

# Does "One-Sphere" System Conform to the Wagner Equation for Simple Binary Dispersions? An Experimental Assessment by Use of a Ball of Glass, Steel or Hydrated Gelatin Suspended in Aqueous Solutions

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*Received July 22, 1985*

The dielectric behavior of a "one-sphere" system in which only one solid sphere of glass, metal or gelatin having a 1-2 mm diameter comprises the suspended phase has been studied. With a glass-bead system of volume fraction below 0.4, changes in its conductivity as a function of bead size was as predictable from the Wagner equation for non-conducting spheres suspended in conductive media. For steel balls suspended in electrolytic solutions, their dielectric dispersions were unexpectedly large with dielectric increments of about  $5 \times 10^6$ . The dispersion behavior could not be predicted from a simple binary mixture of a homogeneous sphere with high conductivity, but was satisfactorily explained by taking account of an additional non-conducting layer with a capacitance of 7-20  $\mu\text{F}/\text{cm}^2$  covering the highly conducting sphere. The large capacitances associated with the steel-ball system was attributable to the electrical double layer formed at the metal/solution interface. Gelatin balls suspended in deionized water, on the other hand, showed dielectric dispersions having dielectric increment of some  $10^2$  and characteristic frequency of  $10^6$ - $10^7$  Hz. In addition, the dispersion curves for the hydrated-gelatin-ball system were significantly broader than the curves of a single relaxation type the Wagner equation should conform to. The spectral broadening here observed was successfully explained by a mechanism based on the reasonable assumption that a frequency dependence predictable from the  $m$ -th power law applies to relative permittivity and conductivity for the suspended phase of hydrated gelatin. It is concluded that even the apparently simplest two-phase systems such as employed here can be the cause of an anomalous dielectric behavior which is too complicated to explain by the direct application of Wagner's theory.

KEY WORDS: Dielectric relaxation/ Interfacial polarization/ Glass bead/  
Gelatin ball/ Steel ball/

## INTRODUCTION

Dielectric dispersions for the suspensions of colloidal particles including biological cells are usually found to take place over a frequency range  $10^2$  to  $10^8$  Hz, and have been extensively as well as intensively studied with a view to elucidating the structural and electrical properties of the particles (for reviews, see Refs. 1-3). In most cases these dielectric dispersions are successfully simulated by dielectric theories based on the interfacial polarization (4-10), but occasionally a marked discrepancy arises between the observed

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dispersion behavior and the theoretically predicted, particularly in the case of biological cells. At least the following two factors may be pointed out as the cause for such a discrepancy: (i) Distribution of relaxation times caused by a particle-to-particle variation of the electrical parameters involved in the suspended phase and (ii) frequency dependence of the properties of the suspended particle itself.

Of these two factors, the second one is particularly interesting because an investigation of the second factor is expected to provide an insight into the fine structure of, and the knowledge of molecular motions involved in, the particle components. In order to extract the frequency-dependent properties from dispersion measurements, we have to minimize, or preferably, to exclude the influence of the first factor by either of the following approaches: One, routinely used, is to make physical properties of given particles as uniform as possible, and the other is to employ a 'one-sphere' suspension such as was earlier introduced by Cole and his co-workers (11, 12) to examine the frequency dependence of membrane impedances for sea urchin and frog eggs. We also have made use of the one-sphere technique in the studies of spherical bilayer lipid membranes (13), fish (*Medaka*) and amphibian (*Xenopus*) eggs (14), and epithelial monolayers cultured on large gelatin balls (15).

During the course of these biological impedance studies a question arose as to whether Wagner's theory on the binary mixtures of spherical particles equally well applies to the 'one-sphere' system where a single, sizeable mass of particle comprises the suspended phase. A quantitative discussion of the dielectric behavior as related to the one-sphere system would then be feasible only after the question above is answered. In the present paper we examine the applicability of the Wagner equation by using the following physicochemical systems: glass beads (as a non-conducting material of frequency-independent nature), steel balls (as an ideally conducting and frequency-independent specimen) and gelatin balls (as a conducting sphere having frequency-dependent electrical parameters).

## MATERIALS AND METHODS

Pyrex glass beads and steel ball bearings were obtained from commercial sources and used as the specimen after a thorough washing with detergents followed by organic solvents. With the steel balls care was taken to minimize the formation of oxides at the surface.

Stable gelatin balls 1-2 mm in diameter were prepared by cross-linking gelatin hydrate. A tuberculin syringe fitted with a #24 needle with its tip cut flat was filled with a warm 10% solution of gelatin and a careful discharge of the content into the air formed a gelatin droplet of approx. 2 mm diameter. The droplet was held in situ for some time at room temperature until gelation completed; it was cut off the needle using a fine nylon fiber and then transferred into a test tube containing a fixative of 2.5% glutaraldehyde/50mM phosphate buffer (pH 7.4) for the purpose of reinforcing the droplet's mechanical stability. Following one day fixation at 4°C, the droplet became moderately elastic (hereafter, the 'gelatin ball') and readily manipulable with forceps. The gelatin balls thus obtained were thoroughly washed with deionized water and then subjected to the permittivity measurements.

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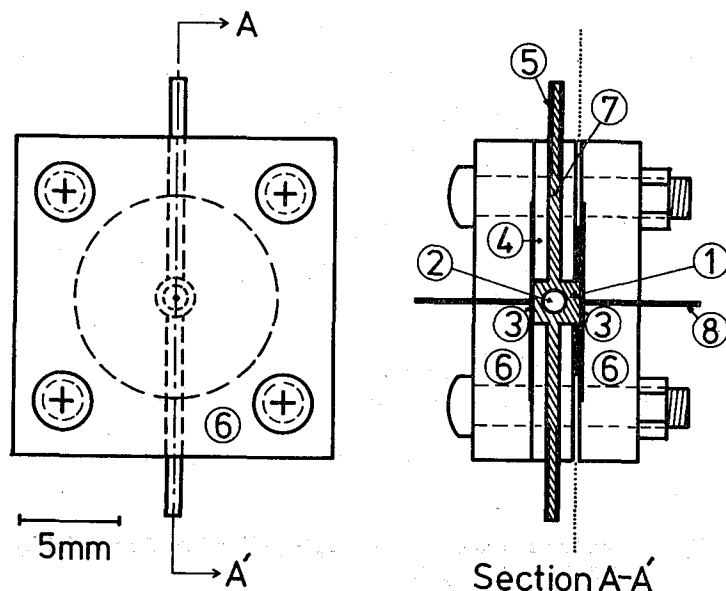


Fig. 1. Diagram of the permittivity cell for one particle suspension. (1) sample cavity ( $6.3\text{mm}^3$ ), (2) sample particle, (3) platinized Pt-disc electrodes, (4) lucite space, (5) stainless tubing (6) lucite block, (7) conduit for circulating medium, and (8) connecting lead to the impedance analyzers. The cell is separable into the two parts along the dotted line.

The volume was determined for each gelatin ball by means of photomicrographic morphometry with an accuracy of 5 %; the sizes of glass beads and steel balls were measured with a micrometer and their volumes estimated to within 1 %.

Figure 1 shows the permittivity cell used which was specially designed for the one-sphere suspension. It was essentially a parallel-plate capacitor of the type that enabled circulation of the suspending medium driven by a peristaltic pump. The test specimen was loaded into the sample cavity and settled in between the electrodes by assembling the cell, as shown in Fig. 2. This flow-through type cell, when arranged as illustrated in Fig. 3, had advantages over a closed type one in respect to both a rapid change of medium and its capability for simultaneous monitoring of the electrical parameters of medium through the sister cell set in tandem.

Equivalent parallel capacitances and conductances for the one-sphere system were measured with Yokogawa-Hewlett-Packard RF and LF impedance analyzers (models 4191A and 4192A) over a frequency range of 10 Hz to 500 MHz. A Yokogawa-Hewlett-Packard LCR Meter (model 4275A) was used for monitoring capacitance and conductance of the medium. These measuring apparatuses were controlled by a Hewlett-Packard 9825A desktop computer.

Data were corrected for residual inductance and stray capacitance arising from the cell assembly by the method described previously (7).

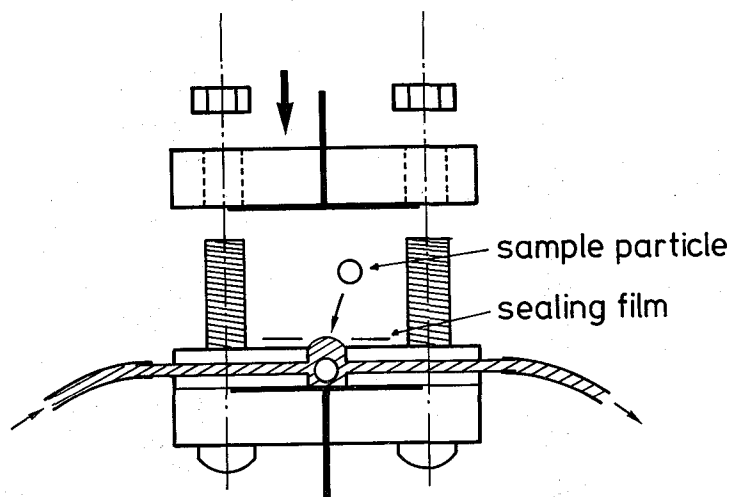


Fig. 2. Loading and assembling a sample particle into the permittivity cell shown in Fig. 1.

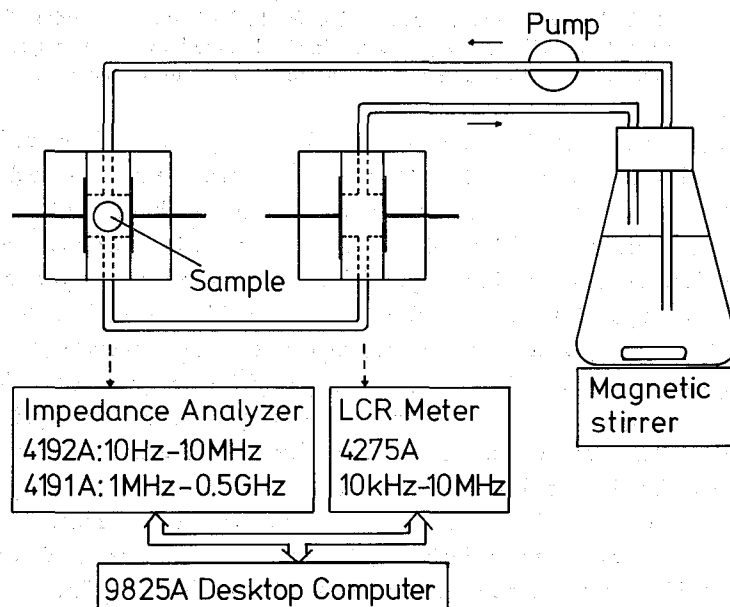


Fig. 3. Experimental arrangement for permittivity measurements. Two permittivity cells for sample suspension and its medium are interconnected with polyethylene tubing for circulating medium.

## RESULTS AND DISCUSSION

### *Glass beads*

Glass beads, because of their homogeneous and non-conductive properties, are suit-

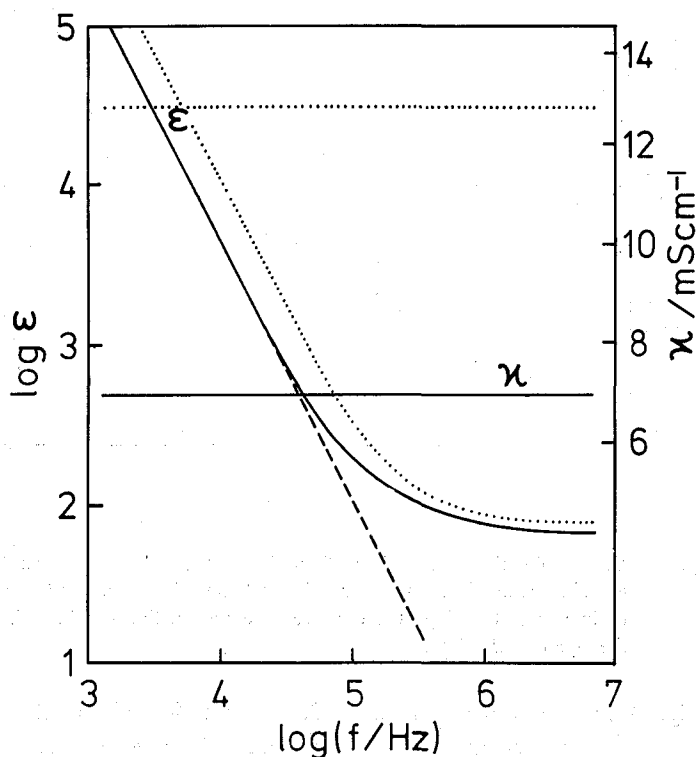


Fig. 4. Plots of relative permittivity  $\epsilon$  and conductivity  $\kappa$  vs. frequency  $f$  for one glass bead suspended in 100 mM KCl. Dotted lines indicate data on medium alone.

able specimens for the test of dielectric theories for a heterogeneous system. Cole and Guttman (12) employed large glass beads to examine the validity of the Wagner equation for one-sphere systems. We also made a similar examination with our permittivity cell which differed from Cole's one in the arrangement of electrodes. Fig. 4 shows an example of dielectric measurements for one glass bead suspended in 100 mM KCl solution. The double-logarithmic plots of permittivity  $\epsilon$  vs. applied frequency  $f$  gave a straight line with a slope of  $-1.6$  below 0.1 MHz, whereas the conductivities  $\kappa$  were independent of frequency over the range 1 kHz to 10 MHz. This feature was also found with a KCl solution alone as the test specimen, whereby being attributable to electrode polarization. Hence, no dielectric dispersion due to interfacial polarization was identified, but in the presence of glass bead the levels of conductivity and permittivity were simply lower than those for the medium.

In the case of non-conducting spheres, the volume fraction  $\Phi$  is calculated from the conductivity of suspension ( $\kappa$ ) and that of medium ( $\kappa_a$ ) by using

$$\Phi = \frac{2(1 - \kappa/\kappa_a)}{2 + \kappa/\kappa_a} \quad (1)$$

which is derived from the Wagner equation. To test for validity of Eq. (1) to this case we plotted the estimated values of  $\Phi$  against the bead volume  $v$  and obtained a linear

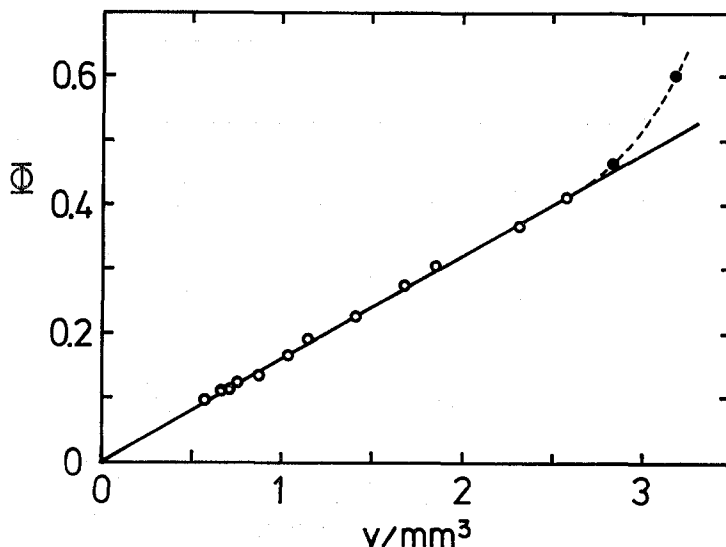


Fig. 5. Volume fraction  $\Phi$  calculated from Eq. (1) vs. glass bead volume  $v$ . The volume of the measuring cell was determined from the reciprocal of the slope for the linear regression line obtained from the open circle data.

correlation (Fig. 5) for the range of  $\Phi$  up to 0.4. Since  $\Phi = v/V$  by definition, where  $V$  is volume of the sample cavity, a linear relationship is expected between  $\Phi$  and  $v$ , and the reciprocal of slope should provide an effective volume of the measuring cell. The actual volume for the present cell of a cylindrical form (2.0 mm diameter  $\times$  2.0 mm length) was 6.28 mm<sup>3</sup>, which was found to be in good agreement with 6.32 mm<sup>3</sup>, a value estimated from Fig. 5. This result indicates that the relation represented by Eq. (1) holds for the one-sphere system with volume fraction below 0.4. Cole and Guttman (12) reported a value of 0.5 as to the applicability limit for volume fraction, which was slightly higher than the present value of 0.4. This discrepancy may be due to a difference between our cell and theirs in the electrode arrangement employed.

#### Steel Ball

Highly conducting spheres like a metal ball, whose conductivity is contrasting to that of the glass beads, have been frequently employed as a specimen of well-defined nature to test the validity of dielectric theories for the binary mixture system (16, 17). We also examined the one-sphere system of a steel ball of 0.79 mm in radius suspended in a series of aqueous KCl solutions ranging from 0 to 100 mM. The dielectric behavior of the system as a function of the salt concentration is shown in Fig. 6, where marked dielectric dispersions of about  $5 \times 10^8$  permittivity units were found except for the case of salt-free media and their characteristic frequencies  $f_c$  were directly proportional to the conductivity of the medium. When the ball was placed in deionized water, because of its far low conductivity, the major portion of the resulting dispersion shifted toward the low-frequency side beyond the measurement range of frequency. Figure 7 shows an example of the complex plane plots for the data in Fig. 6. With 100 mM KCl,

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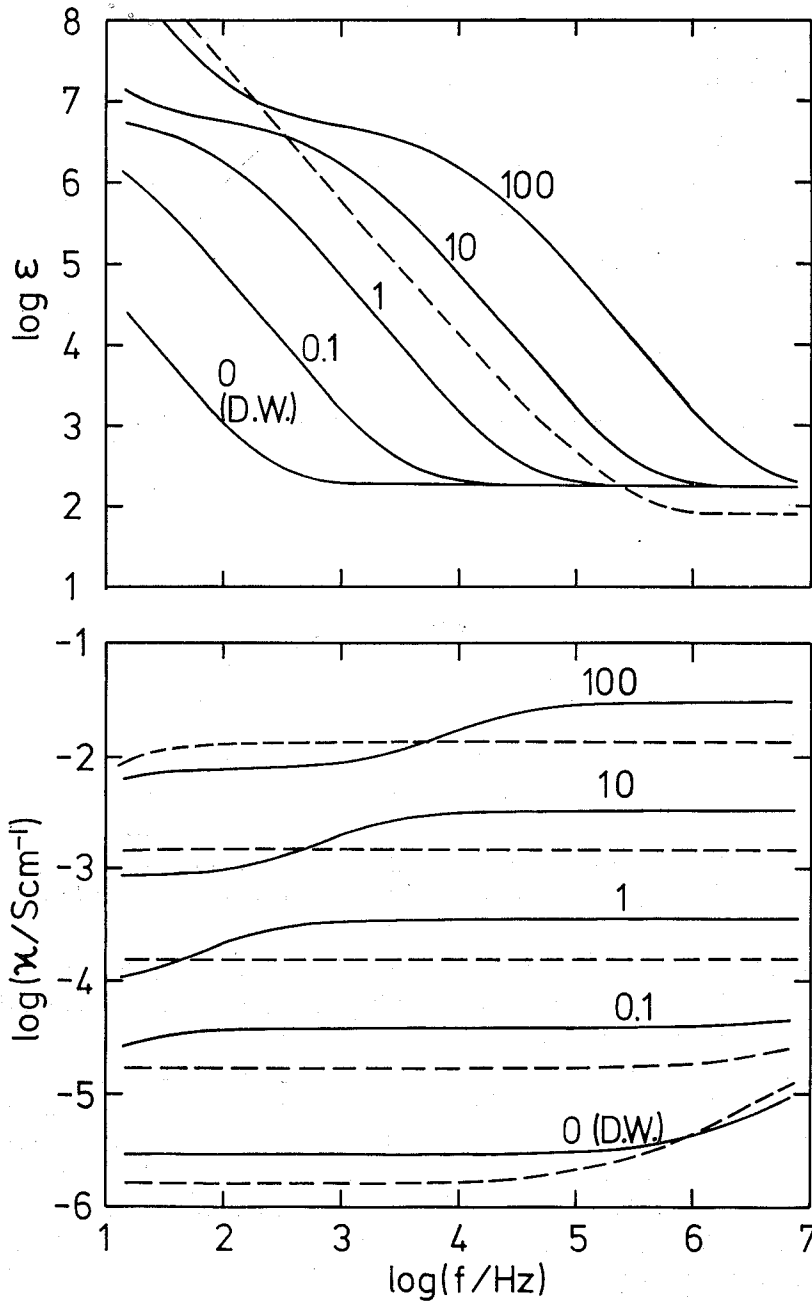


Fig. 6. Plots of relative permittivity and conductivity vs. frequency for one steel ball suspended in different KCl solutions whose concentrations are denoted by numbers beside the curves in mM. Broken lines refer to the suspending medium employed; the permittivity of the suspending medium is shown only for the 100 mM KCl solution.

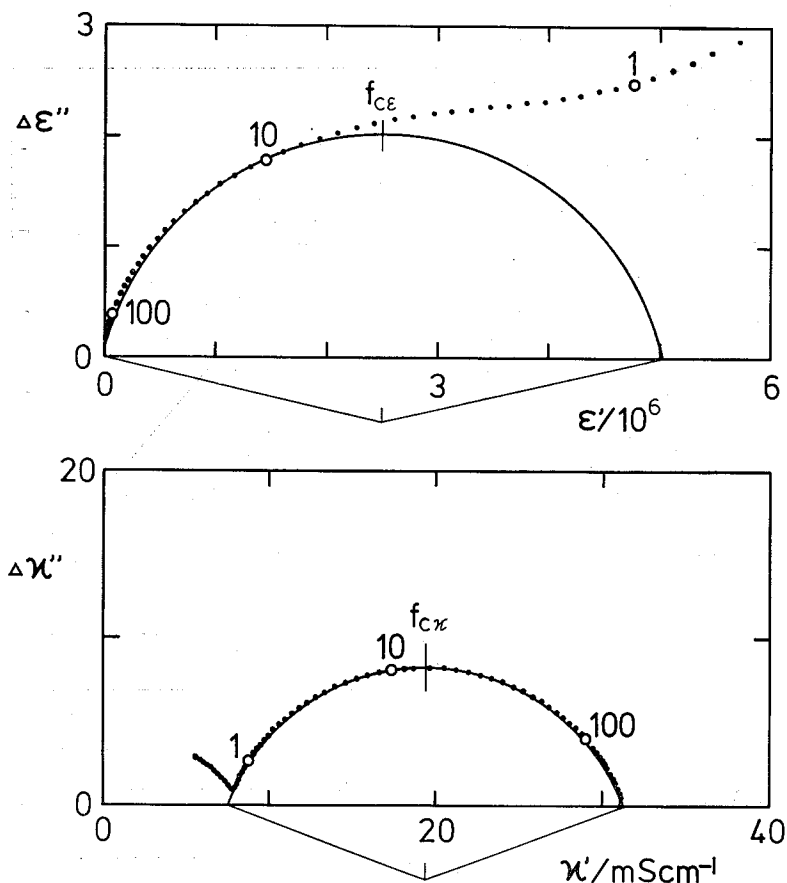


Fig. 7. Complex plane plots of the data obtained with 100mM KCl solution in Fig. 6. The number on each point refers to marker frequency in kHz.

the plots of  $\Delta\epsilon''$  vs.  $\epsilon'$  and  $\Delta\kappa''$  vs.  $\kappa'$  traced circular arcs with depressed centers; similar traces were obtained for the dispersions with 0.1–10 mM KCl. The dielectric parameters of the dispersions in Fig. 6 were those from extrapolation in the complex plane plots and listed in Table 1, where the values of  $\epsilon_h/\epsilon_a$ ,  $\kappa_l/\kappa_a$  and  $\kappa_h/\kappa_a$  (subscripts  $h$  and  $l$  are the limiting values at high and low frequencies, respectively) were independent of KCl concentration and were 2.25, 0.573 and 2.21, respectively, on the average.

If the system of a steel ball placed in an aqueous KCl solution makes a simple diphasic structure in which the conductivity of the ball ( $\kappa_i$ ) is much higher than the medium conductivity ( $\kappa_a$ ), or  $\kappa_a/\kappa_i \ll 1$ , then the limiting relative permittivity and conductivity at low frequencies for the Wagner equation are expressed as

$$\epsilon_l/\epsilon_a = \kappa_l/\kappa_a = (1+2\Phi)/(1-\Phi) \quad (2)$$

From this equation, the values of  $\epsilon_l/\epsilon_a$  and  $\kappa_l/\kappa_a$  are expected to lie between 1 (for  $\Phi=0$ ) and 7 (for  $\Phi=2/3$ ), the latter being the upper limit with the present cell geometry. However, as seen in Table 1, the parameters experimentally obtained were  $7 \times$

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Table 1 Dielectric parameters observed for the one-sphere system of a steel ball and the ambient KCl solutions

| KCl<br>concn. | $\kappa_a$ | $\epsilon_i$ | $\epsilon_h/\epsilon_a$ | $\kappa_l/\kappa_a$ | $\kappa_h/\kappa_a$ | $f_c$ <sup>a)</sup> | $f_c$ <sup>b)</sup> |
|---------------|------------|--------------|-------------------------|---------------------|---------------------|---------------------|---------------------|
| mM            | mS/cm      | $10^6$       |                         |                     |                     | kHz                 | kHz                 |
| 0             | 0.0015     |              | 2.27                    |                     | 2.00                |                     |                     |
| 0.1           | 0.0172     | 5.7          | 2.24                    | 0.608               | 2.24                |                     | 0.011               |
| 1             | 0.1559     | 5.7          | 2.23                    | 0.564               | 2.26                | 0.056               | 0.108               |
| 10            | 1.481      | 5.5          | 2.26                    | 0.561               | 2.26                | 0.525               | 1.14                |
| 100           | 13.66      | 5.0          | 2.26                    | 0.559               | 2.30                | 4.84                | 13.65               |
| mean          |            | 5.5          | 2.25                    | 0.573               | 2.21                |                     |                     |

$\epsilon_a=77$

a) obtained from the plots of  $\Delta\epsilon''$  vs.  $\epsilon'$

b) obtained from the plots of  $\Delta\kappa''$  vs.  $\kappa'$

$10^4$  for  $\epsilon_l/\epsilon_a$  and 0.57 for  $\kappa_l/\kappa_a$ , both being outside the expected range. Thus, the validity of a diphasic model to the present case has been ruled out.

As an alternative, we consider a triphasic structure, or a single-shell model, in which an additional phase intervenes between the steel surface and the bulk solution. The dielectric behavior of one shelled-sphere in suspension can be simulated by the Pauly-Schwan equation as described in a previous paper (13). Here, we tentatively employ the assumptions that the shell phase (of conductivity  $\kappa_s$  and thickness  $d$ ) is thin and non-conducting and the core phase (of conductivity  $\kappa_i$  and radius  $R$ ) is highly conducting, viz.,  $d/R \ll 1$ ,  $\kappa_s/\kappa_a \ll 1$  and  $\kappa_a/\kappa_i \ll 1$ , and so the dielectric parameters may be given by the following simple formulas:

$$\frac{\epsilon_h}{\epsilon_a} = \frac{\kappa_h}{\kappa_a} = \frac{1+2\Phi}{1-\Phi} \quad (3)$$

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

$$\epsilon_l = \epsilon_h + \frac{9\Phi RC_s}{\epsilon_v(2+\Phi)^2} \quad (5)$$

$$f_c = \frac{\kappa_a(2+\Phi)}{2\pi RC_s(1-\Phi)} \quad (6)$$

where  $C_s$  is shell capacitance defined  $C_s = \epsilon_s \epsilon_0 / d$ ,  $\epsilon_s$  is relative permittivity of shell phase and  $\epsilon_v$  permittivity of vacuum. Equation (3) has the same form as Eq. (2), indicating that, under the given condition, the triphasic model is electrically reduced to the diphasic one at the high-frequency limit where the shell phase capacitance is short-circuited. By using  $R=0.79$  mm and  $V=6.3$  mm<sup>3</sup>, already determined from the glass bead experiments, the volume fraction  $\Phi$  is estimated to be 0.33 from  $\Phi=4\pi R^3/3V$ , and then  $\epsilon_h/\epsilon_a = \kappa_h/\kappa_a = 0.25$  from Eq. (3) and  $\kappa_l/\kappa_a = 0.57$  from Eq. (4). These calculations agree well with the observed dielectric parameters in Table 1, indicating that the single-shell

Table 2 Calculation of shell capacitances from Eqs. (5) and (6).

| KCl<br>concn.<br>mM | $C_s/\mu\text{Fcm}^{-2}$ |               |               |
|---------------------|--------------------------|---------------|---------------|
|                     | Eq.(5)                   | Eq.(6)        |               |
|                     |                          | from $f_{ee}$ | from $f_{eh}$ |
| 0.1                 | 11.6                     |               | 10.9          |
| 1                   | 11.6                     | 19.5          | 10.1          |
| 10                  | 11.2                     | 19.7          | 9.1           |
| 100                 | 10.2                     | 19.7          | 7.0           |
| mean                | 11.2                     | 19.6          | 9.3           |

model can be one plausible model for the system of the steel ball immersed in the KCl solutions provided that  $d/R < 1$ ,  $\kappa_s/\kappa_a < 1$  and  $\kappa_a/\kappa_i < 1$ .

Capacitances for the shell (interfacial) layer estimated from Eq. (5) or (6) are 7–20  $\mu\text{F}/\text{cm}^2$  as shown in Table 2, being significantly higher than those of lipid bilayer membranes and comparable to the polarization capacitances due to the electrical double layer arising at the boundary between a metal electrode and an electrolytic solution (18). Provided that the shell consists of an oily contaminant with its permittivity of 2–5, the shell thickness should be 1 to 6 Å. Since this is too small a figure for the realistic oily interface, the oil-layer model seems unlikely. This point might be supported by the fact that the built-up dispersion curves remained unchanged even after the intensive cleansing of the ball surface with organic solvents or detergents.

The impedance of electrical double layers is known to vary depending on both the current density and frequency of the applied ac field (18). This feature is consistent with our findings: (i) The dispersion magnitude and the shell capacitance increased with the current intensity applied above a limit level which was a function of the ac frequency and of the medium conductivity as well, and (ii) the dispersions showed broad spectra which might be due to frequency dependent properties of the shell phase. It appears therefore plausible to choose an electrical-double-layer model for the shell phase.

#### *Gelatin ball*

Gelatin is a denatured collagen having 130–140 acidic and 80–90 basic groups per 1000 amino acid residues (19). Consequently, balls made of hydrated gelatin can be regarded as a conducting sphere containing fixed charges and resemble ion-exchange resins in this respect. Ishikawa, Hanai and Koizumi (9, 10) have extensively studied the dielectric behavior of ion-exchange resins of the dextran gel type. They report that the resin suspensions in low-ionic-strength media gave rise to the dispersion which was assigned to the interfacial polarization. Under such a condition, the conductivity of the resin interior became higher than that of the external media by the possible contribution of movable counterions associated with fixed charges in the resins.

Figure 8 shows the dielectric behavior of a gelatin ball in suspension as a function of the ionic strength of the suspending medium. As illustrated, the ball exhibited a marked

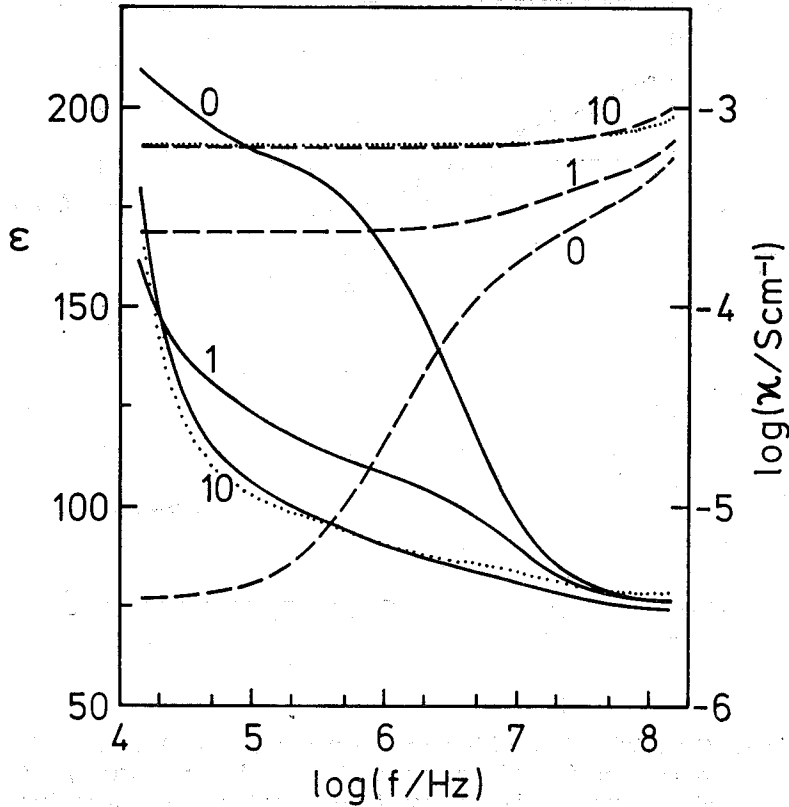


Fig. 8. Plots of  $\epsilon$  (—) and  $\kappa$  (---) vs. frequency for one gelatin ball suspended in different KCl solutions whose concentration are denoted by numbers beside the curves in mM. Dotted lines indicate data on 10mM KCl solution alone.

dielectric dispersion when equilibrated with, and placed in, deionized water, while the dispersion magnitude once attained decreased as the medium ionic strength was raised by successive changes of the circulating medium from pure water to 10 mM KCl solution. Under the final condition of 10 mM KCl the resulting dispersion profiles for both  $\epsilon$  and  $\kappa$  were almost indistinguishable from those of the medium alone. Thus the ionic strength dependence has been demonstrated for the dielectric behavior of the present gelatin-ball suspension as a simple binary system.

As clearly shown in Fig. 9, the observed dispersion curve for the ball equilibrated with deionized water showed a relaxation spectrum broader than a single relaxation (i.e., the Debye type) expected from the Wagner equation:

$$\epsilon^* = \epsilon_a^* \frac{2(1-\Phi)\epsilon_a^* + (1+2\Phi)\epsilon_i^*}{(2+\Phi)\epsilon_a^* + (1-\Phi)\epsilon_i^*} \quad (7)$$

where  $\epsilon^*$  is complex relative permittivity defined as  $\epsilon^* = \epsilon - j\kappa/\omega\epsilon_0$ ,  $j = \sqrt{-1}$ ,  $\omega$  is angular frequency,  $\epsilon_0$  is permittivity of vacuum, and subscripts  $a$  and  $i$  refer to the outer and inner phases, respectively. Apparently, this result is at variance with the result on the

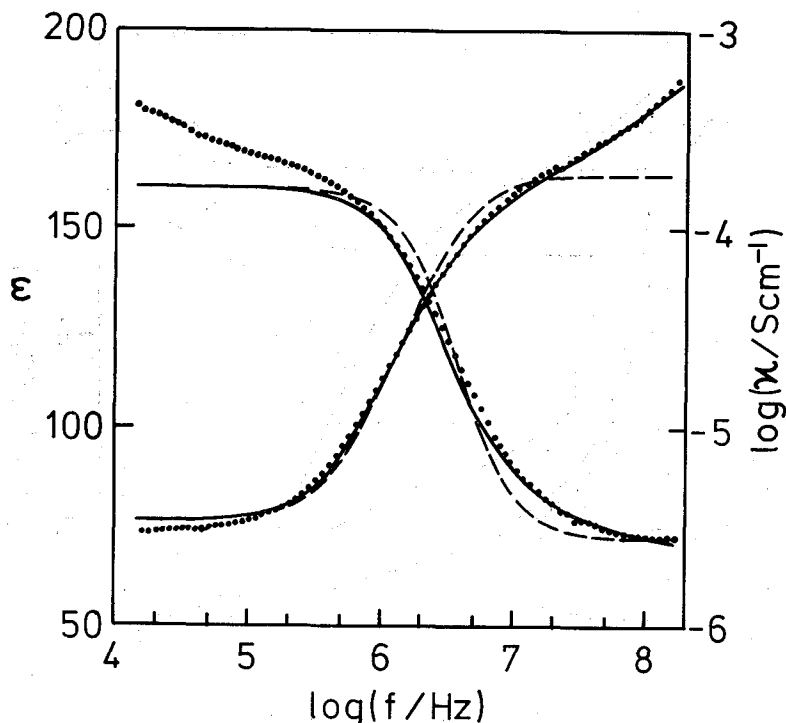


Fig. 9. Curve fittings by the Wagner theory of data (•••••) on one gelatin ball suspended in deionized water, when the phase parameters  $\epsilon_i$  and  $\kappa_i$  are frequency independent (—) and frequency dependent according to the  $m$ -th power law (---).

glass-bead system in that the Wagner equation as one of the pertinent models was applicable to that case.

In order to explain the gap observed between theory and experiment (Fig. 9) we attempted to introduce a certain type of frequency-dependent nature into the parameter  $\epsilon_i^*$  which refers to the suspended phase of hydrated gelatin. After a survey of literature we found that Fricke and co-workers (20, 21) reported an anomalous dielectric behavior for gelatin gel which was ascribed to the relaxation due to the presence of protein-bound water. Quite recently the same topic has been dealt with by Oka et al. (22) who re-examined the anomalous behavior of gelatin gel of concentrations up to 60% and confirmed that the observed dispersions fit to the  $m$ -th power law, or the wedge type relaxation, as earlier pointed out by Hanai (1). Accordingly, our first choice was to assume the  $m$ -th power law to be applicable to the phase parameter of Eq.(7) such that

$$\epsilon_i^* = \epsilon_{ih} + A(j\omega)^{-m} + \frac{\kappa_{i1}}{j\omega\epsilon_v} \quad (8)$$

or alternatively,

$$\epsilon_i = \epsilon_{ih} + (A \cos \frac{\pi}{2} m) \omega^{-m} \quad (9)$$

$$\kappa_i = \kappa_{il} + (A \sin \frac{\pi}{2} m) \varepsilon_v \omega^{1-m} \quad (10)$$

where parameters  $A$  and  $m$  ( $0 < m < 1$ ) are numerical constants dependent on gelatin concentration,  $\varepsilon_{ih}$  is the limiting value of  $\varepsilon_i$  at high frequencies, and  $\kappa_{il}$  the limiting value of  $\kappa_i$  at low frequencies. Combination of Eqs. (7) and (8) gives an expression pertinent to the present system and so allows us to simulate dielectric behavior for the one-sphere system by following the procedure to be detailed in Appendix.

The curve fittings for the measured data were made by using Eqs. (7) and (8) and the resulting best fit curves are shown in Fig. 9, where agreement between the calculated and the measured values is more than satisfactory over the whole dispersion profile. Excellent simulation is also seen in the complex plane plots in Fig. 10. The plot of  $\Delta\varepsilon''$  and  $\varepsilon'$  shows an unusual profile consisting of a circular arc and a subsidiary high-frequency 'tail'.

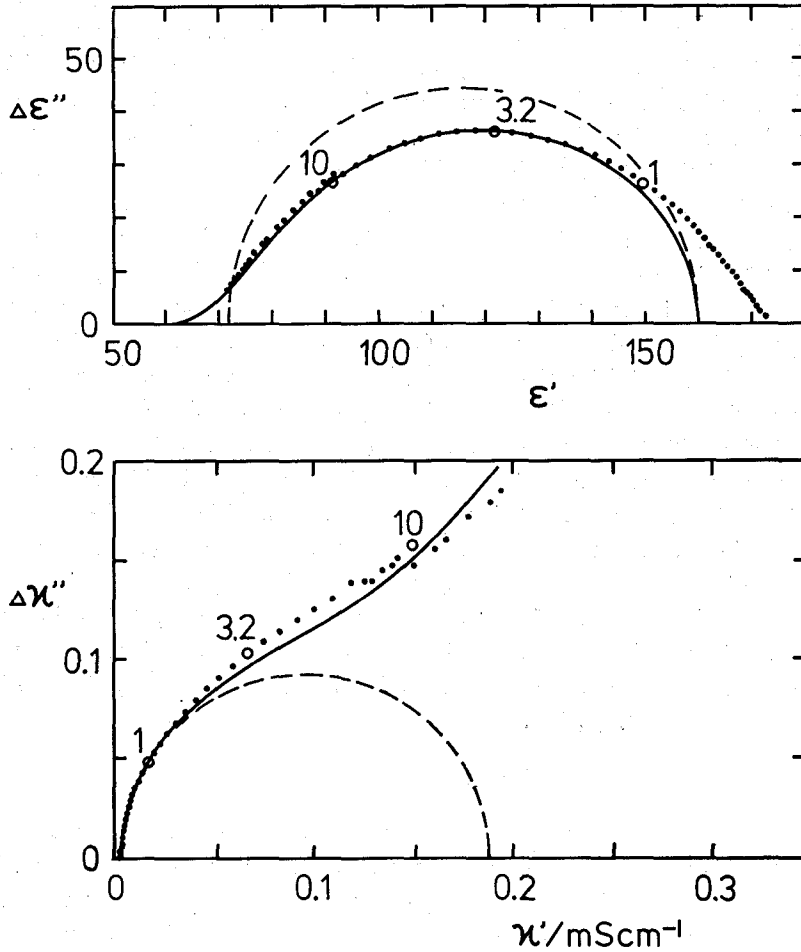


Fig. 10. Complex plane plots of the data in Fig. 9. The number on each point refers to marker frequency in MHz.

Table 3 Estimation of phase parameters for gelatin ball

| Observed parameters           | Estimated phase parameters    |                                  |
|-------------------------------|-------------------------------|----------------------------------|
|                               | Eq. (7)                       | Eqs. (7) and (8)                 |
| $\epsilon_i=160$              | $\kappa_a=1.6 \mu\text{S/cm}$ | $\kappa_a=1.6 \mu\text{S/cm}$    |
| $\epsilon_h=72$               | $\Phi=0.27$                   | $\Phi=0.27$                      |
| $\kappa_i=3.4 \mu\text{S/cm}$ | $\kappa_i=622 \mu\text{S/cm}$ | $\kappa_{ii}=450 \mu\text{S/cm}$ |
| $f_c=3.7 \text{ MHz}$         | $\epsilon_i=62$               | $\epsilon_{ih}=35$               |
|                               |                               | $m=0.34$                         |
| $\epsilon_a=76$               | $\kappa_h=188 \mu\text{S/cm}$ | $A=30000$                        |
| $\kappa_a=1.8 \mu\text{S/cm}$ |                               |                                  |
| $\Phi=0.26$                   |                               |                                  |

Table 3 shows the best-fit parameters employed in Fig. 9. The two curve fittings by Eq. (7) alone and by Eqs. (7) and (8) provided the same values for  $\Phi$  ( $=0.27$ ) and  $\kappa_a$  ( $=1.6 \mu\text{S/cm}$ ); furthermore, these values agreed closely with separate measurements:  $\Phi=0.26$  from the relevant geometry and  $\kappa_a=1.8 \mu\text{S/cm}$  from direct monitoring.

It should be noticed, however, that determination of a unique pair of  $m$  and  $A$  solely from curve fittings via Eqs. (7) and (8) was by no means feasible because changes in  $m$  and  $A$  had a similar effect on the resulting dispersion curves, as will be shown in Appendix. Accordingly, the pair of  $m$  and  $A$  in Table 1 was chosen rather arbitrarily but such that the value of  $m$  be in the range 0.3–0.4 and that of  $A$  in the range  $1 \times 10^4$ – $4 \times 10^4$ , both of which were reported by Oka et al. (22) for a 5–60 % gelatin gel.

The estimated  $\epsilon_{ih}$  is lower than  $\epsilon_a$ , suggesting that the gelatin matrix as a whole had a small permittivity at high frequencies. Oka et al. (22) reported that at the high-frequency region the permittivity of hydrated gelatin gel decrease with increase in the gelatin concentration and that with 40% gelatin gel its permittivity falls to 35, which appears to coincide with the present value of  $\epsilon_{ih}$ . The actual gelatin concentration within the ball was not determined but may have been considerably higher than in the forming solution (10%), since the gelatinous sphere was air dried in the process of formation. In addition to the concentration effect, the lowering of  $\epsilon_{ih}$  may have been partly due to the introduction of cross-linkages between the polypeptide chains.

In spite of complete removal of dialyzable (free) ions from the gelatin gel phase, its conductivity  $\kappa_{ii}$  still remained at a level higher than  $\kappa_a$ . This is explained by the contribution of movable counterions associated with the dissociable groups in gelatin as described by Ishikawa et al. (9, 10).

### CONCLUSION

The dielectric mixture relation for the one-sphere system was examined by use of glass, steel, and gelatin balls suspended in aqueous media. The Wagner equation for a binary mixture suspension was found to be applicable to the glass beads system with the volume fraction up to 0.4 on the assumption of nonconducting spheres. By contrast, the dielectric dispersion curves observed with the steel- and gelatin-ball systems could not be explained in terms of the Wagner equation for a simple binary mixture of a

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frequency-independent, homogeneous sphere and an ambient medium. This, however, does not necessarily mean inapplicability of the Wagner theory to the one-sphere system made of steel or gelatin balls, but rather strongly suggests that the suspended phase carries a complex structure and/or frequency-dependent components. A dielectric model adequate to the steel ball system is the single-shell model where a highly conducting sphere is covered with a thin, non-conducting layer attributable to the electrical double layer arising at the interface between the steel surface and the electrolyte. For the gelatin ball, the frequency dependence obeying the  $m$ -th power law is expected to apply to its internal permittivity and conductivity. Therefore, the Wagner equation combined either with the equation describing the permittivity and conductivity for the shelled-sphere or with the equation for the  $m$ -th power law provided a good simulation for the dielectric behavior of the steel or gelatin ball system, respectively.

### APPENDIX

Here we examine dielectric dispersion curves calculated from text Eqs. (7) and (8) to establish the procedure of the curve fitting for dispersion data on the gelatin balls. Figure 11 shows the variation of dielectric profiles caused by individual changes in the parameters ( $\kappa_{il}$ ,  $\epsilon_{ih}$ ,  $m$  and  $A$ ) from the reference state comparable to the state of the gelatin ball suspended in deionized water. The characteristics of the variation are summarized as follows: (i) The change in  $\kappa_{il}$  strongly influences the dispersion behavior. (ii) Under the condition of  $\kappa_{il} > \kappa_a$ , which is the case for the gelatin ball suspended in deionized water, the effects of  $m$  and  $A$  are restricted to higher-frequency halves of the dispersion curves. (iii) Both an increase in  $m$  and a decrease in  $A$  broaden the dispersion spectra analogously. When  $A=0$ ,  $\epsilon_i$  and  $\kappa_i$  become frequency independent, and then the dispersions exhibit a single relaxation. (iv) A decrease in  $\epsilon_{ih}$  reduces  $\epsilon$  and raises  $\kappa$  at high frequencies.

Next, we briefly consider the limiting permittivities and conductivities at high and low frequencies, which are expressed as

$$\epsilon_h = \epsilon_a \frac{2(1-\Phi)\epsilon_a + (1+2\Phi)\epsilon_{ih}}{(2+\Phi)\epsilon_a + (1-\Phi)\epsilon_{ih}} \quad (A1)$$

$$\kappa_l = \kappa_a \frac{2(1-\Phi)\kappa_a + (1+2\Phi)\kappa_{il}}{(2+\Phi)\kappa_a + (1-\Phi)\kappa_{il}} \quad (A2)$$

$$\epsilon_l = \epsilon_a \frac{\kappa_l}{\kappa_a} + \frac{9(\epsilon_i\kappa_a - \epsilon_a\kappa_{il})\kappa_a\Phi}{[2\kappa_a + \kappa_{il} + \Phi(\kappa_a - \kappa_{il})]^2} \quad (A3)$$

$$\kappa_h = \kappa_a \frac{\epsilon_h}{\epsilon_a} + \frac{9(\kappa_i\epsilon_a - \kappa_a\epsilon_{ih})\epsilon_a\Phi}{[2\epsilon_a + \epsilon_{ih} + \Phi(\epsilon_a - \epsilon_{ih})]^2} \quad (A4)$$

Because  $\epsilon_i \propto \omega^{-m}$  and  $\kappa_i \propto \omega^{1-m}$ , both of Eqs. (A3) and (A4) are a function of  $\omega$ , and thus  $\epsilon_l$  and  $\kappa_h$  essentially have no finite values, but, in a certain frequency range, apparent convergences of  $\epsilon_l$  and  $\kappa_h$  take place under the conditions:  $\epsilon_i \simeq \epsilon_{ih}$  or  $\epsilon_i < \epsilon_a\kappa_{il}/\kappa_a$  for  $\epsilon_l$ ;  $\kappa_i \simeq \kappa_{il}$  or  $\kappa_i < \kappa_a\epsilon_{ih}/\epsilon_a$  for  $\kappa_h$ . In the case of the gelatin ball suspended in deionized water, the condition  $\epsilon_i < \epsilon_a\kappa_{il}/\kappa_a$  is satisfied all over range of measurement frequencies, so that  $\epsilon_l$  has a finite value as shown in Fig. 11.

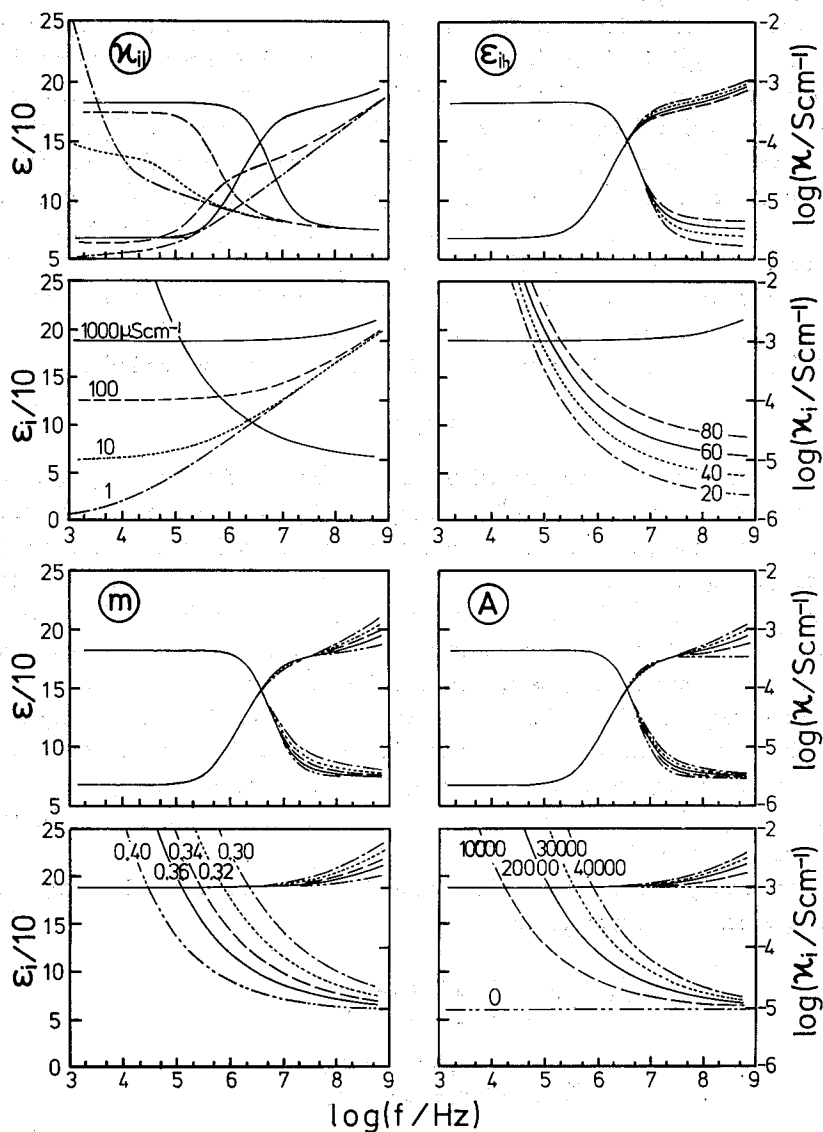


Fig. 11. Variation of dielectric dispersion profiles ( $\epsilon$  and  $\kappa$  vs.  $f$ ) predicted from combination of Eqs. (7) and (8) as a function of encircled parameters. Each figure for  $\epsilon$  and  $\kappa$  is coupled by the figure for  $\epsilon_i$  and  $\kappa_i$  calculated from Eq. (7). Full line curves refer to the reference state defined as:  $\epsilon_a = 80$ ,  $\kappa_a = 1 \mu\text{S/cm}$ ,  $\epsilon_{II} = 60$ ,  $\kappa_{II} = 1 \text{ mS/cm}$ ,  $m = 0.36$ ,  $A = 20000$ , and  $\Phi = 0.3$ .

#### ACKNOWLEDGEMENTS

We wish to thank Professor T. Hanai for pertinent discussion. Thanks are also due to Professor N. Koizumi for his continual encouragement to our dielectric studies. This work was supported in part by the Grant-in-Aid for Scientific Research No. 60770082 from the Ministry of Education, Science and Culture.

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