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# Synthetic Inorganic Ion-Exchangers. Part VIII. Hydrous Cerium(IV) Oxide: Synthesis, Properties, and Ion-Exchange Separations

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## Abstract

Hydrated cerium(IV) dioxide has been synthesized under different conditions. Its physicochemical properties e.g., IR spectra, chemical and thermal stability, pH titration, and ion-exchange properties, have been investigated. Distribution coefficient values of some of the cations on cerium dioxide have been determined. On the basis of distribution coefficients, some selective ion-exchange separations have been reported.

Among the different classes of inorganic compounds, hydrated oxides of metals (*1*) show interesting ion-exchange properties. They act as cation exchangers at higher pH values and as anion exchangers at lower pH values (*2*):

$$\mathrm{MOH} \rightleftarrows \mathrm{MO}^- + \mathrm{H}^+ \qquad (1)$$

$$\mathrm{MOH} \rightleftarrows \mathrm{M}^+ + \mathrm{OH}^- \qquad (2)$$

In this communication the synthesis, IR spectra, chemical stability, thermal stability, pH titration, cation exchange capacity at different pH values of a cerium(IV) dioxide exchanger, distribution coefficient values, and some binary ion-exchange separations using a cerium dioxide column are reported.

## 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 LI-10 (India). For spectrophotometric work, Spectromom 202 (Hungary) was used. Analytical balance OWA Labour type 707.04 (Germany) was used. For column operations, a glass column of internal diameter 1.2 cm and length 20 cm was used.

### Preparation of Hydrated Cerium(IV) Dioxide

Hydrated cerium(IV) dioxide with different degrees of hydration has been synthesised by mixing cerium sulfate and sodium hydroxide solutions. The precipitate was filtered and washed with deionized water, then dried in air, and finally dried over calcium chloride in a vaccum desiccator. Details of synthesis and nature of the product are given in Table 1. The product was converted into the $H^+$-form by treating with 0.1 *N* $H_2SO_4$, washed and dried as before.

## RESULTS AND DISCUSSION

### Composition of Hydrated Cerium(IV) Dioxide

About 0.2 g of the compound was weighed accurately in a silica crucible. It was ignited at 850°C in a muffle furnace and weighed. The difference in weight was the amount of water lost, and the weight of the residue

TABLE 1

Preparation and Composition of Hydrated Cerium(IV) Dioxide

| Batch no. | 0.1 *M* $Ce(SO_4)_2$ in 1.0 *N* $H_2SO_4$ : 1.0 *N* NaOH (vol : vol) | pH of the mother liquor | Stirring time (hr) | $H_2O : CeO_2$ | Physical appearence |
|---|---|---|---|---|---|
| 1[a] | 1 : 2 | 12.5 | 1 | 2.577 | Amber colored, crystalline |
| 2[a] | 1 : 2 | 12.5 | 1 | 3.001 | Yellow amorphous |

[a] For Batch 1, cerium sulfate solution was added to sodium hydroxide solution. For Batch 2, the order of addition was reversed.

was the amount of anhydrous cerium(IV) dioxide. From this result the percentage of water was calculated. $H_2O:CeO_2$ was calculated by employing the equation of Alberti et al. (*3*):

$$\frac{n \times 18}{n \times 18 + CeO_2} = \frac{\%\ \text{weight loss}}{100}$$

where $n$ represents the number of moles of water. Details of the synthesis and composition of cerium dioxide are given in Table 1.

## Chemical Stability

For a detailed study on the stability of the exchanger toward mineral acids, the following method was employed: 0.5 g of the exchanger was taken in a 125-ml bottle, 50 ml of the required solvent was added to the bottle, and the bottle was shaken for 2 days intermittently at room temperature. From the filtrate cerium was estimated spectrophotometrically by the T.T.A. method (*4*).

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

## Heat Treatment

About 1 g of the exchanger was taken in a silica crucible and heated from 100 to 800°C in steps of 100°C. For each step of heating, a separate sample was taken. At 100°C the sample was heated in an air oven, and from 200 to 800°C in a muffle furnace. The percentage of weight loss was plotted against the temperature of heating, and the curve is shown in Fig. 1.

## IR Spectra

The IR spectra reveal a sharp peak at 2850–3000 $cm^{-1}$ which may be due to coordinated water molecules. A sharp peak at about 1650 $cm^{-1}$ corresponds to the deformed vibration of free water molecules. The broad peak at 600–300 $cm^{-1}$ is presumably due to the stretching frequency of the Ce–O bond in the polymeric species.

## pH Titration

Topp and Pepper's method (*5*) was employed for pH titration. Solutions (50 ml) containing 2 $N$ ($MOH + M_2SO_4$), where $M = Na^+$ or $K^+$,

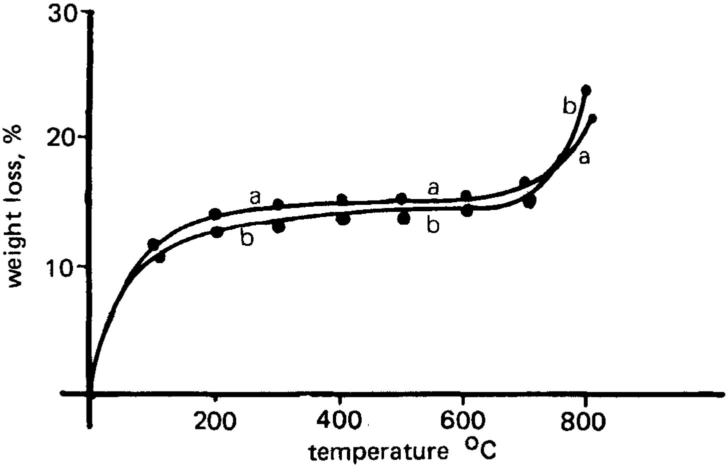

FIG. 1. Weight loss curve of cerium(IV) dioxide: (a) Batch No. 1, and (b) Batch No. 2.

were added to 0.5 g of the exchanger. The metal ion concentration was kept constant while the amount of MOH added was varied. The mixture was shaken intermittently for 2 days at room temperature. The pH of the solution was noted by using a pH meter. The pH of the solution was plotted against the amount of alkali added, and the curves are shown in Figs. 2 and 3. The pH titration curves show only one sharp break, so the exchanger may be compared with a monofunctional strongly acid-type exchanger.

### Ion-Exchange Capacity

The cation exchange capacity of the exchanger ($H^+$ form) was determined at different pH values. One gram of the exchanger was placed in different bottles to which 50 ml of 2 $N$ ($MOH + M_2SO_4$), where M = $Na^+$ or $K^+$, with varying quantities of MOH were added. The mixture was shaken intermittently for 2 days. Aliquots (10 ml) were taken and the excess of alkali was determined by titrating with standard sulfuric acid. From the other portion of the supernatant liquid, the pH was noted by using a pH meter. The exchange capacities for different ions at different pH values are given in Table 2.

The loss in ion-exchange capacity of cerium dioxide was determined

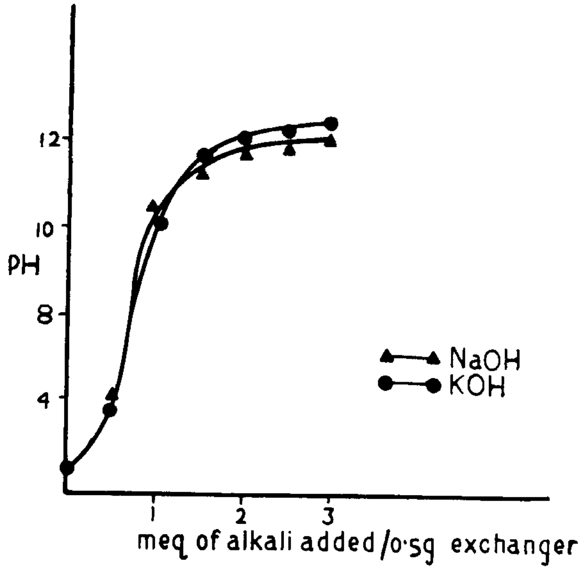

FIG. 2. pH-titration curve for cerium(IV) dioxide (Batch No. 1).

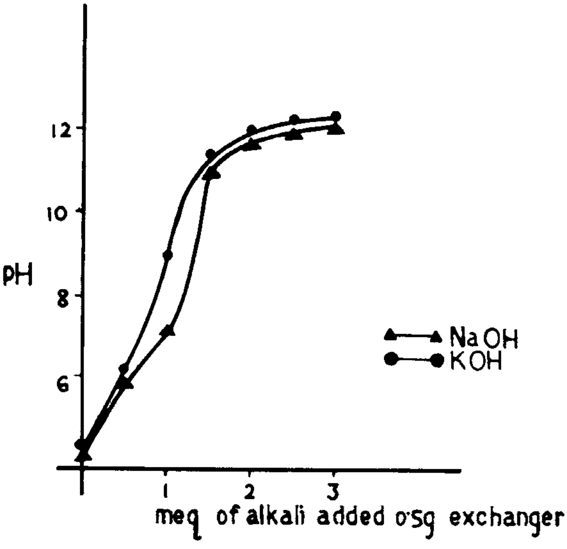

FIG. 3. pH-titration curve for cerium(IV) dioxide (Batch No. 2).

TABLE 2

Cation Exchange Capacity of Cerium Dioxide at Different pH Values

| Ion taken | pH (final) (Batch 1) | Exchange capacity of $CeO_2$ (Batch 1) (meq/g) | pH (final) (Batch 2) | Exchange capacity of $CeO_2$ (Batch 2) (meq/g) |
|---|---|---|---|---|
| $Na^+$ | 4.0 | 0.012 | 4.3 | 0.034 |
| | 6.2 | 0.999 | 6.1 | 0.97 |
| | 10.6 | 1.82 | 7.2 | 1.95 |
| | 12.0 | 2.29 | 11.9 | 2.77 |
| $K^+$ | 4.4 | 0.026 | 4.5 | 0.024 |
| | 6.0 | 0.97 | 6.2 | 0.097 |
| | 10.2 | 1.95 | 9.0 | 1.93 |
| | 11.7 | 2.28 | 11.4 | 2.56 |
| | 12.0 | 2.37 | 12.0 | 2.64 |

after heating it from 100 to 800°C. One gram of the exchanger was heated for 1 hr at the required temperature, and the exchange capacity was determined at pH ~12 with sodium ion by the method given above. The exchanger is fairly stable toward heating up to 700°C (exchange capacity 2.19 meq/g), and the exchange capacity was not lost. At 800°C the exchanger (Batch 2) loses its exchange capacity completely while the exchanger (Batch 1) loses its exchange capacity appreciably (0.77 meq/g).

## Column Elution of Hydrogen Ion

One gram of the exchanger (50–100 mesh size) was placed in a glass column (i.d. 1.2 cm) supported at the bottom with glass wool. A 2 *N* ($NaOH + Na_2SO_4$) solution containing 0.1 *N* NaOH and a 0.4 *N* ($NaOH + Na_2SO_4$) solution containing 0.1 *N* NaOH were separately passed through the column. The effluents were collected in 5 ml fractions, and the amount of alkali consumed was determined by titrating with standard sulfuric acid solution using methyl orange as the indicator.

The amount of hydrogen ion eluted in each fraction was plotted against the volume of effluent. The elution curve is shown in Fig. 4. Almost all the hydrogen ion was released completely after passing 50 ml of the eluent.

## Distribution Coefficient ($K_d$)

The exchanger was converted to the hydrogen form by immersion in 0.1 *N* $H_2SO_4$ followed by washing with deionized water. Due to partial

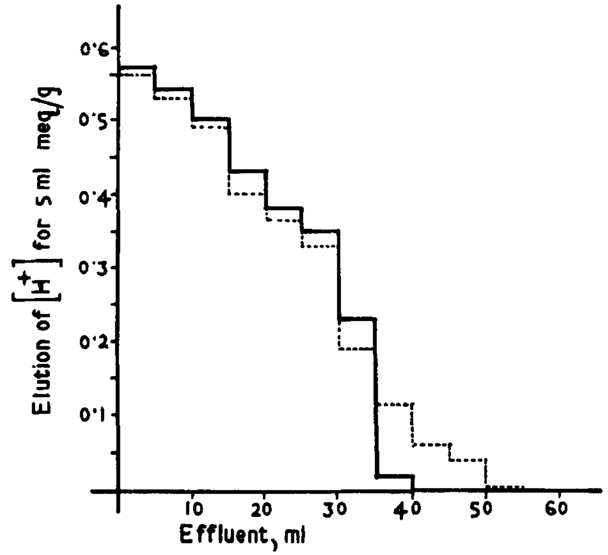

FIG. 4. Elution curve of hydrogen ion of cerium(IV) dioxide: (——) 2 *N* ($Na_2SO_4$ + NaOH), and (----) 0.4 *N* ($Na_2SO_4$ + NaOH).

solubility in the acid, the exchanger was likely to contain partially dissolved cerium(IV) as the complex anion $Ce(SO_4)_3^{2-}$, which is very difficult to remove. This anion hindered the complexometric titration by oxidizing the indicator. To remove the above interference, the exchanger was converted to the $NH_4^+$-form by shaking with 1 *N* $NH_4OH$ for 15 min, washing with deionized water, and drying in an air oven at 110°C for 1 hr. When the exchanger was dried at 110°C, ammonium ion was decomposed and transferred back to the hydrogen form, free from any contamination due to dissolved $Ce(SO_4)_3^{2-}$. By using such an exchanger, the distribution coefficient was measured by following the method reported in an earlier paper (*6*). The concentrations of metal ions were adjusted to about $2 \times 10^{-4}$ *M* and the pH to 5.5 to 6.5. These ions were estimated by using a $2 \times 10^{-3}$ *M* EDTA solution (*7–9*). The results are summarized in Table 3.

## Ion-Exchange Separations

It is evident from studies of $K_d$ values of metal ions on cerium dioxide that some selective ion-exchange separation of copper from other metal ions is feasible. Thus separations of magnesium, zinc, cobalt, and man-

TABLE 3

Distribution Coefficient of Metal Ions on Cerium(IV) Dioxide

| Metal ion | Ionic radii | $K_d$ values at pH 5.5 to 6.5 | |
|---|---|---|---|
| | | Batch 1 | Batch 2 |
| $Mg^{2+}$ | 0.65 | 2.1 | 2.1 |
| $Zn^{2+}$ | 0.75 | 1.6 | 51.7 |
| $Pb^{2+}$ | 1.21 | 42.4 | 72.6 |
| $Cd^{2+}$ | 0.97 | 13.3 | 97.8 |
| $Ca^{2+}$ | 0.99 | 5.8 | 7.7 |
| $Ba^{2+}$ | 1.35 | 5.0 | 2.5 |
| $Sr^{2+}$ | 1.13 | 5.2 | 2.6 |
| $Cu^{2+}$ | 0.92 | 550.3 | T.A.[a] |
| $Co^{2+}$ | 0.72 | 3.0 | 14.6 |
| $Mn^{2+}$ | 0.80 | 5.0 | 28.1 |
| $Ni^{2+}$ | 0.69 | 16.1 | 218.7 |

[a] T.A. = Total adsorption.

ganese from copper have been achieved. A glass column (i.d. 1.2 cm) was filled with 5.0 g cerium dioxide (50–100 mesh size) supported at the bottom with glass wool. The column was washed with deionized water. The pH of the metal ion solutions were adjusted to pH 5.5 to 6.5. The binary mixtures separated and the eluents used are shown in Table 4.

TABLE 4

Separation of Copper from Other Metal Ions on a Cerium Dioxide Column (Batch 1)

| Mixture separated | Eluents | Volume of effluent (ml) | Metals | | % error |
|---|---|---|---|---|---|
| | | | Taken (mg) | Found (mg) | |
| 1. Mg | Water | 30 | 0.09 | 0.093 | +3.3 |
| Cu | 1 *M* $NH_4NO_3$ in 0.15 *M* $HNO_3$ | 30 | 0.27 | 0.26 | −3.7 |
| 2. Zn | Water | 110 | 0.28 | 0.28 | 0.0 |
| Cu | 1 *M* $NH_4NO_3$ in 0.15 *M* $HNO_3$ | 30 | 0.27 | 0.26 | −3.7 |
| 3. Co | Water | 75 | 0.27 | 0.26 | −3.7 |
| Cu | 1 *M* $NH_4NO_3$ in 0.15 *M* $HNO_3$ | 30 | 0.21 | 0.21 | 0.0 |
| 4. Mn | Water | 30 | 0.21 | 0.21 | 0.0 |
| Cu | 1 *M* $NH_4NO_3$ in 0.15 *M* $HNO_3$ | 30 | 0.21 | 0.22 | +4.8 |

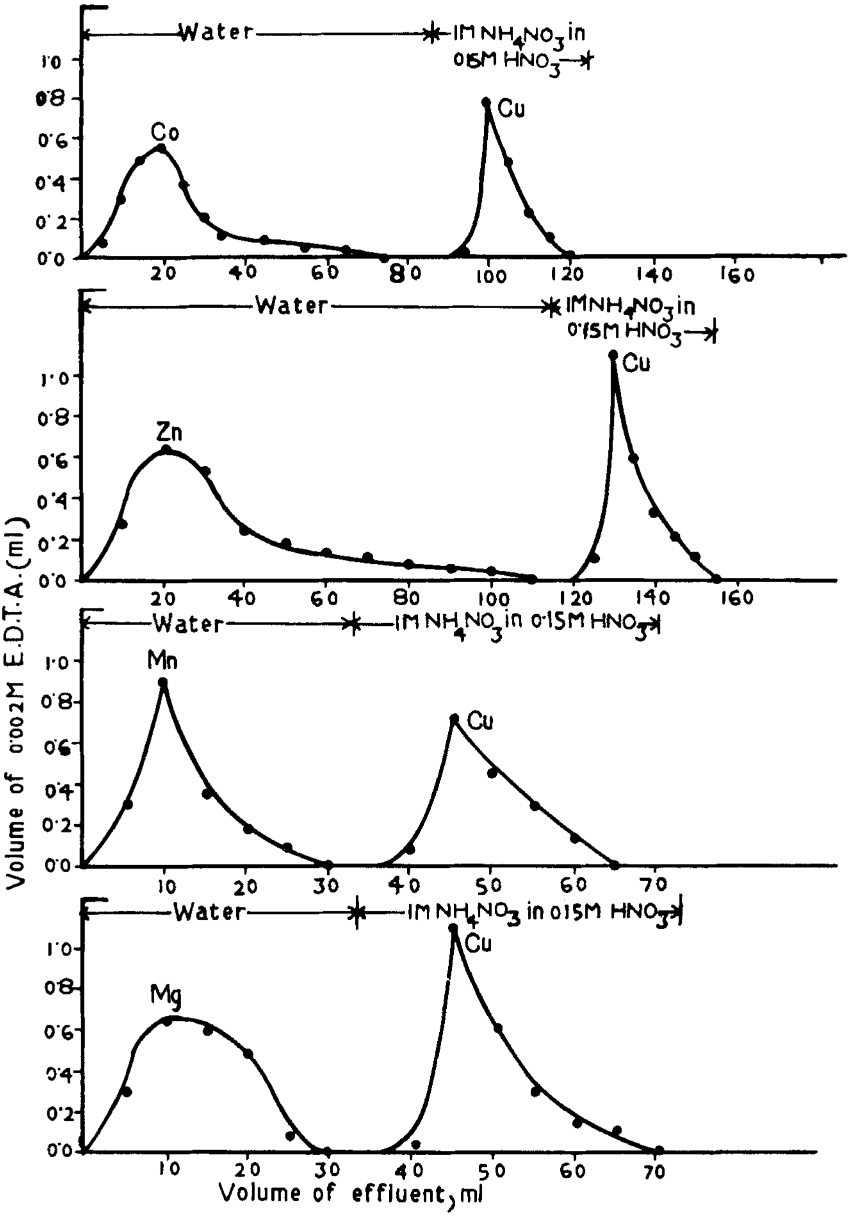

FIG. 5. Binary separation of Co–Cu, Zn–Cu, Mn–Cu, and Mg–Cu on cerium(IV) dioxide column.

## Acknowledgment

Some typical plots of elution curves for metal ions are shown in Fig. 5. The above data show that cerium(IV) dioxide is a good ion exchanger, suitable for some binary ion-exchange separations.

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