Chapter 15
Zeta (ζ) Potential for Micelle and Microemulsion

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Abstract Measurement of zeta potential is not applicable to systems with entangled particles, non-charged particles, and concentrated solutions where the interfacial electrical double layers are depressed. However, dispersibility of charged colloidal particles in aqueous solution can be evaluated by ζ potential. Therefore, this chapter deals with the basics of electrical interface phenomenon and its relationship between surface electric potential, zeta potential, and surface charge density.

15.1 Introduction

Measurement of ζ potential is commonly applied to evaluate the dispersibility of charged solid or liquid fine particles in aqueous electrolyte solutions. As the obtained ζ potential itself would not represent the effect of particle size, unit surface charge should be calculated for the evaluation of the object particle. Unit surface charge can be determined from the ζ potential divided by its surface area.

15.2 What Can Be Known from ζ Potential Measurement

Dispersibility of charged colloidal particles in aqueous solutions can be evaluated by the ζ potential. This method is not applicable to systems with entangled particles, non-charged particles, and concentrated solutions where the interfacial electrical double layers are depressed.

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15.3   Measurement of Zeta (ζ) Potential

Many commercial instruments are available for the measurement of zeta (ζ) potential, and the instruction manual should be referred to for actual measurement. Here, we explain theoretical background and measurements following Nicomp Nano 3000 ZLS (PSS Japan) which we use in our laboratory (Fig. 15.1). The characteristic features of Nicomp Nano 3000 ZLS are its capability for low electric field, reduction against Joule heat effect caused by random movement, short time measurement, high reproducibility and reliability, applicability for nonaqueous solution, and compensational function for the charge polarization indispensable to measure highly salted samples. Figure 15.2 shows the basic principle of the Nicomp system, and Fig. 15.3 shows Nicomp's dip cell.

The procedure for measurement is as follows, and data will be shown automatically.

1. Place the sample into the cell shown in Fig.15.3 (left).
2. Set the electrode as shown in Fig.15.3 (right).
3. Select PALS mode shown on the PC monitor.
4. Set the electric field level (normally 5 v/cm or less, c.a. 2 v/cm).
5. Input the viscosity of the solvent (0.8922 for water under 25 °C) and the reflective index of the solvent (1.33287 for water under 25 °C).

15.4   Important Point for the Measurement

The basic principle of this instrument for ζ potential measurement is electrophoretic light scattering (ELS) with two analytical modes, i.e. frequency analysis and phase analysis. There are limitations in frequency analysis for particles with slow mobility because this method is based on the phase shift of frequency spectrum between the
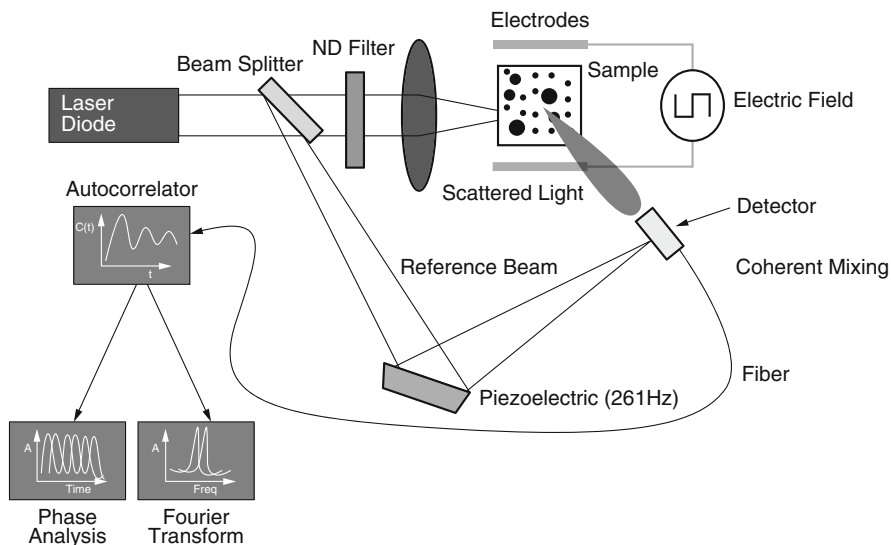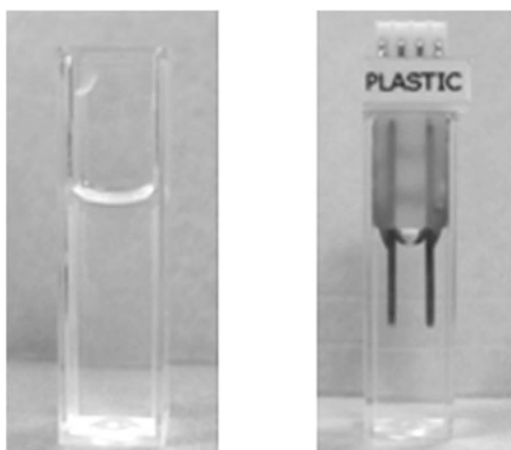
Fig. 15.2 Measurement principle of Nicomp zeta potential analyser

Fig. 15.3 Electrode cell

Nicomp dip cell

particles with and without applied electric field. For example, lower electric field level is preferable to suppress Joule heat and resulted convection heat, but the phase shift will be suppressed, and the S/N ratio lowers and will lose the accuracy of measurement. As a result, it is difficult to measure middle to highly salted samples or organic solvents with a dielectric constant much lower than water, because the particle mobility under electrophoresis is significantly small in both cases.

The value of phase analysis should be noted for these cases, as this method is based on the phase shift from the Doppler effect of the positional change of the particles under electric field application by electrophoresis. This method is insensible to Brownian movement and enables high precision measurement.

15.5 Basics of Electrical Interface Phenomenon [1]

15.5.1 Interfacial Electrical Double Layers

Due to the active Brownian movement in colloidal solutions, coagulation and sedimentation of particles are barely observed under long-term observation despite the frequent collision of particles. Generally, colloidal particles tend to be charged by many causes, such as absorption of ions and electric dissociations. Under different dielectric constants (Dc) between particles and dispersant, larger Dc charges positive, and smaller Dc charges negative. As the total system should remain neutral as a whole, electric charges on particle surfaces have uneven distribution as designated to electrical double layers (EDL). The electric potential difference caused by EDL is called double layer potential (DLP), which exists both on the particle surface and in the surrounding solution, and is determined by the concentration of ions mobile between them. For dissociation of carboxylic groups on the surface, H^+ is the determinant ion. As such, electric properties of solid/liquid interfaces are controlled by DLP.

This EDL concept shown in Fig. 15.4 was proposed by Helmholtz, which explains the electric potential distribution between a flat solid surface with positive charge and the solvent. With the Helmholtz model, EDL can be considered as a planar parallel condenser so that charge density (σ) can be expressed by Eq. (15.1), where ζ is the distance between the positive and negative charges, ε_0 is the dielectric constant for vacuum, and φ_0 is the surface electric potential.

$$\sigma = \frac{\varepsilon_r \varepsilon_0 \phi_0}{\zeta} \tag{15.1}$$

In actuality, electric potential linearly decreases from the solid surface to the bulk solution to become zero, and ions in the solution are attracted to the opposite-charged solid surface while tending to dislocate due to thermal motion at the same time. As a result, the distribution of ions in the EDL is diffusive, determined by the balance between electrostatic attraction and thermal motion. Gouy and Chapman independently proposed diffuse EDL models as shown in Fig. 15.5 with its potential charge profile. Ions with charges opposite to the solid surface distribute widely in the solution, and the average distance from the surface ($1/\kappa$) can be determined by Eq. (15.2) where F is Faraday constant, ε is dielectric constant of the solution, R is Gas constant, T is absolute temperature, and J is ionic strength.

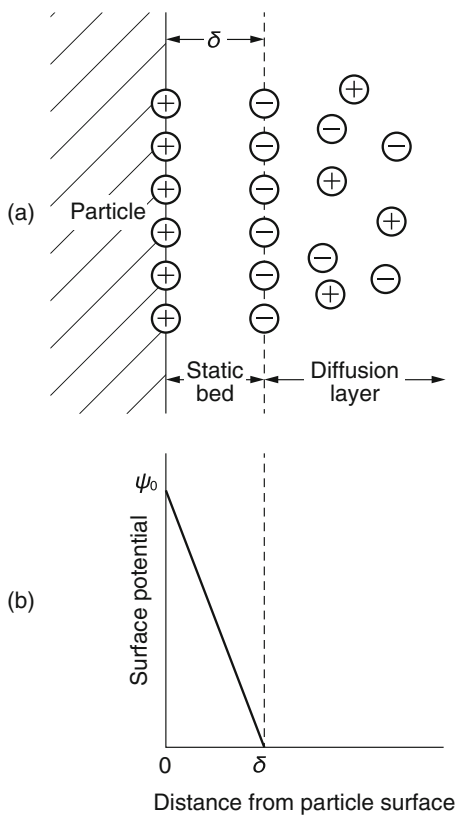**Fig. 15.4** Relationship between electrical double layer of Helmholtz model and change of electric potential

(a) Particle

Static bed

Diffusion layer

(b) ψ_0

Surface potential

0   δ

Distance from particle surface

Fig. 15.5 Relationship between electrical double layer of Gouy-Chapman model and change of electric potential

Particle

$\frac{1}{\kappa}$

ψ

Surface potential

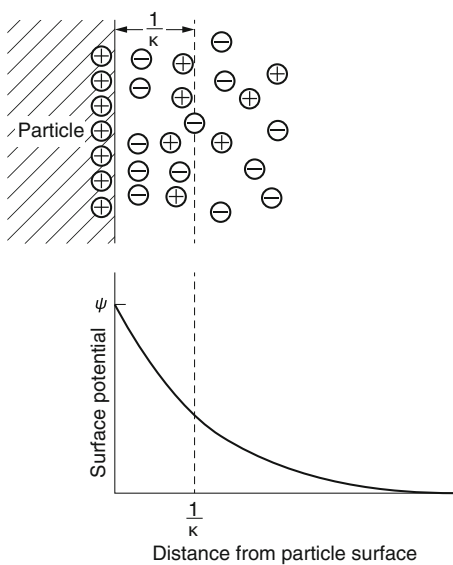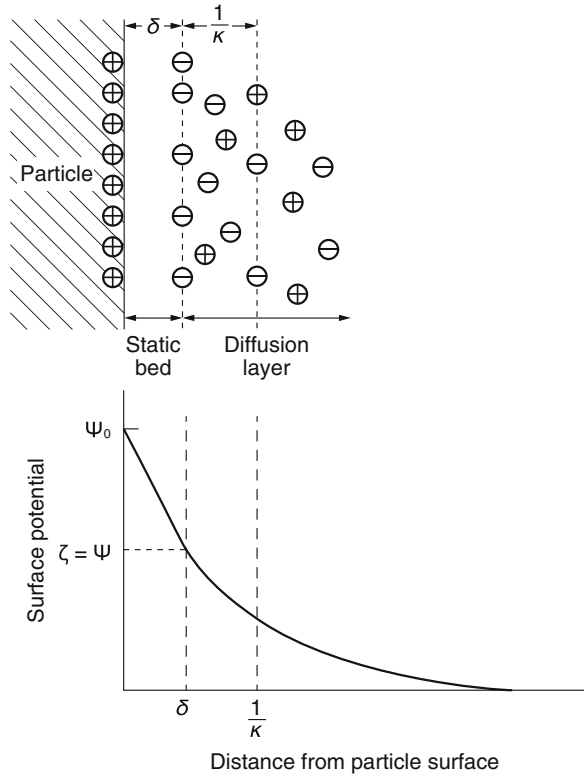$\frac{1}{\kappa}$

Distance from particle surface

Fig. 15.6 Relationship
between electrical double
layer of Stern model and
change of electric potential

$$\kappa = \frac{\left(8\pi F^2\right)^{\frac{1}{2}}}{\left(1000\varepsilon RT\right)^{\frac{1}{2}}\left(J\right)^{\frac{1}{2}}} \qquad (15.2)$$

J is expressed by Eq. (15.3) where Ci and Zi correspond to the concentration and ion valence of ion i.

$$J = \frac{\sum C_i Z_i^2}{2} \qquad (15.3)$$

Increase in the ionic strength by addition of electrolytes in the colloidal solution reduces the thickness $(1/\kappa)$ of EDL from Eqs. (15.2 and 15.3). These equations indicate that the thickness of EDL becomes all the same regardless of the species of ions if the valence of all the ions are equal. In actuality, there are differences in EDL thickness depending on the type of ions. Stern proposed another EDL model to compensate such discrepancies as shown in Fig. 15.6. This model has two layers, an internally fixed Stern layer and a diffuse layer, as a combination of the Helmholtz model and the Gouy-Chapman model. Part of the ions adhere to the Stern layer, and the rest of the ions disperse in the diffuse layer to give a linear potential decrease in

Fig. 15.7 Relationship between potential of solid surface and electrical potential distribution
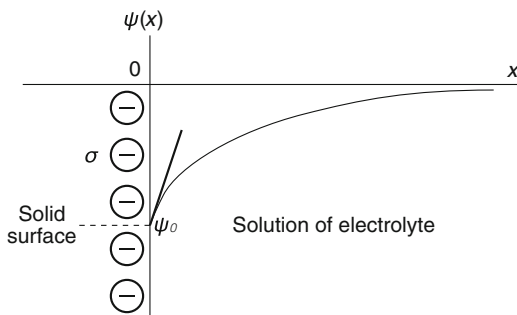
the Stern layer and then exponentially decay in the diffuse layer towards the bulk solution as shown in Fig. 15.6. ζ potential is the electric potential at the plane in between the Stern layer and the diffuse layer called the slipping plane which can be experimentally measured. When the thickness of EDL is negligibly small, it can be equal to the surface potential Ψ. ζ potential correlates to the surface charge density σ and the thickness of EDL ($1/\kappa$) as shown in Eq. (15.4), and ζ increases with the increase of surface charge density or decrease of EDL thickness. ζ potential gives a good indication of the dispersion stability, though DLVO theory is often used for strict discussions.

$$\zeta = \frac{\sigma}{\varepsilon_r \varepsilon_0 \kappa} \tag{15.4}$$

15.5.2 Relationship Between Surface Electric Potential, Z(ζ) Potential, and Surface Charge Density

Figure 15.7 shows electric profiles of charged solid surfaces in electrolyte solutions, where x expresses the distance in the solution from the solid surface and $\Psi(x)$ shows the electric potential of which bulk potential is set to 0 ($\Psi(\infty) = 0$). The solid surface charge is regarded as a constant.

There are two potentials at x = 0. One is $\frac{d\psi}{dx}\big|_{x=+0}$, shown as a tangent thick line in Fig. 15.7, which is the right-side limit value corresponding to the approach from the bulk side which is positive. The other is $\frac{d\psi}{dx}\big|_{x=-0}$ in which the potential value is 0. We take the right-side limit value here for further discussion. Ψ_0 (v) expresses the solid surface potential, and σ (C/m^2) is the surface electric density where the electrolyte is a symmetric type with valence value ν.

$$\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{x=+0} = -\frac{\sigma}{\varepsilon_r\varepsilon_0} \tag{15.5}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{ven}{\varepsilon_r\varepsilon_0}\left[e^{-\frac{\iota e\psi(x)}{kT}} - e^{\frac{ve\psi(x)}{kT}}\right] \tag{15.6}$$

$$\sigma = \sqrt{8CN_A\varepsilon_r\varepsilon_0 kTx10^3}\sinh\left(\frac{ve\psi_0}{2kT}\right) \tag{15.7}$$

where C is concentration (mol/l), N_A is Avogadro's number, e is elementary charge ($e = 1.602 \times 10^{-19}$ C), ε_r is dielectric constant for water (78.5 at 25 °C), ε_0 is dielectric constant for vacuum (78.854×10^{-12}F/m), n is concentration of electrolyte (l/m^3), T is absolute temperature (K), and k is Boltzmann constant (1.38×10^{-23} J/K).

When valence value of the electrolyte is 1 ($v = 1$) and surface potential Ψ_0 (v) is expressed by zeta potential (ζ_0), Eq. (15.7) can be applied to calculate the surface electric potential σ (C/m^2) of the dispersant such as micelles in colloidal solutions by measuring (ζ) vs the concentration of the surfactant.

15.6   Calculation of Surface Electric Potential from the Measured Zeta (ζ) Potential

The zeta (ζ) potential and the particle size of microemulsions consisting of sodium dodecyl-sulphate in 0.086 M NaCl/n-octane/n-hexane are measured at 30 °C. The surface electric potential σ (C/m^2) is calculated by Eq. (15.7) with a valence value 1 as shown in Table 15.1, and both the ζ potential and the particle size are measured.

Table 15.1 Particle sizes and zeta potentials of microemulsion

Concentration of electrolytes (mol/l)	Particle size (diameter) (nm)	Zeta potential (mV)	Surface charge density (C/m^2)
0.08	632	−46.7	①
0.086	34.4	−38.5	②
0.086	48.4	−39.7	③
0.086	55.3	−32.1	④
0.086	61.7	−31.0	⑤

15.7   One-Point Merit for the Determination of Surface Electric Potential

The surface electric potential of particles at a specific concentration and temperature can be determined by measuring the fluid dynamic diameter of particles with dynamic light scattering, which is converted to the surface area. The surface electric potential can be obtained from the surface area by dividing the zeta (ζ) potential as shown in Eq. (15.8), where ζ is zeta potential of the object particle and r is its radius.

$$\zeta/4\pi r^2 \tag{15.8}$$

Reference

1. H. Ohshima, *Theoretical of Colloid and Interfacial Electric Phenomena*, vol 12, 1st edn. (Academic Press, San Diego, 2006)