Preparation and Properties of a Mercury Selective Ion Exchanger Cerium(IV) Selenite

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Synopsis. A new inorganic ion exchanger, cerium(IV) selenite has been synthesized with a cation exchange capacity of 0.98 mequiv g^{-1}. It is fairly stable in water and in dilute solutions of acids, bases and salts. The K_d values for number of metal ions were determined in different solvent systems. The exchanger possesses a high affinity for Hg(II) and hence its separation from certain metal ions have been made.

Selenites of tin,[1] titanium,[2] and tantalum[3] have been synthesized and used for various separations. However, no such studies have so far been reported on cerium(IV) selenite. Our studies on this material reveal that it is highly selective for Hg(II). As mercury is a toxic substance, its determination and separation should be of great importance. In the present report the synthesis and the ion exchange properties of cerium (IV) selenite are described as well as its possible application to separation of Hg(II) from other metal ions.

Experimental

Synthesis. Cerium(IV) selenite was prepared by mixing solutions of sodium selenite (Riedel, Germany) and ammonium cerium(IV) sulfate (British Drug House,England). The solution of 0.05 mol dm^{-3} sodium selenite was added to a solution of 0.05 mol dm^{-3} ammonium cerium(IV) sulfate in the volume ratio of 1:1 at pH 1. The pH was adjusted by adding either nitric acid or aqueous ammonia. The precipitate so obtained was kept standing for 24 h to ensure complete precipitation. It was then filtered, washed with deionized water and dried at 40 °C. The dried product was then converted to H^+ form by treatment with 1 mol dm^{-3} HNO_3.

The ion exchange capacity, which in fact is the capacity to decompose neutral salts, was determined by column operation. A solution of 1.0 mol dm^{-3} of Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} was passed through a column containing 1 g of exchanger. The eluted hydrogen ion concentration was then determined titrimetrically.

To determine the chemical stability, 0.5 g cerium(IV) selenite was shaken with an appropriate solution for six hours in a conical flask. The cerium[4] and selenium[5] released into the supernatant solution were determined by standard methods.

The pH titrations of cerium(IV) selenite were performed with LiOH, NaOH, KOH and aqueous ammonia in the presence of Li^+, Na^+, K^+ and NH_4^+ chlorides, respectively, by the method of Topp and Pepper.[6]

For equilibrium studies 0.5 g of exchanger in H^+ form was shaken with 50 cm^3 solution of 1.0 mol dm^{-3} sodium nitrate. The amount of released H^+ ions in the supernatant solution was determined after appropriate intervals.

The distribution coefficient (K_d values) were determined by shaking 50 cm^3 of 0.001 mol dm^{-3} solution of different metal ions with 0.5 g of the exchanger for six hours at room temperature.[3]

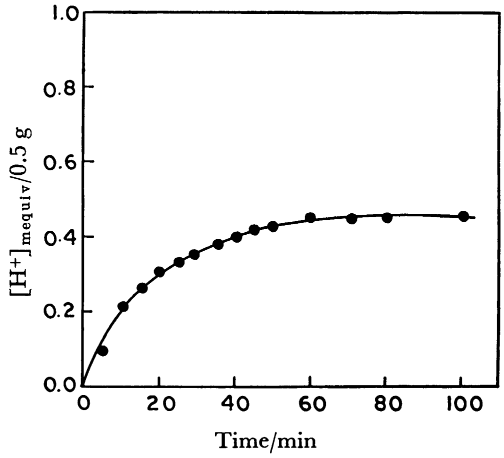

Fig. 1. Attainment of equilibrium of Na^+-H^+ exchange on cerium(IV) selenite.

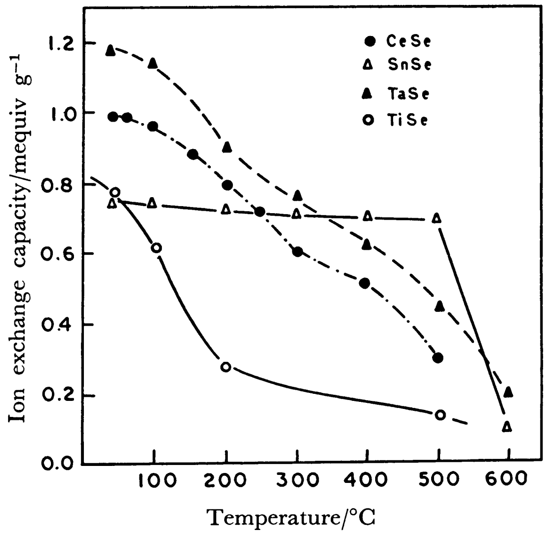

Fig. 2. Ion exchange capacity of various selenites as a function of drying temperature.

Results and Discussion

The hydrogen ion liberation capacity of cerium(IV) selenite for some uni and bivalent metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} were found to be 0.98, 0.86, 0.90, 0.80, 0.82, and 0.85 mequiv g^{-1} respectively.

The equilibrium studies (Fig. 1) show that the equilibrium is attained in 60 min. The effect of drying temperatures of cerium(IV) selenite on the ion exchange capacity (Fig. 2) indicates that the selenite also shows deterioration after 100 °C as in the case of tantalum selenite. The reason for the decrease in capacity with the increase in drying temperature upto 500 °C may be attributed to the loss of structural

Table 1. Some separations on cerium(IV) selenite columns

Separation	Eluent	Elution volume/ml	Amount of cation	
			Loaded mg	Recovered mg
Cd(II)-Hg(II)	Cd(II)-0.01 mol dm^{-3} HNO_3	0.0—80	0.74	0.74
	Hg(II)-0.1 mol dm^{-3} (HNO_3+NaNO_3)	90—160	1.6	1.6
Ni(II)-Hg(II)	Ni (II)-0.1 mol dm^{-3} HNO_3	0.0—70	0.48	0.49
	Hg(II)-0.1 mol dm^{-3} (HNO_3+NaNO_3)	80—160	1.6	1.6
Pb(II)-Hg(II)	Pb (II)-0.01 mol dm^{-3} HNO_3	0.0—90	1.6	1.6
	Hg(II)-0.1 mol dm^{-3} (HNO_3+NaNO_3)	100—170	1.6	1.5

water, selenium and attached replaceable hydrogen ion.

The results of chemical stability test of cerium(IV) selenite revealed that the material is fairly stable (less than 1.2 mg of Se and 0.28 mg of Ce were lost) in demineralized water, 2.0 mol dm^{-3} solution of each of $NaNO_3$, NH_4NO_3, HNO_3, CH_3COOH, HCOOH, and CH_3OH but less stable (3.24 mg of Se and 2.8 mg of Ce were lost) in sulphuric acid of over 2.0 mol dm^{-3}. The pH titration curves (Fig. 3) of the exchanger in H^+ form show bifunctional behaviour.

The chemical analysis revealed that Ce : Se ratio as 1 : 1.1. TGA curve showed the loss of water molecules, 11% at 200 °C. Therefore, the material possibly possesses the empirical formula $CeO_2 \cdot Se(OH)_2O \cdot nH_2O$ with a formula weight of 301 for the anhydride. The value of 'n' the external water molecule per mole of oxide was 2.07.

The analytical importance of cerium(IV) selenite can be deduced from the K_d values of various metal ions in water, 0.1 mol dm^{-3} $NaNO_3$ and in different concentrations of HNO_3. The ion exchanger showed a selective trend in various solution as may be predicted by the K_d values, which are in parentheses *e.g.* in water: Hg^{2+} (total adsorption), Al^{3+} (1160), Pr^{3+} (700), Ho^{3+} (585), Zr^{4+} (470), Y^{3+} (440), Th^{4+} (340), La^{3+} (390), Sm^{3+} (240), Fe^{3+} (240), Ca^{2+} (200), Ba^{2+} (200), Cu^{2+} (170), Mn^{2+} (160), Sr^{2+} (110), Mg^{2+} (100), Zn^{2+} (100), Ni^{2+} (80), Cd^{2+} (68), and Pb^{2+} (55) and in 0.01 mol dm^{-3} HNO_3: Hg^{2+} (2020), Al^{3+} (640), Pr^{3+} (580), Ho^{3+} (400), Y^{3+} (340), Th^{4+} (170), La^{3+} (140), Sm^{3+} (120), Fe^{3+} (180), Ca^{2+} (70), Ba^{2+} (60), Cu^{2+} (120), Mn^{2+} (90), Sr^{2+} (40), Mg^{2+} (50), Zn^{2+} (60), Ni^{2+} (40), Cd^{2+} (20), and Pb^{2+} (10). These indicate that the exchanger shows greatest preference for Hg(II) in solvent media like H_2O and 0.01 mol dm^{-3} HNO_3, where total absorption of Hg(II) was observed. Its elution was possible only when a mixture of 0.1 mol dm^{-3} solution each of HNO_3 and $NaNO_3$ was used. The high affinity of cerium(IV) selenite for Hg(II) paved the way for its separation from most of the metal ions. For separations a glass column of 30 cm in height and of internal diameter 0.69 cm was loaded with 2 g of the exchanger. A solution was then poured into the column. The flow rate was kept 0.5 ml/min. After repeated recyclization the metal ions were eluted with an appropriate solution in which the K_d value was lowest. The separation was practically complete and the order of elution of different metals are shown in Table 1. The separations were quantitative and the errors were within admissible range.

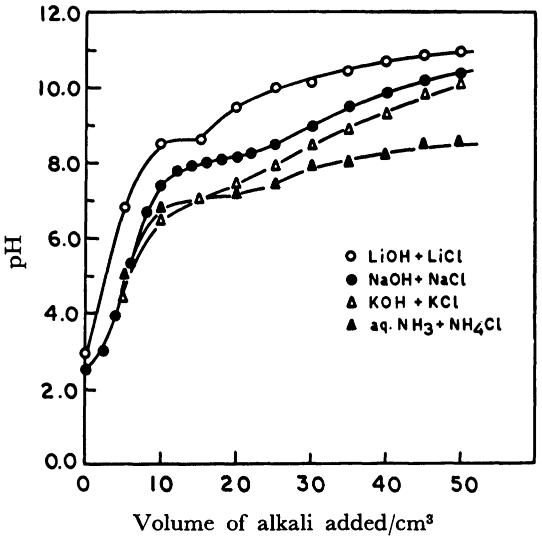

Fig. 3. pH titration curves of cerium(IV) selenite (H^+ form).

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