2274 © 1987 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 60, 2274—2276 (1987) [Vol. 60, No. 6

Synthetic Inorganic Ion-Exchange Materials. XXXXVI. Ion-Exchange Behavior of Titanium(IV) Antimonate Cation Exchanger for Alkali Metal Ions in Ammonium Nitrate Media

Ramesh CHITRAKAR and Mitsuo ABE*
Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152

(Received November 27, 1986)

Synopsis. Titanium(IV) antimonate (TiSbA) showed an extremely high selectivity for lithium ions in ammonium nitrate media, the increased selectivity order for microamounts being $Rb^+<Na^+<Cs^+<K^+\ll Li^+$. The selective separation of lithium ions from other alkali metal ions can be achieved on small columns of TiSbA by a mixed solution of nitric acid and ammonium nitrate.

The synthesis and ion-exchange properties of tin(IV) antimonate and titanium(IV) antimonate (SnSbA and TiSbA) have been studied first by Abe et al.[1-3] Both of SnSbA and TiSbA behave as cation exchangers with high selectivity for lithium ions. The following unusual selectivities for microamounts of alkali metal ions in nitric acid media were observed: $Na^+<K^+<Rb^+<Cs^+\ll Li^+$ on SnSbA,[2] and $Na^+<K^+<Rb^+<Li^+<Cs^+$ on TiSbA[3,4] as compared to increased order of the selectivity with increasing ionic crystal radii for alkali metal ions on a strong acid type polystyrene resin. The high selectivity for lithium on SnSbA and TiSbA can be applied for the recovery of lithium ions from seawater and hydrothermal water.[5,6]

The ion-exchange behavior of various ions on SnSbA and TiSbA has been studied extensively.[7-10]

Isolation of lithium ions from other alkali metal ions on H^+ form TiSbA with nitric acid solution as an eluant is very difficult because of low values of separation factor for pairs of Rb^+-Li^+ and Li^+-Cs^+. It has been known that the selectivity depends much on a variety of solutions used as eluants.

The present work describes the adsorption of alkali metal ions by TiSbA in ammonium nitrate media and the chromatographic separation of lithium from other alkali metal ions.

Experimental

Chemicals. Chemical grade of antimony(V) chloride supplied by Yotsuhata Chemical Co. Ltd., and titanium(IV) chloride supplied by Wako Chemical Co. Ltd., (99% as metal) were used without further purification. The other chemicals were of analytical grade.

Preparation of TiSbA. A 4 M† antimony(V) chloride solution (80 cm^3) was mixed with a 4 M titanium(IV) chloride solution (120 cm^3) at 60 °C and the mixed solutions were immediately hydrolyzed in 4.8 dm^3 demineralized water at the same temperature. The precipitate obtained was kept in mother liquor overnight, filtered and washed with cold demineralized water using a centrifuge operated at 10000 rpm until the pH of supernatant solution was in the range of 1.5—1.8. The product obtained was dried at 60 °C for 4d, ground and sieved to 100—200 mesh size, washed with cold demineralized water in order to remove fine adherent particles, and conditioned with 1 M nitric acid until free from Na^+ ions. The sample was re-washed with demineralized water and air dried.

Preparation of TiSbA in Ammonium Ion Form. The hydrogen form of TiSbA was converted to ammonium form as follows: A solution containing 0.3% aq NH_3 and 0.1 M NH_4NO_3 was passed through a column packed with 10 g of TiSbA in H^+ form until the pH of the effluent was the same as that of the feed solution. Finally, the exchanger was washed with demineralized water and air dried.

pH Titration Curve. The pH titration curve was determined by equilibrating 0.10 g of TiSbA in H^+ form with 10.0 cm^3 of solution containing (NH_4NO_3+HNO_3) or (NH_4NO_3 +NH_3aq) at an ionic strength of 0.1 with intermittent shaking for one week at 30 °C. After equilibrium was attained, the pH of the supernatant solution was measured with a Toa Dempa pH meter, model HM-5B. The concentration of NH_4^+ in the solution was determined as described by Tsuji and Abe.[11]

Distribution Coefficients, (K_d). The K_d values of alkali metal ions were determined by equilibrating 0.10 g of TiSbA in NH_4^+ form with 10.0 cm^3 of 10^{-4} M alkali metal ions, except Li^+ at different concentrations of ammonium nitrate with intermittent shaking at 30 °C. The K_d of Li^+ at an initial concentration of 10^{-4} M showed extremely high values even at 5M NH_4NO_3 solution and could not be determined, because of the detection limit of atomic absorption analysis. Its K_d values were determined at the initial concentration 10^{-3} M of Li^+. The concentrations of metal ions in the solid and liquid phases were deduced from the concentration relative to the initial concentration in the solution. The K_d values were calculated at equilibrium using the following equation:

$$K_d=\frac{\text{Amount of metal ions in exchanger}}{\text{Amount of metal ions in solution}}\times\frac{\text{cm}^3\text{ of solution}}{\text{g of exchanger}}$$

The concentrations of metal ions were determined by using a Varian Techtron 1100 Atomic Absorption Spectrometer.

Column Experiment. Relatively small columns (2 cm× 0.5 cm i.d.) of TiSbA in NH_4^+ form were used during column experiment. The flow rate was regulated by using a high pressure pump (Nihon Seimitsu Kagaku, model NSP-800-5UDX) and the effluents were collected by using a dropping-counting type fraction collector (Ohtaki Works, model UM-160).

Results and Discussion

Characterization of TiSbA. The TiSbA was characterized by X-ray diffraction and thermal analysis. The results showed a good agreement with the previous result.[4] The chemical composition of TiSbA used was determined by chemical analysis and weight loss at 700 °C by assuming that the ignition product was free from water. The empirical formula of TiSbA was $3.1TiO_2\cdot Sb_2O_5\cdot 4.9H_2O$.

pH Titration Curve. The pH titration curve of

---

† 1 M=1 mol dm^{-3}.

NH_4^+ showed apparent monobasic acid behavior which was similar to that reported for alkali metal ions[4] (Fig. 1, top). The dependence of apparent capacity of NH_4^+ on pH (Fig. 1, bottom) is consistent with the titration curve. The uptake of NH_4^+ ions increased with increasing pH of the solution as reported for Na^+ and Li^+ ions. The uptakes of NH_4^+ correspond well to the difference between pH titration curve and blank titration curve, indicating that the ion-exchange reaction is predominant over the whole range of pH studied. Compared with the previous result,[4] the increased order of the uptakes was found to be $Cs^+ < Na^+ < NH_4^+ < Li^+$ at pH 9.

Distribution Coefficients, (K_d). The time dependence of adsorption of alkali metal ions on NH_4^+ form TiSbA in ammonium nitrate was measured in order to determine the equilibrium distribution coefficients. The exchange reaction in ammonium nitrate media was relatively fast and the equilibrium was attained within 24 h for all alkali metal ions studied (Fig. 2), while the reaction for Li^+ and Cs^+ in nitric acid media was slow, about 3 weeks being required for attainment of equilibrium. After equilibration, the K_d values were determined and shown in Fig. 3 as log-log plots of K_d vs. $a_{NH_4NO_3}$. A linear relationship with a slope of -1 was observed for all metal ions studied, indicating an ideal ion-exchange mechanism. The TiSbA in NH_4^+ form showed an extremely high selectivity for Li^+ ion in ammonium nitrate media, the selectivity order being $Rb^+ < Na^+ < Cs^+ < K^+ \ll {}^+Li$, which is not included in the 11 selectivity series predicted by Eisenman.[12] This selectivity is quite different from $Na^+ < K^+ <$

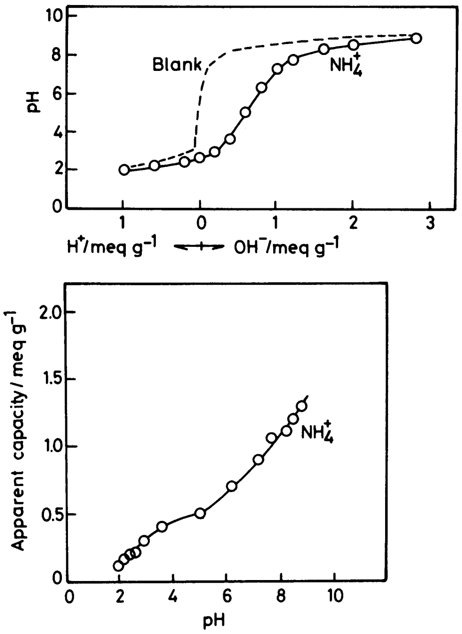

Fig. 1. pH Titration curve (top) and apparent capacity (bottom) of TiSbA.
TiSbA: 0.10 g. Soln.: 0.1 M ($NH_4NO_3+HNO_3$) or ($NH_4NO_3+NH_3aq$). Total vol: 10.0 cm^3. Temp: 30±0.5 °C.

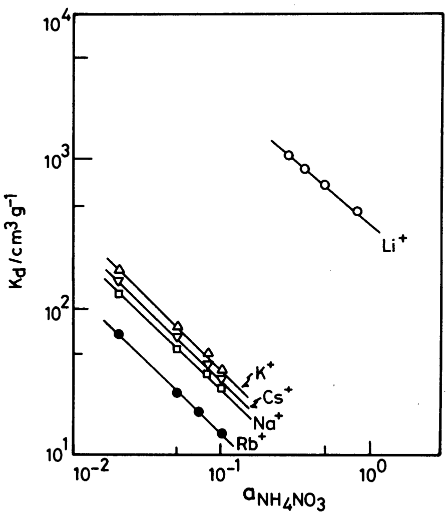

Fig. 3. Log-log plots of K_d values of alkali metal ions on NH_4^+ form TiSbA vs. activity of ammonium nitrate.
TiSbA: 0.10 g. Total vol: 10 cm^3. Other conditions are the same as in Fig. 2.

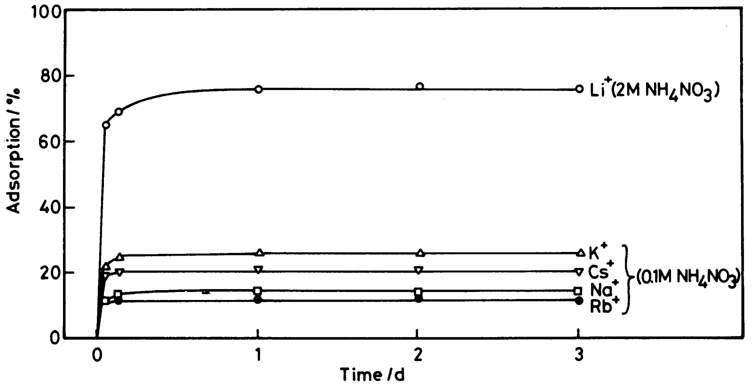

Fig. 2. Time dependence of adsorption of alkali metal ions on NH_4^+ form TiSbA.
TiSbA: 0.25 g. Initial concn of metal ions: 10^{-4} M for Na^+, K^+, Rb^+, and Cs^+, 10^{-3} M for Li^+. Total vol: 25.0 cm^3. Temp: 30±0.5 °C.

Table 1. K_d Values and Separation Factors(α) for Alkali Metal Ions on TiSbA and Bio-Rad AG 50W-X8

Ion exchanger	Media	Parameter								
			Rb^+		Na^+		Cs^+		K^+		Li^+
TiSbA (Ti/Sb=1.5)	0.1 M NH_4NO_3	K_d	14		18		31.3		35.4		$>10^5$
		α		1.3		1.7		1.1		>2800	
TiSbA[4] (Ti/Sb=1.5)	0.1 M HNO_3		Na^+		K^+		Rb^+		Li^+		Cs^+
		K_d	3.8		42		96		220		550
		α		11.1		2.3		2.3		2.5	
Bio-Rad AG 50W-X8[13]	0.1 M HNO_3		Li^+		Na^+		K^+		Rb^+		Cs^+
		K_d	33.1		54		99		118		148
		α		1.6		1.8		1.2		1.2	

$Rb^+<Li^+<Cs^+$ observed on H^+ form TiSbA in acid media.[3,4]

The K_d values and separation factors ($\alpha_A^B=K_{d_B}/K_{d_A}$), for a neighboring pair in NH_4NO_3 media, are summarized in Table 1, in which the K_d values on H^+ form of TiSbA and Bio-Rad AG 50W-X8[13] are included for comparison. The α value for neighboring pairs of alkali metals on H^+ form TiSbA are larger than those reported on Bio-Rad AG 50W-X8. But the values of α for neighboring pairs of alkali metals except Li^+ on NH_4^+ form TiSbA are comparable to Bio-Rad. However, the α value between Li^+ and other alkali metal ions are extremely high i.e. $>2.8\times10^3$.

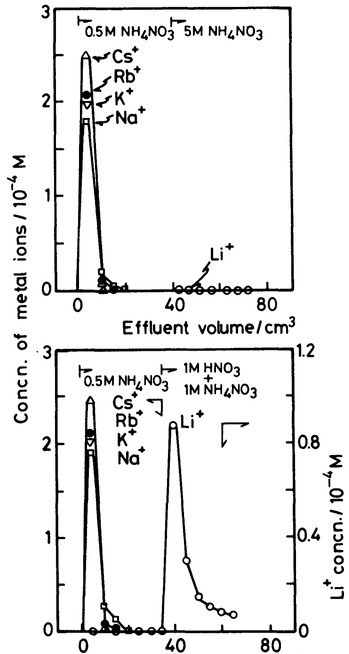

Fig. 4. Elution curves of alkali metals with NH_4^+ form TiSbA.
Column: 1.5 cm×0.5 cm i.d. (0.3 g of TiSbA), Metal ion loading: 1 μmol of each metal ion, Flow rate: 0.12 cm^3 min^{-1}.

Ion-Exchange Separation. It is evident from the studies of K_d values that lithium can be separated from other alkali metals. A solution containing 1 μmol of alkali metal ions was added to the top of the small column (2 cm×0.5 cm i.d.) containing TiSbA in NH_4^+ form. The alkali metals except lithium were eluted with 100% recovery using 0.5 M NH_4NO_3 solution, while the adsorbed lithium could not be eluted even by using 5 M NH_4NO_3 solution as an eluant (Fig. 4, top). The elution of Li^+ was performed with 75% recovery upto 30 cm^3 of the eluant of 1M NH_4NO_3+1M HNO_3 solution (1+1) after elution of other alkali metal ions by a 0.5M NH_4NO_3 solution (Fig. 4, bottom). This procedure is very useful for isolation of lithium from other alkali metal ions.

References

1) M. Abe and T. Ito, *Kogyo Kagaku Zasshi,* **70**, 440 (1967).
2) M. Abe and K. Hayashi, *Solvent Extr. Ion Exch.,* **1**, 97 (1983).
3) M. Abe and M. Tsuji, *Chem. Lett.,* 1561 (1983).
4) M. Abe, R. Chitrakar, M. Tsuji, and K. Fukumoto, *Solvent Extr. Ion Exch.,* **3**, 149 (1985).
5) M. Abe and K. Hayashi, *Hydrometallurgy,* **12**, 83 (1984).
6) M. Abe, R. Chitrakar, and K. Hayashi, "Chemical Separation," ed by C. J. King and J. D. Navratil, Litervan Literature, Denever (1986), Vol. I, p. 187.
7) M. Abe and N. Furuki, *Solvent Extr. Ion Exch.,* **4**, 547 (1986).
8) M. Abe, "Lithium: Current Applications in Science, Medicine, and Technology," ed by R. O. Bach, Wiley-Interscience (1985), p. 1.
9) M. Abe, Y. Kanzaki, and R. Chitrakar, *J. Phys. Chem.,* in press.
10) R. Chitrakar and M. Abe, *Analyst,* **111**, 339 (1986).
11) M. Tsuji and M. Abe, *Bull. Chem. Soc. Jpn.,* **58**, 97 (1985).
12) G. Eisenman, *Biophys. J.,* **2**, 259 (1962).
13) F. W. E. Strelow, R. Rethemeyer, and C. J. C. Bothma, *Anal. Chem.,* **37**, 106 (1965).