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# **JS94**

## **Zeta Potentiometer**

### **Operation Instruction**

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## Chapter 1 Preface

potentiometer is a new product comprises new-type optical system, electrophoresis cell, data sampling unit and data processing unit. It realizes the integration design of data sampling unit controlled by personal computer (PC) and post-data processing unit. Comparing to other like products, it has more outstanding characteristics. This product is the fourth generation of zeta potentiometer designed by Prof. Chen Banglin and has already obtained national patent.

potentiometer can be used for measuring the electrical properties ( $\zeta$ potential) on solid-liquid interface of solid particle in disperse system, and measuring the interface electrical properties of liquid drop of emulsion. It can also be used for measuring isoelectric point and researching on the mechanism of interfacial reaction process. The way of measuring Zeta potential of powder and determining isoelectric point from relational graph of pH and Zeta potential is an important method to understand surface electrical properties of powder, as well as an important manner for surface treatment of powder. Comparing to other like products at home and abroad, it has outstanding superiorities. It can be widely used in the fields of cosmetics, ore dressing, papermaking, health care, building materials, superfine materials, environmental protection, marine chemistry, etc. It is also one of the important instructional apparatuses in such majors as chemistry, chemical engineering, medical science, building materials.

## Chapter 2 General Description of Theory

The content involved in Physical Chemistry of Surfaces is very broad. The electrochemical property of solids in solution, in fact, influences the surface property of solids and charge transfer in boundary region and the speed thereof. A variety of discoveries in electrochemical effect of surfaces of vital importance attract the attention of scientists in variety of fields to perform research on surface electrochemistry.

### 2.1 Double layer

#### 2.1.1 Formation of double layer

In nature, the electrochemical phenomenon on solid surface is ubiquitous when solid contacting with liquid. This causes the liquid surface of liquid-solid interface to be oppositely charged. The interfacial charge influences on the ionic distribution in the medium around the interface, the ions in the medium with opposite charge as the interface are absorbed to the interface (the ions are called counter-ions), while the ions in the medium with same charge as the interface are expelled from the interface (the ions are called co-ions). Meanwhile, the thermal movement of ions impels them to be proportionally mixed together. Therefore, there is a diffuse double layer formed in the charged interface. The term of diffuse means the counter-ions in the surrounding medium of the interface are distributed in the form of diffusion, rather than regularly radiating from the charged interface. For example, the boundary regions of both arterial/vein wall contacting with the blood in human body and colloidal particles in the blood have such double layer structure, which makes blood flow to transport metabolic nutrients smoothly without thrombosis. The double layer theory researches on the diffusion profile and charged interface properties of the counter-ions. Except for external electric field, the formation of double layer of solids in solution can be roughly attributed to the following reasons:

- ① ionization
- ② Ion exchange
- ③ Ion adsorption

According to modern concept, the electron cloud in the solid metals, to some extent, can spread to the solvent molecules layer closely bordering to the solid surface. This will cause the dipoles of solvent molecules or other uncharged molecules tend to orient in the direction of metal surface, i.e. dipole orientation with a greater or less extent. Thus, the ions can be gathered in the molecular layer closely bordering to the interface by

electrostatic force and van der waals force, and form a charge body with the metal.

Besides, for those non-conductive solid matters in the high-velocity fluid (including solution of non-ionized or non-hydrolyzed substances), the transfer of charges generated by phase-phase contact friction from one phase to another phase makes the solid surface charged. Normally, the phase with larger dielectric constant is positive-charged. For example, the flow of benzene in glass tube makes the wall of the glass tube positive-charged, in turn causing discharge and combustion. Such electrochemical phenomenon often occurs in the flow system of industrial production, so that precaution has to be made.

The charged solid surface attracts the ions with opposition charge in the solution to close up to the solid surface and accumulate in the boundary region on the solution side with certain distance to the solid-liquid interface via electrostatic attraction to compensate the charge balance. Supposing the charge on solid surface is  $Q(M)$ , on liquid phase is  $Q(L)$ , their general relation is:

$$Q(M) + Q(L) = 0$$

Thus, forming so called double layer. The charged ions on solid surface are called potential-determining ions. They not only determine the thermodynamic electric potential of surface  $\psi_0$ , but also generate electric-field strength  $(\partial \psi / \partial x)$  in the x direction vertical to the solid surface. The accumulated ions with opposite charge via electrostatic attraction in the solution are called counter-ions.

### 2.1.2 Development history of double layer theory

The double layer theory and zeta-potential research, which relate to many important properties such as adsorption and exchange on liquid-solid interface, are important constituents in surface chemistry.

The development of double layer theory is proposed in the 19th century and has been developed in practice until now. The development processes are as the following:

#### (1) Helmholtz' theory (1853)

Helmholtz firstly introduced a simple double layer model and considered it as a parallel-plate capacitor. One pole-phase of the capacitor is the charged surface of dispersion phase, and the other pole-phase is the adsorbed ions or self-excessive ions closely boarding to the surface or regularly aligned counter-ions in medium. This is called parallel-plate capacitor model, see Figure 1.

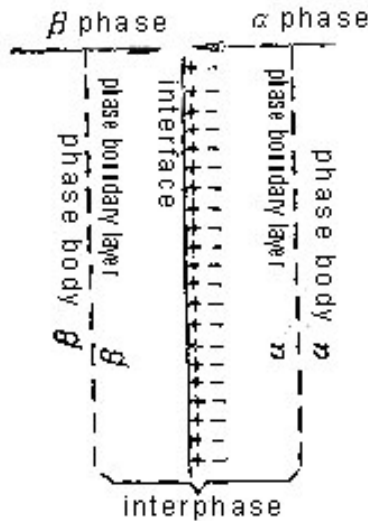


Figure 1 Schematic diagram of phase-phase interface and parallel-plate capacitor model

This double layer model takes consideration completely from the electrostatic view and thinks that the charges with opposite charge are distributed on the two sides of the capacitor via electrostatic attraction. The distance between the charges with opposite charge is  $d$  (approximately the diameter of a molecule) and the electric potential difference is  $\psi$ . The electric potential difference of this double layer can be calculated with Helmholtz equation:

$$\psi = \frac{d \sigma}{\epsilon_0 \epsilon_r} \quad (1)$$

Whereas,  $\epsilon_0$  and  $\epsilon_r$  represent vacuum dielectric constant and relative dielectric constant of medium between two double layers, respectively;

$\sigma$  represents the charged electric quantity per square meter of solid surface (called surface charge density);

Suppose a solid surface adsorbs a single ion layer, the ion is one-valence, the surface area of each ion is  $10^3 \text{ \AA}^2$ , thus the surface charge density of the solid is:

$$\sigma = \frac{\text{Charged electric quantity per iron}}{\text{Solid surface area per iron}} = \frac{1.602 \times 10^{-19}}{10^3 \times (10^{-10})^2} = 0.016 \text{ Coulomb/m}^2$$

Suppose  $\epsilon_r = 80$ , it is known that  $\Psi = 0.1 \text{ V}$ ,  $\epsilon = 8.854 \times 10^{-12} \text{ F/m}$ , thus

$$d = \frac{\Psi \epsilon_0 \epsilon_r}{\sigma} = \frac{0.1 \times 8.854 \times 10^{-12} \times 80}{0.016} = 4.4 \times 10^{-9} \text{ m} = 4.4 \text{ nm} = 44 \text{ \AA}$$

The drawback of this simple model lies in that it does not consider the effect of endless diffusive free movement of counter-ions in medium due to thermal movement, so that it is

impossible for these counter-ions to be regularly aligned. Furthermore, if the double layer exists as shown in the parallel-plate capacitor model, there should be strong electric field, which is apparently disagreed with the fact. This theory cannot explain two main problems. The first one is the difference between  $\zeta$ electric potential (also called zeta potential) and electrode potential (also called thermodynamic electric potential). The second one is the effect of electrolyte to the stability of colloidal sol.

## (2) Gouy-Chapman theory

Gouy and Chapman made suggestions to amend the double layer model proposed by Helmholtz in 1910-1917. They thought that the counter-ions in medium were not only influenced by the electrostatic attraction, but also the diffusion due to thermal movement, therefore, the counter-ions has diffused distribution towards medium by degrees. The density of counter-ions is larger in the region closely boarding to the interface and smaller in the region with farther away from the interface. Thus, a diffuse double layer is formed, wherein the diffuse distance is far larger than the diameter of a molecule. Figure 2 shows the Gouy-Chapman model of diffuse double layer. This theory has certain improvements comparing with the Helmholtz model. However, it still takes considerations only from electrostatic view and does not consider the chemical effect between counter-ions and interface.

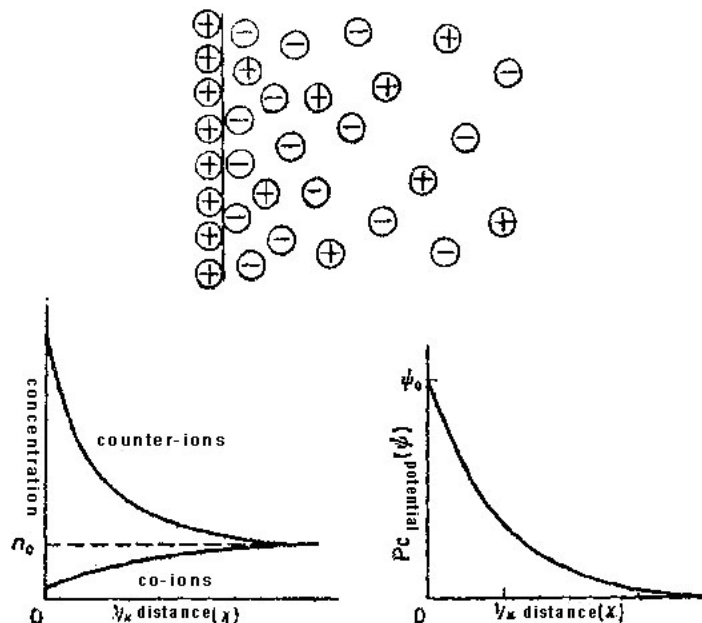


Figure 2 Schematic diagram of Gouy-Chapman model of diffuse double layer

## (3) Stern's theory

In 1924, Stern proposed a double layer model, which combines the Helmholtz model and

Gouy-Chapman model. In this model, the double layer is composed of inner layer and outer layer, wherein the inner layer is similar to the surface very close to the dispersion phase in the Helmholtz model, the external layer is similar to the diffuse layer in the Gouy-Chapman model. The electric potential of the inner layer decreases linearly, and the electric potential of the outer layer decreases exponentially. This theory has more improvements than the former two theories. It can, to some extent, explain the difference between  $\zeta$  electric potential and electrode potential and considers the influence of electrolyte to the stability of colloidal sol. Figure 3 shows the Stern double layer model.

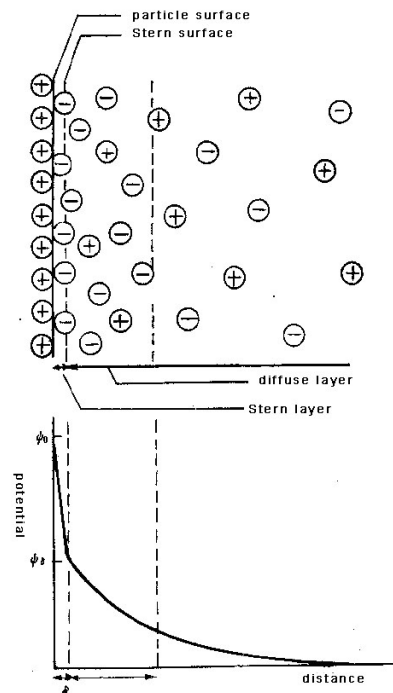


Figure 3 Schematic diagram of Stern double layer model

#### (4) Grahame's theory

In 1947, Grahame further developed the Stern double layer model. He divided the inner layer into two layers, i.e. inner Helmholtz layer and outer Helmholtz layer. He thought that the inner Helmholtz layer composing of non-solvated ions is very close to the interface and behaves same as the inner layer of the Stern model; while the outer Helmholtz layer composing of parts of solvated ions is relatively tightly adsorbed to the interface and is capable of moving with dispersion phase, this layer behaves same as the portion with larger ion density in the outer layer (diffuse layer) of Stern model, which is composed of solvated ions and cannot move with dispersion phase. The potential on the shear surface, which is formed when relative movement between dispersion phase and dispersion medium, is called  $\zeta$  potential (or electrokinetic potential). Figure 4 shows the Grahame model of double layer. According to the view of Grahame, for the potential from dispersion



phase to dispersion medium, it drops steeply in a linear manner from the surface of dispersion phase to the inner Helmholtz layer, and it drops exponentially from the inner Helmholtz layer to outer Helmholtz layer and extending outwardly to diffuse layer. Till now, this theory is still a relatively sound basic theory of double layer. It has strong adaptability and broad applications. The theory of double layer is still progressively developing and perfecting; many theoretical problems are still under dispute.

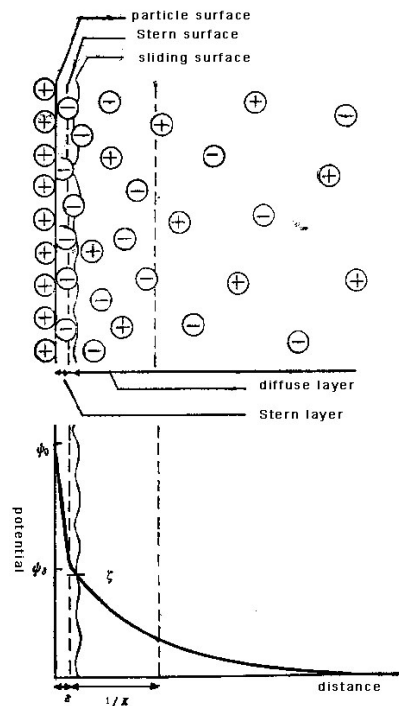


Figure 4 Schematic diagram of Stern-Grahame model of double layer

### 2.1.3 Diffuse double layer model

From the experiments about the electrokinetic phenomena of solid surface in electrolyte solution, it is discovered that the potential value of double layer is always less than surface potential value of solids and takes place large change with the addition of any electrolyte. Parallel-plate capacitor model cannot solve such problems, therefore, diffuse double layer model is proposed. This model explains that although counter-ions are attracted by the electrostatic attraction of solid surface, they still have tendency to diffuse toward and distribute evenly in solution. Therefore, the counter-ions are not likely to line up regularly as in parallel-plate capacitor. In fact, the distribution density of counter-ions is larger in the region close to solid surface, the farther the distance with solid surface, the lower the distribution density of counter-ions. This trend will last until the distribution density of counter-ions in bulk solution does not change any more. Thus the interfacial diffusion layer is formed, as shown in Figure 5.

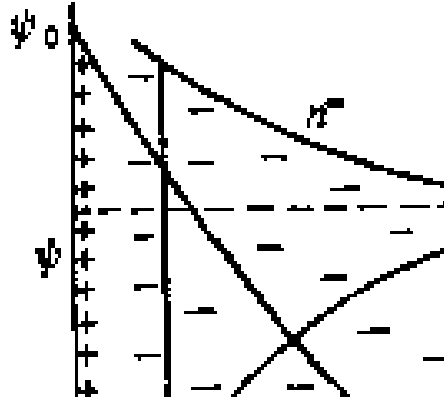


Figure 5 Distribution of positive/negative ions in the boundary layer on solution side according to diffuse double layer model

Suppose the solid surface as a infinitely great plane with even positive charge density, its surface potential is  $\psi_0$ . The distribution of counter-ions, which can be considered as point charges, obeys Boltzmann distribution law. The influence of solvent to counter-ions is only dielectric constant. However, the dielectric constant of solution at different region does not change with the distribution of counter-ions and is a constant under certain temperature.

Because of the uneven distribution of positive/negative ions in the interfacial diffusion layer on solution side, a point in this layer with distance  $x$  to solid surface has potential  $\psi$ , thus, the positive ions at this point has electrostatic potential  $ze\psi$  due to the repulsion by the positive ions on solid surface, and the negative ions at this point has electrostatic potential  $ze\psi$  due to the attraction by the positive ions on solid surface, wherein  $z$  is the absolute value of valence of positive/negative ions. Therefore, the distribution density of positive/negative ions in diffuse layer is:

$$n^+ = n_0 e^{-2e\psi/kT} \quad n^- = n_0 e^{2e\psi/kT} \quad (2)$$

Wherein,  $n^+$  and  $n^-$  represent the number of positive ions and negative ions per unit volume of solution, respectively;

$n$  represents the number of positive ions or negative ions per unit volume of solution ( $m^3$ ) at the place with proper distance to solid surface when solution turns to be electrically neutral ( $\psi=0$ ), (i.e.  $n^+=n^-=n^0$ );

Although the number of negative ions is more than that of positive ions in the boundary layer on solution side near interface, the total amount of net charge in this layer is same as that on solid surface but with opposite sign. If the value of negative charge over positive charge is represented as  $\rho$  (called as volume charge density), thus,

$$\rho = z \ell (n^+ - n^-) = z \ell n_0 \left( e^{-z \ell \psi / kT} - e^{z \ell \psi / kT} \right) \quad (3a)$$

It changes with  $\Psi$  value at different place in boundary layer. If using hyperbolic sine

function  $\sinh(x)$  to express  $\frac{1}{2}(\ell^x - \ell^{-x})$ , thus equation (3a) can be expressed as:

$$\rho = -2 n_0 z \ell \sinh\left(\frac{z \ell \Psi}{k T}\right) \quad (3b)$$

The value of surface charge density on a solid  $\sigma$  equals to the integration from surface ( $x = 0$ ) to infinity ( $x = \infty$ ), but with a opposite sign, i.e.:

$$\sigma = -\int_0^{\infty} \rho dx \quad (4)$$

The above equation reflects the relation between two double layers. One is solid surface with charge density per unit area  $\sigma$ , the other one is a charge layer with opposite charge and diffused distribution toward solution, its volume charge density decreases with the increase of distance  $x$  to interface.

The relation between the potential  $\Psi$  in the boundary layer on solution side arising from double layer and the distance to solid surface belongs to classical electrostatics problem, and can be mathematically treated using Poisson equation, i.e.:

$$\nabla^2 \Psi = -\frac{\rho}{\epsilon_0 \epsilon_r}$$

Where  $\epsilon_0$  and  $\epsilon_r$  are vacuum dielectric constant and relative dielectric constant, respectively;

$\nabla^2$  is a Laplace operational symbol;

$\nabla^2 \Psi$  is the divergence of electric potential gradient at certain point in the boundary layer at solution side

(equal to  $\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}$ ), the relation between  $\nabla^2 \Psi$  and volume charge density at this point can be expressed as:

$$\nabla^2 \Psi = \frac{2 n_0 z \ell}{\epsilon_0 \epsilon_r} \sinh\left(\frac{z \ell \Psi}{k T}\right) \quad (5)$$

Suppose  $x$  is the distance to solid surface in orthogonal direction, and approximately consider  $\Psi$  is a function only associated with  $x$ , therefore,  $\nabla^2 \Psi$  can be simplified as

$\frac{d^2 \Psi}{d x^2}$ , let  $\frac{z \ell \Psi}{k T} = y$ , thus equation (5) can be written as:

$$\frac{d^2 \psi}{d x^2} = \frac{2 n_0 z \ell}{\varepsilon_0 \varepsilon_r} \sinh y \quad (6)$$

Because  $\frac{dy}{dx} = \frac{z \ell}{k T} \frac{d\psi}{dx}$ ,  $\frac{d^2 y}{dx^2} = \frac{z \ell}{k T} \frac{d^2 \psi}{dx^2}$  thus, the following equation can be derived:

$$\frac{d^2 y}{dx^2} = \frac{2 n_0 z \ell^2}{\varepsilon_0 \varepsilon_r k T} \sinh y = K^2 \sinh y \quad (7)$$

Where  $K^2 = \frac{2 n_0 z^2 \ell^2}{\varepsilon_0 \varepsilon_r k T}$ ,  $\frac{1}{k}$  are dimensions associated with distance, termed as effective thickness of diffuse double layer or radius of ionic atmosphere.

#### 2.14 Stern's treatment of double layer

The treatment of diffuse double layer is mainly the contribution of Gouy-Chapman. However, the Gouy-Chapman model draws unrealistic conclusion when the value of  $\psi_0$  is large while the value of  $x$  is small. For example, when  $\psi_0$  increasing, hyperbolic sine function dramatically increases. When  $\psi_0$  is 250 mV and 1:1 electrolyte concentration is

0.1 M,  $\sigma$  value, calculated according to equation (4) is 23 unit charge/Å<sup>2</sup>, i.e. there are 23 monovalence ions existing in such small area. Apparently such charge density is physically impossible. If  $\psi_0$  is 300 mV,  $y_0$  is 12, and  $n_0$  is 10<sup>-5</sup> mol/L (17°C), the calculated local concentration of negative ions in the vicinity of surface is  $n^- = 10^{-3} e^{12} = 160$  mol/L, which is also unrealistic. The above deviations are arisen from the neglect of ionic radius in the assumption. The charges in both situations are regarded as point charges. Thus, large  $\psi_0$  value gives arise to serious deviations. This should be amended, but the treatment of double layer based on the real situation of ionic radius is too difficult. Thus Stern proposed and developed a treatment method to diffuse double layer model, i.e. suppose a plane to divide the region in the vicinity of the plane into two lays, the supposed plane is called Stern plane or outer Helmholtz plane (OHP).

The first layer very close to solid surface, including ions soundly adsorbed on solid surface and water molecules partially participating in salvation, forms an inner fixed layer with double layer, termed Stern layer. It is in harmony with theory of Langmuir single-layer adsorption. The potential in the inner fixed layer drops from surface charge  $\psi_0$  to  $\psi_\delta$  on Stern plane in a linear manner, as shown in Figure 6.

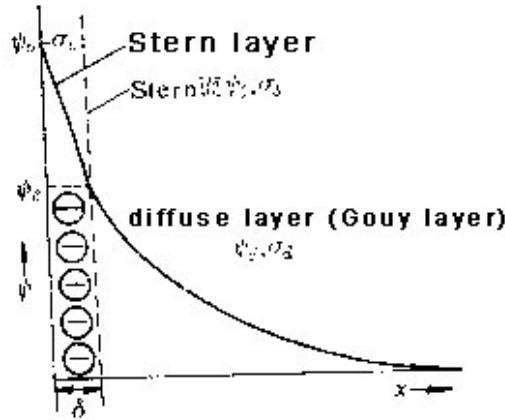


Figure 6 Model of Stern layer

The second layer is called diffuse layer (or Gouy layer). It can be roughly assumed that the potential in this layer drops from  $\psi_0$  to zero with the change of distance  $x$ . He thought the equation proposed by Gouy-Chapman for treating double layer can only be used in diffuse layer. In the equation,  $\psi_0$  is actually  $\psi_\delta$ , thus  $\psi_0$  should be replaced by  $\psi_\delta$ .

The key point of Stern's treatment is to estimate how many ions entering the fixed layer, i.e. the value of  $\psi_0$  (or potential drop from  $\psi_0$  to  $\psi_\delta$ ) and the relation with charge density  $\sigma_\delta$  in Stern layer. He divided the boundary layer and bulk phase (solution) into many sites to be occupied. Suppose the fraction of occupied sites by ions in the boundary layer and bulk phase can be expressed using Boltzmann equation, i.e. all the surface adsorption sites are occupied, the charge density on solid surface can be calculated as:

$$\sigma_0 = z e s_0 \quad (8)$$

The fraction of actually occupied sites can be calculated as:  $\theta = s/s_0 = \sigma_\delta/\sigma_0 \quad (9)$

Wherein,  $s_0$  represents all sites to be occupied by adsorption;

$s$  represents the sites occupied by adsorption;

Whereas, the ratio between the sites occupied and the sites unoccupied should

be  $\frac{\sigma_\delta}{(\sigma_0 - \sigma_\delta)}$ , thus for a dilute solution, Stern though this ratio can be expressed as the following equation:

$$\frac{\sigma_{\delta}}{(\sigma_0 - \sigma_{\delta})} = N_s e^{(ze\psi_{\delta} + \varepsilon)/kT} \quad (10)$$

Wherein,  $N_s$  represent the molar fraction of solute in solution;

$e^{(ze\psi_{\delta} + \varepsilon)/kT}$  represent Boltzmann coefficient. Wherein, the energy  $\varepsilon$  is the sum of electrostatic attraction potential ( $-ze\psi_{\delta}$ ) and any additional attraction potential ( $-\partial$ , could be that due to van der waals force). Thus, the charge density ratio between the fixed layer and diffuse layer  $\sigma_{\delta}/\sigma_0$  can be calculated as:

$$\frac{\sigma_{\delta}}{\sigma_0} = \frac{N_s e^{(ze\psi_{\delta} + \varepsilon)/kT}}{1 + N_s e^{(ze\psi_{\delta} + \varepsilon)/kT}}, \text{ thus } \theta = \frac{B N_s}{1 + B N_s} \quad (11)$$

or

$$\sigma_{\delta} = \frac{\sigma_0}{1 + \frac{1}{N_s} e^{-(ze\psi_{\delta} + \varepsilon)/kT}} \quad (12)$$

Suppose the charge density in diffuse layer is  $\sigma_d$ , because the whole system is electrically neutral, thus, if the solid surface is positively charged, then the values of  $\sigma_{\delta}$  and  $\sigma_d$  are negative, their numerical relation can be expressed as:

$$\sigma_0 = \sigma_{\delta} + \sigma_d \quad (13)$$

Wherein,  $\sigma_d$  can be calculated according to the relation between charge density and surface potential on a solid (equation 14),

$$\sigma = \varepsilon_0 \varepsilon_r \frac{2kT}{ze} x \sinh \frac{y_0}{2} = \sqrt{8\varepsilon_0 \varepsilon_r n_0 kT} \sinh \frac{y_0}{2} \quad (14)$$

It can be simplified as:  $\sigma = \frac{\varepsilon_0 \varepsilon_r \psi_0}{(1/k)}$  (Equation 15)

and then:

$$\sigma_0 = \frac{\sigma_0}{1 + \frac{1}{N_s} e^{-(ze\psi_0 + \varepsilon)/kT}} + \sqrt{8n_0 \varepsilon_0 \varepsilon_r kT} \sinh \frac{ze\psi_{\delta}}{2kT} \quad (16)$$

The following conclusions can be drawn with regard to Stern's treatment of diffuse double layer:

- (1) When solution is diluted, the drop of  $\sigma_d$  is much slower than  $\sigma_\delta$ , the counter-ions mainly appear in diffuse layer, thus the double layer presents the properties of diffuse double layer.
- (2) When solution is concentrated, the value of  $\sigma_\delta$  increases quickly, thus the double layer presents the properties close to Helmholtz parallel-plane capacitor.

Suppose the thickness of Stern layer is  $\delta$ , because the potential in Stern layer is relatively high, thus the  $\psi$ - $x$  curve is approximately a line with slope of:

$$\frac{d\psi}{dx} = \frac{\psi_0 - \psi_\delta}{\delta} \quad (17)$$

Hence, the charge density of Stern layer can be calculated as:

$$\sigma_\delta = \frac{\epsilon_0 \epsilon_r'}{\delta} (\psi_0 - \psi_\delta) \quad (18)$$

Where  $\frac{\epsilon_0 \epsilon_r'}{\delta}$  represents the capacitance  $C_\delta$  of fixed layer;

$\epsilon_r'$  represents local relative dielectric constant or the relative dielectric constant of solid interface layer.

The value of  $\epsilon_r'$  is different with that of the relative dielectric constant of bulk phase (solution). The total capacitance of double layer can be considered composing of capacitance of Stern layer and capacitance of diffuse layer,

$$\text{i.e. } \frac{1}{C} = \frac{1}{C_\delta} + \frac{1}{C_d} \quad (\text{equation 19})$$

Because Stern treated equation 14 and equation 15 by replacing  $\psi_0$  by  $\psi_\delta$ , thus  $C_d$  can be calculated as equation 15, then  $C_d = \epsilon_0 \epsilon_r k$ ; if the solution concentration is quite high, and the value of  $C_d$  turns large enough, then it can be approximately considered that:  $C \approx C_\delta$ .

The aim of Stern's treatment is to try to amend the apparent shortcomings in Gouy-Chapman model. He also noticed the existence of non-coulomb attraction

potential  $\phi$ . However, Stern's treatment (i.e. divide the double layer into two layers, the first layer is fixed (or adsorbed) layer, the second layer is diffuse (or Gouy) layer) has also some problems. For example, the electrokinetic phenomenon indicates that the diffuse layer should be composed of fixed layer and mobile layer. Therefore, the structure of double layer further developed to other models.

## 2.2 Potential-determining layer and Zeta potential

### 2.2.1 Potential-determining ions and potential-determining layer

First of all, the surface potential  $\psi_0$  of solids is discussed by taking colloidal sol of silver iodide at equilibrium of silver iodide saturated water solution at 25°C as example. This experiment indicates that the selective and preferential adsorption of iodine ions on the surface of AgI particles makes AgI particles negatively charged in the saturated solution thereof. However, it can be considered that the concentration of silver ions and iodine ions in solution are approximately same. Thus, from solubility product constant of AgI ( $K_{sp} = 7.5 \times 10^{-17}$ ), the concentration of silver ions (mol/L) is given by:  $[Ag^+] = [I^-] = \sqrt{K_{sp}} = 8.7 \times 10^{-9}$ . If changing the concentration of silver ions and iodine ions in solution by addition of  $AgNO_3$ , AgI particles will be positively charged when the concentration of silver ions reaches above  $3.0 \times 10^{-6}$  mol/L; while if adding KI, AgI particles will be negatively charged when the concentration of silver ions reaches below  $3.0 \times 10^{-6}$  mol/L. When the concentration of silver ions equals to  $3.0 \times 10^{-6}$  mol/L, the surface potential of AgI particles will be zero (actually electrokinetic potential is zero), and the amount of two kinds of ions adsorbed on solid surface turns to be same. The concentration that makes the surface charge on solid surface be zero is called **isoelectric point concentration**. There is no excess charge on solid surface. If the amount of silver ions and iodine ions adsorbed on solid surface is unequal, the solid surface will be either negatively charged or positively charged.

According to the definition of surface excess, the charge density on solid surface is given by:

$$\sigma = e(\Gamma_{Ag^+} - \Gamma_{I^-}) \quad (20)$$

When thermodynamic potential  $\psi_0 = 0$ , the ionic concentration at zero charge point (also called isoelectric point) can be expressed as  $C_{zp}$ , while at any  $\psi_0$  ( $\psi_0 \neq 0$ ), the ionic concentration can be expressed as  $C$ , according to chemical potential equation and Nernst equation:



$$\Delta\mu = kT \ln \frac{C}{C_{zp}} \quad (21)$$

$$\text{or} \quad \psi_0 = \frac{kT}{ze} \ln \frac{C}{C_{zp}} = \frac{2.303RT}{ZF} \log \frac{C}{C_{zp}} \quad (22)$$

Where, F represents Faraday constant.

For monovalent ions, at 25°C,  $\frac{2.303RT}{ZF} = 0.05917V$  or  $\frac{kT}{ze} = 0.02569V$ . The change of

$\psi_0$  can be calculated according to equation 22. For example, for AgI particles in pure water

(or saturated solution thereof), the potential is  $\psi_0 = 25.7 \ln \frac{8.9 \times 10^{-9}}{3.0 \times 10^{-6}} = -150mV$ , which indicates AgI particles are negatively charged.

To summarize, the change of the concentration of silver ions and iodine ions by addition of salts of silver ions or iodine ions can change the surface potential on AgI particles, even change to be zero or change their sign. Therefore, the adsorbed silver ions or iodine ions are called potential-determining ions. The layer comprising one of the ions is called potential-determining layer. Apparently it does not belong to Stern layer. These potential-determining ions are neither always sitting on solid surface, nor same as the composition of solid surface. For example, chloride ions can form stable complex with gold molecules on solid surface. Therefore, they are the potential-determining ions of gold sol. It can be considered that such potential-determining ions are completely separated with solution phase without salvation any more like in solution phase, but that they are chemically bound to solid surface, or even lose their characters completely like silver ions in AgI. Therefore, it is necessary to consider the potential-determining ions separately. The counter-ions adsorbed in Stern layer are solvated. They are fixed in the secondary layer by contacting solid surface via electrostatic interaction or physical adsorption.

From the view of relative flow between solid surface and liquid, the Stern layer is not mobile itself, while it moves with solid surface (or particles). Because the immobility of Stern layer is related to medium (mainly solvent), thus it can not be considered that shear interface should overlap with the boundary of Stern layer. The influence of solvation makes the position of shearing surface sit outside somewhat, therefore, the diffuse layer can be divided into non-shear layer and mobile layer. **The potential on shearing surface (also called sliding surface) exhibits during shearing in electrokinetic phenomenon, so that it is also called electrokinetic potential, as shown in Figure 7.**

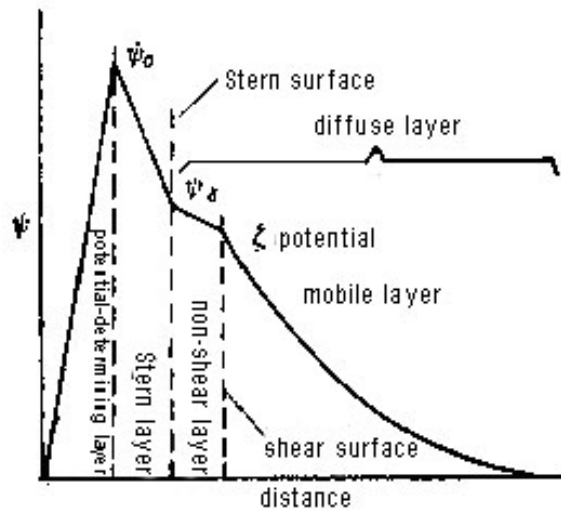


Figure 7 Change of potential with distance when distinguishing potential-determining layer and shear surface

## 2.2.2 $\zeta$ potential and electrokinetic phenomenon

Taking gold sol in a mixed electrolyte solution of sodium chloride and sodium nitrate as an example, first of all, chemisorbed chlorine ions (generally termed specifically adsorbed chlorine ions) form potential-determining inner layer of chlorine ions ( $\psi_0$  value of potential-determining layer is negative), subsequently, Stern layer comprising mainly sodium ions is formed by electrostatic attraction, solvation, van der Waals attraction, etc. In this layer, the potential increases from  $\psi_0$  to  $\psi_\delta$ . Then, in the outward direction, is the non-shear layer of diffuse layer. The potential on shear surface, which is related to electrokinetic phenomenon, equals to  $\zeta$  potential. The whole boundary layer from Stern surface (diffuse layer) is diffusely distributed with positive and negative ions, wherein the ions with opposite charge of potential-determining layer (termed counter-ions) are predominate. With the increasing of distance to interface, the excess counter-ions decrease gradually until zero at certain distance (i.e. solution bulk phase). The range of diffuse double layer is from solid surface to the place where the excess counter-ions are zero. The double layer model of gold sol in the above situation is just an inverted image of Figure 7.

Based on this model, thermodynamic potential can be greatly changed with the change of potential-determining ions until the sign of potential is changed as well. However, the effects of Stern layer and double layer always make potential approach zero. Although  $\zeta$  potential is related to the concentration and properties of all ions in solution, it will be changed with the change of counter-ions in Stern layer, i.e.  $\zeta$  potential drops with the decreasing of  $\psi_\delta$ . The above model separates Stern layer with potential-determining layer.

The aim for that is to emphasize the special role of chemisorbed potential-determining ions played in determination of  $\psi_0$ . If potential-determining ions change,  $\psi_0$  and  $\zeta$  potential will change accordingly.

$\zeta$  potential difference does not strictly exist as phase boundary potential. It can be solely found in fluid zone when relative movement between charged surface and solution bulk phase. Actually, it can be regarded as the phase difference between the point with certain distance to surface and the point on shear surface, which gives rise to electrokinetic phenomenon. Thus,  **$\zeta$  potential can be directly measured based on electrokinetic phenomenon.** Table 1 shows the characteristics of such electrokinetic phenomenon.

Table 1 Electrokinetic phenomenon

Solid surface Electric field	Stationary (e.g. vessel wall or perforated plate; mobile liquid)	Mobile (e.g. colloidal particles; Immobile liquid)
	Applied (along with tangential direction of charged surface)	Induced
	electroosmosis	electrophoresis
	Streaming potential	Sedimentation potential

## Electrophoresis

Electrophoresis is similar to ionic conduction, only the charged particle is macromolecules or colloidal particles. Suppose the applied electric field intensity is  $E$ , the movement velocity of colloidal particles relative to surrounding medium is  $v$ , and take a volume element with area of  $A$  and thickness of  $dx$  at place with distance  $x$  to solid surface, the electric field applied to the charged particles in the volume element exists the volume element an electric field force  $F_{\text{electric}}$ , which equals to the arithmetic product of electric field intensity  $E$  and total net charge, wherein the total net charge involved in the volume element equals to the arithmetic product of volume charge density  $\rho$  and the volume of the volume element. According to Poisson's equation:

$$\rho = -\epsilon_0 \epsilon_r \nabla^2 \psi^2 = -\epsilon_0 \epsilon_r \frac{d^2 \psi}{dx^2}$$

Thus,

$$F_{\text{电}} = E \rho A dx = -E A \epsilon_0 \epsilon_r \frac{d^2 \psi}{dx^2} dx \quad (23)$$

When relative movement takes place between the volume element and solid surface, the viscous force existed on the surface closest to solid surface is given

by:

$$F_{x \rightarrow dx} = \eta A \left( \frac{dv}{dx} \right)_{x+dx}, \text{ the viscous force existed on the volume element equals to the}$$

difference of the above two viscous forces, i.e.

$$F_{\text{粘}} = \eta A \left[ \left( \frac{dv}{dx} \right)_{x+dx} - \left( \frac{dv}{dx} \right)_x \right]$$

If x is quite small, thus

$$\left( \frac{dv}{dx} \right)_{x+dx} \approx \left( \frac{dv}{dx} \right)_x + \left( \frac{d^2v}{dx^2} \right) dx$$

and then:

$$F_{\text{粘}} = \eta A \left( \frac{d^2v}{dx^2} \right) dx \quad (24)$$

When reaching force equilibrium, the electric field force and viscous force are equal in value but opposite in sign, i.e. equation 23 equals to equation 24, thus:

$$\eta \left( \frac{d^2v}{dx^2} \right) = -E \varepsilon_0 \varepsilon_r \frac{d^2\psi}{dx^2} \quad (25)$$

Integrate the above two equations, thus the relation between v and  $\psi$  can be obtained.

First of all, assume  $\eta$  and  $\varepsilon_r$  are all constant. Perform the first

integration:  $\int \frac{d}{dx} \left( \eta \frac{dv}{dx} \right) = - \int E \frac{d}{dx} \left( \varepsilon_0 \varepsilon_r \frac{d\psi}{dx} \right) + C$ , to obtain  $\eta \frac{dv}{dx} = -E \varepsilon_0 \varepsilon_r \frac{d\psi}{dx} + C$

When  $x = \infty$ ,  $\frac{d\psi}{dx} = 0$ ,  $\frac{dv}{dx} = 0$ , thus the integral constant  $C=0$ ; perform the secondary integration with the boundary condition of  $v=0$  ( $\psi=\zeta$ ),  $v=u$  ( $\psi=0$ ), thus:

$$\int_0^v \eta dv = \int_{\zeta}^0 -E \varepsilon_0 \varepsilon_r d\psi$$

The equation of electrophoretic velocity is given by:

$$v = \frac{E \varepsilon_0 \varepsilon_r \zeta}{K \eta} = \frac{E \varepsilon \zeta}{K \eta} \text{ 或 } u = \frac{v}{E} = \frac{\varepsilon \zeta}{K \eta} \quad (26)$$

Where, u represents **electrophoretic mobility, i.e. electrophoretic velocity under unit electric field intensity. Zeta potential is given by:**

$$\zeta = \frac{K u \eta}{\varepsilon} \quad (27)$$

Where, u is electrophoretic mobility of colloidal particles;  $\varepsilon$  and  $\eta$  are dielectric constant of medium and viscosity, respectively;  $\zeta$  is  $\zeta$  potential; K is a constant related to the shape of colloidal particles. This equation not only indicates the dependency relationship between electrophoretic mobility u and  $\zeta$  potential, but also provides a method for measuring  $\zeta$  potential, i.e. calculating  $\zeta$  potential though measuring electrophoretic mobility.

During deduction of the equation, it is assumed that the solid surface is a plane, for other geometric shapes, equation 27 is still suitable as long as the radius of curvature is much larger than the effective thickness of double layer (approximately above 100 times), i.e. the electrolyte concentration is quite high or the curvature of solid surface is quite small (for larger colloidal particles).

## Chapter 3 Components of Apparatus

### 3.1 System parameters

#### Power supply

Supply voltage: 220 V, 50 Hz

Power consumption: 150 W

#### Operating environment

Shock-proof platform

#### Temperature

Temperature: 5°C to 35°C

Recommend to operate in a clean room with constant temperature

#### Measurement range

Suitable for disperse system with particles diameter of 0.5-10  $\mu\text{m}$

pH range: normally operate at 2.0-12.0 (1.6-13.0 is also feasible)

#### Measurement accuracy

Below 5% of systematic error

### 3.2 System components

#### 3.2.1 Hardware components

Figure 8 shows the internal structure of the potentiometer mainframe.

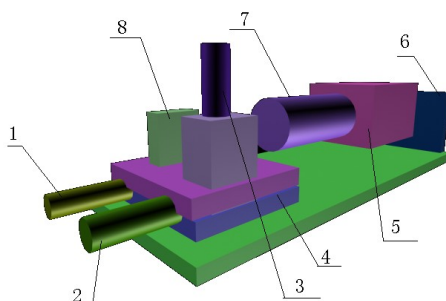


Figure 8 Schematic diagram of the internal structure of the potentiometer mainframe

- |                              |                                |                            |                |
|------------------------------|--------------------------------|----------------------------|----------------|
| 1 Left/right adjusting screw | 2 Focal length adjusting screw | 3 Up/down adjusting screw  | 4. 3D platform |
| 5. CCD components            | 6. Interface panel             | 7. Optical lens components | 8. Sample cell |

Figure 9 shows the structure of the back panel of the apparatus.

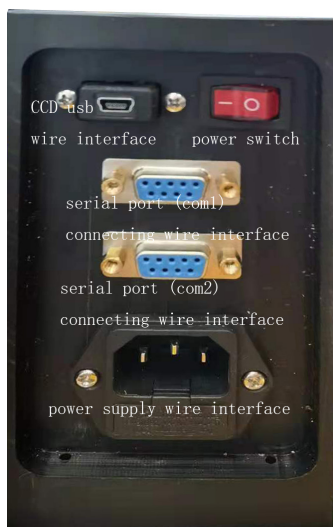


Figure 9 Structural diagram of the back panel of the apparatus

### Electrophoresis cells

Electrophoresis cell is an important component of electrophoresis apparatus. Conventional electrophoresis cell has types of capillary, rectangular, single-tube, duplex-tube, triplex-tube, and etc., both of which have characteristic that electrode is build outside the electrophoresis cell of samples. These types of electrophoresis cell have disadvantages of complex structure, high cost, and high sample dosage (from 10ml to 100ml or so) during measurement, inconvenience for cleaning, and liability for capillary tube to clog. For overcoming the above disadvantages, new type of convenient electrophoresis cell is designed, in which a glass chamber with thickness of 0.5 cm is used, as shown in Figure 10, and electrodes is build inside the cell. Subjecting to precise calculation of micro-flow filed and surface treatment, the electrophoresis chamber and built-in electrodes compose an unique electrophoretic apparatus. The sample dosage during measurement is quite small, only 0.5 ml per time. The new type of electrophoresis apparatus is economical and practical, and convenient for cleaning and using.

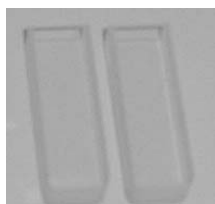


Figure 10 Electrophoresis chamber

### Electrode

A well-designed electrode support and an electrophoresis cylinder compose a cylinder

open-type electrophoresis apparatus by closely fitting. The electrode is made of silver or platinum metals and has stable operational status after surface treatment, as shown in Figure 11 (platinum electrode labeled with P, and silver electrode labeled with A).

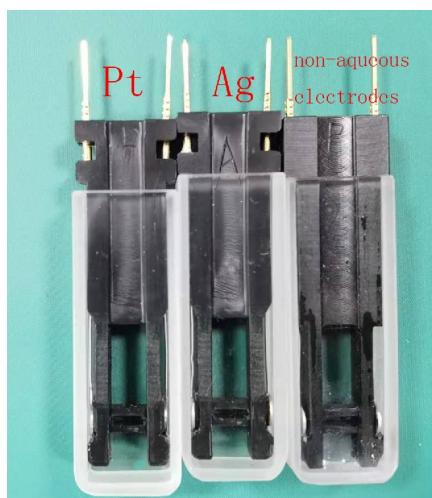


Figure 11 Electrode

### Light source

Conventional zeta potentiometers use incandescent lamp or laser light as light source. The former one has the disadvantages of large power (normally from several to tens of watt) and liability to heat to influence electrophoretic mobility. The latter one has the disadvantages of high cost and short service life. The newly designed potentiometer adopts near-field optical system with semiconductor luminescence component. Its power is only dozens of microwatt, which will not influence measurement environment and measurement accuracy due to heating.

### Power supply

Adopt low-frequency switch power supply with constant voltage, which can prevent polarization and improve measurement speed. Positive/negative change-over time: 0.30-1.20 seconds (continuously adjustable), sampling time: 3-10 seconds. Inter-electrode voltage can be adjusted as required.

### Temperature

Sample environmental temperature automatically and continuously with a probe, send back to computer, adjusting parameters automatically, and calculate Zeta potential.

### Calculation

Adopt multimedia technology to continuously take photos of ultrafine particles (amplification of 1,200 times) under assigned intervals, and perform analysis and calculation based on the resulting four bidirectional grey images.



## Cross sign

Dispose the well-designed cross sign into electrophoresis chamber, put on 3D platform, adjust 3D platform, and identify detection position by observation of clear cross sign on computer screen, as shown in Figure 12



Figure 12 Cross sign

**A serial port connecting wire (as shown in Figure 14)**

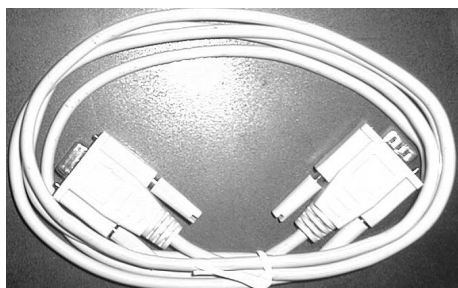


Figure 14 Serial port connecting wire

**A CCD USB wire (as shown in Figure 5)**



Figure 15 CCD USB wire

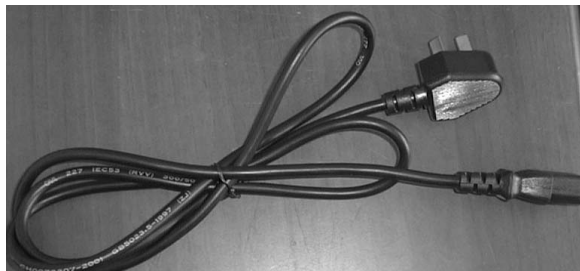
**A mainframe power supply wire (as shown in Figure 16)**

Figure 16 Mainframe power supply wire

**Two electrode wires (one for backup, as shown in Figure 17)**

Figure 17 Electrode wire

**Computer matchable to zeta potentiometer**

If using own computer, the following configurations or higher are recommended:

Memory above 4G

Hard disk with at least 5000M space

### **3.2.2 Software components**

#### **Operating environment**

Windows 7/Windows 10

#### **Bundled software**

The CD disk provided with product normally includes the following contents:

Application software for apparatus;

Introduction and operation manual for apparatus

## Chapter 4 System Installations

### 4.1 System hardware installation

#### 4.1.1 Installation of serial port

Connect the COM1 port of computer with the serial port of the electrophoresis apparatus using the serial port connecting wire provided with the apparatus. The COM1 port of computer is shown in Figure 18, and the connection schematic diagram of the serial port connecting wire is shown in Figure 19.

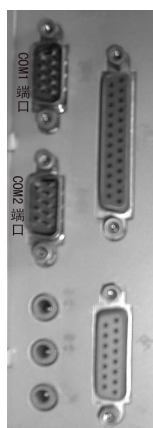


Figure 18 Schematic diagram of COM port

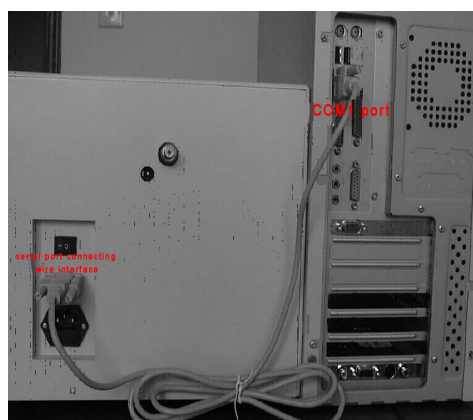


Figure 19 Connection schematic diagram serial port connecting wire

**If you haven't com port on mainboard, you need to install a usb to serial cable.**



**Figure 20** usb to serial cable

## 4.2 System software installation

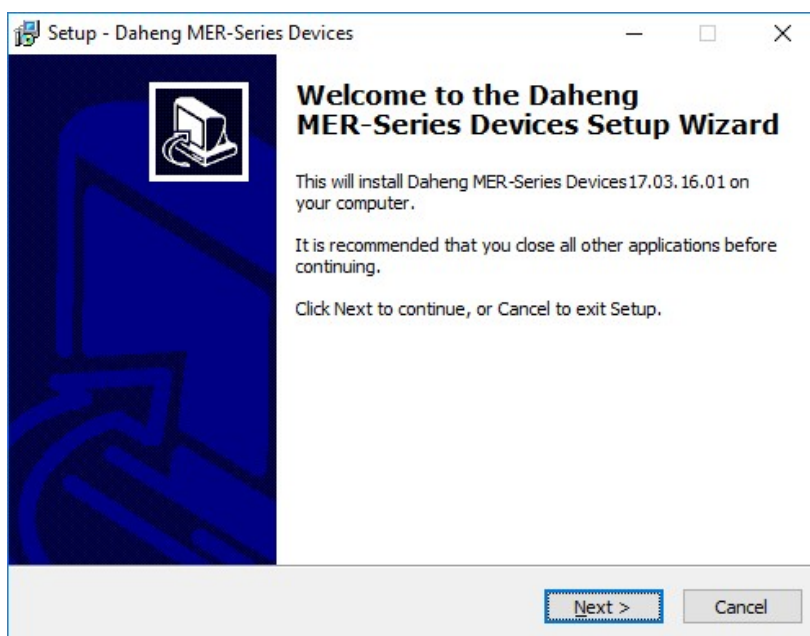
For the zeta potentiometer with computer provided by our company, the software has been installed and the installation software is provided. If customs use their own computer or reinstall system, please following the steps below:

### 4.2.1 CCD drive software

The CCD drive is located in the USB drive directory. Without the CCD drive installed, the CCD cannot work.

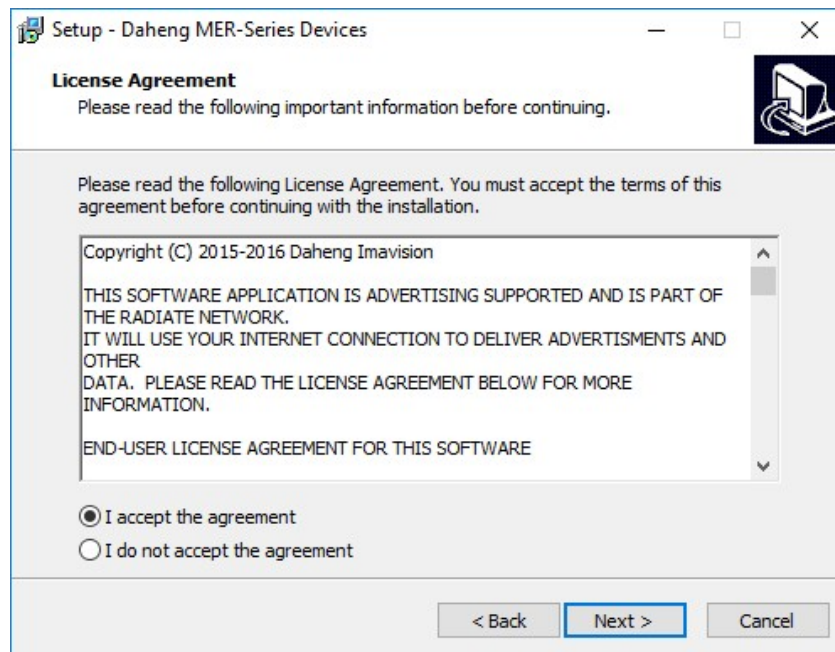
#### (1) Installation of CCD drive program

click the MER\_Setup\_cn\_151130.exe.



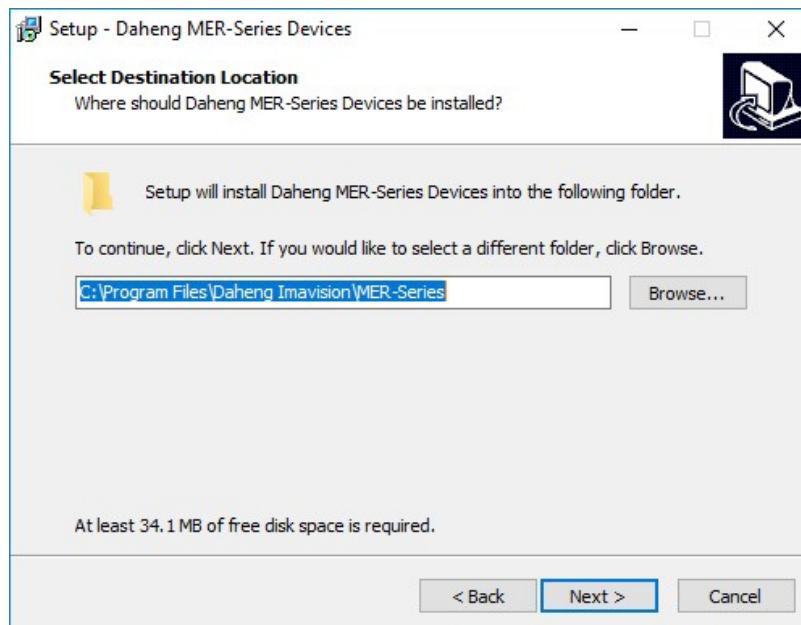
**Figure 21** Drive program installation 1

Click "next" on the screen as shown in Figure 11.



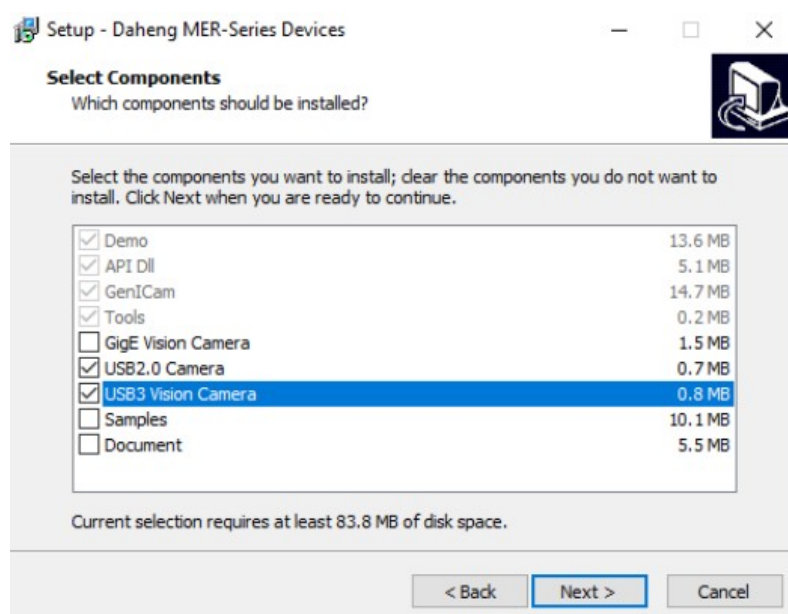
**Figure 22 Drive program installation 2**

Click "I accept this agreement" option and "next", as shown in Figure 22.



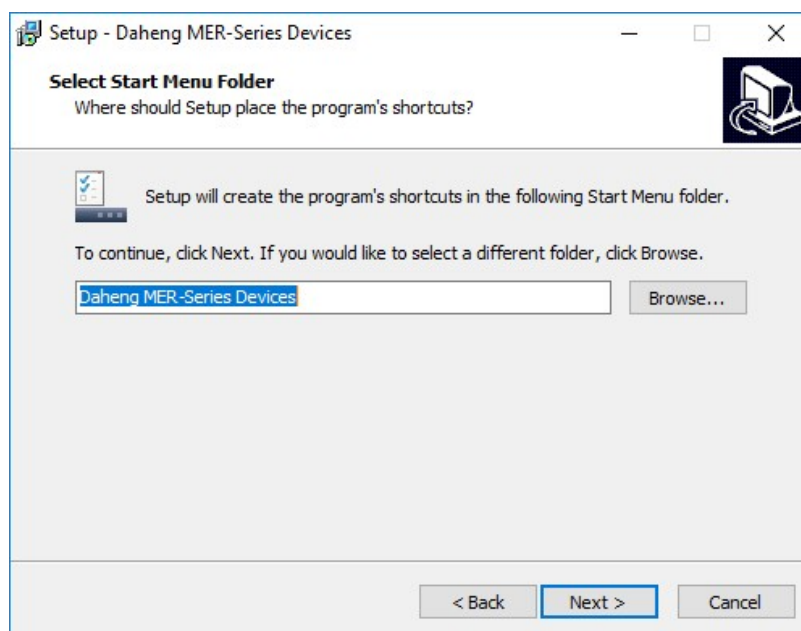
**Figure 23 Drive program installation 3**

The screen shown in Figure 23 will pop out. Do not change the default path. Click "next".



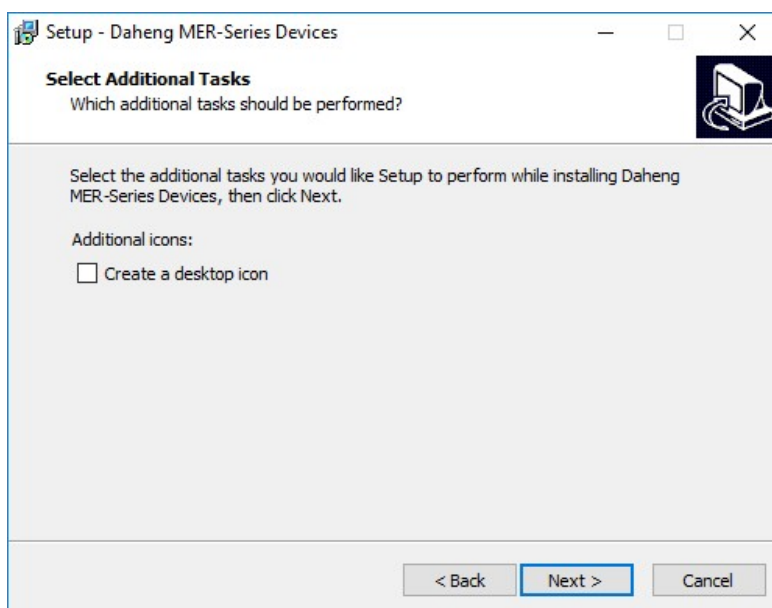
**Figure 24 Drive program installation 4**

The screen shown in Figure 24 will pop out. Do not change the default path. Click "next".



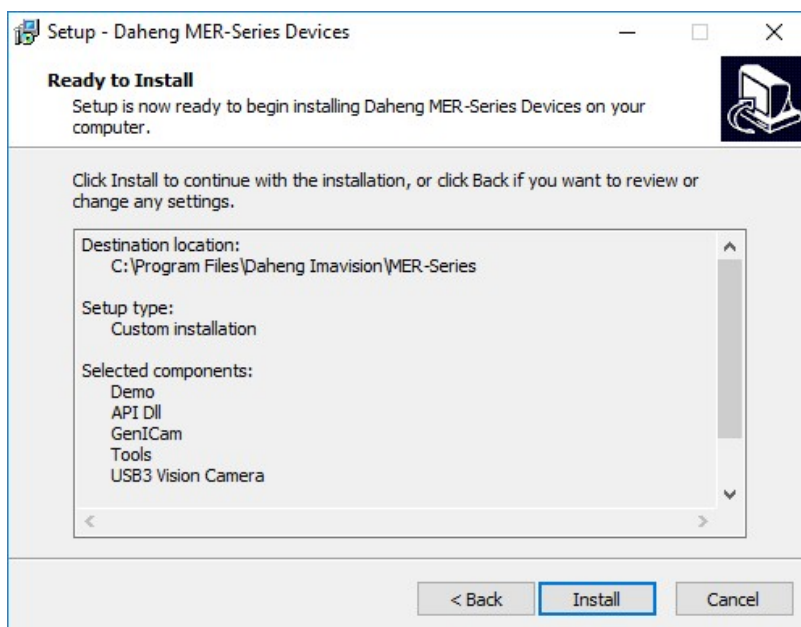
**Figure25 Drive program installation 5**

The screen shown in Figure 25 will pop out. Do not change the default path. Click "next".



**Figure 26 Drive program installation 6**

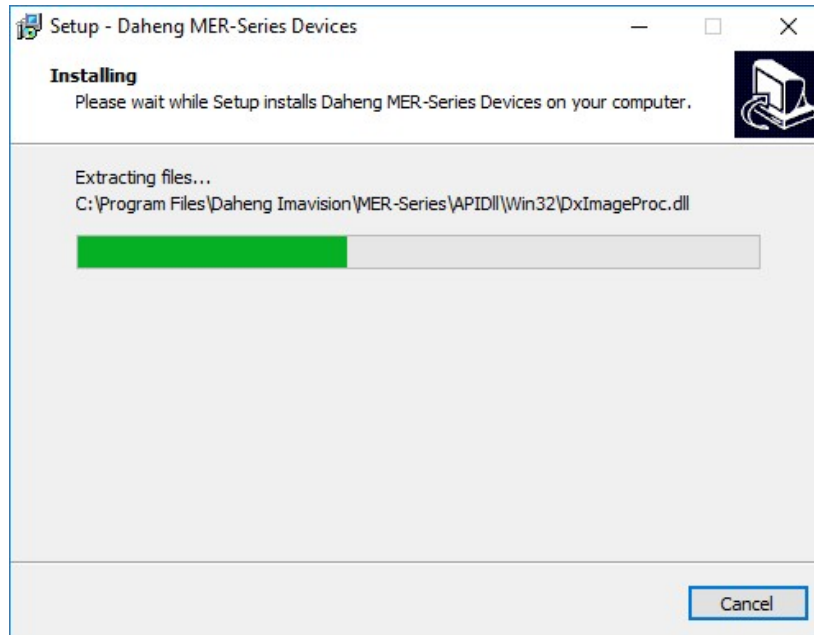
Click "next" on the screen as shown in Figure 26.



**Figure 27 Drive program installation 7**

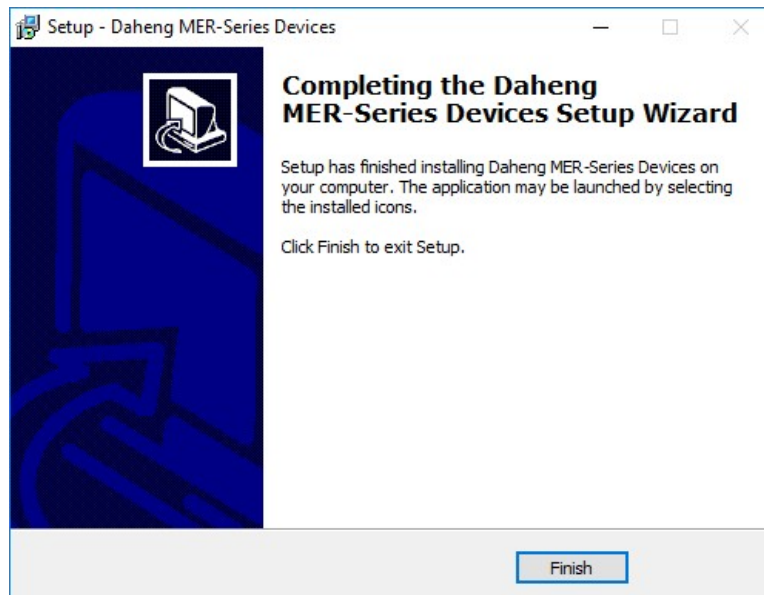
Click "next" on the screen as shown in Figure 27.





**Figure 28 Drive program installation 8**

A program bar will be displayed, as shown in Figure 28.



**Figure 29 Drive program installation 9**

Click "finish" on the screen as shown in Figure 29.

If the drive is properly installed, there will be a graphics processing unit in the device manager under the control panel.

If the drive program is either not installed or installed incorrectly, there will be a graphics processing unit-USB device together with a yellow exclamation point in the device manager under the control panel, as shown in Figure 30.

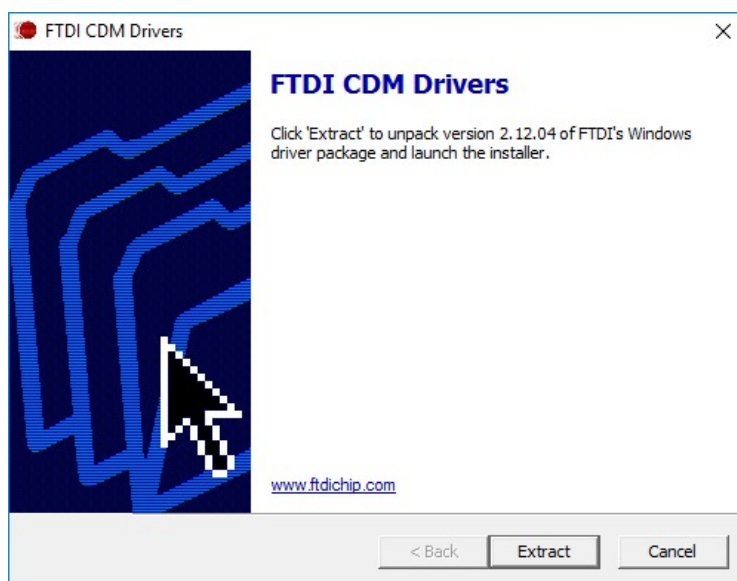




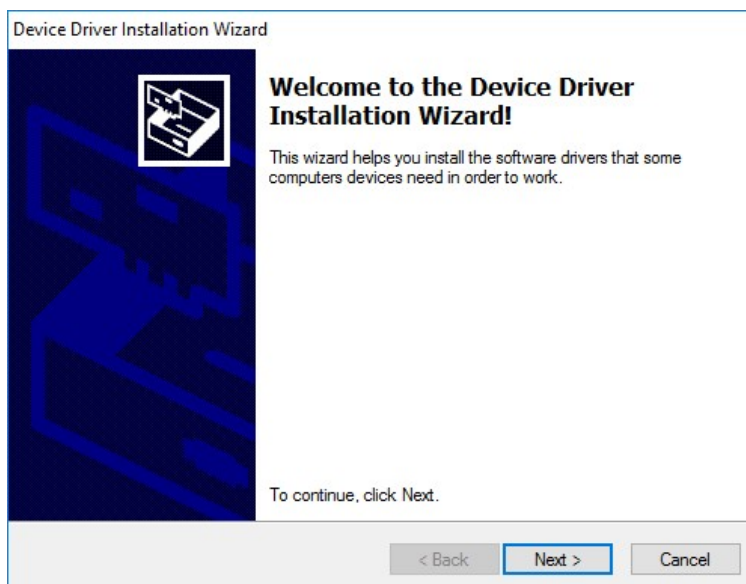
**Figure 30** An unknown USB device found in device manager.

Repeat the CCD drive software installation steps in 4.2.1 to complete installation.

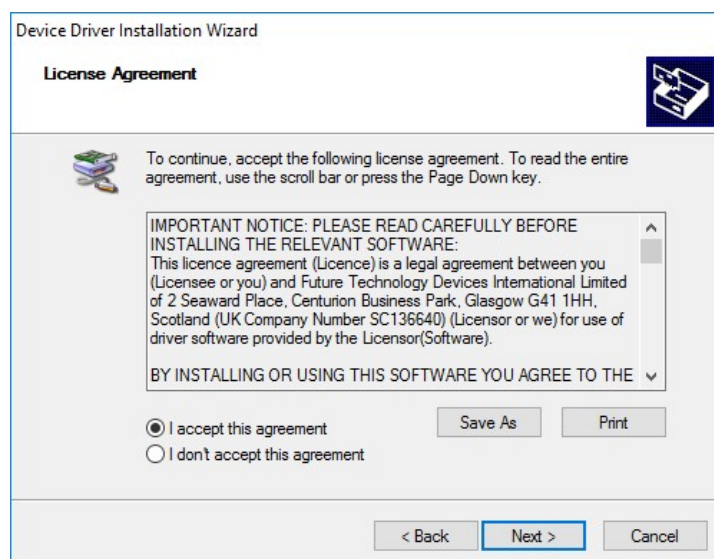
#### 4.2.2 Installation of series port drive software



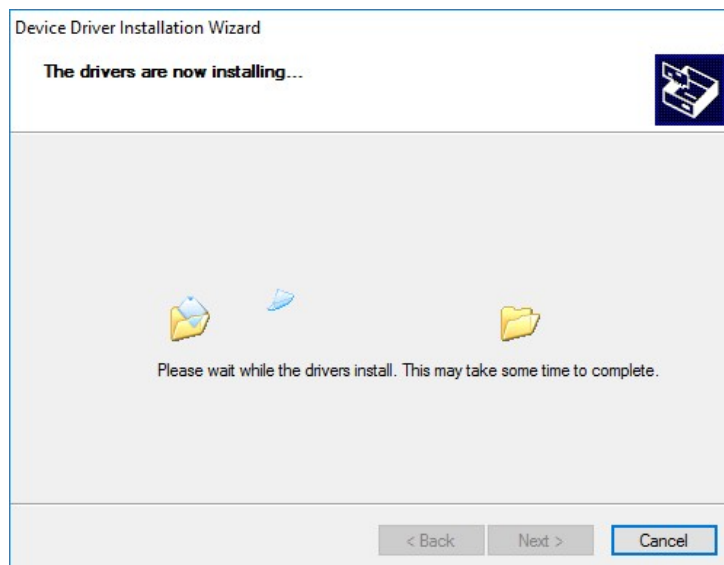
**Figure 31** Installation of series port drive program 1



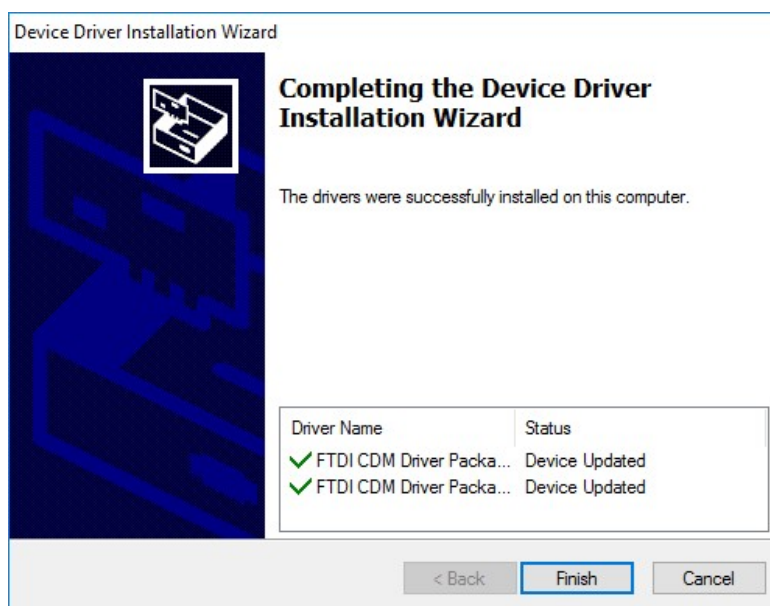
**Figure 32** Installation of series port drive program 2



**Figure 33 Installation of series port drive program 3**



**Figure 34 Installation of series port drive program 4**



**Figure 35 Installation of series port drive program 5**

 USB Serial Port (COM1)

 USB Serial Port (COM2)

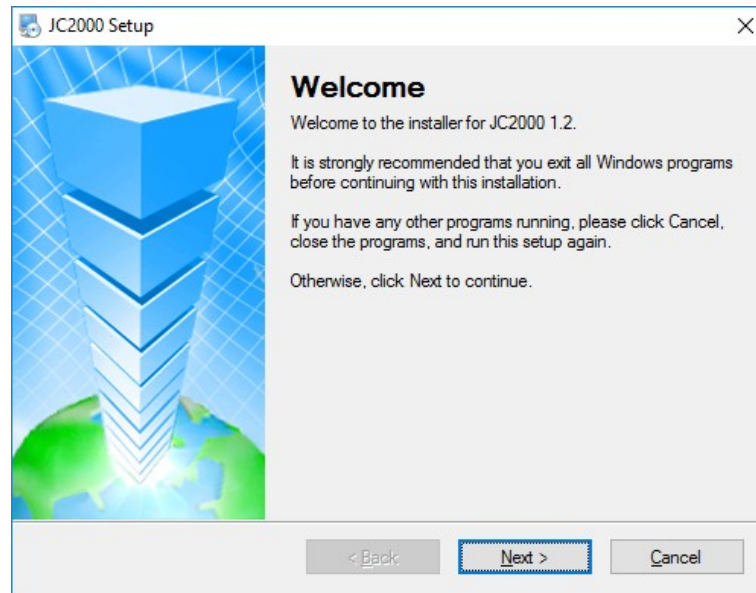
**Figure 36 Installation of series port drive program 6**

In the device manager, change the port number of USB to serial port to com1 and com2

#### **4.2.2 Installation of application software of apparatus**

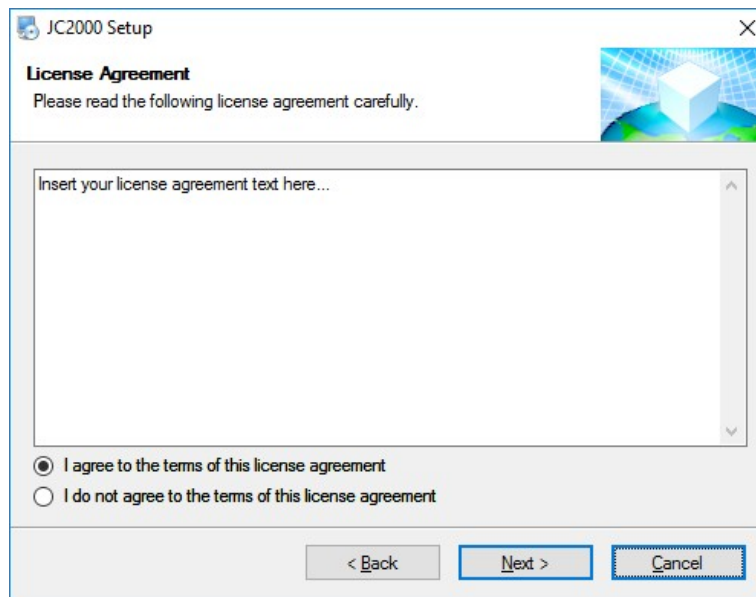
#### **4.2.3 Operating software installation**

Click the "DataBasesetup.exe" in the CD.



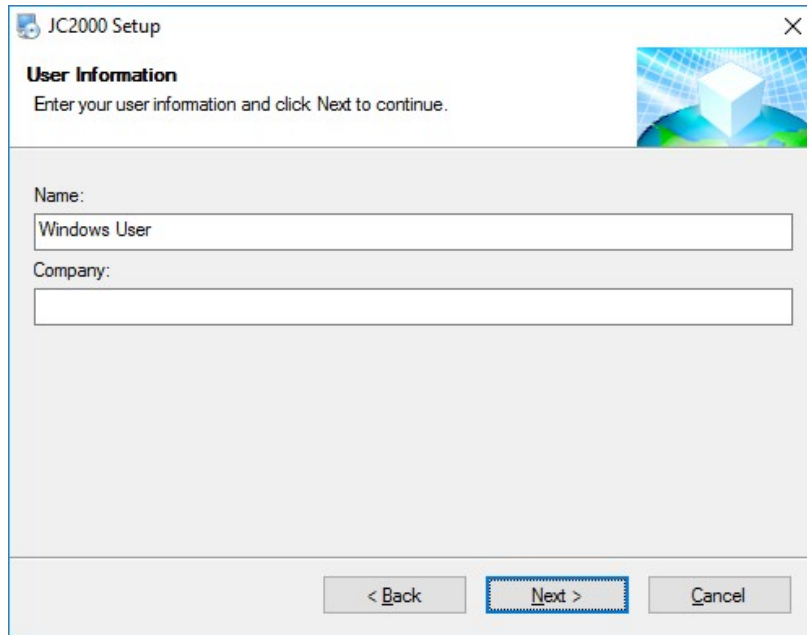
**Figure 27 Installation step 1**

Click "next" on the screen as shown in Figure 28.



**Figure 28 Installation step 2**

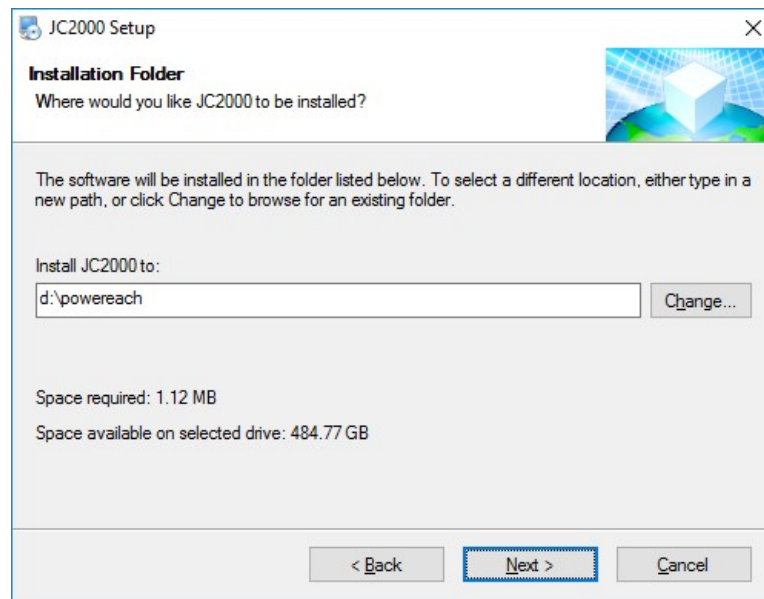
Click "I accept this agreement" and then "next" on the screen as shown in Figure 29.



The screenshot shows the 'JC2000 Setup' window with the 'User Information' tab selected. The window title is 'JC2000 Setup'. Below the title bar, there is a close button (X) and a decorative graphic of a cube on a globe. The main text reads: 'User Information' and 'Enter your user information and click Next to continue.' There are two input fields: 'Name:' with the text 'Windows User' and 'Company:' which is empty. At the bottom, there are three buttons: '< Back', 'Next >' (highlighted with a blue border), and 'Cancel'.

**Figure 29 Installation step 3**

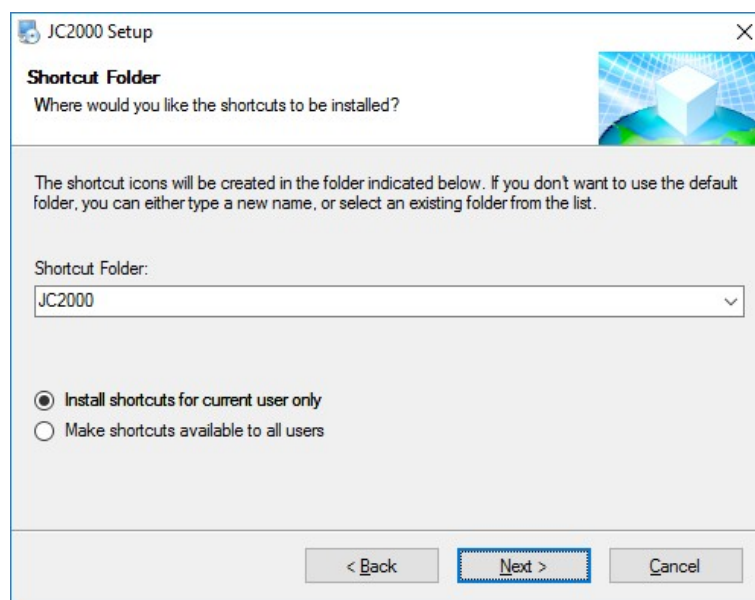
Fill out name and company and then click "next" on the screen as shown in Figure 30.



The screenshot shows the 'JC2000 Setup' window with the 'Installation Folder' tab selected. The window title is 'JC2000 Setup'. Below the title bar, there is a close button (X) and a decorative graphic of a cube on a globe. The main text reads: 'Installation Folder' and 'Where would you like JC2000 to be installed?'. Below this, there is a paragraph: 'The software will be installed in the folder listed below. To select a different location, either type in a new path, or click Change to browse for an existing folder.' There is an input field labeled 'Install JC2000 to:' with the text 'd:\powereach' and a 'Change...' button to its right. Below the input field, it says 'Space required: 1.12 MB' and 'Space available on selected drive: 484.77 GB'. At the bottom, there are three buttons: '< Back', 'Next >' (highlighted with a blue border), and 'Cancel'.

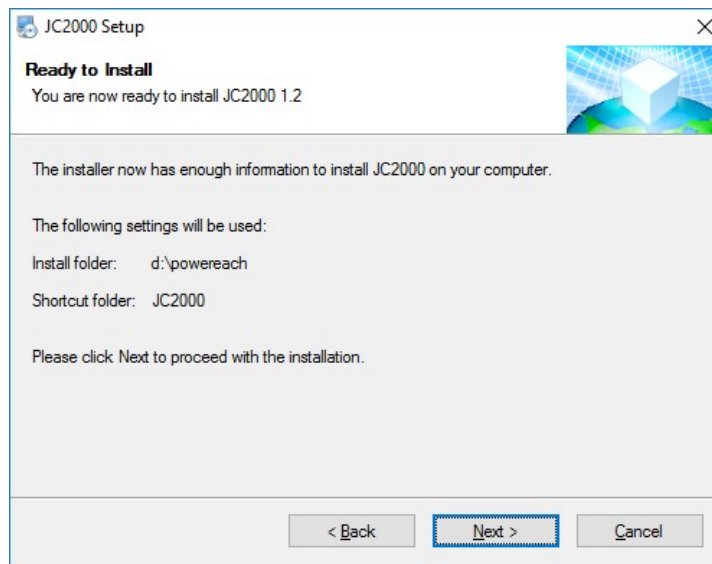
**Figure 30 Installation step 4**

The screen shown in Figure 31 will pop out. Do not change the default path. Click "next".

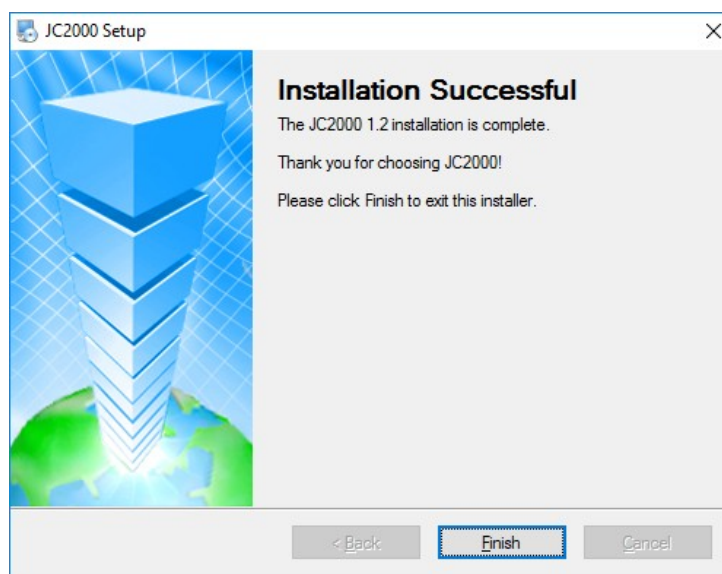


**Figure 31 Installation step 5**

The screen shown in Figure 32 will pop out. Do not change the default path. Click "next".



**Figure 32 Installation step 6**



**Figure 33 Installation step 7**

**Click "finish" on the screen as shown in Figure 33.**

Copy all files in ZetaEn folder under directory of “electrophoresis apparatus” in the CD disk to hard disk, wherein ZetaEn.exe is an executable file.

#### **4.2.3 Display Setting**

Click right button of cursor mouse on desktop, click Property button, click Setting button, Resolution select “1920×1080 Pixel” or above

## Chapter 5 System modular components

The system mainly comprises two modules, which are sampling module and computational analysis module.

### 5.1 Sampling module

This module is the main control module of system operation. It takes charge of initializing multimedia cards and front-single board computer (SBC) and providing users a convenient and integrated operational environment. In this working platform, you can control sampling parameters during sampling, such as real-time output voltage, polarity of electrode, switching speed, etc.; you can input the pH value of sample to be measured; meanwhile, you can observe the movement of particles through video observation window to adjust the region to be saved in disk; you can observe and adjust 3D platform to obtain clear image of cross sign; and you can also acquire the values of environmental parameters in time, such as electric current and temperature.

In the main module, a method for rapid invocation of computational analysis module is also provided to facilitate customer use.

### 5.2 Computational analysis module

This module is for post-treatment and is also an accessory control module of sampling module. It mainly analyses the data images collected by consumers by scaling method to obtain the Zeta potential of particles to be measured under current environmental parameters.



## Chapter 6 Usage of System

### 6.1 Startup

The application software of zeta potentiometer can be started by running ZetaEn.exe file under subdirectory of ZetaEn. Figure 38 shows the main interface of the application software of zeta potentiometer.

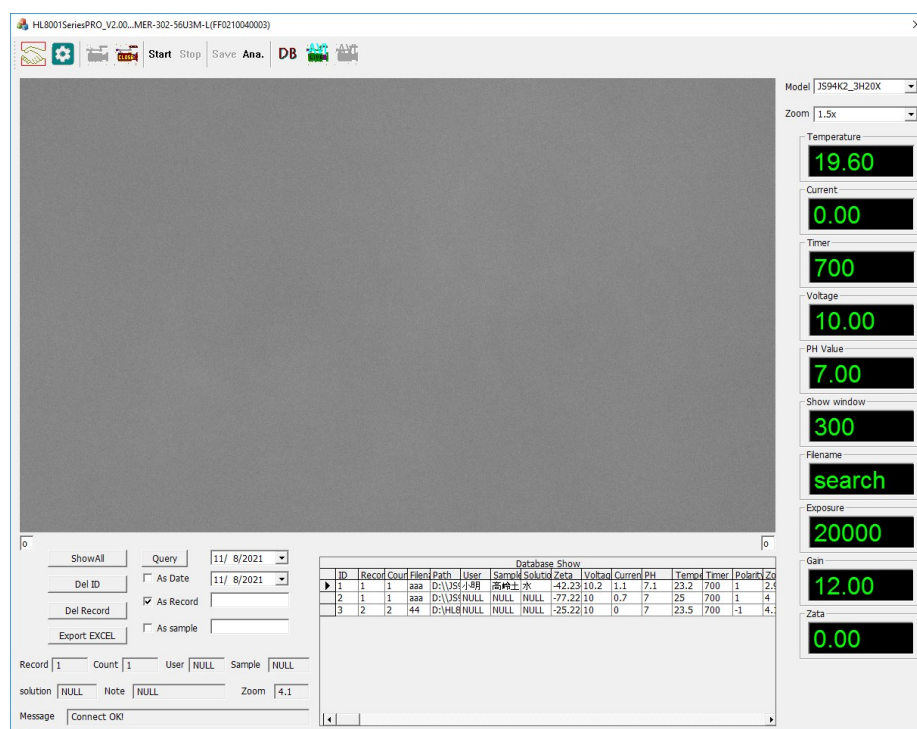


Figure 38 Diagram of the main interface of the application software of zeta potentiometer

### 6.2 Instructions for sampling module

- The large square region on the left of screen is image display region, which displays the current images taken by camera when turning on the camera.
  - The right side of screen is function menus. Now the functions of each menu will be introduced in detail as follows:
- (1) Temperature Menu: to display the environmental temperature in current electrophoresis chamber

Unit: °C

Accuracy: 0.1°C

- (2) Electric current Menu: to display the electric current value in current electrophoresis chamber
  - Unit: mA
  - Accuracy: 0.1mA
  - The working electric current is normally controlled below 18 mA by regulating voltage
- (3) Voltage Menu: to control the value of current output voltage
  - Unit: V
  - Accuracy: 1V
  - Regulating range: 0-200 V
  - Step size: 1V
- (4) Voltage switch Menu: to control the switching period of current polarity of electrode
  - Unit: ms
  - Accuracy: 10 ms
  - Regulating range: 500-1200 ms
  - Step size: 1 ms
- (5) pH value Menu: to input the pH value of solution
  - Regulating range: 0-14
  - Step size: 0.1
- (6) Filename Menu: to give the filenames of image files and data exchange files
  - Composition of filename: a set of image file is composed of the obtained character string and the automatically added 01.bmp, 02.bmp, 03. bmp, and 04.bmp.

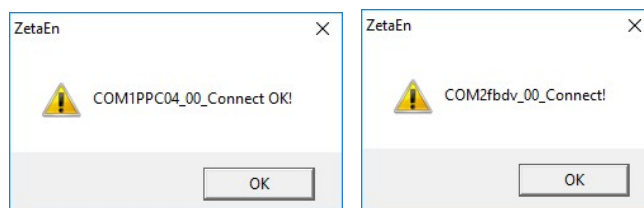
## 6.3 Operational steps

### 6.3.1 Communication

After entering the main interface, please click the ConnectC option and the Connect Zoom option in the Options menu.



"Connected ok" appears, indicating that the communication between the computer and



the instrument is successful.

If an error message appears, please check the connection between the computer and the instrument. After the lens is successfully connected, the lens is automatically initialized to the minimum multiple.



Then click the LIVE button to get image.

### 6.3.2 Focusing and positioning

Rinse the electrophoresis chamber and cross sign with deionized water, inject the sample to be measured into the electrophoresis chamber, insert the cross sign, rinse for several times and completely moisturize the cross sign; inject 0.5 ml of sample into the electrophoresis chamber, incline the electrophoresis chamber, slowly insert the cross sign, approach the surface with cross sign of the quartz plate (with front and back surfaces) to lens, i.e. make the surface with "Front" to face to yourself, and carefully observe (make sure no bubbling); and wipe the outside of dry electrophoresis chamber, stably dispose the electrophoresis chamber inside the sample cell, and slightly press to the end (do not heavily press), as shown in Figure 39.

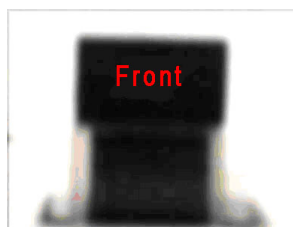


Figure 39 Insertion of cross sign

Adjust up/down and left/right knob and focal length until you can observe clear cross sign image on computer screen, as shown in Figure 40. (Note: Due to different refractive index of each sample, thus it is necessary to re-focusing and re-positioning when using another kind of sample. Once for the same kind of sample)

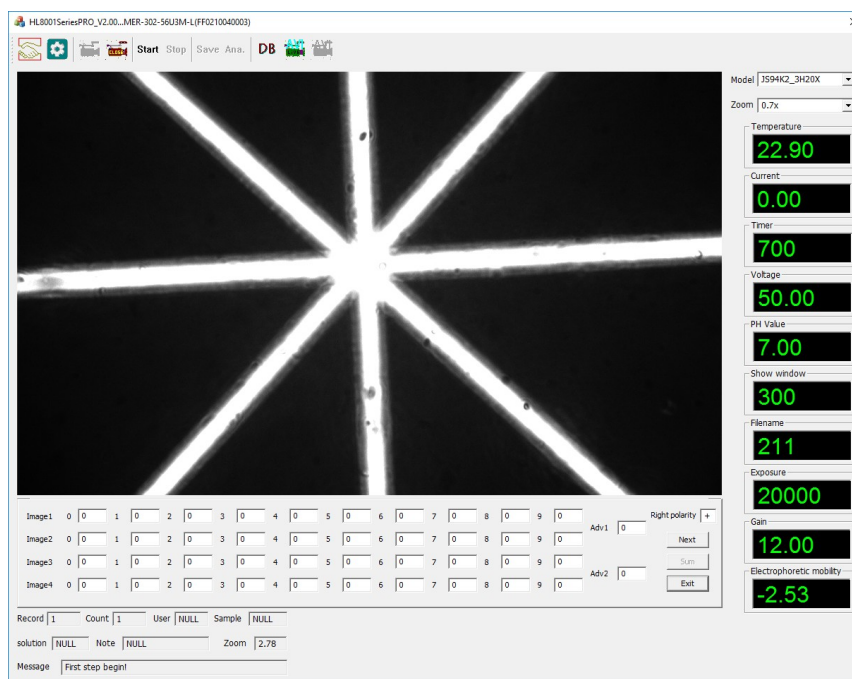


Figure 40 Schematic diagram of focusing of cross sign

### 6.3.3 Sampling

The sample measurement can be started after observing the cross sign. Rinse the electrophoresis chamber and electrode with deionized water, inject the sample to be measured, insert electrode and rinse for several times, and completely moisturize the electrode system;

inject 0.5 ml of sample into the electrophoresis chamber, incline the electrophoresis chamber, slowly insert electrode system, and carefully observing (make sure no bubbling); and wipe the outside of dry electrophoresis chamber, stably dispose the electrophoresis chamber inside the sample cell, slightly press to the end (do not heavily press), and connect with electrode connecting wire, as shown in Figure 41.

(Note: for system in which chloride ions are predominant, Ag electrode is used)

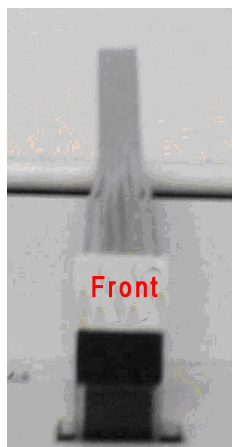


Figure 41 Schematic diagram of connection of electrode

Then, adjust the required voltage; input the pH value of sample; click “Start” button; **give filename**; adjust the particles, which move up & down with the switch of electrode in image, with shortcut keys to locate the particles to be measured inside camera aperture; and click “BMP Save” button immediately. Then system will grab this image for computational analysis.

#### 6.3.4 Setting

Choose the corresponding model. Click the multiple option in the zoom menu, the lens will automatically zoom to the selected multiple. Select the appropriate multiple according to the displayed particle size. as shown in Figure 42.

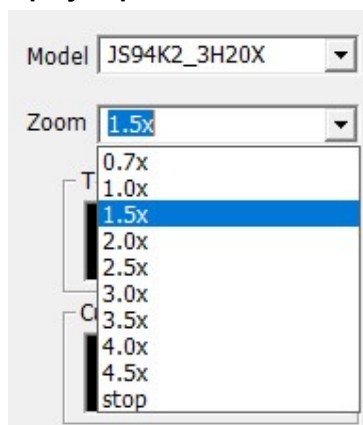


Figure42: Setting dialog box

#### 6.3.5 Image grabbing

click “Start” button, **adjusting the required voltage; input the pH value of sample (pre-measured with pH meter)**; and click “Save” button immediately. Then system will

grab this image for computational analysis.

Start Stop Save Ana.

### 6.3.6 Analysis

Click “Ana” button to enter sub interface of computational analysis. Figure 43 shows the screen layout of computational analysis module.

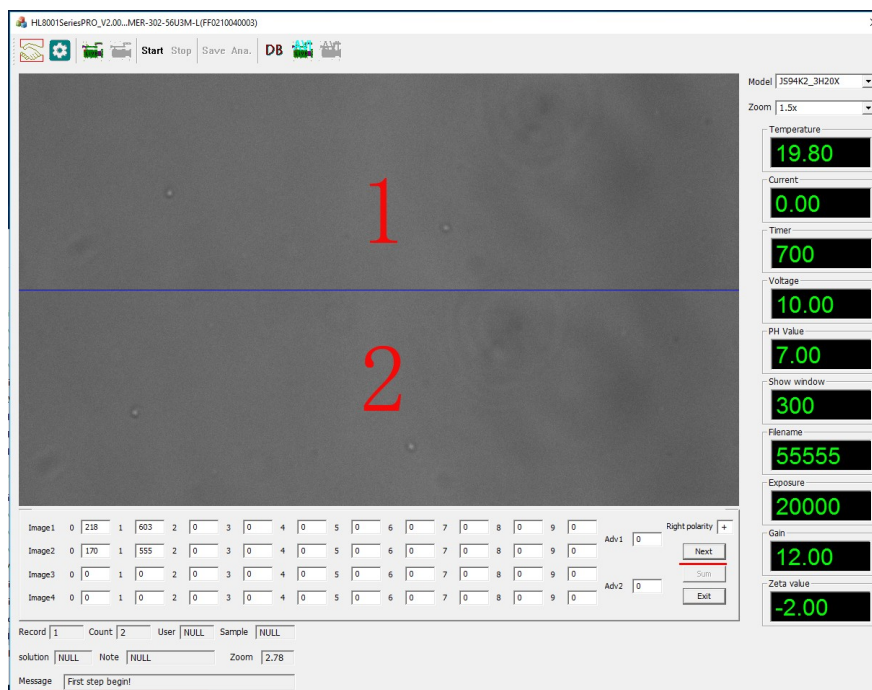


Figure 43 Diagram of main interface of computational analysis

The three rectangular regions on the left side of screen are scaling analysis region 1, 2 , respectively. On the right side of screen, there are three regions, which are, from top to bottom, operational region, environmental parameters region, and cursor positioning data region.

Click “Begin” button, and Select file, as shown in Figure44.

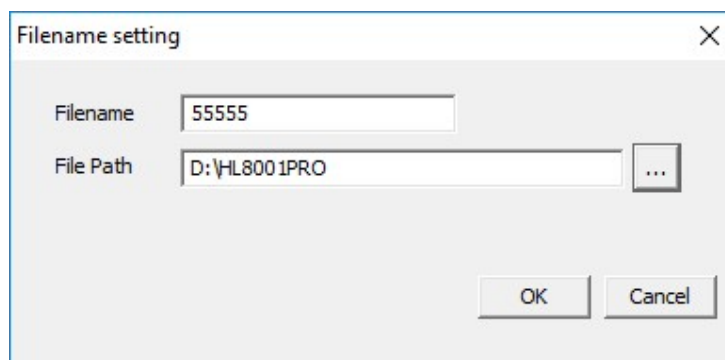
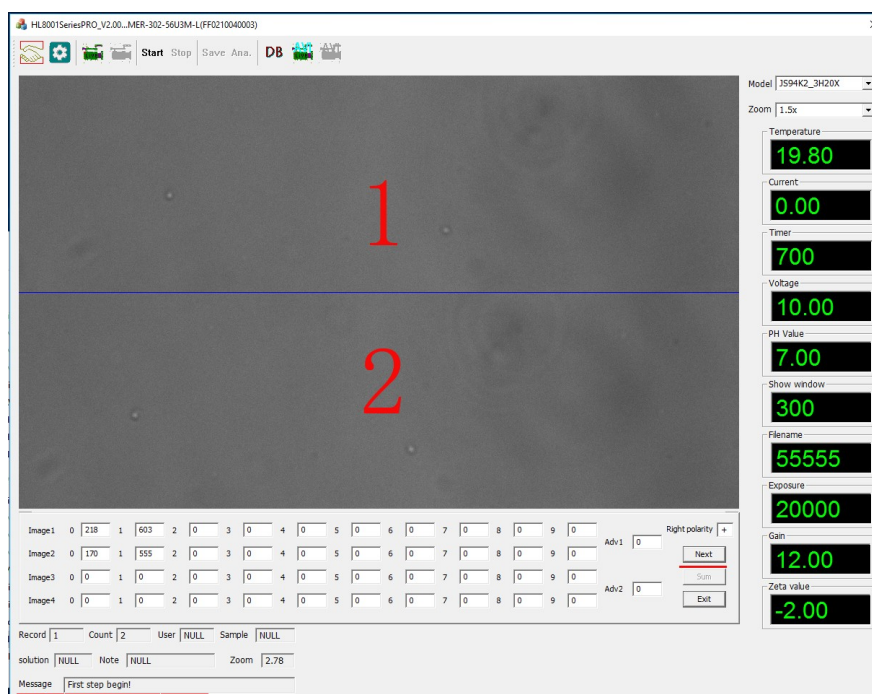


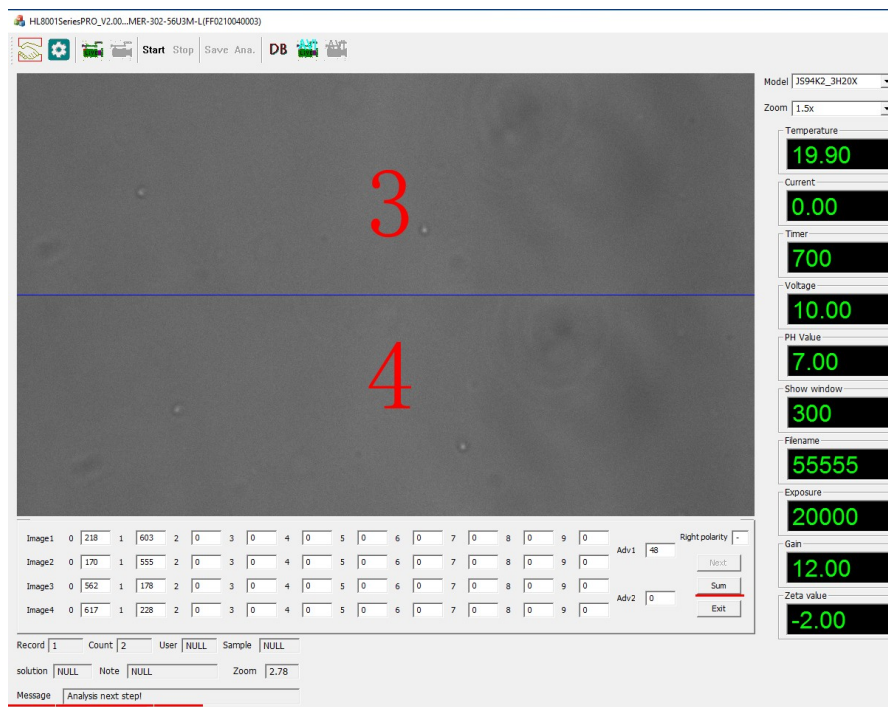
Figure 44 Filename dialog box

Requirement of filename: the filename should be that saved before.

Please click “open” button, system will call out corresponding images and data for your analysis.







The analysis region 1 and 2 shows grey images of particles movement with intervals determined by switching parameters of voltage. When analyzing images, firstly identify a particle in the analysis region 1 where the particle locates and click this point with cursor mouse. The position data thereof will be displayed in “Particle 0” in scaling data region. Then, identify the same particle in the analysis region 2 according to the correlation of particle position. The position data thereof will be displayed in “Particle1” in scaling data region.

Till now, the first set of data is obtained. Subsequently, identify another particle in the analysis region 1 and obtain the second set of data using the same method. In this manner, up to ten sets of data can be obtained. Then, click “Next” button, system will call out the second set of images for your analysis. After you obtain ten sets of data using the same method, click “Sum” button, **System will give analytical results automatically**, as shown in Figure 45.

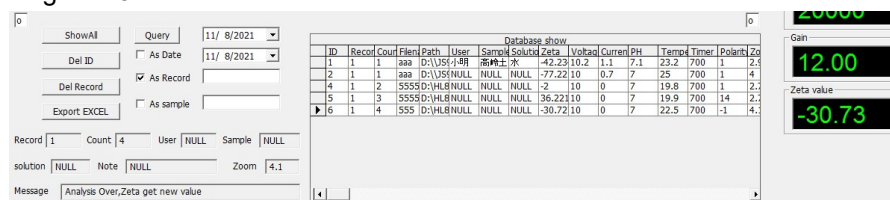


Figure 45 analytical results

Click “EXIT” on the sub interface of computational analysis to terminate computational analysis, return to the main interface and execute next measurement.



If operational mistakes occur during analysis, please click right button of cursor mouse to cancel the input data one by one, and input again. Alternatively, click "CANCEL" button to exit the sub interface, and directly click "Analyzer" to enter again. Then, operate following the above steps.

Note: If the data error is too large, please re-adjust 3D platform and observe cross sign image. Be sure to operate strictly following the above instructions

**Note:**When measuring in a non-aqueous system, the voltage basically needs to be increased, or the liquid needs to be heated. When the voltage is higher than 30V or the temperature is higher than 50 degrees Celsius, the software automatically switches to the calculated value of electrophoretic mobility. For non-aqueous systems, use non-aqueous electrodes.



## Appendix 1 Application example

Put 50 ml NaCl solution with concentration of  $5 \times 10^{-4}$  M in a 100 ml beaker, weigh and add 1 mg R-TiO<sub>2</sub> (Rutile-Titanium) to the solution, dispersing with ultrasonic disperser for 2 min, and measure pH value with pH meter to obtain solution to be measured; then take 1 ml dispersed solution and inject into electrophoresis chamber, insert cross sign, rinse twice, take 0.5 ml dispersed solution and inject into electrophoresis chamber, insert cross sign, and adjust focal length; and subsequently, inject 1 ml dispersed solution into electrophoresis chamber, insert electrode, rinse twice, take 0.5 mL dispersed solution and inject into electrophoresis chamber, insert electrode, and put on 3D platform for measuring to obtain Zeta potential. Rinse the electrophoresis chamber, cross sign and electrode after measurement with deionized water for several times. Dilute the above solution to be measured with dilute acid or dilute base, adjust pH value, and repeat the above steps to measure isoelectric point (to obtain relational graph of Zeta potential versus pH value).

## Appendix 2 Packing list

1. One potentiometer mainframe
2. Ten electrophoresis chambers
3. One platinum electrode
4. One silver electrode
5. One cross sign
6. One electrode wire for backup
7. One serial port extension wire
8. Computer power supply wire
9. One instruction manual
10. USB wire