Asian Journal of Chemistry Vol. 20, No. 8 (2008), 6134-6140

Synthesis, Properties and Analytical Applications of Cerium(IV) Iodoselenite: A New Cation Exchange Material

RAJEEV THOMAS
Department of Chemistry, Mary Matha Arts & Science College
Mananthavady-670 645, India
E-mail: rajeev21567@yahoo.co.in

In order to combine the qualities of inorganic and a stable material with good chromatographic properties, a new inorganic cation exchanger cerium(IV) iodoselenite (CeISe) was synthesized. Sample-1 was chosen for detailed ion exchange studies due to its highest ion exchange capacity, good appearance and chemical stability. Characterization of the resin was done through determination of ion exchange capacity, distribution coefficients for various metal ions, chemical analysis, pH titration, FT-IR spectra and TG thermal analysis. The distribution coefficients (K_d) of 10 metal ions were determined in different electrolyte/electrolyte concentrations. The significance of the exchanger is revealed by the important separations. Based on the difference in distribution co-efficient (K_d) some analytically important binary separations of metal ions Ca^{2+}/Pb^{2+}, Zn^{2+}/Pb^{2+}, Cd^{2+}/Pb^{2+}, Ni^{2+}/Pb^{2+}, Co^{2+}/Pb^{2+} and Hg^{2+}/Pb^{2+} and ternary separations Pb^{2+}/Hg^{2+}/Cd^{2+}, Pb^{2+}/Hg^{2+}/ Zn^{2+} and Pb^{2+}/Hg^{2+}/Co^{2+} have been achieved. Practical utility of the material has been demonstrated by a heavy metal separation. It was found to possess high thermal stability and selectivity for lead, thus making it an important exchanger for the environmentalists.

Key Words: Cerium(IV) iodoselenite, Cation exchanger, Binary and ternary separations.

INTRODUCTION

The ion exchange method is one of the elegant methods used in analytical chemistry. These techniques are used widely for separations involving closely related elements. Separation involving ion exchange method is simple and requires smaller amounts of samples. The separated samples can be determined by instrumental or titrimetric methods. The significance of this method is exposed in large amounts of literature accumulated during last two decades. Nowadays large number of informatives are available in this area[1-9]. Selectivity towards particular metal ion by inorganic ion exchangers[10-15] is one of the important factors for their development and these have extensive applications in separation science specially of heavy metals[16-23].

EXPERIMENTAL

Ceric ammonium nitrate (BDH), sodium selenite (BDH), potassium iodate (E. Merck), double distilled demineralized water were used through out. All other reagents used were analytical grade.

A digital pH meter (Elico, Pvt. Ltd, India model LI-120) with combined glass and calomel electrodes, FT-IR Spectrometer (Bruker IFS 66v FT-IR spectrometer) and thermogravimetric-differential thermal analyzer Perkin-Elmer (Pyres Diamond TG-DTA) in nitrogen atmosphere were used. A glass column (30 cm × 1.1 dia.), chemical balances and calibrated glasswares were used.

Synthesis: The ion exchanger cerium(IV) iodoselenite was synthesized by mixing ceric ammonium nitrate, with a mixture of potassium iodate and sodium selinite in different mole and volume ratios with constant stirring (Table-1). Dilute HNO_3 and NaOH were used to maintain pH at 1.0. The precipitate was allowed to stand for 24 h, filtered, washed first with dil. HNO_3 (pH = 1), then with demineralized water. It was dried at room temperature (30 ºC). The material was then converted to H^+ form by treatment with 1.0 M HNO_3 for 24 h with occasional shaking and intermittent changing of the acid, filtered, washed and dried. The colour of the ion exchanger was orange red.

TABLE-1
CONDITIONS OF PREPARATION OF CERIUM(IV) IODOSELENITE AND ION EXCHANGE PROPERTIES

Sample No.	Cerium(IV) ammonium nitrate (M)	KIO_3 (M)	Sodium selenite (M)	Exchange capacity	Colour	pH (Final)
1	0.10	0.05	0.05	1.56	Reddish orange	1
2	0.10	0.10	0.05	1.39	Reddish orange	1
3	0.10	0.05	0.10	1.42	Reddish orange	1
4	0.05	0.10	0.10	1.52	Orange	1
5	0.05	0.10	0.05	1.53	Orange	1
6	0.05	0.05	0.10	1.49	Reddish orange	1
7	0.05	0.05	0.05	1.50	Reddish orange	1

Ion exchange capacity: The ion exchange capacities of the samples were determined by column operation. The ion exchanger (1.0 g) in the H^+ form was placed in the column with glass wool support, NaCl (1.0 M) was used as the eluent and 150 mL of the eluate was collected in every case. The H^+ ion eluted from the column was determined titrimetrically with standard NaOH using the standard equation. The exchanger can be regenerated thrice without any appreciable loss of exchange capacity. Beyond this 50 % of the capacity was lost. The effect of size and charge of exchanger was studied for all the alkali and alkaline earth metal ions by column method.

Chemical composition: The exchanger 100 mg was ground into fine powder and dissolved in 10 mL of conc. HNO_3, cerium(IV) and iodate were estimated volumetrically and selinite estimated gravimetrically[24,25].

Effect of temperature on exchange capacity: The effect of temperature on the exchange capacity was studied by determining the exchange capacity of the exchanger heated at various temperatures in a thermostatically controlled oven.

pH Titration curves[26]: For pH titration the exchanger 100 mg was placed in 250 mL conical flasks and equimolar solutions of alkali metal chloride and their hydroxides in different volume ratios were added, the final volume being 50 mL to maintain constant ionic strength. The pH of the solution was recorded every 24 h until equilibrium was attained.

Distribution coefficient: Equilibrating the metal ion solution with the exchanger for 6 h at room temperature, distribution studies were carried out for 10 metal ions in demineralized water, 0.1 M, 0.01 M, 0.001 M solutions of HNO_3, 0.1 M, 0.01 M, 0.001 M solutions of NH_4NO_3 and in the mixture of 0.1 M solution HNO_3 0.1 M NH_4NO_3.

Separation of metal ions: Separation studies were carried out with 5 g of exchanger in H^+ form (60-100 Mesh) taken in a glass column (30 cm × 0.69 cm) and 0.005 M metal ion solutions. The rates of flow in all separations were maintained at 0.5 mL/min. Separations were carried out for those metal ions, which are having separation factor greater than five.

Effluent analysis: Effluent analysis were carried out with four different water samples collected from the river basins in Kerala state, India. 1 L of all the samples were acidified with dil. HNO_3 and were concentrated to 200 mL finding out the amount of Pb^{2+} contamination through ion exchange column filled with cerium(IV) iodoselenite (CeISe).

RESULTS AND DISCUSSION

Cerium(IV) iodoselenite obtained was orange red crystalline compound stable in water, acetic acid, 1.0 M aqueous solutions of H_2SO_4, HCl, HNO_3 and 1.0 M aqueous solutions of LiCl, NaCl, KCl, $BaCl_2$ and $CaCl_2$. The chemical composition of the exchanger is found to be 1:2:1. The TG-DTA analysis[27] and chemical composition studies suggests the empirical formula as $CeO_2.I_2O_5.SeO_2.7H_2O$. The sample 1 has promising ion exchange capacity of meq/g. The exchanger could be regenerated thrice without any appreciable loss of exchange capacity; beyond this 50 % of exchange, capacity was lost. The loss in exchange capacity may be due to hydrolysis of the exchanger.

IR spectral data[28-30] of H^+ form of cerium(IV) iodoselenite (dried at 30 ºC) show peaks at 3336, 1619, 1461, 1464, 1384, 1349, 1303, 1036, 814, 707 and 496 cm^{-1}. The peaks at 3336, 1619 cm^{-1} correspond to the vibration of hydroxyl groups and interstitial water. Other peaks at 1036, 814 and 707

cm^{-1} are attributed to iodoselenite and that at 496 cm^{-1} can be assigned to a Ce-O stretching vibration.

The effect of size and charge of metal ion on the ion exchange capacity of the exchanger for alkali and alkaline earth metals follows the sequence:

Li^+ (1.42) < Na^+ (1.56) < K^+ (1.74)
Ba^{2+} (1.96) > Sr^{2+} (1.87) > Ca^{2+} (1.82) > Mg^{2+} (1.53)
(The exchange capacity is given in parenthesis)

The ion exchange capacity increases with decrease in hydrated ionic radii (Table-2). This trend in the exchange capacity suggests that the exchange of these cations take place in the hydrated form.

TABLE-2
CHANGE OF EXCHANGE CAPACITY WITH HYDRATED IONIC RADII

Exchanging ion	Hydrated ionic radii (Å)	Exchange capacity in (meq/g)
Li^+	3.40	1.42
Na^+	2.76	1.56
K^+	2.32	1.74
Mg^{2+}	7.00	1.53
Ca^{2+}	6.30	1.82
Sr^{2+}	6.10	1.87
Ba^{2+}	5.90	1.96

The effect of temperature on ion exchange capacity of the exchanger heated at various temperatures indicates that the ion exchange capacity of the material decreases as the temperature increases. Cerium(IV) iodoselenite after drying at 300 ºC, 90 % ion exchange capacity was lost. Decrease in ion exchange capacity on heating is due to loss of external water (Fig. 1).

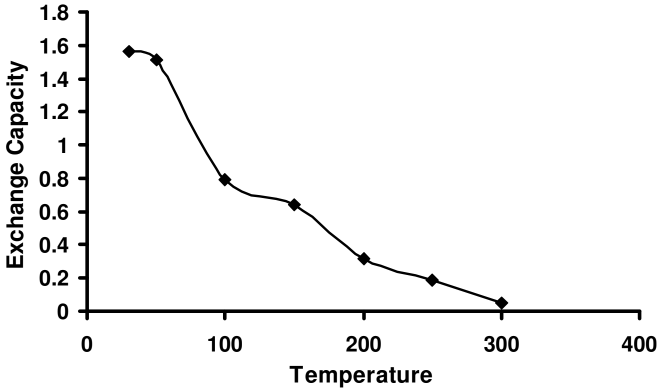

Fig. 1. Effect of temperature on exchange capacity of cerium(IV) iodoselenite

The pH titration curves of cerium(IV) iodoselenite performed in alkali metal chloride/alkali metal hydroxide system (Fig. 2) shows weak dibasic acid behaviour.

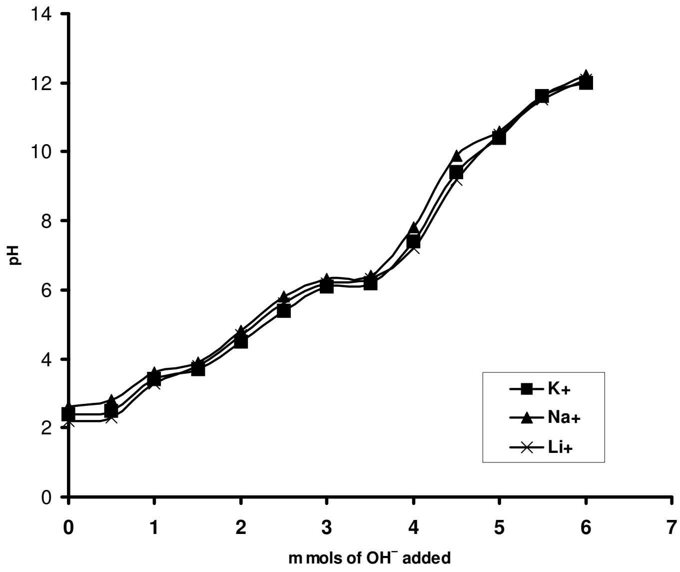

Fig. 2. pH Titration curve-cerium(IV) iodoselenite

Distribution studies of 10 metal ions revealed that (Table-3) cerium(IV) iodoselenite shows higher affinity for Pb^{2+} as compared to the other metal ions. The exchange of metal ions takes place in the order of $Pb^{2+} > Cu^{2+} > Mg^{2+} > La^{2+} > Hg^{2+} > Ca^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$. The electrolyte concentration considerably affects the distribution coefficient. As the electrolyte, concentration increases the distribution coefficient decreases.

Absence of any colour change of the exchanger through out the process indicates that no cerium(III) has been formed.

Analytically important binary and ternary separations were carried out successfully on a column of the exchanger. The recovery range is from 97-100 % with a variation of 1 % repetitive determinations. The results show that cerium(IV) iodoselenite is suitable for certain important binary separations like $Pb^{2+}\backslash Zn^{2+}$, $Pb^{2+}\backslash Cd^{2+}$, $Pb^{2+}\backslash Ni^{2+}$, $Pb^{2+}\backslash Ca^{2+}$, $Pb^{2+}\backslash Co^{2+}$, $Pb^{2+}\backslash Hg^{2+}$ and ternary separations like $Pb^{2+}\backslash Hg^{2+}\backslash Zn^{2+}$, $Pb^{2+}\backslash Hg^{2+}\backslash Cd^{2+}$ and $Pb^{2+}\backslash Hg^{2+}\backslash Co^{2+}$ (Table-4).

The river water analysis showed that the urban industrial area releases considerable amount of Pb^{2+} ions in to the river water (Table-5).

TABLE-3
DISTRIBUTION COEFFICIENTS OF SOME METAL IONS ON CERIUM(IV) IODOSELENITE EXCHANGERAND THE EFFECT OF ELECTROLYTE CONCENTRATION ON DISTRIBUTION COEFFICIENTS

Cation	Taken as	Distilled water	K_d values								
			HNO_3 (M)				NH_4NO_3				AA
			1	0.1	0.01	0.001	1	0.1	0.01	0.001	
Zn^{2+}	SO_4^{2-}	00.00	0.00	00.0	0.00	0.00	0.00	0.00	0.00	00.0	00.00
Co^{2+}	NO_3^-	00.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	00.00
Ni^{2+}	NO_3^-	06.00	0.00	0.00	00.0	05.0	0.00	0.00	0.00	05.0	00.00
Cd^{2+}	NO_3^-	16.00	0.00	10.0	05.0	15.0	0.00	0.00	10.0	10.0	00.00
Ca^{2+}	NO_3^-	20.00	5.00	08.0	08.0	15.0	0.00	00.0	08.0	10.0	00.00
Hg^{2+}	NO_3^-	70.00	22.0	31.0	60.0	64.0	15.0	22.0	55.0	50.0	04.00
La^{3+}	NO_3^-	98.50	40.0	54.0	75.0	90.0	35.0	42.0	65.0	80.0	13.00
Mg^{2+}	NO_3^-	150.0	57.0	74.0	110	140	50.0	70.0	100	135	27.50
Cu^{+2}	SO_4^{2-}	248.0	66.0	136	180	220	100	90.0	150	195	43.00
Pb^{2+}	NO_3^-	780.0	94.0	388	520	740	90.0	350	370	695	69.00

AA = 1:1 Mixture of HNO_3 and NH_4NO_3

TABLE-4
SEPARATION OF BINARY AND TERNARY MIXTURES USING CERIUM(IV) IODOSELENITE ION EXCHANGER

Mixture with eluents	Metal ion (mg)	
	Loaded	Recovered
Zn^{2+} (0.01 M HNO_3)	0.90	0.90
Pb^{2+} (0.01 M HNO_3 + 0.1 M NH_4NO_3)	2.60	2.58
Cd^{2+} (0.01 M HNO_3)	1.20	1.20
Pb^{2+} (0.01 M HNO_3 + 0.1 M NH_4NO_3)	2.60	2.56
Ni^{2+} (0.01 M HNO_3)	2.90	2.88
Pb^{2+} (0.01 M HNO_3 + 0.1 M NH_4NO_3)	2.60	2.55
Ca^{2+} (0.01 M HNO_3)	5.00	4.92
Pb^{2+} (0.01 M HNO_3 + 0.1 M NH_4NO_3)	4.95	4.90
Co^{2+} (0.01 M HNO_3)	6.90	6.80
Pb^{2+} (0.01 M HNO_3 + 0.1 M NH_4NO_3)	4.95	4.90
Hg^{2+} (0.01 M HNO_3)	6.85	6.80
Pb^{2+} (0.01 M HNO_3 + 0.1 M NH_4NO_3)	4.95	4.94
Pb^{2+} – Hg^{2+} – Zn^{2+}		
Pb^{2+} (0.01 M HNO_3 + 0.1 M NH_4NO_3)	9.00	8.46
Hg^{2+} (0.20 M HNO_3)	6.00	5.85
Zn^{2+} (0.10 M HNO_3)	4.80	4.80
Pb^{2+} – Hg^{2+} – Cd^{2+}		
Pb^{2+} (0.01 M HNO_3 + 0.1 M NH_4NO_3)	9.00	8.49
Hg^{2+} (0.20 M HNO_3)	6.00	5.83
Cd^{2+} (0.01 M HNO_3)	3.50	3.50
Pb^{2+} – Hg^{2+} – Co^{2+}		
Pb^{2+} (0.01 M HNO_3 + 0.1 M NH_4NO_3)	2.80	2.80
Hg^{2+} (0.20 M HNO_3)	6.00	5.87
Cd^{2+} (0.10 M HNO_3)	2.80	2.80

TABLE-5
DETERMINATION OF Pb^{2+} CONTAMINATION WITH CERIUM(IV) IODOSELENITE ION EXCHANGER FROM RIVER WATER SAMPLES OF KERALA STATE

Sample 1 Bharathapuzha (Malapuram) river basin Amount/L	Sample 2 Priyar (Aluva) river basin Amount/L	Sample 3 Chaliyar (Calicut) river basin Amount/L	Sample 4 Kabani (Wayanad) river basin Amount/L
0.0156 mg	0.0234 mg	0.0231mg	0.0097 mg

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(*Received*: 23 November 2007; *Accepted*: 4 July 2008) AJC-6659