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Dielectric Studies on Emulsion of Water in Hydrophobic Colloidal Silica-Oil Gel

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Dielectric relaxation due to the interfacial polarization of emulsions of water in a hydrophobic colloidal silica–oil gel (W/(S·O) emulsion, below) was investigated over a wide range of volume fraction of dispersed phase at frequencies ranging from 10 kHz to 3 MHz.

W/(S·O) emulsions without surfactant showed a dielectric relaxation, and the limiting dielectric constants at high and low frequencies were both shown to satisfy the equations given by Wagner's theory[1,2] up to a water volume fraction as high as 0.65. In W/(S·O) emulsions without surfactant, absence of any aggregation of water particles was ascertained by microscopic observation, while aggregation was observed in W/(S·O) emulsions with nonionic surfactant. In emulsions with aggregation, the limiting dielectric constant at low frequencies deviated from both Wagner's and Hanai's theoretical curves, though the limiting dielectric constant at high frequencies was consistent with Hanai's theoretical curve. The dielectric anomaly, *i.e.* the deviation from the theoretical values at low frequencies, may be related to the particle aggregation of w/o emulsions, and it may be possible to make a quantitative evaluation of the colloid-chemical stability of w/o emulsions in terms of particle aggregation.

Keywords——w/o emulsion; interfacial polarization; colloid-chemical stability; aggregation; dielectric measurement; dielectric constant; dielectric loss factor; dielectric relaxation; dielectric anomaly; nonionic surfactant

Quantitative evaluation of the physical characteristics of colloidal dispersion systems is important for predicting the colloid-chemical stability, for quality control and for assessing the texture of emulsion preparations.

Wagner proposed a theory of interfacial polarization for a sparsely distributed dispersion of spherical particles.[1,2] Hanai extended the theory to a higher volume fraction of dispersed phase, and could explain experimental data obtained in practical emulsion systems. However, the observed limiting dielectric constants of practical w/o emulsions at low frequencies were much higher than the values predicted by Hanai's theory.[2-4] Hanai attributed this effect to the instability of the state of aggregation of dispersed particles.[5] From a practical point of view, the degree of the anomaly at lower frequencies was considered to be useful for evaluating the state of aggregation. Particles in w/o emulsions tend, more or less, to aggregate by so-called London van der Waals' force, if the emulsification is dependent upon nonionic surfactant. On the other hand, in W/(S·O) emulsions, water particles can be immobilized in colloidal silica–oil structure and aggregation will be inhibited mechanically without any surfactant.

The purpose of this study was to establish whether the degree of the anomaly, *i.e.* the magnitude of differences between theoretical and observed limiting dielectric constants, is related to the degree of aggregation, and to investigate the dielectric properties of dispersion of W/(S·O) emulsion.

Theoretical

List of Symbols

ε : the dielectric constant
ε_p : the dielectric constant of dispersed phase
ε_m : the dielectric constant of continuous medium
ε_h : the limiting value of ε at high frequency
ε_l : the limiting value of ε at low frequency
κ : the electric conductivity (℧/cm)
κ_p : the electric conductivity of dispersed phase (℧/cm)
κ_m : the electric conductivity of continuous medium (℧/cm)
κ_h : the limiting value of κ at high frequency (℧/cm)
κ_l : the limiting value of κ at low frequency (℧/cm)
Φ : the volume fraction of dispersed phase
f : the frequency (Hz)
f_0 : the relaxation frequency (Hz)
ε^* : the complex dielectric constant
γ : the imaginary part of the complex dielectric constant

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

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

ω : the angular frequency
$\omega=2\pi f$
j : imaginary unit $\sqrt{-1}$
α : the parameter for the distribution of relaxation frequencies can be determined from complex plane plots

The theoretical expressions are as follows, where the dispersed phase is very conductive compared with the continuous medium, that is, $\kappa_p \gg \kappa_m$ (w/o type emulsion).[6]

1. Wagner's Theory

The limiting dielectric constants and conductivities at high and low frequencies are expressed as

$$\varepsilon_h=\varepsilon_m\frac{\varepsilon_p+2\varepsilon_m+2\Phi(\varepsilon_p-\varepsilon_m)}{\varepsilon_p+2\varepsilon_m-\Phi(\varepsilon_p-\varepsilon_m)} \tag{1}$$

$$\varepsilon_l=\varepsilon_m\frac{1+2\Phi}{1-\Phi} \tag{2}$$

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

$$\kappa_l=\kappa_m\frac{1+2\Phi}{1-\Phi} \tag{4}$$

and

$$f_0=\frac{\kappa_p(1-\Phi)}{\varepsilon_p+2\varepsilon_m-\Phi(\varepsilon_p-\varepsilon_m)}\times 1.7975\times 10^{12} \tag{5}$$

2. Hanai's Theory

The limiting values at high and low frequencies are given by

$$\left(\frac{\varepsilon_p-\varepsilon_h}{\varepsilon_p-\varepsilon_m}\right)\left(\frac{\varepsilon_m}{\varepsilon_h}\right)^{1/3}=1-\Phi \tag{6}$$

$$\varepsilon_l=\varepsilon_m\frac{1}{(1-\Phi)^3} \tag{7}$$

$$\kappa_h=\kappa_p\frac{3\varepsilon_h(\varepsilon_h-\varepsilon_m)}{(\varepsilon_p+2\varepsilon_h)(\varepsilon_p-\varepsilon_m)} \tag{8}$$

and
$$\kappa_l=\kappa_m\frac{1}{(1-\Phi)^3} \tag{9}$$

3. Empirical Formula of Cole and Cole[7)]

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

$$\varepsilon^*=\varepsilon-j\gamma=\varepsilon_h+\frac{\varepsilon_l-\varepsilon_h}{1+(jf/f_0)^{1-\alpha}}\quad(0<\alpha<1) \tag{10}$$

Experimental

Materials——Squalane ($\varepsilon_m=2.10$, $\kappa_m=5.64\times10^{-10}$ ℧/cm) of commercial grade (Kuraray Co., Ltd.) hydrophobic colloidal silica (AEROSIL R972, Nippon Aerosil Co., Ltd.) with an electric conductivity of 1×10^{-13} ℧/cm, a particle size of 10—40 nm, and a specific surface area of 120 ± 30 m^2/g (BET absorption method), a nonionic surfactant (sorbitan sesquioleate; NIKKOL SO-15) of commercial grade and water obtained by reverse osmosis ($\varepsilon_p=78.58$, $\kappa_p=2.31\times10^{-6}$ ℧/cm) were used.

Preparation of W/(S•O) Emulsions——Sorbitan sesquioleate was dissolved in warm squalane at a concentration of 0, 0.1, 0.2, 0.3, 0.4, or 0.5% by weight. Hydrophobic colloidal silica (2.0% by weight) was mixed with the squalane. Water was gently and successively added 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)emulsions in which the dispersed particles are fine.

Measurements——Measuring Cell: The measuring cell consisted of a brass cylinder coated with nickel; its empty capacitance was about 16 pF. The cell constant was calibrated accurately by the use of several standard liquids (benzene=2.285, reference=2.284 at 20°C; chloroform=4.772, reference=4.806 at 20°C; methanol =32.06, reference=32.63 at 25°C).

Dielectric Measurement: Both capacitance and conductance were measured over the frequency range of 10 kHz to 3 MHz with a TR-1C type capacitance-conductance bridge[8)] made by Ando Electric Co., Ltd. under non-shearing conditions at 25°C. The measuring circuit is shown in Fig. 1.

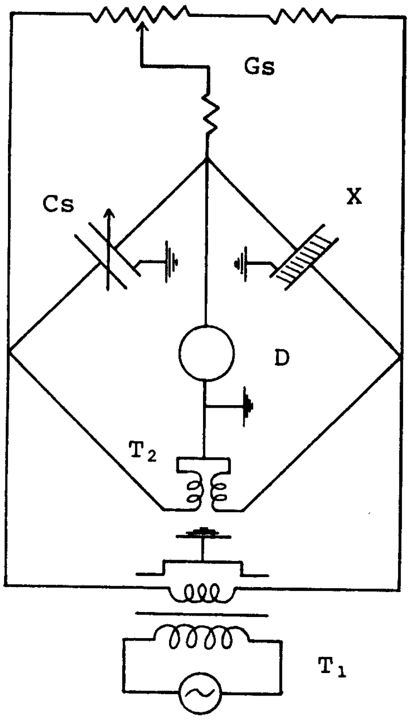
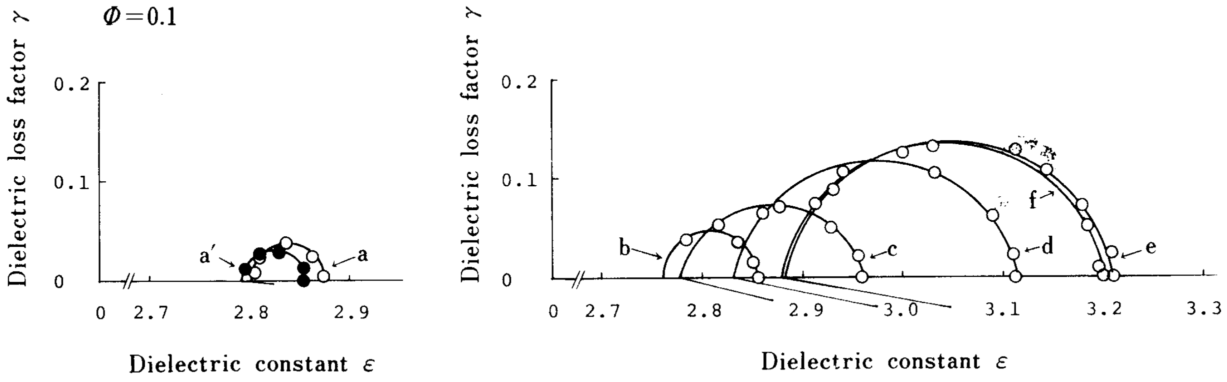


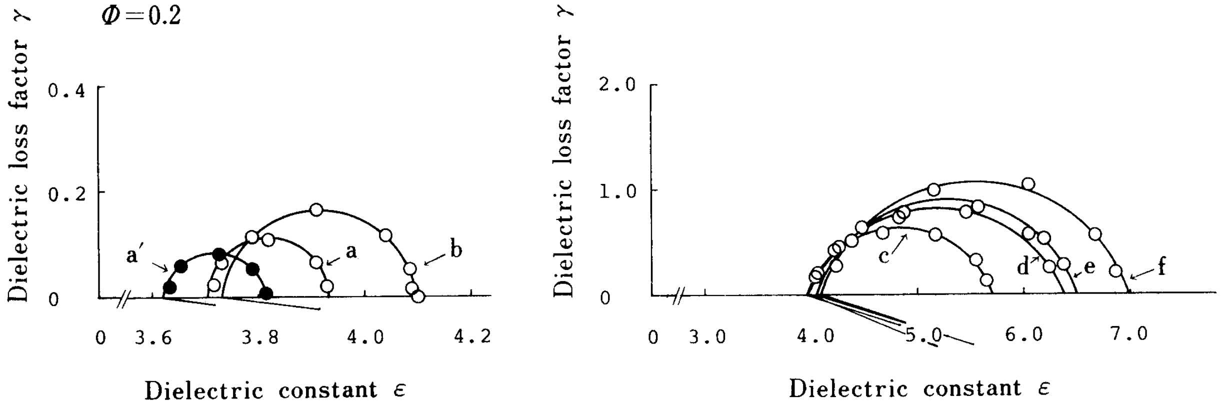
Fig. 1. Schematic Illustration of the Bridge Circuit

Gs: conductance standard.
Cs: capacitance standard.
X: unknown.
T_1: transformer.
T_2: ratio arms.
D: detector.

Results

Dielectric constants, ε, and dielectric loss factors, γ, of W/(S·O) emulsions showed frequency dependence up to 0.65 water volume fraction. Complex plane plots of ε and γ of W/(S·O) emulsions gave a circular arc. Fig. 2 shows the complex plane plots of W/(S·O) emulsions at various water volume fractions. Fig. 3 shows microphotographs of W/(S·O) emulsions at various water volume fractions. Table I summarizes the values of dielectric


Φ=0.1
Dielectric loss factor γ
0.2
0.1
0
0 2.7 2.8 2.9
a′
a
Dielectric constant ε
Dielectric loss factor γ
0.2
0.1
0
0 2.7 2.8 2.9 3.0 3.1 3.2 3.3
b
c
d
e
f
Dielectric constant ε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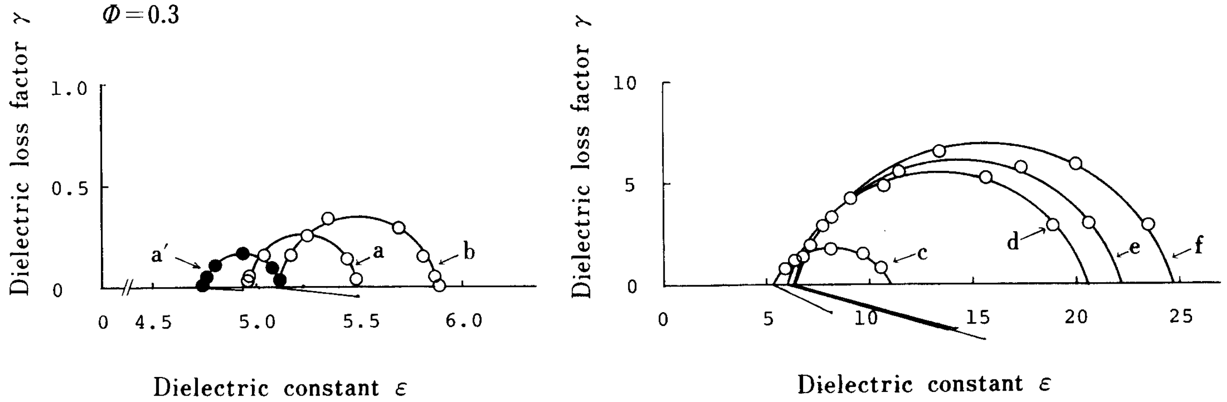
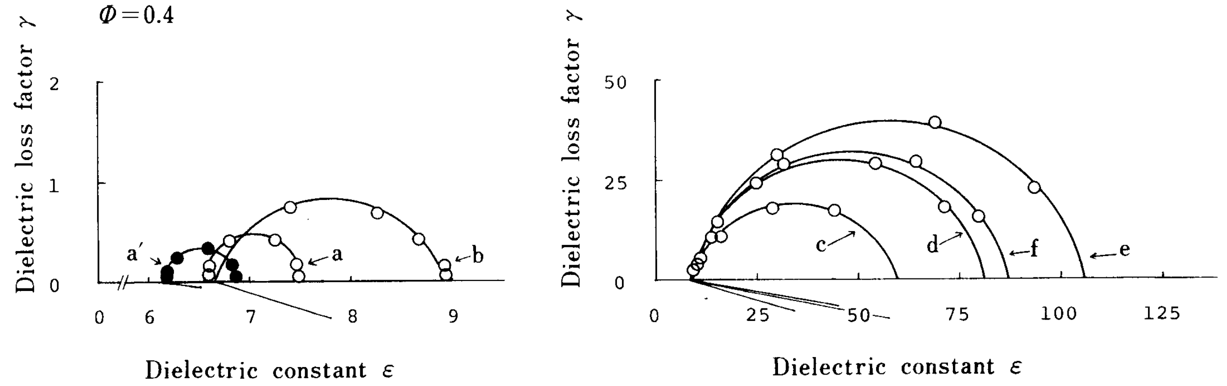
Dielectric loss factor γ
0.4
0.2
0
0 3.6 3.8 4.0 4.2
a′
a
b
Dielectric constant ε
Dielectric loss factor γ
2.0
1.0
0
0 3.0 4.0 5.0 6.0 7.0
c
d
e
f
Dielectric constant ε


Φ=0.3
Dielectric loss factor γ
1.0
0.5
0
0 4.5 5.0 5.5 6.0
a′
a
b
Dielectric constant ε
Dielectric loss factor γ
10
5
0
0 5 10 15 20 25
c
d
e
f
Dielectric constant ε


Φ=0.4
Dielectric loss factor γ
2
1
0
0 6 7 8 9
a′
a
b
Dielectric constant ε
Dielectric loss factor γ
50
25
0
0 25 50 75 100 125
c
d
f
e
Dielectric constant ε

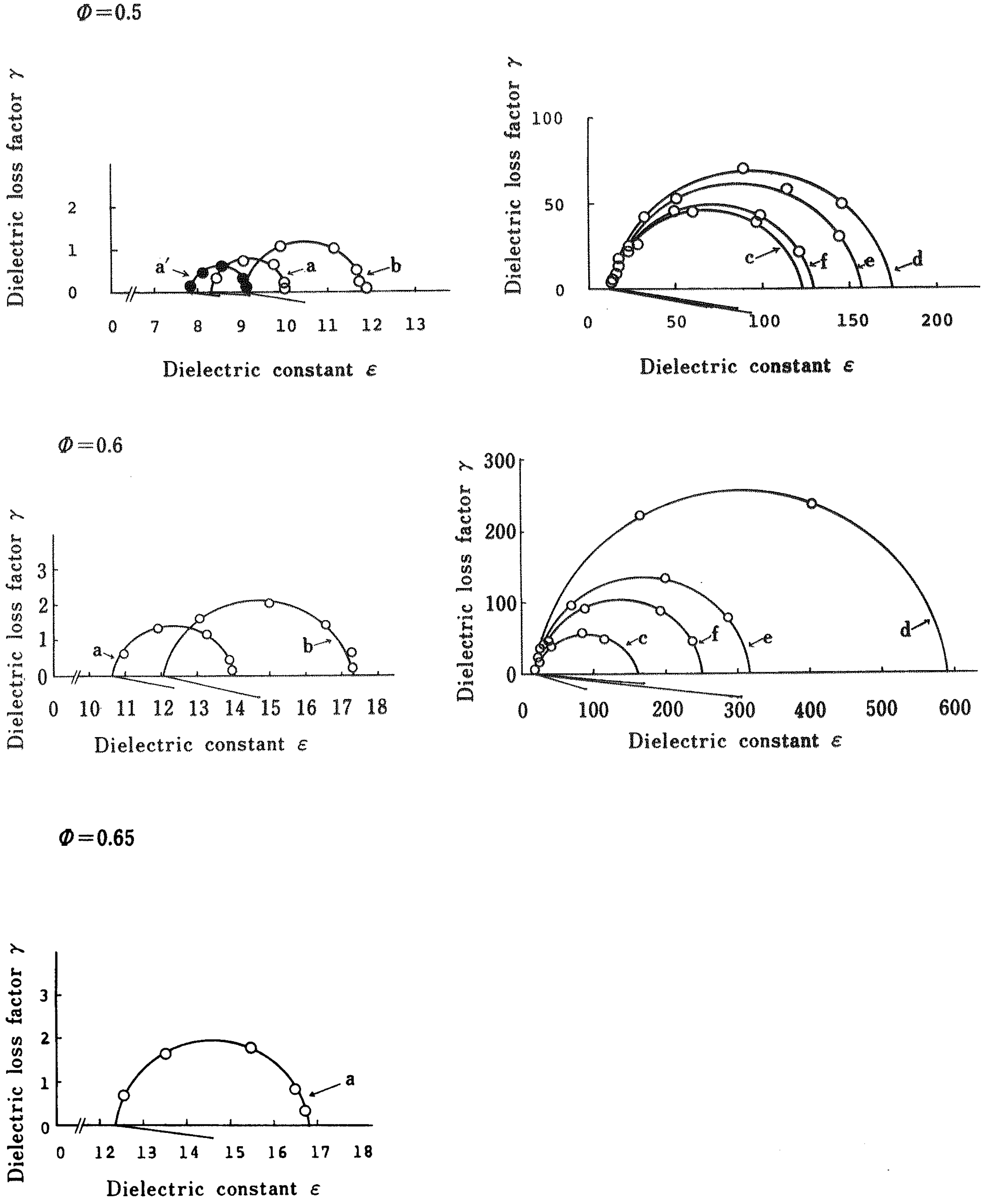
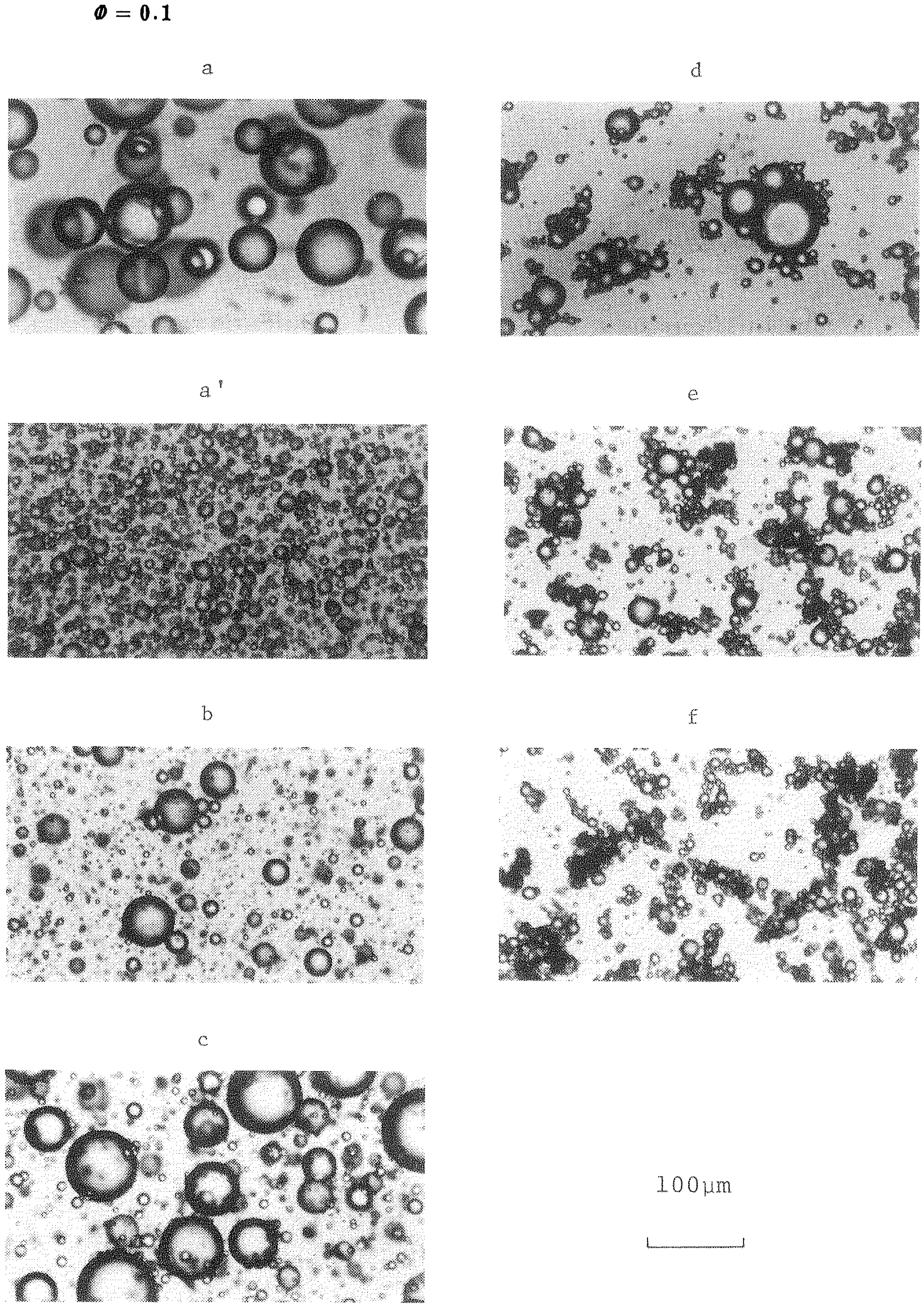


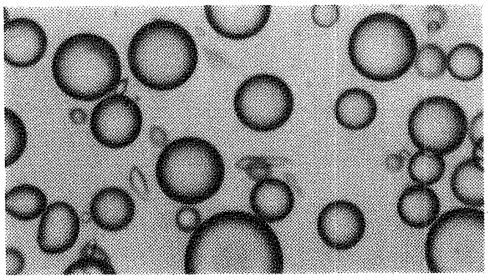
Fig. 2. Complex Plane Plots of the Dielectric Constants, ε, and the Dielectric Loss Factors, γ, of W/(S·O) Emulsions at Various Water Volume Fractions

Concentration of nonionic surfactant:
a, 0% (coarse particles); a', 0% (fine particles); b, 0.1%; c, 0.2%; d, 0.3%; e, 0.4%; f, 0.5%.

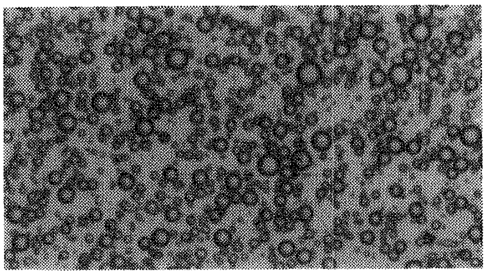

$\Phi = 0.1$
a
d
a'
e
b
f
c
100μm

$\Phi = 0.2$

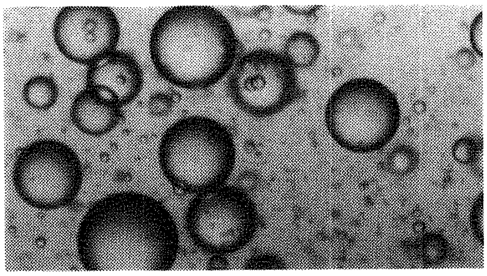
a



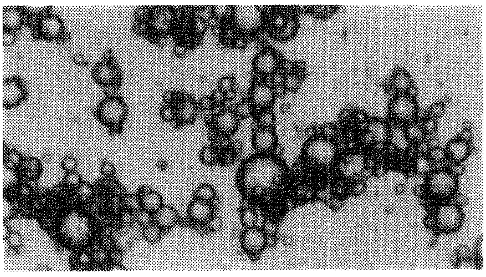
a'



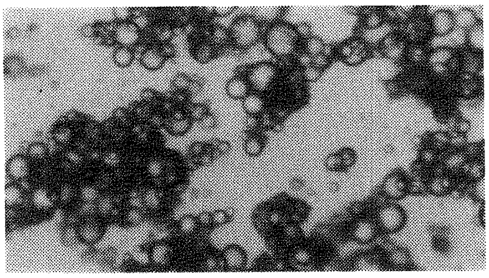
b



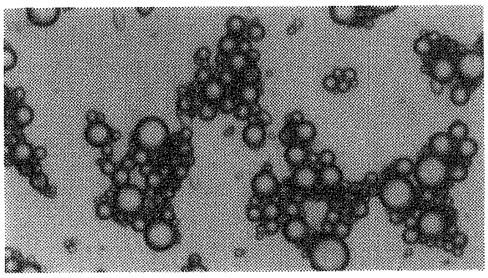
c



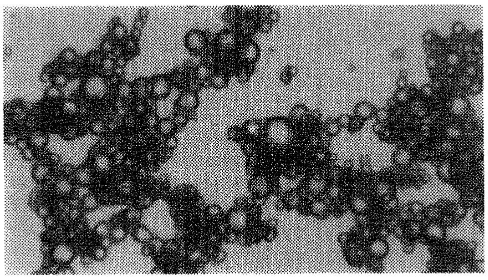
d



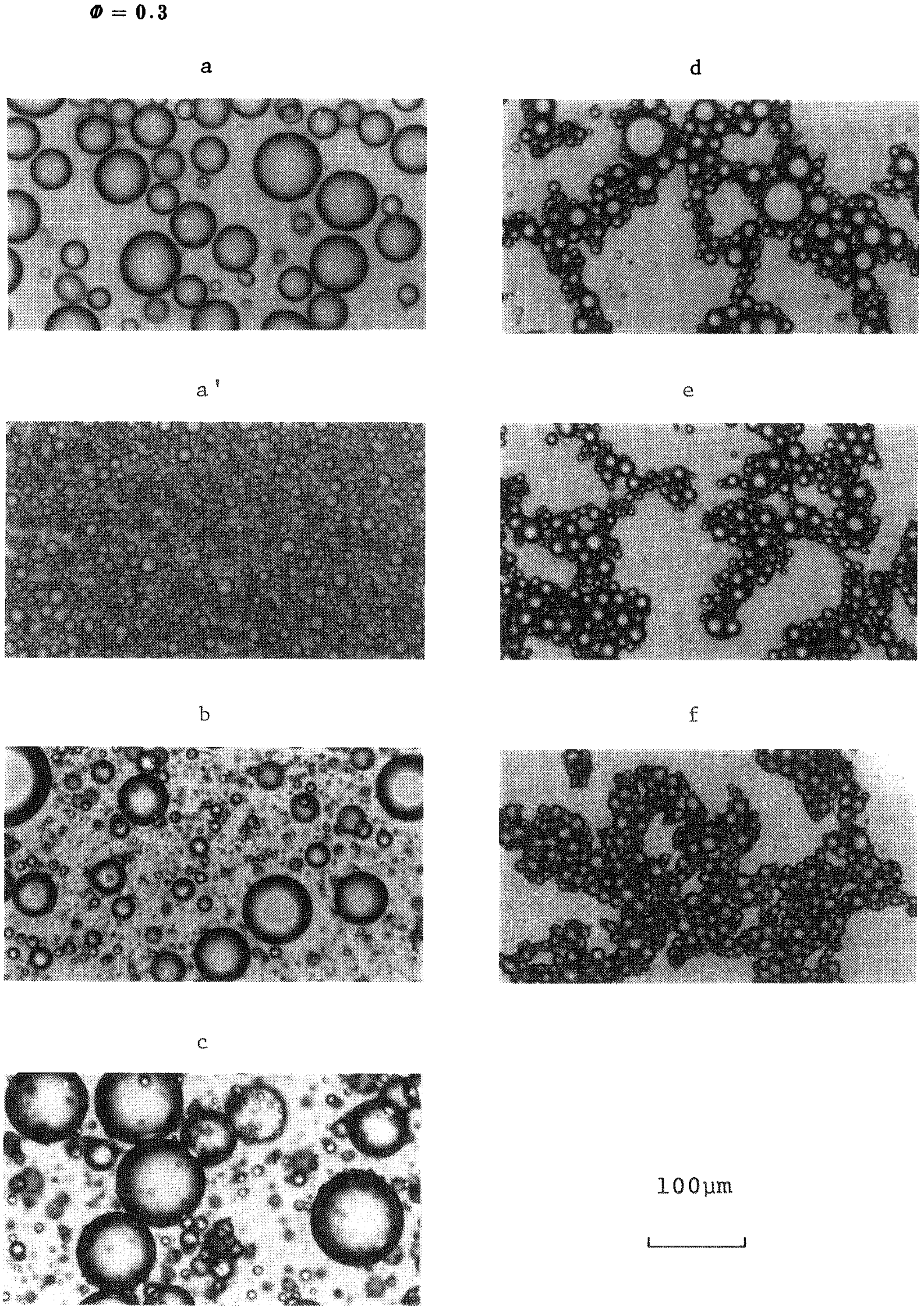
e

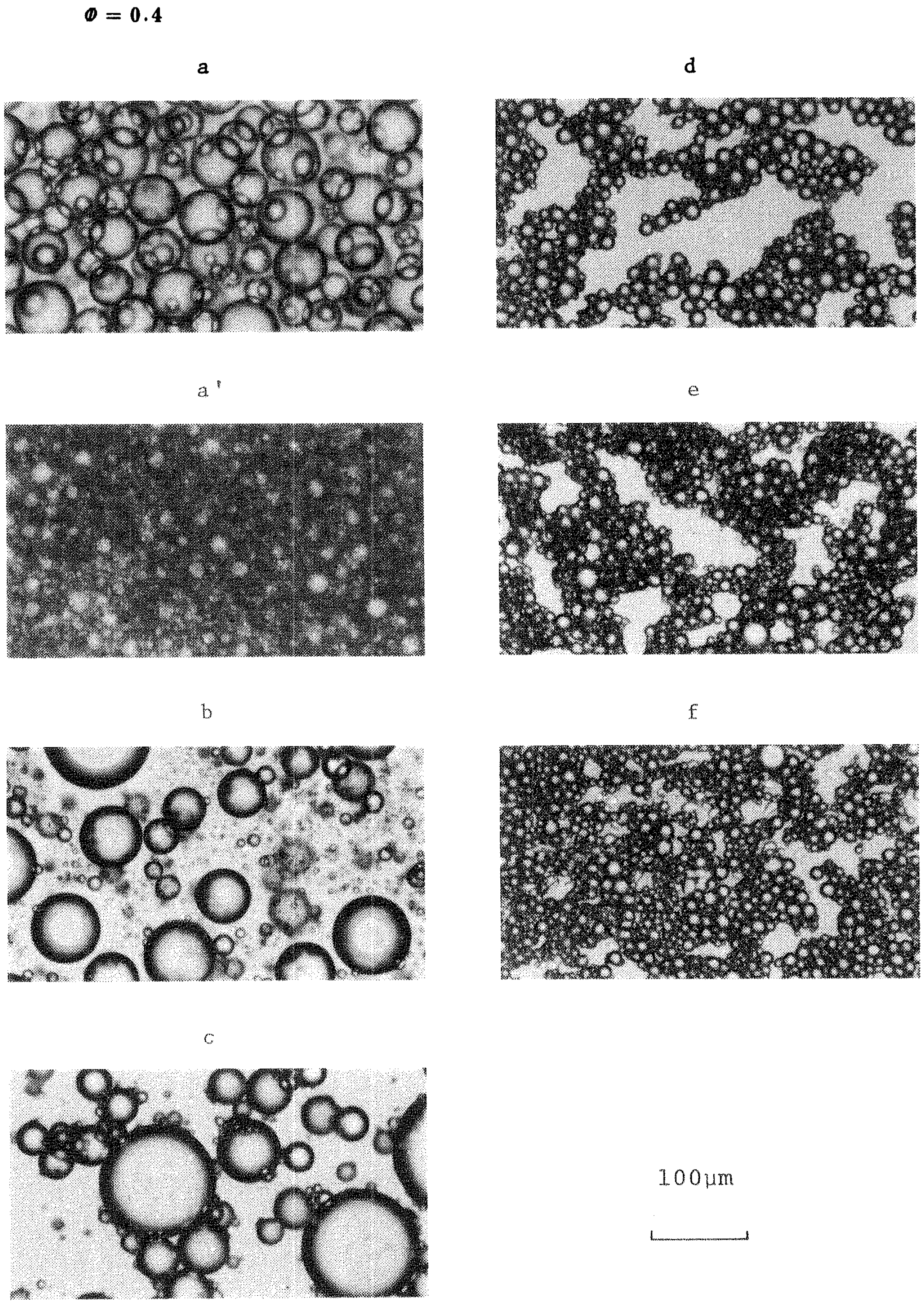


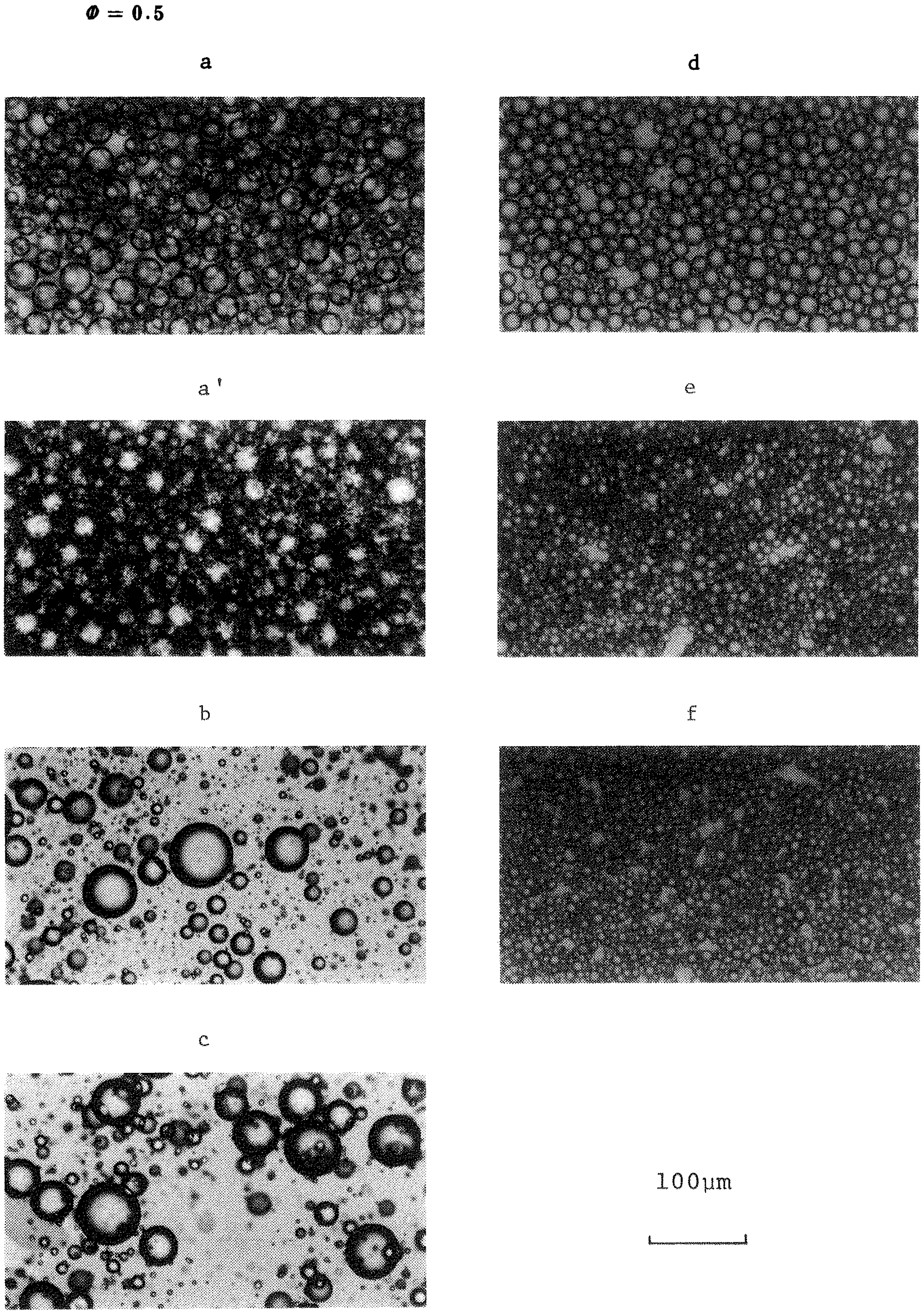
f

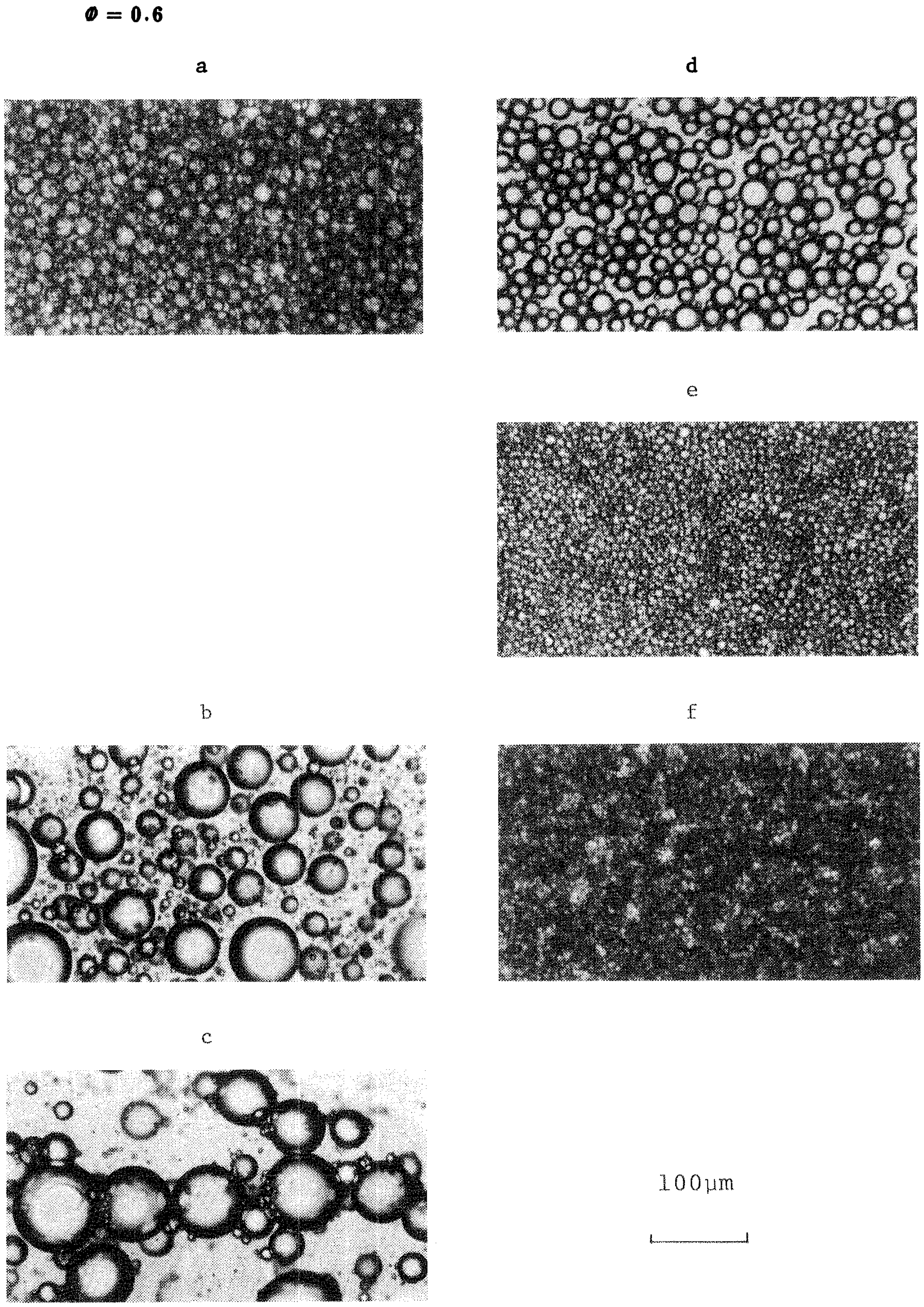


100μm


$\Phi = 0.3$
a
d
a'
e
b
f
c
100μm


$\Phi = 0.4$
a
d
a'
e
b
f
c
100μm


$\Phi = 0.5$
a
d
a'
e
b
f
c
100μm


Φ = 0.6
a
d
e
b
f
c
100μm

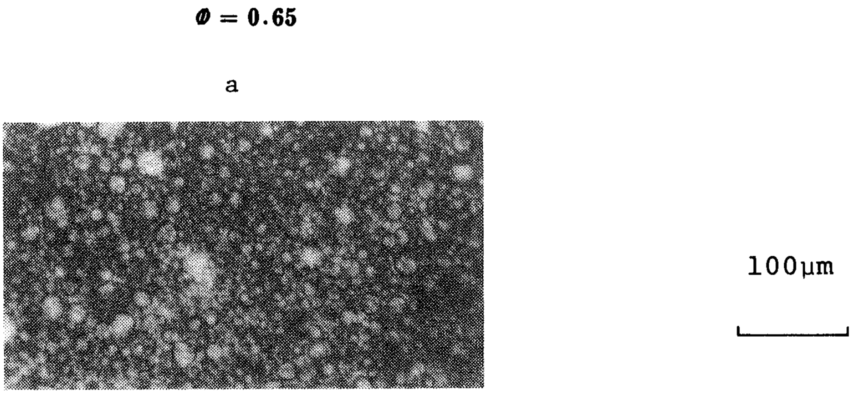


Fig. 3. Microphotographs of Dispersed Particles in W/(S·O) Emulsions at Various Water Volume Fractions

Concentration of nonionic surfactant:
a, 0% (coarse particles); a', 0% (fine particles);
b, 0.1%; c, 0.2%; d, 0.3%; e, 0.4%; f, 0.5%.
a and a' show dispersed particles without aggregation;
b and c show particle aggregation beginning;
d, e, and f show apparent particle aggregation.

parameters obtained from complex plane plots and dielectric loss factor-frequency plots of W/(S·O) emulsions at various water volume fractions.

In Fig. 4, the theoretical values calculated from eqs. (1) and (6) are compared with the observed values of the limiting dielectric constant at high frequencies, ε_h. The observed values without any nonionic surfactant, especially in the case of fine water particles, are much closer to Wagner's theoretical curve than to Hanai's over a wide range of water volume fraction.

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

Φ	Concn. of surfactant (%)	ε_h	ε_l	f_0 (kHz)	α
0.1	$0^{a)}$	2.805	2.875	83.2	0
	$0^{b)}$	2.791	2.858	125.9	0.056
	0.1	2.762	2.856	1819.7	0
	0.2	2.777	2.963	794.3	0.159
	0.3	2.830	3.118	524.8	0.133
	0.4	2.882	3.210	501.2	0.119
	0.5	2.878	3.200	631.0	0.119
0.2	$0^{a)}$	3.703	3.932	100.0	0
	$0^{b)}$	3.620	3.815	89.1	0.097
	0.1	3.732	4.098	851.1	0.080
	0.2	3.965	5.700	186.2	0.207
	0.3	3.970	6.380	158.5	0.256
	0.4	4.050	6.500	158.5	0.200
	0.5	4.090	6.980	158.5	0.211
0.3	$0^{a)}$	4.96	5.47	112.2	0
	$0^{b)}$	4.75	5.12	100.0	0.037
	0.1	5.10	5.89	631.0	0.080
	0.2	5.30	11.00	70.8	0.297
	0.3	6.00	20.06	50.1	0.181
	0.4	6.50	22.20	50.1	0.167
	0.5	6.50	24.70	63.1	0.180
0.4	$0^{a)}$	6.55	7.50	166.0	0
	$0^{b)}$	6.15	6.88	125.9	0.081

Φ	Concn. of surfactant (%)	ε_h	ε_l	f_0 (kHz)	α
0.4	0.1	6.74	8.93	631.0	0.200
	0.2	8.0	59.5	17.8	0.189
	0.3	9.0	81.0	41.7	0.117
	0.4	9.0	106.0	41.7	0.129
	0.5	9.0	87.0	52.5	0.129
0.5	0[a]	8.30	10.00	199.5	0.044
	0[b]	7.78	9.13	125.9	0.067
	0.1	9.05	11.85	602.6	0.106
	0.2	13.0	123.0	20.0	0.117
	0.3	13.0	174.0	28.2	0.111
	0.4	13.0	157.0	50.1	0.098
	0.5	13.0	129.8	58.9	0.117
0.6	0[a]	10.62	14.02	199.5	0.114
	0[b]	—	—	—	—
	0.1	12.03	17.32	371.5	0.141
	0.2	20.0	162.0	21.4	0.184
	0.3	20.0	590.0	15.8	0.128
	0.4	20.0	316.0	39.8	0.058
	0.5	20.0	250.0	56.2	0.058
0.65	0[a]	12.38	16.80	158.5	0.083

[a] In the case of coarse particles.
[b] In the case of fine particles.

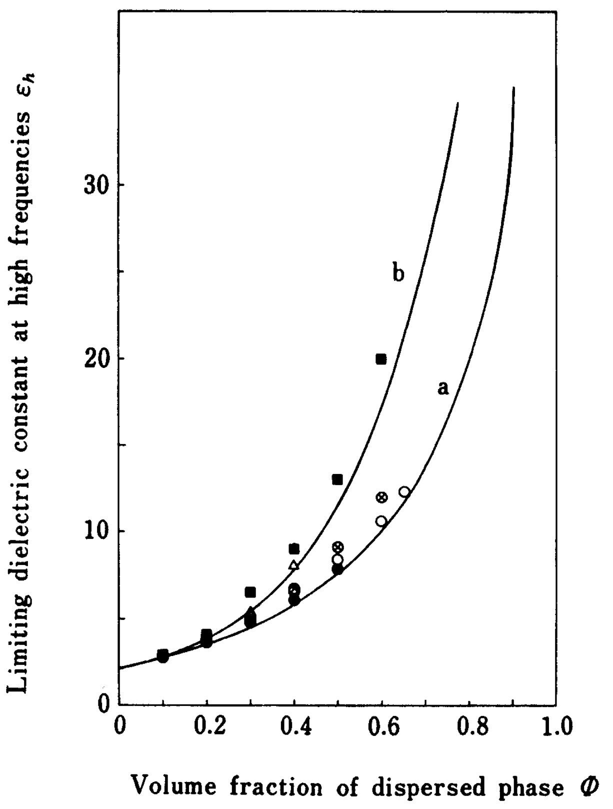


Fig. 4. The Dependence of the Limiting Dielectric Constant at High Frequencies, ε_h, upon Water Volume Fraction of W/(S·O) Emulsions

a: Wagner's theoretical curve according to eq. (1).
b: Hanai's theoretical curve according to eq. (6).
Concentration of nonionic surfactant:
○, 0% (coarse particles); ●, 0% (fine particles);
⊗, 0.1%; △, 0.2%; ▲, 0.3%; □, 0.4%; ■, 0.5%.

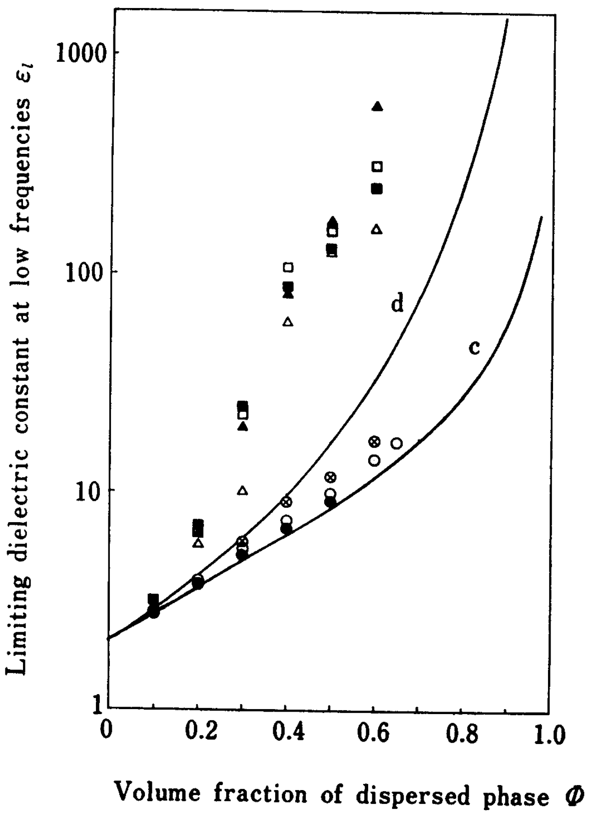


Fig. 5. The Dependence of the Limiting Dielectric Constant at Low Frequencies, ε_l, upon Water Volume Fraction of W/(S·O) Emulsions

c: Wagner's theoretical curve according to eq. (2).
d: Hanai's theoretical curve according to eq. (7).
Concentration of nonionic surfactant:
○, 0% (coarse particles); ●, 0% (fine particles);
⊗, 0.1%; △, 0.2%; ▲, 0.3%; □, 0.4%; ■, 0.5%.

However, those with nonionic surfactant are much closer to Hanai's theoretical curve than to Wagner's over a wide range of water volume fraction.

In Fig. 5, the theoretical values calculated from eqs. (2) and (7) are compared with the observed values of the limiting dielectric constant at low frequencies, ε_l. The observed values without any nonionic surfactant, especially in the case of fine water particles, are also much closer to Wagner's theoretical curve than to Hanai's, but those with nonionic surfactant deviated from both Wagner's and Hanai's theoretical curves. It was found that the observed values with nonionic surfactant were dependent upon the amount of nonionic surfactant and the water volume fraction.

Fig. 6 shows plots of the limiting dielectric constant at low frequencies, ε_l, against surfactant concentration of W/(S·O) emulsions at various water volume fractions. As the amount of surfactant increased, the value of ε_l increased, but in the case of higher volume fractions, where the surfactant concentration was over 0.3% or 0.4%, the value of ε_l gradually decreased.

Discussion

Colloidal silica in the present study is hydrophobic, non-conducting and hyper-fine in particle size. From the characteristics of hydrophobic colloidal silica, it is considered that dispersed particles are immobilized in a hydrophobic colloidal silica–oil gel. It is an unexpected result that the dielectric parameters of W/(S·O) emulsions without surfactant obtained from the present study should satisfy the equations in Wagner's theory better than Hanai's up to a water volume fraction as high as 0.65. In general, the solution given by Wagner's theory[1,2] is not consistent with experimental results especially at high water volume fraction.[9–12] However, since the mutual interaction of dispersed particles may be negligible because of the absence of any aggregation of dispersed particles and large electric resistance among the dispersed particles, it is considered that Wagner's theory is applicable to W/(S·O) emulsions without surfactant.

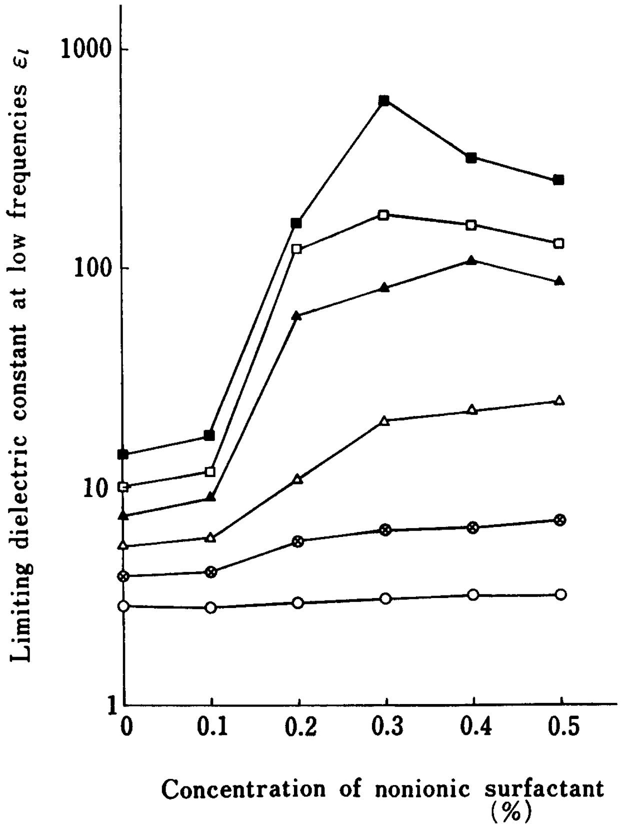


Fig. 6. Plots of the Limiting Dielectric Constant at Low Frequencies, ε_l, Against Surfactant Concentration of W/(S·O) Emulsions at Various Water Volume Fractions

Fraction of dispersed phase:
○, 0.1; ⊗, 0.2; △, 0.3; ▲, 0.4; □, 0.5; ■, 0.6.

Sorbitan sesquioleate, as a nonionic surfactant, is apparently not an agent of aggregation. However, in the present emulsion systems, where water particles are immobilized in hydrophobic colloidal silica–oil gel and particle aggregation is inhibited mechanically, initial addition of sorbitan sesquioleate may weaken the mechanical structure of hydrophobic colloidal silica, which in turn gives rise to aggregation of dispersed particles; further addition of sorbitan sesquioleate produces finer water particles, and aggregation decreases because of the emulsifying effect of sorbitan sesquioleate, as shown in Fig. 3. As shown in Fig. 6, this conclusion may be related to the finding that the values of ε_l decrease over a certain concentration of nonionic surfactant in the case of higher water volume fractions.

The extent of deviation from Wagner's theory was in good agreement with the extent of aggregation as determined by microscopic observation. This information may make it possible to evaluate quantitatively the degree of aggregation as one of the indexes of the colloid-chemical stability of w/o emulsion.

From the theoretical point of view, Wagner's and Hanai's theories are applicable to experimental data only under the condition that mutual interaction of dispersed particles is negligible. It is apparent that w/o emulsions with aggregation show deviation from the theories at lower frequencies. It has been suggested that the interfacial polarization of w/o emulsion is related to ion diffusions on the surfaces of dispersed particles.13) Since the relaxation frequency, f_0, decreased as the degree of particle aggregation increased, and the parameter for the distribution of relaxation frequencies, α, may be related to the magnitude of size distribution of aggregated water particles, as shown in Table I, it may be considered that the dielectric anomaly is related to the anomaly of ion diffusions in interface layers of linked dispersed particles under an alternating current.

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