The Adsorption of Copper(II), Dichromate(II) and Oxalate(II) by Different Samples of Precipitated Hydrous Beryllium Oxide

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In an earlier communication[1] we have described the precipitation of hydrous beryllium oxide by different alkalis, like sodium, potassium and ammonium hydroxides, from a beryllium sulfate solution. It has been shown that hydrous beryllium oxide is always associated with sulfate and sodium or potassium, according to whether the medium of precipitation is acidic or alkaline. This behavior has been attributed to the fact that at lower pH values, the precipitated hydrous oxide is basic in character and adsorbs anions, while at higher pH values it is predominantly acidic in character and preferentially adsorbs cations from the solution (Table IV). This shows, therefore, the amphoteric nature of the hydrous oxide in media of different pH values. It is worthwhile to mention here that, at different stages of precipitation, the ions adsorbed by the hydrous beryllium oxide could not be removed by washing it with hot water or even by heating the precipitated mass.

Extensive studies[2-7] of the adsorption of dyestuffs by precipitated hydrous oxides have been carried out in these laboratories. Tewari, Dey and Ghosh,[8] from a consideration of the adsorption of dyestuffs by hydrous oxides, attempted to elucidate the mechanism of the ageing of metal hydroxide.

It has been thought desirable to study the adsorption of some inorganic ions by different samples of hydrous beryllium oxide, prepared with different amounts of alkali, this paper will record the observation of the association of copper(II), dichromate(II) and oxalate(II) with the samples of hydrous beryllium oxide.

Experimental and Results

Materials.—Beryllium sulfate, copper sulfate, potassium dichromate and sodium thiosulfate solutions of the desired strengths were prepared from B. D. H., AnalaR grade chemicals and standardized by the usual methods (Arthur I. Vogel).

The Preparation of the Samples of Hydrous Oxide.—The samples, A, B and C, of the hydrous oxide were obtained by adding calculated amounts of a standard solution of sodium hydroxide to 500 ml. of a 0.5 M beryllium sulfate solution at 25°C.

A: precipitated with an equivalent sodium hydroxide
B: precipitated with a 10% deficient sodium hydroxide
C: precipitated with a 10% excess sodium hydroxide

These samples were thoroughly washed by decantation with distilled water the washings were free from a majority of the sulfate and hydroxyl ions. (The hydroxyl ions were removed completely, but the last traces of sulfate ions could not be removed completely due to the increasing tendency of the hydrous oxide to form a colloidal solution on further washing.)

These samples were then allowed to age for a month in Jena glass bottles. The volumes of these suspensions were raised by dilution with water to 0.2 M of beryllium oxide per liter after ageing; the pH values of A, B and C were then found to be 6.1, 5.6 and 6.9 respectively.

Adsorption Experiments.—To 5 ml. of suspension (0.001 M), varying amounts of the electrolyte solution were added, and the volumes were raised to 15 ml. The systems were then allowed to equilibrate for 24 hr. at 30°C. In the supernatant liquids, the concentrations of the ions were estimated, copper and dichromate iodometrically and oxalate against a standard permanganate solution. The amounts of ions adsorbed, x/m, where x is the amount of adsorbent adsorbed on m g. of adsorbate, are given below.

TABLE I. ADSORPTION OF CUPRIC IONS BY VARIOUS SAMPLES OF HYDROUS BERYLLIUM OXIDE

Initial concn. $M \times 10^6$	Values of cupric ion adsorbed x/m		
	Sample A	Sample B	Sample C
159.6	88.7	94.2	43.5
128.7	67.2	71.7	34.2
106.0	52.0	55.0	25.9
85.2	37.5	39.7	19.9
53.3	17.0	18.2	10.0
Total:	262.4	278.8	133.5

Adsorptive capacities of samples A, B and C are in the sequence B>A>C.

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[1] R. Dutta and S. Ghosh, *Kolloid-Z*, to be published.
[2] A. K. Dey and S. Ghosh, *Proc. Natl. Acad. Sci. India*, **15A**, 143 (1946).
[3] S. N. Tewari, *Kolloid-Z*, **19**, 128 (1962).
[4] R. B. Hajela and S. Ghosh, *Proc. Natl., Acad. Sci. India*, **28A**, 59, 118, 130 (1959).
[5] S. N. Tewari and S. Ghosh, ibid., **21A**, 29, 41 (1952).
[6] R. Prasad and A. K. Dey, *J. Phys. Chem.*, **65**, 1272 (1961).
[7] R. Prasad and A. K. Dey, *J. Inorg. Nucl. Chem.*, **24**, 1018 (1962).
[8] S. N. Tewari, A. K. Dey and S. Ghosh, *Z. anong. Chem.*, **271**, 150 (1953).

Table II. Adsorption of dichromate ions by various samples of hydrous beryllium oxide

Initial concn. $M \times 10^6$	Values of x/m Sample A	Sample B	Sample C
26.70	11.00	5.75	11.50
21.45	7.90	4.70	9.80
17.75	7.85	4.05	8.50
14.20	6.30	3.40	7.45
Total:	38.55	20.35	42.15

Adsorptive capacities of samples A, B and C in the sequence are C>A>B.

Table III. Adsorption of oxalate ions by various samples of hydrous beryllium oxide

Initial concn. $M \times 10^6$	Values of x/m Sample A	Sample B	Sample C
79.95	26.40	11.85	31.50
53.30	22.65	9.40	25.65
42.60	19.75	7.85	23.40
26.65	13.60	5.70	17.35
Total:	82.40	34.80	97.90

Adsorptive capacities of samples A, B and C in the sequence are C>A>B.

Discussion

The above tables conclusively show that in the case of the adsorption of cupric ions, the amount of adsorption reaches a maximum for sample B, prepared from deficient amount of alkali, and a minimum for sample C, prepared from an excess of alkali, and is in the order of B>A>C. In the case of oxalate and dichromate, the order of adsorption, as noted, is C>A>B, showing thereby that sample C, prepared from an excess of alkali, has the maximum adsorptive capacity for the ions.

It is well known that amphoteric bodies depend on environmental conditions to display their acidic and basic characters. A sample prepared from an excess of alkali should have an acidic character and should adsorb cations. Similarly, an acidic character and should adsorb cations. Similarly, a sample prepared from a deficient quantity of alkali should have a basic property and should preferentially adsorb anions.

In the case of beryllium hydroxide, however, the results show that the adsorption is in the reverse order; i.e., sample C displays a basic character and shows a maximum adsorption for dichromate or oxalate anions. Similarly, sample B shows an acidic character and results in a maximum adsorption for copper cation. It has been explained in an earlier communication,1) that during the precipitation of hydrous beryllium oxide by different alkalis, the precipitated mass always contains sodium or potassium or sulfate according as the medium of precipitation is, respectively, alkaline or acidic (cf. Table IV). Moreover, as has been said earlier, these adsorbed ions could not be removed by either washing with hot water or heating the precipitated mass.

Table IV shows the amounts of beryllium oxide (in mg.) obtained in the residue and SO_3 obtained in the filtrate, when the precipitation of beryllium from beryllium sulfate was carried out with sodium hydroxide. The pH change during the precipitation has also been recorded. It is clear from Table IV that, when the pH of the precipitating medium is made less than 9 by the addition of deficient alkali, the adsorption of SO_3 is prominent on the beryllium oxide precipitate (which is represented by sample B), but that as soon as the pH

Table IV. Precipitation of beryllium hydroxide by sodium hydroxide and estimation of BeO in the residue and SO_3 in the filtrate at different pH values

Beryllium sulphate of 0.1 M taken—20 ml.
Total volume—100 ml.

Ratio Be : OH⁻	pH	BeO obtained, mg. Theoretical calculation	BeO obtained, mg. Experimental	SO_3 obtained, mg. Theoretical calculation	SO_3 obtained, mg. Experimental
1 : 1.0	5.3	25	0.0	160.0	160.0
1 : 1.2	5.65	30	12.4	160.0	158.0
1 : 1.4	5.75	35	26.4	160.0	156.0
1 : 1.6	5.90	40	43.4	160.0	151.0
1 : 1.8	6.20	45	58.6	160.0	149.0
1 : 2.0	9.80	50	63.6	160.0	157.0
1 : 2.2	11.05	50	62.6	160.0	160.5
1 : 2.4	11.35	50	62.0	160.0	160.3
1 : 2.6	11.60	50	61.6	160.0	160.2
1 : 3.0	11.70	50	61.6	160.0	160.1
1 : 4.0	11.85	50	61.5	160.0	160.1

goes above 9 upon the addition of an excess of alkali, sodium ions are preferentially adsorbed by the beryllium oxide (which is represented by sample C).

These results, therefore, conclusively show that sample B, prepared from a deficient quantity of a alkali, which is already associated with anion sulfate, prevents the further association of other oxalate or dichromate anions, and showing thereby the least adsorption value for these anions. Similarly, sample C, prepared from an excess of alkali, is already associated with the cation sodium, prevents the further association of any other cation like copper from the solution.

Summary

Three samples, A, B and C, of hydrous beryllium oxide were prepared by adding different amounts of alkali to a fixed volume of a beryllium sulfate solution.

Sample A prepared with an equivalent amount of alkali, sample B prepared with a 10% deficient amount of alkali, sample C prepared with a 10% excess amount of alkali.

These samples were washed thoroughly and allowed to age for a month. The adsorption capacities of these samples for the ions copper(II), oxalate(II) and dichromate(II) were then studied. The adsorption of copper(II) by different samples was found to be in the order B>A>C, whereas in the case of oxalate and dichromate the order of adsorption, is C>A>B.

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