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PREPARATION AND PROPERTIES OF SOME SALTS OF PERFLUOROOCTANOIC ACID

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SUMMARY

The sodium, potassium, lithium, caesium, barium, calcium, silver, lead and ammonium salts of perfluorooctanoic acid were prepared. Their thermal stabilities, and some spectroscopic data are reported. An attempt is made to correlate some of these measurements with the properties of the metal ions or metals concerned.

INTRODUCTION

The use of perfluorocarboxylic acid salts as intermediates in the synthesis of other fluorinated compounds is well established [1,2,3]. More recently there has been a growing interest in the liquid crystal properties of long-chain perfluorocarboxylic acid salts, in particular the systems caesium perfluorooctanoate/water and lithium perfluorooctanoate/water [4].

It is therefore of some interest to examine the preparation and general properties of such salts. Work on some of these compounds has been carried out previously by Nakayama but no spectroscopic or thermal decomposition data was reported [5].

EXPERIMENTAL

Infrared spectra were measured with a Perkin Elmer 221 or 337 grating instrument. Samples were prepared as nujol mulls on sodium chloride plates. ^{13}C n.m.r. spectra were measured using a Perkin Elmer R32 spectrometer. Thermal gravimetric analysis was carried out using a Dupont Thermal Analyser, model 950.

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Preparation of Salts

The salts were prepared by neutralising aqueous or diethyl ether solutions of perfluorooctanoic acid with either a metal hydroxide or a metal carbonate.

1 Neutralisation by a metal hydroxide

In a typical experiment an aqueous suspension of perfluorooctanoic acid (0.5 g) was neutralised with an aqueous solution of sodium hydroxide using methyl red to indicate the point of neutrality. The salt was filtered off, washed with cold water, and recrystallised from hot water to give 0.51 g of product, m. 273-275°C, ie 97% yield. The potassium salt was prepared in a similar manner.

2 Neutralisation by a metal carbonate

This method was used for salts of barium, calcium, lithium, lead, caesium, silver and the ammonium ion. In a typical experiment lithium carbonate was added to a suspension of perfluorooctanoic acid (0.63 g) in water at 50°C until effervescence ceased and a slight excess of the carbonate remained. Water was removed under vacuum and the salt (0.62 g, 97% yield, m. 219-224°C) allowed to precipitate. Earlier work reported a melting point of 160-190°C.

A similar method was used to prepare the other salts except that in the case of the lead and ammonium salts the reaction was carried out in ether solution.

The melting points, yields and fluorine analysis of all the salts prepared are given in Table 1 below:

Table 1

Salt	mp °C	Yield %	Fluorine analysis % Found	 Theoretical
Li	219-224	97	68.10	67.85
Na	273-275	96	65.17	65.36
K	222-235	95	63.10	63.05
Cs	230d	86	52.08	52.19
Ba	230-240	92	60.94	59.19
Ca	145-155d	97	65.39	65.81
Ag	220-225	88	54.58	54.70
Pb	265-270	80	54.90	55.17
NH_4	157-165	97	64.88	66.12

The thermal stability of these salts was examined using thermal gravimetric analysis the results of which are presented graphically in Figures 1 and 2. In order to facilitate a comparison of the thermal stability of these salts the temperature at which 20% decomposition had occurred is given in Table 2 together with the percentage residue observed and the theoretical percentage residue assuming formation of the corresponding metal fluoride, except in the case of the silver salt which gives a residue of silver metal.

Table 2

Salt	20% decomposition temp °C		Ionic Radii	% Residue of perfluorooctanoates	
	Perfluoro-octanoates	Heptafluoro-butyrates[6]		Found	Theoretical
Li	341	-	0.060	4	6
Ba	320	275	0.135	20	18
Ca	320	-	0.099	10	9
Na	298	235	0.095	9	10
Pb	290	-	0.121	15	24
Ag	287	295	0.126	19	20
K	244	200	0.135	14	13
Cs	237	-	0.169	30	28
NH_4	167	185	0.148		

Some infrared and ^{13}C n.m.r. spectroscopic data of the salts are given in Table 3 below.

Table 3 Spectroscopic Data

Salt	νasym COO cm^{-1}	^{13}C of CO^2 *
Li	1647, 1675, 1698	158.29
Na	1692	158.45
K	1626, 1653, 1667	158.95
Cs	1623, 1658, 1689	158.09
Ba	1637, 1664, 1698	158.66
Ca	1653	158.36
Ag	1610	160.04
Pb	1684	163.71
NH_4	1637, 1698, 1727	159.84

* Chemical shift in p.p.m. downfield from T.M.S.

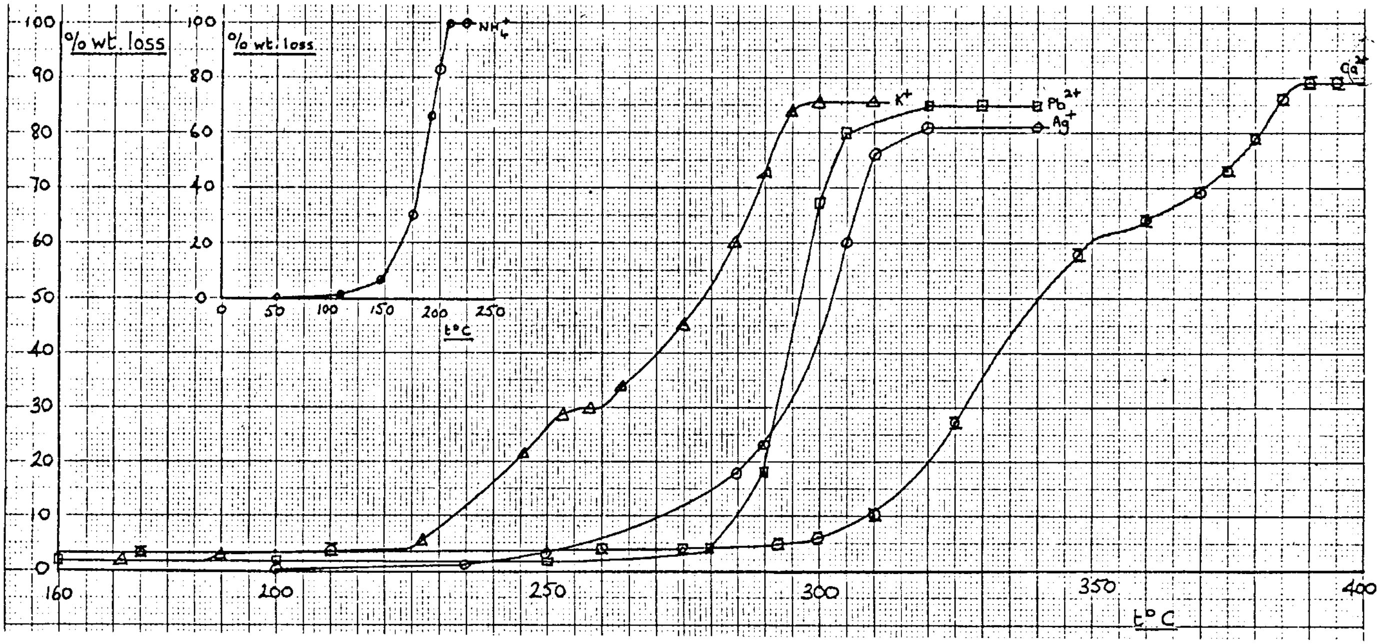

Fig. 1. Thermogravimetric analysis of salts of perfluorooctanoic acid

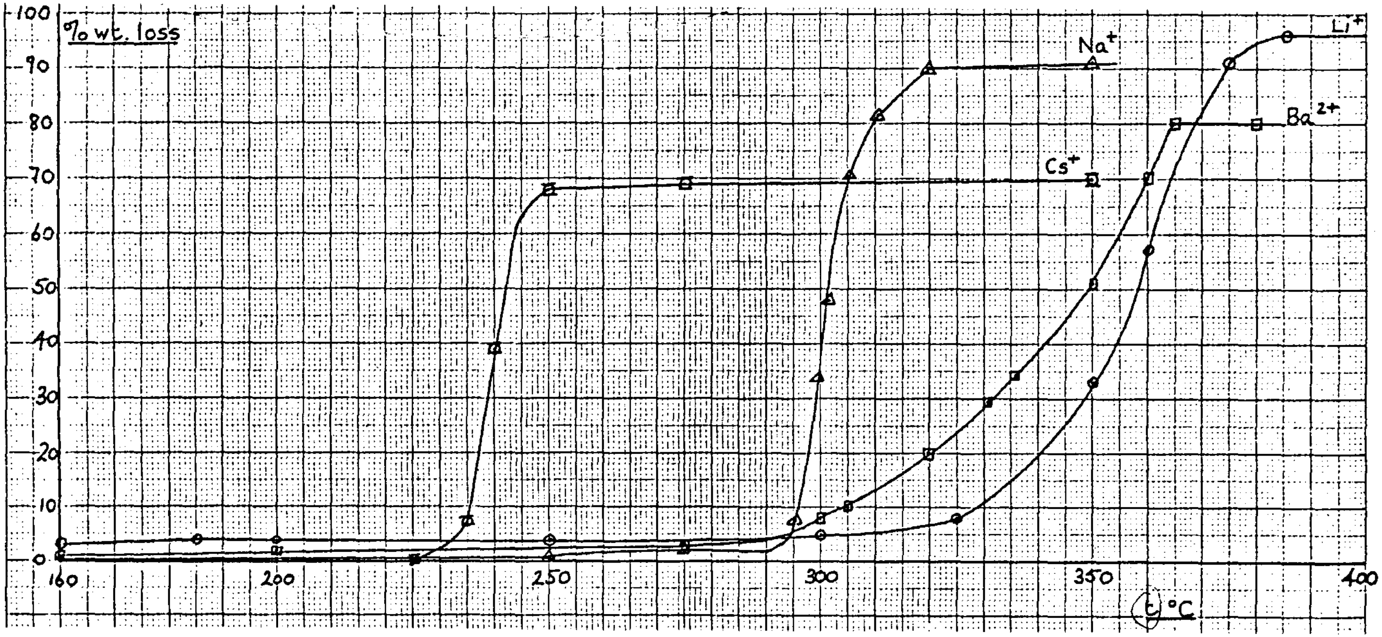

Fig. 2. Thermogravimetric analysis of salts of perfluorooctanoic acid

The Preparation of Mercury derivatives of perfluorooctanoic acid

Preparations in Toluene Solution

Yellow mercuric oxide (2.90 g, 13.39 m. mole) and perfluorooctanoic acid (5.0 g, 12.0 m. mole) were refluxed together in toluene (50 ml) until only a small amount of oxide remained unchanged. The solution was cooled and the excess mercuric oxide (0.35 g, 1.62 m. mole) removed by filtration. The solvent was removed from the filtrate by vacuum distillation to yield an off-white solid (7.3 g, m. 58°C. Found: C, 25.15; F, 40.57, $C_{15}H_7O_2F_{15}H_9$ requires C, 25.54; F, 40.44). Mass spectroscopic analysis revealed the following mast abundant peaks, assignments are given in brackets: 39 (C_3H_3); 51 (C_4H_3); 63 (C_5H_3); 69 (CF_3); 91 (C_7H_7); 100 (C_2F_4); 119 (C_2F_5); 131 (C_3F_5); 169 (C_3F_7); 181 (C_4F_7); 198, 199, 200, 201, 202, 204 (Hg); 289, 290, 291, 292, 293, 295 (HgC_7H_7). The ^{19}F n.m.r. spectrum exhibited the following bands downfield of the CF_3COOH standard: triplets at 4.0 p.p.m. and 38.5 p.p.m. and two broad multiplets centred at ∿ 44.8 p.p.m. and 49.0 p.p.m. The ^{1}H spectrum exhibited triplets at 2.35 and 7.15 p.p.m.

Preparation in Aqueous Solution

Sodium perfluorooctanoate (0.99 g, 2.28 m. mole) in water (50 cc) was cooled to 0°C and treated with an ice-cold solution of mercuric nitrate dihydrate (1.5 g, 4.14 m. mole) in water (5 cc). The resultant precipitate was separated by filtration, washed with ice-cold water to yield a white crystalline solid (1.08 g, m. 155-160°C. Found: C, 18.15; F, 49.57). Mass spectroscopic analysis revealed the following most abundant peaks: 69 (CF_3); 100 (C_2F_4); 119 (C_2F_5); 131 (C_3F_5); 231 (C_5F_9); 281 (C_6F_{11}); 331 (C_7F_{13}) typical of long-chain perfluoroalkyl groups together with a group of peaks around 270 and 370 having an Hg mass isotope pattern and due to $HgCF_3$ and HgC_3F_7 respectively. The ^{19}F n.m.r. spectrum further confirmed the presence of a C_7F_{15} group.

DISCUSSION

The data in Table 2 show that the order of thermal stability for the perfluorooctanoates is: $Li^+ > Ba^{2+} = Ca^{2+} > Na^+ > Pb^{2+} > Ag^+ > K^+ > Cs^+ > NH_4^+$; an overall trend which is paralleled by the work of Lazerte on the perfluorobutanoates [6]. With the exception of Ba^{2+} the decrease in thermal stability is in line with an increase in the ionic radii of the corresponding ions; from 0.06 nm in the case of lithium to 0.148 nm for the ammonium ion.

The percentage residue found, after pyrolysis, agrees in all cases, except for the lead salt, with the theoretical value. In the case of the lead salt a discrepancy of about 37% in the observed weight of the residue was observed. This is even less than would have been expected if the lead salt had decomposed to leave a residue of elemental lead. It is assumed that this loss is due to the formation of volatile perfluoroalkyl lead compounds. Such compounds have been synthesised [1]. Although no attempt was made to identify the volatile products, controlled pyrolysis may well be a useful synthetic route to such compounds.

The infrared absorption frequencies of the asymmetric COO stretching vibration of this series of salts all fall in the range 1610-1698 cm^{-1}, which is within the range previously postulated by other workers for salts of perfluorocarboxylic acids [7,8]. An interesting feature in the present study is the splitting of this absorption into a triplet for the salts of NH_4^+, Li^+, K^+, Cs^+ and Ba^{2+}. A similar splitting has been observed before for metal salts of stearic and lauric acids and a correlation observed between the atomic mass of the metal and the frequency of the asymmetric COO absorption [9,10]. In the present work no such correlation has been observed nor indeed with other simple properties of the metal and metal ions such as electronegativity, ionic radius or charge: radius ratio. Clearly the effect is a complex one and is to a large extent influenced by the nature of the metal carboxylate bonding as well as the site symmetry. The latter is only readily evident from X-ray data, although Deacon and Philips propose useful correlations between the difference $\nu asym\ (CO_2) - \nu sym\ (CO_2)$ and such bonding [8]. In the present work νsym could not be measured owing to overlap with extensive C-F absorption.

The ^{13}C n.m.r. data (Table 3) show a clear relationship between the chemical shift of the carboxyl carbon atom and the electronegativity of the metal in the salt. This is not unexpected since the greater the electronegativity of the metal the more the carboxyl carbon atom will be deshielded.

Attempts to prepare a mercury(II) salt of perfluorooctanoic acid in aqueous solution were unsuccessful even at 0°C. Some decarboxylation had evidently taken place. In toluene solution the reaction of mercury(II) oxide with perfluorooctanoic acid results in mercuration of the toluene to give a mixture of isomers of the compound $CH_3C_6H_4H_9OOC.C_7F_{15}$, as suggested by elemental analysis and spectroscopic data.

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