Synthetic Inorganic Ion-exchange Materials. IX. The Mutual Separation of Alkali Metals with Antimonic Acid

Mitsuo Abe and Takuji Ito

Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo

(Received January 24, 1967)

A previous report[1] has shown that the dried insoluble hydrous oxides of pentavalent metals, such as antimony, tantalum, and niobium have promising cation exchange properties, including high uptakes of certain ions and high resistance against dilute acid and alkaline solutions. Especially, the potassium-ion uptake by hydrous antimony pentoxide, also called antimonic acid, was higher than that by hydrous oxides of any other metal. The ideality of the ion exchange reaction was checked by the potassium-hydrogen and potassium-ammonium ion systems on the antimonic acid[2]; the logarithm of K_d (distribution coefficient) for potassium ions was a linear function of $\log[H^+]$ and of $\log[NH_4^+]$, both with a slope of approximately -1.

In this experiment, an attempt was made to mutually separate alkali metals with the use of the antimonic acid. The antimonic acid was obtained by the hydrolysis of antimony pentachloride in a large amount of water at 30°C, followed by aging it for three days. The granular material was prepared by washing it until it was free from Cl^- and by then drying it at 60°C. The material of a 100—200 mesh size was collected by sieving and then it was pretreated with 6 N nitric acid and 1 M ammonium nitrate solutions in a column.

When a small amount of an alkali metal salt solution is poured down from the top of the column into the antimonic acid in the hydrogen form, hydrogen ions equivalent to the adsorbed cations are liberated, as is illustrated in Fig. 1. The adsorption and the desorption are rapid enough to be used for standard column operation.

The antimonic acid showed an unusual selectivity for alkali metals as compared with the strong acid cation-exchange resins, zirconium phosphate and zirconium tungstate. Alkali metals showed a unique order of selectivity; instead of following the order of atomic numbers, as is commonly observed, sodium ions were more strongly adsorbed than any other alkali metal ions. The adsorbed sodium ions were not eluted even by 10 N nitric acid, but they were easily eluted by a 2 M ammonium nitrate solution.

The two affinity series of a trace amount of alkali metals were, in increasing order, as follows; $Li^+ < K^+ < Cs^+ < Rb^+ < Na^+$ in an acid solution, and $Li^+ < K^+ < Rb^+ < Cs^+ < Na^+$ in an ammonium nitrate solution.

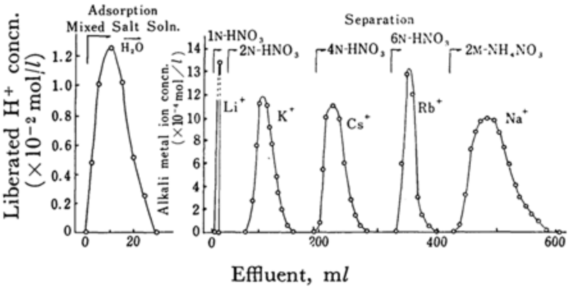

Fig. 1. Adsorption and separation of the alkali metals.
Antimonic acid; 0.8ø×6.0 cm, flow rate; 0.3 ml/min
Alkali metals; Li, 0.01 mmol, Na, 0.1 mmol, K, 0.04 mmol, Rb, 0.04 mmol, Cs, 0.04 mmol

Differences in the selectivity are very large as compared with those of other cation exchangers, and mutual separation can be achieved completely with a small column using both nitric acid and ammonium nitrate solutions, as is illustrated in Fig. 1. The results can also be favorably compared with those of a number of other cation exchangers.

According to Phillips and Kraus,[3] zirconium antimonate also has such an unusual selectivity. The antimonate in thier experiment was described as having an Sb(V)/Zr(IV) ratio somewhat larger than 2 to 1. The results of their experiment on the antimonate were, however, different from ours,[4] showing the relatively small adsorption capacity of 0.2 meq./g for the 0.1 M potassium chloride solution and its usual selectivity. Furthermore, our results revealed that when the material had an Sb(V)/Zr(IV) ratio larger than 1, it contained a considerable amount of antimonic acid.

The antimonic acid used in the present experiment was obtained from antimony pentachloride free from any other metallic impurities.

---

[1] M. Abe and T. Ito, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 1259 (1965).

[2] M. Abe and T. Ito, *ibid.*, **87**, 1174 (1966).

[3] H. O. Phillips and K. A. Kraus, *J. Am. Chem. Soc.*, **84**, 2267 (1962).

[4] M. Abe, T. Kenjo and T. Ito, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **70**, 291 (1967).