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UNDERSTANDING THE BEHAVIOUR OF POLYELECTROLYTE COMPLEXES UNDER DIFFERENT pH

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Introduction. Formation of polyelectrolyte complexes (PECs) is the result of interactions between the amino groups and the carboxyl groups present in chitosan (CS), and hyaluronic acid (HA) respectively. The phase behavior and chain conformation of PECs in salted aqueous solutions of sodium hydroxide causes the charge fraction of these complexes to be adjusted by pH.

Moreover, it can be observed that increasing pH results in higher yielding volume fraction and water content of dense coacervates formed between net pure PECs. This contrast with a decrease in the critical salt concentration is required for coacervation onset, as the charge fraction of PECs decreases accordingly. The hydrophobicity of the PECs solution is linked to a reduction in charge fraction with increasing pH. The strong pH-dependent phase and conformational behaviors suggest a shift in entropic and enthalpic contributions to the thermodynamic energy landscape and chain structural dynamics of polyelectrolyte coacervation involving weak polyelectrolytes in aqueous solutions (1).

Main part. The polyelectrolyte titration technique was based on 1:1, 1:2 and 2:1 molecular ratios adsorption stoichiometry between HA and CS in acetic acid. First, the dissociation behavior of the polyelectrolytes was evaluated by potentiometric titration. It can be analyzed that, NH_2 groups of CS are protonated by the hydrogen ions in the acid giving rise to positively-charged $-\text{NH}_3^+$ groups. In contrast, the negative ionic values of HA are the result of dissociation of $-\text{COO}$ giving rise to $-\text{C}-\text{S}$ and $\text{C}-\text{H}$ in HA molecules. Secondly, the validity of the ideal equilibrium was confirmed by measuring the concentration of NaOH in the polymeric solutions. Hence, the addition of a NaOH deprotonates the $-\text{NH}_3^+$ groups back to NH_2 groups which result in the precipitation of CS and therefore CS exhibits a weak PE behaviour. In CS, the switchover to negative values in the pH range 8–12 is likely due to the screening of NH_2 groups of CS by the excess hydroxide ions from the added alkali. The significant increase in Na^+ and OH^- ions can lead to the disruption of the HA molecules and thereby further exposing the negatively charged groups leading to strong negative ζ -potential as found for pH 11 (2). When complexation between HA and CS takes place, regions of positive and negative charges on both molecules interact with chitosan, creating a dual effect of short-range attraction and long-range repulsion.

Therefore, the addition of an appropriate amount of NaOH can effectively neutralize long-range repulsions while maintaining short-range attractions, leading to optimal binding affinity at specific ionic strengths (3). At the equivalence point, the detection of the endpoint occurs through a rapid potential shift, resulting from an increase in the concentration of chitosan's free cations. Therefore, to anticipate the potentiometric titration curve of polyelectrolytes, it is essential to assess the electrostatic free energy which results in a non-monotonic relationship between the ionic strength and the binding behavior observed in the linear PEs (4).

Conclusion. PECs were developed, and analysis made from all the samples showed that the ionized groups within the polymer and the small ions dispersed in the solvent. The apparent dissociation constant of PEs fluctuated depending on the extent of ionization, influenced by the strong electrostatic potential. The PECs in this study displayed a negative zeta-potential across all pH range, which may have been caused by the dissolution of the HA molecules into the solvent mixture and the higher opposite charge density (2).

References

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