Dielectric Properties of Water-liquid Paraffin Emulsion Systems at the Microwave Frequency of 9.4 GHz

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The state of water contained in emulsions, particularly in o/w emulsions, was studied as a model of water orientation at the peripheries of biomembranes. Dielectric measurements made at microwave frequency on emulsions containing water and liquid paraffin in various ratios with emulsifiers revealed that the o/w emulsions possessed considerably reduced dielectric loss as compared with theoretical values obtained in accordance with the Maxwell-Wagner model, while the dielectric properties of w/o emulsion were in good agreement with the theoretically expected values. The observations seem to be explained by assuming changes in the state of water in the oil-water interfacial layer in o/w emulsions. The preparation of stable emulsions for use in this study is also discussed.

There has been interest in dispersion systems in various industrial fields such as foods, cosmetics, medicines, chemicals, agricultural agents, and polymers. A variety of investigations on emulsions have hitherto been carried out from both practical and theoretical viewpoints. In our previous papers on the state of water in microbiological cells[1] and on the permeability properties bilayer lipid membranes,[2] the structure of water bound to or situated at the membrane peripheries was shown to be important inliving organisms. In the present work we attempt, therefore, to deal with the water contained in emulsions as a model of the bound or peripheral water mentioned above.

In connection with these studies on the behavior of water, the dielectric properties provide an effective indicator of the molecular state of water molecules present in the system. Measurements at microwave frequency appear to be advantageous for this purpose because the dielectric dispersion of bulk water occurs in the microwave frequency range and other coexisting organic molecules have their dispersion ranges at far lower frequencies.

The present paper deals with the preparation of stable emulsions of both w/o and o/w types. The dielectric behavior of these emulsions at 9.4 GHz, and in particular some features of the water phase in o/w emulsions were discussed on the basis of Maxwell-Wagner's dispersion theory.

MATERIALS AND METHODS

Both o/w and w/o types of emulsion containing liquid paraffin in various ratios to water were studied to find the best conditions for preparation using the smallest possible amount of emulsifiers. Studies were made in connection with the types, HLB values and concentrations of the emulsifiers, and the preparative procedures for obtaining stable emulsions. Dielectric measurements were made on these stable emulsions at a microwave frequency.

Preparation of emulsion. Both types of emulsion were prepared as follows. A constant amount of liquid paraffin containing various amounts of an emulsifier mixture was heated up to 80°C and gradually added, with violent agitation, to a predetermined amount of water kept at 82°C. After addition of the water, the mixture was allowed to cool to 35°C with agitation. Sometimes phase inversion was observed during the cooling period. Finally, the precise ratio of oil to water was adjusted by adding a suitable amount of water.

The stability of the emulsion was estimated as usual by standing overnight, followed by inspection for deemulsification of the sample.

The type of emulsion (o/w or w/o) was determined by microscopic observation of emulsion stained with

a water-soluble (methyl orange) or an oil-soluble dye (sudan III) and also by inspection of the features observed when an aliquot of the emulsion was added dropwise into a large amount of water.

Emulsifier. Emulsifiers used were sorbitan-fatty acid esters and their polyoxyethylated derivatives commercially available under the trade name of "Span X" and "Tween X," where "X" indicates the type and number of acyl groups in the fatty acid. Those used were Span 60 (HLB: 4.7), Span 65 (HLB: 2.1), Span 80 (HLB: 4.3); Tween 60 (HLB: 14.9), and Tween 80 (HLB: 15.0). Two of them could be mixed in such a way that the resultant mixture has the desired HLB value. The HLB values examined ranged between 3.0 and 7.0 for w/o type emulsions and between 8.0 and 14.0 for o/w emulsions at 0.5 intervals.

Measurement of dielectric constant. At the microwave frequency of 9.419 GHz, the dielectric constant ε' (real part of a complex dielectric constant) and the dielectric loss ε'' (imaginary part of the same) were measured at 25°C by a standing wave method[1,4] using a cell 0.411 cm in thickness. The same circuit as in our previous work[1] was used and all the microwave components were obtained from Shimada Physical and Chemical Industrial Company, Ltd., Tokyo. The circuit consisted of a klystron power supply (Type 8K030), a klystron mount (2K25, Type 7K350), a standing wave amplifier (Type 3E01), a magic tee, a standing wave indicator, and several variable resistive attenuators. To calculate ε' and ε'' from the amplitude and phase difference of the transmitted wave, the following method of Harris and O'Konski[4] was employed:

$$C \cdot \exp(jc) = \frac{\exp[(k_0-k)d]}{1-(1/4)(1-k/k_0)(1-k_0/k)[1-\exp(-2kd)]}$$

where

$$c = (4\pi/\lambda_1)(y-y_0)$$
$$C = [(\rho_0-1)/(\rho_0+1)][(\rho-1)/(\rho+1)] \quad C<D<1$$
$$= [(\rho_0-1)/(\rho_0+1)][(\rho+1)/(\rho-1)] \quad D<C<1$$
$$= [(\rho_0+1)/(\rho_0-1)][\rho-1)/(\rho+1)] \quad C<D<1$$
$$k_0 = 2\pi j/\lambda_1$$

$C(D)$ and c are the amplitude ratio and the phase shift of the transmitted (reference) wave as referred to the incident wave, λ_1 the wavelength in the empty guide, k the propagation constant, d the length of the sample cuvette, ρ the voltage standing wave ratio, y the position of minimum amplitude in the standing wave, and ρ_0 and y_0 the values of ρ and y with the cuvette empty, respectively. The relationship between k and the complex dielectric constant, $\varepsilon = \varepsilon'-j\varepsilon''$, is given by

$$\varepsilon^* = \frac{(\lambda_1/\lambda_c)^2-(k\lambda_1/2\pi)^2}{(\lambda_1/\lambda_c)+1}$$

where λ_c is the cut-off wavelength for the wave guide.

The numerical values of C and $y-y_0$ were computed from these equations for various sets of ε' and ε'' and tabulated in a number of graphs. The complex dielectric constant of the samples examined was found on the graph by interpolation using the experimental values of C and $y-y_0$. The computation for the graphs was carried out on an OKITAK 5090 computer at the University of Tokyo Data Processing Center.

RESULTS

Preparation of stable emulsion

From the results of a number of combinations of the emulsifiers mentioned above, the most suitable HLB value for obtaining stable w/o emulsions was found to be about 5.0, and that for obtaining stable o/w emulsions to be about 10.0. The stability of the emulsion did not appear to be appreciably affected by the type of emulsifier used. The stable emulsions thus prepared remained unseparated for several days or more after their preparation. These observations are similar to the results of Titus *et al.*[5] who investigated the stability of milk fat-water systems containing various single or binary emulsifier mixtures.

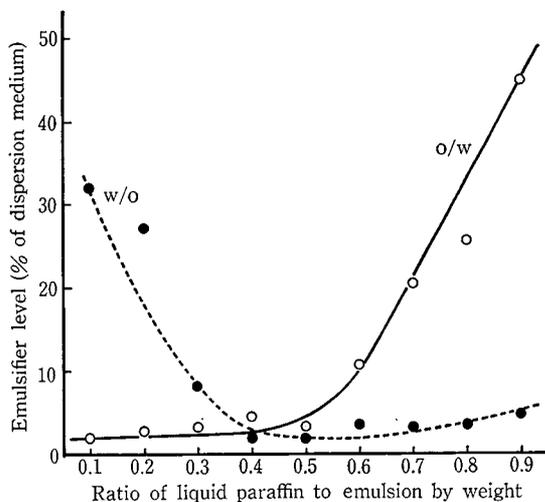Generally, in either type of emulsion, emul-

FIG. 1. Smallest Concentration of Emulsifier Required for Stable Emulsion.

Open circles: o/w emulsion (HLB; 10.0).
Closed circles: w/o emulsion (HLB; 5.0).
The concentration is shown as a percentage by weight of the dispersion medium.

sions composed of about equal amounts of oil and water by weight are the most stable, and moving the ratio away from 5:5 tends to make the emulsion unstable. Thus, the ratio of emulsifier mixture to liquid paraffin necessary for obtaining stable emulsions of unequal composition becomes higher with departure from the ratio of 5:5. Figure 1 illustrates the features mentioned above, where the concentration of the emulsifier in the dispersing medium is plotted against the ratio of oil to water.

Dielectric measurements

The values of the dielectric constant ε' and dielectric loss ε'' of w/o and o/w emulsions containing oil and water in various ratios are shown in Figs. 2 and 3, respectively. ε' and ε'' are the real and imaginary parts of the complex dielectric constant ε^* ($=\varepsilon'-j\varepsilon''$). Throughout the present study, the corrections for ε'' due to direct current conductivity given by Harris and O'Konski[6] were not used, since the emulsions examined were found to possess electric conductivities low enough to make such corrections unnecessary. Scattering of experimental data in these figures seems to be due to the inevitable partial formation of a
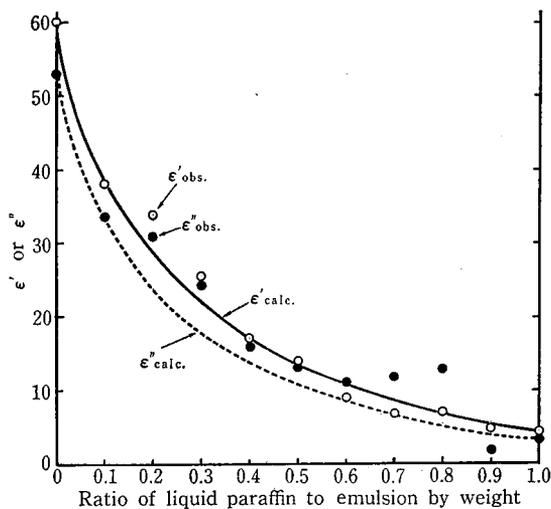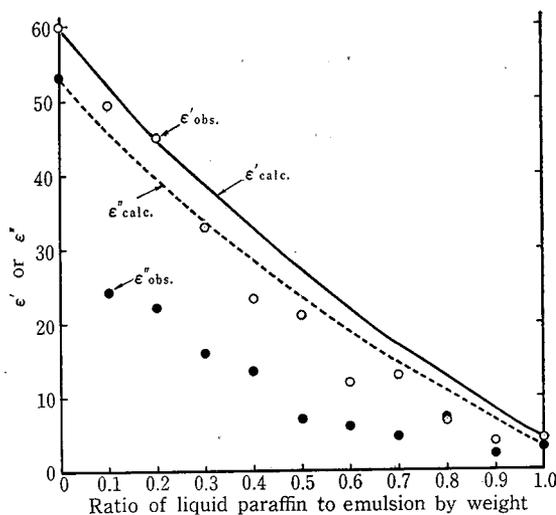

FIG. 3. Dielectric Properties of o/w Emulsion.

Open circles: observed dielectric constant, ε'.
Closed circles: observed dielectric loss, ε''.
Solid line: dielectric constant calculated after the Maxwell-Wagner equation.
Dotted line: dielectric loss calculated after the Maxwell-Wagner equation.

complex emulsion.

In either type of emulsion (w/o or o/w), the values of ε' and ε'' decrease simply from those of bulk water (60 and 53, respectively) to those of liquid paraffin (4.5 and 3.5, respectively). Furthermore, the o/w emulsion is found to have a higher ε' and a considerably lower ε'' compared with w/o emulsion of the same composition.

Figures 2 and 3 include values calculated according to the following simple Maxwell-Wagner equation,[3],[7~12]

$$\varepsilon = \varepsilon_1 \frac{2\varepsilon_1+\varepsilon_2-2p(\varepsilon_1-\varepsilon_2)}{2\varepsilon_1+\varepsilon_2-p(\varepsilon_1-\varepsilon_2)}$$

where ε_1 and ε_2 represent the complex dielectric constants of the dispersion medium and the disperse phase, respectively, and p represents the volume fraction of the disperse phase.

As seen from these figures, the observed values of ε' and ε'' are in fair agreement with those calculated in w/o emulsions, while the observed values, particularly those for ε'', are obviously lower than the calculated ones in o/w emulsions.

In this connection, ε'' was plotted against

FIG. 2. Dielectric Properties of w/o Emulsion.

Open circles: observed dielectric constant, ε'.
Closed circles: observed dielectric loss, ε''.
Solid line: ε' calculated after the Maxwell-Wagner equation
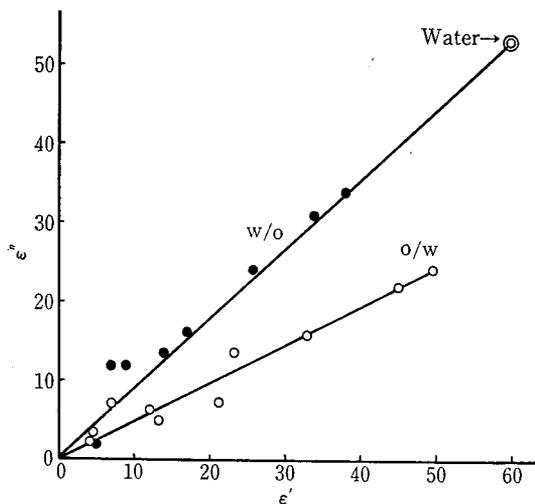Dotted line: ε'' calculated after the Maxwell-Wagner equation.

Fig. 4. Dielectric Loss Plotted against Dielectric Constant.

Open circles: o/w emulsion.
Closed circles: w/o emulsion.
Double circle: pure water.

ε' on a two-dimensional complex space (a "vector" expression) in Fig. 4. As seen in the figure, there are two different groups of the vector, one for w/o emulsions and the other for o/w emulsions. It is found that the vector group of w/o emulsions coincides in its angle with the vector of bulk water, as well as the calculated values for the w/o emulsions, while the group of o/w emulsions has a smaller slope.

DISCUSSION

Since the slopes in Fig. 4 give tan δ and are considered to indicate the state of dipoles contained in this heterogeneous system, it may be suggested that the state of water in the w/o emulsion is the same as or closely similar to that in bulk water, while the state of water in the o/w emulsion should be considerably different from that in bulk water. The fact that the vector of the o/w emulsion possesses similar length and smaller slope compared with the corresponding vector of the w/o emulsion suggests readier rotatability and hence a more loosely arranged structure of water molecules involved in the former type of emulsion.
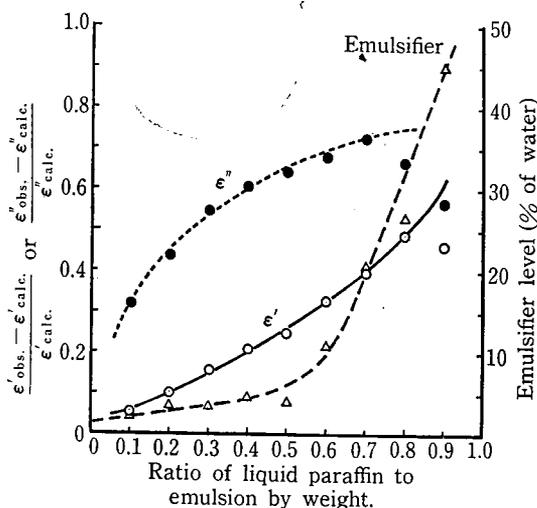

Fig. 5. Relationship between Deviation of Dielectric Constants from the Calculated Value for o/w Emulsion and Emulsifier Content (on the basis of contained water).

Open circles: deviation of ε', $|\varepsilon'_{obs.} - \varepsilon'_{calc.}|/\varepsilon'_{calc.}$
Closed circles: deviation of ε'', $|\varepsilon''_{obs.} - \varepsilon''_{calc.}|/\varepsilon''_{calc.}$
Triangles: emulsifier level (% of water).

In Fig. 5 the deviation of the observed values from those calculated for ε' and ε'' is plotted against the oil-water ratio of o/w emulsions. The concentration of emulsifier (on the basis of water, by weight) is also plotted against the same ratio. It is seen that the deviations increase with emulsifier content. A similar tendency appeared when other proposed equations (e.g., Hanai's equation)[13] were employed. This indicates the possibility that the deviations may arise from the addition of emulsifier.

In this connection, similar dielectric measurements were also carried out with aqueous solutions of the emulsifier used in the present study. Solutions containing 2~20% of emulsifier (HLB=10.0 and 5.0) gave $\varepsilon'=$ 57–63 and $\varepsilon''=$9–10.5. It is clear that, as compared with bulk water, the emulsifier solution has a similar value of ε' and a considerably lower value of ε'', suggesting a remarkable change in the structure of water. In the solutions examined, the emulsifiers aggregate into micelles and thus the extended water-micelle interface appears to be one of the factors responsible for the depression of

ε'' mentioned above.*

No discrepancy between the observed and theoretical values for ε' and ε'' can be seen in the results of Hanai et al.,[13] who investigated a series of emulsions composed of carbon tetrachloride and water in the presence of emulsifier (Tween 20+Span 20) at frequencies ranging from 20 Hz to 5 MHz. Since the frequencies employed by them were far lower than the microwave frequency used in the present work, the inconsistency between these two studies may be ascribed to the existence of dielectric dispersion of water around the microwave frequency used.

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