Boundary-element calculations for dielectric relaxation of water-in-oil-in-water emulsions consisting of spherical droplets with a spheroidal core

Abstract Using the boundary-element method, theoretical calculations were made for the complex permittivity of water-in-oil-in-water emulsions consisting of spherical droplets. A spheroidal inner phase was placed at the center of the droplet. To examine the effects of the shape of the inner phase, the axial ratio of the inner phase was changed by keeping its volume unchanged. The results showed that the dielectric relaxation of the emulsions was markedly affected by the shape of the inner phase. As a detailed analysis, effects of external electric fields directed in the mirror plane and those along the rotation axis of the droplets were examined separately. This showed that the relaxation consisted of two kinds of relaxation terms. The first related to the structure of the droplet parallel to the external field and had similar character to the low-frequency relaxation of emulsions of shelled spheres. The second, found in restricted cases, related to the structure perpendicular to the external field, having character similar to the high-frequency relaxation for the shelled spheres.

Keywords Boundary element method · Dielectric relaxation · Interfacial polarization · Emulsion

Introduction

Several dispersed systems show dielectric relaxation due to interfacial polarization in the radio-frequency region [1–13]. Since the dielectric relaxation of this kind depends on electrical and structural properties of the systems, dielectric spectroscopic techniques serve as nondestructive and in situ methods for the analysis of the interior of the dispersed particles, such as aqueous droplets in frozen water-in-oil (w/o) emulsions [2], biological cells [6–11], ion-exchange resins [12], and microcapsules [13].

In conventional theories of the interfacial polarization for emulsions, models of dispersed particles are limited to layered confocal ellipsoids [14, 15] because of mathematical difficulties. Discrepancies between the structure of such simplified models and that of real droplets reduce the utility of dielectric spectroscopic techniques. Recent progress in theoretical studies [16–20] enabled us to make computer-assisted calculations of the dielectric relaxation using realistic models, to which it was difficult to apply conventional analytical methods.

In the present study, the dielectric relaxation of water-in-oil-in-water (w/o/w) emulsions consisting of spherical droplets is calculated with a method [19] using the boundary-element method (BEM). The shape of the inner phase, which was restricted to spherical in conventional theories, is made spheroidal in the present study. Calculations using these models are situated at the first stage of a series of theoretical examinations about the effects of the internal structure of the droplets using nonconventional models, which will be extended to more complicated specimens in the future, such as flocs in flocculated w/o emulsions [21] and biological cells containing plural intracellular organelles [10]. These calculations are expected to provide guidelines for estimating the detailed structure of the droplets.
Models and method of calculation

Models

The models for the droplets in the w/o/w emulsions are shown in Fig. 1. The outer surface of the droplet is spherical and is represented by

\[ x^2 + y^2 + z^2 = 1. \]  

The inner phase has a spheroidal surface given by

\[ \frac{x^2 + y^2}{R_{in}^2} + \frac{z^2}{R_{s}^2} = 1, \]  

where \( R_{in} \) and \( R_s \) are the semi-axes of the spheroid. The inner phase for model S is spherical (\( R_{in} = R_s = 0.7 \)). By forcing the volume to be constant, the inner phase is modified into oblate spheroids in models O1 (\( R_{in} = 0.88 \)) and O2 (\( R_{in} = 0.95 \)) and into prolate ones in models P1 (\( R_{in} = 0.88 \)) and P2 (\( R_{in} = 0.95 \)). The following values were adopted for relative permittivities \( \varepsilon \) and electrical conductivities \( \kappa \) of the phases: \( \varepsilon_i = \varepsilon_a = 80, \kappa_i = \kappa_a = 1 \text{ mS m}^{-1} \), \( \varepsilon_s = 35, \kappa_s = 0 \), where subscripts \( i \), \( a \), and \( s \) denote the inner phase, a dispersing medium, and the shell-phase, respectively. The values of \( \kappa_i \) and \( \kappa_a \) are typical of aqueous electrolyte solutions [22]. The value of \( \varepsilon_s \) is comparable to the relative permittivity of nitrobenzene [23].

Method of calculation

In a previous study [19], we developed a method of calculating the complex permittivity \( \varepsilon^* \) of emulsions with the BEM, where \( \varepsilon^* \) is represented by \( \varepsilon^* = \varepsilon + i \kappa/(i\omega \varepsilon_{0}) \), with \( \varepsilon, \kappa \), and \( i \) an imaginary unit \( i \), angular frequency \( \omega \) represented by \( \omega = 2\pi f \) in terms of frequency, \( f \), and the permittivity of vacuum, \( \varepsilon_0 \). This method is an extension of the analytical methods using Maxwell–Wagner–Sillars-type mixture equations [14, 24, 25], consisting of the following three steps:

1. When a piece of the droplet is placed in a uniform external electric field \( \mathbf{E}_0(E_{0x}, E_{0y}, E_{0z}) \), a dipole moment \( \mathbf{p} \) is induced. Values of the electric potential \( \phi \) due to \( \mathbf{p} \) are calculated by solving Laplace’s equation numerically using the BEM. Details of the calculations are shown in the Appendix.

2. The values of \( \phi \) at a distant point \( r(x, y, z) \) from the droplet, which is placed at the origin of the Cartesian coordinate system, is represented by

\[ \phi = \frac{1}{4\pi\varepsilon_0}\mathbf{p} \cdot \mathbf{r}, \]  

where \( \varepsilon_0 \) is the complex permittivity of the surrounding medium and \( r = (x^2 + y^2 + z^2)^{1/2} \). The induced moment \( \mathbf{p} \) is represented using a polarizability tensor \( \alpha \) of the droplet as \( \mathbf{p} = \alpha \mathbf{E}_0 \). When the 

\[ \phi = \frac{1}{4\pi\varepsilon_0}\alpha \mathbf{E}_0 \cdot \mathbf{r} \]  

droplet has \( D_{33} \) symmetry, as adopted in the present study, \( x \) is the diagonal consisting of the polarizability components \( \alpha_{yy} \) in the mirror plane (xy-plane) and \( z \) along the rotation axis (z-axis). Hence Eq. (3) is modified to

\[ \phi = \frac{1}{4\pi\varepsilon_0}\alpha \mathbf{E}_0 \cdot \mathbf{r}, \]  

where \( \beta_h \) (k = h, z) is the polarization coefficient defined by \( \beta_h = \alpha_{yy}/(\varepsilon_0 \varepsilon_{0}^*) \) using \( \varepsilon_0, \varepsilon_{0}^* \), and the volume of the droplet \( V \).

In this step, values of \( \beta_h \) are obtained from \( \phi \) using Eq. (4).

3. Using a Maxwell–Wagner–Sillars-type mixture equation, a formula for the equivalent complex permittivity \( \varepsilon^* \) of the emulsion is derived from Eq. (4) as

\[ \frac{\varepsilon^* - \varepsilon_{0}^*}{\varepsilon^* + 2\varepsilon_{0}^*} = \frac{P}{9}(2\beta_h + \beta_z), \]  

where \( P \) is the volume fraction of the emulsion. When \( P \ll 1 \), Eq. (5) becomes [26]

\[ \varepsilon_{eq} = \varepsilon_0 + \kappa_{eq}/(i\omega \varepsilon_0) \equiv (\varepsilon^* - \varepsilon_{0}^*)/P = 2\varepsilon_{eq}^* + \varepsilon_{eq}^*, \]  

where

\[ \varepsilon_{eq} = \varepsilon_{eq}^* + \kappa_{eq}/(i\omega \varepsilon_0) \equiv \varepsilon_h \beta_h \epsilon_{0}/3 \]  

The approximate relations, Eqs. (6) and (7), were used in the present study.

The calculations were made at frequencies from 10 to \( 10^8 \) Hz. The calculations of \( \phi \) in step 1 were carried out using the BEM, in which the surfaces of the droplets were divided into isoparametric elements consisting of ten nodes, with cubic shape functions [27] being used in each of the elements. Preliminary examinations showed that at least three significant figures were attained in the calculations of \( \varepsilon_{eq} \) when the surfaces were divided into more than 288 elements. Analytical equations [28] were used in the calculations for model S since it has a structure of a concentric shell sphere.

Results and discussion

Behavior of \( \beta_h \)

The frequency dependence of \( \beta_h \) for model O2 is shown in Fig. 2. As seen from this figure, the behavior of \( \beta_h \) is dependent on the direction of the external field, \( \mathbf{E}_0 \). \( \beta_h \) shows two-step relaxation that includes two relaxation terms \( h1O \) and \( h2O \) at low and high frequencies, respectively, whereas \( \beta_z \) shows one-step relaxation \( z1O \). Similar behavior of \( \beta_h \) was found for model O1. In models P1 and P2, in contrast, \( \beta_h \) and \( \beta_z \) contained one \( (h1P) \) and two \( (z1P \) and \( z2P) \) relaxation terms, respectively. Since \( R_{in} = R_s \) in model S, \( \beta_h = \beta_z \), which contained two relaxation terms, \( 1S \) and \( 2S \), at low and high frequencies, respectively.

Behavior of \( \varepsilon_{eq}^* \)

The frequency dependence of \( \varepsilon_{eq}^* \) for model O2 is shown in Fig. 3. As seen from this figure, the behavior of \( \varepsilon_{eq}^* \) is