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授与した学位	博 士		
専攻分野の名称	学 術		
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学位授与の要件	自然科学研究科物質科学専攻 (学位規則第 4 条第 1 項該当)		
学位論文の題目	Study on Analysis of Ion Association and Related Reactions in Aqueous Solutions by Electrophoretic and Titrimetric Methods (キャピラリー電気泳動法及び滴定法による水溶液中のイオン会合関連反応の解析に関する研究)		
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#### 学 位 論 文 内 容 の 要 旨

Reaction analysis between cations and various organic compounds in aqueous solutions have been carried out by capillary zone electrophoresis and titration. Complex formation reactions between crown ethers, DB18C6, B18C6, B15C5, B12C4, DB21C7 and DB24C8, and various cations were analyzed by the change in mobility of crown ethers under capillary zone electrophoresis. A good increase in mobility of crown ethers was observed upon increasing metal ion concentrations except for  $\text{Li}^+$  and  $\text{Mg}^{2+}$  in the migrating buffer solutions. The changes in mobility differed from one crown ether to another depending on complexation potential and were explained in terms of size-fit concept and hydration of the cations. Ion association reactions between metal crown ether complexes and pairing anions were also analyzed by measuring the change in mobility of crown ethers. The apparent mobility of crown ethers decreased with increasing pairing anion concentrations in the buffer solutions. The decrease in mobility depended on the hydrophobicity, dispersion of anionic charge and the linear structure of pairing anions. The ion association potential of non-UV-absorbing crown ethers 12C4, 15C5 and 18C6-metal complexes with picrate ion was established through change in mobility of picrate ion. The apparent mobility of picrate ion decreased with increasing concentration of 18C6 in the migrating solution. Upon increasing alkali metal concentration in the presence of 18C6, the apparent mobility of picrate ion decreased up to 15 mM and then started to increase gradually. The decrease was attributed to the interaction between the cationic complex and picrate ion while the increase was attributed to concentrated salt effects and competitive ion association towards the cations between the cationic complex and counter anions. No change in mobility of picrate ion was observed with cationic 12C4 or 15C5. Under titration, concentrated salt effects on the solvolysis rates of aliphatic halides and related compounds were examined in  $\text{MeOH-H}_2\text{O}$  and  $\text{acetone-H}_2\text{O}$  mixed solvents. The first-order reaction rates for typical  $\text{S}_{\text{N}}1$  substrates increased exponentially with increasing concentrations of alkali or alkaline earth metal perchlorates. The addition of nonmetallic salts gave results different from metal salts. For  $\text{S}_{\text{N}}1$ - $\text{S}_{\text{N}}2$  intermediates and typical  $\text{S}_{\text{N}}2$  substrates, the rates were decreased by a decrease in the activity of the solvent. The positive salt effects as demonstrated by metal ions were explained due to change in solvent structure and by a chemical interaction between anions and metal cations. It is proposed that one could simply distinguish  $\text{S}_{\text{N}}1$  from  $\text{S}_{\text{N}}2$  reactions merely by observing a substantial increase in solvolysis rate constant at  $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$  in aqueous mixed solvents.

## 論文審査結果の要旨

In this study, analysis of reactions between cations and various organic compounds in aqueous solutions were carried out by capillary zone electrophoresis and titration. Complex formation reactions between several kinds of crown ethers and various cations were analyzed by the proposed capillary zone electrophoresis method. The changes in mobility differed from one crown ether to another depending on complexation potential and were explained in terms of size-fit concept and hydration of cations. Ion association reactions between metal-crown ether complexes and pairing anions were also analyzed by measuring the change in mobility of crown ethers. The decrease in mobility depended on the hydrophobicity, dispersion of anionic charge and the linear structure of pairing anions. The ion association potential of non-UV-absorbing crown ether-metal complexes with picrate ion was established through change in mobility of picrate ion. Upon increasing alkali metal concentration in the presence of 18C6, the apparent mobility of picrate ion decreased and then started to increase gradually. The decrease was attributed to the interaction between the cationic complex and picrate ion while the increase was attributed to concentrated salt effects and competitive ion association. Under titration, concentrated salt effects on the solvolysis rates of aliphatic halides and related compounds were examined in MeOH-H<sub>2</sub>O and acetone-H<sub>2</sub>O mixed solvents. The first-order reaction rates for typical S<sub>N</sub>1 substrates increased exponentially with increasing concentrations of alkali or alkaline earth metal perchlorates. For S<sub>N</sub>1-S<sub>N</sub>2 intermediates and typical S<sub>N</sub>2 substrates, the rates were decreased by a decrease in solvent activity. The positive salt effects were explained due to change in solvent structure and by a chemical interaction between anions and cations. It is proposed that one could simply distinguish S<sub>N</sub>1 from S<sub>N</sub>2 reactions merely by observing a substantial increase in solvolysis rates at 1.0 M LiClO<sub>4</sub> in aqueous mixed solvents. In this study, the ion association and related reactions in aqueous solutions were analysed by the proposed methods. The study contributes highly to analytical chemistry as well as solution chemistry, and it is worthy of a doctoral (Ph.D) dissertation.