

### 초청강연3

## IONIC RECOGNITION WITH QUINONE-DERIVATIZED CALIXARENES IN SOLUTION AND AT SELF-ASSEMBLED MONLAYERS

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Macrocyclic calix[4]arene compounds are known to act as a selective ionophore especially for Na ion [1]. Simple derivatization with quinone produces independent voltammetric data due to its electrochemical activity in addition to its physical size. Properly functionalized calixarenes can provide excellent ion-binding property due to its rigid three-dimensional cavities for the selective inclusion of inorganic ions or organic cations in aprotic solvents [2]. Not enough solubility of these compounds in water prevents them from wide application in aqueous media. Calix[4]arene with four carboxylic groups in the lower rim, therefore, has attracted attentions with respect to the selective analysis of electrochemically inactive cations such as alkali and alkaline earth metal ions in aqueous media [3]. Quinone-functionalized in the annular frame of the compound as ring members, where two or three carboxylic groups in the lower rim is unchanged show very interesting characteristics such as well-defined redox behavior, selective complexation with  $\text{Ca}^{2+}$  and high solubility in water [4]. It makes the electrochemical reduction of quinone very reversible in the presence of calcium ion and its behavior is not influenced even in the presence of one thousand-fold excess of alkali metal ions including physiologically abundant  $\text{Na}^+$ . This result indicates that the concentration of  $\text{Ca}^{2+}$  in body fluids can be measured without removing  $\text{Na}^+$ , which is one of the most severe interfering ions. And thus in situ monitoring of  $\text{Ca}^{2+}$  is possible, which is essential in physiology and neuroscience.

Also, self-assembled monolayer of these compounds on silver surface and disulfide on gold were obtained through carboxylate and thiol anchoring, respectively. The amount of monolayers was confirmed both by electrochemical (Fig. 1.) and electrochemical quartz crystal microbalance techniques. Similar electrochemical behavior of the self-assembled monolayers

was observed in the presence and absence of calcium ion in the media. This phenomena were obtained irrespective of the procedure when calcium ion was added. In addition, the same electrochemical behavior is obtained no matter the complexation occurred in the solution or on the surface. Therefore, it is also possible to use the self-assembled monolayer surface as a heterogeneous sensing device for calcium ion as well as a stationary phase for ions with different interaction in ion chromatography as a few examples. In this paper, details of the electrochemical property of the monoquinone derivatized calix[4]arene carboxylic acids and self-assembled surface. Also, practical applications towards selective calcium ion detection will be presented.

#### References

- [1] M. Gomez-Kaifer, P.A. Reddy, C.D. Gutsche, L. Echegoyen, *J. Am. Chem. Soc.*, 116, 580, (1994).
- [2] K. M. OConnor, D. W. M. Arrigan and G. Svehla, *Electroanalysis*, 7, 205 (1995), T. D. Chung and Hasuck Kim, *J. Inclusion Phenom. Mol. Recognit. Chem.* 32, 179 (1998), T.D. Chung, Kang S.K., J. Kim, H-s, H. Kim, *J. Electroanal. Chem.*, 438, 71 (1997).
- [3] D. M. Rudkevich, W. Verboom, E. van der Tol, C. van Staveren, F. M. Kaspersen, J. W. Verhoeven and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 131 (1995).
- [4] W.S. Oh, T.D. Chung, J. Kim, Hasuck Kim, D. Hwang, K. Kim, S.G. Rha, J. Choe and S. K. Chang, *Supramol. Chem.*, 9, 221 (1998).