# Dielectric Relaxation of Oil-External Microemulsions

## S. I. Chou[†] and D. O. Shah*

Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, Florida 32611 (Received: March 25, 1980; In Final Form: November 12, 1980)

The dielectric properties of oil-external microemulsions consisting of monodisperse spherical droplets of radii from 115 to 175 Å have been studied over a frequency range from 0.5 to 100 MHz. It is evident that there exist two consecutive relaxation processes within this frequency range, each of which has a well-defined average relaxation time with narrow distribution. A model for the dielectric relaxation of oil-external dispersions with thin shells has been proposed by unifying the theory of double-layer polarization, modified to take into account the finite thickness of the double layer, and the triphasic model of interfacial polarization. According to this model, the low-frequency relaxation time is proportional to the square of the radius of dispersed water droplets and the high-frequency relaxation time is proportional to the radius. Both relationships have been established and can be used to determine the surface charge density and the surface conductivity of oil-external microemulsion droplets. However, the magnitude of the dielectric constant cannot be described by the present model or any other model within the framework of Maxwell-Wagner theory. This inconsistency could be due to the formation of dynamic aggregates of microemulsion droplets under Brownian motion. The effect of substituting $H_2O$ brine by $D_2O$ brine has also been studied. It is shown that, while $H_2O$ and $D_2O$ have nearly identical dielectric constants, the dielectric properties of oil-external microemulsions containing $H_2O$ or $D_2O$ brine are distinctly different. It was found that the surface charge density, the dielectric relaxation times, and the dielectric increment of the $H_2O$ system were ca. 2-4 times higher than those of the $D_2O$ system. These observations indicate the importance of hydration effects on interfacial and double-layer polarizations in microemulsions.

## Introduction

The structure of microemulsions has been extensively studied by Schulman and co-workers using a variety of techniques.[1-5] They conclude that the so-called microemulsions are isotropic, clear or translucent dispersions of oil, water, surfactant, and cosurfactant consisting of spherical droplets with droplet size ranging from 200 to 1000 Å.

Since the droplet sizes of microemulsions fall in between those of true molecular solutions and coarse dispersions, their dielectric properties are of particular interest and can be investigated by two approaches. One can extend the Debye theory,[6] which relates the dielectric constant of solutions to the orientation of molecular dipoles, to colloidal dispersions. Such an approach has been applied to biological systems,[7,8] macromolecules,[9] and reverse micelles.[10] Another approach based on Maxwell's macroscopic theory[11] of interfacial polarization of stratified systems was extended by Wagner[12] to dilute dispersions of spherical particles. Modifications of the Maxwell-Wagner theory to include the effects of particle shape, concentration, and surface phenomena have been presented by a number of investigators.[13-27] This approach has been applied to emulsions,[27] latex dispersions,[28,29] porous plug in electrolyte solutions,[30] polyelectrolytes,[31] membranes,[32,33] micelles,[34] and microemulsions.[35-37] To our knowledge, no existing models can satisfactorily describe the dielectric properties of micellar solutions or microemulsions.

In the present study, the dielectric relaxation of oil-external microemulsions containing various amounts of solubilized brine has been investigated. The effect of $H_2O$ vs. $D_2O$ brine in oil-external microemulsions is studied to show the importance of hydration effects on interfacial and double-layer polarization in microemulsions. A model, which combines the theory of interfacial polarization of dispersion with thin shells[26,27] and the theory of double-

layer polarization,[22-25] is presented to interpret the experimental data.

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†Gulf Research and Development Co., P.O. Drawer 2038, Pittsburgh, PA 15230.

## Experimental Section

Single-phase, oil-external microemulsions were prepared from a petroleum sulfonate (TRS 10-410, mol wt = 418, Witco Chemical Co.), isobutyl alcohol, dodecane (99% pure, Chemical Samples Co.), and 1.5% NaCl brine. Deionized, distilled water ($H_2O$) and $D_2O$ (>99.8% deuterium, Stohler Isotope Chemicals) were used to prepare the brine. The microemulsions were prepared by titrating a mixture of surfactant–oil–brine with alcohol to transparency and then adding 0.01–0.05 g more of alcohol per gram of surfactant, such that the alcohol concentration was the same for $H_2O$ and $D_2O$ systems. The brine-to-surfactant ratios were 1.5, 2.0, 2.5, and 3.0 mL/g, and the oil/surfactant ratio was 17 or 20 g/g, such that the specific conductance (at 1000 Hz) was in a range from $10^{-7}$ to $10^{-4}$ mho/cm. For the brine/surfactant ratio of 3.0 mL/g, the alcohol/surfactant ratio of the $H_2O$ system was higher than that of the $D_2O$ system, in order to form single-phase microemulsions for both systems.

Dielectric measurements were made by a Hewlett-Packard 250B RX meter over a frequency range from 0.5 to 100 MHz at 25 ± 1 °C. A variable-distance dielectric cell similar to the one used by Schwan et al.[28] was employed here. The calculation of the dielectric constant and the conductance of the sample from the measured capacitance and resistance has been given in great detail by Sachs et al.[38] and is briefly described below. The measured resistance ($R_p$) and capacitance ($C_p$) were the resolved parallel components of the equivalent impedance ($Z = X$

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(39) One can define the least-squares method by several different criteria, for example, by minimizing the sum of squares error of $\epsilon'$, $|\epsilon' + j\epsilon''|$, $|(\epsilon' + j\epsilon'')^2|$ or $\epsilon''$. A computer program using an iteration method was written to serve this purpose. The first three criteria yield similar results as the magnitude of $\epsilon'$ is at least twice as large as $\epsilon''$. When the accuracy of experimental data is good, such as for systems shown in Figures 1 and 2, the derived parameters (except for $\tau$, of the $D_2O$ systems) using different criteria differ by ~5% while for other systems they differ by ~5–20%. The difficulties involved here are that the accuracies of $\epsilon'$ and $\epsilon''$ vary from system to system and vary with frequencies. The $\epsilon''$ data are more accurate than the $\epsilon'$ data for the $D_2O$ systems while the reverse is true for the $H_2O$ systems (except that at higher frequencies where the accuracies of $\epsilon'$ and $\epsilon''$ are about the same). Therefore, we have chosen the third and fourth criteria to determine the dielectric parameters for the $H_2O$ systems and $D_2O$ systems, respectively.

(40) Equations 21 and 22 can be derived by simplifying eq 296 and 297 in ref 27, under the conditions: $K_m \ll K_s d/R \ll K_p$ and $\epsilon_m \ll \epsilon_p \ll \epsilon_s d/R$. Equation 34 can be similarly derived by simplifying eq 305 in ref 27 under the above-mentioned conditions.

(41) The droplet size of oil-external microemulsions has been determined by ultracentrifugation, quasi-elastic light scattering, and membrane diffusion measurements. The results by different techniques are in excellent agreement, and it was concluded that the systems under study consist of monodisperse, spherical droplets with radii from 115 to 175 Å. Preprints are shown in the Annual Report, Enhanced Oil Recovery Research Program at the University of Florida, 1979.

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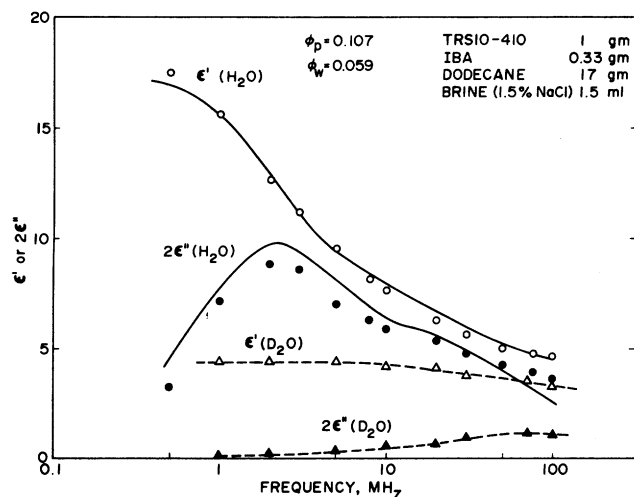(45) C. Tanford, "Physical Chemistry of Macromolecules", Wiley, New York, 1961.

$- j\omega Y$). An elementary network analysis leads to the following expressions for $X$ and $Y$:

$$X = \frac{1/R_p}{1/R_p^2 + \omega^2(C_p - C_T)^2} =$$
$$R^* + \frac{1/R_e}{1/R_e^2 + \omega^2 C_e^2} + \frac{1/R_s}{1/R_s^2 + \omega^2 C_s^2} \quad (1)$$

$$Y = \frac{C_p - C_T}{1/R_p^2 + \omega^2(C_p - C_T)^2} =$$
$$-L^* + \frac{C_e}{1/R_e^2 + \omega^2 C_e^2} + \frac{C_s}{1/R_s^2 + \omega^2 C_s^2} \quad (2)$$

where $C_T$ is the stray capacitance measured as the difference between the measured cell capacitance with air and geometrical air condenser capacitance, $R^*$ and $L^*$ are the series components of the transmission line impedance, $R_e$ and $C_e$ represent the resistance and the capacitance for electrode polarization, $R_s$ and $C_s$ are the sample resistance and capacitance in parallel, and $\omega$ is the angular frequency ($=2\pi f$). The sample capacitance and the conductance ($1/R_s$) vary inversely with the electrode distance ($l$), whereas the transmission line and electrode polarization impedance components are independent of $l$, hence

$$C_s = C_s'/l \qquad R_s = R_s'l \qquad (3)$$

Substituting for $C_s$ and $R_s$ in eq 1 and 2, we have

$$X = R_{tr} + al \qquad Y = -L_{tv} + bl \qquad (4)$$

in which

$$a = \frac{1/R_s'}{(1/R_s')^2 + \omega^2(C_s')^2} \qquad b = \frac{C_s'}{(1/R_s')^2 + \omega^2(C_s')^2} \quad (5)$$

$$R_{tr} = R^* + \frac{1/R_e}{1/R_e^2 + \omega^2 C_e^2}$$

$$L_{tr} = L^* - \frac{C_e}{1/R_e^2 + \omega^2 C_e^2} \qquad (6)$$

The sample capacitance and resistance can be determined by measuring $X$ and $Y$ as a function of $l$. Throughout this study, the linear relationships as demanded by eq 4 were established, and the correlation coefficient of the linear regression was better than 0.99. From the slope of the plots of $X$ and $Y$ vs. $l$, respectively, one can calculate $R_s'$ and $C_s'$ according to eq 7. Thus the transmission line and

$$R_s' = (a^2 + \omega^2 b^2)/a \qquad C_s' = b/(a^2 + \omega^2 b^2) \quad (7)$$

electrode components are eliminated in the calculation of $R_s'$ and $C_s'$. The dielectric constant $\epsilon'$ and the specific conductance $K$ are given by eq 8, where $\epsilon_v$ is the absolute

$$\epsilon' = C_s'/(\epsilon_v A) \qquad K = 1/(R_s'A) \qquad (8)$$

dielectric constant of vacuum ($8.8541 \times 10^{-14}$ f/cm) and $A$ is the electrode area ($4.75$ cm$^2$).

It is interesting to compare the absolute value of the sample impedance $Z_s/l$ with the absolute value of the series impedance $Z_{tr}$ representing the line and electrodes. These parameters are given by eq 9 and 10. Throughout this

$$|Z_s/l| = 1/[(1/R_s')^2 + \omega^2 C_s'^2]^{1/2} \qquad (9)$$

$$|Z_{tr}| = (R_{tr}^2 + \omega^2 L_{tr}^2)^{1/2} \qquad (10)$$

study, $|Z_{tr}|/|Z_s/l|$ was less than $10^{-5}$, indicating that the line and electrode effects were negligible.

The low-frequency limit conductance ($K_l$) was determined by extrapolating the measured conductance to very

**Figure 1.** Dielectric relaxation of oil-external microemulsions from 0.5 to 100 MHz; solubilized brine = 1.5 mL per gram of surfactant. Note that $\phi_w$ is the volume fraction of solubilized brine and $\phi_p$ is the volume fraction of the dispersed phase consisting of all the surfactant, 0.22 g of IBA per gram of surfactant and brine.
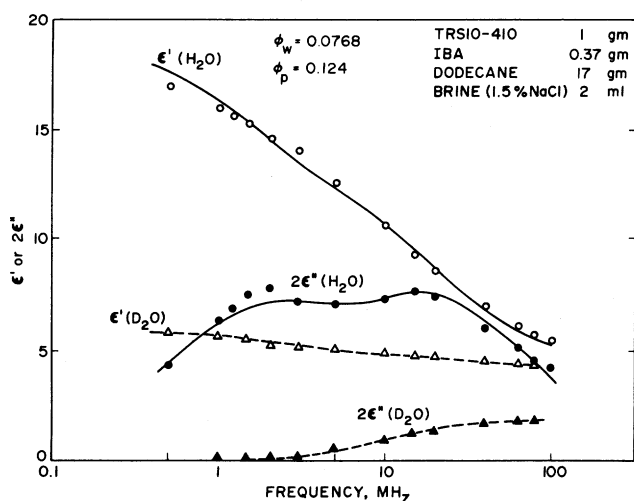


**Figure 2.** Dielectric relaxation of oil-external microemulsions; solubilized brine = 2.0 mL per gram of surfactant.

low frequencies. Except for the $D_2O$ system at low water content, the conductance levels off at a frequency of $\sim 1$ or 2 MHz. The electrical conductance was also measured by a Beckman AC bridge at 1000 Hz, which was close to the extrapolated values within 3–10%. The dielectric loss $\epsilon''$ was calculated by eq 11. The accuracy of the dielectric

$$\epsilon'' = \frac{K - K_1}{\omega \epsilon_v} \qquad (11)$$

constant was estimated to be $\sim 2$–10%, and that of dielectric loss 5–15% depending on the system and frequency.

## Results

The dielectric constant $(\epsilon')$ and the dielectric loss $(\epsilon'')$ of oil-external microemulsions are shown in Figures 1–4 as functions of frequency for various amounts of solubilized brine, respectively. Based on the theory discussed below, these oil-external microemulsions exhibit two consecutive dielectric relaxation processes over a frequency range of 0.5–100 MHz, which are consistent with the experimental data. This behavior is particularly pronounced for microemulsions containing $H_2O$ brine but much less evident for the $D_2O$ systems. The two consecutive relaxation processes are also suggested in the Cole–Cole plot[46] of $\epsilon''$
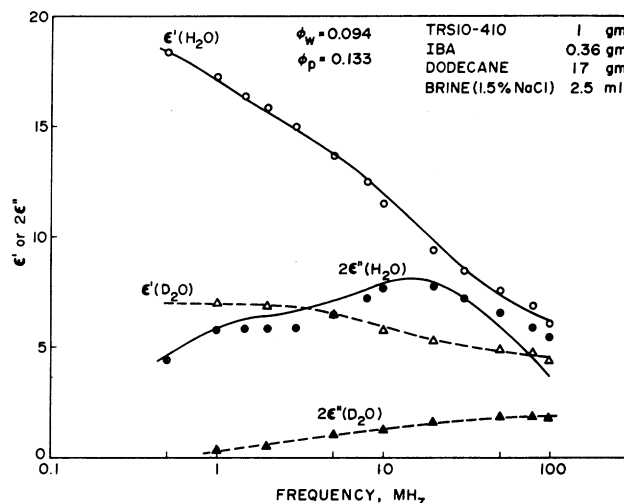


**Figure 3.** Dielectric relaxation of oil-external microemulsions; solubilized brine = 2.5 mL per gram of surfactant.
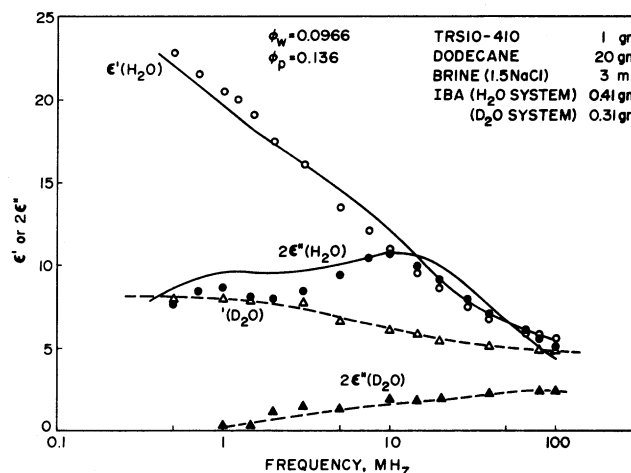


**Figure 4.** Dielectric relaxation of oil-external microemulsions; solubilized brine = 3.0 mL per gram of surfactant. The alcohol concentrations of the $H_2O$ and $D_2O$ systems are slightly different so that both systems can form single-phase microemulsions.
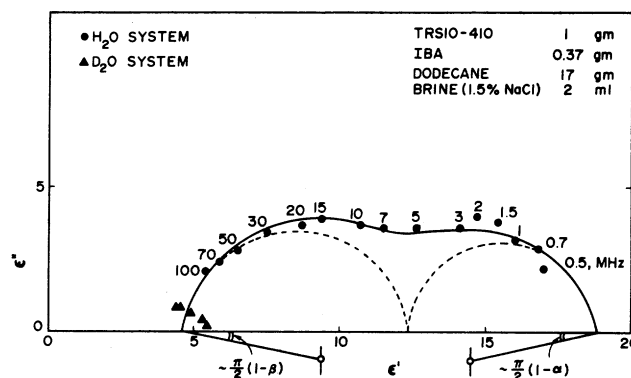


**Figure 5.** Cole–Cole plot of $\epsilon'$ and $\epsilon''$ for the system shown in Figure 2.

vs. $\epsilon'$ in Figure 5. In any event, the dielectric constant and dielectric loss curves in Figures 1–4 are markedly different from those expected for a single relaxation process.[27]

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(46) For a system exhibiting two relaxation mechanisms, the Cole–Cole plot is not very useful in describing the dielectric processes. This is because the two semicircular plots (shown as broken lines in Figure 5) only represent asymptotic relationships between $\epsilon'$ and $\epsilon''$ as the frequency approaches zero or infinity. In general, the data at intermediate frequencies should *not* fall on the semicircles. The solid line in Figure 5 was calculated from eq 14 and 15 by using the appropriate parameters given in Table I.

TABLE I:  Dielectric Relaxation Parameters of Oil-External Microemulsions

| solubilized brine, mL/g of surfactant | $\phi_w$ | $\epsilon_l$ | $\epsilon_i$ | $\epsilon_h$ | $10^{-7}\tau_s$, s | $10^{-9}\tau_2$, s | $\beta$ | $\alpha$ | $K_l$, mho/cm |
|---|---|---|---|---|---|---|---|---|---|
| | | | H$_2$O System | | | | | | |
| 1.5 | 0.059 | 17.7 | 8.4 | 4.1 | 0.80 | 6.5 | 0.97 | 0.87 | $4.0 \times 10^{-6}$ |
| 2.0 | 0.077 | 19.0 | 11.9 | 4.4 | 1.04 | 7.1 | 0.86 | 0.87 | $7.55 \times 10^{-5}$ |
| 2.5 | 0.094 | 20.2 | 13.7 | 4.5 | 1.37 | 8.2 | 0.79 | 0.87 | $9.80 \times 10^{-5}$ |
| 3.0 | 0.097 | 25.8 | 15.7 | 4.5 | 2.1 | 10.5 | 0.83 | 0.85 | $3.25 \times 10^{-5}$ |
| | | | D$_2$O System | | | | | | |
| 1.5 | 0.059 | 4.4 | 4.2 | 3.0 | 0.38 | 2.4 | 0.85 | 0.90 | $1.90 \times 10^{-7}$ |
| 2.0 | 0.077 | 5.7 | 5.4 | 3.2 | 0.43 | 2.7 | 0.78 | 0.83 | $1.26 \times 10^{-7}$ |
| 2.5 | 0.094 | 6.9 | 6.2 | 3.7 | 0.51 | 3.3 | 0.90 | 0.80 | $2.50 \times 10^{-7}$ |
| 3.0 | 0.097 | 8.2 | 7.0 | 4.1 | 0.69 | 3.5 | 0.88 | 0.85 | $1.32 \times 10^{-7}$ |

Although H$_2$O and D$_2$O have nearly identical dielectric constants, the dielectric properties of oil-external microemulsions containing H$_2$O or D$_2$O brine are distinctly different. Qualitatively, the dielectric increment and relaxation times of the H$_2$O systems are much higher than those of the D$_2$O systems at identical compositions. In order to achieve a quantitative understanding of the dielectric phenomena, it is necessary to derive the relaxation times and the low- and high-frequency limits of the dielectric constant as treated below.

The complex dielectric constant $\epsilon^*$ is related to $\epsilon'$ and $\epsilon''$ according to eq 12.[27]  For a system exhibiting two noninteracting relaxations, $\epsilon^*$ can be described by[26,27] eq 13,[26,27] where $\epsilon_l$ and $\epsilon_h$ are the low- and high-frequency

$$\epsilon^* = \epsilon' - j\epsilon'' + \frac{K_l}{j\omega\epsilon_v} \quad (12)$$

$$\epsilon^* = \epsilon_h + \frac{\epsilon_l - \epsilon_i}{1 + (j\omega\tau_s)^\alpha} + \frac{\epsilon_i - \epsilon_h}{1 + (j\omega\tau_2)^\beta} + \frac{K_l}{j\omega\epsilon_v} \quad (13)$$

limits of the dielectric constant, $\epsilon_i$ is the high-frequency limit of the first relaxation as well as the low-frequency limit of the second relaxation, $\tau_s$ and $\tau_2$ are the low- and high-frequency relaxation times, and $1 - \alpha$ and $1 - \beta$ characterize the width of the distribution of each relaxation time. If one compares eq 12 and 13, it can be shown that[27]

$$\epsilon' = \epsilon_h + \frac{(\epsilon_l - \epsilon_i)\left[1 + (\omega\tau_s)^\alpha \cos\left(\frac{\pi}{2}\alpha\right)\right]}{1 + (\omega\tau_s)^{2\alpha} + 2(\omega\tau_s)^\alpha \cos\left(\frac{\pi}{2}\alpha\right)} +$$

$$\frac{(\epsilon_i - \epsilon_h)\left[1 + (\omega\tau_2)^\beta \cos\left(\frac{\pi}{2}\beta\right)\right]}{1 + (\omega\tau_2)^{2\beta} + 2(\omega\tau_2)^\beta \cos\left(\frac{\pi}{2}\beta\right)} \quad (14)$$

$$\epsilon'' = \frac{(\epsilon_l - \epsilon_i)(\omega\tau_s)^\alpha \sin\left(\frac{\pi}{2}\alpha\right)}{1 + (\omega\tau_s)^{2\alpha} + 2(\omega\tau_s)^\alpha \cos\left(\frac{\pi}{2}\alpha\right)} +$$

$$\frac{(\epsilon_i - \epsilon_h)(\omega\tau_2)^\beta \sin\left(\frac{\pi}{2}\beta\right)}{1 + (\omega\tau_2)^{2\beta} + 2(\omega\tau_2)^\beta \cos\left(\frac{\pi}{2}\beta\right)} \quad (15)$$

The experimental data of $\epsilon'$ and $\epsilon''$ were used to fit eq 14 and 15 by the method of least squares[39] to derive the seven parameters: $\epsilon_l$, $\epsilon_i$, $\epsilon_h$, $\tau_s$, $\tau_2$, $\alpha$, and $\beta$. The results are listed in Table I. The $\epsilon'$ and $\epsilon''$ curves shown in Figures 1–4 for the H$_2$O system were calculated by eq 14 and 15 with these parameters. As shown in Figures 1–4, the fitting with

experimental data is in general quite good, but the fitting of $\epsilon''$ at low frequencies is poorer probably because of the lower accuracies of $\epsilon''$ data at low frequencies. The low-frequency relaxation times $\tau_s$ of the D$_2$O systems are only qualitative as the fitting was not very sensitive to the choice of $\tau_s$. The accuracy of other parameters was estimated to be 5–15%. As shown in Table I, the dielectric constant and relaxation times increase with the amount of solubilized brine per gram of surfactant. However, this effect is not equivalent to the effect of increasing the volume fraction of brine ($\phi_w$) in the microemulsions; as in the last two cases in Table I ($\phi_w$ = 0.094 and 0.097), $\phi_w$ values are nearly the same but their dielectric properties differ significantly. The dielectric properties are more closely related to the droplet size in microemulsions, as discussed in the following section.

## Discussion

*Dielectric Relaxation Times.*  The magnitude of the relaxation times can be used to ascertain the mechanism of the relaxation process. The following models are discussed: unmodified Maxwell–Wagner theory of interfacial polarization, surface conductivity, dipole orientation, electrophoretic movement of dispersed particles, triphasic model of interfacial polarization, and double-layer polarization.

According to the Maxwell–Wagner theory[11,12] of interfacial polarization, the dielectric relaxation time is given by eq 16, where $\epsilon_p$, $K_p$, $\epsilon_m$, and $K_m$ are the dielectric con-

$$\tau = \frac{2\epsilon_m + \epsilon_p + \phi(\epsilon_m - \epsilon_p)}{2K_m + K_p + \phi(K_m - K_p)}\, \epsilon_v \quad (16)$$

stant and the specific electrical conductance of the dispersed phase and the medium, respectively, and $\phi$ is the volume fraction of the dispersed phase. Using $\epsilon_m$ = 3, $\epsilon_p$ = 80, $K_m < 10^{-6}$, $K_p$ = 0.023 mho/cm (1.5% NaCl brine), and $\phi \approx 0.1$, we calculated $\tau$ to be $3.0 \times 10^{-10}$ s, which is much smaller than the observed relaxation times ($\sim 10^{-7}$–$10^{-9}$ s), especially for the H$_2$O systems.

O'Konski[20] modified the Maxwell–Wagner theory to include the effect of surface conductivity on the interfacial charge distribution under an applied electric field. His results can be summarized as simply replacing $K_p$ by $K_p + 2\lambda/R$ in the Maxwell–Wagner theory, where $\lambda$ is the surface conductivity and $R$ is the radius of the dispersed particles. For the present system, the relaxation time given by O'Konski's model is nearly identical with that given by the Maxwell–Wagner theory because $K_p \gg 2\lambda/R$ (as a first approximation, take $\lambda = 10^{-9}$ mho and $R \approx 125$ Å).

The orientational relaxation time of a spherical permanent dipole, according to Debye,[6] is given by eq 17,

$$\tau = 4\pi\eta R^3/(kT) \quad (17)$$

where $\eta$ is the viscosity of the medium, $R$ is the radius of the dispersed particle, and $kT$ is the thermal energy term.

For $\eta = 1.42$ cP (dodecane at 25 °C), $R = 125$ Å, the dipole orientation relaxation time was calculated to be $8.5 \times 10^{-6}$ s, which is much higher than the observed relaxation times.

The relaxation time due to electrophoretic movement of the dispersed particle, according to Schwan et al.,[28] is given by eq 18, where $M$ is the molecular weight of dis-

$$\tau = M/(6\pi N_A \eta R) \qquad (18)$$

persed particles, and $N_A$ is Avogadro's number. For $R = 125$ Å and assuming particle density of $\sim 1.0$ g/mL, we calculated $\tau$ to be $2.8 \times 10^{-11}$ s, which is obviously too small.

Since eq 13, in general, can be used to describe the dielectric relaxation of dispersions with shells[21,26,27] (namely, triphasic model of interfacial polarization), it appears relevant to derive the relaxation times according to this model. This model essentially considers the particle (with complex conductance $K_p^*$) and its shell (with complex conductance $K_s^*$) as an equivalent particle (with complex conductance $Y^*$). When one notes that the volume fraction of a spherical particle in the total volume of the particle and its shell is $[(R/(R+d)]^3$, the complex conductance of the equivalent particle is given by eq 19,

$$\frac{Y^* - K_s^*}{Y^* + 2K_s^*} = \left(\frac{R}{R+d}\right)^3 \frac{K_p^* - K_s^*}{K_p^* + 2K_s^*} \qquad (19)$$

where $R$ is the radius of the particle and $d$ is the thickness of the shell. Similarly, the complex conductance of the dispersion $K^*$ is given by eq 20,[12] where $K_m^*$ is the complex

$$\frac{K^* - K_m^*}{K^* + 2K_m^*} = \phi \frac{Y^* - K_m^*}{Y^* + 2K_m^*} \qquad (20)$$

conductance of the dispersion medium. The general solution of eq 19 and 20 in accordance with eq 13 has been described in detail by Pauly and Schwan[26] and by Hanai.[27] In order to have a better understanding of the physical meaning, it is appropriate to derive approximate expressions for the relaxation times. As it can be verified later, the apparent dielectric constant of the shell phase is usually very large. Under this condition and for oil-external dispersions ($K_m \ll K_s$, $K_m \ll K_p$), it can be shown that[40]

$$\tau_s \approx (\epsilon_s/K_s) \, \epsilon_v \qquad (21)$$

$$\tau_2 \approx \frac{\epsilon_p + 2(d/R)\epsilon_s}{K_p + 4(d/R)K_s} \, \epsilon_v \qquad (22)$$

where $\tau_s$ and $\tau_2$ are the low- and high-frequency relaxation times, respectively, and $\epsilon_s$ and $K_s$ are the apparent dielectric constant and the conductance of the shell phase, respectively. The physical meaning, as well as the magnitude, of $\tau_s$ depends on the nature of the shell phase. In the present system, one can consider the shell phase as either the electrical double layer inside the water droplets or the interfacial surfactant/alcohol films. In the latter case, $\tau_s$ would be independent of the size of water droplets or the type of brine ($H_2O$ or $D_2O$), which is obviously incorrect. Therefore we consider the shell phase as the electrical double layer inside the water droplets and have applied the theory of double-layer polarization to interpret $\epsilon_s$ and $K_s$ as shown below.

The theory of double-layer polarization[22-25] essentially introduces new boundary conditions to the Maxwell–Wagner theory by taking into account the electromigration flux and the diffusion currents of counterions inside and across the double layer. Since the thickness of the double layer was assumed to be infinitely small, the theory is valid for $\kappa R \gg 1$, where $\kappa^{-1}$ is the Debye length. It seems more

appropriate to apply the treatment of Schwarz[22] here which is based on the concept of bound ions; i.e., the diffusion of counterions across the double layer is neglected. Under this circumstance, Schwarz derived the complex surface conductivity as

$$\lambda = \frac{j\omega\tau_s\lambda_0}{1 + j\omega\tau_s} \qquad (23)$$

where $\lambda_0$ is the high-frequency limit of surface conductivity and $\tau_s$ is the relaxation time related to the diffusion of counterions in the double layer and is given by[22]

$$\tau_s = e_0^2\sigma_0 R^2/(2KT\lambda_0) \qquad (24)$$

where $e_0$ is the charge of one electron and $\sigma_0$ is the surface charge density. In order to be consistent with the triphasic model in which the thickness of the shell phase is $d$, eq 23 for the surface conductivity should be replaced by an expression for surface conductance $K_s^*$, given by

$$K_s^* = \frac{j\omega\tau_s\lambda_0/d}{1 + j\omega\tau_s} \qquad (25)$$

The complex surface dielectric constant $\epsilon_s^*$ is related to $K_s^*$ by

$$\epsilon_s^* \equiv K_s^*/(j\omega\epsilon_v) \qquad (26)$$

hence

$$\epsilon_s^* = \frac{\lambda_0\tau_s/(\epsilon_v d)}{1 + j\omega\tau_s} \qquad (27)$$

Equations 25 and 27 for the complex surface conductance and the dielectric constant can be realized as the shell phase (double layer) undergoing a Debye-type single relaxation[27] in which

$$K_s^* = K_{sl} + \frac{j\omega\tau_s(K_{sh} - K_{sl})}{1 + j\omega\tau_s} + j\omega\epsilon_{sh}\epsilon_v \qquad (28)$$

$$\epsilon_s^* = \epsilon_{sh} + \frac{\epsilon_{sl} - \epsilon_{sh}}{1 + j\omega\tau_s} \qquad (29)$$

where $K_{sl}$, $K_{sh}$, $\epsilon_{sl}$, and $\epsilon_{sh}$ are the low- and high-frequency limits of surface conductance and the dielectric constant, respectively. If one compares eq 25 and 27-29, it follows that $\epsilon_{sh} = K_{sl} = 0$ and

$$K_s \equiv K_{sh} = \lambda_0/d \qquad (30)$$

$$\epsilon_s \equiv \epsilon_{sl} = \lambda_0\tau_s/(d\epsilon_v) = K_s\tau_s/\epsilon_v \qquad (31)$$

Noting that eq 31 is identical with eq 21, one sees that the polarization of the double layer of small but finite thickness is consistent with the triphasic model of interfacial polarization when the shell phase is taken as the electrical double layer. Substituting eq 24, 30, and 31 into eq 22, we further derive an expression for the high-frequency relaxation time $\tau_2$ as given by

$$\tau_2 \approx \frac{\epsilon_p + \dfrac{e_0^2\sigma_0 R}{kT\epsilon_v}}{K_p + \dfrac{4\lambda_0}{R}} \, \epsilon_v \qquad (32)$$

For the present system $K_p \gg 4\lambda_0/R$, which can be verified later, $\tau_2$ is further simplified to (neglecting the term $4\lambda_0/R$ in eq 32)

$$\tau_2 \approx \frac{\epsilon_p}{K_p}\epsilon_v + \frac{e_0^2 R\sigma_0}{kTK_p} \qquad (33)$$
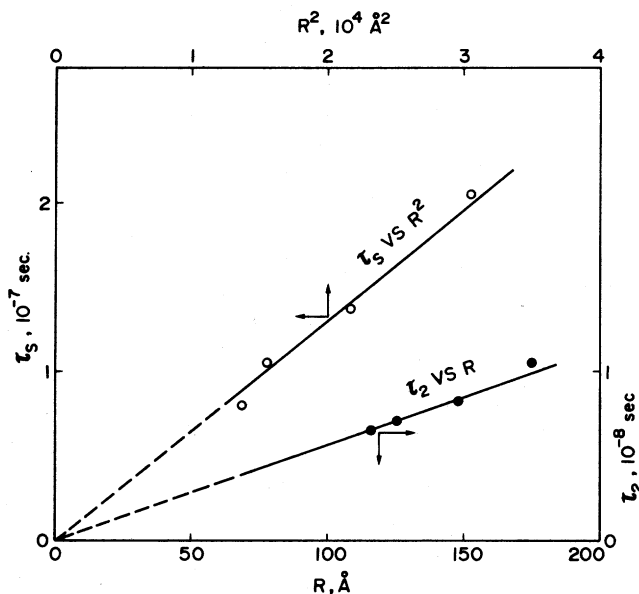
According to eq 24 and 33, the low-frequency relaxation

**Figure 6.** Correlations of the low-frequency relaxation time $\tau_s$ with the square of the radius of water droplets ($R^2$) in microemulsions, and the high-frequency relaxation $\tau_2$ with the radius ($R$).

time is proportional to $R^2$ while the high-frequency relaxation time is proportional to $R$. When the droplet size of microemulsion droplets has been determined independently,[41] these relationships can be verified as shown in Figure 6 (for the $H_2O$ system). Both lines pass through the origin as expected, because the first term in the right-hand side of eq 33 is much smaller than the second term.

It is possible to calculate the surface charge density $\sigma_0$ and the surface conductivity $\lambda_0$ from the measured dielectric relaxation times by using eq 24 and 33. For the $H_2O$ system, $\sigma_0$ was calculated to be $2.1 \times 10^{13}$ cm$^{-2}$ and $\lambda_0$ to be $0.95 \times 10^{-9}$ mho. For a surface area per surfactant molecule of 50 or 100 Å$^2$, the degree of ionization of interfacial surfactant molecules in the $H_2O$ systems would be 10.5% or 21%, respectively. Similarly, $\sigma_0$ of the $D_2O$ system was found to be $6.9 \times 10^{12}$ cm$^{-2}$, and $\lambda_0 \sim 0.86 \times 10^{-9}$ mho. Since $H_2O$ and $D_2O$ are chemically similar, these results indicate the importance of hydration on surface phenomena and double-layer polarization. We have found in another study[42] that the $H_2O$ system is more hydrophilic than the $D_2O$ system in relation to the formation of middle-phase microemulsions, coacervation of aqueous surfactant solution, and surfactant partitioning in oil and brine. These observations are consistent with the present finding where the surface charge density of the $H_2O$ system is higher than that of the $D_2O$ system.

*Dielectric Increments.* The low-frequency limit of the dielectric constant can be derived from the general solutions of eq 19 and 20. It can be shown[40] that for oil-external dispersions ($K_p \gg K_m$, $K_s \gg K_m$)

$$\epsilon_1 = \epsilon_m \frac{1 + 2\phi}{1 - \phi} + \frac{9\phi}{(1 - \phi)^2}\left(\frac{K_m}{K_p}\right)^2\left(\epsilon_p + 2\frac{d}{R}\epsilon_s\right) \quad (34)$$

Equation 34 differs from the unmodified Maxwell–Wagner

theory only in the last term where $\epsilon_p + 2d\epsilon_s/R$ is replaced for $\epsilon_p$. According to eq 34, the dielectric constant of oil-external dispersions should always be small because $(K_m/K_p)^2$ is extremely small even though the term $2d\epsilon_s/R$ can be very large. For $K_p = 0.023$, $K_m \leq 10^{-6}$ mho/cm, $\phi \approx 0.1$, and $2d\epsilon_s/R \approx 2 \times 10^4$, the second term on the right-hand side of eq 34 is negligibly small. Consequently, the calculated $\epsilon_1$ is nearly identical with that by the unmodified Maxwell–Wagner theory ($\sim 3.5$–4.5) and much smaller than the experimental values (see Table I). The reason for this puzzling inconsistency, namely, the excellent agreement of dielectric relaxation times and the lack of fit of the dielectric constant, is still not clear. It was suspected that the mutual polarization of neighboring droplets might be one of the factors. However, analysis of the theory of Günther and Heinricn[43] for multiple moments shows that the increase of the dielectric constant due to mutual polarization is negligibly small for $\phi < 0.2$. A more probable factor may be the aggregation of microemulsion droplets due to the lack of double-layer repulsions.[44] We have found that, for the present system under study, the light scattering second virial coefficient is near zero,[41] indicating the formation of dynamic (temporary) aggregates[45] of microemulsion droplets. In general, the effect of particle aggregation on the increase of the dielectric constant is more pronounced when the ratio of the dielectric constant of the internal phase to that of the external phase is larger.[27] Since the surface charge density and hence the apparent dielectric constant of the solubilized brine is higher in the $H_2O$ system than those in the $D_2O$ system, the dielectric constant of oil-external microemulsions containing $H_2O$ brine is also higher. On the other hand, the drastic difference between $H_2O$ and $D_2O$ containing microemulsions in their dielectric properties may lead one to interpret the data by Debye's theory of permanent dipoles. However, as we have shown that the dipole orientation relaxation time has an order of magnitude of $10^{-6}$ s, the dielectric process occurring in the MHz range is due solely to the polarizability which in essence is of ionic origin.