

Separation of  $\text{Li}^+$  in seawater with synthetic inorganic ion exchangers

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## Summary

Sea water contains lithium ( $170 \mu\text{g/L}$ ), strontium ( $8500 \mu\text{g/L}$ ), rubidium ( $120 \mu\text{g/L}$ ), molybdenum ( $10 \mu\text{g/L}$ ) and others as useful constituents. It is not easy to separate effectively from sea water (concentrated salt solution) by using the conventional method of chemical separation.

Recently, new inorganic ion-exchange materials selective for the above elements have been synthesized by the present authors, et al. That is, antimonite acid with the monoclinic system, antimonates of titanium and tin are selective for lithium. Manganic acid with the tetragonal system is selective for  $\text{K}^+$  and  $\text{Rb}^+$ .

In the present study, new ion-memory ion exchanger selective for lithium ions has been synthesized: 30 g of  $\text{Nb}_2\text{O}_5$  and 8.34 g of  $\text{Li}_2\text{CO}_3$  were mixed thoroughly and heated at  $900^\circ\text{C}$  for 24 h to prepare  $\text{LiNbO}_3$ .

Lithium in  $\text{LiNbO}_3$  was removed by refluxing in 8M  $\text{HNO}_3$  at  $105^\circ\text{C}$ . 8M  $\text{HNO}_3$  was renewed daily. Finally the product was washed with water until pH 7 and air-dried. The niobic acid (C-NbA) belongs to the cubic system (Im3, a, 7.644A) with the chemical composition of  $\text{HNbO}_3$ .

The ion-exchange selectivity was studied for alkali metal ions at low loadings. Plot of  $\text{Log } K_d$  vs pH showed straight line with the slope of -1. It indicates the ion-exchange ideality. The selectivity increased in the order of  $\text{K}^+ < \text{Rb}^+ < \text{Na}^+ < \text{Cs}^+ < \text{Li}^+$  at pH 10. The separation factor attained over 5,500 for the pair of  $\text{Cs}^+ - \text{Li}^+$ . That of  $\text{Na}^+ - \text{Li}^+$  pair showed 6,400.

The pH titration curve indicated that C-NbA behaves as a monobasic acid for lithium ions at both  $30^\circ\text{C}$  and  $60^\circ\text{C}$ . The pH jump was observed at larger amounts of  $\text{OH}^-$  added at  $60^\circ\text{C}$ . It implies the larger uptake for  $\text{Li}^+$  at  $60^\circ\text{C}$ . The titration curves for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  were the same as those of the blank. The uptake for these cations corresponded to those calculated from the pH titration curve. Only  $\text{Li}^+$  was exchanged in the pH range studied ( $4 < \text{pH} < 12$ ). The uptake increased sharply at pH around 6 and attained nearly a constant of 3.1 meq/g at pH 8 at  $30^\circ\text{C}$  and 4.2 meq/g at pH 9 at  $60^\circ\text{C}$ .