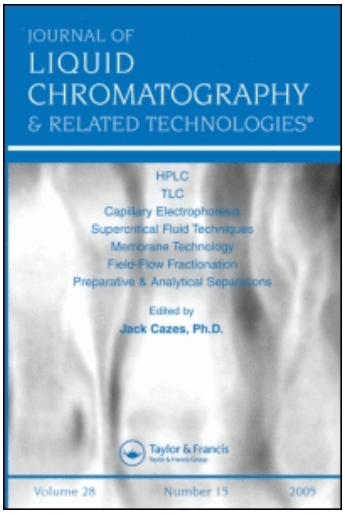

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J. P. Rawat[a]; K. P. Singh Muktawat[a]
[a] Department of Chemistry, Aligarh Muslim University, Aligarh, India

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SYNTHESIS AND ION-EXCHANGE PROPERTIES OF TANTALUM SELENITE AND ITS USE FOR THE SEPARATION OF METAL IONS BY ION-EXCHANGE COLUMN CHROMATOGRAPHY

J.P. Rawat and K.P. Singh Muktawat

Department of Chemistry,
Aligarh Muslim University,
Aligarh-202001 (India).

ABSTRACT

A new inorganic ion-exchanger tantalum selenite has been synthesized by mixing 0.10M Ta_2O_5 and 0.10M Na_2SeO_3. The ion-exchange properties, chemical stability, TGA and IR absorption have been studied. Some industrially important separations of Fe^{3+} from Mn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, VO^{2+}, Al^{3+} and Ba^{2+} from Ca^{2+}, Sr^{2+}, Mg^{2+} have been achieved on the columns of tantalum selenite. Separation of Fe^{3+}-Ni^{2+} can be applied to separate and determine Fe^{3+} from nickel electroplating bath.

INTRODUCTION

Out of the various inorganic ion-exchangers studied recently, the tantalum based ion-exchangers have received scant attention. Studies on tantalum pentoxide have been reported by Abe and Ito (1) and Chidley, et al. (2). Studies on tantalum phosphate by Kraus and Phillips (3), tantalum antimonate by Qureshi,et al.(4) and tantalum arsenate by Rawat and Mujtaba (5) have also been reported. Furthermore, only few studies have been reported on selenite based inorganic ion-exchangers. Costa and Jeronimo (6) prepared zirconium selenite and used for the separation of 1B group metal ions using paper chromatographic technique. Qureshi, et al. (7,8) prepared titanium selenite and stannic selenite and separated metal ions by ion-exchange column chromatography. A search of literature showed that no such studies have been reported on tantalum selenite. Therefore, the studies on tantalum selenite were explored in the field of ion-exchange

chromatography by achieving the selective separation of Fe^{3+} from a number of common interferring metal ions on the column of tantalum selenite. The separation can be applied to the determination of Fe^{3+} content as impurity in nickel electroplating solutions.

MATERIALS AND METHODS

Reagents and Apparatus

Tantalum pentoxide (Fluka), sodium selenite (B.D.H.) were used. A temperature controlled SICO shaker, Bausch and Lomb Spectronic 20 and Elico pH meter model Li-10 were used for shaking, spectrophotometric and pH measurements respectively. For IR studies spectromom 2000 (Budapest) infrared spectrophotometer was used.

Synthesis

The tantalum selenite samples were prepared by mixing 0.1M tantalum pentoxide and 0.1M sodium selenite solution in the ratio 1:1 under conditions given in Table 1. The sodium selenite solution was added to tantalum pentoxide solution and desired concentration of acid was adjusted by adding aqueous ammonia. Sample 3 was prepared by

TABLE 1

Synthesis and Properties of Tantalum Selenite

Sample No.	Conditions of synthesis		Properties		
	Conc.of H_2SO_4 at which exchanger prepared	Temperature at which samples prepared	Appearance of exchanger in H^+ form	Ion-exchange capacity meq/g for H^+	Composition Ta:Se
1	4.50M	25°C	Light red	1.18	1:1.50
2	4.50M	60°C	Light grey	0.96	1:1.45
3	4.50M	Refluxed at 100°C	Light grey	0.50	1:1.38
4	0.10M	25°C	Light red	0.89	1:1.15

refluxing the mother liquor of sample 1 for 24 hours at 100°C. The precipitate was kept overnight with mother liquor. It was filtered off, washed with deminaralized water and dried in oven at 40°C. The dried product broke into small granules when immersed in water. The granules were then dried and placed in 2.0M HNO_3 for 24 hours with occasionally shaking and intermittent changing of acid to convert them into hydrogen form. The chemical composition of the products synthesized was determined by estimating tantalum by Pyrogallol method (9) and selenium by sulpherdioxide method (10).

RESULTS AND DISCUSSION

The condition of synthesis and some basic properties of different sample of tantalum selenite are summarized in Table 1.

Ion-exchange capacity

The ion-exchange capacity of Tantalum selenite (Sample 1) was also determined for different uni and divalent metal ions by column operation and was found to be 1.12, 1.19, 1.45, 1.10, 1.05, 1.12 and 1.30 for Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} respectively. The exchange capacity by gravimetric procedure (11) was also measured as 1.12, 1.18, 1.22 and 1.53 for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} respectively. A comparison of these results with the exchange capacity by column procedure indicates that the exchange capacity by gravimetric procedure is slightly higher than the column procedure capacity. This is due to some adsorption of metal ions on the exchanger (12).

Dissolution of tantalum selenite

To determine the solubility of tantalum selenite in different solvents, 0.5 g of exchanger was taken with 50 ml of the solution concenred at room temperature for 6 hours. After removing the undissolved material tantalum and selenite were determined in the filtrate colorimetrically with pyrogallol (9) and diaminobenzidine (13) respectively. The results show that the amount of tantalum and selenium dissolved in 50 ml is negligible in demineralized water, $NaNO_3$, NH_4NO_3, HNO_3, H_2SO_4, HCl, alcohol and acetic acid. The dissolution of tantalum selenite is upto certain extent in NH_4OH, NaOH and oxalic acid.

The results of Table 1 further reveal that the ion-exchange capacity and chemical stability are considerably affected by the

conditions of preparation. The results are in agreement with the results of Nancollas (14) who found that the method of preparation of amorphous ion-exchanger has a considerable effect on composition and the degree of hydration. These two factors are responsible for the ion-exchange capacity and the chemical stability of the product.

Ion-exchange Potentiometric Titrations

The pH titration of sample 1 were performed by the method of Topp and Pepper (15) with LiOH, NaOH, KOH and aqueous NH_3 with their respective salts of known concentrations. The backward pH titrations were also performed by taking 50 ml NaOH 0.1M with the addition of 0.1M HNO_3 and water to make up the volume 100 ml. After shaking for four hours and the pH was measured. The effect of hydroxyl ion on the pH of equilibrating solutions are given in Figs.1 and 2. These results show that tantalum selenite in hydrogen form behaves as a monobasic acid. The results in Fig.2 forward and backward titration curve for Na^+ ions suggest a reversible behaviour of the exchanger, as a very small hysteresis loop is observed. The concentration of NaOH was 0.1M in which material dissolves negligibly.

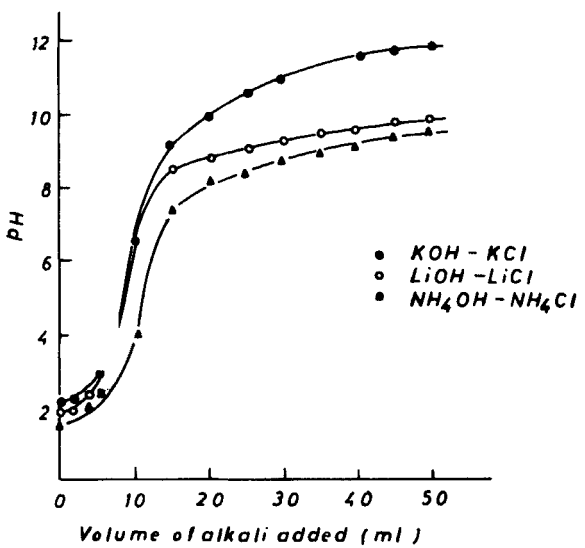

Figure 1 Potentiometric titration for tantalum selenite.

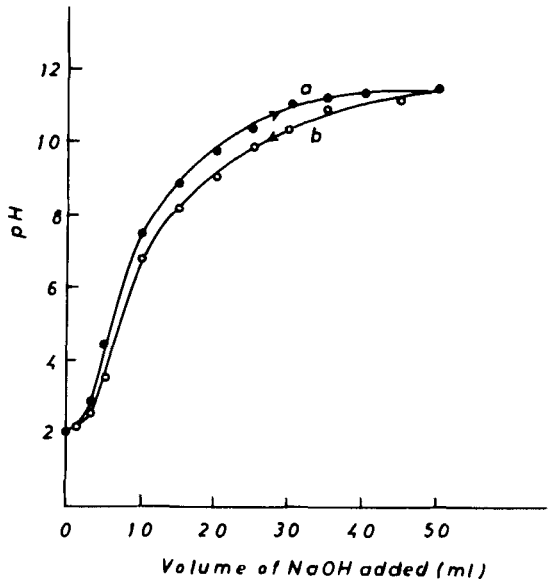

Figure 2 Potentiometric titration for tantalum selenite 'a' Forward, 'b' Backward with 0.1M NaOH and 0.1N NaCl.

IR Absorption Studies

IR spectra of tantalum selenite in hydrogen form were measured in nujol media. The results show that the tantalum selenite gives the characteristic peaks. A broad peak in the range 2900-3600 cm^{-1} with a maxima at 3400 cm^{-1} represents the interstitial water free water with nujol. The strong peak at 1650 cm^{-1} corresponds to the deformation vibration of interstitial water and of OH groups. The weak peaks are at 1150 cm^{-1} and 1050 cm^{-1} and very strong peak is the region 650-900 cm^{-1}. These peaks are due to the stretching vibration of the M-O bond i.e. Ta-O and Se-O. Some of the peaks in this IR spectrum resembles with the IR studies of sodium selenite performed by Millar and Wilkins (16).

Thermal Treatment

To examine the effect of drying temperature on the ion-exchange properties of the material, the sample was dried at various temperatures in a muffle furnace for 2 hours. A decrease in the

ion-exchange capacity with increasing temperature is plotted in Fig.3. Thermogravimetric analysis of sample 1 in hydrogen form was performed at a rate of 5°/min. The results of TGA show that the weight loss of the sample in H^+ form upto 250°C is due to the removal of external water molecules in the structure. Above this temperature upto 500°C the weight loss is nearly constant. It shows that there is no loss of other water molecules. A sharp increase in weight loss is observed when the temperature is raised upto 850°C. Significant structural changes must occur over this temperature range and condensation may take place i.e. may be the formation of oxides.

The effects of the drying temperature on the ion-exchange capacity are given in Fig.3. These results indicate that this ion-exchange material can be used upto 100°C without much loss of ion-exchange capacity. This ion-exchanger, therefore, possesses the higher capacity in comparison to other selenites and tantalum based exchangers. Above 100°C temperature the capacity decreases continuously upto 700°C.

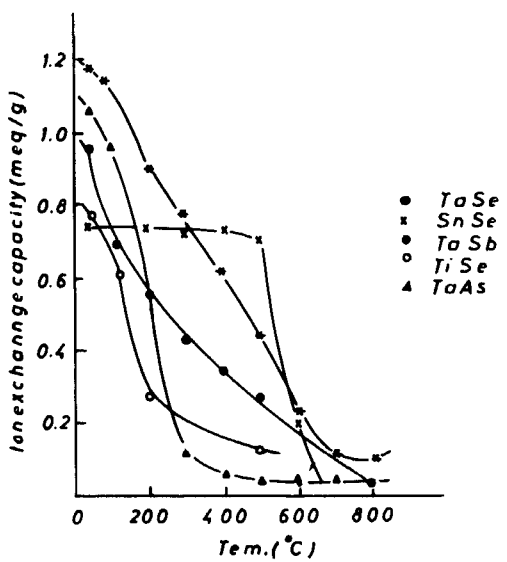

Figure 3 Ion-exchange capacity of various selenites and tantalum based exchangers as a function of drying temperature.

Distribution Studies

Kd values of metal ions were determined by batch process on sample 1 in different systems

$$Kd = \frac{50\ (I-F)}{0.5 \times F}\ ml\ gm^{-1}$$

where I is the volume of 0.002M EDTA used to titrate cation solution initially and F is the EDTA volume needed for cation titration after equilibrium. The total volume of equilibrating solution was 50 ml and 0.5 g exchange was taken. The results are given in Table 2.

Separations

Some analytically important and industrially useful separations were achieved on the basis of Kd values of metal ions.

TABLE 2

Distribution coefficients of metal ions on tantalum selenite

Cation	DMW	0.1M $NaNO_3$	0.1M NH_4NO_3	1.0M HNO_3	0.1M HNO_3	0.01M HNO_3	0.001M HNO_3	0.0001M HNO_3
Ba^{2+}	2210.0	1400.0	1462.0	62.0	328.4	800.0	1180.0	2150.0
Sr^{2+}	8.2	0.0	5.0	2.0	2.6	2.6	7.0	7.0
Mg^{2+}	1.4	1.0	7.0	0.0	4.0	6.5	15.9	16.5
Ca^{2+}	0.0	0.0	0.0	0.0	0.0	0.0	1.5	1.5
Cu^{2+}	22.0	18.0	18.0	2.0	3.0	13.0	17.0	18.0
Mn^{2+}	0.0	0.0	6.0	4.0	6.0	24.0	27.0	27.0
Ni^{2+}	2.4	0.0	2.5	1.0	2.5	2.5	2.5	5.0
Co^{2+}	5.6	4.0	8.2	0.0	1.5	3.8	8.0	15.0
Al^{3+}	21.0	20.0	4.4	0.0	3.0	5.0	6.0	8.0
Fe^{3+}	T.A.	T.A.	1550.0	2.0	7.5	115.0	455.0	780.0
VO^{2+}	30.0	49.0	3.6	7.0	18.0	32.0	40.0	43.0
Zn^{2+}	0.0	9.0	2.0	0.0	6.0	11.0	19.0	19.0

T.A. = Total Adsorption

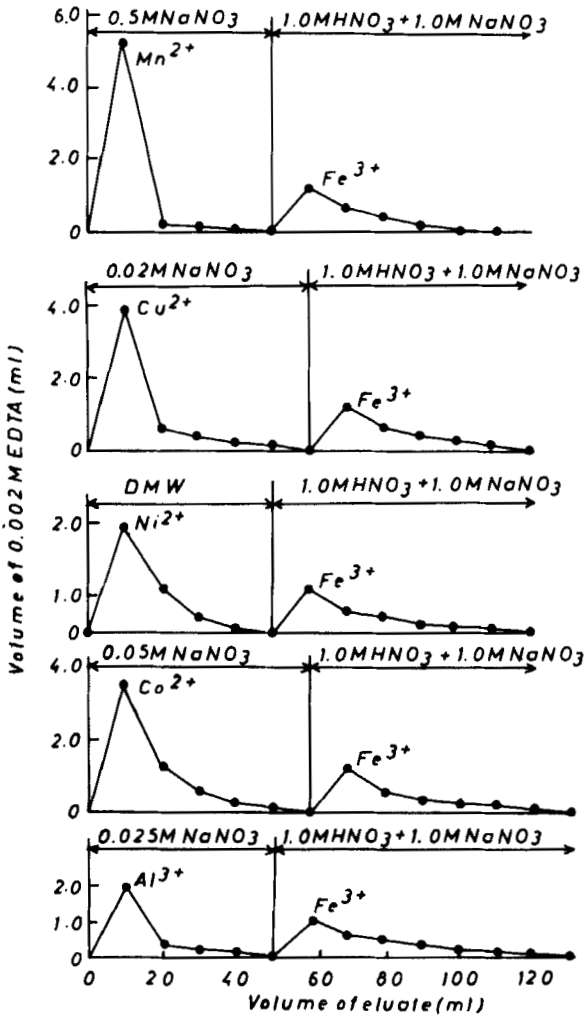

Figure 4a Separations achied on tantalum selenite.

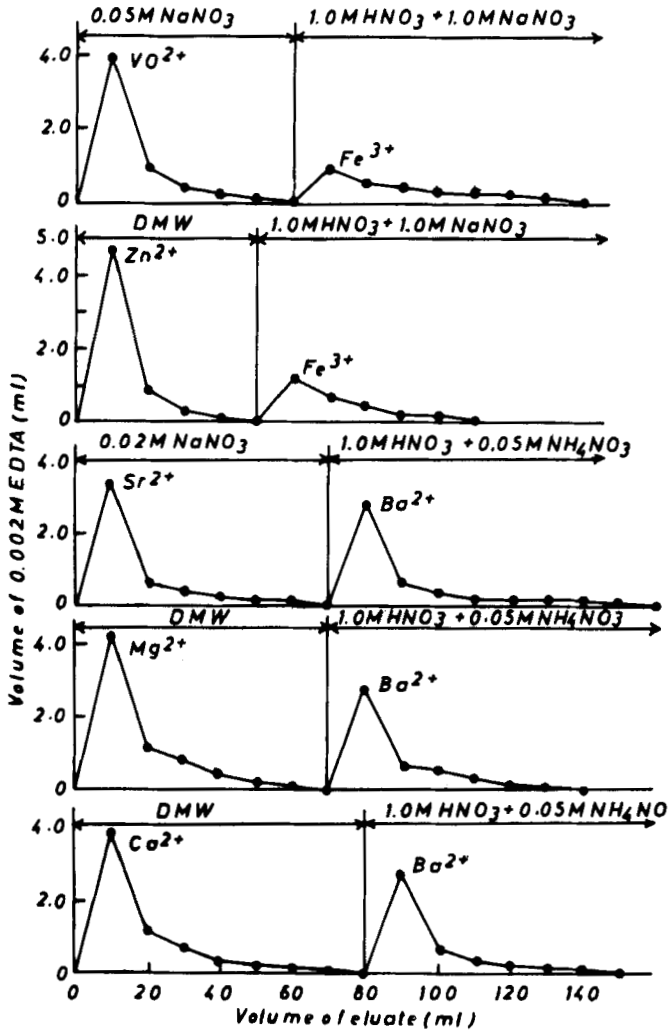

Figure 4b Separations achieved on tantalum selenite.

The separations were performed using the ion-exchange column chromatographic technique. The order of elution and eluents are presented in Fig.4. In order to explain the effectiveness of tantalum selenite for the separation of Fe^{3+} and Ba^{2+} was made. It was found that the selenites of Mg, Ca, Sr, Ni, Cu, Co, Mn, Zn and Al have been prepared by mixing the carbonates of the respective metal ions with selenious acid (17). Except ferric selenite and barium selenite all are soluble in water as well as in dilute mineral acids. Therefore ferric and barium should be adsorbed more strongly than the remaining cations under study. Hence elution of Ma, Ca, Sr, Ni, Cu, Co, Mn, Zn and Al has been made with demineralized water or 0.5M sodium nitrate while the elution of ferric and barrium with 1.0M nitric acid adding 1.0M sodium nitrate or ammonium nitrate. The elution of ferric and barium is not sharper than other metal ions also for the same reason.

The industrial utility of these separations was checked by separating Fe^{3+} from Ni^{2+} in a electroplating bath solution. The presence of Fe^{3+} in the electroplating bath solution of nickel produces black spots on electroplated shiny surfaces. It was found that for two samples taken from the same electroplating bath the iron(III) content was 189 and 201 µg in 2 ml bath solution.

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REFERENCES

1. Abe,M. and Ito,T., Nippon Kagaku Zashi, 86, 1259, 1965.
2. Chidley,B.E., Parkar,F.L. and Tablot,E.A. U.K.Atom.Energy Auth.Res. Group Resp.AERER Rept., 10, 5520, 1966.
3. Kraus,K.A. and Phillips,H.O., Oak Ridge Report ORNL, 50, 2983, 1960.
4. Qureshi,M., Gupta,J.P. and Sharma,V., Anal.Chem., 45, 190, 1973.
5. Rawat,J.P. and Mujtaba,S.Q., Cand.J.Chem., 53, 2685, 1975.
6. Nunes,M.J., DA Costa and Jeronimo,M.A.S., J.Chromatogr., 5, 546, 1961.
7. Qureshi,M., R.Kumar and Rathore,H.S., Anal.Chem., 44, 1081, 1972.
8. Qureshi,M. and Nabi,S.A., Talanta, 19, 1033, 1972.
9. Sandell,E.B., Colorimetric Determination of Traces of Metals, Interscience, New York, 1959, p.697.

10. Wilson,C.L. and Wilson,D.W., Comprehensive Analytical Chemistry, Elsevier Amsterdam, VIC, 1962, p.298.
11. Bunze,K. and Sansoni,B., Anal.Chem., 48, 2279, 1976.
12. Rawat,J.P. and Muktawat,K.P.Singh, Chromatographia, 11, 513 (1978).
13. Furman,N.H., Standard Methods of Chemical Analysis, Van Nostarnd, V.1, 1962, p.930.
14. Sylvia,J.H. and Nancollas,G.H., J.Inorg.Nucl.Chem., 32, 3923, 1970.
15. Topp,N.E. and Pepper,K.W., J.Chem.Soc., 3299, 1949.
16. Miller,F.A. and Wilkins,C.H., Anal.Chem., 24, 1281, 1952.
17. Mellor,J.W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, V.X, Longmans Green & Co., London, 1961, p.829.