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Preparation and Application of Cyclophane Compounds Showing Specific Binding for Lithium

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Summary

Recently lithium ion battery has been increasing its demand because of heavy usage for celluar phones, personal computers, hybrid cars and so on. There is no litium as natural resouces in Japan, thus, we have to import all lithium we need from abroad. It has been known that seawater contains 0.1-0.2 ppm of lithium. If you could get lithium from the seawater, you would supply all lithium that is needed in Japan. However, in seawater many kinds of ions exsit, especially the concentration of sodium ion is up to 10,000 ppm. It costs too much to extract a very small amount of lithium from seawater using the conventional technology.

On the other hand the organic host molecules are weel known to include some ions specifically because the hole in the molecule can fit the size of the ion. So far a large amount of these host molecules have been investigated in terms of recognition of other molecules by weak interactions. Here we have focus on calixarenes that are cyclic compounds consisting of aromatic rings forming the cavity inside of them.

We have prepared three kinds of calixarenes (**5**, **6**, **7**). These compounds are the cyclic structure consisting of four aromatic rings with bridging of propane at 1,3 positions. The substituent on the nitrogen atom is different among calixarenes (**5**, **6**, **7**).

The extraction ability of the compounds (**5**, **6**, **7**) was examined by the liquid-liquid extraction method. The compound was dissolved in chloroform and the metal picrate was dissolved in water. After both solution was mixed and stirred for 1 hr, the amount of the picrate in water was estimated by mesurament of UV-vis spevtra.

The compound **5** shows no ability to bind all alkali metals examined such as Li^+, Na^+, K^+, Rb^+, and Cs^+, which is due to a electron-withdrawing properties of tosyl group on the nitrogen atom. Interestingly stronger binding against Li^+ than other alkali metals was suggested for the compumd **6**. No big difference in extraction of alkali metals was observed for compound **7**.

The conformation of the calixarene binding Li^+ was caliculated using MOPAC. It has been found out that Li^+ binds to three oxgene atoms and one nitrogene atom in cone structure, on the contrary, in 1,3-alternate atructure Li^+ binds to two oxygene atoms and one nitrogene atom. The energy level of the cone structure was lower than that of 1, 3-alterntate by 30 Kcal / mol.

It has been found out that the compound having the hexyl group on the nitrogen atom exhibits strong binding against Li^+ because of small hindrance around the nitrogen atom. Investigations in details are under progress.