# Dielectric Constants of Emulsions

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Dielectric constants and electrical conductivities of oil-in-water (O/W), water-in-oil (W/O), and nitrobenzene-in-water (N/W) emulsions at rest and under shear were measured over a wide range of concentration and at frequencies ranging from 20 cps. to 5 mc.

The 0/W emulsions showed neither dielectric dispersion due to the interfacial polarization nor influence of shearing flow on dielectric properties, the concentration dependence of their dielectric constants and conductivities being expressed best by the equations of the Bruggeman type.

In the case of W/O emulsions, striking dielectric dispersions due to the interfacial polarization were observed at high frequency range above 100 kc. Both the limiting dielectric constants at low frequencies and the conductivities at high frequencies decreased with increasing rate of shear. These shearing effects may be attributable to the breaking up of particle agglomerates, The limiting dielectric constants at high frequencies were subjected to no shearing effect, being expressed best by the Bruggeman equation.

The N/W emulsions, which are a kind of O/W emulsions, showed dielectric dispersion due to the interfacial polarization at high frequency range above 30 kc., whereas no shearing effect on the dielectric properties was found in these systems under the rate of shear up to 40 sec$^{-1}$. The limiting dielectric constants at high frequencies are well expressed by the Bruggeman equation.

These expeaimental results support the theoretical conclusion that the magnitude of dielectric dispereion due to the inteafacial polarization is related not to the emulsion type, but to the correlation among dielectric constants and conductivities of the dispersion medium and the disperse phase.

## 1. INTRODUCTION

Dielectric studies of colloidal or coarse dispersion systems including emulsions have already been made by many investigators.

In earlier investigations,[1] dielectric data of emulsions were discussed without strict distinction between heterogeneous mixtures such as emulsions and homogeneous systems such as molecular solutions. Most of the dielectric measurements were carried out at fixed frequencies and within limitted ranges of concentration.

The recent progress of dielectric measurement has enabled us to determine simultaneously accurate values of both dielectric constant and electrical conductivity over a wide range of frequency. Furthermore, it has become possible, to some extent, by proper choice of emulsifier to prepare stable emulsions of both

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oil-in-water and water-in-oil type over a wide range of concentration, and to choose constituent phases having dielectric constants and electrical conductivities appropriate to the purpose.

In connection with the advanced study of rheology, the influence of shearing flow on the dielectric properties of emulsions may also be a subject of some interest.

It was first found by Parts[2] that heterogeneous dispersion systems show marked changes in dielectric properties on agitation. He reported that the dielectric constant of a printing ink, which is a dispersion system of carbon black in varnish, increased on ceasing the movement. Voet[3] observed that the dielectric constants of various suspensions dispersed in oils decreased on agitation. Bondi and Penther[4] reported the frequency dependence of such an agitation effect for various suspensions. This effect was ascribed to the change in the state of agglomeration of dispersed particles. A similar agitation effect is also expected in the case of emulsions.

From the theoretical point of view, the formulas for the dielectric constant of spherical dispersion systems were proposed by several workers as shown in a subsequent section. Recently Reynolds and Hough[5] discussed relationship between these formulas. The validity of these formulas, however, has not been examined yet for lack of experimental data obtained over a wide range of concentration and for each type of emulsions.

These theoretical formulas for dielectric constant are considered to hold for spherical dispersions composed of non-conductive phases. Dispersion systems composed of two phases having finite conductivities are expected to show a dielectric dispersion, which is a so-called interfacial polarization.

In previous papers,[6,7,8] the Maxwell and the Wagner theory of the interfacial polarization were discussed in detail, and a new theory was proposed for concentrated spherical dispersions.

The dielectric dispersion due to the interfacial polarization has so far been observed in the W/O emulsions only,[9,10,11,12] and none of its examples has been found in usual emulsions of the O/W type yet. This fact was reasonably interpreted by the Wagner and the new theory. According to the new theory it was predicted that, when the dielectric constant of the oil phase is as high as nitrobenzene, the dielectric dispersion due to the interfacial polarization may be observed even in emulsions of the O/W type.

In order to examine the validity of these theoretical formulas and predictions, it is necessary to obtain systematic data over wide ranges of concentration and measuring frequency.

In the present study, the authors intended to observe the dielectric behavior of oil-in-water (O/W), water-in-oil (W/O) and nitrobenzene-in-water (N/W) emulsions over wide ranges of concentration and measuring frequency, and to discuss the results in the light of dielectric theories already proposed.

For the purpose of the consideration on the dielectric constant of O/W emulsions, a non-polar solvent was dispersed in distilled water with the aid of

non-ionic emulsifier. Conductivities of this system were unstable, though its dielectric constants were very reproducible. Hence emulsions of oil dispersed in aqueous potassium chloride solution were used for the consideration on the conductivity. Conductivities of this emulsion were stable enough to be measured, though this system is inadequate for the consideration on dielectric constant owing to the remarkable electrode polarization. Dielectric properties of N/W emulsions, which is a kind of O/W emulsions, were observed in hopes of a dielectric dispersion due to the interfacial polarization in accordance with the prediction from the new theory.

The influence of shearing flow on the dielectric properties was examined for all of these emulsions by use of a rotational viscometer.

## 2. THEORETICAL

### List of Symbols

Symbols used in subsequent sections are as follows.

$\varepsilon_m$, $\varepsilon_p$, $\varepsilon$ : dielectric constants of a continuous medium, a disperse phase and a dispersion system respectively.

$\kappa_m$, $\kappa_p$, $\kappa$ : electrical conductivities of a continuous medium, a disperse phase and a dispersion system respectively.

$\varepsilon_h$, $\varepsilon_l$ : limiting dielectric constants at high and low frequencies respectively.

$\kappa_h$, $\kappa_l$ : limiting electrical conductivities at high and low frequencies respectively.

$\Phi$ : volume fraction of a disperse phase.

### A) Theoretical Formulas for the Dielectric Constant of Spherical Dispersion Systems Composed of Non-Conductive Phases

Theoretical formulas for the dielectric constant of dispersion system of spherical particles are the following.

**i) Rayleigh's equation[13].** Rayleigh discussed an electrostatic field for the case where spherical particles of a disperse phase are arranged regularly at the lattice points of a simple cubic lattice in a continuous medium, and obtained an equation for the dielectric constant of the spherical dispersion system as follows:

$$\varepsilon = \varepsilon_m \left[ 1 + \frac{3\Phi}{\dfrac{\varepsilon_p + 2\varepsilon_m}{\varepsilon_p - \varepsilon_m} - \Phi - 1.65 \dfrac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + \dfrac{4}{3}\varepsilon_m} \Phi^{10/3}} \right]. \qquad (1)$$

**ii) Wiener's equation[14].** For a dilute dispersion, where $\Phi \ll 1$, the term containing $\Phi^{10/3}$ in Eq. (1) may be ignored. Thus Wiener obtained the following equation :

$$\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \Phi . \qquad (2)$$

Equation (2) was also derived by Wagner[15] for a random distribution of of spherical particles as shown later on.

iii) **Bruggeman's equation**[16]. Since Eq. (2) was derived under the condition $\Phi \ll 1$, its validity may be restricted to dilute dispersion systems.

Bruggeman extended Eq. (2) to concentrated dispersions on the assumptions that Eq. (2) holds for infinitesimally increasing processes in concentration of the disperse phase, and that the dispersion system will reach a final concentration by succession of these processes. The equation obtained is as follows:

$$\frac{\varepsilon - \varepsilon_p}{\varepsilon_m - \varepsilon_p} \left(\frac{\varepsilon_m}{\varepsilon}\right)^{1/3} = 1 - \Phi .$$  ( 3 )

iv) **Böttcher's equation**[17]. According to Böttcher, a dispersion system was assumed to be a close mixture composed of two kinds of spherical particles: a disperse phase and a dispersion medium. The environment of these spherical particles may be considered as a continuous dielectric with dielectric constant $\varepsilon$. Thus he derived the following equation for a pherical dispersion:

$$\frac{\varepsilon - \varepsilon_m}{3\varepsilon} = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon} \Phi .$$  ( 4 )

Since there is no distinction between the continuous medium and and the disperse phase of a spherical dispersion in the derivation of Eq. (4), values of $\varepsilon$ given by Eq. (4) remain unchanged on phase inversion of emulsions.

v) **Kubo-Nakamura's equation**[18]. Kubo and Nakamura calculated the infinitesimal increment of electric moment due to addition of a sphere of disperse phase to a continuous medium of dielectric constant $\varepsilon$, and evaluated the corresponding increments of polarization of the dispersion system. The dispersion system was considered to reach a final concentration by successive addition of the spheres of disperse phase. Thus they derived the following equation:

$$\frac{3\varepsilon_p}{(2+C)\varepsilon_p + (1-C)} \log \frac{\varepsilon_p - \varepsilon}{\varepsilon_p - \varepsilon_m}$$

$$- \frac{(2+C)\varepsilon_p - 2(1-C)}{[(2+C)\varepsilon_p + (1-C)](2+C)} \log \frac{(2+C)\varepsilon + (1-C)}{(2+C)\varepsilon_m + (1-C)}$$

$$= \log(1-\Phi), \qquad C = 1 - \frac{4\pi}{9\sqrt{3}} = 0.19387 .$$  ( 5 )

## B) Theoretical Formulas for the Electrical Conductivity of Spherical Dispersion Systems

Since, in electrostatic and quasi-electrostatic fields, the electrical conductivity plays a part analogous to the dielectric constant, it is considered that the forms of equations for the dielectric constant are also available to the conductivity.

i) **Wiener type equation.** Wagner[15] showed that, for a random distribution of spherical particles, the conductivity of a dilute dispersion system is given by the following equation:

$$\frac{\kappa - \kappa_m}{\kappa + 2\kappa_m} = \frac{\kappa_p - \kappa_m}{\kappa_p + 2\kappa_m} \Phi .$$  ( 6 )

Equation (6) has the form similar to Eq. (2) which was derived by Wiener[14] for the dielectric constant of a dilute dispersion of spherical particles.

For O/W emulsions, the conductivity of the continuous medium is much larger than that of the disperse phase, that is $\kappa_m \gg \kappa_p$. Here Eq. (6) is reduced to

$$\frac{\kappa}{\kappa_m} = \frac{2(1-\Phi)}{2+\Phi} .$$ (7)

**ii) Bruggeman type equation.** Analogously to Eq. (3) for the dielectric constant, Rue and Tobias[19] used the following equation:

$$\frac{\kappa-\kappa_p}{\kappa_m-\kappa_p}\left(\frac{\kappa_m}{\kappa}\right)^{1/3} = 1-\Phi .$$ (8)

For O/W emulsions $(\kappa_m \gg \kappa_p)$, Fq. (8) is reduced to

$$\frac{\kappa}{\kappa_m} = (1-\Phi)^{3/2} .$$ (9)

**C) Theoretical Formulas for the Dielectric Constant of Spherical Dispersion Systems Composed of Conductive Phases (Theory of the Interfacial Polarization).[6,7,8]**

It is known theoretically that a spherical dispersion composed of two phases having finite electrical conductivities shows a dielectric dispersion due to a so-called interfacial polarization.

Wagner[15] proposed a theory of the interfacial polarization for dilute dispersion systems. Extending the Wagner theory, one of the present authors (Hanai[6]) proposed a new theory applicable to concentrated dispersion systems.

According to these theories, dielectric dispersions are expected to be found in spherical dispersion systems, the details being described in the previous papers.[6,7,8] The relations necessary for the present considerations concerning limiting values of dielectric constant and conductivity at high and low frequencies are shown below.

From the theoretical point of view of the interfacial polarization in which the finite conductivity of each phase is taken into consideration, the dielectric constant of dispersion system composed of non-conductive phases is considered to correspond to the limiting dielectric constant at high frequencies, and the conductivity of dispersion system is to the limiting conductivity at low frequencies.

**i) Limiting values of dielectric constant and conductivity at high and low frequencies**

**a) Wagner theory**

$$\varepsilon_h = \varepsilon_m \frac{2\varepsilon_m + \varepsilon_p - 2\Phi(\varepsilon_m - \varepsilon_p)}{2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)}$$ (10)

$$\varepsilon_l = \frac{\varepsilon_m(2\kappa_m + \kappa_p)^2 + [(9\varepsilon_p - 2\varepsilon_m)\kappa_m^2 - 8\varepsilon_m\kappa_m\kappa_p + \varepsilon_m\kappa_p^2]\Phi - 2\varepsilon_m(\kappa_m - \kappa_p)^2\Phi^2}{[2\kappa_m + \kappa_p + \Phi(\kappa_m - \kappa_p)]^2}$$

$$= \varepsilon_m \frac{\kappa_l}{\kappa_m} + \frac{9(\varepsilon_p\kappa_m - \varepsilon_m\kappa_p)\kappa_m\Phi}{[2\kappa_m + \kappa_p + \Phi(\kappa_m - \kappa_p)]^2}$$ (11)

$$\kappa_l = \kappa_m \frac{2\kappa_m + \kappa_p - 2\emptyset(\kappa_m - \kappa_p)}{2\kappa_m + \kappa_p + \emptyset(\kappa_m - \kappa_p)} \tag{12}$$

$$\kappa_h = \frac{\kappa_m(2\varepsilon_m + \varepsilon_p)^2 + [(9\kappa_p - 2\kappa_m)\varepsilon_m^2 - 8\kappa_m\varepsilon_m\varepsilon_p + \kappa_m\varepsilon_p^2]\emptyset - 2\kappa_m(\varepsilon_m - \varepsilon_p)^2\emptyset^2}{[2\varepsilon_m + \varepsilon_p + \emptyset(\varepsilon_m - \varepsilon_p)]^2}$$

$$= \kappa_m \frac{\varepsilon_h}{\varepsilon_m} + \frac{9(\kappa_p\varepsilon_m - \kappa_m\varepsilon_p)\varepsilon_m\emptyset}{[2\varepsilon_m + \varepsilon_p + \emptyset(\varepsilon_m - \varepsilon_p)]^2}. \tag{13}$$

Eqs. (10) and (12) are the same as Wiener's equations (2) and (6) respectively.

b) New theory

$$\frac{\varepsilon_h - \varepsilon_p}{\varepsilon_m - \varepsilon_p}\left(\frac{\varepsilon_m}{\varepsilon_h}\right)^{1/3} = 1 - \emptyset \tag{14}$$

$$\varepsilon_l\left[\frac{3}{\kappa_l - \kappa_p} - \frac{1}{\kappa_l}\right] = 3\left[\frac{\varepsilon_m - \varepsilon_p}{\kappa_m - \kappa_p} + \frac{\varepsilon_p}{\kappa_l - \kappa_p}\right] - \frac{\varepsilon_m}{\kappa_m} \tag{15}$$

$$\frac{\kappa_l - \kappa_p}{\kappa_m - \kappa_p}\left(\frac{\kappa_m}{\kappa_l}\right)^{1/3} = 1 - \emptyset \tag{16}$$

$$\kappa_h\left[\frac{3}{\varepsilon_h - \varepsilon_p} - \frac{1}{\varepsilon_h}\right] = 3\left[\frac{\kappa_m - \kappa_p}{\varepsilon_m - \varepsilon_p} + \frac{\kappa_p}{\varepsilon_h - \varepsilon_p}\right] - \frac{\kappa_m}{\varepsilon_m}. \tag{17}$$

Eqs. (14) and (16) are the same as Bruggeman's equations (3) and (8) respectively.

ii) **Case $\kappa_m \gg \kappa_p$ (O/W type emulsion).** Here Eqs. (10)-(17) are reduced to the following respectively.

a) Wagner theory

$$\varepsilon_h = \varepsilon_m \frac{2\varepsilon_m + \varepsilon_p - 2\emptyset(\varepsilon_m - \varepsilon_p)}{2\varepsilon_m + \varepsilon_p + \emptyset(\varepsilon_m - \varepsilon_p)} \tag{18}$$

$$\varepsilon_l = \varepsilon_m \frac{2(1 - \emptyset)}{2 + \emptyset} + \frac{9\varepsilon_p\emptyset}{(2 + \emptyset)^2} \tag{19}$$

$$\frac{\kappa_l}{\kappa_m} = \frac{2(1 - \emptyset)}{2 + \emptyset} \tag{20}$$

$$\frac{\kappa_h}{\kappa_m} = \frac{\varepsilon_h}{\varepsilon_m} - \frac{9\varepsilon_m\varepsilon_p\emptyset}{[2\varepsilon_m + \varepsilon_p + \emptyset(\varepsilon_m - \varepsilon_p)]^2}. \tag{21}$$

b) New theory

$$\frac{\varepsilon_h - \varepsilon_p}{\varepsilon_m - \varepsilon_p}\left(\frac{\varepsilon_m}{\varepsilon_h}\right)^{1/3} = 1 - \emptyset \tag{22}$$

$$\frac{2\varepsilon_l - 3\varepsilon_p}{2\varepsilon_m - 3\varepsilon_p} = (1 - \emptyset)^{3/2} \tag{23}$$

$$\frac{\kappa_l}{\kappa_m} = (1 - \emptyset)^{3/2} \tag{24}$$

$$\frac{\kappa_h}{\kappa_m} = \frac{\varepsilon_h(\varepsilon_h - \varepsilon_p)(2\varepsilon_m + \varepsilon_p)}{\varepsilon_m(\varepsilon_m - \varepsilon_p)(2\varepsilon_h + \varepsilon_p)}. \tag{25}$$

For smaller values of $\varepsilon_p$, Eqs. (18)-(21) of the Wagner theory lead to

$$\varepsilon_l \doteqdot \varepsilon_m \frac{2(1 - \emptyset)}{2 + \emptyset} \doteqdot \varepsilon_h \tag{26}$$

and

$$\frac{\kappa_h}{\kappa_m} \doteqdot \frac{\varepsilon_h}{\varepsilon_m} \doteqdot \frac{2(1 - \emptyset)}{2 + \emptyset} = \frac{\kappa_l}{\kappa_m}, \tag{27}$$

and Eqs. (22)–(25) of the new theory lead to

$$\varepsilon_l \fallingdotseq \varepsilon_m(1-\Phi)^{3/2} \fallingdotseq \varepsilon_h \tag{28}$$

and

$$\frac{\kappa_h}{\kappa_m} \fallingdotseq \frac{\varepsilon_h}{\varepsilon_m} \fallingdotseq (1-\Phi)^{3/2} = \frac{\kappa_l}{\kappa_m}. \tag{29}$$

Hence it is expected from both the Wagner and the new theory that the dispersions of dielectric constants and conductivities are too small to be observed in O/W emulsions having smaller values of $\varepsilon_p$.

The approximate equality between the expressions of $\varepsilon_l$, $\varepsilon_h$, $\kappa_h$ and $\kappa_l$ may not hold in the case of an O/W emulsion in which the disperse phase has a dielectric constant as high as nitrobenzene.

In Table 1 are shown theoretical values of limiting dielectric constants obtained from Eqs. (18), (19), (22) and (23) by using the values $\varepsilon_m = 78.0$ and $\varepsilon_p = 35.15$ corresponding to the case of N/W emulsions.

Table 1. Theoretical values of limiting dielectric constants at high frequencies $\varepsilon_h$ and at low frequencies $\varepsilon_l$ for the nitrobenzene-in-water emulsions.

| Volume fraction of disperse phase $\Phi$ | Wagner theory | | New theory | |
| --- | --- | --- | --- | --- |
| | $\varepsilon_h$ Eq. (18) | $\varepsilon_l$ Eq. (19) | $\varepsilon_h$ Eq. (22) | $\varepsilon_l$ Eq. (23) |
| 0.0 | 78.00 | 78.00 | 78.00 | 78.00 |
| 0.1 | 72.87 | 74.03 | 72.85 | 74.31 |
| 0.2 | 67.96 | 69.80 | 67.88 | 70.81 |
| 0.3 | 63.25 | 65.42 | 63.10 | 67.53 |
| 0.4 | 58.74 | 60.97 | 58.51 | 64.47 |
| 0.5 | 54.42 | 56.51 | 54.12 | 61.66 |
| 0.6 | 50.26 | 52.08 | 49.92 | 59.12 |
| 0.7 | 46.26 | 47.71 | 45.92 | 56.88 |
| 0.8 | 42.42 | 43.42 | 42.13 | 54.99 |
| 0.85 | 40.55 | 41.32 | 40.31 | 54.19 |
| 0.9 | 38.72 | 39.23 | 38.54 | 53.52 |
| 0.95 | 36.92 | 37.18 | 36.82 | 53.01 |
| 0.97 | 36.21 | 36.37 | 36.14 | 52.86 |
| 1.0 | 35.15 | 35.15 | 35.15 | 52.73 |

It should be noticed from Table 1 that the differences between $\varepsilon_l$ and $\varepsilon_h$ are small over the whole range of concentration for the Wagner theory, whereas these differences are large at higher concentrations for the new theory. Consequently N/W emulsions are expected from the new theory to show the dielectric dispersions large enough to be observed at higher concentrations. According to the Wagner theory, the dielectric dispersions in N/W emulsions should be too small to be observed especially at higher concentrations.

iii) **Case $\kappa_p \gg \kappa_m$ (W/O type emulsion).** Here Eqs. (10)–(17) are reduced to the following respectively.

a) Wagner theory

$$\varepsilon_h = \varepsilon_m \frac{2\varepsilon_m + \varepsilon_p - 2\Phi(\varepsilon_m - \varepsilon_p)}{2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)} \tag{30}$$

$$\varepsilon_l = \varepsilon_m \frac{\kappa_l}{\kappa_m} = \varepsilon_m \frac{1 + 2\Phi}{1 - \Phi} \tag{31}$$

$$\frac{\kappa_l}{\kappa_m} = \frac{1 + 2\Phi}{1 - \Phi} \tag{32}$$

$$\frac{\kappa_h}{\kappa_p} = \left[\frac{3\varepsilon_m}{2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)}\right]^2 \Phi . \tag{33}$$

b) New theory

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

$$\varepsilon_l = \varepsilon_m \frac{1}{(1 - \Phi)^3} \tag{35}$$

$$\frac{\kappa_l}{\kappa_m} = \frac{1}{(1 - \Phi)^3} \tag{36}$$

$$\frac{\kappa_h}{\kappa_p} = \frac{3\varepsilon_h(\varepsilon_h - \varepsilon_m)}{(2\varepsilon_h + \varepsilon_p)(\varepsilon_p - \varepsilon_m)} . \tag{37}$$

According to both the Wagner and the new theory, both differences between $\varepsilon_l$ and $\varepsilon_h$ and between $\kappa_h$ and $\kappa_l$ are very large at higher concentrations of W/O emulsions. Therefore remarkable dielectric dispersions due to the interfacial polarization are expected to be observed in W/O emulsions.

## 3. EXPERIMENTAL

### A) Preparation of Emulsions

For almost all cases nujol was weighted with carbon tetrachloride to the same density as the water phase so that emulsions produced may be stable during measurement.

Non-ionic surface active agents were selected as emulsifiers:[20] Tween 20 (Polyoxyethylene sorbitan monolaurate, H.L.B. 16.7), Span 20 (Sorbitan monolaurate, H.L.B. 8.6), Span 60 (Sarbitan mono stearate, H.L.B. 4.7), Arlacel 83 (Sorbitan sesquioleate, H.L.B. 3.7), and Polyoxyethylene glycol cetyl ether ($\overline{DP}$ of the polyoxyethylene group $= 31.3$).

For O/W stystems, stable emulsions were readily obtained by shaking of mixtures of the oil and the water phases.

In the cases of W/O and N/W emulsions, the water phase was gradually poured into the oil phase with vigorous agitation by use of a glass triturator.

For the purpose of conductivity measurements of O/W systems, two kinds of emulsion (I and II) were prepared: Emulsion I were obtained with Span 20 and Tween 20, and Emulsion II with polyoxyethylene glycol cetyl ether.

In Table 2 are tabulated the recipes of emulsions: composition of oil and water phases, emulsifier and its concentration in each phase, method of mixing, particle size of disperse phase and concentration of disperse phase in emulsion.

Table 2. Recipes for preparation of emulsions.

| | O/W emulsion for $\varepsilon$ measurement | O/W emulsion for $\kappa$ measurement | W/O emulsion | N/W emulsion |
|---|---|---|---|---|
| Quantity measured | $\varepsilon$ | $\kappa$ | $\varepsilon$ and $\kappa$ | $\varepsilon$ and $\kappa$ |
| Oil phase | Mixture of nujol, $CCl_4$ and emulsifiers | (I) Mixture of nujol, $CCl_4$ and emulsifier (II) Mixture of tetralin and emulsifier | Mixture of nujol, and $CCl_4$ | Nitrobenzene and emulsifier |
| Water phase | Distilled water | 0.05 N KCl solution and emulsifier | Distilled water and emulsifier | Distilled water and emulsifier |
| Emulsifier | Mixture of Tween 20 (50% wt.) and Span 20 (50%) | (I) Mixture of Tween 20 (50%) and Span 20 (50%) (II) Polyoxyethylene glycoly cetyl ether | Mixture of Arlacel 83 (60%), Span 20 (20%) and Span 60 (20%) | Tween 20 |
| Concentration of emulsifier in oil phase in water phase | 1% wt. 0% | 0.5% 0.5% | 5% 0.5%[a] | 2% 2% |
| Method of mixing | Shaking | Shaking | Stirring with glass triturator | Stirring with glass triturator |
| Particle size | 6~20 $\mu$ | 6~20 $\mu$ | 0.5~1.5 $\mu$ | 1~5 $\mu$ |
| Measuring cell | Concentric cylinders | Platinum wires | Rotational viscometer | Concentric cylinders |
| Cell capacitance | 1.49 $\mu\mu$F | 0.0584 $\mu\mu$F[b] | and 4.74 $\mu\mu$F 17.09 $\mu\mu$F | 1.49 $\mu\mu$F |
| Concentration of disperse phase in emulsion | 0~85% | 0~80% | 0~80% | 50~95% |
| Measuring temperature | 30°C | 25°C | 30°C | 20°C |

a) Translucent owing to poor solubility of emulsifiers in water.

b) Calculated from the relation :

$$\frac{0.08854}{\text{Conductivity cell constant (in cm}^{-1})} = \text{Cell capacitance (in } \mu\mu\text{F)}.$$

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## B) Measuring Cell

The measuring cell of dielectric constant for quiescent state consisted of two concentric platinum cylinders whose empty cell capacitance was $1.49\,\mu\mu\mathrm{F}$. This cell was used for O/W and N/W emulsions.

The electrodes of the conductivity cell consisted of platinum wires, and the cell constant was $1.515\,\mathrm{cm}^{-1}$, which corresponds to $0.0584\,\mu\mu\mathrm{F}$ in empty cell capacitance.

Dielectric measurements of emulsions under shearing stress were carried out with a double cylindrical rotational viscometer of the Green type,[21] the bobs and the cup being made of stainless steel. Two exchangeable bobs were used, being 1.5 and 2.5 cm in diameter respectively and 5.1 cm in length. The cup is 3 cm in inner diameter and 6 cm in inside height. Capacitance and conductance between the bob and the cup filled with a specimen were measured at varying r.p.m. of the cup. The empty cell capacitance was $4.74\,\mu\mu\mathrm{F}$ for the small bob, and $17.09\,\mu\mu\mathrm{F}$ for the large bob. The former was used for W/O emulsions of more than 30%, the latter for less than 20%. The 100, 200 and 300 r.p.m. of the cup correspond to 12.9, 25.8 and 38.7 $\mathrm{sec}^{-1}$ in the mean rate of shear for the specimen respectively.

## C) Dielectric Measurements

Both capacitance and conductance were measured over a frequency range of 20 cps. to 5 mc. by means of a conductance-capacitance bridge[22] which was used in the previous study.[23]

## 4. RESULTS

### A) Dielectric Behavior of O/W Emulsions

**i) Dielectric constant of O/W emulsions**[23]. Dielectric constants and electrical conductivities measured on the O/W emulsion of 70% in concentration at 30°C are plotted against the measuring frequency in Fig. 1. In the lower frequency range the dielectric constant increased rapidly with decreasing frequency, whereas the electrical conductivity remained constant irrespective of the frequency. Above about 5 kc. the observed dielectric constant showed a constant value independent of frequency. Such a frequency dependence of the apparent dielectric constant $\varepsilon_{app}$ is well expressed by the following empirical formula:

$$\varepsilon_{app}-\varepsilon = A\omega^{-m} \tag{38}$$

where $\varepsilon$ is the limiting value of $\varepsilon_{app}$ at high frequencies, $A$ and $m$ are the empirical constants and $\omega$ denotes the angular frequency. The value of $m$ was about 1.7 irrespective of concentration of emulsion. The value of $A$ increased with increasing electrical conductivity of emulsions. Such frequency dependence of dielectric constant was also reported for some other cases.[24,25] This effect may be attributed to the electrode polarization which arises from the electrolytic polarization of ions on electrode surfaces. The limiting value $\varepsilon$ is regarded as the true dielectric constant of emulsion without any contribution of the electrode polarization.
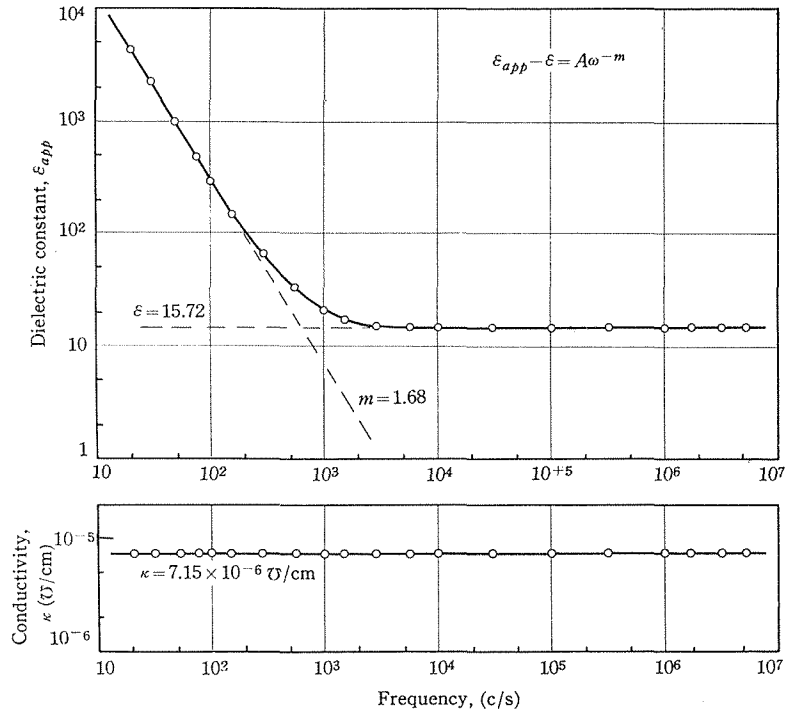
Fig. 1. Frequency dependence of apparent dielectric constant $\varepsilon_{app}$ and electrical conductivity $\kappa$ for the O/W emulsion of 70% in volume concentration at 30°C.

Table 3. Dielectric constants observed and calculated for the O/W emulsions at 30°C.

| Volume fraction of disperse phase $\Phi$ | Dielectric constant $\varepsilon$ | | | | | |
|---|---|---|---|---|---|---|
| | observed | calculated from | | | | |
| | | Kubo-Nakamura Eq. (5) | Wiener Eq. (2) | Rayleigh Eq. (1) | Bruggeman Eq. (3) | Böttcher Eq. (4) |
| 0.0 | 76.80 | 76.80 | 76.80 | 76.80 | 76.80 | 76.80 |
| 0.1 | 65.42 | 68.78 | 66.33 | 66.33 | 66.11 | 65.86 |
| 0.2 | 55.48 | 60.84 | 56.77 | 56.73 | 56.00 | 55.01 |
| 0.3 | 46.36 | 53.02 | 48.01 | 47.76 | 46.50 | 44.28 |
| 0.4 | 38.06 | 45.27 | 39.95 | 39.12 | 37.65 | 33.81 |
| 0.5 | 29.48 | 37.68 | 32.51 | 30.44 | 29.51 | 23.85 |
| 0.6 | 22.28 | 30.21 | 25.62 | 21.24 | 22.13 | 15.06 |
| 0.7 | 15.72 | 22.92 | 19.22 | 10.84 | 15.60 | 8.643 |
| 0.8 | 9.78 | 15.84 | 13.26 | — 1.79 | 10.04 | 5.124 |
| 0.85 | 7.73 | 12.42 | 10.44 | — 9.44 | 7.671 | 4.120 |
| 0.9 | —— | 9.09 | 7.702 | —18.39 | 5.605 | 3.409 |
| 0.95 | —— | 5.83 | 5.058 | —29.15 | 3.873 | 2.890 |
| 1.0 | 2.50 | 2.50 | 2.50 | —42.44 | 2.50 | 2.50 |

The true dielectric constants of O/W emulsions at various concentrations are listed in Table 3, and are plotted against the concentration of oil in Fig. 9. No dielectric dispersion due to the interfacial polarization was found over the present range of frequency. No appreciable change in dielectric constant and conductivity of emulsions was observed on shearing flow.

**ii) Conductivity of O/W emulsions**[26]. Although capacitances of the measuring cell filled with the O/W emulsion show the remarkable dependence of frequency, its conductivities remain constant over the whole range of frequency.

Fig. 2 shows the frequency dependence of capacitance and electrical conductivity for Emulsion I of 70% in volume concentration at 25°C. Such a frequency
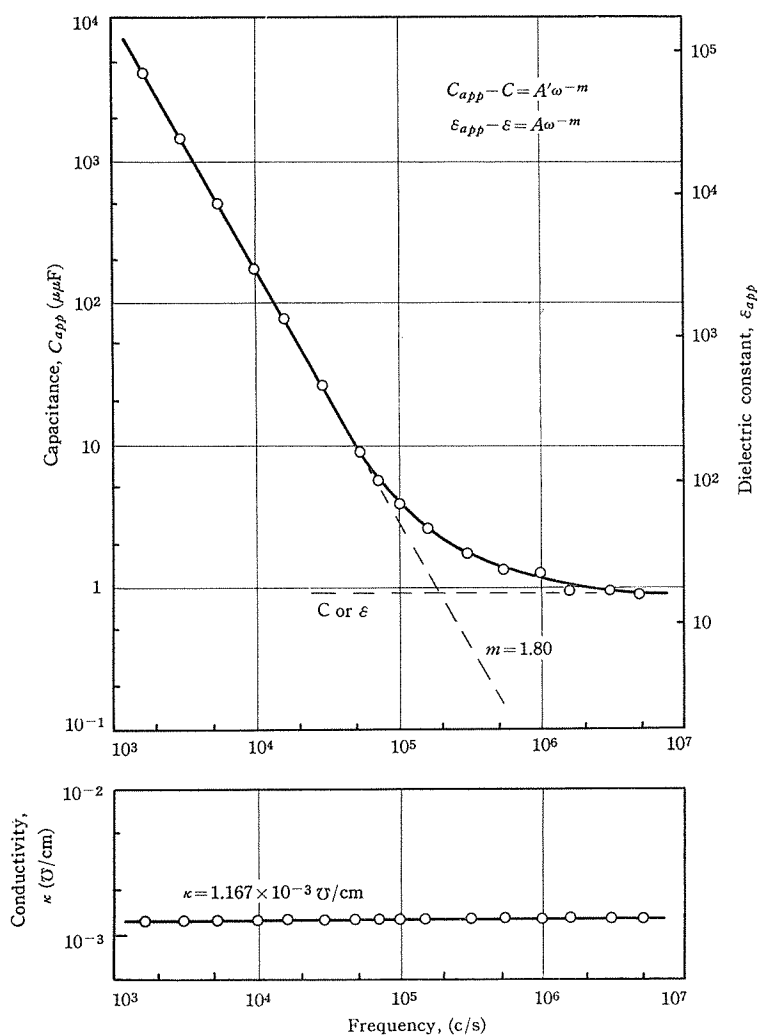


Fig. 2. Frequency dependence of apparent capacitance $C_{app}$ or apparent dielectric constant $\varepsilon_{app}$ and electrical conductivity $\kappa$ for the O/W emulsion of 70% in volume concentration at 25°C.

dependence of the apparent capacitance $C_{app}$ or the apparent dielectric constant $\varepsilon_{app}$ is expressed by the same empirical formula as Eq. (38). The constant $m$ took a value of about 1.8 irrespective of concentration of emulsions. The limiting value of capacitance or dielectric constant at high frequencies was too small to be subjected to quantitative considerations.

This frequency dependence of $C_{app}$ may be attributed to the electrode polarization.

The similar behavior was also found in Emulsion II.

Neither dielectric dispersion due to the interfacial polarization nor appreciable change in the conductivity under shearing flow was observed for the present emulsions.

When the measuring electrodes were coated with platinum black, the electrode polarization was practically reduced and the frequency dependence of capacitance disappeared, whereas the value of conductance still remained unchanged.

The observed values of the relative conductivity $\frac{\kappa}{\kappa_m}$ at various concentrations of Emulsion I and II are shown in Table 4, and are plotted against the concentration of oil in Fig. 10.

Table 4. Electrical conductivities observed and calculated for the O/W emulsions at 25°C.

| Volume fraction of disperse phase $\Phi$ | Relative conductivity $\frac{\kappa}{\kappa_m}$ | | | |
|---|---|---|---|---|
| | observed for | | calculated from | |
| | Emulsion I | Emulsion II | Eq. (7) $\frac{2(1-\Phi)}{2+\Phi}$ | Eq. (9) $(1-\Phi)^{3/2}$ |
| 0.0 | 1.000 | 1.000 | 1.0000 | 1.0000 |
| 0.1 | 0.855 | 0.849 | 0.8571 | 0.8538 |
| 0.2 | 0.714 | 0.694 | 0.7273 | 0.7155 |
| 0.3 | 0.584 | 0.584 | 0.6087 | 0.5857 |
| 0.4 | 0.465 | 0.460 | 0.5000 | 0.4648 |
| 0.5 | 0.353 | 0.354 | 0.4000 | 0.3536 |
| 0.6 | 0.268 | 0.262 | 0.3077 | 0.2530 |
| 0.7 | 0.177 | 0.181 | 0.2222 | 0.1643 |
| 0.8 | 0.0995 | 0.108 | 0.1429 | 0.08944 |
| 0.85 | — | — | 0.1053 | 0.05809 |
| 0.9 | — | — | 0.06897 | 0.03162 |
| 0.95 | — | — | 0.03390 | 0.01118 |
| 1.0 | 0.000 | 0.000 | 0.00000 | 0.00000 |

The electrical conductivity observed for the water phase
$\kappa_m = 6.129 \times 10^{-3}$ ℧/cm    for Emulsion I.
$\kappa_m = 6.855 \times 10^{-3}$ ℧/cm    for Emulsion II.

## B) Dielectric Behavior of W/O Emulsions[27]

The W/O emulsions showed the dielectric behavior very different from that of O/W emulsions in respect of interfacial and electrode polarizations.

Since it was found that dielectric properties of the present W/O emulsions

are influenced by agitation and shearing stress, dielectric measurements were carried out at varying r.p.m. of the cup of the rotational viscometer.

In Figs. 3 and 4 are shown the frequency dependence of dielectric constants $\varepsilon'$, loss factors $\varepsilon''$ and conductivities $\kappa$ at rest and at various r.p.m. of the cup for the W/O emulsion of 80% in volume concentration. These striking dielectric dispersions above 30 kc. may be attributable to the interfacial polarization, which was not found in the O/W emulsions. A gradual increase in the dielectric constant $\varepsilon'$ with decreasing frequency below 1 kc. may be attributed to the electrode polarization, which was much more pronounced in the O/W emulsions than in the present case. A remarkable decrease in the dielectric constant $\varepsilon'$ under shearing stress as seen in Fig. 3 may be attributed to the change in the state of agglomeration of dispersed particles. This phenomenon may be consistent with
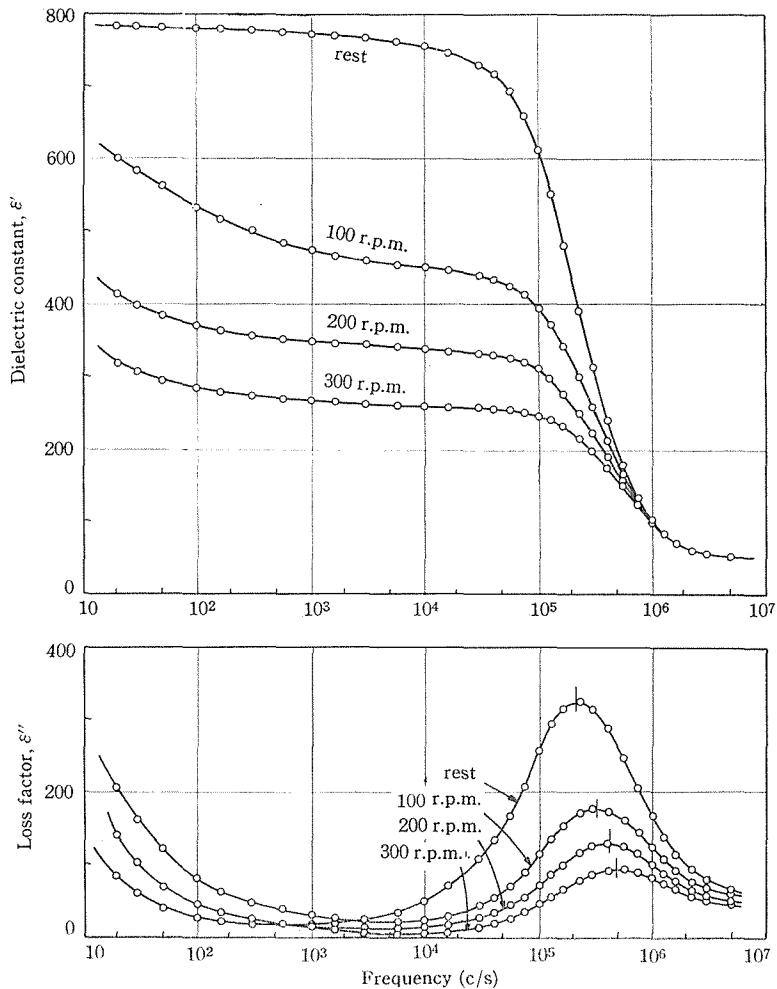
Fig. 3. Frequency dependence of dielectric constants $\varepsilon'$ and loss factors $\varepsilon''$ at rest and at various r.p.m. of the cup for the W/O emulsion of 80% in volume concentration at 30°C.
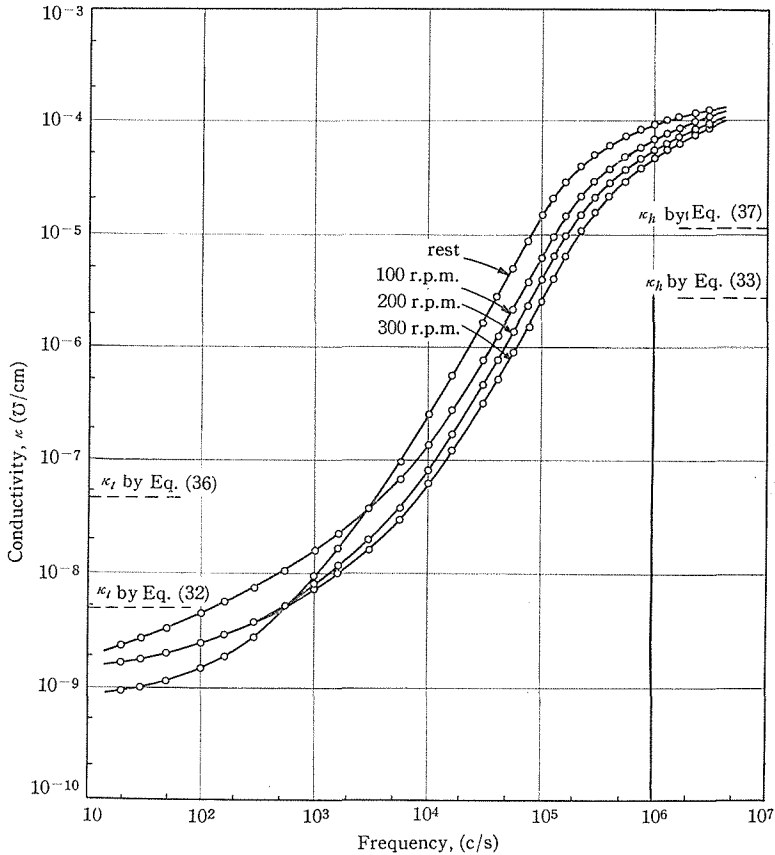
Fig. 4. Frequency dependence of electrical conductivities $\kappa$ at rest and at various r.p.m. of the cup for the W/O emulsion of 80% in volume concentration at 30°C.

that reported by Voet,[3] who measured only the limiting dielectric constants of suspensions at low frequencies.

The complex plane plots of $\varepsilon'$ and $\varepsilon''$ for the W/O emulsion of 80% gave the circular-arcs as shown in Fig. 5. Thus the dielectric dispersions of W/O emulsions are represented approximately by the circular-arc rule

$$\varepsilon' - j\varepsilon'' = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + (jf/f_0)^{1-\alpha}}, \tag{39}$$

where $f$ is the measuring frequency, $f_0$ the critical frequency for which the loss factor is a maximum and $\alpha$ denotes a parameter for the distribution of relaxation times and $j = \sqrt{-1}$.

The limiting dielectric constant at high frequencies $\varepsilon_h$ showed no appreciable change under shearing stress. The values af $\varepsilon_l$ decreased with increasing r.p.m., whereas the critical frequency $f_0$ increased with increasing r.p.m.

The behavior similar to that mentioned above was observed at all other concentrations. Table 5 shows the values of $\varepsilon_h$, $\varepsilon_l$, $f_0$, and $\alpha$ at various r.p.m.

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Table 5. Values of $\varepsilon_h$, $\varepsilon_l$, $\kappa_{100c}$, $\kappa_{f_0}$, $\kappa_{3mc}$, $f_0$ and $\alpha$ at various r.p.m. of the cup for the W/O emulsions at various concentrations $\Phi$.

| Volume fraction of disperse phase $\Phi$ | $\varepsilon_h$ | r.p.m. of the cup | $\varepsilon_l$ | $\kappa_{100c}$ in $10^{-10}$ ℧/cm | $\kappa_{f_0}$ in $10^{-5}$ ℧/cm | $\kappa_{3mc}$ in $10^{-5}$ ℧/cm | $f_0$ in kc. | $\alpha$ |
|---|---|---|---|---|---|---|---|---|
| 0.1 | — | 0 | 3.86 | 0.910 | — | — | — | — |
| | | 100 | 3.60 | 1.43 | — | — | — | — |
| | | 200 | 3.43 | 1.25 | — | — | — | — |
| | | 300 | 3.34 | 1.36 | — | — | — | — |
| 0.2 | — | 0 | 10.93 | 2.35 | — | 0.363 | — | — |
| | | 100 | 8.17 | 4.14 | — | 0.223 | — | — |
| | | 200 | 7.23 | 3.61 | — | 0.156 | — | — |
| | | 300 | 6.91 | 4.04 | — | 0.135 | — | — |
| 0.3 | 6.3 | 0 | 21.6 | 3.52 | 1.410 | 1.297 | 3200 | 0.023 |
| | | 100 | 19.6 | 5.55 | 1.140 | 1.005 | 3230 | 0.036 |
| | | 200 | 15.9 | 4.85 | 0.834 | 0.741 | 3250 | 0.062 |
| | | 300 | 13.8 | 5.30 | 0.653 | 0.586 | 3300 | 0.039 |
| 0.4 | 8.7 | 0 | 45.0 | 3.73 | 0.979 | 2.02 | 1190 | 0.158 |
| | | 100 | 42.6 | 8.17 | 0.746 | 1.633 | 1250 | 0.161 |
| | | 200 | 30.0 | 6.77 | 0.605 | 1.176 | 1300 | 0.169 |
| | | 300 | 24.4 | 7.45 | 0.470 | 0.907 | 1370 | 0.152 |
| 0.5 | 13.3 | 0 | 126.5 | 7.65 | 1.381 | 3.90 | 500 | 0.124 |
| | | 100 | 78.5 | 12.64 | 1.064 | 2.75 | 690 | 0.124 |
| | | 200 | 55.0 | 11.30 | 0.859 | 2.09 | 880 | 0.124 |
| | | 300 | 42.6 | 11.90 | 0.746 | 1.73 | 1040 | 0.111 |
| 0.6 | 18.8 | 0 | 166.3 | 5.97 | 1.717 | 4.81 | 460 | 0.100 |
| | | 100 | 116.5 | 14.32 | 1.474 | 3.94 | 620 | 0.113 |
| | | 200 | 85.7 | 7.39 | 1.306 | 3.21 | 800 | 0.105 |
| | | 300 | 63.5 | 8.40 | 1.120 | 2.59 | 1000 | 0.105 |
| 0.7 | 28.2 | 0 | 346. | 9.66 | 1.886 | 6.22 | 233 | 0.081 |
| | | 100 | 218. | 17.00 | 1.609 | 4.93 | 348 | 0.107 |
| | | 200 | 159. | 16.80 | 1.446 | 4.09 | 460 | 0.111 |
| | | 300 | 119. | 14.92 | 1.306 | 3.60 | 580 | 0.094 |
| 0.8 | 39.0 | 0 | 754. | 14.1 | 4.11 | 13.31 | 224 | 0.062 |
| | | 100 | 450. | 44.8 | 3.21 | 10.41 | 332 | 0.108 |
| | | 200 | 341. | 24.3 | 2.95 | 9.33 | 412 | 0.127 |
| | | 300 | 258. | 23.3 | 2.67 | 8.83 | 492 | 0.083 |

Oil phase : Dielectric constant $\varepsilon_m = 2.50$, conductivity $\kappa_m = 3.83 \times 10^{-10}$ ℧/cm
Water phase: Dielectric constant $\varepsilon_p = 76.8$, conductivity $\kappa_p = 3.13 \times 10^{-5}$ ℧/cm
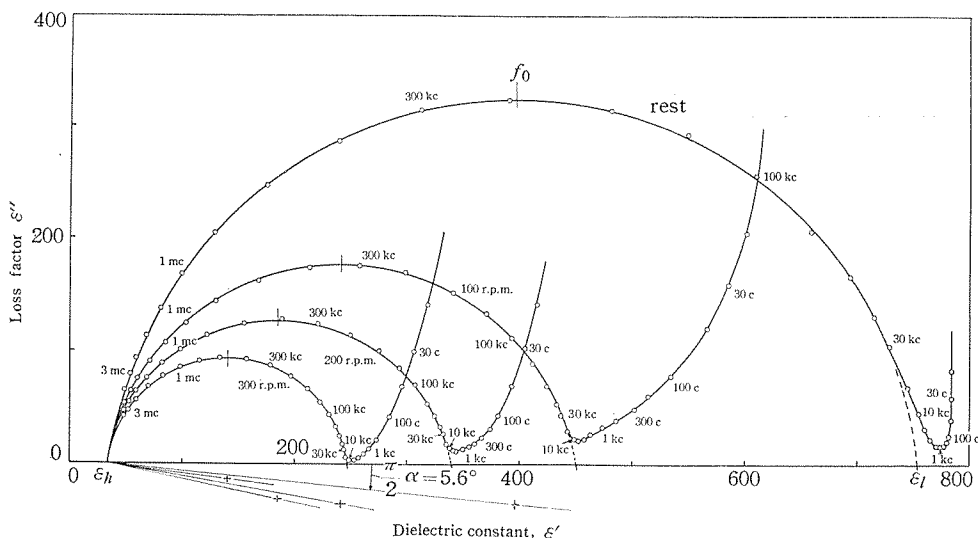
Fig. 5. Complex plane plots of $\varepsilon'$ and $\varepsilon''$ at rest and at various r.p.m. of the cup for the W/O emulsion of 80% in volume concentration at 30°C.

for each concentration.

As seen in Fig. 4, the limiting values of conductivities at low and at high frequencies were not obtained from the present data. In Table 5 are shown the values of conductivity at 100 cps. $\kappa_{100c}$, those at critical frequency $\kappa_{f_0}$, and those at 3 mc. $\kappa_{3mc}$, which are regarded as measures of conductivities at low and at high frequencies respectively.

The dielectric dispersions could not be observed for W/O emulsions at concentrations less than 20%. Since $f_0$ increases with decreasing concentration as seen in Table 5, it seems that the dielectric dispersions in such dilute emulsions shift to the higher frequencies beyond the present measurements.

## C) Dielectric Behavior of N/W Emulsions[28]

The N/W emulsions showed dielectric dispersions due to the interfacial polarization, though these emulsions are considered to be a kind of O/W emulsions.

Fig. 6 shows the frequency dependence of apparent dielectric constants $\varepsilon_{app}$ and conductivities $\kappa$ for the N/W emulsion of 70% in volume concentration.

Rapid increase in dielectric constant at frequencies below 30 kc. may be attributed to the electrode polarization. The frequency dependence of the apparent dielectric constant $\varepsilon_{app}$ for the electrode polarization is well expressed by the following empirical formula similar to Eq. (38)

$$\varepsilon_{app}-\varepsilon' = A\omega^{-m} , \tag{40}$$

where $\varepsilon'$ is the true dielectric constant of emulsion without any contribution of the electrode polarization. The value of $m$ was about 1.7 irrespective of concentration of emulsions.

A dielectric dispersion of $\varepsilon'$ accompanied by a remarkable increase in conduc-
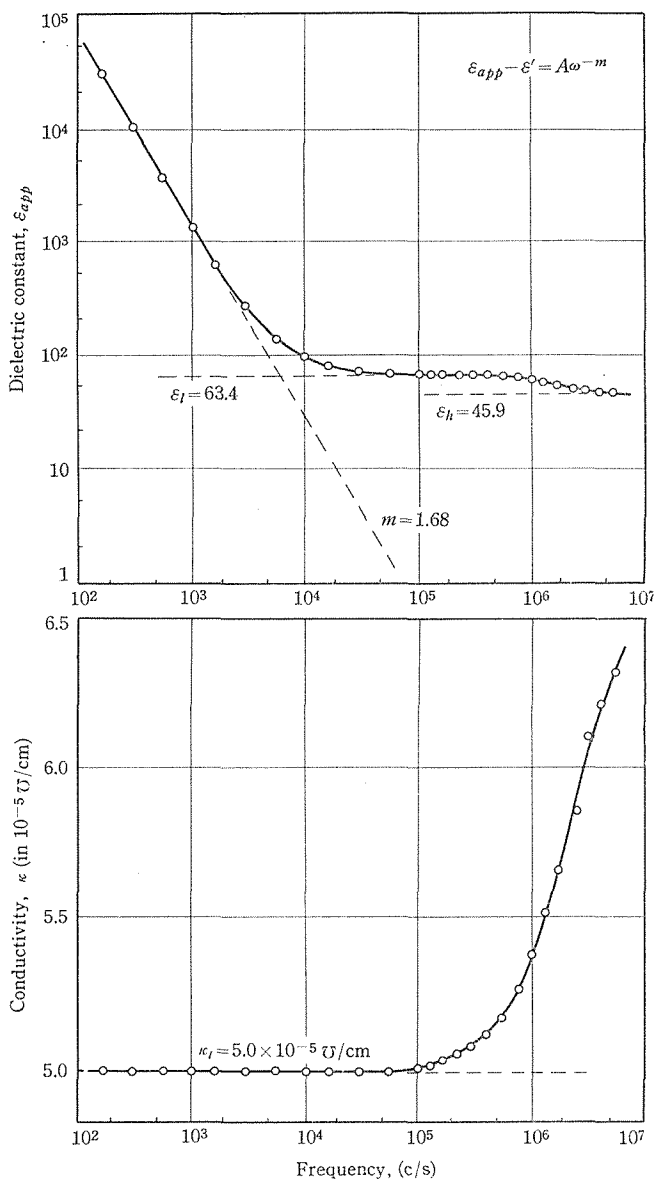
Fig. 6. Freuqency dependence of apparent dielectric constant
$\varepsilon_{app}$ and electrical conductivity $\kappa$ for the nitrobenzene-in-
water emulsion of 70% in volume concentration at 20°C.

tivity with increasing frequency was found at higher frequencies above 100 kc.
The values of $\varepsilon'$ at each frequency were obtained with the aid of Eq. (40) and
values of $A$ and $m$ evaluated from the data at lower frequencies. The loss
factors $\varepsilon''$ associated with the dielectric dispersion of $\varepsilon'$ were calculated from the
following relation:

$$\varepsilon'' = \frac{q}{\omega}(\kappa - \kappa_I),\tag{41}$$

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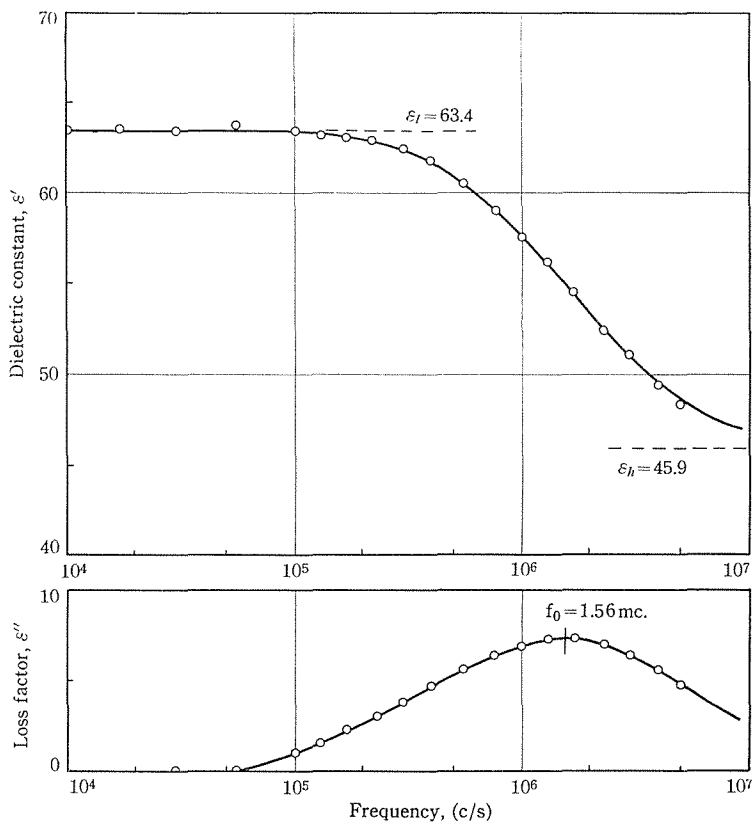


Fig. 7. Frequency dependence of dielectric constant $\varepsilon'$ and loss factor $\varepsilon''$ for the nitrobenzene-in-water emulsion of 70% in volume concentration at 20°C.
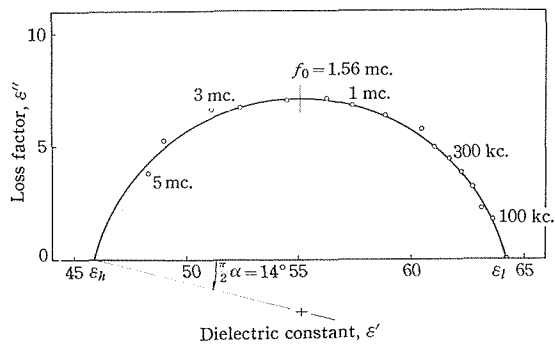


Fig. 8. Complex plane plots of $\varepsilon'$ and $\varepsilon''$ for the nitrobenzene-in-water emulsion of 70% by volume at 20°C.

where a numerical factor $q = 112.94 \times 10^{11}$, and the conductivities are expressed in $\sigma$/cm units. Fig. 7 shows the frequency dependence of $\varepsilon'$ and $\varepsilon''$ obtained through this procedure.

The complex plane plot of $\varepsilon'$ and $\varepsilon''$ for the N/W emulsion of 70% gave a circular-arc as shown in Fig. 8. Thus the dielectric dispersions of N/W emulsions at high frequencies are represented approximately by the same expression as Eq. (39).

No appreciable change in the dielectric constants and the conductivities of the present emulsions was observed under the mean rate of shear up to 40 sec$^{-1}$.

The behavior similar to that mentioned above was observed at all other concentrations. The observed values of $\varepsilon_h$, $\varepsilon_l$, $\kappa_l$, $f_0$ and $\alpha$ at various concentrations of N/W emulsions are listed in Table 6. As seen in Fig. 6, the limiting

Table 6. Values of $\varepsilon_h$, $\varepsilon_l$, $\kappa_l$, $\kappa_{f_0}$, $\kappa_{3mc}$, $f_0$ and $\alpha$ for the nitrobenzene-in-water emulsions at various concentrations $\varPhi$.

| Volume fraction of disperse phase $\varPhi$ | $\varepsilon_h$ | $\varepsilon_l$ | $\kappa_l$ | $\kappa_{f_0}$ | $\kappa_{3mc}$ | $f_0$ | $\alpha$ |
|---|---|---|---|---|---|---|---|
| | | | $f_0$ $\alpha$ in $10^{-5}$ $\sigma$/cm | | | in mc. | |
| 0.5 | 54.0 | 69.0 | 6.78 | 7.29 | 7.62 | 1.70 | 0.256 |
| 0.6 | 49.7 | 66.4 | 6.35 | 6.90 | 7.37 | 1.42 | 0.160 |
| 0.7 | 45.9 | 63.4 | 5.00 | ·5.61 | 6.11 | 1.56 | 0.117 |
| 0.8 | 42.3 | 53.1 | 3.40 | 3.85 | 4.10 | 1.80 | 0.089 |
| 0.9 | 38.7 | 68.0 | 1.71 | 1.82 | 2.30 | 0.149 | 0.080 |
| 0.93 | 38.1 | 53.5 | 1.33 | 1.39 | 1.67 | 0.200 | 0.089 |
| 0.95 | 37.2 | 53.0 | 2.14 | 2.22 | 2.56 | 0.264 | 0.297 |

Water : Dielectric constant $\varepsilon_m = 78.0$, conductivity $\kappa_m = 7.286 \times 10^{-5}$ $\sigma$/cm
Nitrobenzene : Dielectric constant $\varepsilon_p = 35.15$, conductivity $\kappa_p = 0.6429 \times ^{-5}$ $\sigma$/cm

values of conductivities at high frequencies were not obtained from the present data. In Table 6 are shown the values of the conductivities at critical frequency $\kappa_{f_0}$ and those at 3 mc. $\kappa_{3mc}$, which are regarded as measures of the conductivities at high frequencies.

## 5. DISCUSSION

### A) Dielectric Behavior of O/W Emulsions

As shown in the preceding section, both dielectric constants and conductivities of O/W emulsions are found to be independent of measuring frequency. Accordingly it is considered that the values observed may be discussed in the light of theoretical equations (1)–(5).

i) **Dielectric constant of O/W emulsions**[23]. The theoretical values and curves obtained from Eqs. (1)–(5) respectively are given in Table 3 and in Fig. 9 together with our experimental values.

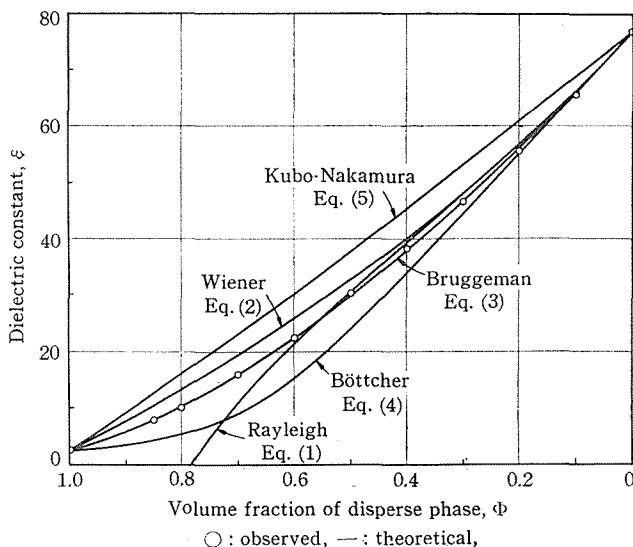The Bruggeman equation fits best to our experimental results over the whole range of concentration.

Fig. 9. Concentration dependence of dielectric constants $\varepsilon$
for the O/W emulsions at 30°C.

**ii) Conductivity of O/W emulsions**[26]. The theoretical values and curves calculated from Eqs. (7) and (9) are shown in Table 4 and Fig. 10 together with our experimental values.

The conductivity of O/W emulsions may be expressed better by Eq. (9) of the Bruggeman type than by Eq. (7) of the Wiener type over the whole range of concentration.

Pearce[29] measured at 400 cps. the conductivities of the system that bakelite hemispheres of about 1 inch in diameter are regularly arranged in tap water, volume concentrations of the disperse phase being less than 45%. This system is an analogue to an O/W emulsion in regular arrangement of spherical particles. His data rather fitted to a curve corresponding to Eq. (7). He carried out no experiment on the conductivity of random dispersions of an O/W type such as actual emulsions.

Meredith and Tobias[30] studied conductivities of a monodisperse system of lucite spheres in rectangular order immersed in water. The conductance of this system showed some deviations from the values calculated from Eq. (7). They presented a modified derivation of Rayleigh's equation (1) for the conductivity of a cubic array of spheres in a continuum. The agreement of the modified equation with experimental data was very satisfactory. A closer examination of theoretical values discloses that this modified equation is numerically very close to Eq. (9) at concentrations less than 60%. Hence it follows that the values observed by them is in agreement with Eq. (9).

Meredith[31] observed conductivities of O/W emulsions at 1 and 10 kc., concentrations being less than 45%. The values observed fell in between those predicted by the Wagner Eq. (6) and by the Bruggeman Eq. (8).
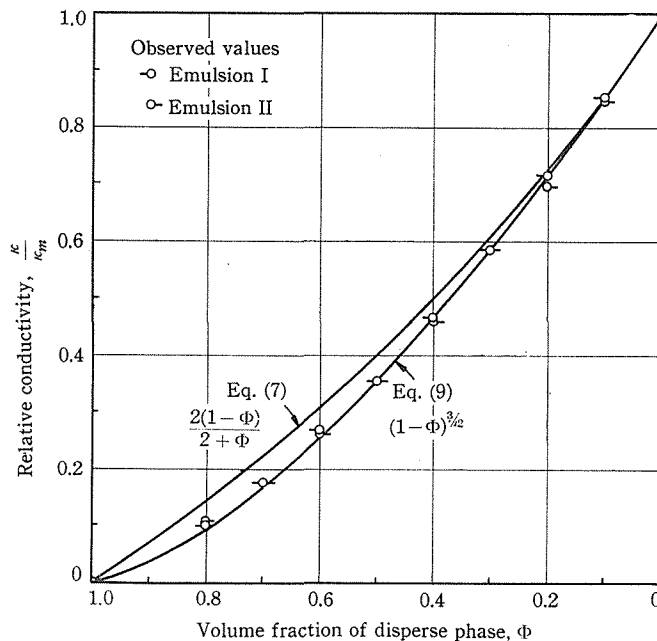
Fig. 10. Concentration dependence of electrical conductivities
$\kappa$ for the O/W emulsions at 25°C.

Rue and Tobias[19] observed conductivities of suspensions of glass beads in ZnBr$_2$ solutions, concentrations of the disperse phase being less than 40%. It was shown from their results that the dependence of the conductivity of dispersion systems on volume fraction was well represented by Eq. (9) for a broad distribution of particle size, whereas data on narrow distribution of size fell between values predicted by Eqs. (7) and (9).

Fricke[32] compared Eq. (6) with the observed conductivity of the dog blood and the sand suspensions in salt solutions, and found that Eq. (6) did not agree with the observed values. He ascribed this disagreement to a non-spherical shape of dispersed particles, and extended Eq. (6) to a dispersion of ellipsoidal particles. Since Eq. (6) was derived for dilute systems, it is not reasonable to apply Eq. (6) to concentrated dispersions. Data cited by Fricke should be compared with Eq. (8) prior to extention to ellipsoidal dispersions.

Considering the results on O/W systems mentioned above, it may be concluded that Eqs. (6) and (7) of the Wiener type is valid for ordered arrangement of uniform size spheres, whereas Eqs. (8) and (9) of the Bruggeman type is valid for random dispersions.

The relation of · present results to the interfacial polarization should be mentioned here. The dielectric constants and the conductivities observed for the present O/W emulsions showed no dielectric dispersion due to the interfacial polarization, being in accordance with Eqs. (22) and (25) respectively. Thus the new theory is quantitatively satisfactory for the dielectric behavior of O/W emulsions.
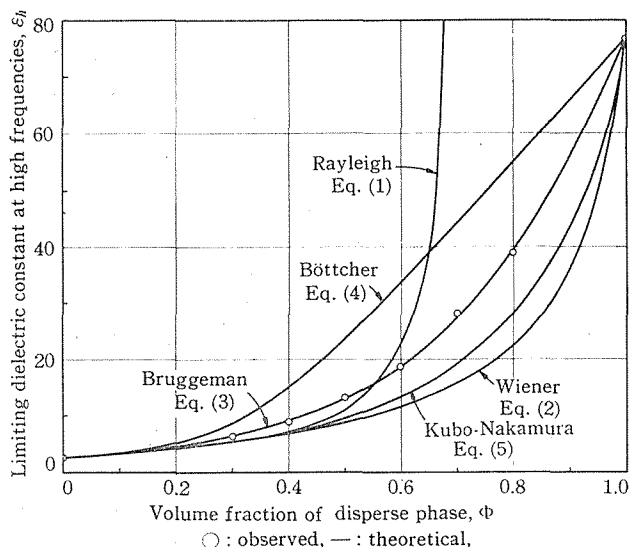
## B) Dielectric Behavior of W/O Emulsions[27]

i) **Limiting dielectric constant at high frequencies** $\varepsilon_h$. The limiting dielectric constant at high frequencies $\varepsilon_h$ is regarded as the dielectric constant of a spherical dispersion system composed of two non-conductive phases. Accordingly it is considered that the observed values of $\varepsilon_h$ may be discussed in the light of theoretical equations (1)–(5).

The theoretical values calculated from these equations are listed in Table 7, and are compared with observed values in Fig. 11. The Bruggeman equation (3)

Table 7. Theoretical values of dielectric constants for the W/O emulsion.

| Volume fraction of disperse phase $\emptyset$ | Dielectric constant $\varepsilon$ calculated from | | | | |
|---|---|---|---|---|---|
| | Böttcher Eq. (4) | Bruggeman Eq. (3) Eq. (34) | Rayleigh Eq. (1) | Wiener Eq. (2) Eq. (30) | Kobo-Nakamura Eq. (5) |
| 0.0 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| 0.1 | 3.409 | 3.317 | 3.250 | 3.249 | 3.15 |
| 0.2 | 5.124 | 4.499 | 4.178 | 4.165 | 4.05 |
| 0.3 | 8.643 | 6.242 | 5.410 | 5.309 | 5.28 |
| 0.4 | 15.06 | 8.852 | 7.271 | 6.780 | 7.01 |
| 0.5 | 23.85 | 12.79 | 10.85 | 8.740 | 9.54 |
| 0.6 | 33.81 | 18.69 | 22.75 | 11.48 | 13.32 |
| 0.7 | 44.28 | 27.33 | −78.28 | 15.59 | 19.08 |
| 0.8 | 55.01 | 39.51 | −11.58 | 22.44 | 28.20 |
| 0.85 | 60.42 | 47.14 | − 7.475 | 27.91 | 34.71 |
| 0.9 | 65.86 | 55.87 | − 5.207 | 36.09 | 43.20 |
| 0.95 | 71.32 | 65.75 | − 3.758 | 49.70 | 54.95 |
| 1.0 | 76.80 | 76.80 | − 2.749 | 76.80 | 76.80 |



Fig. 11. Concentration dependence of limiting dielectric constants at high frequencies $\varepsilon_h$ for the W/O emulsions at 30°C.

or (34) fits best to the observed values over the whole range of concentration.

Recently Naiki, Fujita and Matsumura[33] measured at 2 mc. the dielectric constants of emulsions of water dispersed in kerosene, in transformer oil and in terpene over a concentration range of 0 to 85%. The data were in good agreement with values calculated from the Bruggeman equation over the whole range of concentration. Thus the results obtained by Naiki *et al.* are consistent with the present conclusion.

ii) **Limiting dielectric constant at low frequencies** $\varepsilon_l$. In Fig. 12, the values of $\varepsilon_l$ at rest and at each r.p.m. are compared with those calculated from Eqs. (31) and (35). The values of $\varepsilon_l$ are relatively large at rest, and decrease towards the calculated values with increasing r.p.m. in contrast with $\varepsilon_h$ which is insensitive to shearing stress. Hence this shearing effect on the dielectric constants is considered to become noticeable in the frequency range where the conductivities of constituent phases contribute to the dielectric constants of the dispersion system.
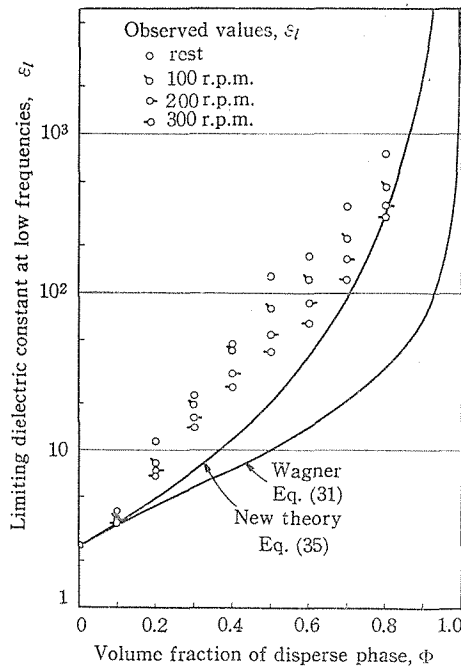


Fig. 12. Concentration dependence of limiting dielectric constants at low frequencies $\varepsilon_l$ for the W/O emulsions at rest and at various r.p.m. of the cup.

The experimental confirmations of the theoretical formulas for $\varepsilon_l$ have already been made by some workers.

Guillien[34] measured the dielectric constants $\varepsilon_l$ of emulsions of mercury in lubricating oil and of mercury in castor oil at concentrations less than 30%. He found the good agreements between observed values of $\varepsilon_l$ and Eq. (35).

Recently Pearce[29] measured at 1 kc. the dielectric constants of emulsions of sea water in fuel oil at concentrations up to 63%. Since the sea water used as the disperse phase has a very high conductivity, the systems of sea water in fuel oil would show the dielectric dispersions due to the interfacial polarization at very high frequencies. The dielectric constants observed by Pearce correspond to the limiting values at low frequencies $\varepsilon_l$. Pearce concluded that the measured dielectric constants agree better with Eq. (35) than with Eq. (31).

iii) **Limiting conductivity at low frequencies $\kappa_l$.** The conductivities below 1 kc. showed no definite tendency of the dependence on shearing stress, and the limiting conductivities at low frequencies $\kappa_l$ were not obtained within the present range of frequency. Hence it is difficult to give a strict consideration on $\kappa_l$.

The values of $\kappa_l$ predictable by Eqs. (32) and (36) are indicated in Fig. 4. It seems that the observed values of $\kappa_l$ are smaller than both theoretical values.

In Fig. 13, the conductivities at 100 cps. $\kappa_{100c}$ are compared with the values calculated from Eqs. (32) and (36), being regarded as a tentative measure of the conductivities at low frequencies. The values of $\kappa_{100c}$ are found to lie below the values calculated from Eq. (32).

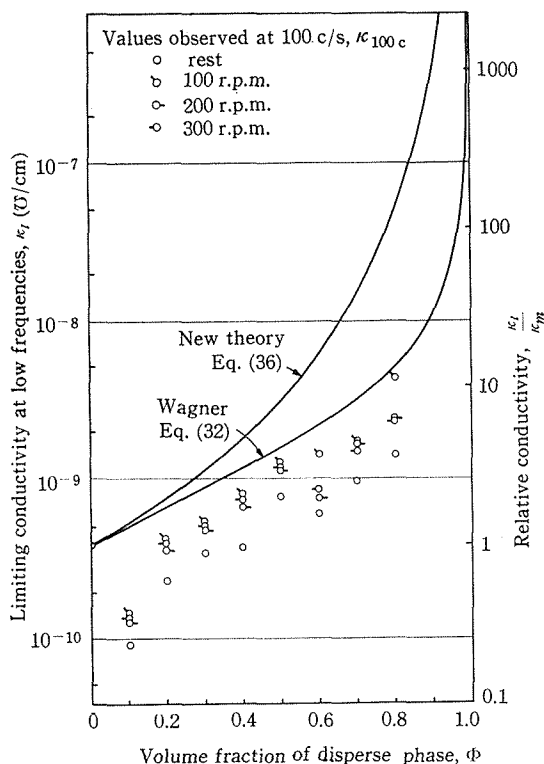The exprimental confirmation of the theoretical formulas for $\kappa_l$ has already been made by some workers.



Fig. 13. Concentration dependence of limiting conductivities at low frequencies $\kappa_l$ for the W/O emulsions.

Meredith[31] observed conductivities of W/O emulsions at 1 and 10 kc., concentrations being less than 50%. The values observed by him may be considered as the limiting conductivity at low frequencies $\kappa_l$, though the dielectric dispersion due to the interfacial polarization was not mentioned in his discussions. The conductivities measured showed the values between Eqs. (32) and (36).

Meredith and Tobias[30] measured conductivities of dispersion systems of brass spheres in a cubic array in tap water. The experimental data fell between values predicted by Eqs. (32) and (36).

iv) **Limiting conductivity at high frequencies** $\kappa_h$. As seen in Fig. 4, the limiting conductivities at high frequencies $\kappa_h$ were not obtained within the present range of frequency. Hence no direct examination of the validity of Eqs. (33) and (37) was successful.

The values of $\kappa_{3mc}$ are given as a tentative measure of the conductivities at high frequencies in Fig. 14 together with curves calculated from Eqs. (33) and (37). There is an overall trend that the experimental values of $\kappa_h$ decrease towards the theoretical values with increasing r.p.m. Such trends for both $\varepsilon_l$ and $\kappa_h$ suggest that the particle agglomerates may be broken up into individual particles under shearing stress.
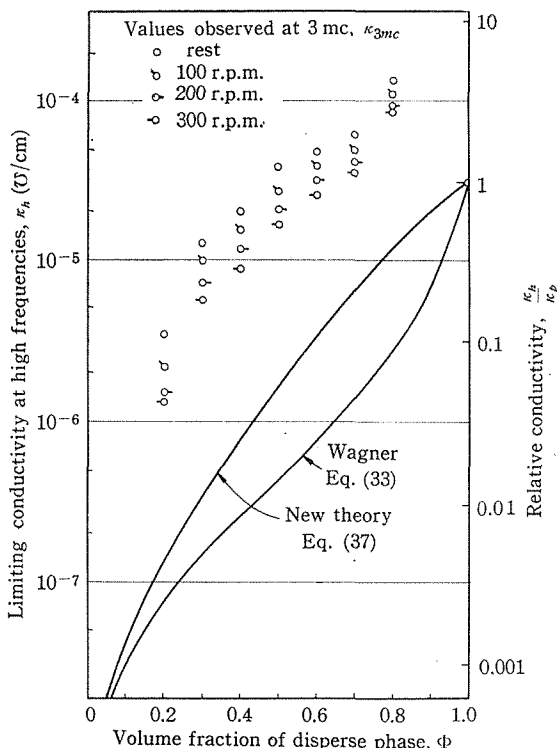


Fig. 14. Concentration dependence of limiting con-
ductivities at high frequencies $\kappa_h$ for the W/O
emulsions at rest and at various r.p.m. of the cup.

**v) Distribution parameter of relaxation times $\alpha$.** As seen in Table 5, observed values of $\alpha$ increased with decreasing concentration. Supposedly the pressent emulsions would not show the single relaxation behavior even at infinite dilution.

According to the Wagner theory,[8] a dilute emulsion composed of dispersed particles of uniform conductivity should show the single relaxation behavior. Some distribution of relaxation times found in the present emulsions may be caused by the non-uniformity in the conductivity of each dispersed particle.

### C) Dielectric Behavior of N/W Emulsions[28]

The frequency dependence of dielectric constant and conductivity observed for the present N/W emulsions is considered to be attributable to the dielectric dispersion expected from the new theory on the interfacial polarization.

Since the condition $\kappa_m \gg \kappa_p$ is not always valid for the present N/W emulsions as seen in Table 6, the experimental results should be discussed in the light of Eqs. (10)–(17) without any restriction on the conductivity.

**i) Limiting dielectric constant at high frequencies $\varepsilon_h$.** Observed values of $\varepsilon_h$ are given by hollow circles in Fig. 15. Curves A and B are the values of $\varepsilon_h$ calculated from Eqs. (14) and (10) respectively. The observed values of $\varepsilon_h$
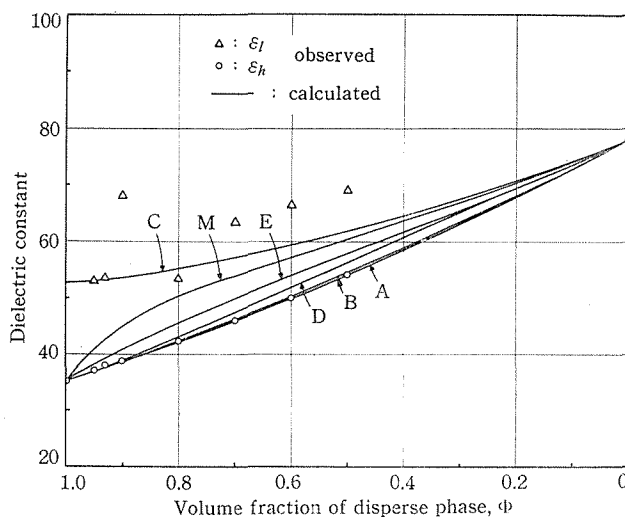


Fig. 15. Concentration dependence of limiting dielectric constants at high frequencies $\varepsilon_h$ and at low frequencies $\varepsilon_l$ for the N/W emulsions.
Curve A, $\varepsilon_h$ calculated from Eq. (14) or Eq. (22) of the new theory;
B, $\varepsilon_h$ calculated from Eq. (10) or Eq. (18) of the Wagner theory;
C, $\varepsilon_l$ calculated from Eq. (23) of the new theory;
D, $\varepsilon_l$ calculated from Eq. (19) of the Wagner theory;
E, $\varepsilon_l$ calculated from Eq. (15) of the new theory by using observed values of conductivities
($\kappa_m = 7.286 \times 10^{-5}$ ℧/cm, $\kappa_p = 6.429 \times 10^{-6}$ ℧/cm)
M, $\varepsilon_l$ calculated from Eq. (15) of the new theory by using the value $\kappa_m = 2.6 \times 10^{-4}$ ℧/cm and the observed value of $\kappa_p$.

are in good agreement with the theoretical curves A and B within experimental errors.

In the case of N/W emulsions, the curve B is very close to the curve A. Therefore it is difficult to decide which curve fits better to the observed values.

**ii) Limiting dielectric constant at low frequencies $\varepsilon_l$.** Triangles in Fig. 15 show the observed values of $\varepsilon_l$. Curve C is calculated from Eq. (23), which is the limiting relation of Eq. (15) in the new theory under the condition $\kappa_m \gg \kappa_p$. Curve E is drawn according to Eq. (15) by using measured values:
$\kappa_m = 7.286 \times 10^{-5} \, \mho/\text{cm}$, $\kappa_p = 6.429 \times 10^{-6} \, \mho/\text{cm}$. Curve D is calculated from Eq. (19) in the Wagner theory.

According to the Wagner theory, the differences between $\varepsilon_l$ and $\varepsilon_h$ are very small both at higher and at lower concentrations, though such differences are rather appreciable at medium concentrations. Hence the Wagner theory is qualitatively inadequate to interpret the striking dielectric dispersions observed for the N/W emulsions.
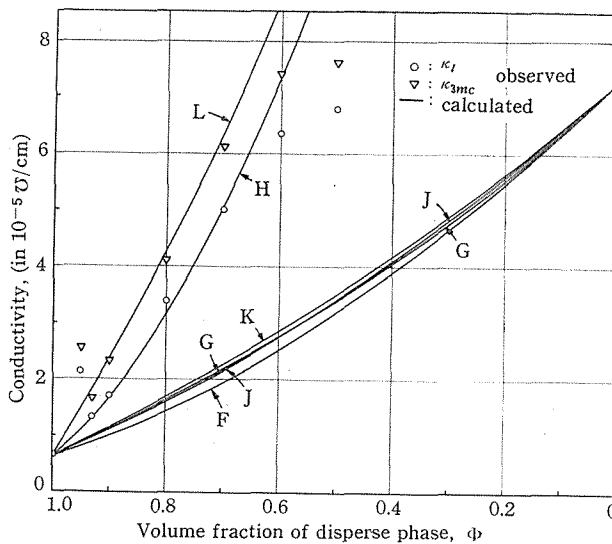


Fig. 16. Concentration dependence of limiting conductivities at low frequencies $\kappa_l$ and at high frequencies $\kappa_h$ for the N/W emulsions.

Curve F, $\kappa_l$ calculated from Eq. (16) of the new theory by using observed values of $\kappa_m$ and $\kappa_p$;

G, $\kappa_l$ calculated from Eq. (12) of the Wagner theory by using observed values of $\kappa_m$ and $\kappa_p$;

H, $\kappa_l$ calculated from Eq. (16) of the new theory by using the value $\kappa_m = 2.6 \times 10^{-4} \, \mho/\text{cm}$ and the observed value of $\kappa_p$;

J, $\kappa_h$ calculated from Eq. (17) of the new theory by using observed values of $\kappa_m$ and $\kappa_p$;

K, $\kappa_h$ calculated from Eq. (13) of the Wagner theory by using observed values of $\kappa_m$ and $\kappa_p$;

L, $\kappa_h$ calculated from Eq. (17) of the new theory by using the value $\kappa_m = 2.6 \times 10^{-4} \, \mho/\text{cm}$ and the observed value of $\kappa_p$.

On the contrary, the considerable differences between $\varepsilon_l$ and $\varepsilon_h$ at higher concentrations are expected from the new theory. The striking dielectric dispersions observed especially at higher concentrations may be interpreted qualitatively in terms of the new theory. As seen in Fig. 15, the observed values of $\varepsilon_l$ is relatively larger than the theoretical ones shown by the curves C and E of the new theory.

iii) **Limiting conductivity at low frequencies $\kappa_l$.** Fig. 16 shows the comparison of observed values of $\kappa_l$ with those given by the theories. Hollow circles show the observed values of $\kappa_l$. Curves F and G are drawn according to Eqs. (16) and (12) respectively by using obrerved values of $\kappa_m$ and $\kappa_p$.

The observed values of $\kappa_l$ is generally larger than the theoretical ones shown by the curves F and G. Observed values of $\kappa_m$ and $\kappa_p$ used here were measured prior to emulsification. It seems possible that the value of $\kappa_m$ changes on emulsification. A curve H is calculated from Eq. (16) by using the value $\kappa_m = 2.6 \times 10^{-4}$ ℧/cm, which is about 3.5 times as large as the observed value. Observed values of $\kappa_l$ fall fairly well on the curve H. It seems plausible that the value of $\kappa_m$ increases on emulsification.

In the conductivity measurement for O/W emulsions, the values of $\kappa_m$ were stabilized by addition of potassium chloride to the water phase. In the case of N/W emulsions, such addition of potassium chloride would keep the values of $\kappa_m$ unchanged on emulsification. The addition of potassium chloride to the water phase, however, results in the remarkable increase in the d.c. conductivity. For systems having a high d.c. conductivity, the measurement of dielectric constants is too inaccurate for the quantitative considerations owing to the electrode polarization, and dielectric dispersions due to the interfacial polarization may shift to higher frequencies beyond the present experimental range.

iv) **Limiting conductivity at high frequencies $\kappa_h$.** In Fig. 16, curves J and K are calculated from Eqs. (17) and (13) respectively by using observed values of $\kappa_m$ and $\kappa_p$. The differences between the curves J and F are larger than those between the curves K and G. Namely the increase in conductivity associated with the dielectric dispersion expected from the new theory is larger than that from the Wagner theory. In fact, as shown in Fig. 6, the remarkable increase in conductivity at higher frequencies was observed in qualitative accordance with the prediction from the new theory.

The values of $\kappa_h$ were not obtained within the present range of frequency. Thus it is difficult to discuss the validity of Eqs. (13) and (17) strictly.

In Fig. 16, a curve L is calculated from Eq. (17) by using the values $\kappa_m = 2.6 \times 10^{-4}$ ℧/cm, which is about 3.5 times as large as the observed value. Triangles in Fig. 16 show the conductivities at 3 mc. $\kappa_{3mc}$, which are regarded as a tentative measure of limiting conductivity at high frequencies. The values of $\kappa_{3mc}$ fall fairly well on the curve L. The observed increase in conductivity associated with the dielectric dispersion is the same order of magnitude as the difference between the curves L and H predicted by the new theory.

The values of $\varepsilon_l$ calculated from Eq. (15) by using the values $\kappa_m = 2.6 \times 10^{-4}$ $\mho$/cm are shown by a curve M in Fig. 15. Observed values of $\varepsilon_l$ is generally larger than those by the curve M.

## 6. CONCLUSIONS

The experimental results and the considerations are summarized in Table 8.

The O/W emulsions showed no dielectric dispersion due to the interfacial polarization, the concentration dependence of the dielectric constant and the conductivity being well represented by equations of the Bruggeman type.

Table 8. Comparision of the results on the dielectric properties of emulsions.

| | O/W emulsion for $\varepsilon$ measurement | O/W emulsion for $\kappa$ measurement | W/O emulsion | N/W emulsion |
|---|---|---|---|---|
| Electrode polarization | | | | |
| frequency range | Below 10 kc. | Below 1 mc. | Below 1 kc. | Below 30 kc. |
| value of exponent $m$ | 1.7 | 1.8 | ⋯ | 1.7 |
| Interfacial polarization | | | | |
| dielectric dispersion | No | No | Remarkable | Appreciable |
| frequency range | — | — | Above 30 kc. | Above 30 kc. |
| complex plane plot of complex dielectric constant | — | — | Circular-arc | Circular-arc |
| concentration dependence of relaxation frequency $f_0$ | — | — | Decrease with increasing concentration | Decrease with increasing concentration |
| concentration dependence of $\varepsilon_h$ | Equation of Bruggeman type | Equation of Bruggeman type | Equation of Bruggeman type | Equation of Bruggeman or Wiener type |
| Shearing effect | No | No | Yes | No |

The W/O emulsions showed striking dielectric dispersion due to the interfacial polarization, the limiting dielectric constant at high frequencies being represented by Bruggeman's equation.

The N/W emulsions, which are a kind of O/W emulsions, showed a dielectric dispersion in accordance with the prediction from the new theory rather than from the Wagner theory.

These experimental results support the theoretical conclusion that the magnitude of dielectric dispersion due to the interfacial polarization is related not to the emulsion type, but to the correlation among dielectric constants and conductivities of the dispersion medium and the disperse phase.

The W/O emulsions showed marked changes in dielectric properties under shearing flow, whereas O/W and N/W emulsions had no shearing effect under the rate of shear up to 40 sec$^{-1}$. The shearing effect found in W/O emulsions may be caused by breaking up particle agglomerates, an exact interpretation being not given yet.

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The influence of particle size on dielectric properties were not found in the present emulsions composed of dispersed particles larger than $0.5\,\mu$ in diameter.

## ACKNOWLEDGEMENTS

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