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Dielectric Studies on Emulsion of Water in Hydrophobic Colloidal Silica–Oil Gel. II

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Dielectric relaxation due to the interfacial polarization of emulsions of water in a hydrophobic colloidal silica–oil gel without any surfactant (denoted as W/(S·O) emulsion, hereinafter) was investigated over a wide range of volume fraction of the dispersed aqueous phase having various electric conductivity values at frequencies ranging from 10 kHz to 3 MHz.

The observed values of the limiting electric conductivities at high frequencies, κ_h , of W/(S·O) emulsion ($\epsilon_{p3} = 78.32$, $\kappa_{p3} = 20.09 \times 10^{-6}$ S/cm) are compared with the values predicted by Wagner's theory [K. W. Wagner, *Arch. Elektrotech.* (Berlin), **2**, 371 (1914)]. The observed values for the case of finely dispersed particles were a little larger than the theoretical values. The values of limiting electric conductivities at low frequencies, κ_l , could not be obtained because they were too small to be determined by the present apparatus. The observed values of the relaxation frequency, f_0 , of the W/(S·O) emulsion showed a good agreement with Wagner's theoretical curve regardless of the dispersed particle size. In W/(S·O) emulsions containing two kinds of dispersed particles having different electric conductivities, the parameter, α , for the distribution of relaxation frequencies as determined from complex plane plots (Cole–Cole plots) became larger than zero, even though the particles were homogeneously dispersed. From the present and previous studies [H. Kaneko and S. Hirota, *Chem. Pharm. Bull.*, **31**, 5, 1445 (1983)], it is considered that new dielectrics are formed by particle aggregation, and the new dielectrics produce a dielectric anomaly at the interface layer of the aggregated particles.

Keywords—interfacial polarization; dielectric relaxation; dielectric measurement; colloid-chemical stability; aggregation; dielectric anomaly; relaxation frequency; w/o emulsion

In the previous study,¹⁾ it was found that dielectric anomaly, *i.e.* deviation between the observed and theoretical limiting dielectric constants at low frequencies, ϵ_l , is related to dispersed particle aggregation, and also that the degree of dielectric anomaly is related to that of particle aggregation on the basis of microscopic observation. From this point of view, it should be possible to make a quantitative evaluation of the colloid-chemical stability of w/o emulsion in terms of particle aggregation by means of dielectric measurement.

Complex plane plots of dielectric constants, ϵ , and dielectric loss factors, γ , of practical w/o emulsion gave a circular arc. The dielectric relaxation of w/o emulsion can be represented as a function of frequency f in the form

$$\varepsilon^* = \varepsilon - j\gamma = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + (jf/f_0)^{1-\alpha}} \quad (0 < \alpha < 1)$$

where ε_h and ε_l are the limiting values of ε at high and low frequencies, respectively, f_0 is the relaxation frequency, α is a parameter of the distribution of relaxation frequencies and $j = \sqrt{-1}$.³⁾ The dielectric parameter, α , of a practical w/o emulsion takes a value between 0 and 1 in most cases.⁴⁾ However, it has so far not been elucidated why this is so. The purpose of the present study is to answer the above question and to investigate the dielectric properties of dispersions of W/(S·O) emulsions containing two kinds of dispersed particles whose electric conductivities are different from each other.

Theoretical

List of Symbols

- ε^* : complex dielectric constant
- ε : dielectric constant
- ε_p : dielectric constant of dispersed phase
- ε_m : dielectric constant of continuous medium
- ε_h : limiting value of ε at high frequency
- ε_l : limiting value of ε at low frequency
- κ^* : complex electric conductivity
- κ : electric conductivity (Ω/cm)
- κ_p : electric conductivity of dispersed phase (Ω/cm)
- κ_m : electric conductivity of continuous medium (Ω/cm)
- κ_h : limiting value of κ at high frequency (Ω/cm)
- κ_l : limiting value of κ at low frequency (Ω/cm)
- Φ : volume fraction of dispersed phase
- f : experimental frequency (Hz)
- f_0 : relaxation frequency (Hz)
- τ : relaxation time (second)

$$\tau = \frac{1}{2\pi f_0}$$

ω : angular frequency

$$\omega = 2\pi f$$

γ : imaginary part of the complex dielectric constant

$$\gamma = \frac{\kappa}{\omega \epsilon_v} = \frac{\kappa}{f} \times 1.7975 \times 10^{12}$$

$$(\epsilon_v = 8.8541 \times 10^{-14} \text{ F/cm})$$

j : imaginary unit $\sqrt{-1}$

α : parameter of the distribution of relaxation frequencies, determined from complex plane plots

The theoretical expressions are as follows,

1. Wagner's Theory (in the Case of w/o Type Emulsion)¹⁾

$$\varepsilon^* = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + j\omega\tau} + \frac{\kappa_l}{j\omega\epsilon_v} \quad (1)$$

$$\varepsilon = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + (\omega\tau)^2} \quad (2)$$

$$\gamma = \frac{\kappa_l}{\omega\epsilon_v} + \frac{(\varepsilon_l - \varepsilon_h)\omega\tau}{1 + (\omega\tau)^2} \quad (3)$$

$$\varepsilon_h = \varepsilon_m \frac{\varepsilon_p + 2\varepsilon_m + 2\Phi(\varepsilon_p - \varepsilon_m)}{\varepsilon_p + 2\varepsilon_m - \Phi(\varepsilon_p - \varepsilon_m)} \quad (4)$$

$$\varepsilon_l = \varepsilon_m \frac{1 + 2\Phi}{1 - \Phi} \quad (5)$$

$$\kappa^* = \kappa_l + \frac{j\omega\tau(\kappa_h - \kappa_l)}{1 + j\omega\tau} + j\omega\epsilon_v\varepsilon_h \quad (6)$$

$$\kappa = \kappa_l + \frac{(\omega\tau)^2(\kappa_h - \kappa_l)}{1 + (\omega\tau)^2} \quad (7)$$

$$\kappa_h = \kappa_p \left[\frac{3\varepsilon_m}{\varepsilon_p + 2\varepsilon_m - \Phi(\varepsilon_p - \varepsilon_m)} \right]^2 \Phi \quad (8)$$

$$\kappa_l = \kappa_m \frac{1 + 2\Phi}{1 - \Phi} \quad (9)$$

and

$$f_0 = \frac{\kappa_p(1 - \Phi)}{\varepsilon_p + 2\varepsilon_m - \Phi(\varepsilon_p - \varepsilon_m)} \times 1.7975 \times 10^{12} \quad (10)$$

2. Empirical Formula of Cole and Cole³⁾

The dielectric relaxation can be represented as a function of frequency f in the following form

$$\varepsilon^* = \varepsilon - j\gamma = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + (jf/f_0)^{1-\alpha}} \quad (0 < \alpha < 1) \quad (11)$$

$$\varepsilon - \varepsilon_h = \frac{(\varepsilon_l - \varepsilon_h) \left[1 + (f/f_0)^{1-\alpha} \cos \left[\left(\frac{\pi}{2} \right) (1 - \alpha) \right] \right]}{1 + 2(f/f_0)^{1-\alpha} \cos \left[\left(\frac{\pi}{2} \right) (1 - \alpha) \right] + (f/f_0)^{2(1-\alpha)}} \quad (12)$$

$$\gamma = \frac{(\varepsilon_l - \varepsilon_h)(f/f_0)^{1-\alpha} \sin \left[\left(\frac{\pi}{2} \right) (1 - \alpha) \right]}{1 + 2(f/f_0)^{1-\alpha} \cos \left[\left(\frac{\pi}{2} \right) (1 - \alpha) \right] + (f/f_0)^{2(1-\alpha)}} \quad (13)$$

Experimental

Materials—Squalane ($\varepsilon_m = 2.10$, $\kappa_m = 5.64 \times 10^{-10}$ U/cm) of commercial grade (Kuraray Co., Ltd.), hydrophobic colloidal silica (AEROSIL R972, Nippon Aerosil Co., Ltd.) with an electric conductivity of 1×10^{-13} U/cm, a particle size of 10–40 nm, and a specific surface area of 120 ± 30 m²/g (BET absorption method), and water obtained by reverse osmosis with various electric conductivities ($\varepsilon_{p1} = 76.95$, $\kappa_{p1} = 5.04 \times 10^{-6}$ U/cm; $\varepsilon_{p2} = 76.66$, $\kappa_{p2} = 8.86 \times 10^{-6}$ U/cm; $\varepsilon_{p3} = 76.99$, $\kappa_{p3} = 17.19 \times 10^{-6}$ U/cm; $\varepsilon_{p4} = 77.66$, $\kappa_{p4} = 41.07 \times 10^{-6}$ U/cm), adjusted by the addition of KCl, were used.

Preparation of W/(S·O) Emulsions—Hydrophobic colloidal silica (2.0% by weight) was mixed with squalane. Water with various electric conductivity values was gently added in portions to the oil phase with vigorous mixing by means of a propeller mixer (max. rpm = 1200), and a homomixer (max. rpm = 5000) in order to prepare W/(S·O) emulsion in which the dispersed particles are fine.

During emulsification, the electric conductivity of the dispersed phase increased slightly owing to ion contamination from colloidal silica–oil gel. In order to determine the practical electric conductivity of the dispersed

phase after emulsification, dispersed phases with various electric conductivities were fractioned by centrifugation from W/(S·O) emulsions. The dielectric constant and electric conductivity of the dispersed phases were $\epsilon_{p1} = 77.12$, $\kappa_{p1} = 9.13 \times 10^{-6} \text{ } \Omega/\text{cm}$; $\epsilon_{p2} = 77.33$, $\kappa_{p2} = 13.09 \times 10^{-6} \text{ } \Omega/\text{cm}$; $\epsilon_{p3} = 78.32$, $\kappa_{p3} = 20.09 \times 10^{-6} \text{ } \Omega/\text{cm}$ or $\epsilon_{p4} = 77.24$, $\kappa_{p4} = 45.95 \times 10^{-6} \text{ } \Omega/\text{cm}$, respectively.

Measurement—Both the capacitance and conductance were measured over frequencies ranging from 10 kHz to 3 MHz by means of a capacitance-conductance bridge as used in the previous study.²⁾

Results

From eq. (7), it can be seen that electric conductivity, κ , takes limiting values, κ_h and κ_l , at high and low frequencies, respectively. Figure 1 shows the frequency dependence of electric conductivities of W/(S·O) emulsions ($\epsilon_{p3} = 78.32$, $\kappa_{p3} = 20.09 \times 10^{-6} \text{ } \Omega/\text{cm}$) up to a water volume fraction of 0.6 in the cases of both coarsely and finely dispersed particles. The electric conductivity in the case of coarse particles at each experimental frequency was a little larger than in the case of fine particles.

In Fig. 2, the theoretical curve of the limiting electric conductivities at high frequencies, κ_h , according to eq. (8) is compared with the observed values. The observed values in the case of fine particles were closer to the theoretical curve than in the case of coarse particles, but were a little larger than the theoretical values. The values of limiting electric conductivities at low frequencies, κ_l , could not be determined because they were too small to determine by using the present apparatus for dielectric measurement.

Figure 3 shows the dielectric loss factor–frequency plots of W/(S·O) emulsions ($\epsilon_{p3} = 78.32$, $\kappa_{p3} = 20.09 \times 10^{-6} \text{ } \Omega/\text{cm}$) in the cases of coarse and fine particles. The relaxation frequency, f_0 , i.e. the frequency at which the dielectric loss factor, γ , was maximum, is shown on the dielectric loss factor–frequency curves for water volume fractions up to 0.6.

In Fig. 4, the theoretical curve of the relaxation frequency, f_0 , according to eq. (10) is compared with the observed values in the case of fine particles in Fig. 3. The dielectric parameters for coarse particles in Fig. 3 gave plots similar to those shown in Fig. 4. The

Fig. 1. The Frequency Dependence of Electric Conductivities, κ , of W/(S·O) Emulsions ($\epsilon_{p3} = 78.32$, $\kappa_{p3} = 20.09 \times 10^{-6} \text{ } \Omega/\text{cm}$) at Various Water Volume Fractions

Volume fraction of dispersed phase
a and a', 0.1; b and b', 0.2; c and c', 0.3; d and d', 0.4; e and e', 0.5; f', 0.6.

○—○, in the case of fine particles; □---□, in the case of coarse particles.

Fig. 2. The Dependence of Limiting Electric Conductivities at High Frequencies, κ_h , of W/(S·O) Emulsions ($\epsilon_{p3} = 78.32$, $\kappa_{p3} = 20.09 \times 10^{-6} \text{ } \Omega/\text{cm}$) upon Volume Fraction of Dispersed Phase

a, Wagner's theoretical curve according to eq. (8);
○, in the case of fine particles; □, in the case of coarse particles.

Fig. 3. Plots of the Dielectric Loss Factors, γ , of W/(S·O) Emulsions ($\epsilon_{p3'} = 78.32$, $\kappa_{p3'} = 20.09 \times 10^{-6} \text{ } \Omega/\text{cm}$) against Frequencies at Various Water Volume Fractions

Volume fraction of dispersed phase

a and a', 0.1; b and b', 0.2; c and c', 0.3; d and d', 0.4; e and e', 0.5; f', 0.6.

Fig. 4. The Dependence of Relaxation Frequency, f_0 , of W/(S·O) Emulsions ($\epsilon_{p3'} = 78.32$, $\kappa_{p3'} = 20.09 \times 10^{-6} \text{ } \Omega/\text{cm}$) upon Volume Fraction of Dispersed Phase in the Case of Fine Dispersed Particles

b, Wagner's theoretical curve according to eq. (10).

observed values of the relaxation frequency, f_0 , showed a good agreement with the theoretical curve regardless of the dispersed particle size.

Figure 5 shows complex plane plots of ϵ and γ of W/(S·O) emulsions in which the electric conductivity of the dispersed phase is $\kappa_{p1'}$, $\kappa_{p2'}$, $\kappa_{p3'}$, or $\kappa_{p4'}$, and those of mixtures of equal amounts of two kinds of W/(S·O) emulsions in which the two electric conductivities of the dispersed particles are $\kappa_{p1'}$ and $\kappa_{p2'}$, $\kappa_{p1'}$ and $\kappa_{p3'}$, or $\kappa_{p1'}$ and $\kappa_{p4'}$, at 0.3 water volume fraction. The dielectric parameters ϵ_h , ϵ_l , f_0 and α can be determined from Figs. 3 and 5. The complex plane plots of the mixtures of W/(S·O) emulsions as shown in Fig. 5 were in good agreement with the plots of arithmetic means of ϵ calculated from eq. (12) or γ calculated from eq. (13) at certain experimental frequencies, using the observed dielectric parameters of W/(S·O) emulsions in which the two electric conductivities of the dispersed particles are $\kappa_{p1'}$ and $\kappa_{p2'}$, $\kappa_{p1'}$ and $\kappa_{p3'}$, or $\kappa_{p1'}$ and $\kappa_{p4'}$, as listed in Table I.

Table I summarizes the dielectric parameters of the W/(S·O) emulsions and of mixtures of equal amounts of W/(S·O) emulsions at various water volume fractions. In the case of W/(S·O) emulsions, f_0 shifted to higher frequency as the electric conductivity of the dispersed phase increased, while the magnitudes of ϵ_h , ϵ_l and α were scarcely affected. On the other hand,

Fig. 5. Complex Plane Plots of the Dielectric Constants, ϵ , and the Dielectric Loss Factors, γ , of W/(S·O) Emulsions and of Mixtures of Equal Amounts of Two Kinds of W/(S·O) Emulsions at 0.3 Water Volume Fraction

Electric conductivity of various W/(S·O) emulsions:

a: $9.13 \times 10^{-6} \text{ U/cm } (\kappa_{p1})$.

b: $13.09 \times 10^{-6} \text{ U/cm } (\kappa_{p2})$.

c: κ_{p1} and κ_{p2} .

d: $9.13 \times 10^{-6} \text{ U/cm } (\kappa_{p1})$.

e: $20.09 \times 10^{-6} \text{ U/cm } (\kappa_{p3})$.

f: κ_{p1} and κ_{p3} .

g: $9.13 \times 10^{-6} \text{ U/cm } (\kappa_{p1})$.

h: $45.95 \times 10^{-6} \text{ U/cm } (\kappa_{p4})$.

i: κ_{p1} and κ_{p4} .

○—○, the observed values; -----, the values calculated from eqs. (12) and (13).

in the case of mixtures of two W/(S·O) emulsions, the parameter α increased, f_0 took an intermediate value, and the determination of f_0 was more difficult since the change in the electric conductivities extended over an apparently broader range of frequency increasing with the difference of electric conductivities of dispersed phase in the two kinds of W/(S·O) emulsions.

Discussion

Water particles of W/(S·O) emulsions in the present study were homogeneous without aggregation. No surfactant was used to prepare the W/(S·O) emulsions.

In Fig. 2, the observed values of κ_h were a little larger than the theoretical values expected from eq. (8). From the fact that the observed values of κ_h were much closer to the theoretical curve when the size of water particles was smaller, particle size might be a cause of the deviation.

From the previous²⁾ and present results of investigations into the dielectric properties of W/(S·O) emulsions in the light of theory, it is possible to say that W/(S·O) emulsion shows a

TABLE I. Values of ε_h , ε_l , f_0 and α of the W/(S·O) Emulsions and Mixtures of W/(S·O) Emulsions at Various Water Volume Fractions

Φ	Conductivity of dispersed phase (Ω/cm)	ε_h	ε_l	f_0 (kHz)	α
0.1	9.13 ($\kappa_{p1'}$)	2.763	2.837	141.3	0
	13.09 ($\kappa_{p2'}$)	2.779	2.852	199.5	0
	$\kappa_{p1'}$ and $\kappa_{p2'}$	2.780	2.852	109.8	0.042
	9.13 ($\kappa_{p1'}$)	2.778	2.852	141.3	0
	20.09 ($\kappa_{p3'}$)	2.776	2.855	426.6	0
	$\kappa_{p1'}$ and $\kappa_{p3'}$	2.784	2.864	199.5	0.079
	9.13 ($\kappa_{p1'}$)	2.785	2.857	141.3	0
	45.95 ($\kappa_{p4'}$)	2.773	2.852	794.3	0
0.2	$\kappa_{p1'}$ and $\kappa_{p4'}$	2.761	2.833	501.2	0.187
	9.13 ($\kappa_{p1'}$)	3.640	3.870	141.3	0
	13.09 ($\kappa_{p2'}$)	3.683	3.903	199.5	0
	$\kappa_{p1'}$ and $\kappa_{p2'}$	3.663	3.891	186.2	0.037
	9.13 ($\kappa_{p1'}$)	3.661	3.878	141.3	0
	20.09 ($\kappa_{p3'}$)	3.638	3.852	398.1	0
	$\kappa_{p1'}$ and $\kappa_{p3'}$	3.682	3.923	223.9	0.076
	9.13 ($\kappa_{p1'}$)	3.670	3.887	141.3	0
0.3	45.95 ($\kappa_{p4'}$)	3.659	3.887	794.3	0
	$\kappa_{p1'}$ and $\kappa_{p4'}$	3.689	3.927	398.1	0.191
	9.13 ($\kappa_{p1'}$)	4.880	5.380	141.3	0
	13.09 ($\kappa_{p2'}$)	4.888	5.380	199.5	0
	$\kappa_{p1'}$ and $\kappa_{p2'}$	4.910	5.436	177.8	0.033
	9.13 ($\kappa_{p1'}$)	4.880	5.390	141.3	0
	20.09 ($\kappa_{p3'}$)	4.883	5.395	354.8	0
	$\kappa_{p1'}$ and $\kappa_{p3'}$	4.910	5.428	208.9	0.080
0.4	9.13 ($\kappa_{p1'}$)	4.870	5.353	141.3	0
	45.95 ($\kappa_{p4'}$)	4.875	5.385	794.3	0
	$\kappa_{p1'}$ and $\kappa_{p4'}$	4.878	5.430	398.1	0.230
	9.13 ($\kappa_{p1'}$)	6.41	7.29	141.3	0
	13.09 ($\kappa_{p2'}$)	6.44	7.33	177.8	0
	$\kappa_{p1'}$ and $\kappa_{p2'}$	6.45	7.38	177.8	0.022
	9.13 ($\kappa_{p1'}$)	6.43	7.32	141.3	0
	20.09 ($\kappa_{p3'}$)	6.47	7.40	380.2	0
0.5	$\kappa_{p1'}$ and $\kappa_{p3'}$	6.46	7.38	208.9	0.068
	9.13 ($\kappa_{p1'}$)	6.44	7.36	131.8	0
	45.95 ($\kappa_{p4'}$)	6.47	7.43	758.6	0
	$\kappa_{p1'}$ and $\kappa_{p4'}$	6.40	7.34	354.8	0.210
	9.13 ($\kappa_{p1'}$)	8.48	10.18	141.3	0
	13.09 ($\kappa_{p2'}$)	8.58	10.25	177.8	0
	$\kappa_{p1'}$ and $\kappa_{p2'}$	8.55	10.15	166.0	0.040
	9.13 ($\kappa_{p1'}$)	8.78	10.45	141.3	0
0.6	20.09 ($\kappa_{p3'}$)	8.75	10.51	331.1	0
	$\kappa_{p1'}$ and $\kappa_{p3'}$	8.57	10.23	208.9	0.064
	9.13 ($\kappa_{p1'}$)	8.48	10.22	131.8	0
	45.95 ($\kappa_{p4'}$)	8.60	10.33	758.6	0
	$\kappa_{p1'}$ and $\kappa_{p4'}$	8.52	10.20	316.2	0.189
	9.13 ($\kappa_{p1'}$)	11.57	14.73	125.9	0.051
	13.09 ($\kappa_{p2'}$)	11.42	14.48	177.8	0.031
	$\kappa_{p1'}$ and $\kappa_{p2'}$	11.80	14.60	177.8	0.044
0.7	9.13 ($\kappa_{p1'}$)	11.30	14.42	125.9	0.026
	20.09 ($\kappa_{p3'}$)	11.63	14.95	316.2	0.026
	$\kappa_{p1'}$ and $\kappa_{p3'}$	11.65	14.89	208.9	0.072
	9.13 ($\kappa_{p1'}$)	11.60	14.76	131.9	0.057
	45.95 ($\kappa_{p4'}$)	11.29	14.50	758.6	0.014
	$\kappa_{p1'}$ and $\kappa_{p4'}$	11.35	14.78	398.1	0.200

good agreement with Wagner's theory. From this point of view, it may be considered that the W/(S·O) emulsion is a suitable model for investigating the dielectric anomaly of practical w/o emulsion, and non-aggregated W/(S·O) emulsions in which the dispersed phase has different electric conductivities were investigated in the present study. In a W/(S·O) emulsion containing two kinds of dispersed particles with different electric conductivities, the parameter α became larger than zero, even though the particles were homogeneously dispersed. From the fact that the parameter α increased as particle aggregation became apparent, the parameter α is considered to reflect the electric irregularity of dispersed particles regardless of particle aggregation in w/o emulsion systems. From this point of view, it may be considered that in practical w/o emulsions, new dielectrics with different relaxation frequencies are formed by particle aggregation, and that the parameter α indicates the degree of irregularity of such aggregation. This was supported by the fact that dielectric constant and dielectric loss factor increased with increasing particle aggregation.²⁾ Since it is considered that the dielectric property of water in aggregated particles does not change, it seems reasonable to consider that the interface layer among water particles plays the most important role in forming new dielectrics. If water particles are surrounded by colloidal silica-oil gel with low electric conductivity, the observed values would relate to the dielectric properties of the water particles, whereas if interface layers exist among water particles, additional dielectric phenomena based on ion diffusion between water particles through the interface layers would have to be taken into account.

References

- 1) K. W. Wagner, *Arch. Elektrotech.* (Berlin), **2**, 371 (1914).
- 2) H. Kaneko and S. Hirota, *Chem. Pharm. Bull.*, **31**, 5, 1445 (1983).
- 3) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
- 4) T. Hanai, "Emulsion Science," ed. by P. Scherman, Academic Press, London and New York, 1968, pp. 353—478.