

## Syntheses of new ionophors for ion selective electrodes

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## Summary

In the qualitative analysis of the alkali metal ion, the electrochemical measurement method with an ion sensor is the most powerful procedure in the view of generality, handiness, and practical use. This measures the concentration of the ion on the basis of the electrochemical potential difference generated on the polymer film such as polyvinyl chloride containing ionophor. Therefore, the development of the selective ion sensor is dependent on how to synthesize selective ionophors. To distinguish alkali metal ions of which chemical properties were analogous each other, the concept of "hole-size selectivity" that the size of a metal ion was recognized by the hole size of an ionophor was taken. A number of macrocyclic ionophors like as crown ethers were designed and synthesized. Especially, recognition of  $\text{Na}^+$  and  $\text{K}^+$  which have high natural abundance has been focused. In the macrocycles having a relatively large cavity, however, the "hole-size selectivity" does not reflect improving the ion selectivity due to the flexibility of their skeleton. It is reported that some ionophoric calix[4]arenes with the cavity size smaller than that of  $\text{Na}^+$  shows excellent  $\text{Na}^+/\text{K}^+$  selectivity. This is a result of making the structure rigid by partially introduction of calixarene structure into a crown ether macrocycles as an ionophor and of the design of the cavity size to be smaller than that of  $\text{Na}^+$ . This attempts us to design  $\text{K}^+$  selective ionophors having larger cavity size than  $\text{K}^+$  with homooxalix[3]arene of which derivatives are known to be ionophors preferring  $\text{K}^+$  as a starting material.

Several ions selective electrodes were prepared from synthesized homooxalix[3]arene derivative and their ion selectivities were estimated. All electrodes showed Nernst response in the range of  $10^{-1}$  to  $10^{-5}$  M of metal concentration. The electrodes containing cone isomer of homooxalix[3]arene showed  $\text{Na}^+$  selectivity among alkali metal cations, whereas these containing partial cone isomer showed  $\text{K}^+$  selectivity. These selectivities are different from the tendency observed in solution. The selectivities are affected by the property of functional groups rather than the cavity size.