INTERPOLYMER REACTIONS AND PHASE BEHAVIOR IN THE LIGNOSULFONATE–CHITOSAN SYSTEM WITH THE FORMATION OF POLYELECTROLYTE COMPLEXES

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Polyelectrolyte complexes (PECs) formed via the interaction of natural polycations and polyanions are of interest both from a fundamental standpoint and because of the possibility of creating new functional materials on their basis. One of the promising systems is the lignosulfonate (LS) – chitosan (CS) pair, in which intermolecular binding is governed by a combination of electrostatic interactions, hydrogen bonding, and cooperative effects, leading to the formation of water-soluble associates and water-insoluble PECs. The aim of this work was to study interpolymer reactions and phase behavior in the LS – CS system using aspartic acid as the medium for chitosan dissolution.

Potentiometric titration of chitosan solutions (0.025 – 0.100 wt%) with lignosulfonate solutions (0.025 – 0.100 wt%) was carried out, and the onset of turbidity was monitored as the beginning of macrophase separation. The resulting precipitate was characterized by FTIR spectroscopy, SEM, and thermal analysis (TGA).

It was found that in all systems the addition of LS causes a gradual increase in pH without a pronounced jump, indicating the progressive nature of the interpolymer interaction. The onset of phase separation was observed at $[\sim(NH_3^+)]/[\sim SO_3^-]$ ratios ranging, depending on the composition, from 0.015 to 0.566. The position of the cloud point depends on the initial concentration of CS and reflects changes in the conditions governing the transition from soluble interpolymer associates to a water-insoluble PEC. In all cases, macrophase separation begins in the region of excess cationic groups of chitosan.

The FTIR spectra of the insoluble PECs indicate the involvement of hydroxyl, amino, carboxyl, and sulfonate groups (3400, 1600, 1380, and 1080 cm^{-1}) in complex formation. According to SEM data, the PEC is characterized by a pronounced plate-like, layered morphology, indicating the formation of ordered aggregates during coagulation of the complex from solution.

The thermal behavior of the PEC differs from that of the initial chitosan: the complex exhibits different ratios of the low-temperature and main mass-loss stages, confirming the formation of a new interpolymer structure rather than simple mechanical mixing of the components.

The results obtained are of interest for the further thermodynamic description of complexation processes and for the targeted design of biopolymer materials based on natural polyelectrolytes.

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