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Systematic Analysis to Determine the Dielectric Phase Parameters from Dielectric Relaxations Caused by Diphasic Structure of Disperse Systems

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A systematic method is proposed to estimate the relative permittivity, the electrical conductivity and the volume fraction of the disperse phase from dielectric relaxation due to diphasic structure in spherical disperse systems. On the basis of Wagner's and Hanai's theory of interfacial polarization, theoretical expressions of practical use are derived for i) a system with non-conducting disperse phase, ii) a system with non-conducting continuous phase, and iii) a general system. Since the relations derived for the general case are of a complicated nature on evaluating the roots, some remarks are given to perform computer-searching for numerical solutions of the equations. The relations derived were applied to dielectric data of an oil-in-water emulsion, a water-in-oil emulsion, and a suspension of Sephadex G-25 in water to estimate the permittivity, the conductivity and the concentration of the disperse phase for the respective systems. For the disperse systems considered, the dielectric relaxation profiles were represented satisfactorily by Hanai's theory.

I. INTRODUCTION

It is known that a heterogeneous structure of disperse systems gives rise to a dielectric relaxation due to interfacial polarization.[1~4] Such dielectric relaxations for suspensions of spherical particles were first pointed out by Maxwell,[5] and afterwards formulated by Wagner[6] in a form convenient for the comparison with experiments. Since closer consideration revealed that Wagner's equation was in poor agreement with experiments at higher concentrations of the suspending particles, Hanai[7,8] proposed an equation which is expected to be applicable to higher concentrations.

These theoretical formulas have so far been used to discuss experimental results of emulsions and suspensions[2,3] with particular reference to the concentration dependence of the limiting relative permittivity and the electrical conductivity at low or high frequencies. Since the dielectric behavior of the disperse systems is characterized by the dielectric phase parameters such as relative permittivities, electrical conductivities and concentrations of the constituent phases, it is possible in principle to estimate the phase parameters of the inner phase from the dielectric data observed for the whole systems. No such attempt, however, has so far been made for disperse systems such as emulsions and suspensions.

On the basis of Wagner's and Hanai's theory of interfacial polarization, a systematic method is proposed, in the present paper, to calculate the relative permittivity, the electrical conductivity and the concentration of the disperse phase by use of data

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on dielectric relaxation caused by diphasic structure of spherical disperse systems. Some examples are given to show the practice of application of the proposed method to emulsions and suspensions.

II. GLOSSARY OF SYMBOLS

ε_a relative permittivity (dielectric constant) of the continuous medium.
κ_a electrical conductivity of the continuous medium, S cm.$^{-1}$
ε_i relative permittivity of the disperse phase.
κ_i electrical conductivity of the disperse phase, S cm.$^{-1}$
ε relative permittivity of the disperse system.
κ electrical conductivity of the disperse system, S cm.$^{-1}$
ε_a^*, ε_i^*, and ε^* are complex relative permittivity of the continuous medium, the disperse phase and the disperse system respectively, being given by

$$\varepsilon_a^*=\varepsilon_a-j\frac{\kappa_a}{2\pi f\epsilon_v}, \tag{1}$$

$$\varepsilon_i^*=\varepsilon_i-j\frac{\kappa_i}{2\pi f\epsilon_v}, \tag{2}$$

and

$$\varepsilon^*=\varepsilon-j\frac{\kappa}{2\pi f\epsilon_v}. \tag{3}$$

f measuring frequency, Hz.
j unit imaginary, $\sqrt{-1}$.
ϵ_v permittivity of a vacuum given by

$$\epsilon_v=\frac{1}{4\pi\cdot 9\cdot 10^{11}}=8.85418\times 10^{-14}\ \text{F cm.}^{-1}$$

Φ volume fraction of the disperse phase.
ε_l limiting relative permittivity at low frequencies.
ε_h limiting relative permittivity at high frequencies.
κ_l limiting conductivity at low frequencies, S cm.$^{-1}$
κ_h limiting conductivity at high frequencies, S cm.$^{-1}$
f_0 relaxation frequency corresponding to a half-value point of the entire dielectric relaxation, Hz.
$\Delta\varepsilon''$ imaginary part of the relative permittivity or loss factor associated with the dielectric relaxation, being expressed as

$$\Delta\varepsilon''=\frac{\kappa-\kappa_l}{2\pi f\epsilon_v}.$$

III. GENERAL EXPRESSIONS OF THE THEORIES OF INTERFACIAL POLARIZATION

1. Wagner Equation[2,6)]

According to Wagner's theory of interfacial polarization, the complex relative permittivity ε^* for a disperse system of spherical particles is given by

$$\varepsilon^* = \varepsilon_a{}^* \frac{2(1-\Phi)\varepsilon_a{}^* + (1+2\Phi)\varepsilon_i{}^*}{(2+\Phi)\varepsilon_a{}^* + (1-\Phi)\varepsilon_i{}^*} . \tag{4}$$

The limiting relative permittivities and conductivities at high and low frequencies are expressed as

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

$$\varepsilon_l = \varepsilon_a \frac{\kappa_l}{\kappa_a} + \frac{9(\varepsilon_i\kappa_a - \varepsilon_a\kappa_i)\kappa_a\Phi}{[(2+\Phi)\kappa_a + (1-\Phi)\kappa_i]^2} , \tag{6}$$

$$\kappa_h = \kappa_a \frac{\varepsilon_h}{\varepsilon_a} + \frac{9(\kappa_i\varepsilon_a - \kappa_a\varepsilon_i)\varepsilon_a\Phi}{[(2+\Phi)\varepsilon_a + (1-\Phi)\varepsilon_i]^2} , \tag{7}$$

$$\kappa_l = \kappa_a \frac{2(1-\Phi)\kappa_a + (1+2\Phi)\kappa_i}{(2+\Phi)\kappa_a + (1-\Phi)\kappa_i} , \tag{8}$$

and

$$f_0 = \frac{(2+\Phi)\kappa_a + (1-\Phi)\kappa_i}{(2+\Phi)\varepsilon_a + (1-\Phi)\varepsilon_i} \cdot \frac{1}{2\pi\epsilon_v} . \tag{9}$$

2. Hanai Equation[2,7]

For a concentrated suspension of spherical particles, Hanai proposed[7,8] the following equation for a complex relative permittivity of the system.

$$\frac{\varepsilon^* - \varepsilon_i{}^*}{\varepsilon_a{}^* - \varepsilon_i{}^*} \left(\frac{\varepsilon_a{}^*}{\varepsilon^*} \right)^{1/3} = 1 - \Phi . \tag{10}$$

The limiting values at high and low frequencies are given by

$$\frac{\varepsilon_h - \varepsilon_i}{\varepsilon_a - \varepsilon_i} \left(\frac{\varepsilon_a}{\varepsilon_h} \right)^{1/3} = 1 - \Phi , \tag{11}$$

$$\varepsilon_l \left(\frac{3}{\kappa_l - \kappa_i} - \frac{1}{\kappa_l} \right) = 3 \left(\frac{\varepsilon_a - \varepsilon_i}{\kappa_a - \kappa_i} + \frac{\varepsilon_i}{\kappa_l - \kappa_i} \right) - \frac{\varepsilon_a}{\kappa_a} , \tag{12}$$

$$\kappa_h \left(\frac{3}{\varepsilon_h - \varepsilon_i} - \frac{1}{\varepsilon_h} \right) = 3 \left(\frac{\kappa_a - \kappa_i}{\varepsilon_a - \varepsilon_i} + \frac{\kappa_i}{\varepsilon_h - \varepsilon_i} \right) - \frac{\kappa_a}{\varepsilon_a} , \tag{13}$$

and

$$\frac{\kappa_l - \kappa_i}{\kappa_a - \kappa_i} \left(\frac{\kappa_a}{\kappa_l} \right)^{1/3} = 1 - \Phi . \tag{14}$$

A theoretical expression of f_0 in Hanai's theory is not derived yet in an analytical form.

According to Wagner's theory so far used, the frequency giving the maximum loss factor is just the same as that giving a half value of the entire dielectric relaxation. In a previous consideration by numerical calculation of Hanai's theory on the frequency dependence of relative permittivity and loss factor,[13] the loss maximum frequency was found to be distinctly lower than the frequency giving the half value of the dielectric relaxation. From an experimental point of view, it is difficult to determine accurately the loss maximum frequency as against the half-value frequency of the dielectric relaxation. In the present paper, therefore, the symbol f_0 is used as the relaxation frequency at which the relative permittivity shows a half value of the entire dielectric relaxation experimentally as well as theoretically.

IV. EXPRESSIONS TO CALCULATE PHASE PARAMETERS FROM DIELECTRIC RELAXATION PARAMETERS

In this Section, expressions are derived to calculate phase parameters such as ε_i, κ_i, κ_a, and Φ from dielectric parameters such as ε_l, ε_h, κ_l, and κ_h.

1. O/W-like System where $\kappa_a \gg \kappa_i$

1-A. Wagner Equation

From Eq. 5 we have

$$\varepsilon_l = \varepsilon_a \frac{(2+\Phi)\varepsilon_h - 2(1-\Phi)\varepsilon_a}{(1+2\Phi)\varepsilon_a - (1-\Phi)\varepsilon_h} . \tag{15}$$

From Eq. 8 we have

$$\Phi = \frac{2(\kappa_a - \kappa_l)}{2\kappa_a + \kappa_l} . \tag{16}$$

Substituting Eq. 16 for Eq. 6 to eliminate κ_l/κ_a, we have

$$\varepsilon_i = \frac{2+\Phi}{9\Phi}\left[(2+\Phi)\varepsilon_l - 2(1-\Phi)\varepsilon_a\right] . \tag{17}$$

Equation 7 is rearranged as

$$\frac{\kappa_h}{\kappa_a} = \frac{\varepsilon_h}{\varepsilon_a} - \frac{9\varepsilon_a \varepsilon_i \Phi}{[(2+\Phi)\varepsilon_a + (1-\Phi)\varepsilon_i]^2} . \tag{18}$$

Equation 9 is simplified as

$$f_0 = \frac{(2+\Phi)\kappa_a}{(2+\Phi)\varepsilon_a + (1-\Phi)\varepsilon_i} \cdot \frac{1}{2\pi\epsilon_v} . \tag{19}$$

1-B. Hanai Equation

Here a condition $\kappa_l \gg \kappa_i$ is adopted in addition to $\kappa_a \gg \kappa_i$ for simplification. Equation 11 is rearranged as

$$\varepsilon_i = \varepsilon_a - \frac{\varepsilon_a - \varepsilon_h}{1 - (1-\Phi)\left(\dfrac{\varepsilon_h}{\varepsilon_a}\right)^{1/3}} . \tag{20}$$

Under the condition $\kappa_l \gg \kappa_i$, Eq. 14 is reduced to

$$\kappa_l = \kappa_a (1-\Phi)^{3/2} . \tag{21}$$

Substituting Eq. 21 for Eq. 12 to eliminate κ_l/κ_a, we have

$$\varepsilon_i = \frac{2}{3}\varepsilon_a - \frac{2}{3}\cdot\frac{\varepsilon_a-\varepsilon_l}{1-(1-\Phi)^{3/2}}\,. \tag{22}$$

Equation 13 is simplified as

$$\frac{\kappa_h}{\kappa_a} = \frac{\varepsilon_h(\varepsilon_h-\varepsilon_i)(2\varepsilon_a+\varepsilon_i)}{\varepsilon_a(\varepsilon_a-\varepsilon_i)(2\varepsilon_h+\varepsilon_i)}\,. \tag{23}$$

2. W/O-like System where $\kappa_a \ll \kappa_i$

In this instance, Φ, ε_i, κ_i, and f_0 can be calculated from ε_l, ε_h, κ_h, and ε_a by using expressions which are derived below.

2-A. Wagner Equation

Equation 8 is reduced to

$$\Phi = \frac{\kappa_l-\kappa_a}{\kappa_l+2\kappa_a}\,. \tag{24}$$

Substituting Eq. 24 for Eq. 6 to eliminate κ_l/κ_a, we have

$$\Phi = \frac{\varepsilon_l-\varepsilon_a}{\varepsilon_l+2\varepsilon_a}\,. \tag{25}$$

Substitution of Eq. 25 for Eq. 5 to eliminate Φ gives

$$\varepsilon_i = \frac{\varepsilon_h(\varepsilon_l+\varepsilon_a)-2\varepsilon_a^2}{\varepsilon_l-\varepsilon_h}\,. \tag{26}$$

Substituting Eqs. 25 and 26 for Eq. 7 to eliminate Φ and ε_i, we have

$$\kappa_i = \kappa_h\frac{(\varepsilon_l-\varepsilon_a)(\varepsilon_l+2\varepsilon_a)}{(\varepsilon_l-\varepsilon_h)^2}\,. \tag{27}$$

Substitution of Eqs. 25, 26, and 27 for Eq. 9 to eliminate Φ, ε_i, and κ_i gives

$$f_0 = \frac{\kappa_h}{\varepsilon_l-\varepsilon_h}\cdot\frac{1}{2\pi\epsilon_v}\,. \tag{28}$$

2-B. Hanai Equation

Here a condition $\kappa_l \ll \kappa_i$ is adopted in addition to $\kappa_a \ll \kappa_i$ for simplification. Equation 14 is reduced to

$$\Phi = 1-\left(\frac{\kappa_a}{\kappa_l}\right)^{1/3}. \tag{29}$$

This Eq. 29 is substituted for Eq. 12 to eliminate κ_l/κ_a, leading to

$$\Phi = 1-\left(\frac{\varepsilon_a}{\varepsilon_l}\right)^{1/3}. \tag{30}$$

Substituting Eq. 30 for Eq. 11 to eliminate Φ, we have

$$\varepsilon_i = \varepsilon_a + \frac{\varepsilon_h-\varepsilon_a}{1-\left(\dfrac{\varepsilon_h}{\varepsilon_l}\right)^{1/3}}\,. \tag{31}$$

Substitution of Eq. 31 for Eq. 13 to eliminate ε_l gives

$$\kappa_l = \kappa_h \frac{1-\dfrac{1}{3}\left(2+\dfrac{\varepsilon_a}{\varepsilon_h}\right)\left(\dfrac{\varepsilon_h}{\varepsilon_l}\right)^{1/3}}{\left[1-\left(\dfrac{\varepsilon_h}{\varepsilon_l}\right)^{1/3}\right]^2} . \tag{32}$$

3. General System

This is general cases without any restriction between κ_a and κ_i.

3-A. *Scheme A* on which Φ, ε_i, κ_i, κ_a, and f_0 can be calculated from ε_l, ε_h, κ_l, κ_h, and ε_a

3-A-a. Wagner Equation

Cumbersome calculations by use of Eqs. 5 to 8 lead to

$$H(\kappa_a) \equiv \sqrt{\frac{\kappa_l\varepsilon_a-\kappa_a\varepsilon_l}{\kappa_h\varepsilon_a-\kappa_a\varepsilon_h}} - \frac{\kappa_a}{\varepsilon_a} \cdot \frac{\varepsilon_l-\varepsilon_h}{\kappa_h-\kappa_l} = 0 . \tag{33}$$

The derivation of this equation is given in Appendix I. Numerical values of κ_a satisfying Eq. 33 can be obtained by means of computer-searching provided that values of ε_l, ε_h, κ_l, κ_h, and ε_a are given from observed data. Some remarks for the computer-searching are given in Appendix II.

Next, Eqs. 5 and 8 are substituted for Eq. 6 to eliminate ε_i and κ_i, the resulting relation being solved for Φ. After tedious calculations, we have

$$\Phi = \frac{(\varepsilon_a\varepsilon_h+\varepsilon_h\varepsilon_l-\varepsilon_a\varepsilon_l)\kappa_a^2-2\varepsilon_a\varepsilon_h\kappa_l\kappa_a+\varepsilon_a^2\kappa_l^2}{(2\varepsilon_a\varepsilon_l+\varepsilon_h\varepsilon_l-2\varepsilon_a\varepsilon_h)\kappa_a^2-2\varepsilon_a\varepsilon_h\kappa_l\kappa_a+\varepsilon_a^2\kappa_l^2} . \tag{34}$$

Alternatively, we have

$$\Phi = \frac{\varepsilon_a\varepsilon_h(\kappa_l-\kappa_a)^2+(\varepsilon_a-\varepsilon_h)(\varepsilon_a\kappa_l^2-\varepsilon_l\kappa_a^2)}{(\varepsilon_a\kappa_l-\varepsilon_h\kappa_a)^2+(\varepsilon_l-\varepsilon_h)(2\varepsilon_a+\varepsilon_h)\kappa_a^2} . \tag{35}$$

An outline of the derivation is shown in Appendix III.

Equations 5 and 8 are rearranged respectively as

$$\varepsilon_i = \varepsilon_a \frac{\Phi(2\varepsilon_a+\varepsilon_h)-2(\varepsilon_a-\varepsilon_h)}{\Phi(2\varepsilon_a+\varepsilon_h)+\varepsilon_a-\varepsilon_h} , \tag{36}$$

and

$$\kappa_i = \kappa_a \frac{\Phi(2\kappa_a+\kappa_l)+2(\kappa_l-\kappa_a)}{\Phi(2\kappa_a+\kappa_l)-(\kappa_l-\kappa_a)} . \tag{37}$$

These Eqs. 35, 36, and 37 can be used for calculating Φ, ε_i, and κ_i.

Relaxation frequency f_0 can be calculated from

$$f_0 = \frac{(2+\Phi)\kappa_a+(1-\Phi)\kappa_i}{(2+\Phi)\varepsilon_a+(1-\Phi)\varepsilon_i} \cdot \frac{1}{2\pi\epsilon_v} . \tag{38}$$

3-A-b. Hanai Equation

For simplicity, we put

$$C \equiv \left(\frac{\varepsilon_h}{\varepsilon_a}\right)^{1/3} \cdot (1-\Phi) . \tag{39}$$

From Eqs. 11, 12, and 14, we have

$$C = \frac{-Q-\sqrt{Q^2-4PR}}{2P} , \tag{40}$$

where

$$P = \left(\frac{\kappa_a}{\kappa_l}+2\right)\varepsilon_l D - 3[\varepsilon_h D - \varepsilon_a(D-1)]D + \left(\frac{\kappa_l}{\kappa_a}-1\right)\varepsilon_a D , \tag{41}$$

$$Q = 3[2\varepsilon_h D - \varepsilon_a(D-1)] - \left[\left(\frac{\kappa_a}{\kappa_l}+2\right)D+3\right]\varepsilon_l - \left(\frac{\kappa_l}{\kappa_a}-1\right)\varepsilon_a D , \tag{42}$$

$$R = 3(\varepsilon_l - \varepsilon_h) , \tag{43}$$

and

$$D = \left(\frac{\varepsilon_a \kappa_l}{\varepsilon_h \kappa_a}\right)^{1/3} . \tag{44}$$

Eventually the function C given by Eq. 40 is a complicated function of κ_a. Details of the derivation are given in Appendix IV.

Next, Eqs. 11 and 14 are substituted for Eq. 13 to eliminate ε_i and κ_i. Thus we have

$$J(\kappa_a) \equiv \kappa_h\left[3-\left(2+\frac{\varepsilon_a}{\varepsilon_h}\right)C\right](1-DC)$$
$$-3\{\kappa_l - [\kappa_a(D-1)+\kappa_l]C\}(1-C) + \kappa_a\left(1-\frac{\varepsilon_h}{\varepsilon_a}\right)C(1-DC) = 0 . \tag{45}$$

The left side of Eq. 45, which is a formula abbreviated as $J(\kappa_a)$, is a function of κ_a provided that ε_l, ε_h, κ_l, κ_h, and ε_a are given through Eqs. 40 and 44. Equation 45 can not be solved for κ_a owing to the complicated functional form. Computers have made it possible to search out a root for $J(\kappa_a)=0$ numerically. Remarks on the computer-searching for $J(\kappa_a)=0$ are given in Appendix V.

By use of numerical values of κ_a thus obtained, values of D can be calculated from Eq. 44. Values of C may be calculated from Eqs. 40, 41, 42, and 43 by use of the values of κ_a and D obtained above.

The rearrangement of Eq. 39 gives

$$\Phi = 1 - \left(\frac{\varepsilon_a}{\varepsilon_h}\right)^{1/3} \cdot C , \tag{46}$$

from which Φ can be calculated. Equations 11 and 14 are rearranged as

$$\varepsilon_i = \frac{\varepsilon_h - \varepsilon_a C}{1-C} , \tag{47}$$

and

$$\kappa_i = \frac{\kappa_l - \kappa_a DC}{1-DC} , \tag{48}$$

which may be used for calculating ε_i and κ_i respectively.

3-B. *Scheme B* on which Φ, ε_i, κ_i, κ_h, and f_0 can be calculated from ε_l, ε_h, κ_l, κ_a, and ε_a.

It is sometimes difficult to obtain observed values of κ_h with required accuracy owing to shift of the dielectric relaxation to somewhat higher frequencies. In such instances, the phase parameters may be determined provided κ_a can be measured instead of κ_h.

3-B-a. Wagner Equation

In this case, Eq. 34 or 35 is used to calculate Φ. Equations 36 and 37 can be used for calculating ε_i and κ_i. Next, κ_h may be calculated from

$$\kappa_h=\kappa_a\frac{\varepsilon_h}{\varepsilon_a}+\frac{9(\kappa_i\varepsilon_a-\kappa_a\varepsilon_i)\varepsilon_a\Phi}{[(2+\Phi)\varepsilon_a+(1-\Phi)\varepsilon_i]^2}\,. \tag{49}$$

Relaxation frequency f_0 can be calculated from Eq. 38. The frequency dependence of ε and κ may be calculated from Eq. 4.

3-B-b. Hanai Equation

In this case, unlike the previous case of κ_h given, the function C given by Eq. 40 is calculated by use of Eqs. 41, 42, 43, and 44 provided that κ_a is given. Values of Φ, ε_i, and κ_i are calculated from Eqs. 46, 47, and 48 respectively. Values of κ_h can be calculated from

$$\kappa_h\left(\frac{3}{\varepsilon_h-\varepsilon_i}-\frac{1}{\varepsilon_h}\right)=3\left(\frac{\kappa_a-\kappa_i}{\varepsilon_a-\varepsilon_i}+\frac{\kappa_i}{\varepsilon_h-\varepsilon_i}\right)-\frac{\kappa_a}{\varepsilon_a}\,. \tag{50}$$

The frequency dependence of ε and κ may be calculated from Eq. 10.[13]

V. APPLICATION AND DISCUSSION

1. Example for an O/W-like System

In this case relevant to usual emulsions of O/W type, the dielectric relaxation is expected to be too small to be observed. For example, we consider a case where $\varepsilon_a=80$, $\varepsilon_i=2$, and $\Phi=0.8$. Calculations by means of Wagner's Eqs. 17 and 15 give values of $\varepsilon_l=13.2653$ and $\varepsilon_h=13.2620$, resulting in a very small dielectric relaxation $\Delta\varepsilon\equiv\varepsilon_l-\varepsilon_h=0.0033$. Likewise Hanai's Eqs. 22 and 20 give values of $\varepsilon_l=9.8871$ and $\varepsilon_h=9.7288$, leading also to a small value $\Delta\varepsilon=0.158$. In view of the measuring accuracy, therefore, it is very difficult to assess the respective values of ε_l and ε_h from observed date. For estimation of the phase parameters in the present case, it is essential to obtain a value of Φ from separate experiments.

In our previous dielectric study of O/W emulsions,[9,10] no appreciable dielectric relaxation was observed in conformity with the theoretical prediction, and the following values were obtained for the O/W emulsion in $\Phi=0.8$: $\varepsilon_l\fallingdotseq\varepsilon_h=9.78$ and $\varepsilon_a=76.8$. By use of these values, the phase parameters were calculated from Wagner's and Hanai's Equations, the results being summarized in Table I. Wagner's Equations seem to give unrealistic values with a negative sign for ε_i, whereas Hanai's Equations give reasonable values for ε_i which can be compared with a directly measured value $\varepsilon_i=2.50$.

Table I. Evaluation of Phase Parameters for an O/W Emulsion

Dielectric Parameters Observed[9]	Phase Parameters Calculated from the Equations	
$\Phi = 0.8$	Wagner Equations	
$\varepsilon_l \fallingdotseq \varepsilon_h = 9.78$	$\varepsilon_i = -1.2973$	from Eq. 17
$\varepsilon_a = 76.8$	$\varepsilon_i = -1.2957$	from Eq. 15
$\varepsilon_i = 2.50$ (oil phase)		
	Hanai Equations	
	$\varepsilon_i = 2.1311$	from Eq. 22
	$\varepsilon_i = 2.2818$	from Eq. 20

2. Example for a W/O-like System

In this case associated with emulsions of W/O type, the marked dielectric relaxation is theoretically expected to be observed. In our previous dielectric measurements of W/O emulsions,[11,12] remarkable dielectric relaxations were observed in accordance with the theoretical prediction. The dielectric data for the emulsion in $\Phi=0.7$ were subjected to the analysis by means of Eqs. 25 to 32 for estimating the values of Φ, ε_i, κ_i, and f_0, the results being listed in Table II together with the dielectric parameters observed. The value of Φ obtained on the preparation of the emulsion is very close to that estimated by Hanai's Eq. 30.

By use of the values of ε_a, κ_a, ε_i, κ_i, and Φ shown in Table II, the frequency dependence of ε, κ, and the loss factor $\Delta\varepsilon''$ is calculated from Eqs. 4 and 10, the resulting theoretical curves being compared with the observed data in Fig. 1. Complex plane plots of the theoretical values are shown in Fig. 2, together with the observed data. The observed data seem to be close to the theoretical curves by Hanai's Eq. 10.

3. Example for a General System

In the case that $\kappa_a \simeq \kappa_i$ and $\varepsilon_a \lesssim \varepsilon_i$, marked dielectric relaxations are theoretically expected to be found. Such examples were observed for suspensions of

Table II. Evaluation of Phase Parameters for a W/O Emulsion

Dielectric Parameters Observed[12]		Phase Parameters Calculated from the Equations		
$\Phi = 0.7$		Wagner Equations		
$\varepsilon_l = 94.0$		$\Phi = 0.9353$		from Eq. 25
$\varepsilon_h = 23.4$		$\varepsilon_i = 31.73$		from Eq. 26
$\kappa_l = 9.256\times10^{-5}$	μS cm^{-1}	$\kappa_i = 7.369$	μS cm^{-1}	from Eq. 27
$\kappa_h = 4.069$	μS cm^{-1}	$f_0 = 103.6$	kHz	from Eq. 28
$\varepsilon_a = 2.12$				
$\kappa_a = 6.178\times10^{-5}$	μS cm^{-1}	Hanai Equations		
$f_0 = 88.0$	kHz	$\Phi = 0.7175$		from Eq. 30
		$\varepsilon_i = 59.49$		from Eq. 31
		$\kappa_i = 16.61$	μS cm^{-1}	from Eq. 32
		$f_0 = 88.52$	kHz	read graphically

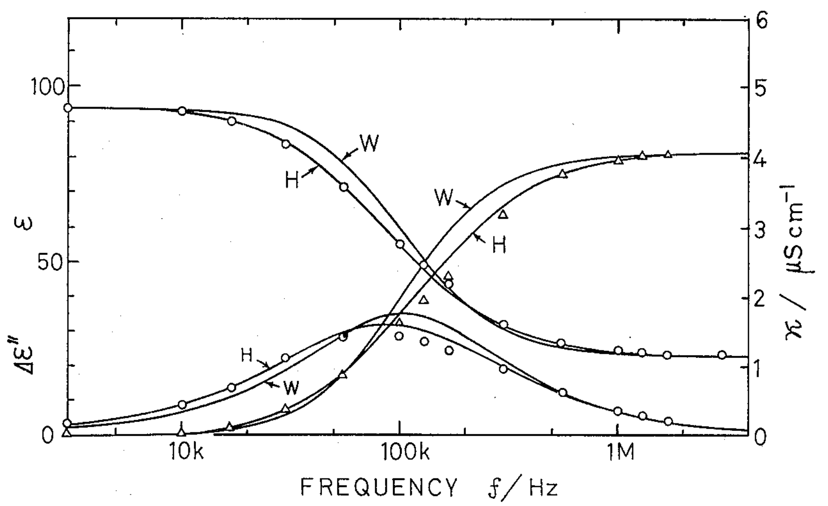

Fig. 1. Frequency dependence of the relative permittivity ε, the electrical conductivity κ and the loss factor $\Delta\varepsilon''=(\kappa-\kappa_l)/(2\pi f\epsilon_v)$ for a W/O emulsion.
The observed values of ε and $\Delta\varepsilon''$ (○), and κ(△) were cited from Reference 12. The theoretical curves W were calculated from Wagner's Eq. 4, and the curves H from Hanai's Eq. 10.

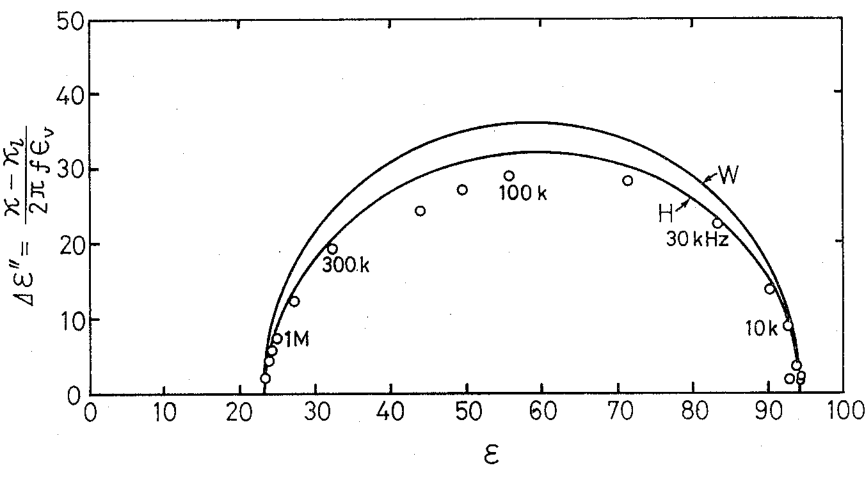

Fig. 2. Complex plane plots of ε and $\Delta\varepsilon''$ for the W/O emulsion.
The same data as shown in Fig. 1. Curve W was calculated from Wagner's Eq. 4, and curve H from Hanai's Eq. 10. Numbers beside the observed points are the measuring frequency.

Sephadex G-25 in water. Sephadex G-25 is spherical beads composed of dextran gel, and possesses the permittivity and the conductivity characteristic of its swollen state in an aqueous phase. Details of the preparation of the suspensions will be reported elsewhere together with the systematic consideration of the dielectric data. Frequency dependence of ε, κ, and $\Delta\varepsilon''$ and the complex plane plots observed for a suspension of Sephadex G-25 in distilled water are shown in Figs. 3 and 4. The

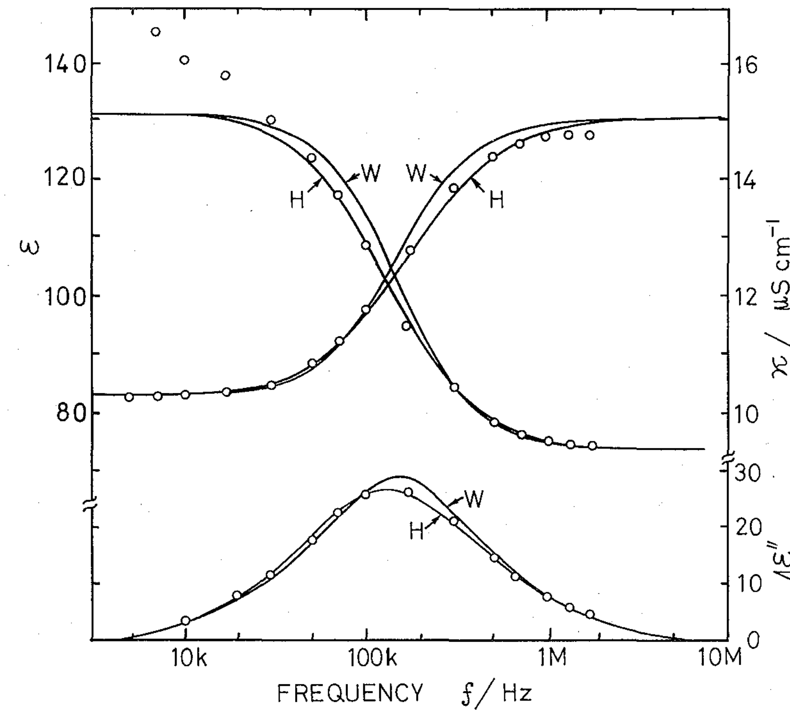

Fig. 3. Frequency dependence of the relative permittivity ε, the electrical conductivity κ and the loss factor $\Delta\varepsilon''=(\kappa-\kappa_l)/(2\pi f\epsilon_v)$ for a Sephadex G-25 suspension. The theoretical curves W were calculated from Wagner's Eq. 4, and the curves H from Hanai's Eq. 10.

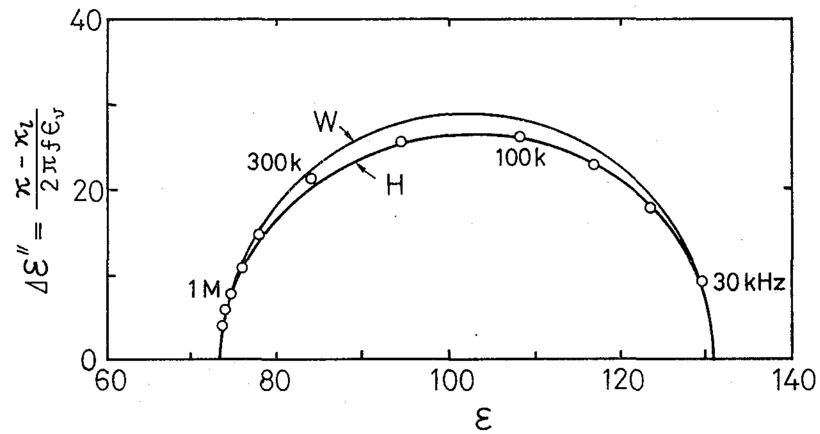

Fig. 4. Complex plane plots of ε and $\Delta\varepsilon''$ for the Sephadex G-25 suspension. The same data as shown in Fig. 3. Curve W was calculated from Wagner's Eq. 4, and curve H from Hanai's Eq. 10. Numbers beside the observed points are the measuring frequency.

Table III. Evaluation of Phase Parameters for a Suspension of Sephadex G-25

Dielectric Parameters Observed		Phase Parameters Calculated from the Equations		
$\varepsilon_l = 131.0$		Wagner Equations		
$\varepsilon_h = 73.4$		$\kappa_a = 3.816$	μS cm^{-1}	from Eq. 33
$\kappa_l = 10.31$	μS cm^{-1}	$\Phi = 0.5873$		from Eq. 35
$\kappa_h = 15.0$	μS cm^{-1}	$\varepsilon_i = 69.43$		from Eq. 36
$\varepsilon_a = 79.29$		$\kappa_i = 22.21$	μS cm^{-1}	from Eq. 37
$\kappa_a = 2.916$	μS cm^{-1}	$f_0 = 146$	kHz	from Eq. 38
$f_0 = 127$	kHz			
		Hanai Equations		
		$\kappa_a = 3.090$	μS cm^{-1}	from Eq. 45
		$\Phi = 0.5720$		from Eq. 46
		$\varepsilon_i = 69.18$		from Eq. 47
		$\kappa_i = 23.13$	μS cm^{-1}	from Eq. 48
		$f_0 = 135$	kHz	read graphically

values of dielectric parameters ε_l, ε_h, κ_l, κ_h, and f_0 can be determined from these results. Values of ε_a and κ_a of the suspending medium being in equilibrium with the Sephadex granules were also measured.

Following the analysis shown in the preceding section, values of κ_a, Φ, ε_i, κ_i, and f_0 were calculated from Eqs. 33, 35, 36, 37, and 38 for Wagner's theory, and from Eqs. 45, 40, 46, 47, and 48 for Hanai's theory in due course. The values thus obtained are summarized in Table III together with the dielectric parameters used. The observed values of κ_a and f_0 seem to be close to the values by Hanai's Equations. As regards the calculated values for Φ, ε_i, and κ_i, no significant differences are found between the two theories.

The frequency dependence of ε, κ, and $\Delta\varepsilon''$ and their complex plane plots were calculated from Eqs. 4 and 10,[18] the theoretical curves being shown in Figs. 3 and 4. The curves calculated from Eq. 10 are satisfactory for representing observed data.

VI. CONCLUSIONS

On the basis of Wagner's and Hanai's theories of interfacial polarization, theoretical expressions of practical use were derived to evaluate the phase parameters from the dielectric parameters characteristic of the dielectric relaxations observed.

i) *O/W-like system where* $\kappa_a \gg \kappa_i$. Values of ε_i and κ_i can be calculated by use of Φ which are obtained from separate experiments.

ii) *W/O-like system where* $\kappa_a \ll \kappa_i$. Values of phase parameters Φ, ε_i, κ_i, and f_0 can be calculated from the dielectric parameters ε_l, ε_h, κ_h, and ε_a which are obtained from dielectric relaxation data observed.

iii) *General system.* (A) Values of the phase parameters Φ, ε_i, κ_i, κ_a, and f_0 can be calculated from the dielectric parameters ε_l, ε_h, κ_l, κ_h, and ε_a. (B) Values of the phase parameters Φ, ε_i, κ_i, κ_h, and f_0 can be calculated from the dielectric parameters ε_l, ε_h, κ_l, κ_a, and ε_a.

For the examples shown in Application, Hanai's Equations were seen to represent satisfactorily the frequency dependence of the data as well as the phase parameters observed.

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APPENDICES

I. Derivation of Eq. 33

Equations 6 and 7 are rearranged respectively as

$$\frac{\kappa_l\varepsilon_a-\kappa_a\varepsilon_l}{\kappa_a^2}=\frac{9(\kappa_i\varepsilon_a-\kappa_a\varepsilon_i)\Phi}{[(2+\Phi)\kappa_a+(1-\Phi)\kappa_i]^2}, \tag{A1}$$

and

$$\frac{\kappa_h\varepsilon_a-\kappa_a\varepsilon_h}{\varepsilon_a^2}=\frac{9(\kappa_i\varepsilon_a-\kappa_a\varepsilon_i)\Phi}{[(2+\Phi)\varepsilon_a+(1-\Phi)\varepsilon_i]^2}. \tag{A2}$$

Equation A1 divided by Eq. A2 leads to

$$\frac{\kappa_l\varepsilon_a-\kappa_a\varepsilon_l}{\kappa_h\varepsilon_a-\kappa_a\varepsilon_h}\cdot\frac{\varepsilon_a^2}{\kappa_a^2}=\left[\frac{(2+\Phi)\varepsilon_a+(1-\Phi)\varepsilon_i}{(2+\Phi)\kappa_a+(1-\Phi)\kappa_i}\right]^2. \tag{A3}$$

Equation 8 is substituted for Eq. 6 to eliminate κ_l. The Eq. 6 subtracted by Eq. 5 is

$$\varepsilon_l-\varepsilon_h=\frac{9(\varepsilon_a\kappa_i-\varepsilon_i\kappa_a)^2\,\Phi(1-\Phi)}{[(2+\Phi)\varepsilon_a+(1-\Phi)\varepsilon_i][(2+\Phi)\kappa_a+(1-\Phi)\kappa_i]^2}. \tag{A4}$$

Equation 5 is substituted for Eq. 7 to eliminate ε_h. The Eq. 7 subtracted by Eq. 8 is

$$\kappa_h-\kappa_l=\frac{9(\varepsilon_a\kappa_i-\varepsilon_i\kappa_a)^2\,\Phi(1-\Phi)}{[(2+\Phi)\kappa_a+(1-\Phi)\kappa_i][(2+\Phi)\varepsilon_a+(1-\Phi)\varepsilon_i]^2}. \tag{A5}$$

Division of Eq. A4 by Eq. A5 gives

$$\frac{\varepsilon_l-\varepsilon_h}{\kappa_h-\kappa_l}=\frac{(2+\Phi)\varepsilon_a+(1-\Phi)\varepsilon_i}{(2+\Phi)\kappa_a+(1-\Phi)\kappa_i}. \tag{A6}$$

Substituting this Eq. A6 for Eq. A3, we have

$$\frac{\kappa_l\varepsilon_a-\kappa_a\varepsilon_l}{\kappa_h\varepsilon_a-\kappa_a\varepsilon_h}=\left(\frac{\kappa_a}{\varepsilon_a}\cdot\frac{\varepsilon_l-\varepsilon_h}{\kappa_h-\kappa_l}\right)^2. \tag{A7}$$

Thus we have, from Eq. A7,

$$\pm\sqrt{\frac{\kappa_l\varepsilon_a-\kappa_a\varepsilon_l}{\kappa_h\varepsilon_a-\kappa_a\varepsilon_h}}=\frac{\kappa_a}{\varepsilon_a}\cdot\frac{\varepsilon_l-\varepsilon_h}{\kappa_h-\kappa_l}, \tag{A8}$$

which leads to Eq. 33 in the text. From the physical point of view, each factor of the right side of Eq. A8 is all positive. Thus a negative sign in front of the radical sign of the left side of Eq. A8 must be ruled out on the evaluation of Eq. A7

II. Some Remarks on the Numerical Searching for κ_a-Values Regarding Eq. 33

The function $H(\kappa_a)$ given by Eq. 33 is composed of two terms as

$$H(\kappa_a)=H_1(\kappa_a)-H_2(\kappa_a)\,, \tag{A9}$$

where

$$H_2(\kappa_a)=\frac{\kappa_a}{\varepsilon_a}\cdot\frac{\varepsilon_l-\varepsilon_h}{\kappa_h-\kappa_l}\,, \tag{A10}$$

and

$$H_1(\kappa_a)=\sqrt{\frac{\kappa_l\varepsilon_a-\kappa_a\varepsilon_l}{\kappa_h\varepsilon_a-\kappa_a\varepsilon_h}}=\sqrt{\frac{\varepsilon_l}{\varepsilon_h}\left(1+\frac{\kappa_h\dfrac{\varepsilon_a}{\varepsilon_h}-\kappa_l\dfrac{\varepsilon_a}{\varepsilon_l}}{\kappa_a-\kappa_h\dfrac{\varepsilon_a}{\varepsilon_h}}\right)}\,. \tag{A11}$$

From this functional form of $H_1(\kappa_a)$ expressed as Eq. A11, it can readily be seen that $H_1(\kappa_a)$ is a modified form of a rectangular hyperbola with two asymptotes

$$H_1(\text{ordinate})=\sqrt{\frac{\varepsilon_l}{\varepsilon_h}}\quad\text{and}\quad\kappa_a(\text{abscissa})=\kappa_h\frac{\varepsilon_a}{\varepsilon_h}\,,$$

and with two intercepts at

$$H_1=\sqrt{\frac{\kappa_l}{\kappa_h}}\quad\text{and}\quad\kappa_a=\kappa_l\frac{\varepsilon_a}{\varepsilon_l}\,.$$

The graphs of $H_1(\kappa_a)$, $H_2(\kappa_a)$, and their composite $H(\kappa_a)$ in brief outline are illustrated in Fig. A1.

The existing domains of $H(\kappa_a)$ of physical significance are

$$0<\kappa_a<\kappa_l\frac{\varepsilon_a}{\varepsilon_l}\qquad\text{termed domain } X, \tag{A12}$$

and

$$\kappa_h\frac{\varepsilon_a}{\varepsilon_h}<\kappa_a\qquad\text{termed domain } Y. \tag{A13}$$

Taking into consideration these limitations, still we find two points X_0 and Y_0 of intersection between the curves $H_1(\kappa_a)$ and $H_2(\kappa_a)$, the corresponding roots being denoted by $\kappa_a=\kappa_{ax}$ and $\kappa_a=\kappa_{ay}$. Further exclusion of the false root for κ_a must be made as the following.

From Eq. 6 we have

$$\varepsilon_l-\varepsilon_a\frac{\kappa_l}{\kappa_a}=\frac{9(\varepsilon_l\kappa_a-\varepsilon_a\kappa_l)\kappa_a\Phi}{[(2+\Phi)\kappa_a+(1-\Phi)\kappa_l]^2}\,. \tag{A14}$$

The sign of the left side of this Eq. A14 is determined according as a factor

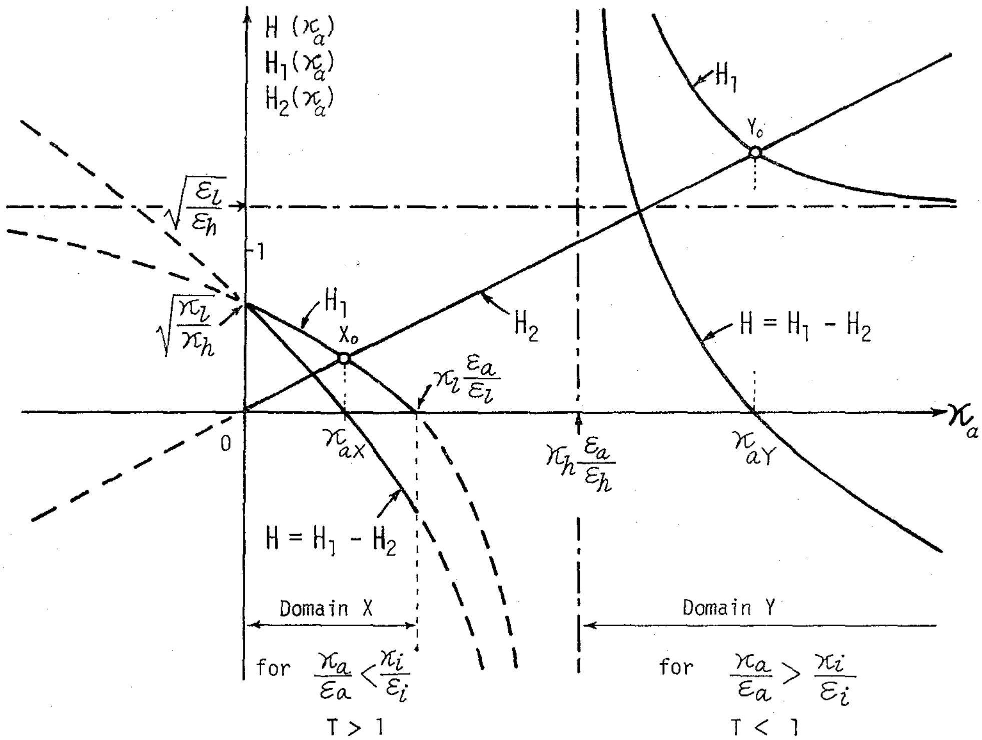

Fig. A1. The brief profiles of functions H_1(Eq. A11), H_2(Eq. A10), and H(Eq. A9) against κ_a.
The chain lines are the asymptotes. The solid curves are the part of physical significance. The dashed curves bear no physical meaning.

$(\varepsilon_i\kappa_a-\varepsilon_a\kappa_i)$ is positive or negative. Thus we have

$$\kappa_l\frac{\varepsilon_a}{\varepsilon_l}<\kappa_a \text{ for } \frac{\varepsilon_i}{\varepsilon_a}>\frac{\kappa_i}{\kappa_a}, \tag{A15}$$

and

$$\kappa_l\frac{\varepsilon_a}{\varepsilon_l}>\kappa_a \text{ for } \frac{\varepsilon_i}{\varepsilon_a}<\frac{\kappa_i}{\kappa_a}. \tag{A16}$$

Similarly, from Eq. 7 we have

$$\kappa_h\frac{\varepsilon_a}{\varepsilon_h}<\kappa_a \text{ for } \frac{\varepsilon_i}{\varepsilon_a}>\frac{\kappa_i}{\kappa_a}, \tag{A17}$$

and

$$\kappa_h\frac{\varepsilon_a}{\varepsilon_h}>\kappa_a \text{ for } \frac{\varepsilon_i}{\varepsilon_a}<\frac{\kappa_i}{\kappa_a}. \tag{A18}$$

For all the cases, we have

$$\varepsilon_l>\varepsilon_h>0 \text{ and } \kappa_h>\kappa_l>0,$$

which lead to

$$\frac{\kappa_h}{\varepsilon_h} > \frac{\kappa_l}{\varepsilon_l} > 0 . \tag{A19}$$

On account of this inequality A19, the relations A15–A18 can be simplified as

$$\kappa_a < \kappa_l \frac{\varepsilon_a}{\varepsilon_l} \text{ (domain } X \text{) for } \frac{\kappa_a}{\varepsilon_a} < \frac{\kappa_i}{\varepsilon_i} , \tag{A20}$$

and

$$\kappa_h \frac{\varepsilon_a}{\varepsilon_h} < \kappa_a \text{ (domain } Y \text{) for } \frac{\kappa_a}{\varepsilon_a} > \frac{\kappa_i}{\varepsilon_i} . \tag{A21}$$

In view of these relations A20 and A21, either domain X or Y should be adopted according as $\kappa_a/\varepsilon_a < \kappa_i/\varepsilon_i$ or $\kappa_a/\varepsilon_a > \kappa_i/\varepsilon_i$.

Now ε_i and κ_i must be eliminated in the relations A20 and A21, since these phase parameters cannot be known before the calculation. By use of Eq. A30 shown later on, Φ is eliminated from Eqs. 36 and 37. The resulting relations are used for representing κ_i/ε_i. After tedious rearrangement of the formulas, we have

$$\frac{\kappa_i}{\varepsilon_i} = \frac{\kappa_a}{\varepsilon_a} T , \tag{A22}$$

where

$$T = \frac{\varepsilon_a V[(V-W)\varepsilon_a(\kappa_l + 2\kappa_a)(\kappa_l - \kappa_a) + VW\kappa_l]}{\kappa_a W[(V-W)\varepsilon_a\{\varepsilon_h(\kappa_l+\kappa_a) - 2\varepsilon_a\kappa_a\} + VW\varepsilon_h]} , \tag{A23}$$

$$V = \varepsilon_a \kappa_l - \varepsilon_h \kappa_a , \tag{A24}$$

and

$$W = \varepsilon_a \kappa_l - \varepsilon_l \kappa_a . \tag{A25}$$

Instead of the relations A20 and A21, discrimination between domains X and Y is expressed as

$$\text{domain } X \left(0 < \kappa_a < \kappa_l \frac{\varepsilon_a}{\varepsilon_l}\right) \text{ when } \frac{\kappa_i \varepsilon_a}{\varepsilon_i \kappa_a} \equiv T > 1 , \tag{A26}$$

and

$$\text{domain } Y \left(\kappa_h \frac{\varepsilon_a}{\varepsilon_h} < \kappa_a\right) \text{ when } \frac{\kappa_i \varepsilon_a}{\varepsilon_i \kappa_a} \equiv T < 1 . \tag{A27}$$

In this instance, an approximate value of κ_a must be measured for estimating a value of T. By use of Eqs. A25, A24, and A23, a value of T can be calculated. Eventually it is concluded in Fig. A1 that a solution $\kappa_a = \kappa_{ax}$ for the point X_0 in domain X should be adopted when $T > 1$, and the other solution $\kappa_a = \kappa_{ay}$ for Y_0 in domain Y when $T < 1$.

III. Derivation of Eq. 34

The expressions of ε_i and κ_i derived from Eqs. 5 and 8 are substituted for two factors $(\varepsilon_i\kappa_a-\varepsilon_a\kappa_i)$ and $[(2+\Phi)\kappa_a+(1-\Phi)\kappa_i]$ to give

$$\varepsilon_i\kappa_a-\varepsilon_a\kappa_i=\frac{9(\varepsilon_h\kappa_a-\varepsilon_a\kappa_l)\varepsilon_a\kappa_a\Phi}{[\Phi(2\varepsilon_a+\varepsilon_h)+(\varepsilon_a-\varepsilon_h)][\Phi(2\kappa_a+\kappa_l)-(\kappa_l-\kappa_a)]}, \tag{A28}$$

and

$$(2+\Phi)\kappa_a+(1-\Phi)\kappa_i=\frac{9\Phi\kappa_a{}^2}{\Phi(2\kappa_a+\kappa_l)-(\kappa_l-\kappa_a)}. \tag{A29}$$

These two factors expressed by Eqs. A28 and A29 are substituted for Eq. 6. Solving the resulting relation for Φ, we have

$$\Phi=\frac{\varepsilon_a(\varepsilon_a\kappa_l-\varepsilon_h\kappa_a)(\kappa_l-\kappa_a)+(\varepsilon_a-\varepsilon_h)(\varepsilon_a\kappa_l-\varepsilon_l\kappa_a)\kappa_a}{\varepsilon_a(\varepsilon_a\kappa_l-\varepsilon_h\kappa_a)(2\kappa_a+\kappa_l)-(2\varepsilon_a+\varepsilon_h)(\varepsilon_a\kappa_l-\varepsilon_l\kappa_a)\kappa_a}. \tag{A30}$$

This Eq. A30 leads to Eq. 34 in the text.

IV. Derivation of Eq. 40

Substitution of Eqs. 47 and 48 for Eq. 12 to eliminate ε_i and κ_i, and rearrangement give

$$\begin{aligned}&\left\{\left(\frac{\kappa_a}{\kappa_l}+2\right)\varepsilon_l D-3[\varepsilon_h D-\varepsilon_a(D-1)]D+\left(\frac{\kappa_l}{\kappa_a}-1\right)\varepsilon_a D\right\}C^2\\&+\left\{3[2\varepsilon_h D-\varepsilon_a(D-1)]-\left[\left(\frac{\kappa_a}{\kappa_l}+2\right)D+3\right]\varepsilon_l-\left(\frac{\kappa_l}{\kappa_a}-1\right)\varepsilon_a D\right\}C\\&+3(\varepsilon_l-\varepsilon_h)=0.\end{aligned} \tag{A31}$$

This quadratic equation for C can be solved as

$$C=\frac{-Q\pm\sqrt{Q^2-4PR}}{2P}, \tag{A32}$$

where P, Q, and R are given by Eqs. 41, 42, and 43 respectively.

Numerical calculations by use of plausible sets of ε_l, ε_h, κ_l, ε_a, and κ_a revealed that the positive sign in front of the radical sign in Eq. A32 always results in unrealistic negative values for ε_i, κ_i, and Φ. Thus the positive sign was ruled out, and Eq. 40 was adopted.

V. Some Remarks on the Numerical Searching for κ_a-Values Regarding Eq. 45

Prior to the evaluation of roots for $J(\kappa_a)=0$, the substantial behavior of $J(\kappa_a)$ must be made clear. After numerical examination of $J(\kappa_a)$-κ_a diagrams for various sets of phase parameters ε_a, ε_i, κ_a, and κ_i, two types of $J(\kappa_a)$ profiles were found in respect of the relative magnitude among κ_i, κ_l, and κ_a provided that $\kappa_a\neq\kappa_i$ and $\varepsilon_a\kappa_i\neq\varepsilon_i\kappa_a$, the typical diagrams for both types being depicted in Fig. A2. The general profile of $J(\kappa_a)$ against κ_a in a range of $\kappa_a>0$ was simulated approximately by a trinomial for κ_a, and possesses three intersections with the axis of abscissas termed L, M, and N in Fig. A2. In the case of $\kappa_a<\kappa_l<\kappa_i$ (W/O-like) shown in Fig. A2(A), the value of κ_a of physical significance was given by the only one point

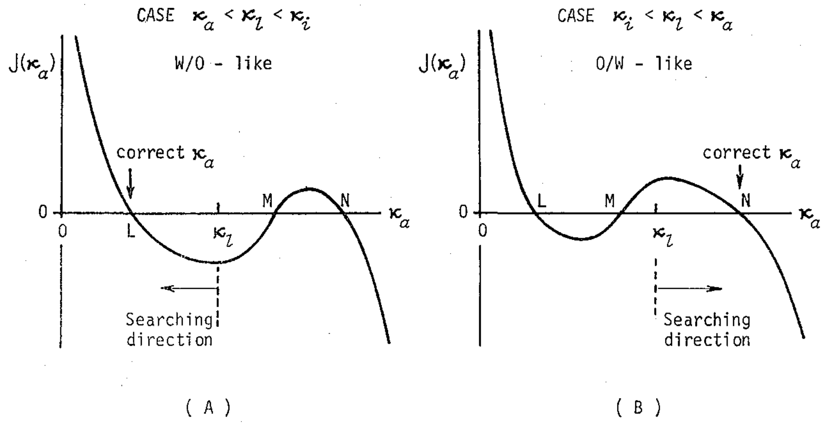

Fig. A2. The brief profiles of the function $J(\kappa_a)$ given by Eq. 45 in a range $\kappa_a > 0$. (A) the case $\kappa_a < \kappa_l < \kappa_i$, (B) the case $\kappa_i < \kappa_l < \kappa_a$. Three points L, M, and N represent the roots of $J(\kappa_a) = 0$.

L located solely lower than the value of κ_l, and other two points *M* and *N* had to be ruled out. In the case of $\kappa_i < \kappa_l < \kappa_a$ (O/W-like) shown in Fig. A2(B), the only one point *N* located solely higher than the value of κ_l showed the value of κ_a of physical significance, and other two points *M* and *L* had to be ruled out. Numerical searching for $J(\kappa_a) = 0$, therefore, can be stated as follows provided that an approximate value of κ_a is known by experiment: The computer-searching should be proceeded from κ_l and towards the lower values of κ_a when $\kappa_a < \kappa_l$. If $\kappa_l < \kappa_a$, then the searching should be proceeded from κ_l and towards the higher values of κ_a.

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