

## ES2

### Electrochemical Recognition of $\text{Ca}^{2+}$ in the Presence of Large Excess of $\text{Na}^+$ Using Calix[4]arenemonoquinone-tricarboxylic acid 과량의 $\text{Na}^+$ 이온이 있을 때 칼릭스아렌모노퀴논을 이용한 $\text{Ca}^{2+}$ 의 전기화학적 감응

김하석, 강선길, 정택동\*, 장석규\*\*

서울대학교 화학과, 서울대학교 의학연구소\*, 중앙대학교 화학과\*\*

Calixarenes have advantages in selectivity, stability and functionalization over other classes of macrocyclic compounds in the analytical applications [1,2]. But only a few reports have been extended to aqueous media because of poor solubility in water. Recently, calix[4]arene with four carboxyl groups in the lower rim has attracted attentions with respect to the selective analysis of electrochemically inactive cations such as alkali and alkaline earth metal ions in aqueous solution [3]. This compound without further modification, however, is electrochemically inactive and thus can not be used in voltammetric analysis. As a redox-active group, quinone can be introduced into the annular frame of this compound as a ring member, where the remaining three carboxyl groups in the lower rim are unchanged. The resulting compound shows very interesting characteristics such as well-defined redox behavior, high solubility in water and selective complexation with  $\text{Ca}^{2+}$ . It makes the electrochemical reduction of quinone enhanced even in the presence of large excess of alkali metal ions including physiologically abundant  $\text{Na}^+$ . Figure 1 shows that  $\text{Ca}^{2+}$  in the range from 0.05 mM to 2.5 mM can be quantified sensitively and accurately in the presence of 0.15 M  $\text{Na}^+$  by square-wave voltammetry. This result indicates explicitly that the concentration of  $\text{Ca}^{2+}$  in body fluids can be measured without separating  $\text{Na}^+$ , which is the most severe interfering ion. Also it suggests possible applications for *in situ* monitoring of  $\text{Ca}^{2+}$ , which is essential in physiology and neuroscience. Other detailed experimental data will be presented.

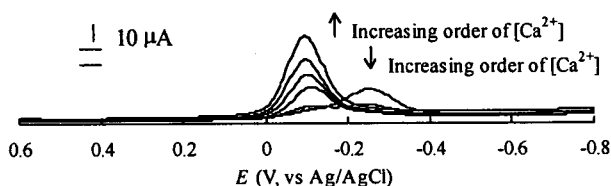


Figure 1. Square-wave voltammograms of 0.5 mM calix[4]arene-tricarboxylic acid upon the quantitative additions of  $\text{Ca}^{2+}$  by 0, 0.05, 0.25, 0.50, 1.00 and 2.50 mM in the presence of 0.15 M  $\text{Na}^+$  in 0.05 M HEPES buffer of pH 7.4.