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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分子科学専攻 (学位規則第4条第1項該当)
学位論文の題目	Studies on Equilibria and Thermodynamics of Weak Ion Association between Inorganic Anions and Symmetrical Tetraalkylammonium Ions in Aqueous and Aqueous-Organic Media (水および水-有機混合溶媒における対称的テトラアルキルアンモニウムイオンと無機陰イオン間の弱いイオン会合の平衡と熱力学に関する研究)
論文審査委員	教授 本水 昌二 教授 山本 俊三 助教授 大島 光子

#### 学位論文内容の要旨

Fairly extensive work has already been done on strong ion association and the knowledge derived is being applied to the separation of metal ions and bulky organic anions. The use of weak ion association in the separation of inorganic anions has received less attention, despite its ever increasing importance in public security, environment and health. The growing need for faster and accurate methods for identification and quantification of inorganic anions makes it necessary to systematically study weak ion association in various types of solutions. Findings from such studies provide data, which can be used for assessment of association theories *e.g.* Bjerrum's theory and comprehensive design of the inorganic anions separation methods by capillary electrophoresis.

Weak ion association equilibria between the inorganic anions and tetraalkylammonium ions  $R_4N^+$  ( $R = Me; Et; Pr; Bu; n\text{-pentyl}, Am$ ) were investigated in aqueous, aqueous-ethanol, aqueous-dioxane and aqueous-acetonitrile media by capillary zone electrophoresis (CZE). Coated and ordinary silica capillaries were used to measure the mobility of inorganic anions as they associated with the tetraalkylammonium of increasing bulkiness at 25°C. Mobility measurements were carried out by applying a negative potential (-10 kV) and anions were detected directly at 220 nm. The measured mobilities, obtained by the classical, Williams-Vigh and improved Williams-Vigh methods were subjected to non-linear least squares method in order to determine the association constant,  $K_{ass}$  and where appropriate the corresponding mobility of the ion associate.

Based on association constants and mobility of the anions in aqueous solutions, the association constants and change in mobility were highest in aqueous-dioxane, followed by aqueous-ethanol and aqueous-acetonitrile, which showed comparable results. Several reversals of migration orders in some organic compositions is evidence that these organic additives changed the selectivities of the inorganic anions. Capillary electrophoretic investigations showed that Bjerrum's theory of association, based on dielectric constant of the solution, failed to account for the small increase in association constant with decrease in dielectric constant. The medium effect and Gibbs free energy of transfer in aqueous-ethanol solution showed that the instabilities of both the anion and the cation led to an increase in association constant as the amount of ethanol in the migrating buffer was increased. Only the instability of the anion in an aqueous-acetonitrile solution was responsible for the increase in association constant by similar thermodynamic treatment of the association data. A capillary electrophoresis method utilizing weak ion association was developed for simultaneous determination of bromate and iodate at ppb level in drinking water. The method incorporated a FESI pre-concentration and had the limit of detection (LOD S/N = 3) of 0.1 ppb and 0.21 for bromate and iodate, respectively.

## 論文審査結果の要旨

In this research, the following subjects have been studied and clarified using the anion mobilities accurately measured by capillary zone electrophoresis (CZE).

The use of weak ion association in the separation of inorganic anions has received less attention, despite its ever increasing importance in public security, environment and human health. The growing need for faster and accurate methods for the identification and the quantification of inorganic anions makes it necessary to systematically study weak ion association in various types of solutions. Findings from such studies provide data, which can be used for assessment of association theories *e.g.* Bjerrum's theory and comprehensive design of the inorganic anions separation methods by capillary electrophoresis.

Weak ion association equilibria between the inorganic anions and tetraalkylammonium ions  $R_4N^+$  ( $R = \text{Me; Et; Pr; Bu; } n\text{-pentyl, Am}$ ) were investigated in aqueous, aqueous-ethanol, aqueous-dioxane and aqueous-acetonitrile media by CZE. Coated and ordinary silica capillaries were used to measure the mobility of inorganic anions as they associated with the tetraalkylammonium of increasing bulkiness at 25°C. Mobility measurements were carried out by applying a negative potential (-10 kV) and anions were detected directly at 220 nm. The measured mobilities, obtained by the classical, Williams-Vigh and improved Williams-Vigh methods were subjected to non-linear least squares method in order to determine the association constant,  $K_{\text{ass}}$  and where appropriate the corresponding mobility of the ion associate.

Based on association constants and mobility of the anions in aqueous solutions, the association constants and change in mobility were highest in aqueous-dioxane, followed by aqueous-ethanol and aqueous-acetonitrile, which showed comparable results. Several reversals of migration orders at certain aqueous-organic compositions is evidence that these organic additives changed the selectivities of the inorganic anions. Capillary electrophoretic investigations showed that Bjerrum's theory of association, based on dielectric constant of the solution, failed to account for the small increase in association constant with decrease in dielectric constant. The medium effect and Gibbs energy of transfer in aqueous-ethanol solution showed that the instabilities of both the anion and the cation led to an increase in association constant as the amount of ethanol in the migrating buffer was increased. Only the instability of the anion in an aqueous-acetonitrile solution was responsible for the increase in association constant by similar thermodynamic treatment of the association data. A capillary electrophoresis method utilizing weak ion association was developed for simultaneous determination of bromate and iodate at ppb level in drinking water. The method incorporated a FESI pre-concentration and had the limit of detection (LOD S/N = 3) of 0.1 ppb and 0.21 for bromate and iodate, respectively.

In view of original/creative contents and results in this research, the committee evaluated the dissertation as PhD degree's worth of research.