

Lecture 14.

Theme. Ionizing macromolecules (polyelectrolytes). Features of the behavior of polyelectrolytes.

Aim: generate the following learning outcomes:

- to relate the effect of charge on the conformation of macromolecules;
- - interpret the interaction of charged circuits with counterions;

Purpose:

To understand the **structure, properties, and solution behavior of polyelectrolytes**, as well as the factors influencing their **ionization and interactions** in solution.

Lecture content:

Ionizing macromolecules (polyelectrolytes).

Chemical and physico-chemical features of the behavior of ionizing macromolecules (polyacids, poly bases and their salts).

Quantitative characteristics of the strength of polyacids and poly bases.

Electrostatic energy of ionized macromolecules. Specific binding of counterions.

Cooperative conformational transformations of ionizing polypeptides in solutions.

Isoelectric and isoionic point. Amphoteric polyelectrolytes.

Concentrated polymer solutions and gels. Association of macromolecules in concentrated solutions and structure formation.

Main Questions:

1. What are polyelectrolytes and how do they differ from neutral polymers?
2. How does ionization affect the behavior of polymer chains in solution?
3. What are the key physical and chemical properties of polyelectrolytes?
4. How do concentration, ionic strength, and pH influence polyelectrolyte behavior?

5. What practical applications rely on polyelectrolyte properties?

Key Theses:

1. Definition and Structure of Polyelectrolytes

- **Polyelectrolytes** are macromolecules containing **ionizable groups** that can dissociate in polar solvents, usually water.
- They can be **cationic** (positively charged), **anionic** (negatively charged), or **ampholytic (zwitterionic)**.
- Examples: **polyacrylic acid (anionic)**, **polyvinylamine (cationic)**, **chitosan (cationic/ampholytic)**.

Structure influences behavior:

- **Charge density:** number of ionizable groups per chain length.
- **Chain flexibility:** flexible chains expand more in solution upon ionization.
- **Hydrophilicity:** highly polar chains dissolve easily in water.

2. Ionization and Chain Behavior

- Ionization generates **electrostatic repulsion** between charged groups along the chain.
- **Chain expansion** occurs in dilute solutions due to repulsion.
- **Counterions** in solution screen charges, affecting chain conformation.

Behavior features:

1. **Extended coil conformation** in dilute solution (high charge, low ionic strength).
2. **Collapse of chains** in high ionic strength due to counterion shielding.
3. **pH-dependent behavior** for weak polyelectrolytes (e.g., polyacids or polybases).

3. Physical Properties of Polyelectrolytes

- **Viscosity:** highly sensitive to ionic strength, concentration, and degree of ionization.
- **Osmotic pressure:** higher than neutral polymers due to counterions.
- **Conductivity:** solutions are electrically conductive due to mobile ions.
- **Non-Newtonian flow:** viscosity may change with shear rate, concentration, or ionic conditions.

4. Chemical Properties and Interactions

- **Electrostatic interactions** with salts, metals, and oppositely charged polymers.
- **Complex formation:** polyelectrolytes can form **polyion complexes** or **coacervates**.
- **Buffering capacity:** weak polyelectrolytes can resist pH changes.

Influencing factors:

- Concentration of polymer and counterions
- Temperature
- Solvent dielectric constant
- pH for weak polyelectrolytes

5. Applications

- Water treatment (flocculants, coagulants)
- Drug delivery systems (controlled release via pH or ionic triggers)
- Superabsorbent materials (e.g., sodium polyacrylate)
- Food industry (thickening, stabilizing agents)
- Polyelectrolyte multilayers in coatings and membranes

Control Questions:

1. List the properties of polyelectrolytes similar to the properties of low molecular weight electrolytes.
2. Define polyelectrolytes and give examples.
3. How does ionization affect polymer chain conformation?
4. Name the causes of the abnormal phenomenon of polyelectrolyte swelling. List the ways to eliminate this phenomenon.

5. Explain the effect of ionic strength on polyelectrolyte solutions.
 6. What are the main physical properties of polyelectrolytes?
 7. How does pH influence the behavior of weak polyelectrolytes?
 8. What is a polyion complex or coacervate?
 9. Define the isoelectric point of polyampholite. Name the methods of its determination.
 10. Define the isoionic point of polyampholite. Name the methods of its determination.
 11. List some practical applications of polyelectrolytes.
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References for lecture content:

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13. <http://www.xumuk.ru/>
14. <http://www.hemi.nsu.ru/>