§ 8.11 Solutions of macromolecules
1. Macromolecules and their solutions

Macromolecules: a chain-like molecule with its molar mass higher than 10000.

**Natural macromolecules**: protein, starch, cellulose;

**Artificial macromolecules**: PE, PP, PS, nylon-66

**Lyophilic sol** – solution of macromolecule

1. Spontaneous dissolution/dispersion;
2. thermodynamically stable;
3. Weak Tyndall effect;
4. High viscosity.
Hermann Staudinger (Mar. 23, 1881-Sep. 8, 1965)

A German organic chemist who demonstrated the existence of macromolecules, which he characterized as polymers. For this work he received the 1953 Nobel Prize in Chemistry.

https://en.wikipedia.org/wiki/Hermann_Staudinger
2. Osmotic pressure of macromolecular solutions

\[ \pi = cRT \]

\[ \pi = \frac{m_B}{M} RT \]

\[ \frac{\pi}{m_B} = \frac{RT}{M} \]

\[ \frac{\pi}{m_B} = RT \left( \frac{1}{M} + A_2m_B + A_3m_B^2 \right) \]

Virial factor

At low molality

\[ \frac{\pi}{m_B} = RT \left( \frac{1}{M} + A_2m_B \right) \]

Valid for polymeric nonelectrolyte

\[ \frac{\pi}{m_B} = \frac{RT}{M} + RTA_2m_B \]

Can be used to determine molar mass of macromolecule
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3. Donnan Effect of macromolecular solutions

polyelectrolyte

NaP $\rightarrow$ Na$^+$ + P$^-$

$\pi = 2cRT$

Na$_z$P $\rightarrow$ zNa$^+$ + P$^{z-}$

$\pi = (z + 1) \ cRT$

It’s hard to determine molar mass of a polyelectrolyte.
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3. Donnan Effect of macromolecular solutions

Two limiting cases:

- $b \ll c \quad \pi = 2cRT$
- $b \gg c \quad \pi = cRT$

When a very large amount of NaCl is present, the Donna effect can be completely eliminated.
4. Viscosity of macromolecular solutions

Newtonian viscosity law: \[ F = \eta A \frac{du}{dx} \]

<table>
<thead>
<tr>
<th>Property</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative viscosity</td>
<td>( \eta_r = \frac{\eta}{\eta_0} )</td>
</tr>
<tr>
<td>Specific viscosity</td>
<td>( \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 )</td>
</tr>
<tr>
<td>Reduced viscosity</td>
<td>( \frac{\eta_{sp}}{c} = \frac{\eta_r - 1}{c} )</td>
</tr>
<tr>
<td>Intrinsic viscosity</td>
<td>( [\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} )</td>
</tr>
</tbody>
</table>

\( c \) is concentration in g/ml
4. Viscosity of macromolecular solutions

Relationship between intrinsic viscosity and molar mass of macromolecule

\[
\left[ \eta \right] = KM^\alpha
\]

For spheric molecule: \( \alpha = 0 \)

For rod-like molecule: \( \alpha = 2 \)

For flexible thread-like molecule: \( \alpha = 0.5\sim1.0 \)

In good solvent: \( \alpha > 0.5 \); in \textit{bad solvent}: \( \alpha \approx 0.5 \)
5. Salting-out of macromolecule

*Salting In*

Addition of salt at low ionic strength can increase solubility of a protein by neutralizing charges on the surface of the protein, reducing the ordered water around the protein and increasing entropy of the system.

*Salting out* (Can be used for *Fractionation*)

If the concentration of neutral salts is at a high level (>0.1 mol/L), in many instances the protein *precipitates*.

This phenomenon apparently results because the excess ions (not bound to the protein) compete with proteins for the solvent. The decrease in solvation and neutralization of the repulsive forces allows the proteins to aggregate and precipitate.
Salting-out effect: Used to selectively precipitate proteins, often with \((\text{NH}_4)_2\text{SO}_4\) which is cheap, effective, does not disturb structure and is very soluble.
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5. Gelation of macromolecule solution

**Gel:** Jelly like material formed by coagulation of a colloidal liquid.

Many gels have a *fibrous matrix* and interstices filled with fluid: gels are *viscoelastic* rather than simply viscous and can resist some mechanical stress without deformation.

**Silica gel:**

\[ \text{Na}_2\text{SiO}_3 + \text{HCl} \quad \text{water content} > 95 \% \]

**Soybean curd:**

Gel: Jelly like material formed by coagulation of a colloidal liquid.
Gels are formed by the interlocking of the dispersed particles in the form of a loose framework inside which liquid or gas dispersion medium is contained.
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5. Gelation of macromolecule solution

**Bicontinuous phase**

Sponge, a solid-gas dispersion system with all the solid phase and gas phase connecting.
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5. Gelation of macromolecule solution

Classification of gels

**On state of phases:**

1) s-l gel: human body, curd, jelly
2) s-g gel: silica gel, sponge

**On mechanical properties:**

1) elastic gels: molecules are held by electrostatic forces
2) rigid gels: silica gel with a network of chemical bonds.
3) thixotropic gels: kieselguhr/water
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5. Gelation of macromolecule solution

thixotropic gels:

syneresis
气凝胶是世界上密度最小的固体之一，其中99.8%以上是空气，所以有非常好的隔热效果，一寸厚的气凝胶相当20至30块普通玻璃的隔热功能。由于里面的颗粒非常小，所以可见光经过它时散射较小，就像阳光经过空气一样。因此，它也和天空一样看着发蓝。在俄罗斯“和平”号空间站和美国“火星探路者”的探测器上都有用到这种材料。图为悬浮在本生灯火焰上的气凝胶及花朵，花朵丝毫没有烧毁。
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5. Gelation of macromolecule solution
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Progress of colloidal chemistry

Prehistorical application: clay, Chinese ink, soybean curd.

Recent
1663, Cassius: Au sol;
1809, Pencc: electrophoresis;
1827, Brown: Brownian movement;
1857, Tyndall: Tyndall effect

1861, Graham, colloid chemistry;
1903, Zsigmondy: Ultramicroscopy;
1907, BanmapH, nature of colloids Ostwald: dispersed system
1923, T. Svedberg, Ultracentrifuge;
1930s, Staudingur, macromolecules