Specific Counterion Interactions in Aqueous Polyelectrolyte Systems

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Polyelectrolytes are macromolecules with charged repeating units along with corresponding counterions that can dissociate in water. These counterions strongly influence the properties of polyelectrolyte aqueous solutions, from affecting the chain hydration to altering electrostatic interactions and transport characteristics such as ionic conductivity. Consequently, investigating the impact of different types of counterions on polyelectrolyte behaviour is essential.

In general, ions can be broadly classified into two groups based on their specific interactions with other charged moieties, as well as their affinity for water molecules [1] . Weakly hydrated ions - which interact better with ionic species and less with water molecules (e.g., SCN^-) - are referred to as Chaotropes, whereas strongly hydrated ions - which preferentially interact with water rather than ionic groups (e.g., F^-) - are classified as Kosmotropes. By incorporating these counterions with different affinities towards polyelectrolyte's ionic groups, the specific ion effect can be systematically studied by methods such as freezing point depression and ion-selective potentiometry.

Freezing point depression, as a well-established colligative property, can be a reliable tool to study the specific counterion effect of electrolyte and polyelectrolyte aqueous solutions [2] . Generally, the freezing point of water decreases upon the introduction of ions due to changes in the entropy of the solution by the ions' entropy of mixing. Polyelectrolytes on the other hand, affect freezing point depression in a more complex manner, as the presence of polymer chains introduces an additional configurational entropy contribution. In these systems, the extent of freezing point depression depends not only on ion concentration, but also on polymer characteristics and counterion chemistry [3] . These dependencies make freezing point measurements a valuable analysis for gaining insight into the specific ionic interactions in such systems.

Furthermore, electrochemical measurements can provide additional insight on the into the ion-specific behaviour of different counterions. One approach is the ion-selective potentiometry. In this method, by employing ion-selective electrodes that measure the activity a specific ion in a polyelectrolyte solution, the specific interactions between various counterions and ionic species along the polymer chains can be studied [4] .

In this regard, we study the effect of various anions (such as F^-, I^-, SCN^-) on the freezing point behaviour of poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (pMETAC). Also, the ion-selective electrode potentiometry technique is implemented to further investigate the ion-ion specific interaction of tertiary ammonium groups and corresponding Chaotropic and Kosmotropic anions. To do so, the polyelectrolytes are first synthesized via the polymerization of 2-(methacryloyloxy)ethyl trimethylammonium chloride (METAC), followed by ion-exchange processes to obtain polyelectrolytes with the desired counterions.

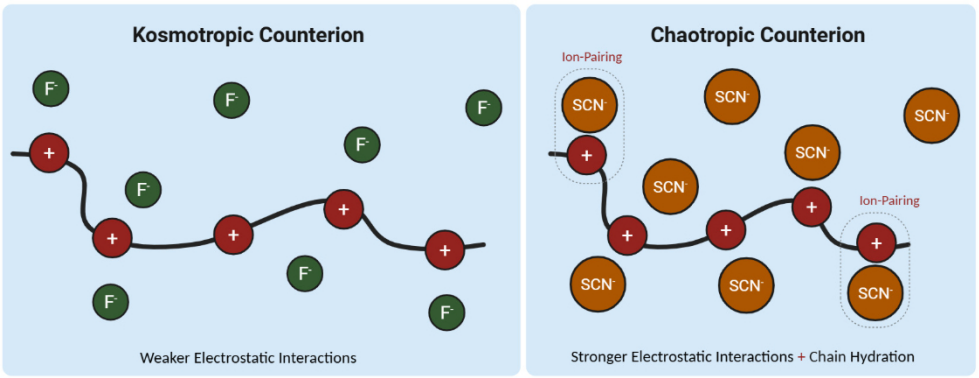

Fig.1 Different effect of kosmotropic and chaotropic counterions

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