CH2203 Physical Chemistry

Solutions and Colloids

James Pickering

Overview

This course forms half of the module CH2203 Physical Chemistry and generally is based on the physical chemistry of things in the solution phase.

This course was written by Shengfu Yang (his slides and recordings are available on the Blackboard site), who normally delivers the lectures. **Shengfu's notes are the most complete resource for this course, and Shengfu is the one who has written the exam**.

However, this year due to a number of problems of people being unavailable, I am delivering the lectures in DLI. To make things worse, I cannot stay in DLI for two weeks to do this, because I have too many teaching commitments at Leicester!

So, we have 10 sessions together in DLI to cover this part of the module. This is fewer than usual, but I think we can actually cover all the content if we focus. **These notes are my condensed interpretation of Shengfu's slides**, and are what I will base my delivery on when lecturing in DLI.

These notes follow the order of Shengfu's lectures almost entirely, but have been condensed in places (I will tell you where). They are a bit 'rough and ready' - as we say in English - as I had to do this at short notice and did not have much time to prepare. This means:

- There are no figures (pictures/graphs) in these notes. I will sketch them on the chalkboard and nicer versions are in Shengfu's notes.
- There are a lot of new words in this module, so I have tried to add Chinese translations to the ones that may be most unfamiliar. But these have mostly been done using Wiki or Google translate, so they might not be 100% accurate...

For the course, you have a range of materials:

- These notes, which are what I will follow when lecturing in DLI. They follow the structure of Shengfu's slides.
- Shengfu's original slides, which will have more detail and more pictures in them.
- Recordings of Shengfu delivering the course from previous years.

Overall, I think this will be the most useful way to approach things - and you'll benefit from seeing how two different people (me and Shengfu) interpret and approach the same material.

Finally, as I said, I only got very short notice of being asked to come and deliver this course, and it is also a course I have not delivered before. So please bear with me, we are all learning as we go along! When I am in DLI, I'll spend as much time as possible in C07 so you can find me to ask any extra questions you have.

Lecture 1

Solutions

This lecture roughly corresponds to Lecture 1 and 2 in Shengfu's slides.

1.1 Basic Definitions

Key definitions:

- **Solution** (溶液): a *homogeneous* mixture of **solute** and **solvent**, where the particle size is less than 1 nm.
  - Example: salt water (salt dissolved in water), or 白酒 (alcohol dissolved in water).
- **Suspension** (悬浊液): a *heterogeneous* mixture containing large ($> 1\,\mu m$) particles. The particles are large enough to undergo *sedimentation*, and are not dissolved in the solvent (insoluble).
  - Example: muddy water (clay suspended in water), or 珍珠奶茶 (large bubbles suspended in tea).
- **Colloid** (膠體) a *heterogeneous* mixture containing smaller particles (between 5 and 1000 nm) that are insoluble, but small enough to be dispersed without sedimentation.
  - Example: cow's milk (fats dispersed in water), or 豆奶 (fats dispersed in water).

Homogeneous (同質) means that the mixture is uniform, and does not contain two visible phases. *Heterogeneous* (異質) means that the mixture clearly contains two separate parts or phases.

The formation of a solution is a **physical process, not a chemical one**:

- No covalent bonds are formed or broken when something dissolves into a solution.
- You can extract the solute in a *chemically unchanged* form from the solvent (compare $Zn(NO_3)_2$ in water to Zn metal in HCl).

There are many different kinds of solvent and solute:

- The **solute** is the thing that is present in smaller quantities than the **solvent**.
- The physical state of the solvent is what determines the physical state of the mixture.

- If the solute makes a homogeneous mixture, then it is *soluble*.

Solvents do not always need to be liquids (e.g. supercritical fluids), and solutes do not always need to be solids (e.g. can dissolve gas in liquid: carbonated drinks). We can broadly split solutes into those that are **electrolytes** (电解质 - e.g. salts) that create conductive solutions, and **non-electrolytes** (非电解质 - e.g. sugar) that do not.

Why do we need solvents? Consider the simplified exothermic chemical reaction below, happening in a vacuum:

$$A(g) + B(g) \longrightarrow AB(g)$$

In the absence of any solvent, or third body, can A and B collide to form AB? We need something to take away the energy released on forming the AB.

Solvents allow chemistry to happen, by providing a place for released energy to go. They also help to stabilise intermediates and separate solute molecules. Reaction rates can depend strongly on solvents – think about an S_N1 reaction in a polar vs non-polar solvent. Which is fastest?

Clearly we need to understand interactions in solutions to understand chemistry!

1.2 Interactions in Solutions: Macro

There are three kinds of interaction in solution:

- Solvent – Solvent interaction.
- Solute – Solute interaction.
- Solvent – Solute interaction.

The relative strengths of these interactions dictate the way the solution forms.

For a solution to form spontaneously, we need:

$$\Delta G_{sol} = \Delta H_{sol} - T\Delta S_{sol} < 0$$

Where ΔG_{sol} is the change in Gibbs' energy on formation of a solution, and so on. Thus, we require that:

$$\Delta H_{sol} < T\Delta S_{sol}$$

We can think of the solution as forming in three steps, and consider the enthalpy and entropy changes in each case:

1. Separate the solute into particles
2. Separate the solvent to make space for the solute.
3. Mix the solute and solvent.

The enthalpy and entropy changes are summarised in Table 1.1

Process	ΔH	ΔS
1. Separate solute	>0	>0
2. Separate solvent	>0	>0
3. Mix	<0	>0

Table 1.1: Enthalpy and entropy changes on solution formation.

Our overall enthalpy and entropy changes are the sum of the changes at each step (Hess' Law):

$$\Delta H_{\text{sol}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$
$$\Delta S_{\text{sol}} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

Clearly from Table 1.1 we can see that $\Delta S_{\text{sol}} > 0$ in all cases. The question is therefore about the enthalpy changes. Note that ΔH_1 and ΔH_2 are positive, but ΔH_3 is negative. We have three options:

1. $|\Delta H_1 + \Delta H_2| = |\Delta H_3|$
   - Here $\Delta H_{\text{sol}} = 0$ and so $\Delta G_{\text{sol}} < 0$, driven by entropy.
   - Example: solution of benzene and CCl_4
2. $|\Delta H_1 + \Delta H_2| < |\Delta H_3|$
   - Here $\Delta H_{\text{sol}} < 0$ and so $\Delta G_{\text{sol}} < 0$, driven by enthalpy and entropy.
   - Example: solution of NaOH and water.
3. $|\Delta H_1 + \Delta H_2| > |\Delta H_3|$
   - Here $\Delta H_{\text{sol}} > 0$ and so the sign of ΔG_{sol}, depends on the size of ΔH_{sol} compared to $T\Delta S_{\text{sol}}$. This explains why increasing the temperature can make things more soluble.
   - Example: solution of NaCl and water.

But, what is happening *at a molecular level?*

1.3 Interactions in Solutions: Micro

There are a number of interactions that occur between molecules. From strongest to weakest:

- Ion – ion interactions.
- Ion – dipole interactions.
- Dipole – dipole interactions (Keesom forces)
- Dipole – induced dipole interactions (Debye forces)
- Induced dipole – induced dipole interactions (London dispersion forces).

The last three of these *together* are known as **van der Waals** forces.

Not all molecules experience all these forces. All molecules experience dispersion forces, but other forces require there to be permanent dipoles in the molecule. **Polarity**, the presence of a permanent dipole in a molecule, is very important for how it behaves as a solvent.

Question: is salt (NaCl) more soluble in water (polarity: 1.8 D), or acetone (polarity: 2.9 D)?

Clearly the polarity of an isolated molecule is not the whole story. What matters is how good the collection of molecules as a solvent is at screening and separating charges. This is captured by a quantity called the **relative permittivity** (相對電容率), ϵ_r. It is also sometimes called the **dielectric constant**.

A useful way to think about ϵ_r is to think of it as a measure of how good the solvent is at screening charges from each other. We can see this if we consider the force, F, between two charges using Coulomb's Law:

$$F = \frac{1}{4\pi\epsilon_0\epsilon_r}\frac{q_1 q_2}{r}$$

Thus, as ϵ_r increases, the force between the charges drops, as they are more effectively screened from each other.

In the example given above, even though water is less polar than acetone, it has a much higher relative permittivity ($\epsilon_r(\text{water}) = 78$, $\epsilon_r(\text{acetone}) = 20$), which explains why it is better at solvating the ions in NaCl.

We can think about how these forces will lead to the structuring of solvents around ions, and other things (drawings on the chalkboard, or see Shengfu's slides).

We will come back to these ideas again and again later. Now, we will move onto thinking about how particles and molecules move through solutions.

Lecture 2

Transport in Solutions I

This lecture roughly corresponds to Lecture 3 and a bit of 4 in Shengfu's slides.

2.1 Chemical Potential

It's useful to think about the energy of solutions and mixtures as we change their composition. This is neatly captured by the concept of the **chemical potential** (化学势), μ.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Where μ_i is the chemical potential of component i in the mixture, G is the Gibbs' energy of the mixture, and n_i is the number of moles of component i.

In words, the chemical potential tells us how the **energy of the system changes as we change the amount of one component**. It is called a potential because molecules will want to move from areas of high chemical potential to low – just like a ball rolling down a hill (gravitational potential).

Chemical Potential in Solution

Chemical potentials of molecules in solution depend strongly on concentration. For an **ideal solution**, we can write the chemical potential of component i as:

$$\mu_i = \mu_i^0 + RT \ln x_i$$

Where x_i is the **mole fraction** (摩尔分数) of component i; and μ_i^0 is the chemical potential of a pure liquid (i.e. where $x_i = 1$). An **ideal solution** is one where $\Delta H_{\text{sol}} = 0$. The mole fraction is simply defined as:

$$x_i = \frac{n_i}{n_{total}}$$

i.e. the fraction of the total moles that are component i.

The $RT \ln x_i$ term is an entropic term (can be derived – come and ask for details), and is always < 0 because $0 \leq x_i \leq 1$. That is, the chemical potential of the component in solution is lower than the pure component. You can think of this as being related to how entropically, things tend to drive towards more disorder. At very low x_i, the potential will tend to some lower limit, known as μ_i^∞. This corresponds to infinite dilution, and the particles in solution behaving independently, like an ideal gas.

In reality, most solutions are not ideal, and $\Delta H_{sol} \neq 0$. In this case, we substitute the mole fraction x_i for the **activity** (活性度), a_i:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

Where $a_i = f_i x_i$, and f_i is the *activity coefficient*. Activity is the effective concentration of a species in a mixture. **For all of our purposes in this course, we will consider the activity and concentration to be equivalent.**.

External Electric Fields

It'll be useful (trust me) to think about how the chemical potential is affected by external electric fields. For instance, we might be interested in **electrolysis**, or how **batteries** work - these involve the interaction of external electric fields with our solutions.

If we apply an external electric field with voltage V to our solution, then the chemical potential of component i is given by:

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F V \tag{2.1}$$

Where z_i is the charge of component i, and F is the Faraday constant ($F = N_A e$).

2.2 Origin of Transport in Solutions

Species in solution will want to move from areas of high μ to low μ. Thus, if we have a solution where μ varies with position, x, then it is intuitive that the velocity of species i, v_i will be given by:

$$v_i = m_i \left(\frac{\partial \mu_i}{\partial x} \right)$$

Where m_i is a proportionality constant to be worried about later.

If we stick Equation 2.1 into the above, we get:

$$v_i = m_i \left[RT \left(\frac{\partial \ln a_i}{\partial x} \right) + z_i F \left(\frac{\partial V}{\partial x} \right) \right]$$

Now letting $a_i = c_i$ (activity $\rightarrow$ concentration), and defining the **flux**, j_i, as the rate of concentration transfer ($j_i = v_i c_i$), we find:

$$j_i = m_i c_i \left[RT \left(\frac{\partial \ln c_i}{\partial x} \right) + z_i F \left(\frac{\partial V}{\partial x} \right) \right]$$

Which simplifies to:

$$j_i = m_i RT \left(\frac{\partial c_i}{\partial x} \right) + m_i c_i z_i F \left(\frac{\partial V}{\partial x} \right) \tag{2.2}$$

Think about the units here and convince yourself it all makes sense. The **flux** has units of $\mathrm{mol\,m^{-2}\,s^{-1}}$, so you can think of it as the amount of moles flowing through a unit area in a unit time.

The only way that $j_i \neq 0$ and we have transport through the solution is if either of the two derivative terms are non-zero:

- If $\left(\frac{\partial c_i}{\partial x} \right) \neq 0$, then we have a **concentration gradient** as the concentration of species i, c_i, changes with position, x. This leads to a process called **diffusion** (扩散作用).

- If $\left(\frac{\partial V}{\partial x}\right) \neq 0$, then we have a **potential gradient** as the applied potential V changes with position, x. This leads to a process called **migration** (迁移).

Diffusion will affect all particles, as it just requires there to be a concentration gradient. **Migration** will only affect charged particles, as it requires that particles respond to the applied electric field. We will think about migration first.

2.3 Ion Migration: Conductivity

Ion migration is what makes electrolyte solutions able to conduct electricity. Electrolyte solutions are *second class conductors* (in contrast to metals, which are *first class conductors*).

Conductance (导电), G is the quantity that tells you how conducting a solution/material is.

$$G = \frac{1}{R}$$

Where R is the **resistance** (阻电) measured in ohms (Ω). The unit for conductance is the *Siemens* (S), or sometimes the *mho*, Ω^{-1}.

Conductance, like resistance, is an *extensive property* that depends on the size and shape of the conductor. **Conductivity** (电导率), κ, is the equivalent *intensive property* that is independent of size and shape. For a conductor of length L and area A:

$$\kappa = G\frac{L}{A}$$

The quantity L/A is known as the *cell constant* in electrochemistry.

For a solution, conductivity depends on the number of ions present, and so on the concentration of the solution. Therefore, it is common to define the **molar conductivity**, Λ_m:

$$\Lambda_m = \frac{\kappa}{c}$$

Using Λ_m allows conductivity of solutions with different concentrations to be compared.

2.3.1 Strong and Weak Electrolytes

Electrolytes can be **strong** or **weak**, depending on how fully they dissociate in solution.

- **Strong electrolytes** dissociate fully into ions in solution.
- **Weak electrolytes** dissociate partially into ions in solution.

Clearly this will depend on the solvent though (e.g. salt is a strong electrolyte in water, but would be very weak in petrol).

2.3.2 Conductivity of Electrolyte Solutions

Conductivity of electrolyte solutions varies with the type of electrolyte (strong or weak) and with concentration. Strong and weak electrolytes exhibit different dependence of conductivity (κ or Λ_m) on concentration (c) (see chalkboard in lecture).

- For strong electrolytes:

  - Absolute conductivity (κ) *increases* with increased c, as there are more ions.
  - Molar conductivity (Λ_m) *decreases* slightly with increased c, as ion-ion interactions reduce ion **mobility** (more on that later).

- For weak electrolytes:
  - Absolute conductivity (κ) *stays fairly constant* with increased c, as increased c lowers the degree of dissociation, reducing the fraction of ions produced at high c (see later).
  - Molar conductivity (Λ_m) *decreases* strongly with increased c, for the same reason as above.

Strong electrolytes obey **Kohlrausch's Law**:

$$\Lambda_m = \Lambda_m^\infty - Y_k\sqrt{c}$$

Λ_m^∞ is the *conductivity at infinite dilution* - i.e. in the limit of no ion-ion interaction. Y_k is an empirical constant.

Weak electrolytes do not obey the law above as written, because the degree of dissociation of the electrolyte (α) varies with concentration. If we think about a generic 1:1 electrolyte, we can show that:

$$K = \frac{\alpha^2 c}{1-\alpha} \quad (\approx \alpha^2 c, \text{ as } \alpha << 1)$$

where K is the equilibrium constant for dissociation. Here it is clear that as c increases, α must decrease to keep K constant. Thus, the molar conductivity of a weak electrolyte depends on α:

$$\Lambda_m = \alpha\Lambda_m^\infty$$

Combining the two previous equations leads to the **Ostwald Equation**:

$$\frac{1}{\Lambda_m} - \frac{1}{\Lambda_m^\infty} = \frac{\Lambda_m c}{(\Lambda_m^\infty)^2 K}$$

The Ostwald Equation can be used to calculate K and Λ_m^∞ from measured values of Λ_m and c.

Experiments into conductivity by Kohlrausch led to the discovery that the molar conductivities of different ions in the same solution are additive in the limit of infinite dilution:

$$\Lambda_m^\infty = \nu_+\lambda_+ + \nu_-\lambda_-$$

Where ν_+ is the stoichiometric coefficient of the cation, and λ_+ is the **ionic conductivity** of the cation, and so on for the anion. This is known as the **law of independent ion migration**.

This observation led to the discovery that ions in solution have different conductivities, which implies that different ions have different **mobility** in solution. This is the topic for next time.

Lecture 3

Ions in Solution I

This lecture roughly corresponds to Lecture 4 and 5 in Shengfu's slides.

3.1 Ion Mobility and Conductivity

Why do different ions have different conductivities in solution? The answer is due to their different **mobility** (電気移動度).

Consider a positive ion in solution, under an electric field $\vec{E}$ (drawn on chalkboard in lecture). The forces on the ion are:

- A force from the electric field (the potential gradient) in one direction, $\overrightarrow{F_E}$.
  - $\overrightarrow{F_E} = ze\vec{E}$ (Coulomb's law).
- A drag/friction force, in the opposite direction $\overrightarrow{F_D}$.
  - $\overrightarrow{F_D} = 6\pi\eta a\vec{v}$ (Stokes' law).
  - η is the **viscosity** (黏度) of the solution, a is the **hydrodynamic radius** of the ion, and $\vec{v}$ is the velocity of the ion.

Note that we are emphasising that these forces are vector quantities that act in a specific *direction*, using the vector notation $\vec{v}$.

When these two forces are balanced ($\overrightarrow{F_E} = \overrightarrow{F_D}$), we can find the **terminal velocity** or the **drift velocity** of the ion, $\overrightarrow{v_{\text{drift}}}$:

$$\overrightarrow{v_{\text{drift}}} = \frac{ze\vec{E}}{6\pi\eta a}$$

We then define the **mobility** of the ion, u, as the ratio of the magnitudes of the drift velocity to the field:

$$u = \frac{|\overrightarrow{v_{\text{drift}}}|}{|\vec{E}|} = \frac{|z|e}{6\pi\eta a} \tag{3.1}$$

Here, we can see that higher charges lead to higher mobility, and that higher viscosity leads to lower mobility, etc...

The mobility of a typical ion is on the order of $5 \times 10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$, however H^+ and OH^- ions have much higher mobility (36.3 and $20 \times 10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$ respectively).. This is due to **proton-passing** mechanisms that allow ions to be moved very quickly.

So how does the mobility of an ion u_i link to the conductivity of that ion λ_i? The relationship is straightforward, they are directly proportional:

$$\lambda_i = |z| F u_i$$

Thus, we see that a higher **mobility** leads to a higher **conductivity**.

The problem that now arises is that when we measure these quantities, we don't measure individual conductivities λ_+ and λ_-, but the overall molar conductivity Λ_m^∞. Remember that for a simple 1:1 electrolyte:

$$\Lambda_m^\infty = \lambda_+ + \lambda_-$$

Thus, we measure the sum of the individual conductivities. It would be nice to have a way to measure them individually. This is where measurement of the **transport number** is useful.

3.2 Transport Numbers

Electric current (I) passed through a solution is carried by the ions in the solution. The **transport number**[1], t_i of an ion is the **fraction of the total current carried by that ion**:

$$t_i = \frac{I_i}{I_{\text{total}}}$$

The amount of current carried by an ion, I_i, is proportional to $\nu_i \lambda_i$, such that:

$$t_i = \frac{\nu_i \lambda_i}{\sum_j \nu_j \lambda_j}$$

From these equations it is clear that $0 < t_i < 1$ and that $\sum_i t_i = 1$.

For a simple 1:1 electrolyte, the utility of the transport number becomes obvious:

$$t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda_+}{\Lambda_m^\infty} \tag{3.2}$$

Thus, if we can measure t_+ and Λ_m^∞, we can calculate λ_+, which was our aim. An analogous equation applies for the anion transport number, t_-.

Note that you could rewrite Equation 3.2 in terms of ion mobilities, as:

$$t_+ = \frac{u_+}{u_+ + u_-} \tag{3.3}$$

3.3 Determining Transport Numbers

The question now becomes: 'how do we determine the transport number?'. We learn two methods in this course: **Hittorf's Method** and the **Moving Boundary Method**. Both methods are based on Equation 3.3 – if you can measure the mobilities of different ions, you can measure the transport numbers.

We will talk about these in detail in the lecture, and do some example calculations, using some of the figures from Shengfu's slides.

[1] I couldn't find a Chinese translation for this, maybe one of you can help me?

Lecture 4

Ions in Solution II

This lecture roughly corresponds to Lecture 6 in Shengfu's slides.

4.1 Interactions between Ions

We've talked about ionic mobility and conductivity, but to fully understand these, we need to understand the different interactions that occur between ions in solution. Ions in solution, with no external electric field applied, will undergo:

- **Thermal motion:** creating disorder (thermal energy $= k_B T$).
- **Ion-solvent interaction:** creating order.
- **Ion-Ion interaction:** creating order.

These interactions increase as the number of ions increase, and cause the Λ_m of strong electrolytes to slowly decrease as c increases (example: ion pairing, which reduces the effective concentration of ions at high c). Overall, these interactions lead to the arrangement of solvent and ions around any specific ion in solution to not be random, but be ordered.

An ion in solution is *on average* surrounded by more counter-ions than ions of the same charge. This surrounding of a cation by anions (and vice versa) is what we call the **ionic atmosphere**[1].

The problem of understanding and modelling ionic atmosphere is a huge one (try and calculate the number of ions and number of interactions for a typical solution) – the number of particles is too large even for the best supercomputers we have today. We need an approximation to simplify things.

4.2 The Debye-Hückel Approximation

The **Debye-Hückel Approximation** (DHA) is the approximation we need. A full mathematical treatment of the DHA is beyond what we can do here, but the fundamental ideas are that:

- We are considering the ionic atmosphere around a given central ion.
- The central ion has a discrete charge.

[1] I am reliably informed that a reasonable translation is 离子氛 – thanks to Li Qianhao!

- The solvent is a continuous dielectric – i.e. we do not worry about individual solvent molecules, but we do consider the average effect of the solvent when considering how charges interact with each other.
- The counter-ions that surround the central ions smear out into a continuous **ionic atmosphere**.

Overall, we can then picture a single ion in solution as surrounded by an atmosphere of counter-ion, such that overall the system is electrically neutral. I will draw it on the chalkboard in the lecture. The effect of this ionic atmosphere is to **screen** the rest of the solution from feeling the full charge from the central ion.

The DHA leads to a modified potential, $V_{DH}(r)$ that describes the electrostatic interaction between particles at a distance r:

$$V_{DH}(r) = V_C(r) \exp\left(-\frac{r}{L_D}\right) \tag{4.1}$$

Where:

- $V_C(r)$ is the normal Coulomb potential in the solvent.
- L_D is the **Debye-Hückel Length**, which tells you about the **extent of the ionic atmosphere.**

4.2.1 The Debye-Hückel Length

Note that Equation 4.1 is just a combination of the ordinary Coulomb potential[2]

$$V_C(r) = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r r}$$

multiplied by a factor that accounts for the **screening** of charges by the ionic atmosphere:

$$\exp\left(-\frac{r}{L_D}\right)$$

This factor is just an exponential decay with a characteristic decay length of L_D, and will always be < 0 (i.e. it screens the solution from feeling the full Coulomb potential from the central ion, V_C). It is useful to try and sketch graphs of $V_C(r)$ and $V_{DH}(R)$ to understand the effect (we will do this in the lecture):

- $V_{DH} < V_C$ in all cases, due to screening.
- If L_D is large, then $\exp\left(-\frac{r}{L_D}\right) \to 1$, and $V_{DH} \approx V_C$, and the screening is ineffective (ionic atmosphere too diffuse and extended).
- If L_D is small, then $\exp\left(-\frac{r}{L_D}\right) \to 0$, and so $V_{DH} << V_C$, and the screening is very significant (ionic atmosphere very tight and condensed).

The charge distribution around the central ion, $\rho(r)$ is proportional to $4\pi r^2 V_{DH}(r)$. It is simple to show that the position of maximum charge is when $r = L_D$ – i.e. L_D is the thickest point of the ionic atmosphere. We will go through the derivation on the chalkboard.

[2]Note that it explicitly includes the permittivity of the solvent, ϵ_r.

It can be shown[3] that:

$$L_D = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{N_A} \frac{1}{I}}$$

Where I is the **ionic strength**, given by:

$$I = \sum_i c_i z_i^2 e^2$$

Considering the various factors in this equation (which we will do together on the chalkboard), makes it clear what affects the ionic atmosphere and amount of screening. For example:

- As T increases, L_D increases: because the ions are more free to move at higher temperatures as they have more thermal energy, which increases L_D and reduces screening.
- As c (concentration) increases, L_D decreases: because as more charges are added to the solution, the counter-ions crowd more closely around the central ion, reducing L_D and increasing screening.

4.3 Ionic Atmospheres In Electric Fields

Previously we considered the mobility of an ion in solution in an applied electric field $\vec{E}$, and the interplay of the Coulomb and drag/friction forces. We can expand on this picture now we understand the ionic atmosphere.

I will draw it on the chalkboard (and see Shengfu's slides). Now we have more forces to think about, as we have to think about the central ion and the ionic atmosphere:

1. A force from the electric field on the central ion, $\overrightarrow{F_E}$, the **electromotive force**.
    - This moves the central ion in the direction of the applied field, $\vec{E}$.
2. A force from the electric field on the surrounding atmosphere $\overrightarrow{F_{el}}$, the **electrophoretic force**.
    - This opposes $\overrightarrow{F_E}$, and causes increased drag (*electrophoretic drag*, or *electrophoretic retardation*).
3. A force that attracts the central ion to the centre of the ionic atmosphere, $\overrightarrow{F_R}$, the **relaxation force**.
    - This opposes $\overrightarrow{F_E}$ and causes increased drag.
4. The **Stokes drag force** described earlier, $\overrightarrow{F_D}$, is also present.

We can see that the effect of these forces around the ionic atmosphere is to **reduce** the ion mobility in solution (relative to an ion with no atmosphere). Under an electric field, the shape of the ionic atmosphere is distorted away from being spherical. This distortion of the shape is known as the **asymmetric effect** or **relaxation effect**.

Enough about ions for now. Next time we talk about **diffusion**.

[3] I am not exactly sure how, hopefully I find out before I come to China...

Lecture 5

Diffusion

This lecture roughly corresponds to Lecture 7 in Shengfu's slides.

5.1 Fick's First Law

Going back to Equation 2.2:

$$j_i = m_i RT\left(\frac{\partial c_i}{\partial x}\right) + m_i c_i z_i F\left(\frac{\partial V}{\partial x}\right) \tag{5.1}$$

We said that the first term was identified with **diffusion**, and the second term with **migration**, i.e:

$$j_i = j_{i,\text{dif}} + j_{i,\text{mig}}$$

Let's look at the first term. **Fick's First Law** of diffusion says that that flux due to diffusion, $j_{i,\text{dif}}$ is given by:

$$j_{i,\text{dif}} = D\left(\frac{\partial c_i}{\partial x}\right) \tag{5.2}$$

Where D is the **diffusion coefficient**[1]. The physical meaning of D is hopefully intuitive from the equation above.

If we compare Equation 5.2 to the first term of Equation 5.1, we can see that:

$$D = m_i RT \tag{5.3}$$

However, we didn't ever actually find out what m_i was, and said we would *worry about it later*. Well, later is now.

5.2 Einstein Equation(s)

Ultimately what we would like to do is find a way to link the **diffusion coefficient**, D, to the **ion mobility**, u_i. We can do this and figure out m_i at the same time (nice).

Look back at the migration term of Equation 2.2:

$$\overrightarrow{j_{i,\text{mig}}} = m_i c_i z_i F\left(\frac{\partial V}{\partial x}\right) = m_i c_i z_i F\vec{E}$$

[1] You will see many books that define this law with $-D$ rather than D. The reason is that j is in the opposite direction to the concentration gradient (i.e. if concentration is higher on the left of the solution, then the flux flows from the left to the right), but ultimately it doesn't affect the results we need. I will leave it defined with D to keep it consistent with Shengfu's slides.

Also note that the migration flux is given by:

$$\overrightarrow{j_{i,\text{mig}}} = \vec{v_i} c_i$$

Note in general the flux, j is a vector quantity, $\vec{j}$. I left this out earlier as I didn't want things to look messy, but will add it back now. Recall that $\vec{v_i}$ is the velocity of the ion. Recall also the definition of ion mobility:

$$u_i = \frac{|\vec{v_i}|}{|\vec{E}|}$$

Combining these three equations leads us to the result that:

$$m_i = \frac{u_i}{z_i F} \tag{5.4}$$

Now, we have to make some subtle arguments. At equilibrium, in our solution, there must be no net flux. This means that the flux due to migration and the flux due to diffusion must be equal and opposite. The practical result of this is that Equation 5.3 and Equation 5.4 must both hold simultaneously. Thus we can say that:

$$D = \frac{u_i R T}{z_i F} \tag{5.5}$$

Equation 5.5 is called the **Einstein Equation**. It provides the link between **ion mobility** and the **diffusion coefficient**. **Note that Equation 5.5 only works for ions**.

We can also develop Equation 5.5 a little further and include the effect of solvent viscosity. Recall that the **Stokes drag force** (friction from the viscosity of the solvent) is given by:

$$\overrightarrow{F_D} = 6\pi\eta a \vec{v}$$

Which led to an equation for the mobility including viscosity:

$$u_i = \frac{|z|e}{6\pi\eta a} \tag{5.6}$$

If we combine Equation 5.6 and Equation 5.5, we get:

$$D = \frac{k_B T}{6\pi\eta a} \tag{5.7}$$

Equation 5.7 is the **Stokes-Einstein Equation**. It works to describe diffusion coefficients of ions *and* neutrals.

5.3 Fick's Second Law

Fick's Second Law of diffusion states that:

$$\left(\frac{\partial c}{\partial t}\right) = D\left(\frac{\partial^2 c}{\partial x^2}\right) \tag{5.8}$$

Where x is position, c is concentration, t is time, and D is the diffusion coefficient.

Equation 5.8 is a beautiful and intuitive equation, which has a similar form to many other analogous equations in physics and chemistry like the *Heat Equation*. We will talk about it extensively in the lecture. As an exercise, show that the solution to the equation is given by a function of the form:

$$c \propto \exp\left(-A\frac{x^2}{t}\right)$$

Where A is a constant to be determined.

Various integrations of the solution to Equation 5.8 lead to a couple of illustrative results. Firstly, the average distance travelled by a species in solution is:

$$\langle x \rangle = 2\sqrt{\frac{Dt}{\pi}}$$

This illustrates that the larger D is, the greater the average distance travelled by a species in solution.

Secondly, we can calculate the **root-mean-square (rms)** distance:

$$x_{RMS} = \sqrt{2Dt}$$

This is called the **Einstein-Smoluchowski Equation**[2]. This provides another link between the *microscopic* (distance x moved by an individual particle) and the *macroscopic* (diffusion coefficient). Neat.

That's it for solution transport. Next time we are onto **colloids**. Get your tofu ready.

[2]Depending on which book you read, it seems people can't all agree what to call these things.

Lecture 6

Colloids I

This lecture roughly corresponds to Lecture 9 and a bit of 10 in Shengfu's slides.

6.1 Colliodal Suspensions

In Lecture 1 we defined a **colloid** (膠體) as *heterogeneous* mixture containing smaller particles (between 5 and 1000 nm) that are insoluble, but small enough to be dispersed without sedimentation. This was true, but actually colloids exist more generally (they do not have to be in the liquid phase). Colloids have two parts:

- A **dispersed phase** (分散剂), which is the phase of the colloidal particles.
- A **continuous phase** (分散质), which is the phase that the particles are dispersed in.

We will talk about a number of examples, and see Shengfu's slides for extensive examples.

Colloids are interesting because while they look stable (e.g. milk can happily sit in a refrigerator for a long time), they are actually inherently *unstable*. Essentially, a colloid, or a **colloidal suspension** (the same thing), consists of particles that are **kinetically trapped** in this unstable state. That means it is possible to break apart the suspension and cause it to **flocculate** (絮凝) or **coagulate** (凝固) or 'crash out' (informal term).

Colloids are incredibly widespread. I will bring some examples with me.

6.2 Forming Colloids

To form a colloid, we need a way to *disperse* a number of small particles into soution. There are basically two approaches:

- **Dispersion**, or a **top-down** approach.
  - Here you break down a bulk material into the colloidal particles, which are then dispersed in the continuous phase.
- **Condensation**, or a **bottom-up** approach.
  - Here you grow the colloidal particles from smaller ones, via **nucleation** and **growth**.

Controlling the size of the colloidal particles is a key consideration, as the properties of the colloid depend very strongly on particle size.

In a *bottom-up* approach, this can be controlled through the processes of nucleation and growth, by controlling the amount of material available

- In **nucleation** (at low density of material), we form lots of small (<500 nm) particles, usually from a **supersaturated** solution. We want to maximise this step.
- in **growth** (at higher density of material), the small particles **aggregate** and get larger. We usually want to minimise this step.

If we do this right, we end up with our colloidal particle dispersed through our continuous phase. We can characterise the size of the colloidal particles by calculating the **dispersity** (分散度), Đ, (called the **polydispersity** or **polydispersity index** in some books).

$$Đ = \frac{M_{av}(\text{mass})}{M_{av}(\text{number})}$$

Where:

$$M_{av}(\text{number}) = \frac{\sum_i n_i M_{r,i}}{\sum_i n_i} \quad M_{av}(\text{mass}) = \frac{\sum_i n_i M_{r,i}^2}{\sum_i n_i M_{r,i}}$$

Are the **number average** and **mass average** molecular masses. $M_{r,i}$ is the molar mass of particle i, and n_i is the number of moles of particle i. We will do an example to illustrate, but in the *monodisperse* case:

$$M_{av}(\text{number}) = M_{av}(\text{mass}) \rightarrow Đ = 1$$

In the polydisperse case:

$$M_{av}(\text{number}) < M_{av}(\text{mass}) \rightarrow Đ > 1$$

If a colloidal suspension is **polydisperse**, it consists of a number of different particle sizes. If it is **monodisperse**, it consists of particles of similar size. Usually monodisperse colloids are what we want.

6.3 Stability of Colloids I

Colloidal particles in suspension move around due to the available thermal energy, in a process called **Brownian Motion** (this ultimately is the origin of diffusion). They are also affected by **gravity**[1]. Let's think about **gravity** initially.

6.3.1 Sedimentation

We can imagine a colloidal particle in suspension (drawn on chalkboard). Clearly the important forces are the **force due to gravity**, $\overrightarrow{F_g}$ and the **buoyancy force**, $\overrightarrow{F_b}$. The net force:

$$\overrightarrow{F_{net}} = \overrightarrow{F_g} - \overrightarrow{F_b} = V\Delta\rho g$$

Where $\Delta\rho = \rho_{disp} - \rho_{cont}$, the difference in densities between the dispersed phase (the particle) and the continuous phase (the solution). The difference in density affects the tendency of the solution to crash out:

[1] This is interesting, because molecules undergo Brownian motion but are too small to be affected much by gravity. Larger objects are affected by gravity but are too small to undergo Brownian motion. Colloidal particles are in the middle so affected by both.

- If $\Delta\rho > 0$, then the particle is denser than the continuous phase, and the tendency is for the particles to settle at the bottom. This is known as **sedimentation** (沉降).
- If $\Delta\rho < 0$, then the particle is less dense than the continuous phase, and the tendency is for the particles to settle at the top. This is known as **creaming**[2].

We can imagine that both the density of the particle and viscosity of the continuous phase will affect these processes. We define the **sedimentation coefficient**, s, as:

$$s = \frac{v_t}{g}$$

Where v_t is the terminal velocity of the particle and g is the acceleration causing it (here gravity). We will show that for sedimentation under gravity, s is given by:

$$s = \frac{m}{f}\left(1 - \frac{\rho_{cont}}{\rho_{disp}}\right)$$

Where m is the mass of the particle and f is the **friction factor** that we have discussed in the context of Stokes' law previously. The unit of the sedimentation coefficient is seconds, but is often referred to in **Svedbergs**, where one Svedberg is 1×10^{-13} s. **Note** that a *high* value of s means *faster* sedimentation (s is **not** the time taken to sediment!).

From Stokes' Law, for a spherical particle the friction factor is given by:

$$f = 6\pi\eta a$$

Recall that a is the hydrodynamic radius, and η is the viscosity of the continuous phase.

We can go on to show (will be done on chalkboard in lecture) that the sedimentation coefficient for a spherical particle is given by:

$$s = \frac{2r^2\Delta\rho}{9\eta}$$

Doing some calculations of typical values for s (in lecture) will show that *sedimentation by gravity of colloidal particles takes a very long time*. One way to increase the sedimentation rate is to apply more force to the colloidal particles using a **centrifuge** - see Shengfu's slides for more details.

6.3.2 Diffusion vs Sedimentation

Recall that **diffusion** was the motion of particles from areas of **high** concentration to **low**. Sedimentation is the opposite: particles to move from areas of **low** concentration to **high**.

We can thus think of diffusion and sedimentation as having opposite effects on colloidal particles – they fight each other!

Next time we will continue thinking about the stability of colloidal particles.

[2] Can't find a Chinese translation for this either...

Lecture 7

Colloids II

This lecture roughly corresponds to Lecture 11 and 12 in Shengfu's slides.

7.1 Stability of Colloids II

We said previously that colloids were:

- **Kinetically stable**, as there is a big activation barrier to them crashing out of solution (i.e. the sedimentation/coagulation/etc is very slow).
- **Thermodynamically unstable**, as the energy of the colloidal system is not at the global minimum of the two-component system (i.e. the colloid being crashed out into sediment or similar *is* ultimately more stable than it being dispersed as a colloid).

For example, if you churn milk a lot, it irreversibly turns into butter (the fats that were dispersed in the water crash out and coagulate).

It will be useful to think about the interactions between colloidal particles so we can understand these effects more deeply.

7.1.1 Intermolecular Interactions

We listed types of intermolecular interactions before:

- Ion – ion interactions (r^{-1}).
- Ion – dipole interactions (r^{-4})
- Dipole – dipole interactions (r^{-6}).
- Dipole – induced dipole interactions (r^{-6}).
- Induced dipole – induced dipole interactions (r^{-6}).

It will now be useful to think about the **length scale** of these interactions. The length scale is a measure of the distance over which the interaction acts. For example, the Coulomb interaction:

$$V_C \propto \frac{1}{r}$$

Scales with $1/r$. So if the distance increases by a factor of 2, the interaction energy goes down by a factor of 2.

For **van der Waals** interactions between two molecules (the bottom three of the interactions listed above), the length scale is much shorter:

$$V_{vdw} \propto \frac{1}{r^6}$$

So, if the distance between two molecules increases by a factor of 2, the van der Waals interaction strength drops by a factor of $2^6 = 64$. Other length scales are annotated on the list above, in brackets next to the interactions.

7.1.2 Interactions between Colloidal Particles

The above interactions were for molecules. A colloidal particle is made of a large number of molecules, so we have to sum the interactions over a large number of molecules.

If we just consider neutral colloids, then we only have vdW interactions to think about. The mathematics for doing this quite involved, but essentially the result is the **short range vdW interactions between molecules become longer range when between colloidal particles**. The exact length scale varies with particle geometry, but it is between r^{-2} and r^{-1} (compared with r^{-6} for molecules).

However, colloidal particles in aqueous solution are not usually completely electrically neutral, so there are other interactions to consider.

7.2 Electrical Double Layers

A charged colloidal particle[1] will order solvent molecules (and any other ions in solution - such as salts) in a similar way to that described in the Debye-Hückel Approximation earlier.

A useful way to think about this is to imagine a charged surface immersed in an ionic solution. This surface could be the surface of our colloid, for example. If we imagine this for a **positively charged surface**:

- Near the surface, there is a very dense, ordered structure of anions. This is the **Stern Layer**.
- Further from the surface, there is still ordering of the solution, but the ordering is more diffuse. This is the **Diffuse Layer**.
- Very far from the surface, we return to unordered bulk solution.

Together these layers are called the **Electrical Double Layer** (双电层). This model is called the **Stern Model** of a charged interface. These layers affect the stability of colloidal particles, as if two particles approach each other then the electrical double layers will repel each other. This is called **double layer repulsion**.

The idea of the electrical double layer is similar to the Debye-Hückel model for charges around an ion in solution. In fact, the thickness of the diffuse layer is given by the Debye-Hückel parameter

[1] I know, we just said that we were treating interactions between neutral colloids - but the surface of a colloidal particle can still be charged, due solution pH and other factors, so this is OK.

L_D. The electric potential at the interface, ϕ, has to obey **Poisson's Equation**, which for small ϕ takes the form[2]

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}r^2} = k^2\phi$$

The solution to this equation, with the boundary condition that $\phi \to 0$ as $r \to 0$, leads to a similar expression to that which we got from the Debye-Hückel screening:

$$\phi(r) = \phi_0 \exp(-kr)$$

Where we can identify:

$$k = \frac{1}{L_D}$$

7.2.1 Slipping Plane and Zeta Potential

The reason it is called a **double layer** is because of the tight Stern layer and more loose diffuse layer. As the particle moves around in solution, it will drag the Stern layer along with it, but at some distance from the particle surface the solution does not move with the particle. We can define the **slipping plane** or **shear plane** as this point: the point where mobile solution molecules are separated from those that are stationary and attached to the particle.

The **zeta potential** (ζ potential) is the **potential difference at the slipping plane**. ζ will give us a useful measure of the stability of a colloidal dispersion:

- If $|\zeta|$ is big: there will be big electrostatic repulsion between colloidal particles, keeping them separate and dispersed.
- If $|\zeta|$ is small: there will be low electrostatic repulsion between colloidal particles, meaning they can get closer and increasing the chance of them crashing out of solution.

Next time we will see how the presence of these double layers, with the other interactions, combine together to give us a complete picture of the interactions between colloidal particles. We will be able to fully explain how to make things like tofu and butter. How exciting.

[2] In general $\frac{\mathrm{d}^2\phi}{\mathrm{d}r^2} = k^2 \sinh\phi$, and the equation given is a useful limiting case for small ϕ. See Shengfu's notes for a bit more detail.

Lecture 8

Colloids III

This lecture roughly corresponds to Lecture 13 in Shengfu's slides.

8.1 DLVO Theory

Last time we saw the different kinds of interactions between colloidal particles:

- **Attractive interactions**: van der Waals interactions (long range: r^{-1} or r^{-2}).
- **Repulsive interactions**:
  - The double layer repulsion (intermediate range: e^{-r}).
  - Hard-sphere repulsion (very short range: r^{-12}).

We can see the typical length scales of these interactions in the list above. Note that the exact length scale of the vdW interactions depends on the particle geometry. We have also introduced the **hard-sphere repulsion**, which is an extremely short range and highly repulsive interaction that occurs when two colloidal particles actually touch.

If we combine all these interactions together:

$$V_{\text{total}} = V_{\text{hard sphere}} + V_{\text{double layer}} + V_{\text{vdW}}$$

We end up with the **Derjaguin–Landau–Verwey–Overbeek model**. I can't pronounce all these names properly, so we call it the **DLVO model** for short.

8.1.1 DLVO Behaviour

The exact form of the DLVO potential varies with the specific system under consideration, but we can make a useful approximate expression which will illustrate most of the physics:

$$V_{\text{DLVO}} \sim \frac{1}{r^{12}} + \exp\left(-\frac{r}{L_D}\right) - \frac{1}{r^2} \tag{8.1}$$

I've left out a bunch of constants that make the units actually make sense, because it's much more important to understand the physical behaviour of the system than to do numerically accurate calculations. Note that the form of Equation 8.1 changes depending on the geometry of the system (e.g. different shape colloids), but the physics is similar in all cases. *See Shengfu's notes for some more rigorous explanation of calculation using the DLVO model.*

The most useful thing we can do to understand stability of colloids is to plot the DLVO potential as a function of particle separation r for a range of cases and see if we can understand what is going on. We will do this on the chalkboard, but the key points are that we find:

- A **primary minimum**, which is deep. At this separation, the colloidal particles have **coagulated** and **irreversibly** bound together.
- A **secondary minimum**, which is shallow. At this separation, the colloidal particles have **flocculated** and **reversibly** bound together.
- An **energy barrier** separating the two minima. The height of this barrier determines the stability of the colloidal suspension.

Remember that the thermal energy available to the colloidal particles is $k_B T$. We will talk a lot about the well depths and barrier heights relative to $k_B T$.

We will spend a while talking about this, and looking at some illustrative example cases. It really is very cool.

8.2 Manipulating Colloidal Suspensions

A useful thing to think about is the effect of adding an electrolyte (salt) to the colloidal suspension:

- More salt $\rightarrow$ more ions in solution.
- More ions $\rightarrow$ decreased L_D.
- Decreased $L_D \rightarrow$ lower $zeta$ potential.
- Lower $\zeta \rightarrow$ **lower barrier, deeper secondary minimum.**

Thus we can, for example, make our colloidal suspension more likely to coagulate by adding salt.

8.2.1 豆腐

When you make tofu (豆腐), you add $MgCl_2$ or $CaSO_4$ to boiled soy bean milk. Adding this salt makes the proteins and fats in the milk coagulate into 豆花, which is then pressed into 豆腐.

A similar process is used in Europe to make various kinds of cheese and other dairy products. Unfortunately, the climate is too cold in summer to grow soy beans in most of Europe, so we never figured out the joys of 豆腐.

8.2.2 Schulze-Hardy Rule

One rule relating to this is the **Schulze-Hardy Rule**, which says that the **valency** of the salt ions (i.e. how charged they are) is the most important factor in determining how much they affect colloidal stability. The Schulze-Hardy rule says that the **critical coagulation concentration**:

$$\text{Critical Coagulation Concentration} \propto \frac{1}{z^6}$$

Where z is the valency of the salt ion.

Next time we are going to talk about **micelles**.

Lecture 9

Surfactants and Micelles

This lecture roughly corresponds to Lecture 14 in Shengfu's slides.

9.1 Surfactants

A **surfactant** (表面活性剂) is a molecule that has both:

- A **hydrophobic** (疏水性) part that is not soluble in aqueous solvents, such as a long alkyl chain (but is soluble in non-polar solvents, like fats or oil).
- A **hydrophilic** (親水性) part that is soluble in aqueous solvents, such as a carboxylic acid group.

These molecules will tend to gather at the interface between polar and non-polar phases, and so are active at surfaces: hence the name, **surfactant**.

Soap is the classic example of a surfactant. Oil and grease (dirt) sticks to the **hydrophobic** part of the surfactant, and then the whole dirt+surfactant combination can be washed off in water, which interacts with the **hydrophilic** part of the surfactant.

9.1.1 Surface Tension and Monolayers

Imagine a beaker of water open to the air. The water molecules at the surface of the water don't want to be at the surface, but would rather be in the bulk solution where they can be surrounded by other water molecules. This produces **surface tension** (表面张力), because the molecules want to move to minimise the area of the surface open to the air.

If we add a small amount of surfactant to this water:

- The hydrophilic parts of the surfactant point into the water.
- The hydrophobic parts point into the air.

Overall this reduces the surface tension, because now there are no water molecules facing the air: the surfactant has covered the surface.

When the surfactant has completely covered the surface, we say that a **monolayer** (单层) has been formed. It is called a **mono**layer because it is one molecule thick.

9.2 Micelles

As we add surfactant to our system, we will observe the surface tension lowering. Once we have formed a monolayer, the surface tension will no longer drop. At this point, the surface is 'full' and any extra surfactant has to go somewhere else. The extra surfactant will then form **micelles** (胶束), and the concentration of surfactant at which this happens is called the **critical micelle concentration**, or **CMC**.

A **micelle** is a self-assembly of surfactant molecules such that the hydrophilic parts point outwards and the hydrophobic parts point inwards[1]. In this way the micelle can happily exist in bulk aqueous solution.

9.2.1 Thermodynamics of Micellisation

Imagine the equilibrium between monomer surfactants S, and micelles M. Assume that it takes n surfactants to make a micelle:

$$\mathrm{S} \rightleftharpoons \frac{1}{\mathrm{n}}\mathrm{M}$$

We can define the equilibrium constant, K, of this reaction in terms of the mole fraction of surfactant, x_S, and micelle, x_M:

$$K = \frac{x_\mathrm{M}^{\frac{1}{n}}}{x_\mathrm{S}}$$

We can then link K to the Gibbs' energy of micellisation, ΔG_mic:

$$\Delta G_\mathrm{mic} = -RT \ln K = -RT \ln \left(\frac{x_\mathrm{M}^{\frac{1}{n}}}{x_\mathrm{S}} \right)$$

At the CMC, we know that $x_\mathrm{M} << x_\mathrm{S}$ and that $x_\mathrm{M} << 1$. Thus for Gibbs' energy expression reduces to:

$$\Delta G_\mathrm{mic} \approx RT \ln x_\mathrm{CMC}$$

Where x_CMC is the mole fraction of S at the CMC. Thus, if we can determine the CMC, we can determine ΔG_mic. Finally, if we can determine ΔG_mic at a range of temperatures, we can calculate the usual set of thermodynamic parameters relating to the micellisation:

$$\Delta S_\mathrm{mic} = -\frac{\mathrm{d}\Delta G_\mathrm{mic}}{\mathrm{d}T}$$

$$\Delta H_\mathrm{mic} = \Delta G_\mathrm{mic} + T\Delta S_\mathrm{mic}$$

We will think about what these equations tell us and see some examples in the lecture.

[1] You can also have a **reverse micelle**, which is the other way around and stable in oil.

Lecture 10

Measurement of Colloidal Particles

This lecture roughly corresponds to Lecture 15 in Shengfu's slides.

This will be kept relatively brief as Shengfu's slides are very comprehensive and I want us to have some time to look at some past exam problems in the actual lecture.

10.1 Microscopy

Colloidal particles are very small ($<\mu m$) and thus are difficult to observe using optical microscopy. The **diffraction limit** sets an effective lower limit on the size of an object resolvable using optical microscopy. Visible light has a wavelength of around 0.5 µm, and so observing particles around this size is impossible with optical microscopy.

10.1.1 Electron Microscopy

One way to lower the diffraction limit is to use a radiation source that has a much smaller wavelength. **Electron microscopy** allows this by using high-energy electrons[1], which have a much shorter characteristic wavelengths.

There are two main types of electron microscope:

- A **Transmission Electron Microscope (TEM)** – where electrons are focussed onto a sample, and the **transmitted** electrons are imaged.
  - A TEM tells you more about the internal structure of samples.
- A **Scanning Electron Microscope (SEM)** – where the electrons are **scattered** off the sample.
  - An SEM measurement tells you more about the surface morphology of samples.

10.2 Light Scattering

Light scattering (scattering of photons in the optical energy region) is another key technique used in investigating colloidal dispersions. Unlike microscopy, the particles are not individually resolved and imaged, but a **scattering pattern** from the **scattered light** can be detected – and various properties of the scattered light can tell you things about your colloidal dispersion. One classic technique here is **Dynamic Light Scattering (DLS)**, which is very widely used[2]

[1] Think about the de Broglie wavelengths of electrons and try and work out the kinds of energy needed.
[2] If a questionably rigorous technique for a lot of samples. I am a bit of a DLS sceptic.

10.2.1 Rayleigh and Mie Scattering

Light scattering is a *vast* topic, and rigorous treatments of it are very complex[3].

Fundamentally there are a number of different regimes of light scattering, and the one we care about in this context is **Rayleigh scattering**, which happens when the particles are much smaller than the wavelength of light. Rayleigh scattering is a limiting case of **Mie Scattering**, which is a more complex model. We will draw some pictures on the chalkboard in the lecture.

10.2.2 Neutron and X-Ray Scattering

X-rays are much shorter wavelength than visible light, and so can resolve smaller particles. **X-ray scattering** is a commonly used technique in investigating small particles, and can detect very small particles. Fundamentally, it occurs by the same physical process as other kind of light scattering (interaction between electric field of light with electrons on molecules/particles).

Neutron scattering , on the other hand, is different. Neutrons interact directly with the **nuclei** in molecules and so is very sensitive to things like **isotopic substitution**. Both techniques are widely used in analytical chemistry.

That's it for this whistlestop tour of Shengfu's parts of CH2203. I hope this brief handout is also useful as we do the lectures – even if it was mostly written for my benefit to get all the material clear in my head! **Please also watch Shengfu's recordings** – he knows this material better than I do and wrote the original course.

[3] I used to do a lot of nonlinear light scattering spectroscopy – it is *complicated*, let me tell you...