

### **Evaluation of Colloids by Dielectric Spectroscopy**

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#### 1. Introduction



A colloidal dispersion is a suspension of fine particles composed of molecular assemblies. Since there are interfaces between the particles and the surrounding medium, the colloidal dispersion is regarded as a heterogeneous system. In general, heterogeneous systems are expected to show dielectric relaxation caused by interfacial polarization due to the build-up of charge on the boundaries between the different materials. Indeed, when the permittivity (or dielectric constant) of colloidal dispersions is measured over a wide frequency range, we often observe dielectric relaxation (or dielectric dispersion), in which the permittivity decreases with increasing frequency. The underlying relaxation mechanisms differ from that of pure polar liquids, in which the molecular dipoles change their orientation depending on the applied electric field. Analyzing the dielectric relaxation by an appropriate theory based on interfacial polarization provides valuable information on the structural and electrical properties of colloidal particles [1-7]. In addition, dielectric spectroscopy (or measurements of permittivity as a function of frequency) is suited for in situ characterization of colloidal dispersions because it is a nondestructive method. Hence, the dielectric method described in this article will provide one of the most promising methods for quality control in factories and for continuous monitoring of microbial conditions in brewing.

2. What is permittivity (or dielectric constant)?

Although the permittivity of materials is usually measured by applying an ac field, we first for the sake of simplicity deal with permittivity in a static (dc) electric field. Let us consider a parallel plate capacitor consisting of two flat metal plates separated by a constant distance (Figure 1). When one plate is given a positive charge and the other a negative charge of the same magnitude Q, an electric field is produced in the space between the plates. The charge Q on the plates (termed true charge) is directly proportional to the voltage V between the plates.

$$Q = CV$$

where *C* is the capacitance. When the space is empty, the voltage *V* is given by  $V=Q/C_0$ , where  $C_0$  is the capacitance for the empty capacitor. When an electrically-neutral material is inserted between the plates, positive and negative charges are separated in the material by the charge

on the plates. The induced charge of magnitude *P*, therefore, appears at the surfaces of the material, having opposite polarity to the true charge. The induced charge neutralizes a part of the true charge, resulting in the reduction of voltage between the plates; the voltage is given by  $V=(Q-P)/C_0$ . Alternatively, the voltage is expressed as V=Q/C with the capacitance *C* for the capacitor filled with the material. Hence, the capacitance ratio  $C/C_0$ , that is the relative permittivity  $\varepsilon$ , is

$$\varepsilon = \frac{C}{C_0} = \frac{Q}{Q - P} = \frac{1}{1 - P/Q} \tag{2}$$

The relative permittivity depends on the polarizability of materials. For example, the *P*/*Q* ratio for benzene is 0.6 and thus the relative permittivity becomes 2.5. The relative permittivity of water is 78 at 25°C since *P*/*Q*=0.987. Heterogeneous systems, such as emulsions and biological cell suspensions, frequently show a huge relative permittivity exceeding one thousand. In this case, the value of P approaches that of *Q*; *P*/*Q*=0.999 for  $\varepsilon$ =1000.



Since the capacitance of a parallel plate capacitor is proportional to the surface area S of the plates and to the inverse of the distance d between the plates, the capacitance of the empty capacitor  $C_0$  is

$$C_0 = \varepsilon_0 \frac{S}{d} \tag{3}$$

where  $\varepsilon_0$  is the permittivity of vacuum ( $\varepsilon_0$ =8.8541 pF/m). The capacitance  $C_0$  of the empty capacitor is called the 'cell constant', which is used for the conversion of the measured capacitance into the relative permittivity. The capacitance *C* of the capacitor filled with the material with permittivity  $\varepsilon$  is

$$C = \varepsilon C_0 = \varepsilon \varepsilon_0 \frac{S}{d} \tag{4}$$

When the material is not a pure dielectric, conductive current is observed in proportion to the applied voltage. The conductance is expressed as

$$G = \kappa \frac{S}{d} = \kappa \frac{C_0}{\varepsilon_0} \tag{5}$$

where  $\kappa$  is the conductivity of the material. The conductivity is called the 'dc conductivity', which is distinguished from the 'ac conductivity' attributed to the dielectric nature of the material in an ac field, which is described in the next section.

**3. Description of dielectrics in an ac field** Here we describe how to express the dielectric behavior of materials in an ac field. When a sinusoidal voltage of angular frequency  $\omega$  (=2 $\pi f$ , f is frequency) and amplitude  $V_0$  is applied to a capacitor, we can write

$$V = V_0 \cos \omega t \tag{6}$$

The charge Q on the plates of an empty capacitor is given by

$$Q = C_0 V_0 \cos \omega t \tag{7}$$

The current is obtained by differentiating the charge Q with respect to t.

$$I_{C0} = \frac{dQ}{dt} = C_0 V_0 \omega \cos\left(\omega t + \frac{\pi}{2}\right)$$
(8)

The wave of current precedes that of the voltage by 90 degrees. For convenience, we can introduce complex expressions for the voltage and current as:

$$V^* = V_0 \exp(j\omega t) = V_0(\cos\omega t + j\sin\omega t)$$
(9)

$$I_{C0}^* = C_0 \frac{dV^*}{dt} = j\omega C_0 V^* = C_0 V_0 \omega \left[ \cos\left(\omega t + \frac{\pi}{2}\right) + j\cos\omega t \right]$$
(10)

where  $j = \sqrt{-1}$  and the asterisk refers to the complex quantity. The voltage *V* and current  $I_{c0}$  correspond to the real parts of *V*\* and  $I_{c0}$ \*, respectively. In the case of the capacitor filled with a material, the polarization of the material takes a certain time and thus some delay of the current occurs compared with the current for the empty capacitor. Thus, the phase angle between the current and the voltage becomes smaller than 90 degrees as shown in Figure 2a. The current has two components: the current  $I_{c}^{*}$  in phase with the ac voltage and the charging or displacement current  $I_{c}^{*}$  out of phase by 90 degrees.

$$I_C^* = j\omega C V^* \tag{11}$$

$$I_G^* = G_{ac} V^* \tag{12}$$

where  $G_{ac}$  is the 'ac conductance'. The total current is

$$I^* = I^*_C + I^*_G = (j\omega C + G_{ac})V^*$$
(13)

This relation is represented by an equivalent circuit of capacitance C in parallel with a conductance  $G_{ac}$  (Figure 2b). Using the complex conductivity  $G^*$  defined by



Equation (13) can be rewritten as  $I^*=G^*V^*$ , in the form of Ohm's law for a static field. Integrating the complex current  $I^*$  provides the relationship between the charge  $Q^*$  and the voltage  $V^*$  as

$$Q^* = \int I^* dt = \int (j\omega C + G_{ac}) V^* dt = \left(C + \frac{G_{ac}}{j\omega}\right) V^*$$
(15)

Equation (15) thus has the same form as Equation (1), with the complex capacitance  $C^*$  defined as

$$C^* = C + \frac{G_{ac}}{j\omega} = C - j\frac{G_{ac}}{\omega} = \frac{G^*}{j\omega}$$
(16)

As an analogy of the definition of static relative permittivity, the complex relative permittivity  $\varepsilon^*$  can be defined by the ratio of the complex capacitance  $C^*$  to the capacitance  $C_a$  for the empty capacitor.

$$\varepsilon^* = \frac{C^*}{C_0} = \frac{C}{C_0} - j\frac{G_{ac}}{\omega C_0} \tag{17}$$

Using the relative permittivity  $\varepsilon(=C/C_0)$  and conductivity  $\kappa(=G_{ac}\varepsilon_0/C_0)$ , the complex relative permittivity can be expressed as

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon - j\frac{\kappa}{\omega\varepsilon_0} \tag{18}$$

where  $\varepsilon'$  is the real part of  $\varepsilon^*$  and  $\varepsilon''$  is the imaginary part, called the loss factor.

4. **Dielectric relaxation** When dielectric measurements are carried out over a wide frequency range, we sometimes observe dielectric behavior in which the permittivity decreases and the conductivity increases with increasing frequency (Figure 3a), a phenomenon called dielectric relaxation (or dispersion). A single dielectric relaxation is characterized by a set of parameters, called dielectric parameters, i.e.,  $\varepsilon_l$  and  $\varepsilon_h$  are the limiting values of relative permittivity at low and high frequencies respectively,  $f_0$  is the characteristic frequency,  $\kappa_l$  and  $\kappa_h$  are the limiting values of conductivity at low and high frequencies respectively, and  $\Delta \varepsilon$  (= $\varepsilon_l$ - $\varepsilon_h$ ) is the magnitude of dielectric relaxation. Instead of the conductivity  $\kappa$ , the loss factor  $\varepsilon^{"}(=\kappa/\omega\varepsilon_{0})$  may also be plotted against frequency, giving rise to a peak at the characteristic frequency  $f_{0}$ (Figure 3b). If the dc conductivity  $(=\kappa_{l})$  is not negligible, the loss factor is calculated from  $\varepsilon^{"}=(\kappa-\kappa_{l})/\omega\varepsilon_{0}$ . The complex plane plot, called the Cole-Cole plot, is also used for the analysis of dielectric relaxation (Figure 3c). In the Cole-Cole plot the loss factor is plotted against relative permittivity, tracing a semicircular, circular or skewed arc.



For dielectric relaxation in the radio frequency range, the chief mechanisms are orientation of polar molecules in an electric field and interfacial polarization at the boundary between materials with different electrical properties. Although the dielectric relaxation of a heterogeneous system includes both mechanisms, the main concern is interfacial polarization because, in general, the magnitude of the relaxation due to interfacial polarization is much larger than that due to orientation of polar molecules. Therefore, if the interest is in molecular polarization in heterogeneous systems, it should be discussed after careful consideration of the interfacial polarization.

Next, we shall discuss the dielectric relaxation due to interfacial polarization in the case of a water-in-oil emulsion (Figure 4). When a static field is applied, ions in the water droplets move to and stay at the water-oil interface, polarizing the emulsion. The polarization occurs in an alternating field whose frequency is sufficiently low, resulting in a high relative permittivity at low frequencies. The relative permittivity decreases with increasing frequency because the polarization is slow compared with the speed of the alternating field. The delay of the polarization results in the increase in conductivity at high frequencies as described above.



Figure 4. Polarization of a W/O emulsion in an ac field.

In order to analyze the dielectric behavior of suspensions of spherical particles quantitatively, several mixture equations were proposed. Here, we shall confine our attention to Hanai's equation [8, 9], which provides better simulation for various colloidal dispersions over a wide range of volume fraction up to 0.8. When spherical particles of complex relative permittivity  $\varepsilon_p^*$  are suspended in the medium of  $\varepsilon_a^*$  at volume fraction  $\Phi$  (Figure 5), the complex relative permittivity of the suspension  $\varepsilon^*$  is

$$\frac{\boldsymbol{\varepsilon}^* - \boldsymbol{\varepsilon}_p^*}{\boldsymbol{\varepsilon}_a^* - \boldsymbol{\varepsilon}_p^*} \left(\frac{\boldsymbol{\varepsilon}_a^*}{\boldsymbol{\varepsilon}^*}\right)^{1/3} = 1 - \Phi \tag{19}$$



Figure 5. An electrical model for a suspension of spherical particles.



#### 5. Emulsion

#### 5.1 Water-in-Oil (W/O) emulsion [10, 11]

In the case of a water-in-oil (W/O) emulsion, where water droplets are suspended in an oil phase, we may assume that the conductivity of the oil phase is much lower than that of the water droplets. In this case the following approximate equations are derived from Equation (19).

$$\Phi = 1 - \left(\frac{\varepsilon_a}{\varepsilon_l}\right)^{1/3} \tag{20}$$

$$\kappa_a = \kappa_l (1 - \Phi)^3 \tag{21}$$

$$\varepsilon_p = \varepsilon_a + \frac{\varepsilon_h - \varepsilon_a}{1 - \left(\frac{\varepsilon_h}{\varepsilon_l}\right)^{1/3}} \tag{22}$$

$$\kappa_p = \kappa_h \frac{1 - \frac{1}{3} \left(2 + \frac{\varepsilon_a}{\varepsilon_h}\right) \left(\frac{\varepsilon_h}{\varepsilon_l}\right)^{1/3}}{\left[1 - \left(\frac{\varepsilon_h}{\varepsilon_l}\right)^{1/3}\right]^2}$$
(23)

Using these equations we can estimate the volume fraction  $\Phi$  of the water droplets, the conductivity  $\kappa_a$  of the oil phase, and the relative permittivity  $\varepsilon_p$  and conductivity  $\kappa_p$  of the water phase from the dielectric parameters ( $\varepsilon_l$ ,  $\varepsilon_h$ ,  $\kappa_l$  and  $\kappa_h$ ) observed for the W/O emulsion and the relative permittivity  $\varepsilon_a$  measured separately for the oil phase.

Figure 6 shows an example of dielectric measurements for a W/O emulsion. The oil phase was a mixture of kerosene and carbon tetrachloride (72:28 V/V). The W/O emulsion was prepared by mixing distilled water with the oil containing 0.4% (V/V) Span 80 as an emulsifier. The volume fraction of the water in the emulsion was 0.75. Dielectric relaxation is clearly found, from which the dielectric parameters are extracted. Using the dielectric parameters, the phase parameters are calculated from Equations (20)-(23), as listed in Table 1. The volume fraction is consistent with the volume ratio of water in the emulsion. The values of  $\kappa_p$  and  $\varepsilon_p$  are in good agreement with the conductivity and relative permittivity of the water phase separated from the oil phase by centrifugation after the measurement.



Figure 6. Dielectric relaxation of a W/O emulsion.

The open circles indicate the measured data. The solid lines are the theoretical curves.

#### Table 1. Dielectric analysis for a W/O emulsion.

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Measured dielectric parameters

\varepsilon_r=121, \varepsilon_n=30.6, \kappa_r=1.27 nS/cm, \kappa_n=0.700 µS/cm, f_0=11.3 kHz

Volume fraction in preparation

\Phi=0.75

The parameters of the oil and water phases separated from the emulsion after its

dielectric measurement

\varepsilon_a=2.23, \varepsilon_p=78.5, \kappa_p=3.09 µS/cm
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Estimated phase parameters \Phi=0.736, \kappa_a=0.023 nS/cm, \epsilon_p=79.6, \kappa_p=2.93 \muS/cm
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### 5.2 Oil-in-Water (O/W) emulsion [12-14]

For oil-in-water (O/W) emulsions, in which oil droplets are suspended in a water phase, the conductivity of the oil droplets is negligibly small compared with that of the aqueous phase. Assuming that  $\kappa_p <<\kappa_a$  we obtain the following equations from Equation (19):

$$\varepsilon_l = \frac{3}{2}\varepsilon_p + \left(\varepsilon_a - \frac{3}{2}\varepsilon_p\right)(1 - \Phi)^{3/2}$$
(24)

$$\left(\frac{\varepsilon_h - \varepsilon_p}{\varepsilon_a - \varepsilon_p}\right) \left(\frac{\varepsilon_a}{\varepsilon_h}\right)^{1/3} = 1 - \Phi \tag{25}$$

$$\kappa_l = \kappa_a (1 - \Phi)^{3/2} \tag{26}$$

$$\kappa_h = \kappa_a \frac{\varepsilon_h (\varepsilon_h - \varepsilon_p) (2\varepsilon_a + \varepsilon_p)}{\varepsilon_a (\varepsilon_a - \varepsilon_p) (2\varepsilon_h + \varepsilon_p)}$$
(27)

Using these equations, we can assess the magnitude of dielectric relaxation of O/W emulsions. When the relative permittivity is 78 for the water phase and 2.5 for the oil phase and the volume fraction is 0.7, the magnitude of the relaxation  $\Delta \epsilon$  becomes 0.15, which is too small to detect.

In general, most O/W emulsions do not give a detectable relaxation magnitude as expected from the numerical assessment. However, the use of an oil with a higher relative permittivity value leads to a definite dielectric relaxation. Figure 7 shows an example with a nitrobenzene( $\epsilon$ =35)/water emulsion.



Figure 7. Dielectirc relaxation of a nitrobenzene/water emulsion.

6. Ion-exchange resin particles [15-19] Column chromatography is widely used for separation of ions and organic molecules. One of the packing materials is ion-exchange resin, whose electrical properties can be evaluated by dielectric spectroscopy. As an example we describe the dielectric analysis of Sulfopropyl(SP)-Sephadex beads. The beads are swollen in water to be spheres of about 100  $\mu$ m in diameter. The matrixes of the beads have negative fixed charges, whose density is about 0.25 mole/dm<sup>3</sup>.

The relative permittivity and conductivity of a bed of the SP-Sephadex beads in distilled water show a typical dielectric relaxation as shown in Figure 8. Since the interior of the bead has movable counter-ions around the fixed charges, the conductivity of the bead is higher than that of the external medium (distilled water), i.e.,  $\kappa_p > \kappa_a$ . However, the assumption of  $\kappa_p >> \kappa_a$  that holds for W/O emulsions is not necessarily applicable to the ion-exchange resin beads because the conductivity of the beads depends on the fixed charge density. The analysis for the ion-exchange resin beads, therefore, is based on the following general equations derived without approximations.



$$P = \left(\frac{\kappa_a}{\kappa_l} + 2\right) \varepsilon_l D - 3[\varepsilon_h D - \varepsilon_a (D - 1)] D + \left(\frac{\kappa_l}{\kappa_a} - 1\right) \varepsilon_a D$$
(30)

$$Q = 3[2\varepsilon_h D - \varepsilon_a (D-1)] - \left[ \left( \frac{\kappa_a}{\kappa_l} + 2 \right) D + 3 \right] \varepsilon_l - \left( \frac{\kappa_l}{\kappa_a} - 1 \right) \varepsilon_a D$$
(31)

$$C = \frac{-Q - \sqrt{Q^2 - 4PR}}{2P} \tag{32}$$

$$f(\kappa_a) \equiv \left[3 - \left(2 + \frac{\varepsilon_a}{\varepsilon_h}\right)C\right](1 - DC)\kappa_h - 3\{\kappa_l - [\kappa_a(D - 1) + \kappa_l]C\}(1 - C)$$

$$+\kappa_a \left(1 - \frac{\varepsilon_h}{\varepsilon_a}\right) C(1 - DC) = 0 \tag{33}$$

$$\Phi = 1 - \left(\frac{\varepsilon_a}{\varepsilon_h}\right)^{1/3} C \tag{34}$$

$$\varepsilon_p = \frac{\varepsilon_h - \varepsilon_a C}{1 - C} \tag{35}$$

$$\kappa_p = \frac{\kappa_l - \kappa_a DC}{1 - DC} \tag{36}$$

Figure 9. Flow chart of the computer program for

estimated by a successive approximation.  $K_{a,i}$  is an initial value of  $K_a$ .

dielectric analysis of ion-exchange resins.  $K_a$  is



Use of these equations enables us to calculate the phase parameters ( $\kappa_a$ ,  $\Phi$ ,  $\varepsilon_p$ ,  $\kappa_p$ ) from the dielectric parameters ( $\varepsilon_v$ ,  $\varepsilon_h$ ,  $\kappa_l$ ) and the relative permittivity of the medium  $\varepsilon_a$  according to the flow chart shown in Figure 9. The phase parameters estimated for the dielectric relaxation shown in Figure 8 are listed in Table 2. The internal conductivity of the ion-exchange resin is much higher than the external conductivity. With the estimated internal conductivity Ishikawa et al. discussed the mobility of counter ions and the interactions between the counter ions and the fixed ionic residues in the ion-exchange resin [16-19].

Table 2. Dielectric analysis for an ion-exchange resin suspension.

Measured dielectric parameters  $\epsilon_{r}$ =855.6,  $\epsilon_{b}$ =66.3,  $\kappa_{r}$ =0.303 mS/cm,  $\kappa_{b}$ =10.3 mS/cm,  $f_{o}$ =13.1 MHz

The phase parameters measured for the external medium  $\epsilon_{a}\text{=}76.0,\,\kappa_{a}\text{=}2.35\,\mu\text{S/cm}$ 

Estimated phase parameters  $\Phi$ =0.568,  $\kappa_{a}$ =25.6  $\mu$ S/cm,  $\varepsilon_{b}$ =59.4,  $\kappa_{b}$ =16.9 mS/cm

7. Microcapsules [20-23] Microcapsules are widely used in pharmaceutical, food and industrial fields. There are many kinds of microcapsules made from various materials. Here, we choose polystyrene microcapsules because of their simple and well-defined structure. Polystyrene microcapsules have the shell-sphere structure in which an aqueous core is covered with a thin insulating shell of polystyrene. Thus, the polystyrene microcapsule is represented by the 'single-shell' model shown in Figure 10. The complex relative permittivity ε\* of the microcapsule suspension is given by Equation (19)

$$\frac{\boldsymbol{\varepsilon}^* - \boldsymbol{\varepsilon}_p^*}{\boldsymbol{\varepsilon}_a^* - \boldsymbol{\varepsilon}_p^*} \left(\frac{\boldsymbol{\varepsilon}_a^*}{\boldsymbol{\varepsilon}^*}\right)^{1/3} = 1 - \Phi \tag{19}$$

with the equivalent complex relative permittivity  $\varepsilon_p^*$  of the shell-sphere consisting of the core of  $\varepsilon_i^*$  and the shell of  $\varepsilon_s^*$ . The  $\varepsilon_p^*$  is expressed as

$$\varepsilon_p^* = \varepsilon_s^* \frac{2(1-\nu)\varepsilon_s^* + (1+2\nu)\varepsilon_i^*}{(2+\nu)\varepsilon_s^* + (1-\nu)\varepsilon_i^*}$$
(37)

where  $v = (1-d/R)^3$ , *d* is the shell thickness, and *R* is the radius of the shell-sphere.



Figure 11 shows the results of dielectric measurements for a dense suspension of polystyrene microcapsules. Unlike W/O emulsions there are two relaxations, which correspond to the inner and outer interfaces of the shell. When the KCl concentration of the inner aqueous phase is fixed, only the low-frequency relaxation, termed the P-relaxation, shifts to lower frequencies with decreases in the KCl concentration of the outer aqueous phase. On the other hand, the high-frequency relaxation, termed the Q-relaxation, depends only on the inner KCl concentration. This suggests that the P-relaxation is attributed to the polarization at the outer interface and the Q-relaxation is due to the polarization at the inner interface.



The double relaxation is characterized with the dielectric parameters indicated in Figure 12. They are the two characteristic frequencies  $f_p$  and  $f_q$  for the P-and Q-relaxations, respectively, the low-frequency limits of the relative permittivity  $\varepsilon_i$  and conductivity  $\kappa_p$  the high-frequency limits of the relative permittivity  $\varepsilon_h$  and conductivity  $\kappa_h$ , and the relative permittivity  $\varepsilon_m$  in the middle of the two relaxations.



Figure 12. Dielectric relaxation of a dense suspension of polystyrene microcapsules.

The open circles indicate the measured data and the solid lines are the theoretical curves.

The relationships between the dielectric parameters and the phase parameters are derived from Equations (19) and (37) assuming that the conductivity of the shell phase is much less than that of the outer and inner aqueous phases. The equations are as follows:

$$f(\Phi) \equiv \frac{\kappa_m}{\kappa_l} (1-\Phi)^{1/2} - \frac{\varepsilon_m + 2\varepsilon_a - 3\varepsilon_a (1-\Phi) \left(\frac{\varepsilon_m}{\varepsilon_a}\right)^{1/3}}{3\varepsilon_m - (2\varepsilon_m + \varepsilon_a)(1-\Phi) \left(\frac{\varepsilon_m}{\varepsilon_a}\right)^{1/3}} \left(\frac{\varepsilon_m}{\varepsilon_a}\right)^{4/3} = 0$$
(38)

$$\kappa_a = \frac{\kappa_l}{\left(1 - \Phi\right)^{3/2}} \tag{39}$$

$$\varepsilon_{ql} = \varepsilon_a + \frac{\varepsilon_m - \varepsilon_a}{1 - (1 - \Phi) \left(\frac{\varepsilon_m}{\varepsilon_a}\right)^{1/3}}$$
(40)

$$v = \frac{\varepsilon_{ql} - \varepsilon_s}{\varepsilon_{ql} + 2\varepsilon_s} \tag{41}$$

$$d = R(1 - v^{1/3}) \tag{42}$$

$$\varepsilon_{qh} = \varepsilon_a + \frac{\varepsilon_h - \varepsilon_a}{1 - (1 - \Phi) (\frac{\varepsilon_h}{\varepsilon_a})^{1/3}}$$
(43)

$$\varepsilon_i = \frac{\varepsilon_{qh}(\varepsilon_{ql} + \varepsilon_s) - 2\varepsilon_s^2}{\varepsilon_{ql} - \varepsilon_{qh}}$$
(44)

$$\kappa_{qh} = \frac{1}{3(\varepsilon_a - \varepsilon_h)} \bigg[ (\varepsilon_a - \varepsilon_{qh})(2\varepsilon_h + \varepsilon_{qh}) \frac{\kappa_h}{\varepsilon_h} - (\varepsilon_h - \varepsilon_{qh})(2\varepsilon_a + \varepsilon_{qh}) \frac{\kappa_a}{\varepsilon_a} \bigg]$$
(45)

$$\kappa_{i} = \kappa_{qh} \frac{\left(\varepsilon_{ql} + \varepsilon_{i} + \varepsilon_{s}\right)^{2}}{\left(\varepsilon_{ql} + 2\varepsilon_{s}\right)\left(\varepsilon_{ql} - \varepsilon_{s}\right)}$$
(46)

Figure 13 shows a flow chart describing the procedure for estimation of the phase parameters from the dielectric parameters using Equations (38)-(46). According to the flow chart we can calculate the volume fraction, the shell thickness, and the relative permittivity and conductivity of the inner aqueous phase. Table 3 shows the results for the data shown in Figure 12. The theoretical curves calculated from the estimated phase parameters are in good agreement with the observed curves. The same dielectric analysis is also applicable to similar microcapsules with an insulating shell, such as polymethylmethacrylate microcapsules [22, 23]. For microcapsules with a leaky shell, however, the rather simple analysis described is no longer applicable and more sophisticated methods are required such as computer-assisted curve fitting using the general equations without the assumptions.

Table 3. Dielectric analysis of a microcapsule suspension.

Measured dielectric parameters  $\epsilon_{i}$ =156.0,  $\epsilon_{n}$ =103.6,  $\epsilon_{o}$ =62.0,  $\kappa_{i}$ =0.424  $\mu$ S/cm,  $\kappa_{n}$ =0.787  $\mu$ S/cm,  $\kappa_{h}$ =79.2  $\mu$ S/cm,  $f_{p}$ =14 kHz,  $f_{q}$ =3.4 MHz

Measured phase and morphological parameters  $\epsilon_a{=}80.0,\,\epsilon_s{=}2.65,\,R{=}175\,\mu\text{m}$ 

Estimated phase parameters  $\Phi$ =0.575,  $\kappa_a$ =1.53 µS/cm,  $\epsilon_i$ =86.7,  $\kappa_i$ =350 µS/cm, d=3.7 µm



Figure 13. Flow chart of the computer program for dielectric analysis of polystyrene microcapsules.  $\Phi$  is estimated by a successive approximation.  $\Phi$ , is an initial value of  $\Phi$ .

## 8. Biological cells and their models

#### 8.1 Liposomes [24]

Liposomes are vesicles with lipid bilayer membranes which are spontaneously formed by mixing phospholipids in an aqueous medium. The liposomes are regarded as a model of biological cells. Figure 14 shows the dielectric relaxation obtained for lecithin liposomes of a few  $\mu$ m in diameter suspended at  $\Phi$ =0.45. Although liposomes are represented by the shell-sphere model as well as microcapsules, the suspension of the liposomes did not show the double relaxation of the polystyrene microcapsules. According to numerical assessments using Equations (19) and (37), this is because the membrane is very thin and the conductivity of the internal phase is similar to that of the external medium.



Figure 14. Dielectric relaxation of a liposome suspension.

#### 8.2 Biological cells [25-35]

Biological cells are also represented by the shell-sphere model. The thickness of the plasma membrane is 5-10 nm, the same order as that of liposome membranes. Hence, biological cells hold for the conditions that d/R <<1. The conductivity of the plasma membrane of viable cells is negligibly small compared with that of the external medium and the cytoplasm. Using these assumptions, the following equations are obtained:

$$\Phi = 1 - \left(\frac{\kappa_l}{\kappa_a}\right)^{2/3} \tag{47}$$

$$C_m = \frac{\varepsilon_s \varepsilon_0}{d} = \frac{2\varepsilon_0}{3R} \left[ \frac{\varepsilon_l - (1 - \Phi)^{3/2} \varepsilon_a}{1 - (1 - \Phi)^{3/2}} \right] = \frac{2\varepsilon_0}{3R} \left[ \frac{\varepsilon_l \kappa_a - \kappa_l \varepsilon_a}{\kappa_a - \kappa_l} \right]$$
(48)

$$\varepsilon_{i} = \frac{\varepsilon_{h} \left(\frac{\varepsilon_{a}}{\varepsilon_{h}}\right)^{1/3} - \varepsilon_{a}(1-\Phi)}{\left(\frac{\varepsilon_{a}}{\varepsilon_{h}}\right)^{1/3} - (1-\Phi)}$$
(49)

$$\kappa_{i} = \frac{\kappa_{h} \left(\frac{3}{\varepsilon_{h} - \varepsilon_{i}} - \frac{1}{\varepsilon_{h}}\right) - \kappa_{a} \left(\frac{3}{\varepsilon_{a} - \varepsilon_{i}} - \frac{1}{\varepsilon_{a}}\right)}{3 \left(\frac{1}{\varepsilon_{h} - \varepsilon_{i}} - \frac{1}{\varepsilon_{a} - \varepsilon_{i}}\right)}$$
(50)

The volume fraction is obtained from Equation (47) with the values of  $\kappa_i$  and  $\kappa_a$  observed for the suspension and for the medium, respectively. With the mean radius of the cell estimated by microscopy, the membrane capacitance is calculated from Equation (48). The relative permittivity and conductivity of the cytoplasm are estimated from Equations (49) and (50). Figure 15 shows the dielectric relaxation of the suspension of human erythrocytes (red blood cells) that are swollen in hypotonic medium. Since the swollen erythrocyte is spherical and has no intracellular structure, the shell-sphere model is applicable to it. The results are shown in Table 4. With the value of 0.66  $\mu$ F/cm<sup>2</sup> for the membrane capacitance, the thickness of the hydrophobic region in the plasma membrane is estimated to be 2.5-3.7 nm assuming that its relative permittivity is 2-3.

Table 4. Dielectric analysis of a human erythrocyte suspension.

Measured dielectric parameters  $\epsilon_{r}$ =2195,  $\epsilon_{h}$ =67,  $\kappa_{r}$ =3.65 mS/cm,  $\kappa_{h}$ =6.98 mS/cm,  $f_{0}$ =2.6 MHz

Measured phase and morphological parameters  $\epsilon_a$ =78,  $\kappa_a$ =8.57 mS/cm, *R*=3.4  $\mu$ m

Estimated phase parameters  $\Phi$ =0.434,  $C_m$ =0.66 µF/cm<sup>2</sup>,  $\varepsilon_i$ =54,  $\kappa_i$ =5.2 mS/cm



Figure 15. Dielectric relaxation of a human erythrocyte suspension.

Since most cells have organelles in the cytoplasm unlike erythrocytes, their electrical models become complicated. Yeast cells with a large vacuole and lymphocytes with a sizable nucleus are represented by the 'double-shell' model [27, 28] (Figure 16a). With such a complicated model, the phase parameters can no longer be simply calculated from the dielectric parameters as described above but can be estimated through computer-assisted curve fitting. For the non-spherical cells, such as E. coli and intact erythrocyte, the shell-ellipsoid model (ellipsoid covered with a thin shell) is available [29, 30] (Figure 16b).



# (b) Shell-ellipsoid model.

#### 8.3 Dielectric monitoring of yeast in fermentation [36-38]

Since the magnitude of the dielectric dispersion  $\Delta \varepsilon$  is proportional to the cell concentration  $N_c$  for a dilute cell suspension(P << 1), the cell concentration in cell culture can be monitored by the dielectric method. The relation between  $\Delta \varepsilon$  and  $N_c$  is expressed as

$$\Delta \varepsilon \approx \frac{9\Phi RC_m}{4\varepsilon_0} = \frac{3\pi R^4 C_m}{\varepsilon_0} N_c \tag{51}$$

where  ${\it R}$  is the cell radius and  ${\it C}_{\rm m}$  is the membrane capacitance, which is regarded as a constant (usually between 0.5-2  $\mu$ F/cm<sup>2</sup> depending on the cell type). The magnitude of the dielectric dispersion is proportional to the 4th-power of the cell radius. The sensitivity of the dielectric method for measuring cell concentration depends on the cell radius. In the case of yeast cells, which have a radius of a few µm, the detection limit is about

10<sup>7</sup> cell/ml. When the relative permittivity of the culture broth is monitored during cultivation, the cell growth curve can be obtained. A typical result for yeast cell culture is shown in Figure 17, where the increment of the relative permittivity is plotted logarithmically versus cultivation time. There are two phases in the plots, which correspond to the logarithmic growth phase (up to 10 hr) and the stationary phase. The generation time or growth rate of the yeast is calculated from the slope of the straight line in the logarithmic growth phase.





The dielectric monitoring of cell growth in culture has several advantages over conventional methods as follows: (1) real-time and automated monitoring, (2) applicability to turbid and colored culture medium, (3) direct measurement of cell number or mass and (4) counting of only viable cells because dead cells, which have plasma membranes which are leaky to ions, are not polarized. These advantages enable continuous monitoring and control of fermentation in brewing.

9. A summary of dielectric behavior of colloidal dispersions [39]
The characteristics of dielectric behavior in colloidal dispersions are summarized in Table 5. The number of dielectric relaxations theoretically expected for a colloidal dispersion is identical to the number of different interfaces found in it. In practice, however, all relaxations predicted are not observed because of the limited frequency range and the limited sensitivity of the measurements. With reference to the examples described in this article, the structure and electrical properties of the colloidal dispersion concerned would be determined from its dielectric relaxation using an appropriate model.

Colloidal dispersion		Number of dielectric relaxations	Models
Emulsions	W/O type	1	Sphere
	O/W type	0-1	Sphere
Ion-exchange resin particles		1	Sphere
Microcapsules		2	Shell-sphere
Liposomes		1	Shell-sphere
Biological cells	Erythrocyte	1	Shell-sphere
	Yeast Lymphocyte	1-3	Double-shell
	E. coli	>2	Shell-ellipsoid

Table 5. Summary of the dielectric behavior of colloidal dispersions.

In this article I have dealt with colloidal dispersions with relatively large particles whose radius *R* is much larger than the Debye screening length *l*, which is a measure of the thickness of the diffuse double laver surrounding the particles. Under the conditions of R >> l, dielectric relaxation of colloidal dispersions can be interpreted by interfacial polarization alone. However, when the radius of particles approaches the Debye screening length, dielectric behavior of colloidal dispersions is influenced by electrodiffusion processes in the vicinity of particle surfaces [3]. For these systems, therefore, more sophisticated models should be used, instead of the interfacial polarization models.

10. Dielectric measurement In order to study the dielectric relaxation of a colloidal dispersion, it is [40, 41]necessary to measure its permittivity and conductivity over a wide frequency range. Recently, instruments suited for dielectric spectroscopy have become commercially available. Although well-advanced instruments enable us to easily get accurate dielectric spectra without knowledge on dielectric measurement, it is worth noting that dielectric measurement includes various errors to be corrected.

> The raw data include errors due to stray capacitance and residual inductance arising from the measurement cell (or electrodes) and its connecting leads. Correction for the stray capacitance and the residual inductance, therefore, is requisite, especially at high frequencies (>10 MHz). For details of the correction, readers are referred to Refs. 40 and 41.

In addition, electrode polarization due to the electrical double layer between electrode surfaces and electrolytes becomes a serious problem at low frequencies (<1 MHz). When an electrolyte solution (e.g., a 100-mM KCl solution) is measured, an enormous increase in capacitance is seen at low frequencies (Figure 18, the capacitance of the electrolyte should be independent of frequency). The increase in capacitance at low frequencies is not due to the intrinsic property of the electrolyte solution but due to the electrode polarization artifact which depends on the surface properties and geometry of the electrodes and conductivity of the solution. For example, the use of platinized Pt electrodes (Pt-black electrodes) reduces the artifact above 100 Hz compared with the use of bare (bright) Pt electrodes, as shown in Figure 18.



Figure 18. Frequency dependence of capacitance and conductance of a capacitor filled with a 100 mM KCI solution.

The open circles indicate data obtained with bright Pt electrodes and the closed circles indicate data obtained with platinized Pt electrodes.

However, a new technique which is free from electrode polarization has been developed recently. The method is based on electromagnetic induction and uses a probe, consisting of two concentric toroidal coils covered with epoxy resin, which is immersed in the sample. Although the frequency range is limited to between 200 kHz and 20 MHz at present, the method is a promising new tool for evaluation of the dielectric properties of colloidal dispersions.

#### Nomenclature C = Capacitance(F, Farad) $G = \text{Conductance (S, Siemens, inverse } \Omega \text{ (Ohm)})$ I = Current(A, Ampere)Q = Charge(C, Coulomb)V = Voltage (V, Volt)f = Frequency (Hz, Hertz) $\Phi$ = Volume fraction $\epsilon$ = Permittivity (F/m, Farad per meter) or relative permittivity $\kappa$ = Conductivity (S/m, Siemens per meter) $\omega$ = Angular frequency (=2 $\pi f$ , rad/s) 1. van Beek L.K.H., Dielectric Behaviour of Heterogeneous Systems. References In Progress in Dielectrics. vol.7, Edited by J.B. Birks, London Heywood Books, pp.69-114 (1967)Hanai T., Electrical Properties of Emulsions. In Emulsion Science. Edited by P.Sherman, 2.Academic Press, pp.353-478 (1968) 3. Dukhin S.S., Dielectric Properties of Disperse Systems. In Surface and Colloid Science. Vol.3, Edited by E. Matijevic, John Wiley & Sons, pp.83-165 (1971) Pethig R., Dielectric and Electronic Properties of Biological Materials. John Wiley & Sons 4. (1979)5. Clausse M., Dielectric Properties of Emulsions and Related systems. In Encyclopedia of Emulsion Technology. Vol.1, Edited by P. Becher, Marcel Dekker, pp.481-715.(1983) 6 Foster K.R., Schwan H.P. Dielectric Properties of Tissues. In Handbook of Biological Effects of Electromagnetic Fields. Edited by C. Polk and E.Postow, CRC Press, pp.27-96, (1986) Takashima S., Electrical Properties of Biopolymers and Membranes. Adam Hilger (1989) 7. 8. Hanai T., Kolloid Zeitschrift, 171, 23-31 (1960) Hanai T., Kolloid Zeitschrift, 175, 61-62 (1961) 9. Hanai T., Kolloid Zeitschrift, 177, 57-61 (1961) 10 11. Hanai T., Imakita T., Koizumi N., Colloid Polymer Sci, 260, 1029-1034 (1982) Hanai T., Koizumi N., Gotoh R., Kolloid Zeitschrift 167, 41-43(1959) 12. 13. Hanai T., Koizumi N., Gotoh R., Kolloid Zeitschrift 171, 20-23(1960) Hanai T., Koizumi N., Gotoh R., Kolloid Zeitschrift 184, 143-148 (1962) 14. Ishikawa A., Hanai T., Koizumi N., Japanese J. Appl. Phys., 20, 78-86 (1981) 15. Ishikawa A., Hanai T., Koizumi N., Japanese J. Appl. Phys., 21, 1762-1768 (1982) 16. Ishikawa A., Hanai T., Koizumi N., Japanese J. Appl. Phys., 22, 942-947 (1983) 17. Ishikawa A., Hanai T., Koizumi N., Colloid & Polym. Sci., 262, 477-480 (1984) 18. Ishikawa A., Hanai T., Koizumi N., Colloid & Polym. Sci., 263, 428-432 (1985) 19

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