

Cd-ox	Cd- $\alpha$ -ala	Cd- $\beta$ -ala
log $\beta_{01}$ = 2.94	log $\beta_{10}$ = 4.40	log $\beta_{10}$ = 3.70
log $\beta_{02}$ = 4.30	log $\beta_{20}$ = 7.40	log $\beta_{20}$ = 5.75
log $\beta_{03}$ = 5.44	log $\beta_{30}$ = 9.50	log $\beta_{30}$ = 6.85

The studies were made at two fixed concentrations (0.01 and 0.1 M) of oxalate so chosen that predominantly one and two oxalate ions per Cd(II) ion would exist respectively in the Cd-oxalate system. The functions  $F_{00}$ ,  $F_{10}$ ,  $F_{20}$  and  $F_{30}$  were calculated following the method of Schaap and McMasters<sup>5</sup>. The functions  $A$ ,  $B$ ,  $C$  and  $D$  were calculated by Leden's<sup>6</sup> extrapolation method. From the values of  $B$  and  $B'$  at two different concentrations of oxalate ions, the formation constants of  $[\text{Cd}(\alpha\text{-ala}/\beta\text{-ala})(\text{ox})]^-$  and  $[\text{Cd}(\alpha\text{-ala}/\beta\text{-ala})(\text{ox})_2]^{3-}$  have been calculated. The values are as follows :

$\alpha$ -alanine	log $\beta_{11}$ = 6.20	log $\beta_{12}$ = 7.30
$\beta$ -alanine	log $\beta_{11}$ = 5.40	log $\beta_{12}$ = 6.78

From the values of  $C$  and  $C'$  the formation constants (log  $\beta_{21}$ ) were calculated for both the amino acids. The average values for log  $\beta_{21}$  are 8.60 and 6.88 for  $\alpha$ -ala and  $\beta$ -ala respectively. The average values of  $D$  and  $D'$  were obtained as 9.49, 6.85 which are in agreement with log  $\beta_{30}$  values found experimentally (9.5, 6.85).

The mixing constant,  $K_M = \beta_{11}/\sqrt{(\beta_{02}\beta_{20})}$  and stabilization constants (log  $K_S = \log K_M - \log 2$ )<sup>7</sup> were calculated for the above systems. The values obtained are :

$\alpha$ -ala	log $K$ = 0.350	log $K_S$ = 0.049
$\beta$ -ala	log $K_M$ = 0.375	log $K_S$ = 0.074

The positive values of mixing constants and stabilization constants show that the ternary complexes are slightly more stable than the binary complexes; also, the values are more positive for  $\beta$ -alanine than for  $\alpha$ -alanine. The positive values of stabilization constants have also been observed by Brookes and Pettit<sup>8</sup>, Gergely and Sovago<sup>9</sup> and Ting and Wancollas<sup>10</sup>.

The equilibria between various species formed in solution in the two ternary systems, Cd-ox- $\alpha$ -ala and Cd-ox- $\beta$ -ala are shown in Figs 1 A and B. The numerical values are the log  $K$  values and Y and X refer to oxalate and  $\alpha$ -ala/ $\beta$ -ala respectively.

The stability constants of mixed ligand complexes were also calculated by the method of Watters and De Witt<sup>11</sup>. The results obtained are as under :

$\alpha$ -ala :	log $\beta_{11}$ = 5.74,	log $\beta_{12}$ = 7.26,	log $\beta_{21}$ = 8.60
$\beta$ -ala :	log $\beta_{11}$ = 4.86,	log $\beta_{12}$ = 6.38,	log $\beta_{21}$ = 6.84

It can be seen that it is easier for  $\alpha$ -ala/ $\beta$ -ala to add to  $[\text{Cd}(\text{ox})]$  than to  $[\text{Cd}(\alpha\text{-ala}/\beta\text{-ala})]$ , thus formation of ternary complex is more favoured than that of the binary complex. The log  $K$  values for substitution are 2.30 and 1.70, while there is no tendency to substitute (ox) due to weaker nature of the oxalate ligand. The higher experimental values

may be accounted for by the electrostatic and steric factors as also concluded by Hughes *et al.*<sup>12</sup>.

A comparison of the present data with those reported in our previous communications<sup>1,2</sup> reveals that the stability of the ternary complexes  $[\text{Cd}(\text{aa})_n(\text{ox})_{2-n}]$  decreases in the order: gly >  $\alpha$ -ala > val >  $\beta$ -ala which is in agreement with the increasing bulkiness of the alkyl group and the expected relative behaviour of the amino acids. It is interesting to note that the binary complexes of  $\beta$ -alanine are much weaker than those of  $\alpha$ -alanine as expected on account of the larger size of ring in the case of  $\beta$ -alanine chelates. But in ternary system there is not much of difference in the stabilities which may be due to the fact that amino acid occupies one axial and the equatorial position in the ternary systems.

## References

1. AGGARWAL, A. R., ARORA, H. K., PANDEYA, K. B. & SINGH, R. P., *J. inorg. nucl. Chem.*, **43** (1981), 601.
2. AGGARWAL, A. R., PANDEYA, K. B. & SINGH, R. P., *Ann. Chim. (Rome)*, (in press).
3. NAGESWARA, RAO, S. G. & SUBRAHAMANYA, R. S., *Proc. Indian Acad. Sci.*, **60** (1964), 165.
4. DEFORD, D. D. & HUME, D. N., *J. Am. chem. Soc.*, **73** (1951), 5321.
5. SCHAAP, W. B. & MCMASTERS, D. L., *J. Am. chem. Soc.*, **83** (1961), 4699.
6. LEDEN, I., *Z. phys. Chem.*, **188** (1941), 160.
7. JAIN, S. L., KISHAN, J., & KAPOOR, R. C., *Indian J. Chem.*, **18A** (1979), 133.
8. BROOKES, G. & PETTIT, L. D., *J. chem. Soc.*, (1977), 1918.
9. GERGELY, A. & SOVAGO, I., *J. inorg. nucl. Chem.*, **35** (1973), 4355.
10. TING, P. I. & WANCOLLAS, G. H., *Inorg. Chem.*, **11** (1972), 2414.
11. WATTERS, J. I. & DEWITT, J., *J. Am. chem. Soc.*, **82** (1960), 1333.
12. HUGHES, E. D., INGOLD, C. K., PATAI, S. & POCKER, Y., *J. chem. Soc.*, (1957), 1206.

## Synthesis & Ion-exchange Properties of Niobium Selenite : Separation of La-Th, Th-Cu, Pb-Cd, Zn-Pb & La-Ce

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A new inorganic ion-exchanger, niobium selenite, has been prepared by mixing 0.1M niobium pentoxide and 0.1M sodium selenite in different ratios. Its ion-exchange capacity, composition, chemical stability etc. have been determined. Distribution studies have been carried out to study its selectivity. On the basis of differential selectivity a number of separations have been achieved.

INORGANIC ion-exchangers of the type of zirconium phosphate have received considerable attention because of their high selectivity which is based upon their rigid structure of definite pore size. Materials based on niobium have, however, not received the same attention though a number of

niobium salts have been used as exchangers<sup>1-7</sup>. We report here the preparation and ion-exchange properties of niobium selenite. Its analytical utility was explored by achieving some important binary separations.

Temperature controlled SICO shaker was used for shaking. Bausch and Lomb spectronic 20 (U.S.A.) and ELICO pH meter model LI-10 were used for spectrophotometric and pH measurements respectively.

Niobium pentoxide, selenium dioxide and ammonium sulphate were BDH reagents. All the other reagents and chemicals were BDH reagents of AR grade. Selenium dioxide was dissolved in water. Niobium pentoxide (20 g) was heated with 500 ml of conc. sulphuric acid containing 200 g of ammonium sulphate and the clear solution obtained was diluted with water to 750 ml to get a solution 0.1M in niobium.

**Synthesis** — Niobium selenite was prepared by adding 0.1M solution of niobium pentoxide to 0.1M sodium selenite solution in various ratios. The precipitate so obtained was kept for 24 hr, filtered and washed with demineralized water, dried at 40°C in a temperature-controlled oven. The dried product was then kept in 2.0M nitric acid to convert it to H<sup>+</sup> form, washed to make it acid-free and dried again at 40°C. Three different samples were prepared at pH equal to zero by changing the mixing ratio of Nb : Se as 1 : 1, 1 : 2 and 2 : 3 for sample Nos 1, 2 and 3 respectively.

The ion-exchange capacity of various samples of niobium selenite was determined by column operation as usual. The H<sup>+</sup> liberation ion-exchange capacity by KNO<sub>3</sub> (0.1M) was found to be 0.95, 1.04 and 0.90 meq/g for sample Nos. 1, 2 and 3 respectively. In order to see its working capacity as ion-exchanger, the capacity was determined for mono and divalent cation solutions. On sample No. 2 i.e. containing Nb : Se in the ratio of 1 : 2, the ion-exchange capacity was 1.04, 0.4, 0.8 and 0.4 for K<sup>+</sup>, Sr<sup>2+</sup>, Li<sup>+</sup> and Ba<sup>2+</sup> ions respectively.

The sample No. 2 was dried at different temperatures in a muffle furnace for 1 hr and the ion-exchange

capacity for 1.0 MK<sup>+</sup> was found to be 1.04, 1.00, 0.70 and 0.40 meq/g for products dried at 100°C, 200°C, 400°C and 600°C respectively. Sample 2 was studied in detail because of its stability and ion exchange capacity were higher than those of other two samples.

**pH-titration** — pH-titrations were performed by shaking 0.5 g of niobium selenite (sample No. 2) with 0.1M solution of NaOH, LiOH, KOH and their salts. The contents of the flask were shaken for 4 hr and the pH of the supernatant solutions were measured. The results are shown in Fig. 1.

**Distribution coefficient** — The distribution studies were carried out for metal ions by batch process in the usual manner. After allowing the attainment of equilibrium by shaking the metal ion solution with exchanger beads for 6 hr at room temperature, the *K<sub>d</sub>* values for metal ions were calculated by using the following expression,

$$K_d = \frac{I - F}{F} \times 100 \text{ ml g}^{-1}$$

where *I* is the amount of 0.002M EDTA consumed by the original solution and *F* is the volume of EDTA

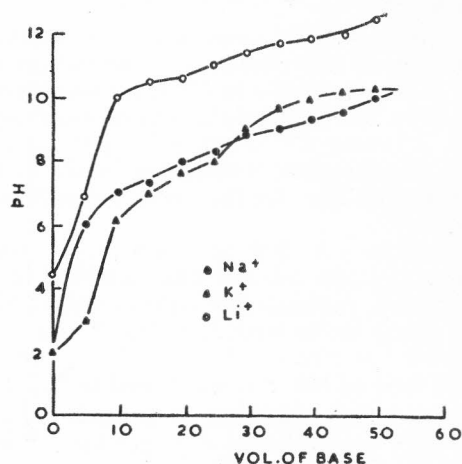


Fig. 1 — pH titration curve of niobium selenite with added salts

TABLE I — SEPARATIONS ACHIEVED USING NIOBIUM SELENITE

Mixture loaded	Cation eluted	Eluent	Total volume of effluent collected (ml)	Amount loaded (μg)	Amount found (μg)	Error (%)
Th <sup>4+</sup> -Cu <sup>2+</sup>	Th <sup>4+</sup>	2.0 M HNO <sub>3</sub>	70 ml	1972.25	1925.84	2.33
	Cu <sup>4+</sup>	0.01M HNO <sub>3</sub>	80 ml	648.108	622.69	3.92
Th <sup>4+</sup> -La <sup>3+</sup>	Th <sup>4+</sup>	2.0M HNO <sub>3</sub>	80 ml	1972.25	1925.84	2.35
	La <sup>3+</sup>	D.M.W.	60 ml	611.16	583.38	4.54
Pb <sup>2+</sup> -Cd <sup>2+</sup>	Pb <sup>2+</sup>	0.01M HNO <sub>3</sub>	90 ml	1450.4	1376.52	5.71
	Cd <sup>2+</sup>	0.1M HNO <sub>3</sub>	90 ml	899.2	854.24	5.00
Zn <sup>2+</sup> -Pb <sup>2+</sup>	Zn <sup>2+</sup>	D.M.W.	60 ml	542.57	522.96	3.60
	Pb <sup>2+</sup>	0.01M HNO <sub>3</sub>	80 ml	1450.4	1376.52	5.71
La <sup>3+</sup> -Ce <sup>3+</sup>	La <sup>3+</sup>	D.M.W.	50 ml	611.16	583.38	4.54
	Ce <sup>3+</sup>	0.01M HNO <sub>3</sub>	60 ml	840.72	812.69	3.33

consumed after equilibrium. The total volume of solution was 50 ml and the amount of exchanger used was 0.5 g. The  $K_d$  values are obtained in the following order :

In DMW :  $\text{Th}^{4+} > \text{Ba}^{2+} > \text{Yt}^{3+} > \text{Hg}^{2+} > \text{Dy}^{3+} > \text{In}^{3+} > \text{Th}^{3+} > \text{Pb}^{2+} > \text{Pr}^{3+} > \text{Sm}^{3+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Ce}^{3+} > \text{Sn}^{2+} > \text{Mg}^{2+} > \text{La}^{3+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Ho}^{3+} > \text{Gd}^{3+} > \text{Ca}^{2+}$ .

In 0.01M  $\text{HNO}_3$  :  $\text{Pb}^{2+} > \text{Ba}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+} > \text{Sn}^{2+} > \text{Mg}^{2+} > \text{Th}^{4+} > \text{Ca}^{2+} > \text{La}^{3+} > \text{Ho}^{3+} > \text{Pr}^{3+} > \text{Tb}^{3+} > \text{Hg}^{2+} > \text{In}^{3+} > \text{Gd}^{3+} > \text{Sm}^{3+} > \text{Ce}^{3+} > \text{Yt}^{3+} > \text{Dy}^{3+}$ .

In 0.05M  $\text{HNO}_3$  :  $\text{Hg}^{2+} > \text{Ba}^{2+} > \text{Pr}^{3+} > \text{Th}^{4+} > \text{Mn}^{2+} > \text{Ho}^{3+} > \text{Tb}^{3+} > \text{Sm}^{3+} > \text{Pb}^{2+} > \text{Sn}^{2+} > \text{Zn}^{2+} > \text{Dy}^{3+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ce}^{3+} > \text{In}^{3+} > \text{Mg}^{2+} > \text{Yt}^{3+} > \text{Ca}^{2+} > \text{a}^{3+} > \text{Gd}^{3+}$ .

In 0.1M  $\text{HNO}_3$  :  $\text{Th}^{4+} > \text{La}^{3+} > \text{Ce}^{3+} > \text{Gd}^{3+} > \text{Tb}^{3+} > \text{Sm}^{3+} > \text{Hg}^{2+} > \text{In}^{3+} > \text{Ho}^{3+} > \text{Yt}^{3+} > \text{Pr}^{3+} > \text{Mg}^{2+} > \text{Ba}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Sn}^{2+} > \text{Dy}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+}$ .

In 1%  $\text{NH}_4\text{NO}_3$  :  $\text{Th}^{4+} > \text{Ce}^{3+} > \text{Yt}^{3+} > \text{Gd}^{3+} > \text{Dy}^{3+} > \text{Ba}^{2+} > \text{Pr}^{3+} > \text{Zn}^{2+} > \text{La}^{3+} > \text{Cd}^{2+} > \text{Sm}^{3+} > \text{Hg}^{2+} > \text{Tb}^{3+} > \text{Cu}^{2+} > \text{In}^{3+} > \text{Mn}^{2+} > \text{Sn}^{2+} > \text{Mg}^{2+} > \text{Ho}^{3+} > \text{Pb}^{2+} > \text{Ca}^{2+}$ .

**Separations** — Separations were tried on the basis of difference in  $K_d$  values. For separation studies 2.0 g of niobium selenite in  $\text{H}^+$  form was taken in a glass column 30 cm in height and of inner diameter 0.69 cm. The rate of flow was 0.5 ml/min and 10 ml fractions of effluent were collected for the metal ion determination. The results are summarized in Table 1.

**Composition** — A 200 mg portion of the well powdered niobium selenite was dissolved in 10 ml sulphuric acid, niobium was determined gravimetrically by precipitation with cupferron<sup>10</sup> and selenium was estimated gravimetrically by hydrogen sulphide<sup>11</sup>. The mole ratio of Nb : Se was found to be 2 : 1.

Niobium selenite behaves as a weak cation exchanger with ion-exchange capacity for  $\text{K}^+$  ions as 1 meq/g of the exchanger. The ion-exchange capacity varies with the nature of the metal ion.

Heat treatment of the material shows no appreciable loss of ion-exchange capacity upto 200°C and hence it can be used at high temperature which is an advantage over the organic resins.

The results of the pH-titration of niobium selenite with NaOH-NaCl, LiOH-LiCl and KOH-KCl (Fig. 1) indicate that the reagent behaves as a mono-functional weak acid in  $\text{H}^+$  form.

The order of the  $K_d$  values with different metal ions indicates differential selectivity. On the basis of large difference in  $K_d$  values separations quantitatively achieved are : La-Th, Th-Cu, Pb-Cd, Zn-Pb, La-Ce (Table 1).

**References**

1. QURESHI, M., RAWAT, J. P. & GUPTA, A. P., *J. Chromatography*, **118** (1976), 167.
2. GUPTA, J. P., NOWELL, D. V., QURESHI, M. & GUPTA, A. P., *J. inorg. nucl. Chem.*, **40** (1970), 545.
3. PHILLIPS, H. O. & KRAUS, K. A., *Rep. U.S. Atomic Energy Comm.*, **81** (1962), 3320.

4. EGOROV, YU. V., SUKHAREV, YU. I. & PUSTOVALOV, N. N., *Otkrytiya, Izobert, Prom-obraztry, Tovarnyc Znaki*, **22** (1969), 46.
5. SUKHAREV, YU. I., EGOROV, YU. V. & PUSTOVALOV, N. N., *Zh. neorg. Mater*, **16** (1971), 1026.
6. SUKHAREV, YU. I. & EGOROV, YU. V., *Izv. Akad. Nauk SSSR, neorg Mater*, **4** (1968), 996.
7. SUKHAREV, YU. I. & EGOROV, YU. V., *Izv. Akad. Nauk SSSR, neorg Mater*, **7** (1971), 1948.
8. KOLTHOFF, I. M. & ELVING, P. J., *Treatise on analytical chemistry*, Part II, Vol. 6 (Interscience Publishers, New York), 297.
9. FURMAN, N. H., *Standard methods of chemical analysis* (D. Van Nostrand Company, Princeton, New Jersey, New York), 1962, 930.
10. LUNDELL, G. E. F. & HOFFMAN, J. I., *Outline methods of chemical analysis* (Wiley, New York), 1958, 117.
11. KOLTHOFF, I. M. & ELVING, P. J., *Treatise on analytical chemistry*, Part II, Vol. 7, (Interscience Publishers, New York), 1961.

**Potentiometric Studies on the Complex Formation of Some Ln(III) Ions with 4-Nitrocatechol**

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The interaction of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) and Y(III) with 4-nitrocatechol has been investigated potentiometrically in aqueous medium at 25° and at ionic strengths of 0.05, 0.1, 0.15 and 0.2M ( $\text{KNO}_3$ ). The proton-ligand formation constants and metal-ligand formation constants have been calculated using the Calvin-Bjerrum titration technique as modified by Irving and Rossotti. The thermodynamic formation constants have also been determined. The order of stabilities of the lanthanide complexes with the above ligand is found to be : La(III) < Ce(III) ~ Pr(III) < Nd(III) < Sm(III) < Gd(III) < Y(III) < Tb(III) < Dy(III) < Ho(III).

COMPLEXATION reactions of 4-nitrocatechol have been reported<sup>1-3</sup> with a few metal ions. However, no work is reported with Ln(III) ions. We report here the results of our study on Ln(III)-4-nitrocatechol systems employing Calvin-Bjerrum<sup>4,5</sup> titration technique as modified by Irving and Rossotti<sup>6</sup>.

The Ln(III) nitrates (Indian Rare Earths Ltd) were dissolved in  $\text{CO}_2$ -free doubly distilled water and standardized by the oxalate method<sup>7</sup>. All the other chemicals used were of AR grade. pH was measured with a Phillips pH meter (PR 9405 M) with glass (PV 9012) calomel assembly.

The experimental method employed consists of pH titrations of the following mixtures thermostated at 25° against 0.4N NaOH : (i)  $4 \times 10^{-3}M \text{HNO}_3$ , (ii)  $4 \times 10^{-3}M \text{HNO}_3 + 3 \times 10^{-3}M$  ligand and (iii)  $4 \times 10^{-3}M \text{HNO}_3 + 3 \times 10^{-3}M$  ligand +  $5 \times 10^{-4}M$  metal ion solution. The concentrations of the common ingredients were same in different cases. An appropriate quantity of potassium nitrate (2.0M) was added