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# Colloid and Interface Chemistry for Water Quality Control

# 水质控制胶体与界面化学

Qing Chang 常青 著

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·北京·

本书介绍水质控制所涉及的胶体与界面化学的基本原理和方法。第 1 至 7 章为胶体化学部分，包括胶体化学的简史与基本概念、扩散与布朗运动、沉降、渗透压、光学性质、流变性质、电学性质。第 8 至 10 章为界面化学部分，包括液体的表面、溶液的表面、固体的表面等。第 11 章介绍粗分散体系，包括乳状液、泡沫、凝胶等。

本书的特点是紧密联系水质控制理论与技术，推理严谨细致，简明扼要，并附有必要的案例解析，易学易懂。附录中给出了常用物理常数、水的物理化学常数，以及常见各种液体的表面张力、常用表面活性剂的 HLB 值等，方便读者使用。

本书可作为给水排水工程、环境工程、环境科学等专业的研究生教学用书，也可供水处理科技工作者参考。

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# Preface

Colloid and interface chemistry is one of the most important scientific bases of water quality control. It is related to nearly all of the principles of water treatment, including coagulation-flocculation, sedimentation, adsorption, filtration, flotation, oil separation, membrane separation, sludge dewatering, scaling-corrosion inhibitor, and environmental catalysis. The need for water quality control has quickly increased for decades because people pay more and more attention to drinking water safety and water environment protection. Decision-making in matters relating to water quality control requires a sound understanding of basic principles of colloid and interface chemistry; therefore, the publication of this book is quite relevant at present.

This book was completed on the basis of my teaching materials in the School of Environmental and Municipal Engineering at Lanzhou Jiaotong University of China. It provides students the most basic knowledge of colloid and interface chemistry. Chapters 1–7 introduce colloid chemistry including Chapter 1 "Brief History of Colloid and Interface Chemistry and Basic Concepts," Chapter 2 "Diffusion and Brown Motion," Chapter 3 "Sedimentation," Chapter 4 "Osmotic Pressure," Chapter 5 "Optical Properties," Chapter 6 "Rheology Properties," Chapter 7 "Electric Properties"; Chapters 8–10 introduce interface chemistry including Chapter 8 "Surface of Liquid," Chapter 9 "Surface of Solution," and Chapter 10 "Surface of Solids"; Chapter 11 "Emulsion, Foam, and Gel" introduces the coarse dispersion system. As a classical science, colloid and interface chemistry has been developing for more than a century and encompasses a large amount of knowledge, but this book focuses on that which can be applied to water treatment and is closely related to the practices of water treatment and water purification; therefore, students and specialists in the area will find it very useful.

This book is characterized by concision, and the main basic principles and theories are introduced and described. It is easy to read and understand. I think textbooks should not be designed simply as a collection of facts but rather an introduction to ways of thinking about the world. Questions and exercises as well as their solutions have been given throughout the book so that readers can check their understanding of the text. Both traditional and some newly developed knowledge are included to reflect the latest advances of the discipline.

I hope this book will be used as a reference book or a text book for undergraduate students and graduate students who are majoring in water quality control to help them understand the problems and difficult points in their studies. It could also be used as a reference for researchers and engineers as well as graduate students in other majors for further study. In addition, it is quite suitable for researchers and engineers to quickly consult relevant information that they encounter in their work because of the book's brevity and clarity.

It is always a pleasure to thank my editor Gang Wu who has contributed so generously with illustrations and helpful suggestions to improve the book. My appreciation also goes to Dr Pengyu Liu for his work on the figures. Finally, I am very grateful for the financial support from the National Natural Science Foundation of China (No. 21277065) in preparation of this book.

**Qing Chang**
Lanzhou Jiaotong University
Lanzhou, Gansu, China
October, 2015

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## Chapter 1

# Brief History of Colloid and Interface Chemistry and Basic Concepts

### Chapter Outline

## 1.1 ORIGIN OF THE TERM "COLLOID"

The system formed by dispersing one kind of substance in another kind of substance is referred to as a dispersion system. The former is called the dispersed phase, and the latter is the dispersion medium. For example, dispersing sodium chloride (NaCl) in water is a dispersion system. Here the sodium chloride is the dispersed phase, and the water is the dispersion medium. Generally, the dispersed phase contains particles of various sizes. The smaller the particle, the higher the dispersion degree; the larger the particle, the lower the dispersion degree.

As early as 1861, Graham studied the permeability of various dispersion systems through parchment paper. The device for this study is shown in Fig. 1.1.

According to the permeability characteristics obtained in Graham's experiment, the dispersion systems studied were divided into two types as follows:

1. *True solution*: The diffusion is faster, and the permeation is easier. Crystal is obtained after evaporation to dryness, for example, sugar, inorganic salt, and urea.
2. *Colloid*: The diffusion is slower, and the permeation is more difficult. An amorphous substance is obtained after evaporation to dryness. "Colloid' means the substance does not easily permeate through parchment paper, for example, gelatin, aluminum hydroxide, and polysilicic acid.

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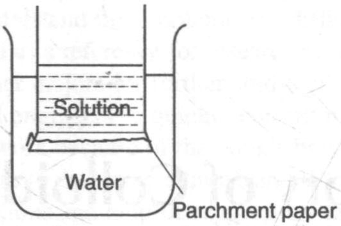

**FIGURE 1.1 Device for the Graham experiment.**

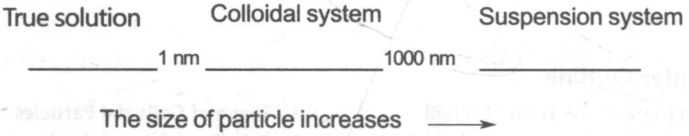

**FIGURE 1.2 A type of dispersion system.**

Afterward, the experiment of Beŭmph proved that the two types of dispersion systems can be transformed into each other; for example, if we disperse NaCl in water, we will obtain a true solution; if we disperse NaCl in alcohol, we will obtain a colloid system. There are many such instances that indicate that the terms "colloid" and "true solution" do not represent the essence of the material; instead, they represent two different forms of the substance. The difference between them is only the size of the particles or the dispersion degree, as shown in Fig. 1.2.

Now it is widely accepted that the system in which a particle has at least one dimension in the range of 1–1000 nm is considered a colloid system. Therefore, the size of the particle is the only criterion used to determine if the dispersion system is a colloid system. Linear dimension rather than particle weight, or the number of atoms in a particle, defines the colloid size range.

## 1.2 CLASSIFICATION OF THE COLLOIDAL SYSTEM

Although the size of particles in a colloid system is in the range of 1–1000 nm, the properties are not always the same. According to the different properties of particles, the colloid system can be grouped into two general classifications:

1. *Sol*: There are interface and interface-free energies between the dispersed phase and the dispersion medium. It is a thermodynamically unstable, irreversible system and not easily reconstituted after phase separation. This is often called a lyophobic colloid.

2. *The solution of macromolecular material*: There are no interface and interface-free energies between the dispersed phase and the dispersion medium. It is a thermodynamically stable system and can be recovered after separation. This is often called a lyophilic colloid.

There are some similar properties and some different properties between the two kinds of colloid systems. The properties that are related to particle size are similar, but the properties that are related to interface are different. For example, dynamics properties, optical properties, rheology properties, etc., are similar, but electrical properties, adsorption properties, etc., are different.

Although the size of the particles in the suspension system is greater than that in the colloid system, there is also greater interface between the dispersed phase and the dispersion medium in the suspension system, and many properties of the suspension system are similar to that of the colloid system; therefore, the study on the suspension system is generally included in the category of colloid chemistry.

Generally speaking, natural water, industrial west water, and domestic sewage not only contain dissolved salts, becoming true solutions, but also contain colloid and suspension particles, becoming colloid systems and suspension systems; therefore, they are complicated and integrated systems. Because particle separation is one of the most important tasks of water treatment, colloid and interface chemistry is very important for researchers and engineers who engage in water treatment and water environment protection.

In another way, colloid systems can also be grouped according to the kinds of dispersed phases and dispersion mediums, as in Table 1.1.

**TABLE 1.1** Classification of Colloid Systems

| Dispersed phase | Dispersion medium | Name | Example |
|---|---|---|---|
| Liquid | Gas | Liquid aerosol | Fog |
| Solid | Gas | Solid aerosol | Smoke, dust |
| Gas | Liquid | Foam | Foam on soap solutions |
| Liquid | Liquid | Emulsion | Milk |
| Solid | Liquid | Sol | Paint |
| Gas | Solid | Solid foam | Foamed plastic |
| Liquid | Solid | Solid emulsion, gel | Pearl |
| Solid | Solid | Solid suspension system | Alloy |

As far as water treatment is concerned, sol, emulsion, and foam are very important. The natural turbid water belongs to sol and suspension dispersion systems. The industrial or domestic oil wastewater often forms emulsion. The wastewater that contains protein or surfactant generally produces foam. Essentially, the effect of water treatment is to destroy the stabilities of the colloidal dispersion systems.

## 1.3 DISPERSION DEGREE AND SPECIFIC SURFACE AREA

Generally, the dispersion degree of multiphase dispersion systems can be represented by the specific surface area $A_0$:

$$A_0 = \frac{A}{V} \tag{1.1}$$

where $A$ is the total surface area of dispersed substance, and $V$ is the total volume of dispersed substance. Therefore, the specific surface area is the surface area of the substance's unit volume (or unit mass). Its value quickly increases with the decrease in particle size. When a cube 1 cm in length is divided into smaller cubes, the specific surface area will increase as shown in Table 1.2.

It can be seen that the smaller the cubes, the greater the specific surface area. As we know, the size of colloidal particles is within the range of 1–1000 nm; therefore, the colloid system has great specific surface area, and its surface effect is very significant. In fact, many principles of colloid chemistry belong to interface chemistry.

**TABLE 1.2 Division of Cubes and Increase of Specific Surface Areas**

| Length of side (cm) | Cube numbers | Specific surface area ($cm^{-1}$) |
|---|---|---|
| 1 | 1 | 6 |
| $10^{-1}$ | $10^3$ | $6 \times 10$ |
| $10^{-2}$ | $10^6$ | $6 \times 10^2$ |
| $10^{-3}$ | $10^9$ | $6 \times 10^3$ |
| $10^{-4}$ | $10^{12}$ | $6 \times 10^4$ |
| $10^{-5}$ | $10^{15}$ | $6 \times 10^5$ |
| $10^{-6}$ | $10^{18}$ | $6 \times 10^6$ |
| $10^{-7}$ | $10^{21}$ | $6 \times 10^7$ |

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**Example 1.1 Variation of Specific Surface Area with Geometry**

A material of density $\rho$ exists as uniform cylindrical particles of radius $R_c$ and length $L$. Derive an expression for $A_0$ for this material and examine the limiting forms when either $R_c$ or $L$ is very small.

Solution: The area of each cylindrical particle equals the sum of the areas of both ends and the cylindrical surface:

$$A = 2\left(\pi R_c^2\right) + 2\pi R_c L$$

The volume of each cylindrical particle equals $\pi R_c^2 L$, and its mass is given by $\rho\pi R_c^2 L$.

For an array of $n$ cylindrical particles, the total area per total mass equals $A_0$ and is given by

$$\begin{aligned} A_0 &= \frac{n\left(2\pi R_c^2 + 2\pi R_c L\right)}{n\rho\pi R_c^2 L} \\ &= \frac{2\left(R_c^2 + R_c L\right)}{\rho R_c^2 L} \\ &= \left(\frac{2}{\rho}\right)\left(\frac{1}{R_c} + \frac{1}{L}\right) \end{aligned}$$

For a thin rod, $L \gg R_c$:

$$A_0 \approx \frac{2}{\rho}\frac{1}{R_c}$$

For a flat disk, $R_c \gg L$:

$$A_0 \approx \frac{2}{\rho}\frac{1}{L}$$

---

## 1.4 SHAPE OF COLLOIDAL PARTICLES

Particle shape has very important effects on the properties of colloid systems. For example, polystyrene latex has very low viscosity and flows easily, even if its concentration increases to 10~20%, because the particle is spherical; vanadic oxide has very high viscosity and cannot flow, even if its concentration decreases to 0.01%, because the particle is filamentous.

Polyacrylamide is usually used as the flocculant in water treatment. Its macromolecule is a very long chain, and its viscosity is very high. Before using, it should be diluted in order to add it into water easily; for example, the concentration should be in the range of 0.05~0.1% in laboratory experiments.

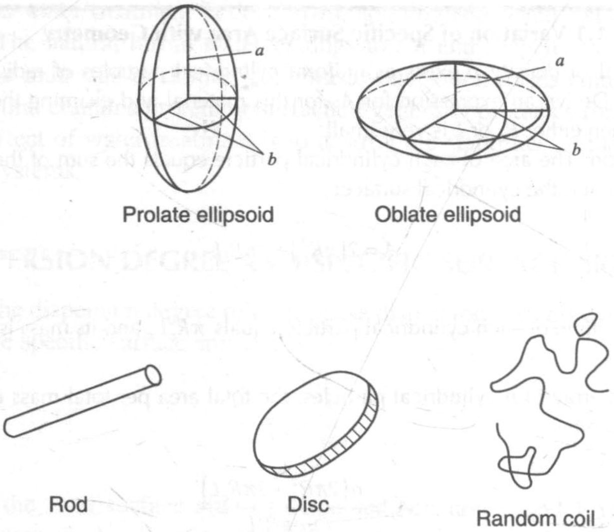

**FIGURE 1.3 Representations of nonspherical particles.**

The particle shape can be grouped into three types as follows:

1. *Sphere*: It is generally characterized by its radius.
2. *Ellipsoids of revolution*: They are generally characterized by their axial ratio, which is the ratio of the single half-axis (a) to the radius of revolution (b), as shown in Fig. 1.3. The axial ratio is greater than 1 for a prolate ellipsoid and less than 1 for an oblate ellipsoid. If a $\gg$b, the particle will be a rod, and if a $\ll$b, the particle will be a disc.
3. *Threadlike macromolecule*: It is a random coil and can be characterized by its molecular weight.

## 1.5 POLYDISPERSITY AND THE AVERAGE SIZE OF COLLOIDAL PARTICLES

The dispersion system in which the molecular weights or the sizes of all particles are the same is termed a monodispersed system. This kind of system is very rare in nature, but synthetic polymers can possibly be this kind of system; for example, polystyrene latex might be a monodispersed system. The dispersion system in which the molecular weights or sizes of particles are not identical is termed polydispersed system. This kind of dispersion system is very general; for example, all natural waters and polluted natural waters are polydispersed. For polydispersed systems, the size of the particle is generally characterized by average diameter or average molecular weight. The former is suitable for sol, and the latter is suitable for macromolecule solutions.

1. Average diameter

   There are three kinds of average diameters.

   **a.** Number average diameter $\bar{d}_n$

   Number average diameter is obtained by averaging the diameters to the particle numbers:

$$\bar{d}_n = \frac{\sum n_i d_i}{\sum n_i} = \sum f_i d_i \tag{1.2}$$

   where *n* is the particle number, subscript *i* indicates the particle size, *d* is the particle diameter, and *f* is the weighting factor:

$$f_i = \frac{n_i}{\sum n_i} \tag{1.3}$$

   The average diameter obtained using a microscope is the number average diameter.

   **b.** Area average diameter $\bar{d}_s$

   Area average diameter is a root mean square value converted from the average particle areas obtained from the adsorption experiment. If *A* represents the area of the particle, the average area of particles can be expressed as

$$\bar{A} = \frac{\sum n_i A_i}{\sum n_i} = \frac{\sum n_i \pi d_i^2}{\sum n_i} = \pi \sum f_i d_i^2 \tag{1.4}$$

   or

$$\bar{A} = \pi\left(\bar{d}_s\right)^2 \tag{1.5}$$

   Combining Eqs. (1.4) and (1.5) gives

$$\pi \sum f_i d_i^2 = \pi\left(\bar{d}_s\right)^2$$

$$\bar{d}_s = \left(\sum f_i d_i^2\right)^{\frac{1}{2}} \tag{1.6}$$

   **c.** Volume average diameter $\bar{d}_v$

   Volume average diameter is converted from the average particle volume obtained from the density. If *V* represents the volume of particles, the average volume of particles can be expressed as

$$\bar{V} = \frac{\sum n_i V_i}{\sum n_i} = \frac{\sum n_i \frac{\pi}{6} d_i^3}{\sum n_i} = \frac{\pi}{6} \sum f_i d_i^3 \tag{1.7}$$