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Dielectric Studies of Emulsions of Polyol in Hydrophobic Colloidal Silica–Oil Gel[1-3]

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The dielectric relaxation due to the interfacial polarization of emulsions of either polyol or aqueous solutions of polyol in a hydrophobic colloidal silica–oil gel (P/(S·O) emulsions) was investigated over a wide range of volume fractions of the dispersed phase at frequencies ranging from 10 kHz to 3 MHz.

P/(S·O) emulsions without surfactant showed dielectric relaxation, and the limiting dielectric constants at high and low frequencies, ε_h, ε_l, limiting dielectric conductivity at high frequency, κ_h, and relaxation frequency, f_0, were shown to satisfy the equations given by Wagner's theory[4] up to a dispersed phase fraction as high as 0.6. In P/(S·O) emulsions without surfactant, the absence of any particle aggregation was ascertained by microscopic observation. When the polyol was diglycerin, several dispersed phases with different dielectric constants were obtained at different mixing ratios of water and diglycerin. It was found that the values of ε_l changed markedly on the addition of surfactant, increasing as the dielectric constant of the dispersed phase, ε_p, became larger. In P/(S·O) emulsions with surfactant, particle aggregation was found by microscopic observation. The f_0 values of P/(S·O) emulsions with particle aggregation were smaller than in those without particle aggregation, in spite of the increase in electric conductivity of the dispersed phase brought about by the addition of a surfactant. It should be noted that the magnitude of the dielectric anomaly[1] varies with the magnitude of ε_p even if the added amount of surfactant is the same.

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

In the manufacture of water-in-oil type emulsions whose dispersed phase contains proteins such as enzymes and hormones, polyol is useful for the chemical stabilization of the proteins in the water phase.[5]

The dielectric properties of emulsions of water in hydrophobic colloidal silica–oil gel have been elucidated in previous studies.[1-2] In cases where the dispersed phase contains polyol, the dielectric properties are considered to be different from those of plain water emulsions because the dielectric constant of polyol is different from that of water. The purpose of the present study was to investigate the dielectric properties of emulsions of either polyol or aqueous solutions of polyol in hydrophobic colloidal silica–oil gel (P/(S·O) emulsions). In the present study, diglycerin and sorbitol were used as the polyols.

Theoretical

List of Symbols

ε^*: complex dielectric constant
ε: dielectric constant
ε_p: dielectric constant of dispersed phase
ε_m: dielectric constant of continuous phase
ε_h: limiting value of ε at high frequency

ε_l: limiting value of ε at low frequency
κ: electric conductivity ($\mho$/cm)
κ_p: electric conductivity of dispersed phase ($\mho$/cm)
κ_m: electric conductivity of continuous medium ($\mho$/cm)
κ_h: limiting value of κ at high frequency ($\mho$/cm)
κ_l: limiting value of κ at low frequency ($\mho$/cm)
Φ: volume fraction of dispersed phase
f: experimental frequency (Hz)
f_0: relaxation frequency (Hz)
γ: imaginary part of the complex dielectric constant

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

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 for Water-in-Oil Type Emulsions (W/O Emulsions)

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

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

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

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

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. Empirical Formula of Cole and Cole⁶⁾

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

$$\varepsilon^*=\varepsilon-j\gamma=\varepsilon_h+\frac{\varepsilon_l-\varepsilon_h}{1+(jf/f_0)^{1-\alpha}} \quad (0<\alpha<1) \tag{6}$$

Experimental

Materials——Squalane ($\varepsilon_m=2.10$, $\kappa_m=5.64\times 10^{-10}\,\mho$/cm) of commercial grade (Kuraray Co., Ltd.), hydrophobic colloidal silica (AEROSIL R972, Nippon Aerosil Co., Ltd.) with an electric conductivity of $1\times 10^{-13}\,\mho$/cm, a particle size of 10—40 nm and a specific surface area of $120\pm 30\,\mathrm{m^2/g}$ (BET adsorption method), sorbitan sesquioleate (NIKKOL SO-15, Nikko Chemicals Co., Ltd.) of commercial grade, diglycerin (Tokyo Kasei Co., Ltd.) of reagent grade, sorbitol (Towa Chemical Industry Co., Ltd.) of commercial grade, and water obtained by reverse osmosis ($\varepsilon_p=78.58$, $\kappa_p=2.31\times 10^{-6}\,\mho$/cm) were used.

Preparation of P/(S·O) Emulsions——(1) Diglycerin (100% (v/v))/(S·O) Emulsion (Water Weight Fraction of Dispersed Phase: 0): Sorbitan sesquioleate was dissolved in warm squalane (70—80 °C) at a concentration of 0%, 0.5%, 1.0% or 2.0% by weight, and hydrophobic colloidal silica (2.0% by weight) was mixed with the squalane. The oil phase was cooled to room temperature. Diglycerin ($\varepsilon_p=35.03$, $\kappa_p=0.18\times 10^{-6}\,\mho$/cm at 10 kHz) was gently added to the oil phase, which was then vigorously agitated by means of a propeller mixer (max. rpm = 1200) and then a homomixer (max. rpm = 5000) in order to prepare diglycerin (100% (v/v))/(S·O) emulsion with finely dispersed

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particles.

(2) Diglycerin (75% (v/v))/(S·O) Emulsion (Water Weight Fraction of Dispersed Phase: 0.215): In this and the following five paragraphs, the methods of preparation using aqueous solutions of diglycerin or sorbitol, instead of diglycerin alone, are described. The methods employed were otherwise the same as in paragraph (1). First, 75% (v/v) of aqueous solution of diglycerin ($\varepsilon_p=48.45$, $\kappa_p=9.78\times10^{-6}$℧/cm at 1 MHz) was used.

(3) Diglycerin (50% (v/v))/(S·O) Emulsion (Water Weight Fraction of Dispersed Phase: 0.443): In this case, 50% (v/v) of an aqueous solution of diglycerin ($\varepsilon_p=59.76$, $\kappa_p=51.70\times10^{-6}$℧/cm at 1 MHz) was used.

(4) Diglycerin (25% (v/v))/(S·O) Emulsion (Water Weight Fraction of Dispersed Phase: 0.702): Here, 25% (v/v) of an aqueous solution of diglycerin ($\varepsilon_p=68.16$, $\kappa_p=91.24\times10^{-6}$℧/cm at 1 MHz) was used.

(5) Sorbitol (75% (w/v))/(S·O) Emulsion (Water Weight Fraction of Dispersed Phase: 0.395): Next, 75% (w/v) of an aqueous solution of sorbitol ($\varepsilon_p=66.01$, $\kappa_p=1.47\times10^{-6}$℧/cm at 1 MHz) was used.

(6) Sorbitol (50% (w/v))/(S·O) Emulsion (Water Weight Fraction of Dispersed Phase: 0.570): Then, 50% (w/v) of an aqueous solution of sorbitol ($\varepsilon_p=71.35$, $\kappa_p=3.06\times10^{-6}$℧/cm at 1 MHz) was used.

(7) Sorbitol (25% (w/v))/(S·O) Emulsion (Water Weight Fraction of Dispersed Phase: 0.766): Finally, 25% (w/v) of an aqueous solution of sorbitol ($\varepsilon_p=74.59$, $\kappa_p=5.67\times10^{-6}$℧/cm at 1 MHz) was used.

Preparation of Emulsion of Water in a Hydrophobic Colloidal Silica–Oil Gel (W/(S·O) Emulsion)——W/(S·O) emulsion was prepared as described in our previous reports.[1-2)]

Measurements——Both capacitance and conductance were measured over frequencies ranging from 10 kHz to 3 MHz by means of a capacitance–conductance bridge, as in the previous study.[3)]

Results

In Fig. 1, for diglycerin (50% (v/v))/(S·O) emulsion without any surfactant, and in Fig. 2, for sorbitol (75% (w/v))/(S·O) emulsion without any surfactant, the theoretical values calculated from Eqs. 1, 2, 3 and 5 are compared with the observed values of limiting dielectric constants at high and low frequencies, ε_h, ε_l, limiting electric conductivity at high frequency, κ_h, and relaxation frequency, f_0. The observed values were shown to satisfy the equations given by Wagner's theory up to a dispersed phase fraction as high as 0.6, independent of the size of the dispersed particles. The values of limiting electric conductivity at low frequency, κ_l, could not be obtained because they were too small to be determined by the apparatus employed.

The dielectric parameters of other P/(S·O) emulsions in Table I gave plots similar to those shown in Figs. 1 and 2.

Figure 3 showed microphotographs and the particle size distribution of diglycerin (100% (v/v))/(S·O) emulsion, diglycerin (75% (v/v))/(S·O) emulsion, diglycerin (50% (v/v))/(S·O) emulsion and diglycerin (25% (v/v))/(S·O) emulsion in which the volume fraction of the dispersed phase was 0.3 at various concentrations of surfactant. It was found that particle aggregation occurred in the emulsion and that the emulsifying effect of surfactant, the micronizing action on dispersed particles due to the decrease of interfacial tension, became more distinct with increasing ε_p.

Figure 4 showed the complex plane plots of the dielectric constant, ε, and dielectric loss factor, γ, of the P/(S·O) emulsions in Fig. 3. It was found that the values of ε_l rose as ε_p increased in the presence of surfactant, but decreased with increasing surfactant concentration in the P/(S·O) emulsions with larger ε_p.

Table II summarizes the values of dielectric parameters of P/(S·O) emulsions in which the volume fraction of the dispersed phase is 0.3 at various concentrations of surfactant, obtained from complex plane plots and from plots made of dielectric loss factor against frequency in accordance with the method described in a previous study.[2)] In the emulsions whose dispersed phase was an aqueous solution of sorbitol, the values of ε_l increased with rise in the value of ε_p analogous to the case of the emulsions whose dispersed phase was an aqueous solution of diglycerin.

The relaxation frequency, f_0, of P/(S·O) emulsions with particle aggregation was smaller than without particle aggregation, in spite of the increase in the electric conductivity of the

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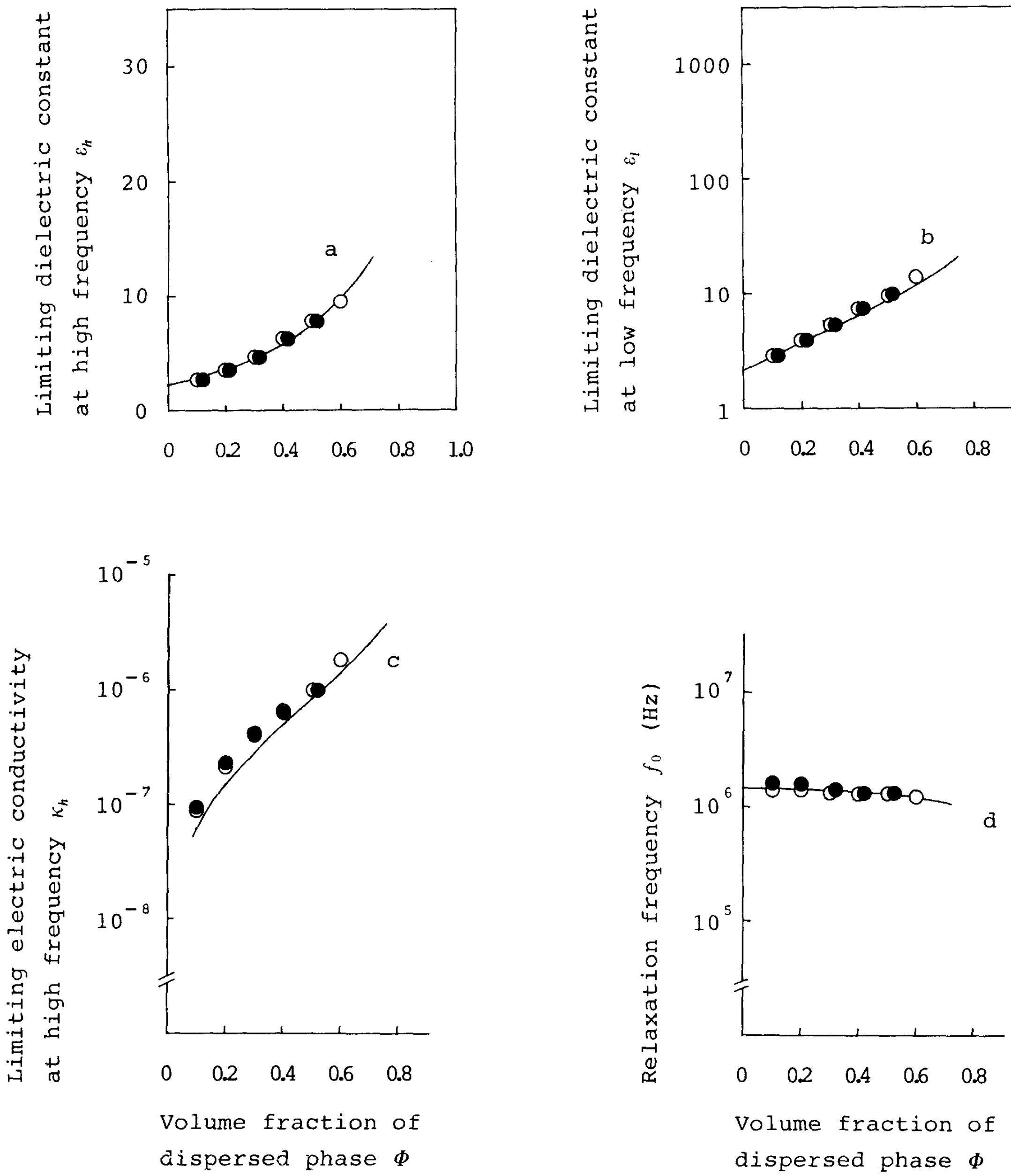

Fig. 1. The Dependence of the Limiting Dielectric Constants at High and Low Frequencies, ε_h, ε_l, the Limiting Electric Conductivity at High Frequency, κ_h, and Relaxation Frequency, f_0, upon the Volume Fraction of the Dispersed Phase of Diglycerin (50% (v/v))/(S·O) Emulsion

a: Wagner's theoretical curve according to Eq. 1. b: Wagner's theoretical curve according to Eq. 2. c: Wagner's theoretical curve according to Eq. 3. d: Wagner's theoretical curve according to Eq. 5.

○, coarse particles; ●, fine particles.

The range of average size of dispersed particle: coarse particles, 11.17—25.89 μm; fine particles, 3.07—6.13 μm.

dispersed phase generated by the addition of surfactant.

Discussion

From the results shown in Figs. 1, 2 and Table I, it was found that the observed values of

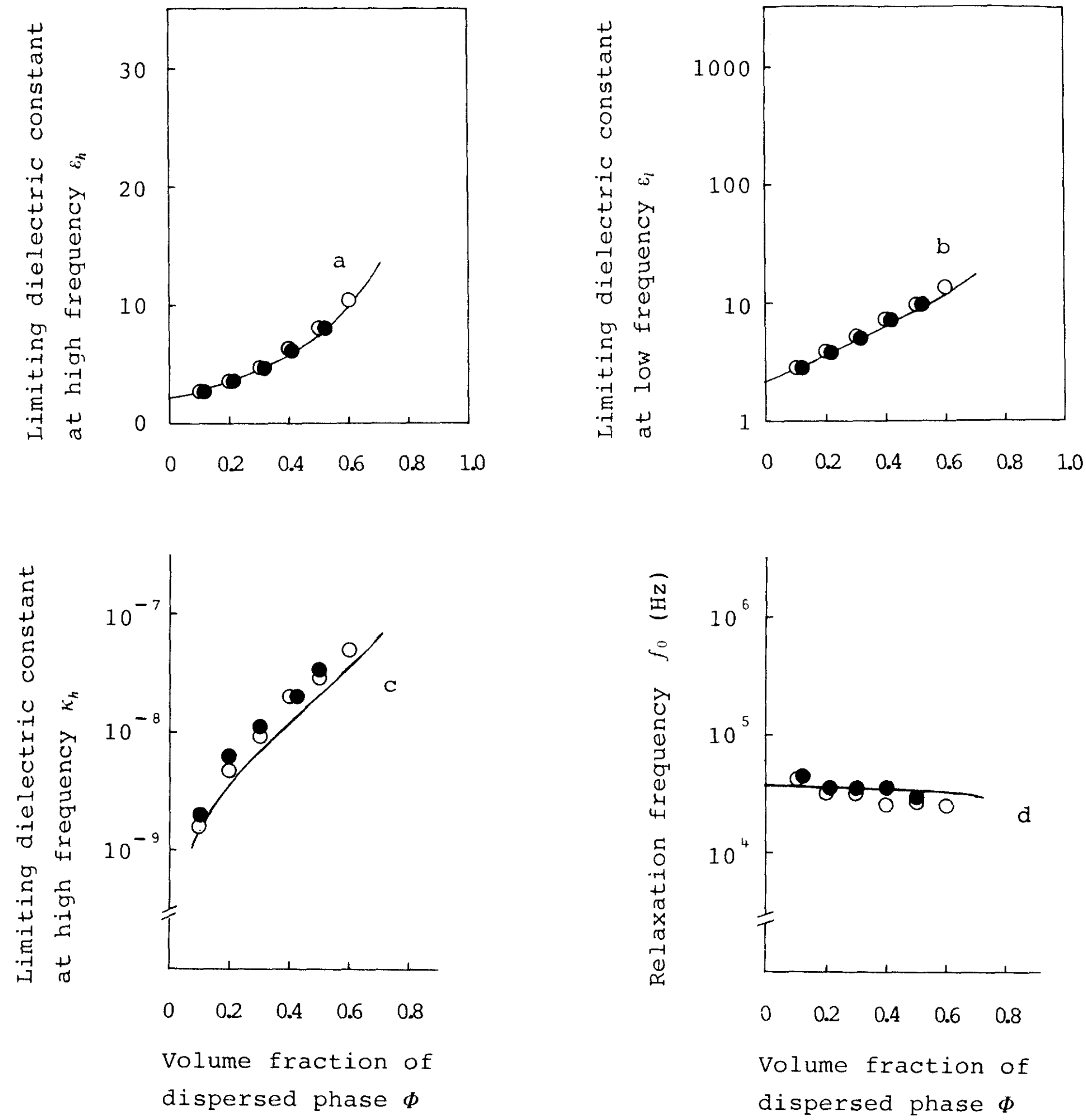

Fig. 2. The Dependence of the Limiting Dielectric Constants at High and Low Frequencies, ε_h, ε_l, the Limiting Electric Conductivity at High Frequency, κ_h, and the Relaxation Frequency, f_0, upon the Volume Fraction of the Dispersed Phase of Sorbitol (75% (w/v))/(S·O) Emulsion

a: Wagner's theoretical curve according to Eq. 1. b: Wagner's theoretical curve according to Eq. 2. c: Wagner's theoretical curve according to Eq. 3. d: Wagner's theoretical curve according to Eq. 5.

○, coarse particles; ●, fine particles.

The range of average size of dispersed particle: coarse particles, 21.10—47.12 μm; fine particles, 6.20—8.71 μm.

dielectric properties of P/(S·O) emulsions whose dispersed phase had different dielectric constants and electric conductivities were in good agreement with Wagner's theoretical curves, as was the case for W/(S·O) emulsion.[1] It is considered that this result may also be applicable to other polyols.

In the previous study,[1] it was found that the degree of particle aggregation in W/(S·O) emulsions increased with increasing surfactant. However in this study, the degree of particle aggregation in P/(S·O) emulsion at constant surfactant concentration was found to increase with increasing ε_p due to dilution with water. In the case of sorbitol (75% (w/v))/(S·O)

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Table I. Values of ε_h, ε_l, α, κ_h and f_0 of P/(S·O) Emulsions at Various Volume Fractions of the Dispersed Phase

P/(S·O) emulsion	Φ	ε_h	ε_l	α	$\log \kappa_h$ (℧/cm)	f_0 (kHz)
Diglycerin	0.1	2.718[a)]	2.885	0	−8.88	6.8
(100% (v/v))/		2.726[b)]	2.897	0	−8.83	7.6
(S·O) emulsion	0.2	3.518	4.002	0	−8.50	7.6
		3.562	4.050	0	−8.43	8.3
$\varepsilon_p = 35.03$	0.3	4.09	5.95	0	−8.30	5.0
		4.68	5.62	0	−8.30	7.6
	0.4	5.97	8.40	0	−8.03	5.0
		5.85	7.40	0	−8.13	7.6
	0.5	7.68	11.62	0	−7.80	5.1
		7.15	9.97	0	−7.82	7.6
	0.6	9.22	14.59	0.033	−7.65	5.6
		—	—	—	—	—
Diglycerin	0.1	2.737	2.850	0	−7.55	3.2×10^2
(75% (v/v))/		2.737	2.850	0	−7.62	3.2×10^2
(S·O) emulsion	0.2	3.568	3.912	0	−7.12	3.2×10^2
		3.479	3.812	0	−7.20	3.2×10^2
$\varepsilon_p = 48.45$	0.3	4.62	5.27	0	−6.83	3.0×10^2
		4.27	4.89	0	−6.97	3.0×10^2
	0.4	5.93	7.27	0	−6.63	2.7×10^2
		5.92	7.26	0	−6.70	2.8×10^2
	0.5	7.75	9.95	0	−6.35	2.5×10^2
		7.76	10.15	0	−6.43	2.8×10^2
	0.6	9.72	13.90	0.022	−6.18	2.5×10^2
		—	—	—	—	—
Diglycerin	0.1	2.717	2.822	0	−7.05	1.4×10^3
(50% (v/v))/		2.717	2.840	0	−7.03	1.6×10^3
(S·O) emulsion	0.2	3.582	3.868	0	−6.68	1.4×10^3
		3.532	3.820	0	−6.63	1.6×10^3
$\varepsilon_p = 59.76$	0.3	4.68	5.23	0	−6.40	1.3×10^3
		4.62	5.17	0	−6.38	1.4×10^3
	0.4	6.13	7.18	0	−6.18	1.3×10^3
		6.15	7.13	0	−6.21	1.3×10^3
	0.5	7.77	9.47	0	−6.00	1.3×10^3
		7.73	9.77	0	−6.00	1.3×10^3
	0.6	9.50	13.75	0.042	−5.73	1.3×10^3
		—	—	—	—	—
Diglycerin	0.1	2.693	2.822	0	−6.82	2.5×10^3
(25% (v/v))/		2.681	2.806	0	−6.88	2.5×10^3
(S·O) emulsion	0.2	3.553	3.862	0	−6.40	3.6×10^3
		3.478	3.762	0	−6.45	4.0×10^3
$\varepsilon_p = 68.16$	0.3	4.63	5.28	0	−6.10	2.6×10^3
		4.35	4.94	0	−6.20	3.2×10^3
	0.4	6.35	7.12	0	−6.00	1.3×10^3
		6.27	7.03	0	−6.05	1.3×10^3
	0.5	8.20	9.87	0	−5.88	1.3×10^3
		8.12	9.70	0	−5.92	1.3×10^3
	0.6	10.05	13.17	0.023	−5.78	1.5×10^3
		—	—	—	—	—
Sorbitol	0.1	2.750	2.826	0.030	−8.80	41.69
(75% (w/v))/		2.727	2.821	0.091	−8.70	44,67
(S·O) emulsion	0.2	3.653	3.929	0	−8.32	31.62
		3.587	3.820	0.011	−8.20	35.48

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TABLE I. (continued)

P/(S·O) emulsion	Φ	ε_h	ε_l	α	$\log \kappa_h$ (℧/cm)	f_0 (kHz)
$\varepsilon_p=66.01$	0.3	4.745	5.258	0	−8.03	31.60
		4.640	5.090	0	−7.95	37.20
	0.4	6.38	7.45	0	−7.70	25.12
		6.13	7.10	0.046	−7.70	35.48
	0.5	8.02	9.80	0	−7.53	26.92
		8.02	9.75	0	−7.46	30.20
	0.6	10.49	13.53	0	−7.30	25.12
Sorbitol (50% (w/v))/ (S·O) emulsion	0.1	2.838	2.753	0	−8.30	63.1
		2.819	2.741	0	−8.40	75.9
	0.2	3.700	3.952	0	−7.90	67.6
		3.608	3.820	0.033	−7.78	89.1
$\varepsilon_p=71.35$	0.3	4.78	5.27	0	−7.70	63.1
		4.57	4.98	0	−7.65	69.2
	0.4	6.28	7.19	0	−7.43	63.1
		5.98	6.77	0	−7.43	67.6
	0.5	8.06	9.87	0.078	−7.20	60.3
		7.90	9.36	0	−7.23	66.1
	0.6	10.90	14.03	0.022	−6.95	58.9
Sorbitol (25% (w/v))/ (S·O) emulsion	0.1	2.759	2.839	0	−8.23	100.0
		2.713	2.783	0	−7.92	239.9
	0.2	3.675	3.900	0	−7.73	89.1
		3.569	3.757	0	−7.62	169.8
$\varepsilon_p=74.59$	0.3	4.85	5.32	0	−7.53	100.0
		4.77	5.21	0	−7.32	141.3
	0.4	6.38	7.30	0	−7.33	83.2
		6.37	7.25	0	−7.16	131.8
	0.5	8.25	9.83	0	−7.03	100.0
		7.97	9.47	0	−6.93	125.9
	0.6	10.83	13.82	0.047	−6.80	107.2

a) Coarse particles. *b*) Fine particles.

emulsion, whose ε_p is the same as that of diglycerin (25% (v/v))/(S·O) emulsion, the value of ε_l of the emulsion when the surfactant concentration was 0.5% differed from that of diglycerin (25% (v/v))/(S·O) emulsion. It is thought that the value of ε_l is affected by the state of orientation of the surfactant molecules at the interface based on the magnitude of hydrophilic interaction between the hydrophilic moiety of surfactant molecules and dispersed phases.

From the previous[1-3] and present studies, the factors relating to the magnitude of the value of ε_l are considered to be: (1) the size of aggregated particle clusters and (2) the thickness of the interface layer after particle aggregation. The value of ε_l is postulated to increase with the size of aggregated particle clusters (a "plus effect"), and to decrease as the thickness of the interface layer formed by many surfactant molecules increases (a "minus effect"). For a more detailed explanation of the above hypothesis, see the schematic illustration of the state of dispersion in P/(S·O) emulsions with and without surfactants shown in Fig. 5. Colloidal silica is hydrophobic, non-conducting and hyper-fine in particle size. From the characteristics of hydrophobic colloidal silica, dispersed particles are immobilized in a hydrophobic colloidal silica–oil structure without any surfactant. In Fig. 5-(a), hydrophobic colloidal silica particles coated dispersed particles which are separated from each other, and dispersed particle

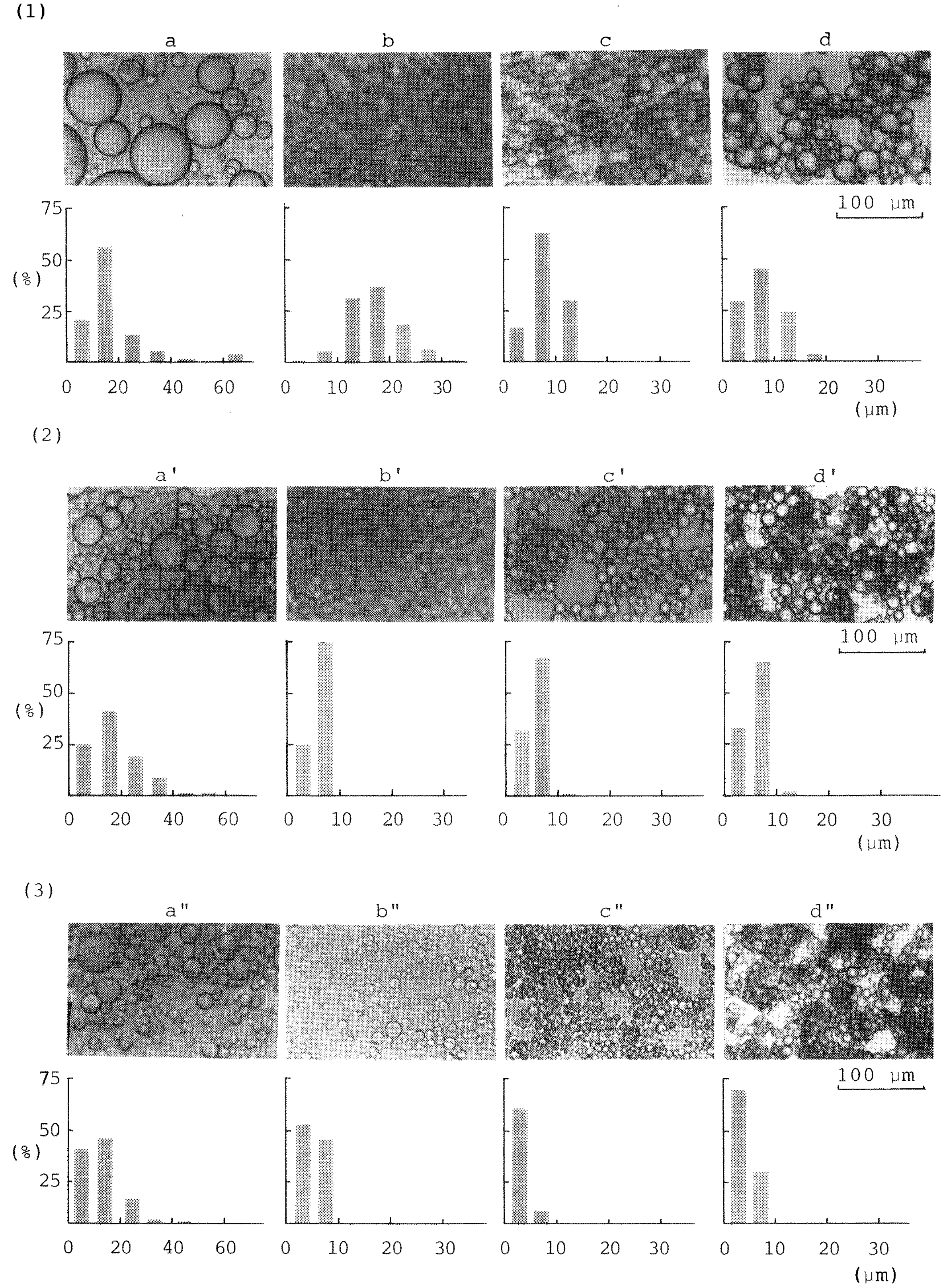

Fig. 3. Microphotographs and Particle Size Distributions of P/(S·O) Emulsions ($\Phi=0.3$) at Various Concentrations of Surfactant

Concentration of surfactant: (1) 0.5%, (2) 1.0%, (3) 2.0%.

a, a′ and a″: Diglycerin (100% (v/v))/(S·O) emulsion. b, b′ and b″: Diglycerin (75% (v/v))/(S·O) emulsion. c, c′ and c″: Diglycerin (50% (v/v))/(S·O) emulsion. d, d′ and d″: Diglycerin (25% (v/v))/(S·O) emulsion.

Average size of dispersed particles: a, 18.90 µm; a′, 18.43 µm; a″, 12.82 µm. b, 17.09 µm; b′, 13.26 µm; b″, 10.16 µm. c, 14.63 µm; c′, 12.08 µm; c″, 7.18 µm. d, 15.61 µm; d′, 12.04 µm; d″, 8.43 µm.

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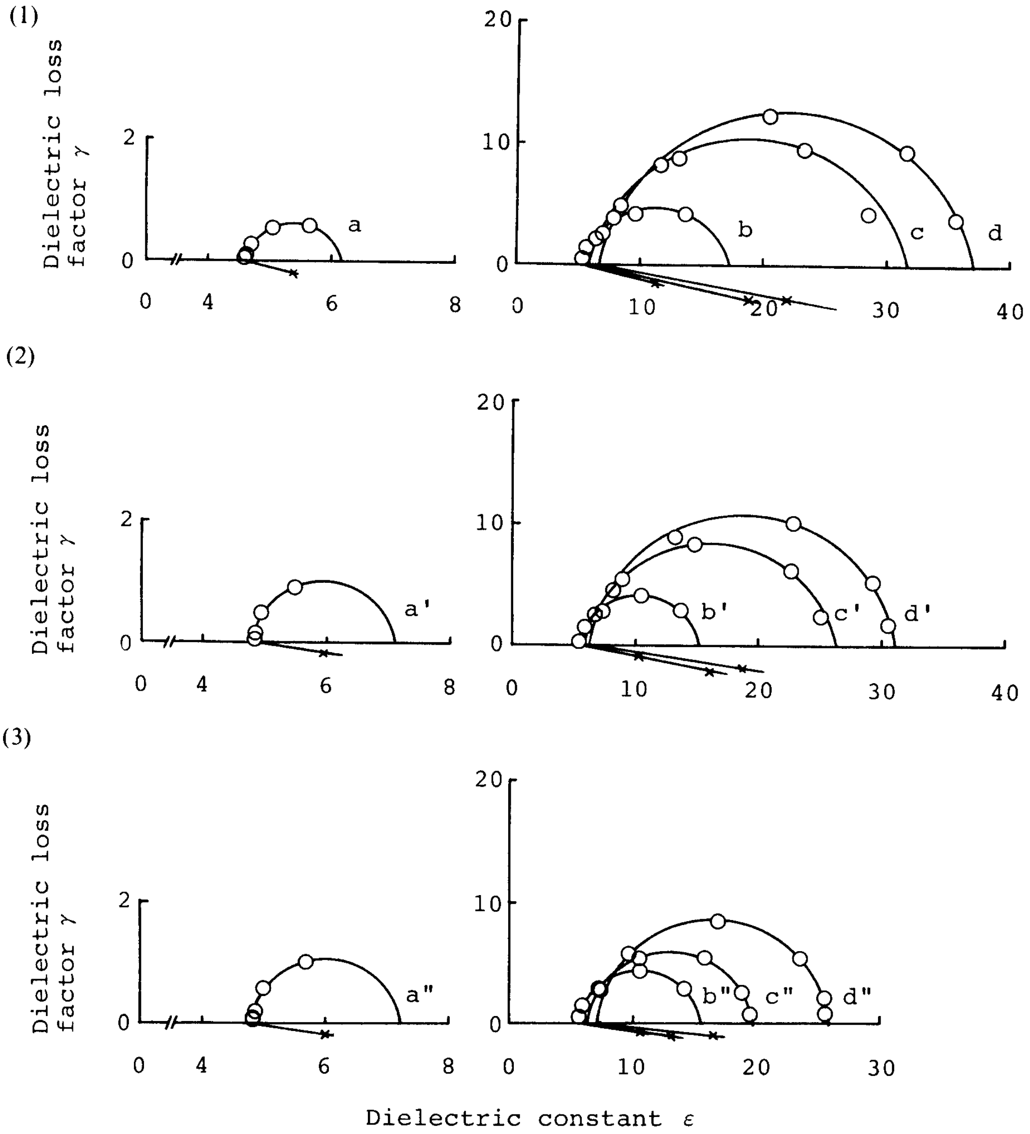

Fig. 4. Complex Plane Plots of ε and γ of P/(S·O) Emulsions at Various Concentrations of Surfactant

Concentration of surfactant: (1) 0.5%, (2) 1.0%, (3) 2.0%.
a, a′ and a″: Diglycerin (100% (v/v))/(S·O) emulsion. b, b′ and b″: Diglycerin (75% (v/v))/(S·O) emulsion. c, c′ and c″: Diglycerin (50% (v/v))/(S·O) emulsion. d, d′ and d″: Diglycerin (25% (v/v))/(S·O) emulsion.

aggregation is inhibited mechanically. Here, the magnitude of the dielectric constant of the dispersed particles is independent of the state of particle dispersion. In Fig. 5-(b), particle aggregations are caused by the addition of surfactant. In this case, although a thin surfactant layer, instead of hydrophobic colloidal silica particles, is present on the surface of the dispersed particles, the value of ε_l increases, because the plus effect predominates over the minus effect caused by the surfactant molecules. In Fig.5-(c), the thickness of the thin surfactant layer between aggregated particles increases on the addition of large amount of surfactant, and then the value of ε_l becomes smaller than that in Fig. 5-(b). Here the distance between the aggregated particles is affected by the physicochemical properties, such as the magnitude of dielectric constant related to London–van der Waals' force and the state of orientation of the surfactant molecules on the interface layer of dispersed particles. In P/(S·O) emulsions keeping the particle size and surfactant concentration constant, the distance

TABLE II. Values of ε_h, ε_l, α and f_0 of P/(S·O) Emulsions ($\Phi=0.3$) at Various Concentrations of Surfactant

P/(S·O) emulsion	Concentration of surfactant (%)	ε_h	ε_l	α	f_0 (kHz)
Diglycerin	0.5	4.58	6.17	0.153	5.0
(100% (v/v))/(S·O)	1.0	4.81	7.09	0.094	5.0
emulsion ($\varepsilon_p=35.03$)	2.0	4.80	7.21	0.092	6.3
Diglycerin	0.5	5.2	17.3	0.152	17.8
(75% (v/v))/(S·O)	1.0	5.2	15.2	0.122	26.3
emulsion ($\varepsilon_p=48.45$)	2.0	5.5	15.5	0.091	31.6
Diglycerin	0.5	5.9	31.7	0.142	50.1
(50% (v/v))/(S·O)	1.0	5.8	26.3	0.123	70.8
emulsion ($\varepsilon_p=59.76$)	2.0	6.2	19.3	0.097	169.8
Diglycerin	0.5	6.8	37.0	0.114	74.1
(25% (v/v))/(S·O)	1.0	6.3	31.1	0.092	151.4
emulsion ($\varepsilon_p=68.16$)	2.0	7.0	25.9	0.069	331.1
Sorbitol	0.5	5.7	21.7	0.150	11.2
(75% (w/v))/(S·O)	1.0	6.2	30.0	0.131	14.8
emulsion ($\varepsilon_p=66.01$)	2.0	6.2	29.6	0.140	23.4
Sorbitol	0.5	6.2	30.0	0.144	22.4
(50% (w/v))/(S·O)	1.0	6.2	32.0	0.133	39.8
emulsion ($\varepsilon_p=71.35$)	2.0	6.5	30.0	0.094	89.1
Sorbitol	0.5	6.7	46.3	0.121	35.5
(25% (w/v))/(S·O)	1.0	6.3	34.6	0.123	75.9
emulsion ($\varepsilon_p=74.59$)	2.0	7.3	32.1	0.070	199.5

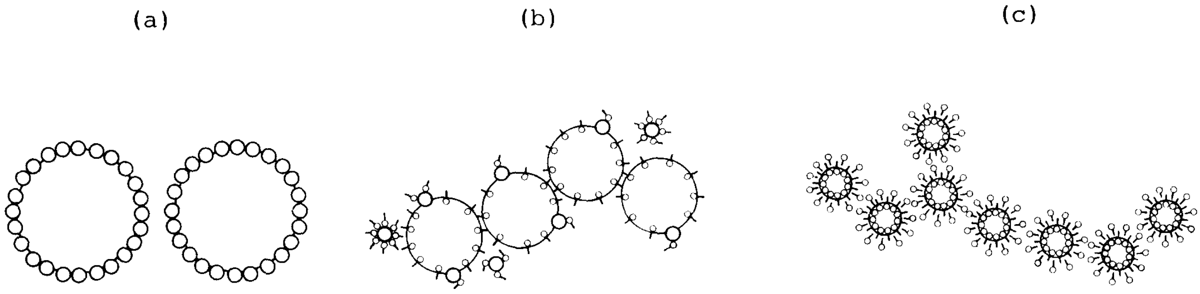

Fig. 5. Schematic Illustrations of Interface Layers of Dispersed Particles in P/(S·O) Emulsions with and without Surfactant

Concentration of surfactant: (a) none, (b) low, (c) high.

(a) The surface of the dispersed particles is occupied completely by hydrophobic colloidal silica particles.

(b) Hydrophobic colloidal silica particles on the surface of dispersed particles are coated by surfactant molecules and removed from the dispersed particles. Surfactant molecules replace the hydrophobic colloidal silica particles on the surface of the dispersed particles, but have poorer dispersing effects, and so aggregation results.

(c) Hydrophobic colloidal silica particles are coated by surfactant molecules and adsorption on the surface of the dispersed particles cannot take place as it can in the case of (b). A large amount of surfactant molecules is adsorbed on the surface of the dispersed particles.

The size of dispersed particles becomes smaller with increasing concentration of surfactant based on the emulsifying effect of surfactant. The size of aggregated particle clusters in (c) is larger than that in (b) and the thickness of the interface layer between the aggregated particles in (c) is also larger than that in (b).

○, hydrophobic colloidal silica particle; -o, surfactant molecule.

between the aggregated particles with large dielectric constant becomes smaller than that in the case with small dielectric constant.

In the emulsion whose dispersed phase was an aqueous solution of sorbitol, the minus

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effect of the surfactant was shown only in sorbitol (25% (w/v))/(S·O) emulsion. In sorbitol (75% (w/v))/(S·O) or sorbitol (50% (w/v))/(S·O) emulsions, it is considered that the minus effect is more than counteracted by the increase of the plus effect based on the increase of particle cluster size.

The size of the aggregated particle clusters can be observed by microscopic examination, but it is not possible to measure the thickness of the surfactant layer between aggregated particles. However, if the above hypothesis were correct, the thickness of the surfactant layer, when the size of dispersed particles is kept constant, could be estimated by means of dielectric measurements.

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