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Numerical Estimation in a Theory of Interfacial Polarization Developed for Disperse Systems in Higher Concentrations

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Numerical calculations are carried out to obtain solutions of a theoretical expression of interfacial polarization, which was proposed by Hanai [Kolloid Z., 171, 23 (1960)], applicable to concentrated disperse systems of spherical particles. It is found that the dielectric relaxation characterized by the changes in the dielectric constants and the electrical conductivities extends over an apparently broader range of frequency in comparison with a single relaxation system, and that the complex plane plots of the complex dielectric constants show remarkable depression from a semicircle. Some comparisons of the limiting dielectric constants and electrical conductivities at low and high frequencies are made between the present results and those by approximate equations so far used. The relaxation frequency giving the maximum loss factor is found to be strongly dependent on the concentration of the disperse phase and to reduce to very low values at higher concentrations in conformity with experimental results.

I INTRODUCTION

As is well known, a heterogeneous system of spherical particles dispersed in a continuous phase shows a dielectric relaxation due to interfacial polarization. The dielectric relaxation has been discussed by many workers\(^1\) qualitatively in the light of Wagner's theory. Since closer consideration revealed that Wagner's theory was in agreement with experimental results only at lower concentrations of the disperse phase, Hanai\(^2,3\) proposed a theory which is expected to be applicable to higher concentrations.

According to our dielectric study of water-in-oil (W/O) emulsions\(^4,6\) remarkable dielectric relaxations were observed in accordance with Hanai's theory, and the limiting dielectric constants at high frequencies showed excellent agreements with the theory. In our previous work on the dielectric relaxations of W/O emulsions,\(^5\) the limiting dielectric constants at low frequencies were also in good agreements with the theory as far as the W/O emulsions are prepared by minimal use of emulsifiers.

The expression of this theory is of a functional form including a cubic root of complex variable, and is impossible to be rearranged so that the relaxation frequency may be numerically calculated. Hence the comparison was not made between the theoretical and the experimental values.

Clausse\(^6,7,8,9\) performed computer analyses of this theoretical expression for the purpose of discussing his data on emulsions. Nevertheless it is still necessary for the discussion of our experimental data to estimate the results by using our measured values on the constituent phases.

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Numerical Estimation in a Theory of Interfacial Polarization

In the present paper, the expression of Hanai's theory is calculated by means of a programmable calculator, giving the frequency dependence of the dielectric constants, the electrical conductivities, and the loss factors. The limiting dielectric constants and the electrical conductivities at low and high frequencies and the relaxation frequencies are evaluated as well, and are compared with those from approximate formulas and experimental values.

II GLOSSARY OF SYMBOLS

\( \varepsilon_a \) dielectric constant of the continuous medium.
\( \kappa_a \) electrical conductivity of the continuous medium, S cm\(^{-1}\).
\( \varepsilon_i \) dielectric constant of the disperse phase.
\( \kappa_i \) electrical conductivity of the disperse phase, S cm\(^{-1}\).
\( \varepsilon \) dielectric constant of the disperse system.
\( \kappa \) electrical conductivity of the disperse system, S cm\(^{-1}\).
\( \varepsilon_a^* \), \( \varepsilon_i^* \) and \( \varepsilon^* \) are complex dielectric constant of the continuous medium, the disperse phase and the disperse system respectively, being given by

\[
\varepsilon_a^* = \varepsilon_a - j \frac{\kappa_a}{2 \pi f \varepsilon_s},
\]

\[
\varepsilon_i^* = \varepsilon_i - j \frac{\kappa_i}{2 \pi f \varepsilon_s},
\]

and

\[
\varepsilon^* = \varepsilon - j \frac{\kappa}{2 \pi f \varepsilon_s}.
\]

\( f \) measuring frequency, Hz.
\( j \) unit imaginary, \( \sqrt{-1} \).
\( \varepsilon_s \) dielectric constant of free space given by

\[
\frac{1}{4 \pi \varepsilon_0} = 8.8542 \times 10^{-14} \text{ F cm}^{-1}.
\]

\( \Phi \) volume fraction of the disperse phase.
\( \varepsilon_l \) limiting dielectric constant at low frequencies.
\( \kappa_l \) limiting conductivity at low frequencies, S cm\(^{-1}\).
\( \varepsilon_h \) limiting dielectric constant at high frequencies.
\( \kappa_h \) limiting conductivity at high frequencies, S cm\(^{-1}\).
\( f_0 \) relaxation frequency giving the maximum loss factor, Hz.

III COMPUTER EXPERIMENTS ON NUMERICAL CALCULATIONS OF HANAI'S EQUATION

For a complex dielectric constant of a disperse system in which spherical particles are dispersed in a continuous medium by a volume fraction \( \Phi \), Hanai\(^{2,3} \) derived the following equation

\[
\frac{1}{1 - \Phi} \frac{\varepsilon^* - \varepsilon_i^*}{\varepsilon_a^* - \varepsilon_i^*} \left( \frac{\varepsilon_a^*}{\varepsilon_i^*} \right)^{1/3} = 1.
\]
By cubing the both sides of Eq. (4), we have the cubic equation with respect to $\varepsilon^*$ as

$$\varepsilon^* - 3\varepsilon^*\varepsilon^* + \left\{3\varepsilon^* + \frac{1}{\varepsilon_a^*} \left(1 - \frac{\varepsilon_a^*}{\varepsilon_*} \right) \right\} = 0.$$  

(5)

Numerical evaluation of the solution was carried out by a calculator, Yokogawa-Hewlett-Packard Model 10, with a programming of the following steps.

(a) Substitution of numerical values of $\varepsilon_a$, $\kappa_a$, $\varepsilon_i$, and $\kappa_i$, and an arbitrary value of $\varepsilon_1$ into Eqs. (1) and (2) gives values of $\varepsilon_a^*$ and $\varepsilon_2^*$.
(b) The coefficients of the cubic Eq. (5) can be determined by substituting $\varepsilon_a^*$, $\varepsilon_2^*$, and an arbitrary value of $\Phi$.
(c) By the use of a computer programme "Roots of Polynomial with Complex Numbers" (Model 10, MATH PAC III–3), we obtain three roots of Eq. (5) designated by $\varepsilon_1^*$, $\varepsilon_2^*$, and $\varepsilon_3^*$.
(d) Among the three roots $\varepsilon_1^*$, $\varepsilon_2^*$, and $\varepsilon_3^*$, we have to choose only one solution satisfying Eq. (4) by means of the following criterion. Since Eq. (5) is derived by cubing Eq. (4), respective substitution of the three roots $\varepsilon_1^*$, $\varepsilon_2^*$, and $\varepsilon_3^*$ into a function

$$F(\varepsilon^*) = \frac{1}{1 - \Phi} \frac{\varepsilon^* - \varepsilon_i^*}{\varepsilon_a^* - \varepsilon_i^*} \left(\frac{\varepsilon_a^*}{\varepsilon_*}\right)^{1/3}$$  

(6)

is to give

$$F(\varepsilon_1^*) = 1 + 0j = e^{i0}.$$  

(7)

$$F(\varepsilon_2^*) = -\frac{1}{2} + \frac{\sqrt{3}}{2}j = e^{i(2\pi/3)}$$  

(8)

and

$$F(\varepsilon_3^*) = -\frac{1}{2} - \frac{\sqrt{3}}{2}j = e^{i(-2\pi/3)}$$  

(9)

respectively. When each of the three roots is thus substituted into $F(\varepsilon^*)$ given by Eq. (6), the roots which lead to either Eq. (8) or Eq. (9) should be ruled out, and only one root giving Eq. (7) adopted as the solution of Eq. (4).
(e) The root is regarded as $\varepsilon^*$ of Eq. (3), giving the values of $\varepsilon$, $\kappa$, and $\varepsilon''$ for the disperse system.

IV RESULTS

In our previous measurements on W/O emulsions, remarkable dielectric relaxations were observed, and the relaxation frequencies were reported without comparison with those by Eq. (4). Hence, in the present work, the frequency profile of the complex dielectric constant was calculated by using numerical values of $\varepsilon_a$, $\kappa_a$, $\varepsilon_i$, and $\kappa_i$ reported in the previous paper.

The results calculated for $\Phi=0.8$ are shown in Figs. 1 and 2. For comparison, theoretical curves of a single relaxation system, the so-called dielectric relaxation in the Debye type, are shown with dashed curves in Figs. 1 and 2. The decrease in $\varepsilon$ and the increase in $\kappa$ with increasing frequency for Eq. (4) are seen to extend over an apparently
Fig. 1. Comparison of the frequency dependence of dielectric constant $\varepsilon$, electrical conductivity $\kappa$, and loss factor $\varepsilon''$. The solid curves are calculated from Equation (4) with volume fraction $\Phi=0.8$ and values of phase parameters shown in Table I. The dashed curves indicate a single relaxation system with the same values of $\varepsilon_i$, $\varepsilon_h$, $\kappa_i$, and $\kappa_h$ as those calculated from Equation (4). As regards the loss factor, curves of $\varepsilon''=(\kappa-\kappa_i)/2\pi f\varepsilon_0$ are depicted in the figure.

Fig. 2. Complex plane plots of the dielectric constants and the loss factors. The solid curve is given by Equation (4), the dashed curve (semicircle) by a single relaxation system. The same data as shown in Fig. 1.

a broader range of frequency in comparison with a single relaxation system, being simulated by system with some distribution of relaxation times. The frequency profile of the loss factor $\varepsilon''=(\kappa-\kappa_i)/2\pi f\varepsilon_0$ for Eq. (4) seems to be asymmetric with respect to log ($f/f_0$).

In Table I are summarized the values of $\varepsilon_i$, $\varepsilon_h$, $\kappa_i$, $\kappa_h$, and $f_0$ thus calculated from Eq. (4) for various values of $\Phi$. Since $f_0$ cannot be evaluated at $\Phi=0$ owing to no dielectric relaxation, the value of $f_0$ at $\Phi=0.0001$ is calculated instead.
Values of Limiting Dielectric Constants $\varepsilon_l$, $\varepsilon_h$, and Limiting Conductivities $\kappa_l$, $\kappa_h$ at Low and High Frequencies, and Relaxation Frequencies $f_0$ at Various Volume Fractions $\Phi$

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<th>$\Phi$</th>
<th>$\varepsilon_l$</th>
<th>$\varepsilon_h$</th>
<th>$\kappa_l$</th>
<th>$\kappa_h$</th>
<th>$f_0$</th>
<th>$\varepsilon_l$</th>
<th>$\kappa_l$</th>
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<tr>
<td></td>
<td>$\mu$S cm$^{-1}$</td>
<td>$\mu$S cm$^{-1}$</td>
<td>kHz</td>
<td>kHz</td>
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<td>kHz</td>
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<td>77.5</td>
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Values of the phase parameters used for the calculation are cited from the previous work.5) Outer oil phase: Dielectric constant $\varepsilon_o = 2.10$, conductivity $\kappa_o = 6.55 \times 10^{-11}$ S cm$^{-1}$

Inner aqueous phase: Dielectric constant $\varepsilon_i = 77.5$, conductivity $\kappa_i = 24.5 \times 10^{-6}$ S cm$^{-1}$

V DISCUSSION

Comparison of the Present Values with Those Obtained from Approximate Equations.

In our previous papers4,5 only the limiting cases at high and low frequencies for Eq. (4) were discussed owing to the difficulty of numerical calculations at arbitrary frequencies, and the following relations were derived from Eq. (4).

Irrespective of the emulsion type, we have, at high frequencies ($f \to \infty$),

$$\frac{\varepsilon_h - \varepsilon_i}{\varepsilon_a - \varepsilon_i} \left( \frac{\varepsilon_a}{\varepsilon_h} \right)^{1/3} = 1 - \Phi, \quad (10)$$

and

$$\kappa_h \left( \frac{3}{\varepsilon_h - \varepsilon_i} - \frac{1}{\varepsilon_h} \right) = 3 \left( \frac{\kappa_a - \kappa_i}{\varepsilon_a - \varepsilon_i} + \frac{\kappa_i}{\varepsilon_h - \varepsilon_i} \right) - \kappa_a \quad (11)$$

and, at low frequencies ($f \to 0$),

$$\varepsilon_i \left( \frac{3}{\kappa_i - \kappa_i - \kappa_i} - \frac{1}{\kappa_i - \kappa_i} \right) = 3 \left( \frac{\varepsilon_a - \varepsilon_i}{\kappa_a - \kappa_i} + \frac{\varepsilon_i}{\kappa_i} \right) - \frac{\varepsilon_a}{\kappa_a} \quad (12)$$

and

$$\frac{\kappa_i - \kappa_i}{\kappa_a - \kappa_i} \left( \frac{\varepsilon_a}{\kappa_i} \right)^{1/3} = 1 - \Phi, \quad (13)$$

For the W/O type emulsions ($\kappa_i \gg \kappa_a$), Eqs. (10), (11), (12), and (13) reduce to

$$\frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i - \varepsilon_a} \left( \frac{\varepsilon_a}{\varepsilon_h} \right)^{1/3} = 1 - \Phi, \quad (14)$$

(252)
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\[ \kappa_h = \kappa_I \frac{3\epsilon_h (\epsilon_h - \epsilon_a)}{\epsilon_I + 2\epsilon_h (\epsilon_h - \epsilon_a)} \]  \quad (15)

\[ \epsilon_I = \frac{\kappa_I (\kappa_I - \kappa_I)}{\kappa_a (\kappa_I + 2\kappa_I)} \]  \quad (16)

and

\[ \frac{\kappa_I - \kappa_I}{\kappa_I} \left( \frac{\kappa_a}{\kappa_I} \right)^{1/3} = 1 - \Phi. \]  \quad (17)

If it is allowed, further, to put \( \kappa_I \gg \kappa_I \), Eqs. (16) and (17) reduce to

\[ \epsilon_I = \epsilon_a \frac{1}{(1 - \Phi)^2}, \]  \quad (18)

and

\[ \kappa_I = \kappa_a \frac{1}{(1 - \Phi)^2}. \]  \quad (19)

In our previous papers, Eqs. (14), (15), (18), and (19) were eventually used for comparison between theories and experiments.

In order to examine the accuracy of the approximation, the values of \( \epsilon_h, \kappa_h, \epsilon_I, \) and \( \kappa_I \) are calculated from the equations shown above. It is found that the values of \( \epsilon_h, \kappa_h, \epsilon_I, \) and \( \kappa_I \) calculated from Eqs. (10), (11), (12), and (13) are in perfect agreement with those from Eq. (4) listed in Table I.

As regards the approximate equations for \( \kappa_I \gg \kappa_I \), the values of \( \kappa_a \) from Eq. (15) are in good agreement with those from Eq. (4) at higher values of \( \Phi \), and show smaller values by about 0.1% than those of Eq. (4) at less than \( \Phi = 0.3 \), such differences being insignificant in practice. The values of \( \epsilon_I \) from Eq. (16) are in good agreement with those from Eq. (4) in a whole range of \( \Phi \).

The approximate equations (18) and (19) simplified by the condition \( \kappa_I \gg \kappa_I \) show appreciable deviation from Eq. (4), the calculated values being listed in Table I. The values of \( \epsilon_I \) and \( \kappa_I \) by Eqs. (18) and (19) show the differences of more than 1% from those by Eq. (4) at \( \Phi = 0.9 \).

Comparison of the Relaxation Frequency

Most interesting is the profile of the concentration dependence of \( f_0 \) values, which are shown in Table I. For comparison, the values from Wagner's expression given by

\[ f_0 = \frac{\kappa_I + 2\kappa_a - \Phi (\kappa_I - \kappa_a)}{\epsilon_I + 2\epsilon_a - \Phi (\epsilon_I - \epsilon_a)} \frac{1}{2\pi \epsilon_0} \]  \quad (20)

are also shown in Table I.

Figure 3 shows theoretical curves for the concentration dependence of \( f_0 \). At lower concentrations, the curve by Eq. (4) is very close to that by Wagner's theory, whereas at higher concentrations the curve by Eq. (4) shows much lower values than that by Wagner's theory. In Fig. 3 are shown the observed data, which showed the remarkable dependence on the concentration similar to the tendency shown by Eq. (4). It is thus concluded that the concentration dependence of \( f_0 \) by Eq. (4) explains the experimental results fairly well. It is desired that values of \( \kappa_I \) is controlled experimentally by the use of salt solutions in definite concentrations to obtain more reliable values of \( f_0 \).
Fig. 3. Concentration dependence of relaxation frequency $f_0$ calculated from Equation (4) (Curve A) and from Wagner's Equation (20) (Curve B). Values of the phase parameters used for the calculation are shown in Table I. The circles in the figure are the experimental data cited from the previous paper.\(^9\)

**REFERENCES**


