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SYNTHESIS, ION-EXCHANGE BEHAVIOUR AND ANALYTICAL APPLICATIONS OF STANNOUS FERROCYANIDE

SEPARATION OF Mg–Ca, Mg–Ba, Mn–Co, Mn–Ni AND Y–Th

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SUMMARY

Stannous ferrocyanide has been synthesized as an inorganic ion exchanger having an Sn:Fe ratio of 1:1 and a cation-exchange capacity of 2.03 mequiv./g (dry-weight). It is fairly stable in water and dilute solutions of acids, sodium and ammonium salts and reducing agents such as hydrazine sulphate, ascorbic acid and tartaric acid. Ion distribution studies of twenty-eight metals have been made on this ion exchanger, and on the basis of these studies five binary separations (Mg–Ba, Mg–Ca, Mn–Co, Mn–Ni and Y–Th) have been achieved on its column. Papers impregnated with stannous ferrocyanide have also been used for eighteen other separations. A tentative structure of this compound is proposed on the basis of chemical analysis, pH titrations, thermogravimetry, IR spectrophotometry and the aqueous chemistry of tin and the ferrocyanide ion.

INTRODUCTION

Metal ferrocyanides have been used as inorganic ion exchangers. Thus, the scavenging properties of nickel, copper, ferric and zinc ferrocyanides for the recovery of caesium from uranium fuel wastes have long been known[1–4]. BAETSLE *et al.*[5] discussed the exchange of ^{137}Cs with ferrocyanide molybdate, and gave some structural evidence based on X-ray studies. They also used[6] molybdenum and tungsten ferrocyanides for the separation of ^{137}Cs and ^{90}Sr from fission products in an acidic medium. Extensive sorption studies have been made of fission products such as Sr, Ce, Ru, Zr, Rb and Cs on potassium hexacyanocobalt(II)ferrate(II)[7], tungsten ferrocyanide[8,9], vanadium ferrocyanide[10,11] and titanium ferrocyanide[12]. Exchangers, more selective for ^{137}Cs, were prepared by replacing potassium with different amines[13] in potassium hexacyanocobalt(II)ferrate(II). Ferrocyanides mixed with organic resins have also received attention. Thus, Amberlite IRA-904 anion exchanger in the copper ferrocyanide form has been found[14,15] to be specific for ^{137}Cs and, therefore, has been used successfully for its isolation from sea-water. The

TABLE I

SOLUBILITY OF STANNOUS FERROCYANIDE IN DIFFERENT SOLVENTS

Solvent	*Solubility (mg/50 ml)*	
	Fe	*Sn*
Distilled water	0.105	0.11
0.1 M HCl	0.225	0.20
0.1 M H_2SO_4	0.30	0.24
0.1 M $HClO_4$	0.095	0.31
0.05 M HNO_3	0.01	0.00
0.1 M HNO_3	0.095	0.13
0.5 M HNO_3	0.135	0.128
1.0 M HNO_3	0.37	0.112
2.0 M HNO_3	0.40	0.272
5% $NH_2OH \cdot HCl$	0.125	0.27
1% Hydrazine sulphate	0.13	0.51
1% Ascorbic acid	0.135	0.34
1% Tartaric acid	0.155	0.36
1% Oxalic acid	0.17	0.61
1 M $NaNO_3$	0.025	0.04
1 M NaCl	0.012	0.04
1 M NH_4Cl	0.075	0.112
1 M NH_4NO_3	0.04	0.46
1 M $K_4Fe(CN)_6$	Almost complete dissolution of the exchanger; solution turns green and turbid	
1% Na_2SO_3	Complete dissolution	
1% Na_2CO_3	Complete dissolution	

TABLE II

DISTRIBUTION COEFFICIENTS OF METAL IONS ON STANNOUS FERROCYANIDE

Metal ions	*K_d (ml/g)*		*Metal ions*	*K_d (ml/g)*	
	Demineralised water	*0.05 M HNO_3*		*Demineralised water*	*0.05 M HNO_3*
Mg^{2+}	68.00	0.00	Cd^{2+}	2350	47
Al^{3+}	$>$ 5700	285	In^{3+}	269	46
Ca^{2+}	$>$ 9900	1500	Ba^{2+}	$>$9300	3100
Sc^{3+}	$>$ 6750	382	La^{3+}	$>$3000	1500
VO^{2+}	$>$11050	829	HfO^{2+}	$>$4000	$>$4000
Mn^{2+}	$>$11000	$>$11000	Hg^{2+}	$>$5800	550
Co^{2+}	$>$ 9800	$>$ 9800	Pb^{2+}	$>$9900	137
Ni^{2+}	$>$11500	$>$11500	Bi^{3+}	$>$5000	450
Cu^{2+}	$>$31000	37.5	Ce^{3+}	$>$6800	1625
Zn^{2+}	1357	18	Pr^{3+}	$>$7550	2450
Ga^{3+}	$>$ 6200	3100	Nd^{3+}	$>$8000	$>$8000
AsO_3^{3-}	0.00	0.00	Sm^{3+}	$>$6450	$>$6450
Y^{3+}	$>$ 9400	3100	Th^{4+}	$>$5400	33
Zr^{4+}	$>$ 1700	16	UO_2^{2+}	3800	3800

exchange of alkali metals has been studied on zinc and copper ferrocyanides[16,17]. VOL'KHIN *et al.*[18] used a mixed ferrocyanide, rubidium–nickel ferrocyanide, for the separation of rubidium and potassium. A rapid separation of sodium, potassium, rubidium and caesium has recently been achieved[19] by thin-layer chromatography on zinc ferrocyanide.

It is clear, therefore, that most of the work on metal ferrocyanides has been concentrated on the separation of alkali metals and fission products. They have not been used for the separation of common metal ions owing to their low stability. Their chief advantage is their high ion-exchange capacity. We showed recently[20] that stannic ferrocyanide has useful properties as an inorganic ion exchanger. However, it is not very stable. Stannous ferrocyanide is more stable, has a high ion-exchange capacity, and can be used for numerous column separations of metal ions. It has also been used in paper chromatography. The present report summarizes our studies on this ion exchanger.

EXPERIMENTAL AND RESULTS

Reagents and apparatus

Stannous chloride dihydrate and potassium ferrocyanide were obtained from B.D.H., Great Britain, and the other chemicals used were of reagent grade. Whatman No. 1 filter-paper was used in the paper chromatographic studies.

The spectrophotometry, X-ray studies, IR studies, pH measurements and thermogravimetry were performed using the Bausch and Lomb Spectronic-20 colorimeter, the Philips X-ray unit, the Perkin-Elmer Model 137 spectrophotometer and a Stanton thermobalance type H-4, respectively.

Synthesis, ion-exchange capacity and solubility

Stannous ferrocyanide precipitates were obtained at different pHs (0–10), component concentrations (0.02–0.25 M) and volume ratios of mixing (1:1, 1:2 and 2:1). The precipitates were digested at room temperature for 24 h, filtered, washed with water and then dried at 40°. They were immersed in water to give shiny blue particles. After drying, the particles were ground and screened into the desired mesh sizes. The solubilities of all the samples were determined[20] in water and in 0.1 M nitric acid by shaking 500 mg of the exchanger with these solvents at room temperature (30 ± 2°) for 6 h to attain equilibrium. The sample prepared by mixing a 0.05 M solution of stannous chloride (in 4 M hydrochloric acid) and aqueous potassium ferrocyanide, at pH 0.1 and in the volume ratio 1:1, was selected for further studies. Its ion-exchange capacity[20] was 2.03 mequiv./g (dryweight) and the Sn:Fe ratio[20] was 1. Its solubility in various solvents is given in Table I.

Distribution coefficients

The distribution studies were carried out for all metal ions by the batch process in the usual manner[20] after attaining equilibrium by shaking the metal solution with the exchanger beads for 6 h at room temperature. The K_d values observed in demineralized water and 0.05 M nitric acid are summarized in Table II.

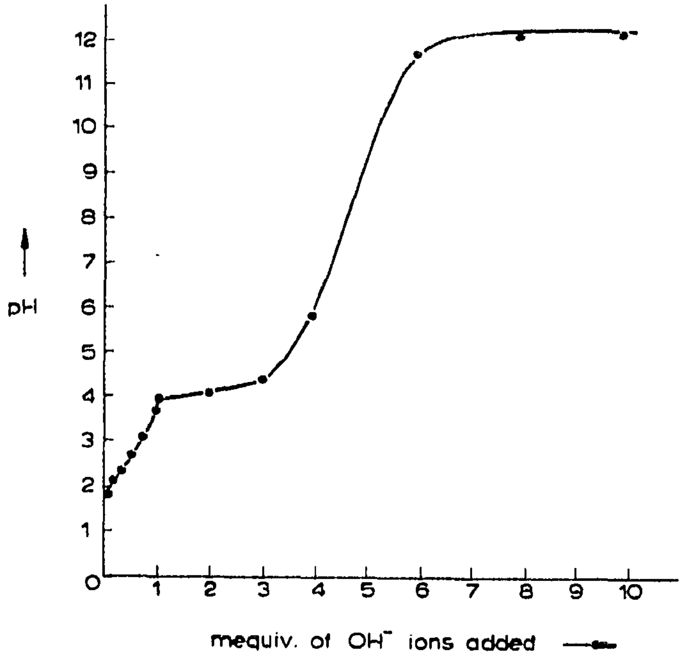

Fig. 1. pH titration graph for stannous ferrocyanide. Exchanger, 0.5 g; titrant, sodium hydroxide–sodium chloride solution.

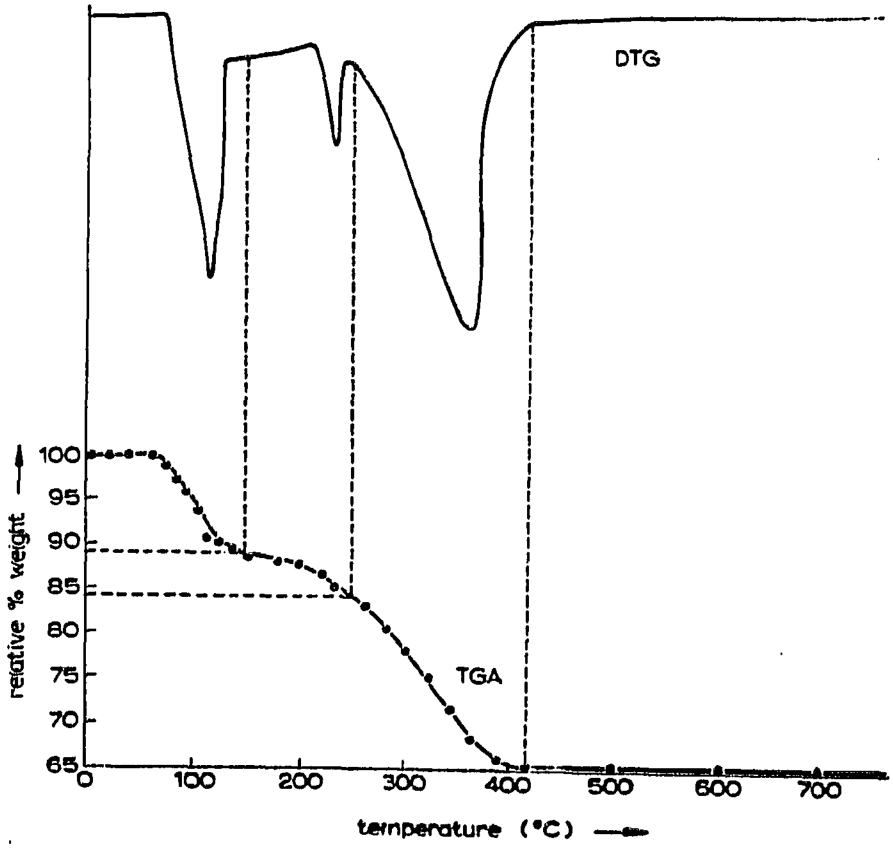

Fig. 2. Thermogravimetric (TGA) and differential thermogravimetric (DTG) curves for stannous ferrocyanide.

pH titrations, thermogravimetry, X-ray diffraction and IR spectrophotometry

pH titrations were performed by the method of TOPP AND PEPPER[21] (Fig. 1). For thermogravimetry the heating rate was set at 4°/min (Fig. 2). X-ray diffraction studies revealed that the exchanger is amorphous at room temperature and this behaviour applies up to 300°. It becomes poorly crystalline above 300°, and at 800° it gives a good X-ray pattern. The IR spectrum (Fig. 3) was obtained by the potassium bromide disc method.

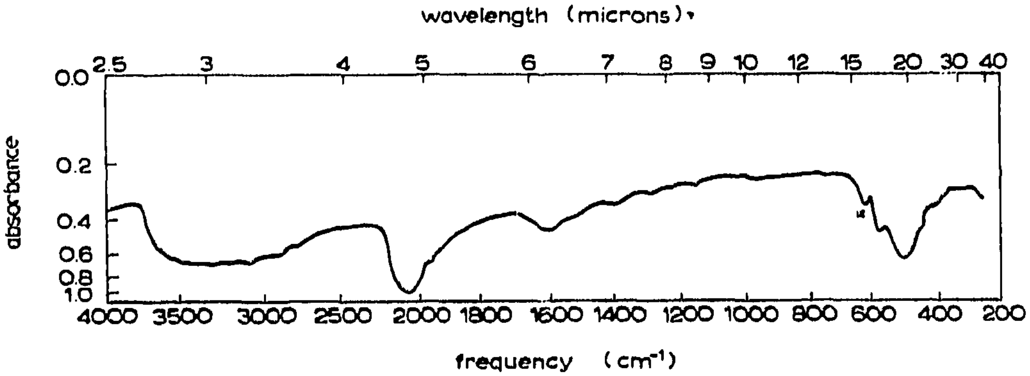

Fig. 3. IR spectrum of stannous hexacyanoferrate(II).

Separations on columns

On the basis of the K_d values, five separations were achieved on the column of stannous ferrocyanide by the usual method[22]. The details of the separations are summarized in Table III.

TABLE III

QUANTITATIVE SEPARATIONS OF METAL IONS ON COLUMNS OF STANNOUS FERROCYANIDE

Separation achieved	*Exchanger taken (g)*	*Metal ions taken + weight (μg)*		*Eluent*
Mg^{2+}–Ba^{2+}	1	Mg^{2+}	(94.815)	Mg^{2+}; 0.005 M HNO_3
		Ba^{2+}	(651.365)	Ba^{2+}; 0.1 M HNO_3
Mg^{2+}–Ca^{2+}	1	Mg^{2+}	(94.815)	Mg^{2+}; 0.005 M HNO_3
		Ca^{2+}	(202.404)	Ca^{2+}; 0.1 M HNO_3
Mn^{2+}–Co^{2+}	1	Mn^{2+}	(250.29)	Mn^{2+}; 1 M $NaNO_3$ + 0.1 M HNO_3 (1:1)
		Co^{2+}	(388.74)	Co^{2+}; 2 M HNO_3
Mn^{2+}–Ni^{2+}	1	Mn^{2+}	(250.29)	Mn^{2+}; 1 M $NaNO_3$ + 0.1 M HNO_3 (1:1)
		Ni^{2+}	(284.16)	Ni^{2+}; 2 M HNO_3
Th^{4+}–Y^{3+}	1	Y^{3+}	(257.82)	Y^{3+}; 1 M $NaNO_3$ + 0.1 M HNO_3 (1:1)
		Th^{4+}	(649.70)	Th^{4+}; 2 M HNO_3

Separations on papers

For paper chromatography of the metal ions, the paper strips were impregnated in the usual manner[23], first by dipping them in a 0.25 M solution of stannous chloride, drying and then dipping in a 0.25 M solution of potassium ferrocyanide. The excess reagent was washed away with distilled water and the strips were then dried and used as such. In Table IV are summarized the important binary separations

TABLE IV

BINARY SEPARATIONS ACHIEVED ON STANNOUS FERROCYANIDE PAPERS

Pairs of values in brackets are first the R_L value and then the R_T value.

Solvent systems	*Separations achieved*
0.1 M HNO_3 + 0.2 M NH_4NO_3 (2:1)	Ca^{2+} (0.82, 0.66)–Ba^{2+} (0.58, 0.32)
	Mg^{2+} (0.98, 0.84)–Sr^{2+} (0.40, 0.18)
	Mg^{2+} (0.92, 0.80)–Ba^{2+} (0.70, 0.34)
0.5 M HNO_3 + 2 M NH_4NO_3 (1:1)	Ca^{2+} (0.00, 0.00)–Sr^{2+} (0.93, 0.81)
	Cr^{3+} (0.00, 0.00)–Al^{3+} (0.96, 0.87)
	Ga^{3+} (0.87, 0.00)–Al^{3+} (1.00, 0.93)
	In^{3+} (0.21, 0.00)–Al^{3+} (1.00, 0.87)
	Zr^{4+} (0.21, 0.00)–Th^{4+} (0.93, 0.68)
	Ca^{2+} (0.00, 0.00)–Ba^{2+} (1.00, 0.93)
2 M HNO_3 + 2 M NH_4NO_3 (1:1)	Sb^{3+} (0.15, 0.00)–Pb^{2+} (1.00, 0.75)
	Cu^{2+} (0.25, 0.00)–Pb^{2+} (0.93, 0.75)
	Cd^{2+} (0.50, 0.03)–Pb^{2+} (1.00, 0.84)
	Ag^{+} (0.12, 0.00)–Pb^{2+} (0.93, 0.75)
	Hg^{2+} (0.25, 0.00)–Pb^{2+} (0.86, 0.62)
	As^{3+} (0.12, 0.00)–Pb^{2+} (1.00, 0.86)
	Ga^{3+} (0.40, 0.00)–Al^{3+} (0.97, 0.68)
4 M HNO_3 + 0.8 M $NaNO_3$ (1:1)	Ag^{+} (0.13, 0.00)–Tl^{+} (0.92, 0.34)
	Zr^{4+} (0.50, 0.00)–La^{3+} (1.00, 0.75)

achieved in some solvent systems, along with the R_L and R_T values of the migrating spots.

Thermal stability

Samples of the exchanger (1 g) were heated to different temperatures and their ion-exchange capacities were determined[20] to observe the effect of heat (Table V).

TABLE V

EFFECT OF HEAT ON THE ION-EXCHANGE CAPACITY OF STANNOUS FERROCYANIDE

Temperature (°C)	*Ion-exchange capacity (mequiv./g, dry weight)*	*Colour of beads*
40	2.03	Blue-black
100	2.03	Blue-black
200	0.54	Dirty black
300	0.12	Brownish black
400	0.00	Brown

DISCUSSION

Stannous ferrocyanide shows a high stability in aqueous and acidic solutions. It is clear from Table I that solutions of different salts such as $NaNO_3$, NaCl, NH_4NO_3 and NH_4Cl dissolve this ion exchanger to a negligible extent. Certain reducing agents, such as hydroxylamine hydrochloride, hydrazine sulphate and ascorbic acid, do not have any effect. However, the exchanger is decomposed by solutions of $K_4Fe(CN)_6$ (1 M), Na_2CO_3 (1%) and Na_2SO_3 (1%). It is more stable than stannic ferrocyanide;

the hydrous SnO_2 obtained by slow hydrolysis of the stannic salts is readily soluble[24] in acids and bases. Because of its comparatively high stability, stannous ferrocyanide has been used successfully in column and paper chromatography. As a result, five binary separations have been achieved on its column (Table III). Also, impregnated papers have been used for eighteen other separations of metal ions (Table IV).

Distribution studies (Table II) revealed that the exchanger has a high affinity for almost all metal ions in distilled water, with the exception of Mg^{2+} and In^{3+}. This may be due to the great tendency of ferrocyanide to form a large number of insoluble metal salts. When the interaction of various metal ions with ferrocyanide was observed under the experimental conditions, it was noticed that Al^{3+}, Cr^{3+}, Ca^{2+}, Ba^{2+} and Mg^{2+} do not form precipitates with potassium ferrocyanide. However, apart from Mg^{2+}, all these cations have high K_d values. The magnesium is anomalous probably as a result of its comparatively higher hydrated radius. With a decrease in pH (0.05 M nitric acid), the affinity of the exchanger for the metal ions generally decreases, which is in accordance with the normal behaviour of an ion-exchange material.

From the aqueous chemistry of ferrocyanides[25], it can be seen that in acidic solutions ferrocyanide exists according to the following equilibrium:

$$H_2Fe(CN)_6^{2-} \overset{H^+}{\rightleftharpoons} H_3Fe(CN)_6^- \overset{H^+}{\rightleftharpoons} H_4Fe(CN)_6$$

A small amount of Fe^{2+} is oxidized to Fe^{3+}, and prussian blue might have been formed, thus giving an octahedral network for the exchanger. Tin(II) exists[26] in the solution as:

$$3\ Sn^{2+} + 4\ H_2O \rightleftharpoons [Sn_3(OH)_4]^{2+} + 4\ H^+$$

As the solution at the time of mixing was highly acidic, the most probable species present would be Sn^{2+}. On mixing the two solutions at pH 0.1, a white gel was produced, which on digestion at room temperature for 24 h turned bluish in colour, probably owing to the formation of prussian blue. When the precipitates were dried at 40° for several days, they turned blue-black. A stable blue-black[27] SnO might have been formed at this stage, which perhaps could be incorporated into the network of prussian blue. Sn(II) has a lone pair of electrons unused in bonding, thus giving a ψ-octahedral geometry[27] to SnO. On the basis of the super-complex structures ascribed [28] to the ferrocyanides of Cu(II), Co(II), Ni(II) and Mn(II), the composition of stannous ferrocyanide may be represented as $Sn[SnFe(CN)_6]$. Treatment with dilute nitric acid converts it to the hydrogen form, which on chemical analysis gives an Sn:Fe ratio of 1:1. This suggests, therefore, that the Sn(II) represented outside the bracket is weakly bonded and is replaced by a hydrogen ion.

The IR spectrum (Fig. 3) of the compound shows sharp and strong peaks at 510, 590 and 2040 cm^{-1}, and a broad but strong peak at 3000–3500 cm^{-1}. The first two peaks correspond[29] to the stretching frequencies of Sn–O and M–C bonds of $Fe(CN)_6^{4-}$. The characteristic frequency of the ferrocyanide ion[30] is 2170–2040 cm^{-1}, and this was shown by the material. The fourth peak (3000–3500 cm^{-1}) is due to the presence of free water and OH groups[31]. Free water also absorbs at 1600 cm^{-1}.

On the basis of the aqueous chemistry of tin(II) and ferrocyanides, chemical analysis of the material, the pH titration curve (Fig. 1), the thermogram (Fig. 2) and the definite supporting evidence from the IR spectrum, the following formula may be proposed for this ion exchanger:

$$[\mathrm{SnO \cdot H_4Fe(CN)_6 \cdot 2.5\ H_2O}]_n$$

The exact number of water molecules (2.5) per molecular unit of the exchanger was calculated with the help of the thermogram. The weight loss (11%) at 150° is due to the removal of external water molecules. Above this temperature, the weight loss corresponds to the condensation process, with elimination of one more water molecule. The second peak in the thermogram clearly indicates this process. Cyanogen starts to be liberated[32] at 237°. The third peak, therefore, represents this step. This process continues up to 400°, when the weight becomes constant owing to the formation[33] of the oxides and iron carbide (FeC_2). However, as the exchanger is amorphous in character, X-ray analysis cannot be helpful in ascertaining the exact structure.

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