Chem. Pharm. Bull.
33(12)5484—5494(1985)

Effects of Particle Size and Stabilizing Agents upon Dielectric Properties of Water-in-Oil Type Emulsions[1-4]

HIDEO KANEKO* and SADAO HIROTA

Pharmaceutical Formulation Research Center, Research Institute,
Daiichi Seiyaku Co., Ltd., 16–13, Kitakasai 1-chome,
Edogawa-ku, Tokyo 134, Japan

(Received April 11, 1985)

The dielectric relaxation due to the interfacial polarization of water-in-oil type emulsions (W/O emulsions) was investigated at frequencies ranging from 10 kHz to 3 MHz.

In preparing W/O emulsions, differences of mixing or micronizing efficiency arise between bench-scale and production-scale apparatus owing to the difference of mixing or shear rate. Therefore, the size of dispersed particles can be regarded as an index of the mechanical effect arising from the mixing apparatus. Firstly, the relationship between the size of dispersed particles and the dielectric properties of W/O emulsions was investigated. It was found that 1 d after preparation, the degree of particle aggregation leveled off and became fairly steady, and the values, for W/O emulsions with coarse particles, of the limiting dielectric constant at low frequency, ε_l, and parameter α, indicating the distribution of relaxation frequencies, determined from complex plane plots, were greater than for those for emulsions with fine particles. The value of ε_l is thought to be related to the thickness of the surfactant layer between aggregated particles rather than to the size of particle clusters, but the relation becomes more ambiguous as the concentration of surfactant becomes higher. Relaxation frequency, f_0, decreases with increasing particle aggregation.

Secondly, in order to obtain good emulsification in the W/O emulsion, the stabilizing effects of 23 stabilizing agents upon the state of dispersion of W/O emulsion were evaluated by dielectric measurement. Primary emulsifiers for micronizing dispersed particles, such as polyoxyethylene (POE) (6) sorbitan monooleate, secondary emulsifiers for protecting interface membranes, such as phytosterol, and lipojelling additives, such as aluminum stearate, decreased the value of ε_l of W/O emulsions.

From the present study, it was concluded that dielectric evaluation can be applied to examine the mechanical effects on emulsification and to as an aid in the selection of optimum additives and vehicles for a W/O emulsion.

Keywords——interfacial polarization; dielectric relaxation; dielectric measurement; colloid-chemical stability; aggregation; W/O emulsion; stabilizing agent

The dielectric properties of emulsions of water, polyols and aqueous solutions of polyols in hydrophobic colloidal silica–oil gel have been investigated.[1-4] Hydrophobic colloidal silica has been suitable for the purposes of the previous investigations, but it cannot be used generally as an emulsifier for preparing any water-in-oil type emulsion.

In the present study, the dielectric properties of water-in-oil type emulsions without hydrophobic colloidal silica (W/O emulsions) were studied keeping two practical problems in mind. Firstly, the size of dispersed particles affects the viscosity regarded as an important property of a W/O emulsion.[5] From this point of view, it is necessary to obtain the same size of dispersed particles between bench-scale and production-scale preparations by the control of mixing rate or mixing time. The effect of the size of dispersed particles in the W/O emulsions upon the dielectric properties, especially on the limiting dielectric constant at low frequency, ε_l, and the parameter of distribution of relaxation frequencies, α, were therefore investigated.

Secondly, the HLB (hydrophilic–lipophilic balance) method is not very useful for preparing W/O emulsions, because the range of HLB values in which good W/O emulsions can be prepared is narrow (between 3 and 6—7),[6)] and HLB is not generally such a predominant factor in the stability of W/O emulsions as it is in the case of oil-in-water type emulsions. In order to obtain good emulsification in W/O emulsions, it is necessary to use stabilizing agents——primary emulsifiers for micronizing dispersed particles, secondary emulsifiers for protecting interfacial membranes and lipojelling additives for preventing particle aggregation. The effect of these stabilizing agents upon the dielectric properties of W/O emulsions was also examined.

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 (℧/cm)
κ_p: electric conductivity of dispersed phase (℧/cm)
κ_m: electric conductivity of continuous phase (℧/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 frequency, determined from complex plane plots

Empirical Formula of Cole and Cole[7)]

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

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

Experimental

Materials——Squalane ($\varepsilon_m=2.10$, $\kappa_m=5.64\times 10^{-10}$ ℧/cm) of commercial grade (Kuraray Co., Ltd.), sorbitan sesquioleate (NIKKOL SO-15, Nikko Chemicals Co., Ltd.) of commercial grade, various stabilizing agents (see Table I) and water obtained by reverse osmosis ($\varepsilon_p=78.58$, $\kappa_p=2.31\times 10^{-6}$ ℧/cm) were used.

Preparation of W/O Emulsion——Sorbitan sesquioleate 0.5 g, 1.0 g or 2.0 g was dissolved in warm squalane (70—80 °C) (total volume: 70 ml). The squalane was cooled to room temperature. Then, 30 ml of water was gently added to the oil phase with vigorous agitation by means of a propeller mixer (max. rpm = 1200) for 1 min or 10 min. Coarse particles were obtained on agitation for 1 min and fine particles were obtained on agitation for 10 min.

Preparation of W/O Emulsion Containing Additional Stabilizing Agents——Various stabilizing agents (see Table I) at concentrations of 0.1%, 0.2% or 0.5% by weight were dissolved in warm squalane (70—80 °C) containing 0.5% sorbitan sesquioleate (total volume: 70 ml). The squalane was cooled to room temperature. Finally, 30 ml of water was gently added to the oil phase and the whole was vigorously agitated by means of a propeller mixer (max. rpm = 1200) for 10 min.

Measurement——Both capacitance and conductance were measured over the frequency range from 10 kHz to

TABLE I. List of Stabilizing Agents

Stabilizing agent	Trademark/grade	HLB[a] value	Manufacturer
Primary emulsifiers			
Sorbitan monooleate	NIKKOL SO-10	4.3	Nikko Chemicals Co., Ltd.
POE[b] (6) sorbitan monooleate	NIKKOL TO-106	10.0	Nikko Chemicals Co., Ltd.
Diglyceryl monooleate	NIKKOL DGMO-C	5.5	Nikko Chemicals Co., Ltd.
Diglyceryl dioleate	NIKKOL DGDO	7.5	Nikko Chemicals Co., Ltd.
Decaglyceryl dioleate	NIKKOL Decaglyn 2-O	10.0	Nikko Chemicals Co., Ltd.
Decaglyceryl trioleate	NIKKOL Decaglyn 3-O	6.5	Nikko Chemicals Co., Ltd.
Decaglyceryl pentaoleate	NIKKOL Decaglyn 5-O	4.0	Nikko Chemicals Co., Ltd.
POE (2) oleyl ether	NIKKOL BO-2	7.5	Nikko Chemicals Co., Ltd.
POE (7) oleyl ether	NIKKOL BO-7	10.5	Nikko Chemicals Co., Ltd.
POE (2) monooleate	NIKKOL MYO-2	4.5	Nikko Chemicals Co., Ltd.
POE (6) monooleate	NIKKOL MYO-6	8.5	Nikko Chemicals Co., Ltd.
Secondary emulsifiers			
Cholesterol	Reagent grade		Nikko Chemicals Co., Ltd.
Cholesteryl stearate	Reagent grade		Nikko Chemicals Co., Ltd.
Phytosterol	Reagent grade		Eisai Co., Ltd.
POE (10) phytosterol	NIKKOL BPS-10	12.5	Nikko Chemicals Co., Ltd.
POP–POE–POP copolymer	UNISAFE IP-225		Nippon Oil & Fats Co., Ltd.
Lanolin	SPM		Takasago Perfumery Co., Ltd.
Liquid lanolin	Reagent grade		Nikko Chemicals Co., Ltd.
L-α-dipalmitoyl phosphatidyl choline	Reagent grade (content: >99%)		Nippon Oil & Fats Co., Ltd.
Lipojelling additives			
Aluminum monostearate	Reagent grade		Kishida Chemical Co., Ltd.
Paraffin	Reagent grade 135 °F		Nippon Oil Co., Ltd.
Cetanol	Reagent grade		Nikko Chemicals Co., Ltd.
Bephenyl alcohol	Reagent grade		Nikko Chemicals Co., Ltd.

a) Hydrophilic–lipophilic balance. *b*) Polyoxyethylene.

3 MHz by means of a capacitance–conductance bridge, as in the previous study.[1]

Results

Figure 1 shows microphotographs and plots of ε_l and $\log f_0$ against storage time of W/O emulsions with coarse particles and fine particles immediately after preparation and 1, 2 and 7 d after preparation at various concentrations of sorbitan sesquioleate. It was found that the value of ε_l rapidly increased up to 1 d after preparation, and then decreased or increased slowly during storage. The value of ε_l where the particles were fine was greater than in the case of coarse particles immediately after preparation, and this tendency was more marked at lower concentrations of sorbitan sesquioleate. The differences in the values of ε_l due to the differences of particle size in the dispersed phase were apparent at various concentrations of sorbitan sesquioleate, and the higher the concentration was, the smaller the ε_l value both with coarse and with fine particles. The value of the relaxation frequency, f_0, decreased as the particle aggregation increased.

Table II summarizes the values of the dielectric parameters of the W/O emulsions with coarse particles and with fine particles at various storage times. Parameter α of the W/O emulsions with coarse particles was larger than when the particles were fine, 1 d after preparation.

Table III summarizes the values of the dielectric properties of W/O emulsions containing 23 stabilizing agents. Several primary emulsifiers with micronizing action, such as po-

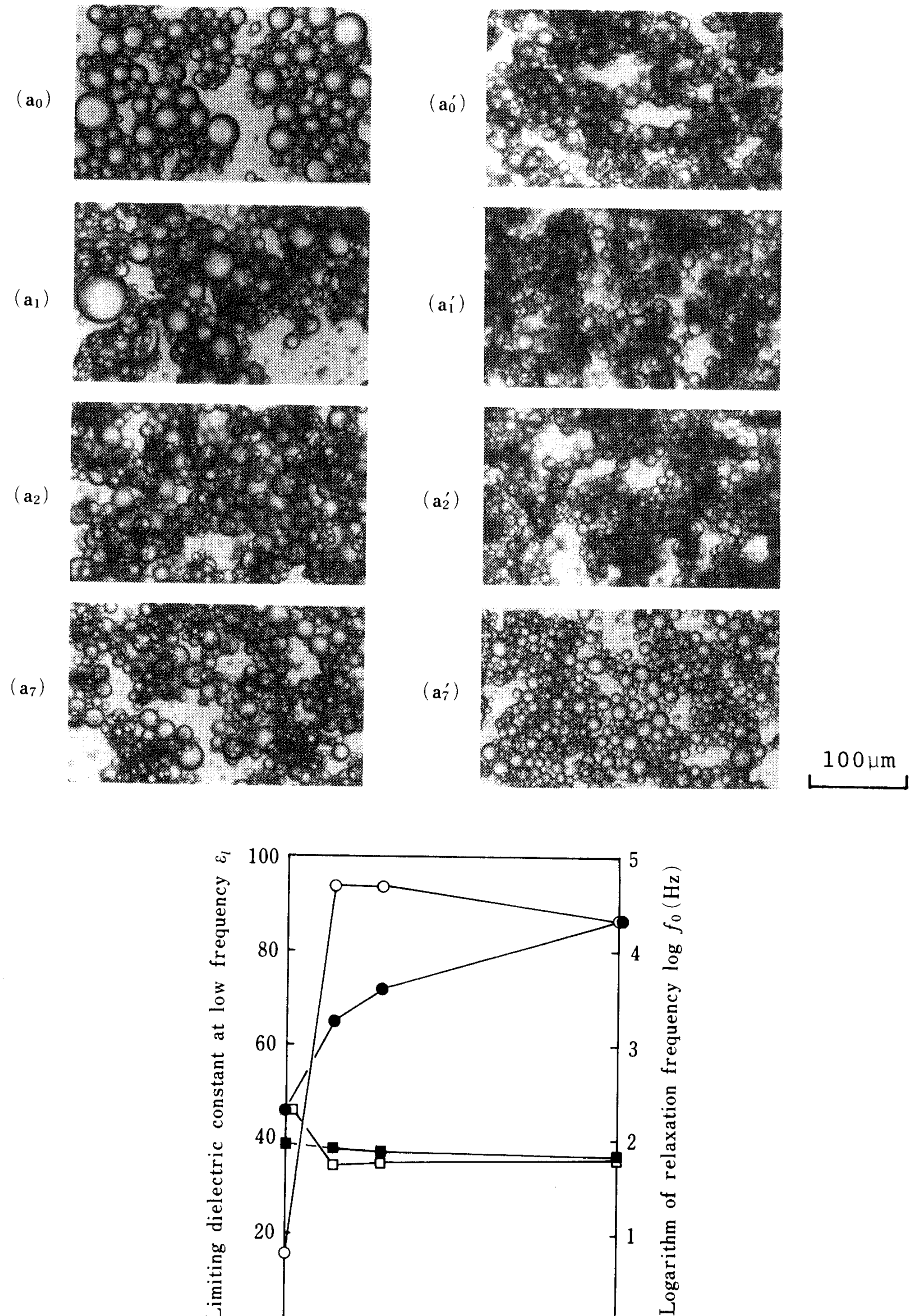

Fig. 1

lyoxyethylene (POE) (6) sorbitan monooleate, decaglyceryl esters, POE (2) oleyl ether, POE (7) oleyl ether and POE (6) monooleate, decreased the values of ε_l and α at concentrations of 0.1% or more. Thus, the primary emulsifiers with higher HLB values can be said to have the effect of decreasing the value of ε_l regardless of their chemical structure. Several secondary emulsifiers with the property of protecting the interfacial membrane, such as phytosterol and

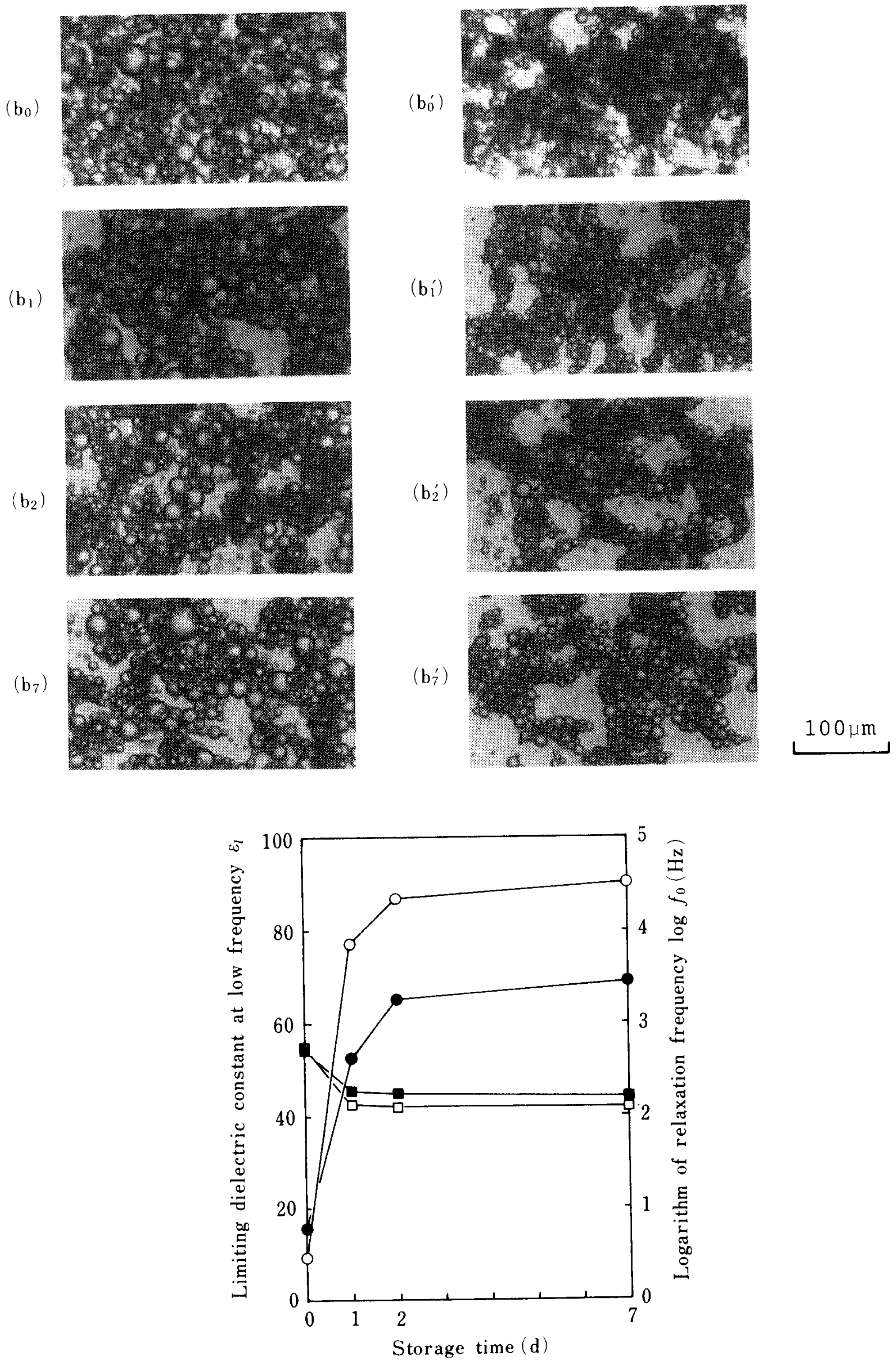

Fig. 1

liquid lanolin, decreased the value of ε_l, but L-α-dipalmitoyl phosphatidyl choline immediately decreased the value of ε_l, then increased both it and α during storage. Lipojelling additives with emulsifying action, such as aluminum stearate, decreased the value of ε_l. Secondary emulsifiers and the lipojelling additives have the effect of decreasing the value of ε_l above 0.2%. No effect of lipojelling additives without emulsifying action, such as paraffin and

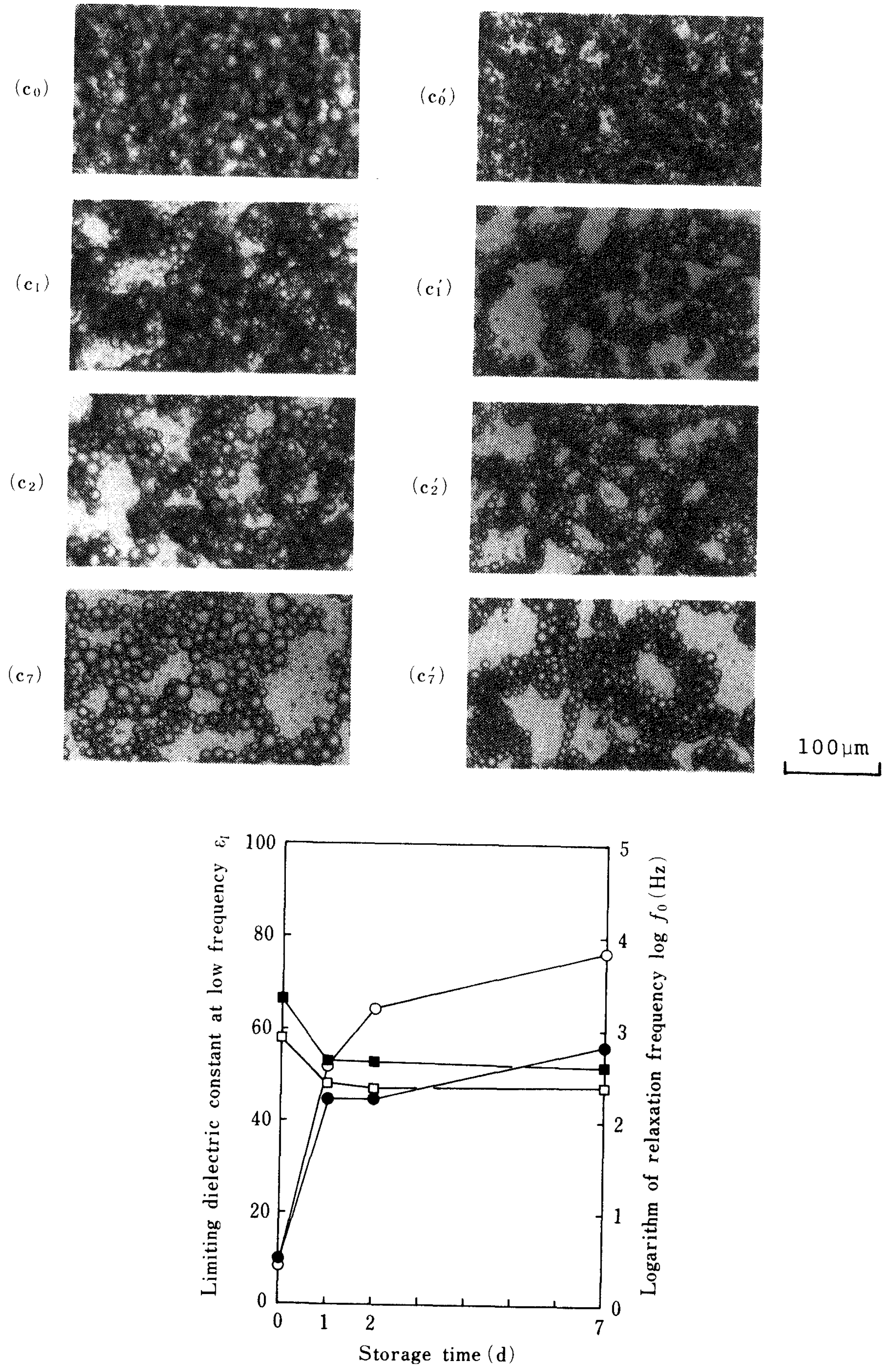

Fig. 1. Microphotographs of Dispersed Particles and Plots of Limiting Dielectric Constant, ε_l, and Relaxation Frequency, f_0, against Storage Time of W/O Emulsion ($\Phi = 0.3$) with Coarse and Fine Disperse Particles

(1) 0.5% sorbitan sesquioleate, (2) 1.0% sorbitan sesquioleate, (3) 2.0% sorbitan sesquioleate.

(a_0), (a_0'), (b_0), (b_0'), (c_0), (c_0'): immediately after preparation. (a_1), (a_1'), (b_1), (b_1'), (c_1), (c_1'): at 1 d after preparation. (a_2), (a_2'), (b_2), (b_2'), (c_2), (c_2'): at 2 d after preparation. (a_7), (a_7'), (b_7), (b_7'), (c_7), (c_7'): at 7 d after preparation.

○, coarse particles (ε_l); ●, fine particles (ε_l); □, coarse particles (f_0); ■, fine particles (f_0).

TABLE II. Values of ε_h, ε_l, f_0 and α of W/O Emulsions at Various Concentrations of Sorbitan Sesquioleate

Concentration of sorbitan sesquioleate (%)	Average size of dispersed particles (μm)		Storage time (d)	ε_h	ε_l	f_0 (kHz)	α
0.5	Coarse particles	13.00	0	6.7	14.8	199.5	0.023
		12.24	1	8.2	93.0	52.5	0.074
		12.40	2	8.2	93.8	56.2	0.074
		12.60	7	8.2	86.5	63.1	0.057
	Fine particles	8.72	0	8.2	46.0	89.1	0.087
		7.44	1	8.2	65.3	79.4	0.024
		9.76	2	8.2	72.0	74.1	0.043
		10.20	7	8.2	86.5	67.6	0.057
1.0	Coarse particles	14.60	0	6.5	9.4	562.3	0.003
		11.88	1	8.3	77.3	134.9	0.048
		9.76	2	8.3	87.0	125.9	0.033
		10.60	7	8.6	90.3	125.9	0.030
	Fine particles	7.16	0	7.4	15.8	524.8	0.013
		6.92	1	8.3	52.8	190.5	0.014
		7.92	2	8.4	65.3	177.8	0.014
		9.16	7	9.0	69.3	162.2	0.014
2.0	Coarse particles	12.64	0	6.3	8.3	794.3	0
		10.40	1	7.9	51.8	251.2	0.070
		10.84	2	9.2	64.1	223.9	0.022
		9.72	7	9.2	76.8	239.9	0.050
	Fine particles	7.84	0	6.8	10.0	2089.3	0
		7.72	1	8.2	42.8	446.7	0.022
		7.08	2	8.2	42.8	436.5	0.022
		8.96	7	9.2	56.6	398.1	0

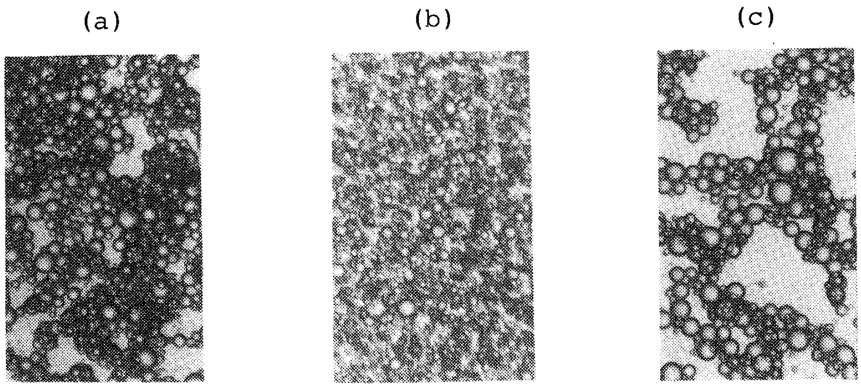
(a) (b) (c)

Fig. 2. Microphotographs of Dispersed Particles of W/O Emulsion and W/O Emulsions Containing Stabilizing Agent at 7 d after Preparation

(a) W/O emulsion containing 0.5% sorbitan sesquioleate, (b) W/O emulsion containing 0.5% sorbitan sesquioleate and 0.5% POE (6) sorbitan monooleate, (c) W/O emulsion containing 0.5% sorbitan sesquioleate and 0.5% paraffin.

cetanol, upon the values of ε_l and α of W/O emulsions was observed at 0.5%.

Figure 2 shows microphotographs of W/O emulsion alone, containing 0.5% POE (6) sorbitan monooleate, and containing 0.5% paraffin at 7 d after preparation. The results in Fig. 2 are consistent with those in Table III.

TABLE III. Effect of Various Stabilizing Agents upon Values of ε_h, ε_l, f_0 and α for W/O Emulsion

Stabilizing agent	Storage time (d)	Concentration of stabilizing agent (%)	ε_h	ε_l	f_0 (kHz)	α
None	0	—	7.5	46.5	89.1	0.111
	7	—	8.0	86.0	67.6	0.044
Primary emulsifiers						
Sorbitan monooleate	0	0.1	8.2	55.8	100.0	0.076
		0.2	8.3	53.7	141.3	0.067
		0.5	9.5	40.0	281.8	0.056
	7	0.1	8.2	99.0	79.4	0.036
		0.2	8.2	63.2	141.3	0.064
		0.5	8.0	35.0	269.2	0.069
POE (6) sorbitan monooleate	0	0.1	7.2	27.5	158.5	0.100
		0.2	7.1	19.8	166.0	0.100
		0.5	7.1	14.2	234.4	0.100
	7	0.1	6.8	22.1	177.8	0.077
		0.2	7.1	13.0	426.6	0.056
		0.5	6.8	11.1	831.8	0
Diglyceryl monooleate	0	0.1	8.2	57.3	79.4	0.109
		0.2	8.0	43.0	100.0	0.108
		0.5	8.0	28.2	177.8	0.077
	7	0.1	8.0	86.8	70.8	0.056
		0.2	8.0	64.0	83.2	0.050
		0.5	8.2	62.3	100.0	0.020
Diglyceryl dioleate	0	0.1	7.9	75.2	70.8	0.142
		0.2	8.2	55.0	95.5	0.070
		0.5	8.0	41.8	141.3	0.067
	7	0.1	8.3	94.5	63.1	0.044
		0.2	8.0	78.1	79.4	0.056
		0.5	8.3	71.2	100.0	0
Decaglyceryl dioleate	0	0.1	8.0	40.1	70.8	0.144
		0.2	7.2	39.3	63.1	0.133
		0.5	5.1	5.9	831.8	0
	7	0.1	7.5	31.7	166.0	0.106
		0.2	6.0	11.0	501.2	0.112
		0.5	—	—	—	—
Decaglyceryl trioleate	0	0.1	8.3	51.0	63.1	0.071
		0.2	8.0	44.7	56.2	0.080
		0.5	7.3	31.3	50.1	0.092
	7	0.1	6.8	17.0	223.9	0.081
		0.2	6.8	13.9	426.6	0.063
		0.5	6.6	11.5	707.9	0.044
Decaglyceryl pentaoleate	0	0.1	7.6	48.2	79.4	0.100
		0.2	7.3	41.4	79.4	0.110
		0.5	7.5	36.3	79.4	0.130
	7	0.1	8.0	68.1	75.9	0.036
		0.2	8.0	50.2	79.4	0.018
		0.5	7.0	23.0	141.3	0.037
POE (2) oleylether	0	0.1	8.0	33.0	125.9	0.050
		0.2	6.8	17.5	177.8	0.043
		0.5	7.1	18.0	269.2	0.058
	7	0.1	8.5	98.0	70.8	0.048
		0.2	7.3	35.4	104.7	0.026
		0.5	6.1	11.4	354.8	0.052

TABLE III. (continued)

Stabilizing agent	Storage time (d)	Concentration of stabilizing agent (%)	ε_h	ε_l	f_0 (kHz)	α
POE (7) oleylether	0	0.1	7.2	17.3	234.4	0.033
		0.2	7.0	13.0	446.7	0.063
		0.5	—	—	—	—
	7	0.1	6.5	15.4	223.9	0.048
		0.2	6.8	13.8	524.8	0.013
		0.5	—	—	—	—
POE (2) monooleate	0	0.1	8.0	50.5	89.1	0.080
		0.2	8.0	37.0	125.9	0.044
		0.5	8.0	33.0	177.8	0.048
	7	0.1	8.0	98.0	63.1	0.066
		0.2	8.0	102.6	75.9	0.078
		0.5	7.8	82.8	112.2	0.078
POE (6) monooleate	0	0.1	6.7	18.3	213.8	0.078
		0.2	6.5	11.9	501.2	0.056
		0.5	6.8	11.2	707.9	0.037
	7	0.1	6.5	22.7	134.9	0.059
		0.2	5.9	11.4	354.8	0.064
		0.5	5.9	9.1	676.1	0.022
Secondary emulsifiers						
Cholesterol	0	0.1	7.5	51.7	79.4	0.090
		0.2	8.2	61.3	67.6	0.062
		0.5	8.3	41.2	83.2	0.077
	7	0.1	8.5	100.5	63.1	0.048
		0.2	8.2	98.0	60.3	0.047
		0.5	9.6	131.2	50.1	0.053
Cholesteryl stearate	0	0.1	7.7	54.7	79.4	0.148
		0.2	7.8	50.4	83.2	0.128
		0.5	8.8	43.8	151.4	0.123
	7	0.1	8.2	76.8	67.6	0.044
		0.2	8.1	77.0	70.8	0.048
		0.5	7.9	69.5	158.5	0.056
Phytosterol	0	0.1	8.3	53.2	79.4	0.068
		0.2	7.9	54.8	75.9	0.111
		0.5	8.0	37.0	100.0	0.080
	7	0.1	8.3	92.0	63.1	0.062
		0.2	8.3	78.8	67.6	0.046
		0.5	8.0	53.3	75.9	0.059
POE phytosterol	0	0.1	8.2	47.8	117.5	0.082
		0.2	8.6	55.0	63.1	0.109
		0.5	—	—	—	—
	7	0.1	8.1	72.6	79.4	0.070
		0.2	8.5	74.0	85.1	0.081
		0.5	—	—	—	—
POP–POE–POP copolymer	0	0.1	7.8	23.0	166.0	0.108
		0.2	7.7	25.3	158.5	0.144
		0.5	7.3	27.5	158.5	0.158
	7	0.1	7.2	83.0	41.7	0.119
		0.2	—	—	—	—
		0.5	—	—	—	—

Table III. (continued)

Stabilizing agent	Storage time (d)	Concentration of stabilizing agent (%)	ε_h	ε_l	f_0 (kHz)	α
Lanolin	0	0.1	8.1	57.3	70.8	0.089
		0.2	8.3	51.7	66.1	0.078
		0.5	8.0	48.0	79.4	0.076
	7	0.1	8.8	118.3	53.7	0.057
		0.2	8.5	96.8	60.3	0.054
		0.5	8.2	92.0	60.3	0.059
Liquid lanolin	0	0.1	7.9	50.8	79.4	0.069
		0.2	8.0	40.8	100.0	0.056
		0.5	7.5	38.0	112.2	0.070
	7	0.1	9.0	78.1	67.6	0.053
		0.2	8.2	66.1	66.1	0.020
		0.5	7.8	44.0	93.3	0
L-α-dipalmitoyl phosphatidyl choline	0	0.1	7.2	20.0	158.5	0.081
		0.2	7.8	27.0	85.1	0.090
		0.5	—	—	—	—
	7	0.1	7.2	257.0	20.9	0.124
		0.2	7.8	105.5	28.2	0.213
		0.5	—	—	—	—
Lipojelling additives						
Aluminum stearate	0	0.1	6.3	28.6	177.8	0.109
		0.2	6.0	21.7	269.2	0.133
		0.5	7.7	22.0	166.0	0.189
	7	0.1	8.6	72.8	147.9	0.020
		0.2	8.3	50.7	316.2	0.031
		0.5	8.7	33.0	676.1	0.046
Paraffin	0	0.1	8.2	51.1	79.4	0.089
		0.2	8.2	52.3	70.8	0.059
		0.5	8.1	44.0	79.4	0.037
	7	0.1	8.0	102.8	60.3	0.070
		0.2	8.0	87.6	60.3	0.098
		0.5	8.0	84.0	60.3	0.048
Cetanol	0	0.1	7.7	58.3	70.8	0.108
		0.2	8.3	52.9	85.1	0.052
		0.5	8.3	47.0	79.4	0.058
	7	0.1	8.5	104.0	58.9	0.059
		0.2	8.6	107.9	56.2	0.042
		0.5	8.9	101.0	60.3	0.022
Bephenyl alcohol	0	0.1	8.0	50.1	93.3	0.071
		0.2	7.9	44.2	85.1	0.087
		0.5	7.9	41.0	100.0	0.047
	7	0.1	8.3	93.5	63.1	0.052
		0.2	8.2	92.0	67.6	0.054
		0.5	8.0	72.0	70.8	0.081

Discussion

As shown in Fig. 1, the ε_l of W/O emulsion with fine particles is larger than that of emulsion with coarse particles immediately after preparation. This is considered to be due to the particle clusters formed.[3] The rapid increase of ε_l up to 1 d after preparation was attributed to the decrease of the distance between the aggregates, *i.e.*, the decrease of thickness of the surfactant layer on the dispersed particles. The value of ε_l in the case of fine particles becomes smaller than that with coarse particles 1 d after preparation. It is therefore assumed that the density of surfactant molecules in the surfactant layer when the particles are fine is lower, but that the distance between particles is greater than with coarse particles due to the difference of magnitude of London–van der Waals' force. The value of ε_l is affected by both the increase in the size of the particle clusters and the decrease in the thickness of the surfactant layer between aggregated particles.

Parameter α with coarse particles is always larger than in the case of fine particles 1 d after preparation, which suggests that there is non-uniformity in the thickness of the surfactant layer on dispersed particles in particle clusters——a non-uniformity resulting from particle size variation. In other words, the magnitude of parameter α can be used to estimate the non-uniformity of particle size in the dispersed phase.

The values of ε_l and α are affected by the difference of particle size in the dispersed phase of W/O emulsions. Dielectric measurement can thus probably be used to obtain valid figures for mechanical effect based on the particle size variation in W/O emulsions.

As shown in Table III, ε_l decreased on the addition of primary emulsifiers with a higher HLB value and of lipojelling additives, and the stabilizing agents are presumed to be adsorbed on the surface of particles, preventing access by other particles in the neighborhood. This view is supported by the microscopic findings shown in Fig. 2. In order to prevent particle aggregation, the concentration of the lipojelling additive without emulsifying action must be higher than 0.5%.

From the results of the present study, it is concluded that dielectric evaluation can be employed to examine the effects of various factors on emulsification and as an aid for the selection of optimum additives and vehicles for a W/O emulsion.

References

1) H. Kaneko and S. Hirota, *Chem. Pharm. Bull.*, **31**, 1445 (1983).
2) H. Kaneko and S. Hirota, *Chem. Pharm. Bull.*, **32**, 1683 (1984).
3) H. Kaneko and S. Hirota, *Chem. Pharm. Bull.*, **33**, 1775 (1985).
4) H. Kaneko and S. Hirota, *Chem. Pharm. Bull.*, **33**, 5167 (1985).
5) E. G. Richardson, *J. Colloid Sci.*, **8**, 367 (1953).
6) G. Proserpio, *Cosmetics & Toiletries*, **96**, 5, 31 (1981).
7) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).