Effect of Thermodynamic Factors on Colloid Stability

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Abstract: Colloid is more and more widely used in daily life. No matter medical application, or food additive in the food industry, or electrolyte in the lead battery, all are deeply connected with it. Among them, the stability of colloid is an important direction for people to explore. According to DLVO theory, the stability of colloid is determined by the height of energy barrier. In this paper, the effect of temperature on colloid aggregation or sedimentation will be discussed by calculating and observing the settling process of colloid. This paper will also put forward the optimum temperature position to keep the highest energy barrier height and the way to estimate the value of energy barrier by reaction, which gives new possibilities for controlling colloid stability.

1. Introduction
At present, few people have systematically studied the influence of temperature or other thermodynamic factors on the stability of colloids, because the influence of temperature change on colloids is relatively complex. For example, surface potential parameters, surface potential or Hamaker constant and other parameters will affected colloid stability. In this paper, these parameters will be discussed and analyzed one by one, and the results will be obtained through calculation. Some parameters will vary when temperature varies in consideration of different colloid molecules. This paper provides a qualitative analysis method.

2. DLVO Theory
In the colloid deposition experiment, according to DLVO theory[1], we can use the energy barrier height to discuss the stability of colloid. The classical DLVO theory explores the relationship between colloidal repulsive potential energy, gravitational potential energy and colloidal precipitation. This relationship can be observed visually by the potential energy curve of colloid. There are two kinds of interaction forces between charged colloidal particles. One is the electrostatic repulsive force on the double layer overlaps part, the other is the long-range van der Waals suction between particles. The potential energy of colloidal particles can be expressed as follows:

\[ V_i = V_e + V_d \]  \hspace{1cm} (1)

Classical DLVO theory has been used for a long time, but in recent years, it has been found that there are many special interaction forces between hydrophilic and hydrophobic particles, which play a decisive role in the stability of colloidal dispersion systems. Classical DLVO theory cannot explain the condensation and dispersion behavior of these systems. Therefore, an extended DLVO theory is put forward to explain them[2].

\[ V = V_{ER} + V_{WA} + V_{SR} + V_{HR} + V_{HA} + V_{MA} \]  \hspace{1cm} (2)

In the formula, \( V_{ER} \) is spatial repulsive potential energy, \( V_{HR} \) is hydration interaction repulsive
energy, $V_{HA}$ hydrophobic interaction attraction energy, $V_{MA}$ is magnetic attraction potential energy.

This paper will use the traditional DLVO theory to analyze and explore the influence of temperature on the energy barrier by calculation.

![Potential energy curves between particles](image)

Fig. 1. Potential energy curves between particles

It is not difficult to see that curve 1 is the repulsive force of double layer overlap, and curve 2 is van der Waals force produced by gravity, and the addition of the two forms curve 3, the potential energy curve of particles. Among them, the wave peak of the potential energy curve is the energy barrier between the particles, and the wave valley on the right is the second minimum. If the potential energy of the particle falls into this range, a reversible aggregation process will be formed, the structure is relatively loose, and a little external interference will be destroyed. This system has thixotropy or shear dilution. The wave valley on the left is the first minimum, and the precipitation of colloidal particles here is very close. If the colloidal particles are to settle, they must exceed the height of the energy barrier to further aggregate. If the energy barrier is small, the colloidal particles are prone to aggregation and precipitation, which is unstable. DLVO theory suggests that the general barrier height should be higher than 15 kT, which can prevent the settlement caused by thermal movement. Therefore, the height of energy barrier determines whether the colloid is stable, and there are many influencing factors of energy barrier, which are mainly reflected in the change of gravity and repulsive force. In this paper, magnesium hydroxide colloid is taken as an example to calculate, and the trend of estimating colloidal energy barrier and qualitative analysis of potential energy by theoretical method is put forward[3].

3. Influencing Factors of Van Der Waals Force

Molecules can be seen as many nuclei, and colloidal molecules also adsorb a lot of electrons which are moving around.

When the colloidal molecules are close to each other, the atoms or groups in the colloidal molecules will produce van der Waals attraction, which will reduce the energy of the system; when the molecules draw closer, the repulsive force of electron clouds will increase instantly and the energy of the system will increase. Van der Waals force includes directional force, induction force and dispersion force. Except for some molecules with strong polarity (such as water molecules), the dispersion force plays a major role in most of the other molecules. Especially for macroscopic objects, the dispersion force is much larger than the directional force and the induction force, so we mainly discuss the dispersion force.

Imagining a colloidal molecule as a sphere and consider the interaction between the two particles. A formula for the dispersion energy of the interaction between two spheres and particles can be obtained:

$$U = -\frac{A}{12} \left[ \frac{\sigma^2}{R^2 - 4\sigma^2} + \frac{2\sigma^2}{R^2} + 2\ln(1 - \frac{4\sigma^2}{R^2}) \right]$$

In the formula, $U$ is dispersion energy, $\sigma$ is colloidal particle radius, $R$ is colloidal particle distance, $A$ is the famous Hamaker constant, also known as long-range attraction constant. Hamaker constant is fixed and its value is between $10^{-19} \sim 10^{-20}$.
The calculation of Hamaker constant is very complex, which is generally calculated by two ways: macro method and microcosmic method. Recently, researchers proposed a very novel method, which is also closely related to DLVO theory, to calculate the Hamaker value of colloid.

The theory is based on DLVO theory and assumes that colloids are at the turning point of critical agglomeration (the turning point between slow precipitation and rapid precipitation). In this case, the barrier of the colloid is equal to 0, that is, the van der Waals force is equal to the repulsive force of the double layer. The Hamaker value of a colloid can be estimated by calculating the critical concentration of the colloid.[4]

\[
U_R = U_d = -\frac{A}{12} \left[ \frac{a^2}{R^2 - 4a^2} + \frac{2a^2}{R^2} + 2 \ln(1 - \frac{4a^2}{R^2}) \right]
\]  

(4)

The repulsive force of the electric double layer will be explained later.

At the same time, the size of dispersion energy can be expressed as follows:

\[
U = \frac{I \alpha^2}{3} \times \frac{1}{r^6} \times \frac{1}{(4\pi\varepsilon_0)^2}
\]

(5)

\(\alpha\) is polarizability, \(I\) is ionization energy and \(r\) is distance. Dispersion force is also related to these three parameters.

Because the Hamaker constant is around \(10^{-19} \sim 10^{-20}\), the values calculated by the macro method and the microscopic method are a bit different. In this paper, the Hamaker constant is approximately regarded as a constant value. From this, the van der Waals force can be calculated.

4. Repulsive Force of Double Layer Overlap

According to the theory of double electric layer, charged colloid will attract the counterions around to form double electric layer. Because of the requirement of electric neutrality, the electric quantity of counterion is equal to the electric quantity of colloid surface. Some counterions combine with the surface closely to form an adsorption layer (or Stern layer). The rest of the ions are diffused in the solution, forming a diffusion layer (or Gouy layer). When two charged colloidal particles are close, their diffusion layers overlap, resulting in electrostatic repulsion. The electrostatic repulsion effect can be expressed as follows[5]:

\[
U_x = \frac{64\pi n_0 kT\alpha^2}{\kappa^2} \exp(-D\kappa)
\]

(6)

In the form, \(n_0\) is the number of ions per unit volume, that is, the concentration is multiplied by the Avogadro constant, \(a\) is the radius of colloidal particles, \(k\) is Boltzmann constant and \(T\) is temperature. These are all values, but \(\kappa\) is variable, we call it the Debye-Huckel parameter, and its reciprocal, \(\frac{1}{\kappa}\), is Debye length, characterization of the thickness of diffused double layer. \(\kappa\) can be calculated by the following formula:

\[
\kappa = \left( \frac{2F^2I}{\varepsilon cRT} \right)^{\frac{1}{2}}
\]

(7)

In the form, \(F\) is Faraday constant; \(R\) is molar gas constant; \(I = \frac{1}{2} \sum z_i c_i^2\) is ionic strength. \(c_i\) is Molar concentration of ions. \(z_i\) is valence.

\(\varepsilon\) is dielectric constant.

The relationship between \(\kappa\) and temperature can be explored by this formula to, using Matlab to
draw the curve:

![Graph 1](image1)

Fig. 2. The relationship between $\kappa$ and temperature (290K-340K).

![Graph 2](image2)

Fig. 3. The relationship between $\kappa$ and temperature (0K-340K).

It's easy to see that in the 290K to 340K range, the change of $\kappa$ is approximate to a linear change, which is not significant. After calculation, the range from 290K to 340K reduced by about 8%.

$\gamma_0$ is the potential parameter of the colloid surface, it can be calculated by the following formula:

$$
\gamma_0 = \frac{\exp(ze\varphi_0 / 2kT) - 1}{\exp(ze\varphi_0 / 2kT) + 1}
$$ (8)

In the form, $\varphi_0$ is the surface potential of colloid. At present, the surface potential is difficult to measure directly, only through complex inversion operation[6].

With Poisson-Boltzmann form, we can get:

$$
\gamma = \gamma_0 \exp(-\kappa D)
$$ (9)

$$
\gamma_0 \exp(-\kappa \xi) = \frac{\exp(ze\varphi / 2kT) - 1}{\exp(ze\varphi / 2kT) + 1}
$$ (10)

So:

$\varphi$ is the potential of a certain place and $x$ is the distance from this place to the colloidal surface.

In order to facilitate our operation, researchers can study the critical precipitation state of colloid. When the diffusion layer is severely compressed, the thickness of the double electric layer is approximately equal to the thickness of the sliding layer, so we can measure the $\xi$ potential of the critical precipitation, and get $\kappa \xi = 1$.

The scale between the surface potential and the zeta potential can be seen in the following graph:

![Graph 3](image3)

Fig. 4. Surface potential and zeta potential
At room temperature, the effect of temperature on surface potential and zeta potential of different colloidal particles is unclear. For example, the higher the temperature of silica sol is, the lower the zeta potential is, and also less stable the colloid is. Zeta potential is widely used to judge the stability of colloid in general. At the same temperature, the higher the zeta potential is, the more stable the colloid is. If the temperature varies greatly, the colloid stability needs to be calculated separately. In this paper, it assumes that the surface potential is unchanged and discusses the effect of temperature on the stability. In fact, the potential may or may not change, and it can be determined by matter.

Here we can look at the variation of potential parameters with temperature:

![Fig. 5. Variation of potential parameters with temperature](image)

The parameter calculated in the formula is magnesium hydroxide colloid, which is taken as an example. With the temperature increasing, the potential parameters are getting smaller.

Combined with the chart above, here we can draw the electrostatic interaction curve of colloidal particles:

![Fig. 6. Electrostatic interaction of colloids The y-coordinate is k](image)  
![Fig. 7. Electrostatic interaction of colloids The y-coordinate is kT](image)

When the top curve is 330K, Ur varies with distance. From top to bottom, they are 320K, 310K, 300K and 290K. It is worth noting that the longitudinal coordinate unit of the curve is not kT, so it is necessary to adjust the left unit, that is, divide by its corresponding temperature.

We can see that the distance between the curves becomes smaller, but still the higher temperature has a larger repulsive force, indicating that it has a large energy barrier value.

This computational idea provides a very good reference for the theoretical exploration of colloidal energy barrier value, and clarifies the variation of energy barrier value and colloid stability under different parameters. It is more reasonable to explain the theory that the object which has a larger Zeta value will be more stable when the temperature is constant.

5. **Calculating the Energy Barrier Value from a Macroscopic Point of View**

It is very troublesome to calculate the energy barrier value from the microscopic point of view. For
example, it is unnecessary to measure the Zeta potential, particle radius and some other data which is
tedious. Here is a convenient way to estimate the energy barrier directly by the reaction rate.

It is known that there are two kinds of reaction rates in flocculation and precipitation. One is called
rapid flocculation, and the other is slow flocculation. Slow flocculation is caused by the existence of
flocculation energy barrier, so the energy barrier value can be calculated by ingenious method according
to the rate of slow flocculation.

The slow flocculation rate constant $k_s$ can be expressed as follows:

$$K_s = \left[ -\frac{dN}{dt} \right]_s = \frac{4\pi DN^2}{\int_{d}^{\infty} \exp\left(\frac{V_x}{KT}\right) dr}$$

(11)

Take a diagram of colloidal precipitation as an example:

The longitudinal coordinate, is the precipitation height of the colloid, which can be measured directly,
and the slow settling rate at the beginning of settlement can be obtained directly by experiments.

The slow reaction rate at different temperatures was recorded and a table was obtained.

![Colloidal precipitation](image)

According to formula (11):

$$\ln \frac{k_{s,1}}{k_{s,2}} = \frac{\Phi}{kT_2} - \frac{\Phi}{kT_1}$$

(12)

So

$$\Phi = \ln \frac{k_{s,1}}{k_{s,2}} \times \frac{T_1 - T_2}{kT_1T_2}$$

(13)

$\Phi$ is the energy barrier of the colloid.

6. Discussion

From the analysis above, we can simplify the complex problems and find out the relationship between
temperature and barrier size. In the actual situation, different colloid molecules have different specific
ways to analyze as temperature affects its surface potential and other parameters in different ways. This
paper just provides an analysis model and a simple calculation of energy barrier value through the macro
method. It will be much more convenient to choose the most appropriate temperature storage colloid
when the equipment condition is insufficient.

7. Conclusion

This paper introduces how to discuss the influence of temperature on energy barrier value by calculation.
Obviously, the influence of temperature on different colloidal molecules is different, and is affected by
the type of ions in colloidal solvent. According to the content of this paper, it only needs to calculate the
surface potential parameters of colloid and Hamaker constant, and then the influence of temperature on
the energy barrier value can be discussed directly. The subsequent studies will also focus on this part,
and will select some substances to explore the changes of surface potential and surface potential parameters under temperature changes.

The simple method of calculating the surface potential parameter and Hamaker constant is also introduced in this paper. It provides a method to estimate the energy barrier value, which is to measure the precipitation rate using macro method, and it provides a reference for researchers.

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