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Dielectric measurement of a single sub-millimeter size microcapsule

K. Asami and K. S. Zhao[1]

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
[1] Department of Chemistry, Northeast Normal University, Changchun, China

Abstract: A new technique is described for measuring dielectric dispersion of a single microcapsule in suspension over a frequency range from 1 kHz to 10 MHz. It was applied to polystyrene microcapsules which showed a two-step dielectric dispersion, that is, a superposition of two Debye type dispersions. The dielectric dispersion was analyzed by an electrical model in which a spherical core covered with a shell is immersed in a continuous phase, yielding the phase parameters related to the microcapsule: the wall thickness, the permittivity and conductivity of the core phase. The advantage of this technique is that it can characterize individual microcapsules, whereas the conventional method provides average properties of many microcapsules. Hence, the technique enables us to directly determine the distributions of the phase parameters and to exactly examine the relationship between the dielectric behavior and the microcapsule structure simultaneously observed by microscopy.

Key words: Dielectric dispersion – polystyrene microcapsule – interfacial polarization – single-capsule measurement – three-terminal method

Introduction

Dielectric techniques are useful to elucidate the structural and electrical properties of microcapsules that are widely used in pharmaceutical, food, and industrial fields. Zhang et al. [1, 2] reported that a dense suspension of polystyrene microcapsules showed a two-step dielectric dispersion that was caused by charging process at the two interfaces of the capsule wall. The analysis of the dielectric dispersion by a dielectric theory based on interfacial polarization provided the structural and electrical parameters of the microcapsules, namely, the wall thickness, the internal permittivity and conductivity, and the external conductivity. This method, however, has the following limitations, because the analysis is based on the assumption that all microcapsules have uniform structural and electrical parameters. Prior to the dielectric measurements, it is necessary to fractionate microcapsules, although available fractionation techniques cannot make microcapsules uniform in all electrical and structural parameters but only in size and density (or wall thickness). When there is a distribution of the internal conductivity, which usually results from some variations in the ion leakage rate through the walls, the dielectric theory becomes complicated [3, 4] and the analysis is possible only under limited conditions [5]. The experimental limitations and theoretical complexity might be circumvented by a new technique that analyzes dielectric behavior of a single microcapsule.

Asami et al. developed a technique measuring a single millimeter-size sphere in suspension, by which glass, gelatin and steel beads [6], spherical bilayer lipid membranes [7], fish eggs [8], and gelatin balls covered with a biological cell monolayer [9] were studied. Because this technique was based on the two-terminal method, a closed-type chamber was needed for the measurements in order to avoid the fringing field at the edge of electrodes. In this study, we adopt the three-terminal method, which eliminates the fringing field effects and enables us to design an open-type chamber, in which a sub-millimeter microcapsule can be easily manipulated. The purpose of this paper is, therefore, to describe the technique for single-microcapsule measurements with a three-terminal chamber. As an example of its application, polystyrene microcapsules are measured and the results are analyzed by a dielectric theory based on a simple shell-sphere model.

Theory

For a polystyrene microcapsule in suspension, we assume an electrical model (Fig. 1), in which a spherical core (of complex relative permittivity ε_i^*) covered with a shell (of ε_s^*) is immersed in a continuous phase (of ε_a^*). The complex relative permittivities are defined as $\varepsilon^* = \varepsilon - j\kappa/\omega\varepsilon_v$, where ε is relative permittivity, κ conductivity, ε_v permittivity of vacuum ($\varepsilon_v = 0.088541$ pFcm^{-1}), $\omega = 2\pi f$, f frequency and $j = \sqrt{-1}$. The complex relative permittivity of the whole system ε^* is given by Maxwell [10] and Wagner [11]:

$$\varepsilon^* = \varepsilon_a^* \frac{2(1-\Phi)\varepsilon_a^* + (1+2\Phi)\varepsilon_c^*}{(2+\Phi)\varepsilon_a^* + (1-\Phi)\varepsilon_c^*}, \tag{1}$$

where Φ is the volume fraction of the shell-sphere occupied in the system and the equivalent complex relative permittivity of the shell-sphere ε_c^* is expressed by the equation derived by Maxwell [10]:

$$\varepsilon_c^* = \varepsilon_s^* \frac{2(1-v)\varepsilon_s^* + (1+2v)\varepsilon_i^*}{(2+v)\varepsilon_s^* + (1-v)\varepsilon_i^*}, \tag{2}$$

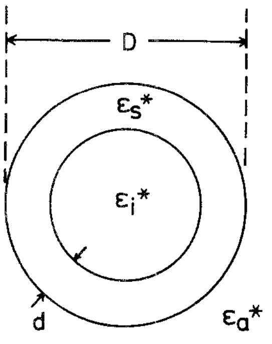

Fig. 1. An electrical model of a microcapsule in suspension. ε_s^*, ε_i^*, and ε_a^* are the complex relative permittivities of the shell, core and external phase, respectively; d is the shell thickness; D is the outer diameter

where $v = (1 - 2d/D)^3$, d is the thickness of the shell, and D is the outer diameter of the shell-sphere. Rearranging Eqs. (1) and (2), we obtain:

$$\varepsilon^* = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_m}{1 + j\omega\tau_p} + \frac{\varepsilon_m - \varepsilon_h}{1 + j\omega\tau_q} + \frac{\kappa_l}{j\omega\varepsilon_v}. \tag{3}$$

This equation indicates that the model shows a two-step dielectric dispersion composed of two subdispersions of Debye type, which are termed P- and Q-dispersion. The six parameters ε_h, ε_m, ε_l, $\tau_p(=1/2\pi f_p)$, $\tau_q(=1/2\pi f_q)$ and κ_l are called dielectric parameters and are obtainable from dielectric measurements (see Fig. 5). The relationships between the dielectric parameters and the structural and electrical parameters of the shell-sphere, called phase parameters, have been obtained by Pauly and Schwan [12] and Hanai [13]. In the case of polystyrene microcapsules that hold for the conditions that $\kappa_s \ll \kappa_a, \kappa_i$, the relationships are approximated as:

$$\kappa_l = \kappa_a \frac{2(1-\Phi)}{2+\Phi}, \tag{4}$$

$$\varepsilon_h = \varepsilon_a \frac{2(1-\Phi)\varepsilon_a + (1+2\Phi)\varepsilon_{ch}}{(2+\Phi)\varepsilon_a + (1-\Phi)\varepsilon_{ch}}, \tag{5}$$

$$\varepsilon_l = \varepsilon_a \frac{\kappa_l}{\kappa_a} + \frac{9\Phi\varepsilon_{cl}}{(2+\Phi)^2}, \tag{6}$$

$$\varepsilon_m = \varepsilon_h + \frac{\varepsilon_v\varepsilon_a - \kappa_a\tau_q}{\varepsilon_v(\tau_p - \tau_q)}\left[\left(\frac{\kappa_l}{\kappa_a} - \frac{\varepsilon_h}{\varepsilon_a}\right)\tau_p + \left(\frac{\varepsilon_l}{\kappa_a} - \frac{\varepsilon_a\kappa_l}{\kappa_a^2}\right)\varepsilon_v\right], \tag{7}$$

where ε_{ch} and ε_{cl} are the limiting relative permittivities of ε_c at high and low frequencies, respectively:

$$\varepsilon_{ch} = \varepsilon_s \frac{2(1-v)\varepsilon_s + (1+2v)\varepsilon_i}{(2+v)\varepsilon_s + (1-v)\varepsilon_i}, \tag{8}$$

$$\varepsilon_{cl} = \varepsilon_s \frac{1+2v}{1-v}. \tag{9}$$

In addition, the limiting conductivity at high frequencies κ_h is given by

$$\kappa_h = \kappa_l + (\varepsilon_m - \varepsilon_h)\varepsilon_v/\tau_q + (\varepsilon_l - \varepsilon_m)\varepsilon_v/\tau_p = \kappa_a \frac{\varepsilon_h}{\varepsilon_a} + \frac{9(\kappa_{ch}\varepsilon_a - \kappa_a\varepsilon_{ch})\varepsilon_a\Phi}{[(2+\Phi)\varepsilon_a + (1-\Phi)\varepsilon_{ch}]^2}, \tag{10}$$

where κ_{ch} is the limiting conductivity of κ_{c} at high frequencies:

$$\kappa_{\mathrm{ch}} = v\kappa_{\mathrm{i}}\left[\frac{3\varepsilon_{\mathrm{s}}}{(2+v)\varepsilon_{\mathrm{s}} + (1-v)\varepsilon_{\mathrm{i}}}\right]^2 . \tag{11}$$

Materials and methods

Preparation of microcapsules

Polystyrene microcapsules were prepared by an interfacial polymer deposition technique as reported previously [1, 14]. The internal aqueous phase of the capsules contained 3 mM KCl and 0.1% (w/v) gelatin. The capsules were stored in a 3 mM KCl solution at room temperature before dielectric measurements.

Dielectric measurement

For measuring a single microcapsule in suspension, we designed a chamber that permits the three-terminal measurement, which is free from an error inherent in the fringing field in the two-terminal method. In the chamber (see Fig. 2), a common electrode (5 mm × 3 mm) is parallel to a measuring electrode (1.2 mm × 1 mm) and a guard electrode, which lie on the same plane through a narrow gap of about 0.1 mm and are held at the same potential. The distance between the common and measuring electrodes is about 0.9 mm and platinum plates are used for the three electrodes. The chamber was fixed on a hand-made test fixture (not shown), which was mounted on an inverted phase contrast microscope (Olympus CK2). The fixture was connected to a Hewlett-Packard 4192A LF Impedance Analyzer via 1 m 50-ohm coaxial cables.

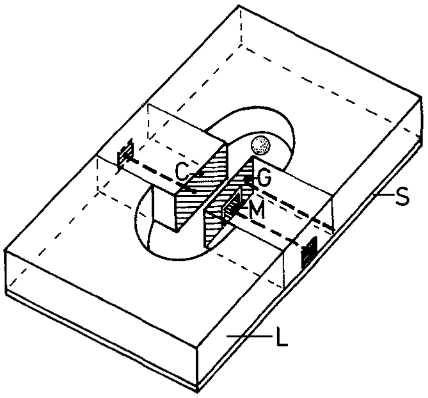

Fig. 2. A schematic representation of the three-terminal chamber used for the dielectric measurements of a single microcapsule in suspension. *C*, *M*, *G* are common, measuring and guard electrodes, respectively; *S*, slide glass; *L*, Lucite. The thick broken lines indicate leads that connect the electrodes and the contacts, which are used for the connection with an impedance analyzer

The measuring procedure consists of the following steps. First, a microcapsule was rinsed several times with distilled water and was introduced into the chamber filled with distilled water. The microcapsule was moved to the area between the electrodes by manipulating it with a piece of nylon thread under the microscope and then capacitance C and conductance G were measured with the Impedance analyzer in its parallel circuit mode between 1 kHz and 10 MHz. Secondly, the microcapsule was removed from the area between the electrodes, and capacitance C' and conductance G' were measured again. Finally, the diameter of the microcapsule was determined with the microscope and the temperature of the medium in the chamber was directly measured with an electric thermometer with a needle-type thermistor.

The capacitance C measured for a microcapsule in suspension includes an error inherent in electrode polarization at low frequencies and is represented by

$$C = C_{\mathrm{s}} + C_{\mathrm{e}} + C_0 , \tag{12}$$

where C_{s} is the capacitance of the specimen, C_{e} is the capacitance due to the electrode effect, and C_0 is the stray capacitance. For calculating C_{s} from C, we have to estimate C_{e} and C_0. The estimation is carried out with the aid of the capacitance C' measured for the medium:

$$C' = C_{\mathrm{a}} + C'_{\mathrm{e}} + C_0 , \tag{13}$$

where C_{a} is the capacitance of the medium itself, in this case distilled water, which is frequency independent below about 100 MHz, and C'_{e} is the capacitance for the electrode effect. With the values of C' at high frequencies, in this case above 200 kHz, where there is no influence of electrode polarization ($C'_{\mathrm{e}} \cong 0$), the term $C_{\mathrm{a}} + C_0$ was found to be slightly frequency dependent and be approximately expressed as:

$$C_{\mathrm{a}} + C_0 = a + b \log f , \tag{14}$$

where a and b are constants. Subtracting the value of $C_a + C_0$ (calculated from Eq. (14)) from the value of C' at each frequency, we can obtain the frequency dependence of C_e'. Using the relationship described in the Appendix, the curve of C_e is constituted by shifting the curve of C_e' along the axis of frequency by multiplying the frequency value of each data points of C_e' by a factor of G_l/G', where G_l is the conductance measured in the presence of the microcapsule at low frequencies (around 10 kHz) and G' is the medium conductance.

When the sum of the C_e and $C_a + C_0$ estimated above is denoted by C'' and the relative permittivity of the medium is equal to that of water ε_w, the relative permittivity ε of the specimen is calculated from:

$$\varepsilon = (C - C'')/C_l + \varepsilon_w \,, \tag{15}$$

where C_l is the dielectric cell constant. The conductivity κ is calculated from $\kappa = G\varepsilon_v/C_l$. The value of C_l was 0.01 pF for the chamber used.

Results

Effectiveness of three-terminal method for single-capsule measurements

We used a three-terminal chamber to avoid the fringing field effect, which is inevitable in the two-terminal measurement. If the three-terminal method works ideally with the chamber, the measurement would be confined to the measuring electrode area (the M-area indicated in the inset of Fig. 3) and would be not infuenced by materials in the guard electrode area (the G-area). We, therefore, examine the effectiveness of the three-terminal method for single-capsule measurements in this regard. Figure 3 shows frequency dependence of the capacitance and conductance obtained by changing the position of a microcapsule from the G-area to the M-area. When the microcapsule was just outside of the M-area (Position 2), the measured capacitance and conductance were almost the same as those obtained when it was positioned out of the electrode area (Position 1).

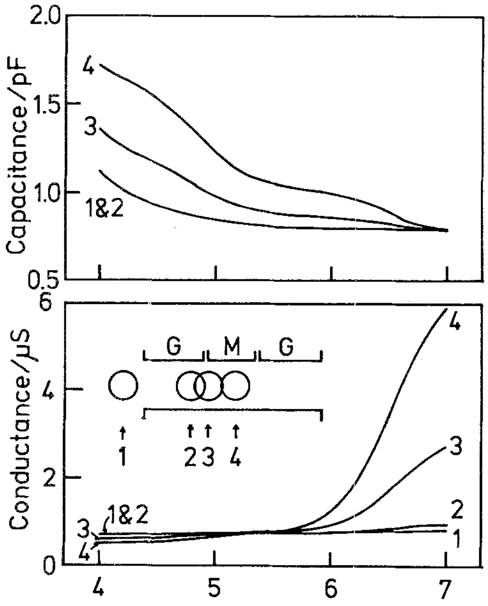

Fig. 3. Frequency dependence of the capacitance and conductance obtained by changing the position of a microcapsule between the electrodes. The number of the curves refers to the position shown in the inset. M and G indicate the measuring and guard electrode area, respectively

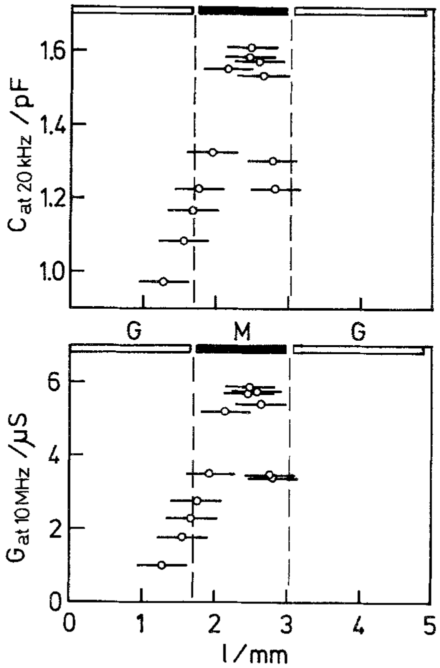

Fig. 4. The low frequency capacitance (at 20 kHz) and the high frequency conductance (at 10 MHz) are plotted against the position of a microcapsule. M and G indicate the measuring and guard electrode area. The horizontal bars indicate the diameter of the microcapsule

When the microcapsule was moved to the *M*-area (Position 3), the measured capacitance and conductance show frequency dependence, i.e., dielectric dispersion. The maximum intensity of the dielectric dispersion was obtained when the whole of the microcapsule was inside the *M*-area (Position 4). Figure 4 shows the position dependence of the low frequency capacitance (at 20 kHz) and the high frequency conductance (at 10 MHz), which change critically at the boundary between the *G* and *M* area. This result indicates that the fringing field effect is satisfactorily eliminated in the three-terminal chamber.

Phenomenological analysis

Figure 5 shows the frequency dependence of the relative permittivity and conductivity obtained by correcting the data of Curve 4 in Fig. 3 for electrode polarization. The complex plane plots of the same data are also shown in Fig. 6. The dielectric dispersion was phenomenologically expressed by a two-step dispersion composed of two Debye type subdispersions as has been predicted by the dielectric theory described in the theory section. Agreement between the measurements and the curves calculated from Eq. (3) with the best-fit parameters shown in Table 1 (Specimen 1) is more than satisfactory; the average deviation of the measurements from the best-fit curve is less than 0.3 dielectric unit. The curve-fitting was made by means of a nonlinear least squares method with the Gauss–Newton algorithm. Table 1 shows the dielectric parameters obtained with several microcapsules from the same batch.

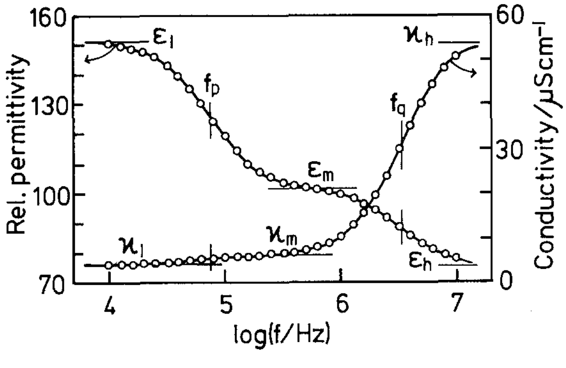

Fig. 5. Frequency dependence of the relative permittivity and conductivity of a single microcapsule in suspension, which is calculated from the data of Curve 4 in Fig. 3. The open circles represent measurements; the solid curves are the best-fit curves calculated from Eq. (3) with the best-fit dielectric parameters (ε_h, τ_p, τ_q, ε_l, ε_m and κ_l) shown in Table 1 (Specimen 1). The curves also agree with the theoretical curves calculated using the shell-sphere model with the parameters in Table 2 (Specimen 1)

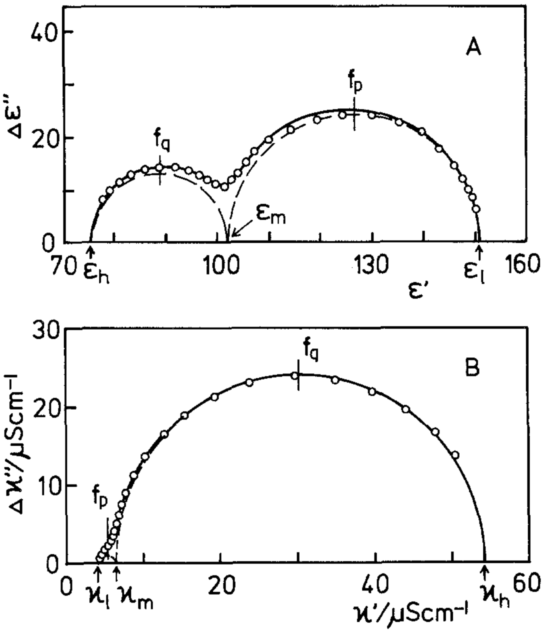

Fig. 6. Complex plane plots of the data in Fig. 5. A) the complex relative permittivity plane plots, $\Delta\varepsilon'' = (\kappa - \kappa_l)/\omega\varepsilon_v$ and $\varepsilon' = \varepsilon$; B) the complex conductivity plane plots, $\Delta\kappa'' = (\varepsilon - \varepsilon_h)\omega\varepsilon_v$ and $\kappa' = \kappa$. The solid curves are a superposition of two Debye type dispersions, each of which is indicated by the broken line

Table 1. Dielectric parameters obtained by fitting the data of single-capsule measuremens with Eq. (3) consisting of two Debye forms

Specimen No.	D μm	κ_l μS/cm	ε_l	ε_m	ε_h	f_p kHz	f_q MHz
1	780	4.28	151.0	101.7	75.3	74.1	3.25
2	740	5.32	129.7	93.6	75.2	89.1	4.58
3	710	3.89	202.7	106.6	76.2	43.1	3.12
4	740	5.41	139.6	97.6	75.6	88.7	4.11

Analysis based on shell-sphere model

Using the dielectric parameters estimated above, we can calculate the phase parameters κ_a, Φ, d, ε_i and κ_i of the microcapsules from the alternative forms of the relationships described in the theory section. The calculation is made according to a procedure analogous to that of Zhang et al. [1, 2]. Rearranging Eq. (7), we obtain:

$$A(\kappa_l/\kappa_a)^3 + B(\kappa_l/\kappa_a)^2 + C(\kappa_l/\kappa_a) + D = 0 \,, \tag{16}$$

where

$$A = -(\varepsilon_a \varepsilon_v)^2/\kappa_l \,,$$

$$B = \varepsilon_a \varepsilon_v(\tau_p + \tau_q + \varepsilon_l \varepsilon_v/\kappa_l) \,,$$

$$C = -\varepsilon_v[\varepsilon_m(\tau_p - \tau_q) + \tau_q(\varepsilon_l + \varepsilon_h)] - \kappa_l \tau_p \tau_q \,,$$

$$D = (\varepsilon_h/\varepsilon_a)\kappa_l \tau_p \tau_q \,.$$

By solving this cubic equation with the measured dielectric parameters (ε_h, τ_p, τ_q, ε_l, ε_m and κ_l) and the measured ε_a, we obtain the value of the κ_l/κ_a ratio and then the value of κ_a. The volume fraction Φ is calculated from the κ_l/κ_a ratio using the equation obtained from Eq. (4):

$$\Phi = \frac{2(1 - \kappa_l/\kappa_a)}{2 + \kappa_l/\kappa_a} \,. \tag{17}$$

Since the relative permittivity determined for polystyrene films is available to that of the shell phase, i.e., $\varepsilon_s = 2.65$ [1], the wall thickness d is estimated from the following equations:

$$d = D(1 - v^{1/3})/2 \,, \tag{18}$$

$$v = (\varepsilon_{cl} - \varepsilon_s)/(\varepsilon_{cl} + 2\varepsilon_s) \,, \tag{19}$$

$$\varepsilon_{cl} = \left[\varepsilon_l - \varepsilon_a \frac{\kappa_l}{\kappa_a}\right] \frac{(2 + \Phi)^2}{9\Phi} \,. \tag{20}$$

Equations (19) and (20) are obtained from Eqs. (9) and (6), respectively. The relative permittivity of the aqueous core phase ε_i is calculated from the equations derived from Eqs. (5) and (8):

$$\varepsilon_i = \varepsilon_s \frac{2(1 - v)\varepsilon_s - (2 + v)\varepsilon_{ch}}{-(1 + 2v)\varepsilon_s + (1 - v)\varepsilon_{ch}} \,, \tag{21}$$

$$\varepsilon_{ch} = \varepsilon_a \frac{2(1 - \Phi)\varepsilon_a - (2 + \Phi)\varepsilon_h}{-(1 + 2\Phi)\varepsilon_a + (1 - \Phi)\varepsilon_h} \,. \tag{22}$$

The conductivity of the core phase κ_i is determined from the alternative forms of Eqs. (10) and (11):

$$\kappa_i = \frac{\kappa_{ch}}{9v}\left[2 + v + (1 - v)\frac{\varepsilon_i}{\varepsilon_s}\right]^2 \,, \tag{23}$$

$$\kappa_{ch} = \left(\kappa_h - \kappa_a \frac{\varepsilon_h}{\varepsilon_a}\right) \frac{[(2 + \Phi)\varepsilon_a + (1 - \Phi)\varepsilon_{ch}]^2}{9\Phi\varepsilon_a^2} + \kappa_a \frac{\varepsilon_{ch}}{\varepsilon_a} \,. \tag{24}$$

The results obtained by these calculations with the data in Table 1 are shown in Table 2. The external conductivity κ_a calculated is in good agreement with the measured κ_a. The mean value of the effective volume V_c between electrodes (calculated from $V_c = \pi D^3/6\Phi$) was 1.0 mm^3, being close to the volume expected from the measuring electrode area and the distance between the common and measuring electrodes. The values of the wall thickness d estimated show some scatter between 2 and 5 μm. These values are similar to those obtained by Zhang et al. [1, 2]. The internal permittivity ε_i is slightly higher than the relative permittivity of pure water, which might be partly due to the presence of gelatin, which is requisite for the microcapsule preparation as an emulsifier.

Table 2. Phase parameters calculated from the data shown in Table 1 using a shell-sphere model on the assumption that $\kappa_s \ll \kappa_a, \kappa_i$

Specimen No.	Observed		Calculated					
	ε_a	κ_a μS/cm	Φ	κ_a μS/cm	ε_i	κ_i μS/cm	d μm	V_c*) mm^3
1	78.6	6.75	0.248	6.41	94.5	373	4.60	1.01
2	78.6	6.72	0.216	7.51	97.9	471	5.20	1.00
3	77.8	5.64	0.201	5.35	86.1	386	2.40	0.94
4	78.6	7.47	0.217	7.65	95.7	464	4.60	0.99

*) V_c is the effective volume of the measuring chamber, which is calculated from $V_c = \pi D^3/6\Phi$.

The internal conductivity κ_i is similar to the conductivity of a 3 mM KCl solution that was loaded in the microcapsule preparation, but slightly varies from capsule to capsule. The diverse values indicate variations in ion cncentration in the core phase, which result from various degrees of ion loss from the microcapsules in distilled water.

Discussion

The present study demonstrates the utility of a new dielectric technique for characterization of individual polystyrene microcapsules and its suitability for determination of their electrical and structural parameters. In addition, the three-terminal measurement employed in this technique is effective for the single-capsule measurements.

All of the measured dielectric dispersion curves were phenomenologically expressed by a superposition of two Debye forms as expected from the theory based on the shell-sphere model. In most cases, the analysis with the shell-sphere model on the assumption that the wall conductivity is much less than the conductivity of the internal and external aqueous phases, i.e., $\kappa_s \ll \kappa_a$, κ_i, provided reasonable values of the phase parameters, and agreement between theoretical and experimental curves was satisfactorily. However, some of the microcapsules yielded inconsistent results; the calculation with the estimated phase parameters failed to reconstitute their measured dielectric dispersion curves. This may indicate that the assumption for κ_s does not hold for some microcapsules. Hence, we assess the effect of κ_s on the dielectric parameters and on the errors in the estimation of the phase parameters. The calculation of the dielectric parameters is made using Pauly–Schwan's general equation with the following phase parameters: $\varepsilon_a = 80$, $\varepsilon_s = 2.65$, $\varepsilon_i = 80$, $\kappa_a = 5\ \mu$S/cm, $\kappa_i = 500\ \mu$S/cm, $\Phi = 0.2$, $D = 700\ \mu$m, $d = 3\ \mu$m and κ_s is varied from 0 to 10 nS/cm. As shown in Table 3, the effects of κ_s are confined to the dielectric parameters related to the P-dispersion, namely, κ_l, ε_l and f_p, and become considerable above 5 nS/cm for κ_s or 10^{-3} for the κ_s/κ_a ratio. Next, using these calculated dielectric parameters, we estimated the errors in phase parameters calculated from the Eqs. (16–24), which are derived on the assumption of $\kappa_s \ll \kappa_a$, κ_i. The results are summarized in Table 4. It is clear that the errors become serious in calculation of Φ and κ_i when κ_s is above 5 nS/cm. From this assessment, we believe that polystyrene microcapsules with leaky walls (whose κ_s is more than 5 nS/cm) may be always included to some extent in the same preparation.

Table 3. Effect of change in κ_s on dielectric parameters. The effects are represented by the differences (%) from the reference dielectric parameters that are calculated from Pauly–Schwan's equation with the following phase parameters: $\varepsilon_a = 80$, $\varepsilon_s = 2.65$, $\varepsilon_i = 80$, $\kappa_a = 5\ \mu$S/cm, $\kappa_s = 0\ \mu$S/cm, $\kappa_i = 500\ \mu$S/cm, $\Phi = 0.2$, $D = 700\ \mu$m, and $d = 3\ \mu$m. The reference dielectric parameters are: $\kappa_l = 3.6365\ \mu$S/cm, $\varepsilon_l = 172.2$, $\varepsilon_m = 104.9$, $\varepsilon_h = 76.4$, $f_p = 46.5$ kHz and $f_q = 4.34$ MHz

κ_s/nS cm^{-1}	0.5	1	5	10
κ_l	+ 0.61	+ 1.18	+ 5.69	+ 10.89
ε_l	− 0.58	− 1.16	− 5.28	− 9.81
ε_m	0	0	0	0
ε_h	0	0	0	0
f_p	+ 0.43	+ 0.86	+ 4.30	+ 8.60
f_q	0	0	0	0

Table 4. Errors in calculation of phase parameters on the assumption of $\kappa_s \ll \kappa_a$, κ_i. The phase parameters are calculated from Eqs. (16–24) with the dielectric parameters shown in Table 3. The errors are represented by the differences (%) from the true phase arameters: $\kappa_a = 5.0\ \mu$S/cm, $\Phi = 0.2$, $d = 3\ \mu$m, $\varepsilon_i = 80$, $\kappa_i = 500\ \mu$S/cm

κ_s/nScm^{-1}	0.5	1	5	10
κ_a	0	0	0	0
Φ	− 1.5	− 3.5	− 16.5	− 31.0
d	− 0.33	− 0.66	− 3.33	− 8.33
ε_i	− 0.63	− 1.25	− 6.75	− 15.0
κ_i	+ 1.12	+ 2.24	+ 11.42	+ 23.58

The analysis of the microcapsules with leaky walls or the estimation of κ_s is quite important because the permeability of drugs in the wall and the ability to retain materials in the microcapsule constitute main concerns in pharmaceutical and industrial applications. We are developing a method to analyze without the assumption for κ_s and the details will be discussed in a subsequent paper.

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Appendix

Electrode polarization is due to an electrical double layer caused at the boundary between electrodes and electrolyte solutions, resulting in a steep increase in capacitance at low frequencies. The curve of the capacitance for the electrode effect shifts to higher frequency with increasing the conductance of the specimen. Figure 7a shows frequency dependence of the capacitance measured for KCl solutions with various conductivities, which are superimposable on each other by shifting the curves along the axis of logarithmic frequency. In orer to obtain the relationship between the frequency shift and the specimen conductance G, the values of frequency f at which the same capacitance value is obtained are extracted from every curves in Fig. 7a and are plotted against the conductance G as shwon in Fig. 7b, where f_r and G_r are corresponding to the reference solution. It is obvious from the plots that the frequency is linearly related to the conductance, that is, $f/f_r = a\,G/G_r + b$, where a and b are constants. The mean values of a and b estimated by a least squares method were 0.97 and 0.01 and the correlation coefficient was 0.9998. Hence, the relationship is roughly represented as $f/f_r = G/G_r$.

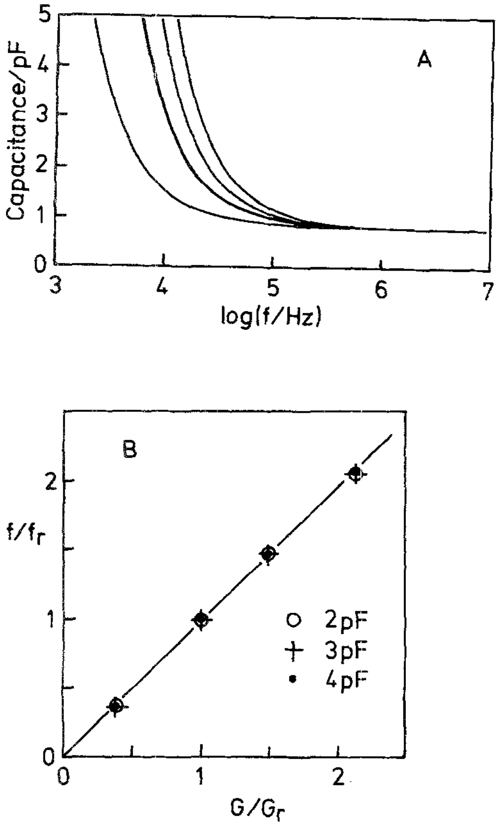

Fig. 7. The capacitance due to electrode polarization. A) Frequency dependence of the capacitance of KCl solutions with various conductivities. B) The relationship between the frequency shift and the specimen conductance. The frequencies f where the capacitance vaue is 2, 3 and 4 pF are extracted from every curve in (A) and are divided by those of the reference solution whose curve is indicated by the thick curve in (A). The frequency ratio f/f_r is plotted against the condutance ratio G/G_r, where the subscript r refers to the reference solution

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Authors' address:

Dr. Koji Asami, Associate Professor
Institute for Chemical Research
Kyoto University
Uji, Kyoto 611
Japan