Lecture 13.

Theme. Phase diagrams of polymer solutions. Raoult's law. State equation for a polymer. Thermodynamic quality of solvent.

Aim: generate the following learning outcomes:
- explain the concepts of "bad", "good", "ideal" solvent in relation to polymer solutions;
- formulate the change in thermodynamic functions during the dissolution of polymers;
- describe the concepts of "second virial coefficient", "Huggins constant", "Flory temperature".

Purpose:

To understand the **phase behavior of polymer solutions**, the applicability of **Raoult's law**, the **equation of state for polymers**, and the concept of **thermodynamic solvent quality** affecting polymer solubility.

Lecture content:
Hydrodynamic properties of macromolecules in solutions.
Phase diagrams of polymer-solvent systems. Critical dissolution temperatures.
Thermodynamic behavior of macromolecules in solutions and their features in comparison with the behavior of molecules of low-molecular substances.
Deviations from ideality and their causes.
The equation of state of the polymer in solution.
The second virial coefficient and θ -temperature (θ -conditions).

Main Questions:

1. How are phase diagrams of polymer solutions constructed and interpreted?
2. What is Raoult's law and how does it apply to polymer solutions?
3. What is the equation of state for polymers?
4. What defines the thermodynamic quality of a solvent?

5. How do polymer-solvent interactions determine solution behavior and phase separation?

Key Theses:

1. Phase Diagrams of Polymer Solutions

- Phase diagrams illustrate **regions of polymer solubility, miscibility, and phase separation** depending on **temperature, polymer concentration, and solvent type**.
- **Types of polymer solution phase diagrams:**
    1. **UCST (Upper Critical Solution Temperature):** above a certain temperature, polymer and solvent are completely miscible.
    2. **LCST (Lower Critical Solution Temperature):** below a certain temperature, polymer and solvent are miscible; above it, phase separation occurs.

Key points:

- Phase diagrams are influenced by polymer molecular weight, solvent quality, and temperature.
- Critical point: polymer concentration and temperature at which phase separation begins.

2. Raoult's Law

- Raoult's law states that the **partial vapor pressure of a solvent in a solution** is proportional to its **mole fraction.**

  For polymer solutions:

- Due to large molecular size of polymers, the mole fraction of polymer is **very small**, so solvent vapor pressure is only slightly reduced.
- Deviations from ideal Raoult behavior are common due to **polymer-solvent interactions**.

3. Equation of State for Polymers

- Polymer solutions do not obey ideal gas laws; instead, **modified equations of state** describe their behavior, considering **chain length, volume, and interactions**.

Significance:

- Describes **thermodynamic behavior**, including **swelling, phase separation, and osmotic pressure**.

4. Thermodynamic Quality of Solvent

- **Solvent quality** measures how favorably a solvent interacts with a polymer:
    1. **Good solvent:** polymer-solvent interactions dominate; chains expand; polymer dissolves easily.
    2. **Theta solvent:** polymer behaves ideally; chain interactions with solvent and itself are balanced.
    3. **Poor solvent:** polymer-polymer interactions dominate; chains collapse; phase separation occurs.

Factors affecting solvent quality:

- Polar vs non-polar interactions
- Hydrogen bonding capacity
- Temperature and pressure

5. Summary of Relationships

- Phase behavior, osmotic pressure, and solubility are **thermodynamically linked** through polymer-solvent interactions.
- Raoult's law provides a **baseline for ideal behavior**, but polymers often deviate due to chain size and interaction effects.
- Equation of state and Flory-Huggins theory allow **quantitative prediction of phase diagrams and solvent effects**.

Control Questions:

1. What information does a polymer solution phase diagram provide?
2. Explain the difference between UCST and LCST behavior.
3. State Raoult's law and describe its limitations for polymer solutions.
4. Write the Flory-Huggins equation of state for polymers and explain each term.
5. Define the concepts of "good", "bad" and ideal solvent for polymers.
6. Define thermodynamic solvent quality and give examples of good, theta, and poor solvents.
7. Name the methods for determining the second virial coefficient.
8. Name the main cause of endothermic dissolving of flexible-chain polymers.

9. How does polymer molecular weight affect phase separation?
10. Why do polymer solutions often deviate from ideal solution behavior?

References for lecture content:

1. Introduction to Polymer Science and Chemistry: A Problem-Solving Approach, Second Edition 2nd Edition / by Manas Chanda, CRC Press; 2nd edition (January 11, 2013)
2. Polymer Chemistry 2nd Edition / by Paul C. Hiemenz, Timothy P. Lodge, CRC Press; 2nd edition (February 15, 2007)
3. Семчиков Ю.Д. Высокомолекулярные соединения: Учебник для вузов. М.:Академия, 2003, 368 .
4. Киреев В.В. Высокомолекулярные соединения. Учебник. М.: -Юрайт.-2015. – 602 с.
5. Зезин А.Б. Высокомолекулярные соединения. Учебник и практикум. М.: -Юрайт.-2017. – 340 с.
6. В.Н.Кулезнев, В.А.Шершнев. Химия и физика полимеров. М.: Колос С, 2007.- 366с.
7. Тугов И.И., Кострыкина. Химия и физика полимеров. –М: Химия,1989. -430с.
8. Ергожин Е.Е., Құрманәлиев М.Қ. Жоғары молекулалық қосылыстар химиясы. Алматы, 2008, 407 б.
9. Абдықалыкова Р.А. Полимерлерді хим. түрлендіру ж/е модиф. //Оқу құр. -Қазақ унив.-2003.-44 б.
10. Абдықалыкова Р.А., Рахметуллаева Р.К., Үркімбаева П.И. Оқу құралы. Алматы, «Қазақ университеті», 2011. -177 бет
11. Қаржаубаева Р.Ғ. Полимерлеу процестерінің химиясы //Оқу құр. -Қазақ унив.-2002, 80б.

Internet resources:

12. http://www.pslc.ws/index.htm
13. http://www.xumuk.ru/
14. http://www.hemi.nsu.ru/