

Capillary electrophoresis for chiral analysis of diquats and determination of binding constants of their complexes with sulfated cyclodextrins

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Gold statement

- A new CE method for chiral analysis of diquats, new functional organic molecules, was developed.
- The (*P*)- and (*M*)-enantiomers of diquats were separated with high resolution in a short time.
- The binding constants of diquat complexes with highly sulfated cyclodextrins were determined.

Introduction

Diquats (DQs) – derivatives of the widely used herbicide diquat represent a new type of functional organic molecules [1]. These chiral *N*-heteroaromatic dicationic molecules comprising 2,2'-bipyridine moiety can be potentially used as catalysts, dyes, redox indicators, DNA intercalators, chiral selectors or as building blocks in supramolecular chemistry. Prior to these applications, the chiral purity of the (*P*)- and (*M*)-enantiomers of the particular DQs has to be checked. Hence, the aim of this work was to develop a suitable capillary electrophoresis (CE) method for chiral analysis of DQs.

Body

The (*P*)- and (*M*)-enantiomers of eleven diquats were resolved by CE using highly sulfated α -, β - and γ -cyclodextrins (*S*- α -, *S*- β - and *S*- γ -CDs) as chiral additives of the aqueous background electrolyte (BGE) composed of 22/35 mM sodium phosphate, pH 2.5. Interactions of dicationic diquats with sulfated CDs resulted in formation of negatively charged complexes [2] that were separated at reversed voltage polarity in hydroxypropylcellulose coated fused silica capillary within a short time of 5–8 min. From *S*-CDs tested, the *S*- γ -CD separated enantiomers of all eleven DQs (100% success rate), followed by the *S*- β -CD with ten DQs (91%) and the *S*- α -CD with nine resolved DQs (82%). The highest resolution and separation efficiency were achieved in above BGE containing 6 mM *S*- β -CD. In addition, strength of the complexes of DQs enantiomers with *S*-CDs was assessed. The apparent stability constants of the DQ-CDs complexes were estimated from the CE measured dependence of effective electrophoretic mobilities of (*P*)- and (*M*)-enantiomers of DQs on the concentrations of *S*-CDs in the BGE using the nonlinear regression analysis [3]. The DQs enantiomers formed strong complexes with all three types of *S*-CDs, the apparent stability constants of these complexes were in the range $(7.80\text{--}547.4) \times 10^3$ L/mol.

Conclusion

CE using randomly highly sulfated CDs as chiral selectors proved to be a suitable method for the fast, high-resolution separations of enantiomers of a series of eleven new diquat derivatives and for quantitative estimation of the strength of their complexes with sulfated CDs.

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References

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