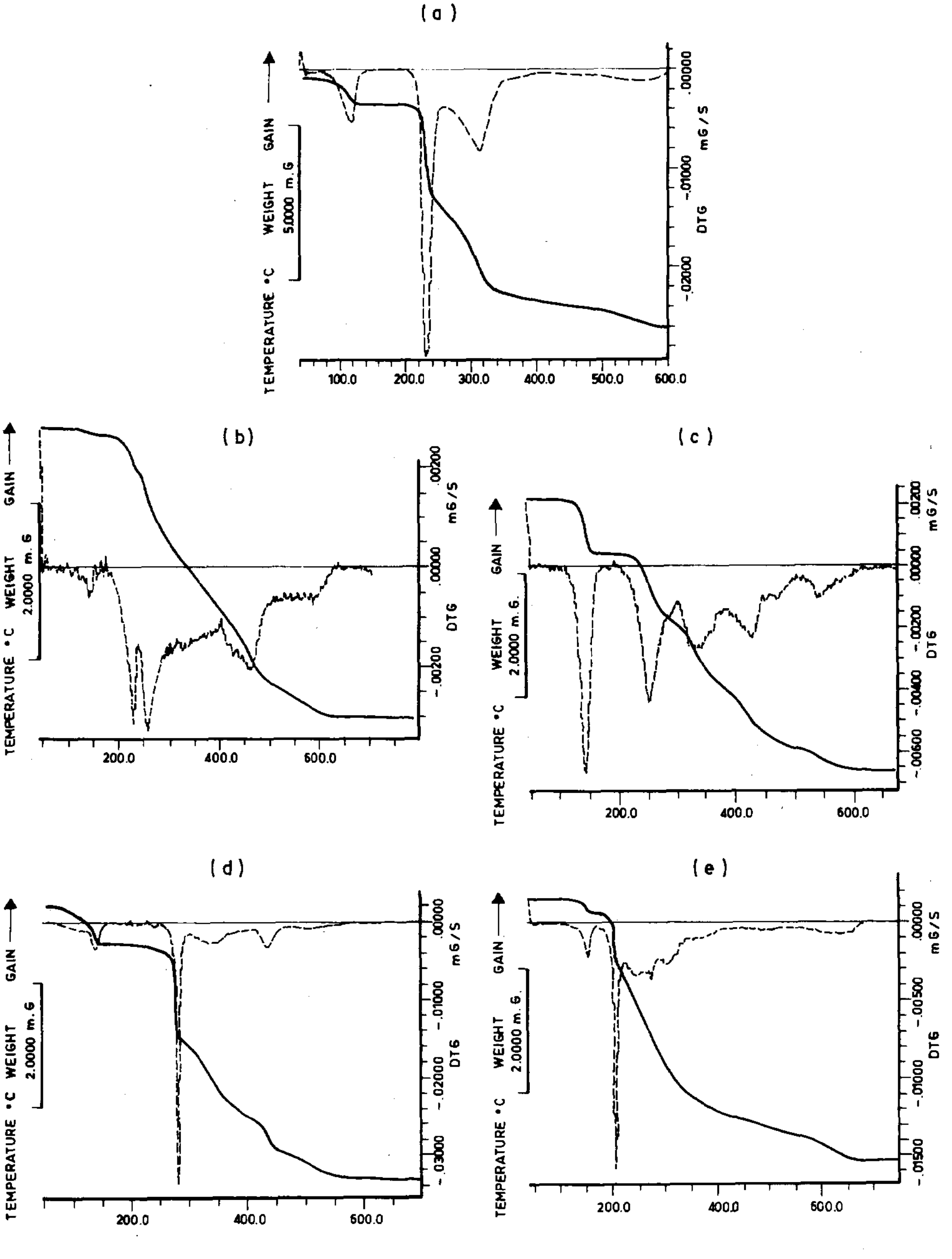

Fig. 1. TG and DTG plots of monomethyl-violuric acid (a), Li(AMV)·H_2O (b); Na(AMV)·2 H_2O (c); K(AMV)·H_2O (d); and NH_4(AMV)·0.5 H_2O (e).

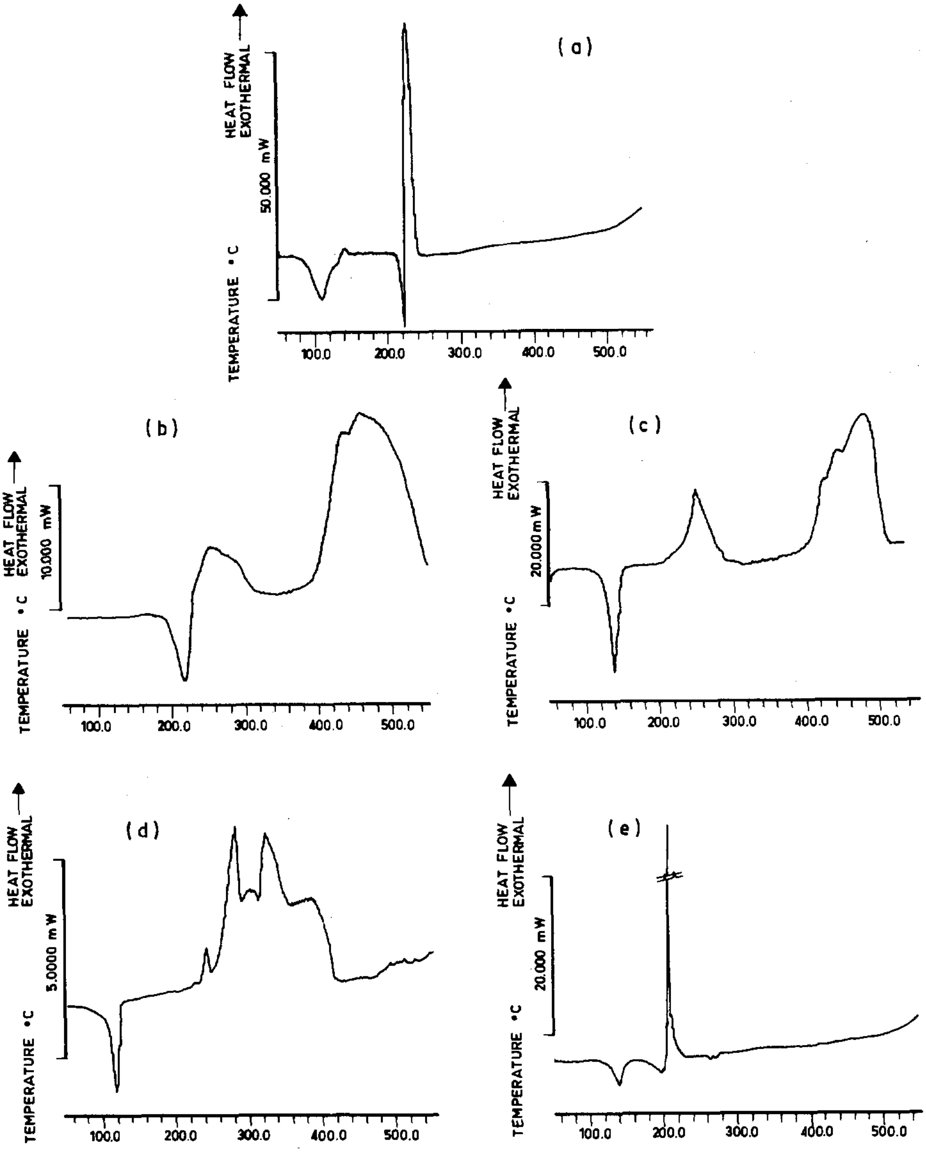

Fig. 2. DSC curves of HAMV $\cdot H_2O$ (a); Li$(AMV)_2 \cdot H_2O$ (b); Na(AMV)$\cdot 2\ H_2O$ (c); K(AMV) $\cdot H_2O$ (d); and NH_4(AMV)$\cdot 0.5\ H_2O$ (e).

For sodium monomethyl violurate dihydrate, dehydration starts at 100°C and finishes at 160°C. In this temperature range the experimental weight loss is 15.43%, which corresponds to two molecules of water. The enthalpy of dehydration calculated from the corresponding DSC curve of Fig. 2 is 25.2 kcal mole^{-1}. The anhydrous salt is stable from 160°C to 210°C. A fast decomposition occurs between 210 and 305°C, followed by slow decomposition from 305°C to the end of the run at 700°C. The percentage weight of the residue at 700°C (22.9%) corresponds to Na_2CO_3.

The thermogravimetric curve of potassium monomethyl violurate monohydrate shows no weight loss until 70°C, at which point it loses 8.39% weight in one step at 160°C; this weight loss corresponds to the elimination of one molecule of water. The enthalpy of dehydration calculated from the DSC curve of Fig. 2 is 8.4 kcal $mole^{-1}$. The anhydrous salt is stable up to 260°C; from this temperature up to the end of the run a very rapid weight loss occurs. The final weight % is 29.64%, which is slightly less than the 30.44% required for the formation of K_2CO_3.

The thermal study of ammonium monomethyl violurate hemihydrate indicates that dehydration of this salt takes place in the temperature range 125–160°C. The observed weight loss in this temperature range is 4.80%, which is in good agreement with the theoretical value for the elimination of 0.5 molecules of water (4.57%). The dehydration enthalpy calculated for this elimination is 7.3 kcal $mole^{-1}$. The anhydrous salt is stable from 160 to 195°C. Between 195 and 205°C a rapid decomposition occurs, followed by slow decomposition at about 670°C. At this point total combustion of the salt occurs.

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