

Effect of Calix[4]pyrrole as Addition Reagent on Anions Separation in Capillary Zone Electrophoresis (CZE)

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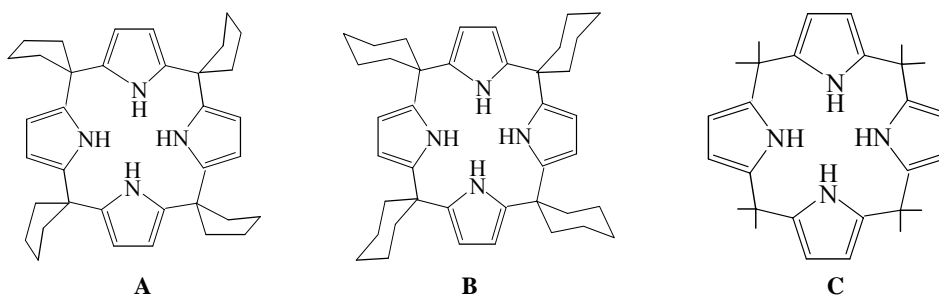
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Abstract: Supramolecular interaction of calix[4]pyrroles with several inorganic anions is reported by addition of calix[4]pyrroles to background electrolyte (BGE) in CZE. The retention time (t_R) of all anions increased with increasing concentration of calix[4]pyrroles. The effect on F^- is most evident.

Keywords: Supramolecular interaction, calix[4]pyrroles, CZE, retention time.

Calixpyrroles, as new macrocyclic receptors, have gain increasing interest in host-guest chemistry. Pioneering work in this area by Sessler and co-workers have evidenced that calix[4]pyrroles are effective anion binding agents and have used for anion binding, sensing and new anion separation technologies^{1, 2}. In this letter, we report that calix[4]pyrroles **A**, **B** and **C**^{3,4} (**Scheme 1**) can serve as additives in CZE for the separation of halide ions.

Scheme 1



When analyzing anions with CZE, the migrate velocity of anions can be described as $u = u_{ep} + u_{eo}$, where u_{ep} is the electrophoresis velocity, u_{eo} , electroosmotic flow velocity that is nearly in direct proportion to charge density. Either of their changing can result the alteration of u , which is described as t_R in the experiment.

Addition of calix[4]pyrrole **A**, **B** or **C** to BGE in CZE caused the different extent changes of t_R of the analytes. All the t_R increased with increase in the concentration of calix[4]pyrrole (**Figure 1**). However, the increase order of t_R is $F^- > Cl^- > Br^- > I^-$, which

is consistent with the interaction abilities of calix[4]pyrroles with halide ions⁵. Owing to the interaction, analyte alters from single anion to “calix[4]pyrrole-anion”, which results in decrease of charge density and thus decrease in u_{ep} , so t_R is increased.

Addition of calix[4]pyrroles influences t_R of F^- significantly. The dependence of t_R of F^- on the concentration of the calix[4]pyrroles **A**, **B** and **C** is shown in **Figure 2**. It suggests that the influence of compound **C** on F^- is most evident, which can be due to less steric hindrance of the compound **C** than that of **A** and **B**. The preliminary results showed that the calix[4]pyrroles, as additives in CZE, could affect the separation of halide ions. Moreover, the stability constant of the interaction of calix[4]pyrrole with anions might be determined by this new method. Further works on these are in progress.

Figure 1 Dependence of t_R of Br^- , Cl^- , I^- , F^- on the concentration of compound **C**

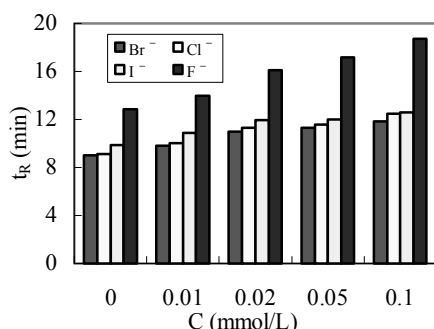
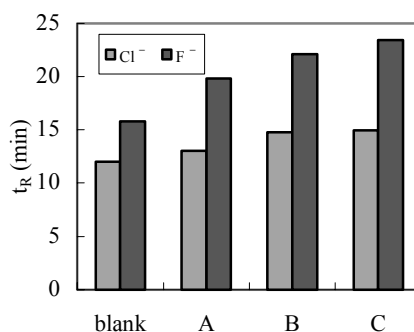


Figure 2 Dependence of t_R of Cl^- , F^- on the concentration of compound **A**, **B**, **C**



electrolyte: 85% (5.0 mmol/L K_2CrO_4 + 0.04 mmol/L TTAB + 4% $n-C_4H_9OH$ pH = 7.4) + 15% THF (different concentration of **C** (**Figure 1**); 0.05 mmol/L of Compound **A**, **B**, and **C** (**Figure 2**))
 Capillary: $60 \times 50 \mu m$ I. D. fused-silica; applied voltage: -10 kV (**Figure 1**); -12 kV (**Figure 2**)
 Detection: indirect 254 nm; $T=20^\circ C$.

Acknowledgment

This work was supported by the Nature Science Foundation of Gansu Province (NO. A52).

References

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Received 20 October, 2000