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Trioxomonofluorovanadates(V)

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Abstract

The isolation and characterization of salts of trioxomonofluorovanadate(V), $M^I_2VO_3F \cdot xH_2O$ where $M^I = Na^+$ ($x = 6$), K^+ ($x = 0.5$), NH_4^+ ($x = 1$), $\frac{1}{2}Ca^{2+}$ ($x = 0.5$), $\frac{1}{2}Mg^{2+}$ ($x = 0.5$), $\frac{1}{2}Ba^{2+}$ ($x = 1$) are described. The IR spectra of these compounds support the polymeric nature and existence of $-V-O-V-$ chains The TG data reveal a loss of water at around 80 °C. A comparison of the X-ray diffraction data for $K_2VO_3F \cdot 0.5H_2O$ with those for KVO_3 reveals the absence of KVO_3 in $K_2VO_3F \cdot 0.5H_2O$.

Introduction

Through conductometric titrations of the system M^IVO_3–M^IF ($M = Na^+$ and K^+) at different concentrations, the authors have found that these two reactants react in a 1:1 molar ratio. From an aqueous mixture of KVO_3 and KF in a 1:1 molar ratio, $K_2VO_3F \cdot 0.5H_2O$ has been isolated.

Earlier physicochemical studies [1] on the M^IVO_3–HF system ($M = K^+$ and NH_4^+) revealed the formation of $VO_2F_2^-$ and $HVO_2F_3^-$ ions in solution at molar ratios of 1:2 and 1:3 respectively of these two reactants, but the presence of the VO_3F^{2-} ion was not indicated.

We have isolated several trioxomonofluorovanadates with the general formulae $M^I_2VO_3F \cdot xH_2O$ ($M^I = Na^+$ K^+ and NH_4^+) and $M^{II}VO_3F \cdot xH_2O$ ($M^{II} = Ca^{2+}$, Ba^{2+} and Mg^{2+}). These were prepared by various methods and characterized by elemental analyses, solubility determinations, ion-exchange, thermogravimetry, X-ray and IR spectral studies.

Experimental

Ammonium metavanadate was prepared from vanadium pentoxide (Riedel-de Haen) according to Audrieth [2]. Potassium and sodium metavanadates were prepared by the reaction between ammonium metavanadate and the requisite amount of anhydrous K_2CO_3 or Na_2CO_3 in water followed by evaporation of the reaction mixture on a water bath. The products after recrystallization from water were dried to constant weight and analyzed. Potassium fluoride was fused in a platinum crucible before use. Other reagents were of AR grade.

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Vanadium, fluorine and nitrogen were estimated as reported earlier [3]. Sodium, potassium and calcium were determined by flame photometry (Systronics Digital Flame Photometer, FPM 125). Barium and magnesium were estimated gravimetrically as barium sulphate and magnesium pyrophosphate, respectively [4]. The analytical data are recorded in Table 1. Thermogravimetric analyses were undertaken in air up to a temperature of 500 °C in a manually operated apparatus, the rate of heating being maintained at 2° per min IR spectra were recorded using KBr discs on a Perkin-Elmer spectrophotometer over the range 400–4000 cm^{-1}.

Potassium trioxomonofluorovanadate, $K_2VO_3F \cdot 0.5H_2O$, was prepared by adding solid potassium fluoride (2.0 g) to a potassium metavanadate solution (4.8 g KVO_3 dissolved in 50 ml water). The resulting clear light yellow solution (pH 6.8) was evaporated on a water bath. Light yellow polyhedral crystals were separated from the concentrated solution. These were filtered, dried over fused $CaCl_2$ *in vacuo* to constant weight and analyzed.

The potassium compound was also obtained through the following procedures:

(a) The requisite amounts of KVO_3 and KF (1:1 molar ratio) were fused in a platinum crucible and the cold mass extracted into 2% aqueous KF solution. On concentrating the resulting solution over a water bath, a light yellow crystalline precipitate separated. This was filtered, dried as before and analyzed.

(b) A concentrated aqueous solution of $K_3V_2O_4F_5$ [5] was evaporated *in vacuo* over fused $CaCl_2$. After 3–4 d, light yellow crystalline substances were deposited on the walls of the vessel. The mother liquor was decanted off, the crystals filter pressed, dried as before and analyzed.

$Na_2VO_3F \cdot 6H_2O$, $(NH_4)_2VO_3F \cdot H_2O$, $MgVO_3F \cdot 0.5H_2O$ and $CaVO_3F \cdot 0.5H_2O$ were prepared by passing a concentrated aqueous solution of the potassium salt (1.5 g $K_2VO_3F \cdot 0.5H_2O$ dissolved in 25 ml water) through a cation-exchange resin (Amberlite IR-120 column in the Na^+, NH_4^+, Mg^{2+} and Ca^{2+} forms, respectively). The effluents were evaporated *in vacuo* separately in a desiccator over fused $CaCl_2$ for 4–5 d when light yellow sodium and ammonium salts and almost white calcium and magnesium salts were obtained. These were filter pressed, dried as before and analyzed. Barium trioxomonofluorovanadate, $BaVO_3F \cdot H_2O$, was isolated as a yellow precipitate on adding 5% aqueous $BaCl_2$ solution to a concentrated aqueous solution of the potassium salt. The precipitates were separated out immediately. These were filtered, dried and analyzed.

Results and discussion

Compounds containing VO_3F^{2-} groups are crystalline and non-hygroscopic solids, except the Mg and Ca salts which are slightly hygroscopic in air. The Mg salt decomposes slowly to a brownish mass on storing. The Na, K and NH_4 salts are highly soluble in water but insoluble in common organic

TABLE 1

Analytical and IR data for trioxomonofluorovanadates

Compounds	Found (Calcd.) (%)			IR spectral data[a]			
	N/M	V	F	ν(V=O)	ν(–V–O–V–)	ν(V–F)	ν(V–OH$_2$)
$Na_2VO_3F \cdot 6H_2O$	17.24 (16.91)	19.12 (18.75)	6.55 (6.99)	950(s)	730(s)	530(s)	870(s)
$K_2VO_3F \cdot 0.5H_2O$	38.36 (38.11)	25.67 (24.85)	9.39 (9.26)	970(s) 900–940(d)	690–760(b)	570(s)	850(m)
$(NH_4)_2VO_3F \cdot H_2O$	16.52 (16.23)	30.49 (29.65)	11.22 (11.05)	930(s)	700(m)	500(s) 550(w)	850(m)
$BaVO_3F \cdot H_2O$	51.10 (50.25)	19.21 (18.66)	7.13 (6.95)	930(s)	670–690(b)	500(s) 540(w)	840(s)
$CaVO_3F \cdot 0.5H_2O$	24.44 (23.95)	30.48 (30.54)	11.20 (11.38)	900(s)	670–720(b)	510(s)	840–850(b)
$MgVO_3F \cdot 0.05H_2O$	16.04 (16.06)	33.51 (33.71)	12.48 (12.56)	–	–	–	–
Na_2VO_3F	28.11 (28.05)	31.20 (31.10)	11.64 (11.59)	–	–	–	–
K_2VO_3F	39.87 (39.85)	25.92 (25.99)	9.67 (9.68)	980(s) 930–950(b)	670–730(b)	520(s)	–
$BaVO_3F$	53.80 (53.78)	20.05 (19.97)	7.45 (7.44)	–	–	–	–

[a] Observed frequencies in cm^{-1}; s = strong, m = medium, w = weak, b = broad, d = doublet.

solvents. These salts could not be recrystallised from water. After one week, a brown precipitate which is probably hydrated vanadic acid separated from the solution of the potassium salt. Barium and calcium salts are slightly soluble in water, their solubilities being 0.1841 and 0.0874 g l^{-1}, respectively, at 27 °C.

When an aqueous solution of the potassium salt was passed through a cation-exchange resin (Amberlite IR-120, H^+ form) column, the fluoride was obtained quantitatively as hydrofluoric acid in the effluent, while vanadium remained attached to the column and was subsequently eluted using 4 M HCl solution. This observation indicates that the potassium salt is hydrolyzed at low pH when it comes into contact with a cation-exchange resin (H^+ form). The complex ion, however, remained stable on a resin column in the Na^+ or NH_4^+ form (vide isolation). It was also observed that the VO_3F^{2-} ion remained completely absorbed on an anion-exchange resin (Dowex 21K, Cl^- form) column without any decomposition and was retained as such on subsequent elution with 1 M NaCl solution.

The thermograms of $K_2VO_3F \cdot 0.5H_2O$, $Na_2VO_3F \cdot 6H_2O$ and $BaVO_3F \cdot H_2O$ indicated that these substances were thermally stable up to 80 °C, after which they lost weight up to 450 °C, 460 °C and 360 °C, respectively. The rate of decomposition of the potassium salt was, however, very slow. The observed losses at these temperatures corresponded to the calculated values for the complete removal of the water molecules present in these compounds. Isothermal heating of the compounds was carried out at 450 °C, 460 °C and 360 °C, respectively and the corresponding anhydrous products were obtained. The complete removal of water from these compounds at such high temperatures reveals that such water was probably part of the coordinatively bonded molecules.

$(NH_4)_2VO_3F \cdot H_2O$ was stable up to 80 °C and then decomposed rapidly up to 450 °C. At around 450 °C the residue was brown and contained V_2O_5 contaminated with a lower valent oxide.

The powder X-ray diffraction photographs of $K_2VO_3F \cdot 0.5H_2O$ and KVO_3 were recorded using Ni-filtered CuK_α radiation. Such diffraction data ruled out the possibility of KVO_3 contamination in $K_2VO_3F \cdot 0.5H_2O$.

The IR spectral data of $M^I_2VO_3F \cdot xH_2O$ ($M = K^+, Na^+, NH_4^+, \frac{1}{2}Ca^{2+}, \frac{1}{2}Ba^{2+}$) and anhydrous K_2VO_3F are given in Table 1. The strong absorption band between 900–970 cm^{-1} was assigned to $\nu(V{=}O)$ [6, 7]. The characteristic $-V-O-V-$ bands [6–9], observed in the region 670–760 cm^{-1}, suggested that these compounds are probably polymeric in nature. The spectra also showed strong absorption in the 500–570 cm^{-1} region, probably due to $\nu(V-F)$ [6, 7]. In addition to the appearance of ν(OH)(stretching) and ν(HOH) (bending) frequencies at *c.* 3400 cm^{-1} and in the 1600–1650 cm^{-1} region, respectively, the potassium, sodium and barium compounds exhibited sharp absorption bands between 840–870 cm^{-1}, a diagnostic region for coordinated water molecules [10]. The TGA data (*vide supra*) of these compounds also supported the presence of coordinatively bonded water molecules. Anhydrous K_2VO_3F, did not show bands at *c.* 3400 cm^{-1}, 1600

cm^{-1} and in the 840–870 cm^{-1} region. The spectra of the ammonium salt showed characteristic ν(N−H) bands at *c*. 1400 cm^{-1} and 3200 cm^{-1} [10].

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