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Synthetic Inorganic Ion-Exchangers. Part XII. Hydrous Cerium(IV) Oxide: Anion-Exchange Properties and Some Ion-Exchange Separations

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NOTE

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Abstract

The anion-exchange behavior of hydrated cerium(IV) oxide has been studied. The distribution coefficients of several anions on cerium dioxide were determined. On the basis of the distribution coefficients some selective ion-exchange separations of anions are reported.

INTRODUCTION

The hydrous oxides of metals possess both cation and anion exchange properties at pH values above and below their isoelectric points. In Part VIII (*1*) of this series, the cation exchange behavior of hydrous cerium(IV) oxide and some selective separations of metal ions on the exchanger column were reported. Two varieties of hydrous cerium(IV) oxide were prepared. These were hard, crystalline, and suitable for column operations. The isoelectric point of cerium(IV) oxide has been reported to be about pH 7.0 by Abe (*2*). In the present work the anion exchange properties of this exchanger have been explored. The distribution coefficients of several anions were determined, and on the basis of these values several ion-exchange separations of anions were achieved.

EXPERIMENTAL

Reagents

All the chemicals used were of analytical grade (B.D.H., E. Merck, or S. Merck).

Apparatus

pH measurements were made with an ELICO pH meter, Model No. LI-10 (India). For spectrophotometric work, Spectromom Model 202, Budapest (Hungary) was used.

Preparation

Hydrated cerium(IV) oxide of different degrees of hydration was synthesized as described in our earlier paper (*1*). The mixture was digested for 1 hr at room temperature. The precipitate was filtered and washed with deionized water, then dried in air, and finally dried over calcium chloride in a vaccum desiccator. The product was converted into the H^+ form by treating with 0.1 N H_2SO_4 and 1 N NH_4OH, washed, and dried as before at 110°C.

RESULTS AND DISCUSSION

Composition

The exchanger was heated to 800 °C in a muffle furnace. From the weight loss, the percentage of water was calculated and the ratio of $H_2O:CeO_2$ was determined as described earlier (*1*).

The ratio of H_2O: CeO_2 of Batch 1 was 2.577 and that of Batch 2 was 3.001.

Chemical Stability

Half a gram of the exchanger was shaken with 50 ml of different acids of varying strength intermittently for 2 days at room temperature. From the filtrate, cerium was estimated spectrophotometrically by the T.T.A. method (*8*).

The exchanger is fairly stable in water, 0.1 N HNO_3, 0.1 N H_2SO_4, and 0.1 N $HClO_4$.

pH Titration

Topp and Pepper's method (*3*) was applied for pH titration. Solutions containing either 100 ml of free acid (H_2SO_4 or HNO_3) or acid mixed mixed with its corresponding salt (Na_2SO_4 or $NaNO_3$), having SO_4^{2-} or NO_3^- constant at 0.1 *N*, were added to 0.5 g of the exchanger. The mixture was shaken intermittently for 2 days at room temperature. The pH of the solutions was plotted against the amount of acid added. The curves show only one sharp break, so the exchanger shows a monofunctional nature.

Anion-Exchange Capacity

The anion-exchange capacity of the exchanger was determined at different pH values. Half a gram of the exchanger was shaken with 100 ml of $H_2SO_4 + Na_2SO_4$ or $HNO_3 + NaNO_3$, with varying amounts of H_2SO_4 or HNO_3. The strength of $[NO_3]^-$ or $[SO_4]^{2-}$ was kept constant at 0.1 *N*. The mixture was shaken intermittently for 2 days. Aliquots (10 ml) were taken, and the excess of acid was determined by titrating with standard NaOH solution. The pH was noted from an aliquot of the supernatant liquid. The exchange capacities for different ions at different pH values are given in Table 1.

The anion exchange capacity decreases with increasing temperature as in the case of cation-exchange capacity (*1*): Batch 1, 0.84 (200°C); 0.04 (600°C) meq/g.

DISTRIBUTION COEFFICIENTS

The exchanger was converted to the H^+ form as reported earlier (*1*). By using this exchanger (Batch 1), the distribution coefficients of several anions were determined at pH 2 and at pH 6. Arsenate, ferricyanide, vanadate, and chromate were determined volumetrically by standard methods (*4*, *5*). Phosphate was determined colorimetrically by the heteropoly blue method (*5*), while tungstate and molybdate were determined by the thiocyanate method (*7*, *8*). The results are summarized in Table 2.

It is evident from studies of the K_d values of anions on cerium dioxide that some selective separations of vanadate, arsenate, phosphate, and tungstate from other anions are feasible. Thus separation of dichromate from arsenate and phosphate, ferricyanide from phosphate and arsenate, and tungstate from phosphate and arsenate have been achieved. Although

TABLE 1

Anion-Exchange Capacity of Cerium Dioxide at Different pH Values

Anion taken	pH (final), (Batch 1)	Exchange capacity (Batch 1) (meq/g)	pH (final), (Batch 2)	Exchange capacity (Batch 2) (meq/g)
SO_4^{2-}	6.5	0.5	4.35	0.94
	3.3	1.68	2.90	1.30
	2.6	1.50	2.5	1.4
	2.45	1.76	2.3	1.42
	2.30	1.76	2.2	1.52
	2.20	1.76	2.1	1.56
NO_3^-	6.4	0.25	2.26	0.54
	2.8	0.64	2.20	0.62
	2.3	0.81	2.05	0.66
	2.05	0.86	1.90	0.68
	1.95	0.88	1.80	0.68
	1.80	0.92	1.75	0.68
	1.75	0.92		

TABLE 2

Distribution Coefficients of Anions on Ce(IV) Dioxide

Anion taken	K_d values pH 2	K_d values pH 6
WO_4^{2-}	300	11.1
MoO_4^{2-}	75	36.3
$Fe(CN)_6^{3-}$	2.1	1.01
VO_3^-	1420	143
AsO_4^{3-}	270	49
PO_4^{3-}	226	55
$Cr_2O_7^{2-}$	13	9.7

the K_d values at pH 2 are higher and the anion exchange is more pronounced than at pH 6, the quantitative elutions of the anions from the exchanger at pH 2 were difficult, probably due to formation of stable ceric compounds in the column itself. These difficulties were overcome by using pH 6 where distinct anion-exchange properties were noticeable.

A glass column (i.d. 1.2 cm) was filled with 5 to 6 g of exchanger (50–100 mesh) supported at the bottom with glass wool. The pH of the anions

TABLE 3

	Mixtures loaded (mg)		Eluents (volume, ml)		Recovery (%)
1.	$Cr_2O_7^{2-}$,	4.35	1% $(NH_4)_2SO_4$	(30)	103.7
	AsO_4^{3-},	8.58	3 *N* NaOH	(25)	95.3
2.	$Cr_2O_7^{2-}$,	4.58	1% $(NH_4)_2SO_4$	(30)	103.7
	PO_4^{3-},	3.1	3 *N* NaOH	(40)	96.7
3.	$Fe(CN)_6^{3-}$,	3.32	1% $(NH_4)_2SO_4$	(30)	101.0
	AsO_4^{3-},	8.58	3 *N* NaOH	(25)	96.1
4.	$Fe(CN)_6^{3-}$,	3.32	1% $(NH_4)_2SO_4$	(30)	101.02
	PO_4^{3-},	3.1	3 *N* NaOH	(40)	94.5
5.	WO_4^{2-},	1.58	0.5 *N* NH_4OH	(15)	95.0
	AsO_4^{3-},	8.58	3 *N* NaOH	(30)	97.7
6.	WO_4^{2-},	1.58	0.5 *N* NH_4OH	(20)	102.5
	PO_4^{3-},	3.1	3 *N* NaOH	(35)	93.6

was kept at 6. The binary mixtures were separated, and the eluents used are shown in Table 3.

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