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Dielectric Studies on Emulsion of Aqueous Agarose Gel in Hydrophobic Colloidal Silica–Oil Gel[1]

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In order to characterize the state of aggregation, dielectric relaxation due to interfacial polarization of a system of aqueous agarose gel particles dispersed in a squalane medium jellified by hydrophobic colloidal silica (denoted below as G/(S·O) emulsion) was investigated over a frequency range from 10 kHz to 3 MHz.

The value of the parameter α, a measure of the distribution of relaxation frequency determined from complex plane plots, was zero when there was no aggregation. It was positive while aggregation was progressing and fell toward zero as the aggregation approached the steady state during storage. When the dependence of α on the uniformity of particle size was taken into account, the transient characteristics of dielectric relaxation represented by the positive value of α seemed to indicate that the mode of ion diffusion through the interface layer between particles in contact changed depending on the magnitude and particle size variation of particle clusters. Microscopic observation during aggregation supported the hypothesis that positive α appeared during the progressive stage of aggregation as a result of a transient deviation from uniformity of aggregation. The influence of aggregation on other dielectric parameters is also discussed.

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

In the previous study[1] on W/(S·O) emulsion without particle aggregation, *i.e.*, an emulsion of water in a hydrophobic colloidal silica–oil gel, the dielectric parameter α in Cole and Cole's empirical formula was found to be related to electric irregularity, *i.e.*, nonuniformity of electric conductivity in the dispersed particles.

In W/(S·O) emulsion with particle aggregation, the parameter α is positive in spite of the uniform electric conductivity of dispersed particles.[2] It is considered that the electric irregularity in the emulsion is caused by the new dielectrics with different relaxation frequencies formed by particle aggregation.

However, the nature of the electric irregularity in the new dielectrics has not yet been clarified. The purpose of the present study was to elucidate this point and to investigate the dielectric properties of a system of aqueous agarose gel particles dispersed in a squalane medium jellified by hydrophobic colloidal silica (denoted below as G/(S·O) emulsion) with various concentrations of surfactant and various sizes of dispersed particles.

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: electric conductivity ($\mho$/cm)
κ_p: electric conductivity of dispersed phase ($\mho$/cm)
κ_m: electric conductivity of continuous medium ($\mho$/cm)
Φ: volume fraction of dispersed phase
f: experimental frequency (Hz)
f_0: relaxation frequency (Hz)

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

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

Empirical Formula of Cole and Cole[3)]

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 ($\varepsilon_m=2.10$, $\kappa_m=5.64\times 10^{-10}\,\mho$/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 range of 10—40 nm, and a specific surface area of $120\pm 30\,\mathrm{m}^2/\mathrm{g}$ (BET adsorption method), sorbitan sesquioleate (NIKKOL SO-15, Nikko Chemicals Co., Ltd.) of commercial grade, agarose (Type VI, Sigma Chemical Co., Ltd.) of commercial grade and water obtained by reverse osmosis ($\varepsilon_1=79.34$, $\kappa_1=3.11\times 10^{-6}\,\mho$/cm) were used. Reagent-grade KCl was added to increased the conductivity of the water ($\varepsilon_2=79.26$, $\kappa_2=39.93\times 10^{-6}\,\mho$/cm).

Preparation of G/(S·O) Emulsion without Particle Aggregation——A 2.0 g sample of hydrophobic colloidal silica was mixed with squalane (total volume: 57.5 ml). The oil mixture was warmed to 70—80 °C. Then 30 ml of 0.3% aq. agarose solution (70—80 °C) with low or high electric conductivity ($\varepsilon_{p1}=79.00$, $\kappa_{p1}=9.24\times 10^{-6}\,\mho$/cm; $\varepsilon_{p2}=79.99$, $\kappa_{p2}=47.47\times 10^{-6}\,\mho$/cm) was gently added to the oil phase with vigorous agitation by means of a propeller mixer (max. rpm = 1200). The emulsions were cooled to room temperature. Samples of 0.5, 1.0 or 2.0 g of sorbitan sesquioleate were dissolved in warm squalane (total volume: 12.5 ml). Then, 12.5 ml of a sorbitan sesquioleate solution cooled to room temperature was added to each emulsion with vigorous agitation by means of a propeller mixer (max. rpm = 1200).

Preparation of G/(S·O) Emulsion with Particle Aggregation——First, 0.5, 1.0 or 2.0 g of sorbitan sesquioleate was dissolved in warm squalane (70—80 °C), then 2.0 g of hydrophobic colloidal silica was added (total volume: 70 ml). Next, 30 ml of 0.3% aq. agarose solution (70—80 °C) of low or high electric conductivity ($\varepsilon_{p1}=79.00$, $\kappa_{p1}=9.24\times 10^{-6}\,\mho$/cm; $\varepsilon_{p2}=79.99$, $\kappa_{p2}=47.47\times 10^{-6}\,\mho$/cm) was added to the oil phase, either with gentle agitation by means of a propeller mixer (max. rpm = 200) in order to prepare G/(S·O) emulsions in which the dispersed particles were coarse, or with vigorous agitation by means of a propeller mixer (max. rpm = 1200) in order to prepare such emulsions with fine dispersed particles. These emulsions were cooled to room temperature.

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.[2)]

Results

Figure 1 shows microphotographs of G/(S·O) emulsions with the lower-conductivity dispersed phase ($\varepsilon_{p1}=79.00$, $\kappa_{p1}=9.24\times10^{-6}$ ℧/cm) with various sizes of dispersed particles with and without particle aggregation at various concentrations of surfactant immediately after preparation and 1 d after preparation.

Figure 2 shows the complex plane plots for G/(S·O) emulsions with the lower-conductivity dispersed phase ($\varepsilon_{p1}=79.00$, $\kappa_{p1}=9.24\times10^{-6}$ ℧/cm) in the presence of particle aggregation with various sizes of dispersed particles at various concentrations of surfactant, immediately after preparation, and 1, 2 and 7 d after preparation. The dielectric parameters, ε_h, ε_l, f_0 and α of the G/(S·O) emulsions were affected by surfactant concentration, particle size and storage time. High values for parameter α were observed immediately after the beginning of distinct particle aggregation ($\varepsilon_l>10$), and low values were seen after storage. The values of parameter α of the G/(S·O) emulsions ($\varepsilon_l>10$) with coarse particles were larger than when the particles were fine at all surfactant concentrations. The rate of decrease of parameter α at 2.0% surfactant concentration was faster than at 0.5%. The complex plane plots of G/(S·O) emulsions with the higher-conductivity dispersed phase ($\varepsilon_{p2}=79.99$, $\kappa_{p2}=47.47\times10^{-6}$ ℧/cm) gave plots similar to those shown in Fig. 2.

Table I summarizes the values of the dielectric parameters obtained from complex plane plots and plots of dielectric loss factor against frequency for G/(S·O) emulsions at various concentrations of surfactant.

Figure 3 shows the relaxation frequency, f_0, of G/(S·O) emulsions at various concentrations of surfactant. It was found that the values of f_0 of G/(S·O) emulsions with particle aggregation were smaller than those of G/(S·O) emulsions without particle aggregation, and were dependent upon the electric conductivity of the dispersed particles.

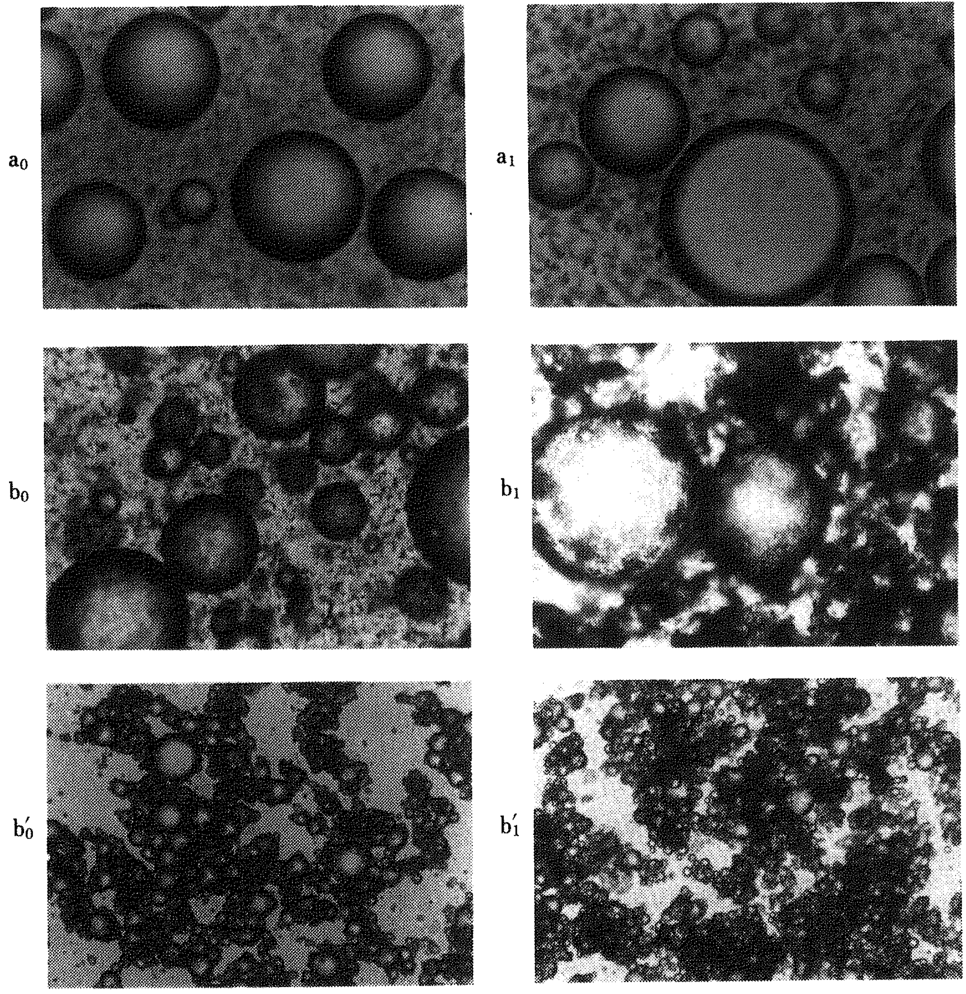
Discussion

In the present study, in order to elucidate the effect of particle aggregation, dispersed water particles were prepared in a gel with agarose. In this way, size changes of dispersed particles were prevented during the study.

The different preparation procedures for G/(S·O) emulsions resulted in particle aggregation in some emulsions and no aggregation in others. Thus, particle aggregation is related to the adsorption of colloidal silica on dispersed water particles, *i.e.*, in the case of G/(S·O) emulsions without particle aggregation, colloidal silica particles are tightly adsorbed onto the surface of the dispersed particles and the surface is completely occupied by colloidal silica particles, whereas in the case of G/(S·O) emulsions with particle aggregation, the adsorption of colloidal silica particles onto the surface of the dispersed particles was prevented by a surfactant. Thus, imperfect adsorption of colloidal silica on the surface of the dispersed particles gives rise to particle aggregation.

The results shown in Fig. 2 indicate that the transient dielectric irregularity reflects changing modes of ion diffusion through the interface layer among aggregated particles based on the magnitude and particle size variation of particle clusters. The dielectric irregularity disappears during storage when there is a large amount of surfactant. This phenomenon suggests that the electric conductivity of the surface layer of aggregated particles becomes uniform after storage of the emulsions.

concentration of surfactant: 0.5%



concentration of surfactant: 1.0%

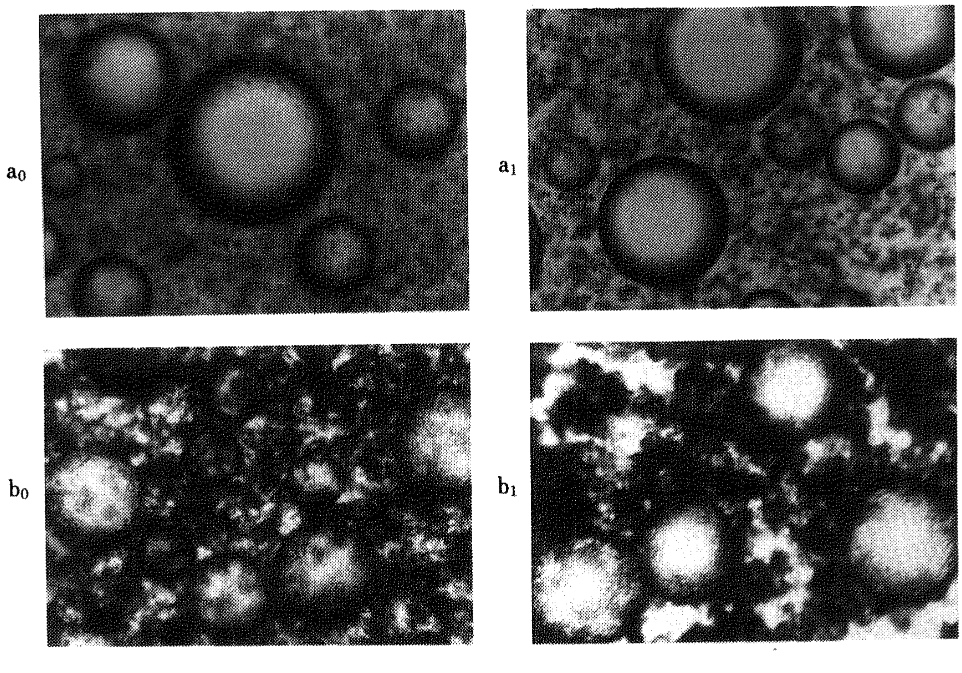
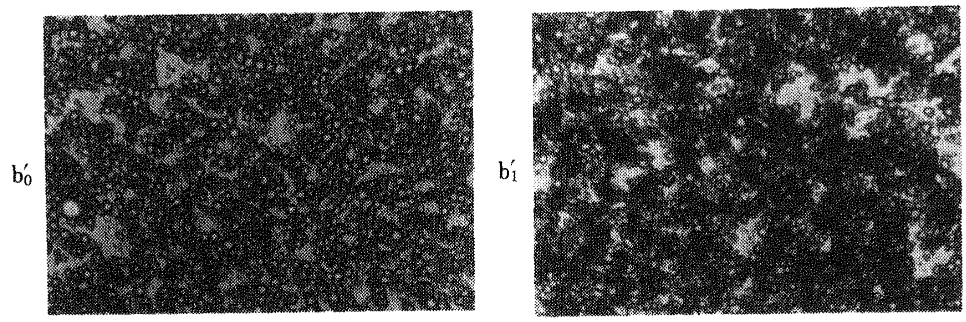


Fig. 1



concentration of surfactant: 2.0%

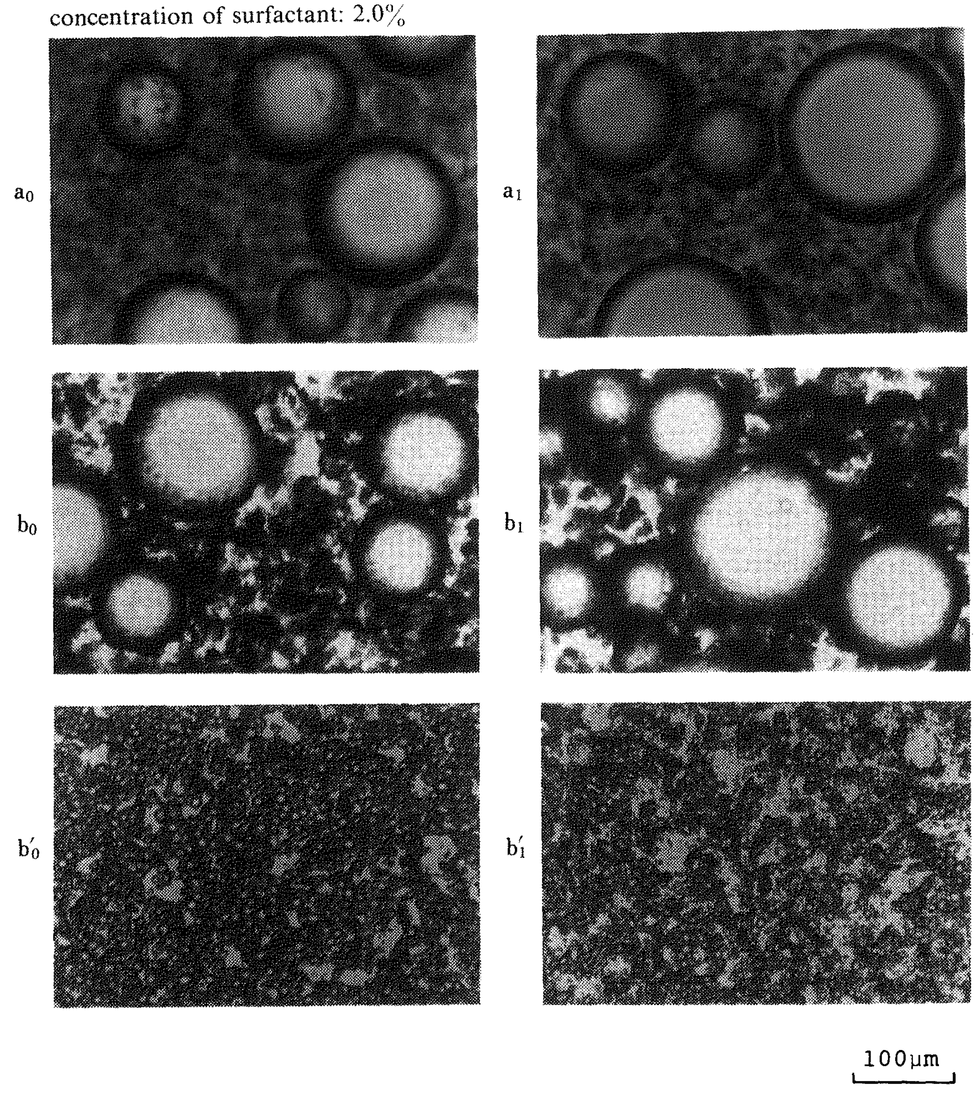


Fig. 1. Microphotographs of Dispersed Particles in G/(S·O) Emulsions with the Lower-Conductivity Dispersed Phase ($\varepsilon_{p1}=79.00$, $\kappa_{p1}=9.24\times10^{-6}$℧/cm) at Various Concentration of Surfactant

a_0, b_0, b_0': immediately after preparation. a_1, b_1, b_1': 1 d after preparation. a_0, a_1: G/(S·O) emulsion without particle aggregation. b_0, b_1: G/(S·O) emulsion with coarse-particle aggregation. b_0', b_1': G/(S·O) emulsion with fine-particle aggregation.

The increase of f_0 during storage, shown in Fig. 3, was probably caused by ion contamination from colloidal silica or nonionic surfactant in the oil phase. This is supported by the fact that the electric conductivity of 30 ml of water containing 2.0 g of colloidal silica is

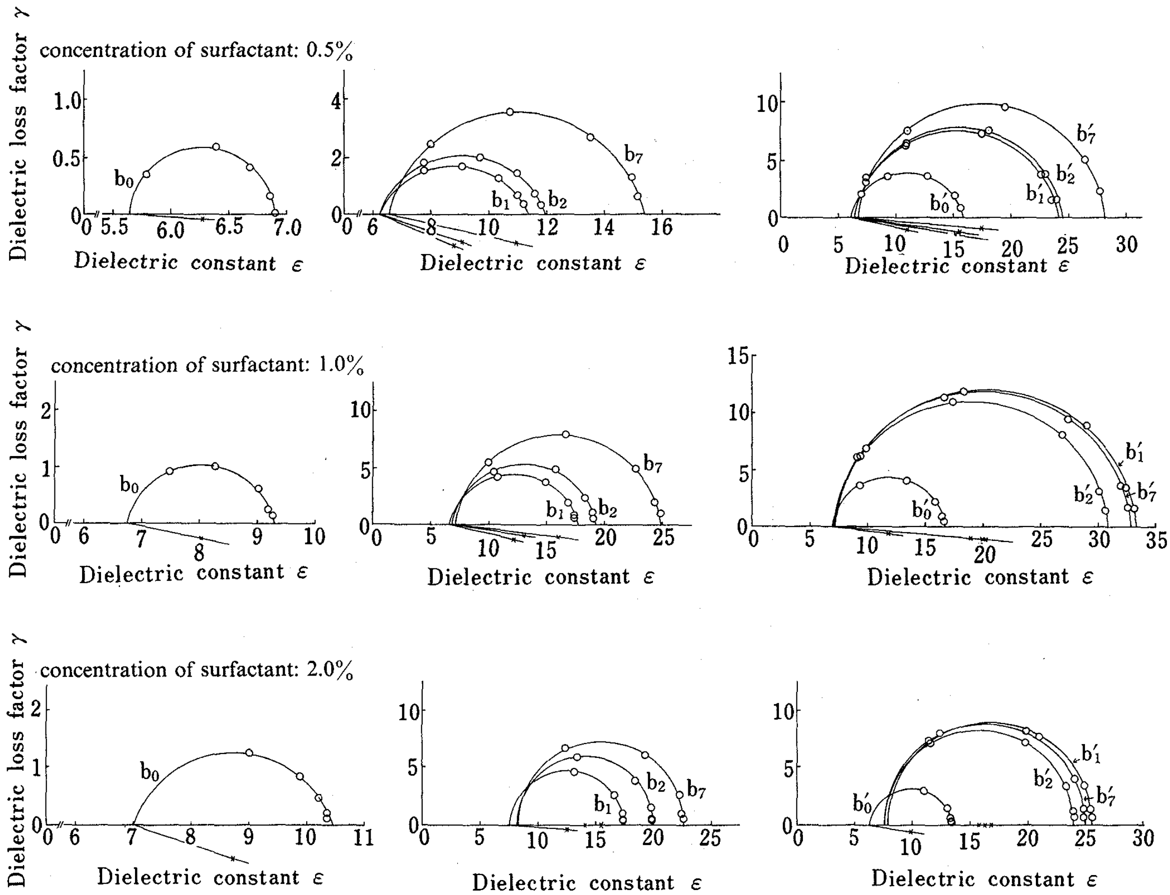


Fig. 2. Complex Plane Plots of Dielectric Loss Factor, γ, against Dielectric Constant, ε, for G/(S·O) Emulsions with the Lower-Conductivity Dispersed Phase ($\varepsilon_{p1}=79.00$, $\kappa_{p1}=9.24\times10^{-6}$ ℧/cm) with Particle Aggregation at Various Concentrations of Surfactant

b_0, b_1, b_2, b_7: with coarse particles. b_0', b_1', b_2', b_7': with fine particles. b_0, b_0': immediately after preparation. b_1, b_1': 1 d after preparation. b_2, b_2': 2 d after preparation. b_7, b_7': 7 d after preparation.

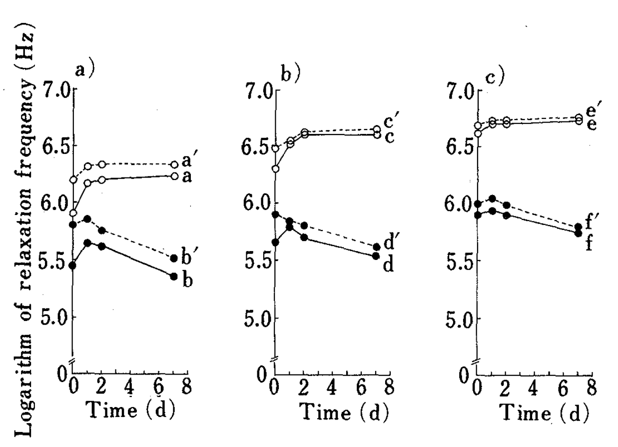


Fig. 3. Plots of the Logarithm of Relaxation Frequency, f_0, against Storage Time

a) concentration of surfactant: 0.5%, b) concentration of surfactant: 1.0%, c) concentration of surfactant: 2.0%. a, c, e: G/(S·O) emulsion with the lower-conductivity dispersed phase ($\varepsilon_{p1}=79.00$, $\kappa_{p1}=9.24\times10^{-6}$ ℧/cm) without particle aggregation. a′, c′, e′: G/(S·O) emulsion with the higher-conductivity dispersed phase ($\varepsilon_{p2}=79.99$, $\kappa_{p2}=47.47\times10^{-6}$ ℧/cm) without particle aggregation. b, d, f: G/(S·O) emulsion with the lower-conductivity dispersed phase with coarse-particle aggregation. b′, d′, f′: G/(S·O) emulsion with the higher-conductivity dispersed phase with coarse-particle aggregation.

7.44×10^{-6} ℧/cm, and that of 30 ml of water containing 0.5 g of nonionic surfactant is 44.58×10^{-6} ℧/cm. The results in Fig. 3 and Table I suggest that the new dielectrics regarded as the origin of the dielectric anomaly[2] have a small relaxation frequency, and that this frequency is influenced by the electric conductivity of the dispersed particles. This supports

Table I. Values of ε_h, ε_l, f_0 and α of G/(S·O) Emulsions

Concn. of surfactant (%)	Aggregation	Particle size	Time (d)	G/(S·O) emulsion with the lower-conductivity dispersed phase[a]				G/(S·O) emulsion with the higher-conductivity dispersed phase[b]			
				ε_h	ε_l	f_0 (kHz)	α	ε_h	ε_l	f_0 (kHz)	α
0.5	(−)	Coarse	0	5.268	5.875	794.3	0	5.336	6.010	1584.9	0
			1	5.290	5.940	1479.1	0	5.300	5.978	2089.3	0
			2	5.292	5.965	1584.9	0	5.212	5.888	2138.0	0
			7	5.222	5.862	1698.2	0	5.325	6.040	2138.0	0
	(+)	Coarse	0	5.64	6.90	281.8	0.043	5.46	6.95	631.0	0.048
			1	6.21	11.38	426.6	0.258	5.93	10.63	707.9	0.211
			2	6.21	11.93	416.9	0.211	6.35	11.88	562.3	0.147
			7	6.55	15.40	234.4	0.143	7.08	19.48	331.1	0.100
		Fine	0	6.20	15.80	158.5	0.137	6.50	19.70	199.5	0.113
			1	6.40	24.20	141.3	0.107	6.25	20.20	199.5	0.103
			2	6.40	24.50	134.9	0.089	6.70	27.90	177.8	0.069
			7	6.75	28.20	125.9	0.058	6.90	24.80	177.8	0.059
1.0	(−)	Coarse	0	5.270	5.945	1995.3	0	5.320	6.100	3020.0	0
			1	5.230	6.025	3311.3	0	5.252	6.080	3548.1	0
			2	5.235	6.020	3981.1	0	5.200	5.953	4168.7	0
			7	5.260	5.978	3981.1	0	5.140	5.860	4466.8	0
	(+)	Coarse	0	6.74	9.30	446.7	0.131	6.52	9.32	794.3	0.099
			1	6.70	17.75	602.6	0.147	6.72	17.56	676.1	0.133
			2	6.80	19.25	501.2	0.102	7.10	19.20	631.0	0.091
			7	7.20	24.80	338.8	0.078	7.75	25.20	416.9	0.031
		Fine	0	6.80	16.70	446.7	0.081	6.90	20.70	398.1	0.072
			1	7.20	33.30	233.9	0.056	7.20	33.20	316.2	0.044
			2	7.00	30.85	223.9	0.056	7.50	30.70	316.2	0.026
			7	7.10	32.85	208.9	0.056	7.30	28.00	302.0	0.022
2.0	(−)	Coarse	0	5.268	6.135	4168.7	0	5.240	6.200	4786.3	0
			1	5.240	6.195	5011.9	0	5.295	6.278	5370.3	0
			2	5.240	6.190	5011.9	0	5.272	6.215	5370.3	0
			7	5.210	6.072	5370.3	0	5.202	6.110	5888.4	0
	(+)	Coarse	0	7.00	10.44	794.3	0.203	6.63	11.68	1000.0	0.113
			1	7.50	17.50	851.1	0.048	8.00	17.35	1122.0	0.011
			2	8.20	20.00	794.3	0	8.40	20.20	955.0	0
			7	8.25	22.68	537.0	0	8.25	20.22	631.0	0
		Fine	0	6.25	13.50	891.3	0.103	6.81	15.79	851.1	0.067
			1	7.80	25.60	524.8	0	7.50	20.60	631.0	0
			2	7.60	23.95	501.2	0	7.80	24.80	501.2	0
			7	7.60	25.00	478.6	0	7.80	27.20	501.2	0

a) $\varepsilon_{p1}=79.00$, $\kappa_{p1}=9.24\times10^{-6}$ ℧/cm. *b)* $\varepsilon_{p2}=79.99$, $\kappa_{p2}=47.47\times10^{-6}$ ℧/cm.

the contention that the dielectric anomaly is related to the ion diffusion among water particles through the interface layer of aggregated particles.

References

1) H. Kaneko and S. Hirota, *Chem. Pharm. Bull.*, **32**, 1683 (1984).
2) H. Kaneko and S. Hirota, *Chem. Pharm. Bull.*, **31**, 1445 (1983).
3) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).