Control of Particle Alignment in Water by an Alternating Electric Field

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We attempted to align a large number of silica particles dispersed in aqueous solution by controlling the alternating electric field between the two electrodes (400 μm apart). Relatively large particles (9.9 μm) were found to align forming strings in the direction parallel to the electric field while relatively small particles (2.0 and 4.9 μm) were observed to align making stripes in the direction perpendicular to the field. The number of stripes formed by particles between the electrodes increased with increasing frequency of the alternating field. This peculiar perpendicular particle alignment appeared when the contribution to particle alignment of electroosmotic flow exceeded that of dielectric polarization and the osmotic flow was found to be stronger around the particles than in the vicinity of the electrode surface.

1. Introduction

Colloid crystals in which fine particles of colloidal dimensions are orderly arranged two- or three-dimensionally have recently attracted attention because they can be used as a template for constructing tiny structures by using the gaps between arranged particles[1] and applied to an optical element that is called photonic crystal and allows control of light freely.[2]

The preparation methods of colloid crystals are divided into two categories, one that permits the crystal to grow spontaneously and the other that makes colloidal particles gather and arrange themselves orderly driven by external stimuli to form a crystal. The former category includes a method that uses the balance between the attractive forces of colloidal particles and the repulsive forces arising from surface forces and enables the particles to form a spatial arrangement through the control of salt concentration.[3] Also, a technique was developed to make three-dimensional colloid crystals by using the sedimentation of colloidal particles due to gravitational force.[4] However, these methods are apt to cause defects in the highly ordered structures and permit no choice of desired particle arrangement because they are based on the self-organization of particles. On the other hand, the methods belonging to the latter category use external stimuli that can restrict the movement of colloidal particles against the interparticle repulsive forces. For instance, microneedle,[5,6] laser,[7,8] and scanning probe for atomic force microscope[9] are used as external stimuli to arrange particles one by one on the substrate. Although these methods are advantageous to detailed construction of structures, they are lacking in simplicity because they need much time and high skills to manipulate particles one by one and require expensive equipment. In addition, there are some other methods including those in which an electron beam or an ion beam is used to depict charged latent images on the substrate and oppositely charged particles are electrostatically attached to the depicted images,[10] and particles are dispersed as aerosol or suspension and the resultant dispersion is sprayed onto desired spots on the substrate.[11] These methods do not permit the reversible control of particle arrangements even though they are simple and enable choice of a desired arrangement.

Meanwhile, an electric field is commonly used in the field of biochemistry for cell fusion[12] and separation of live and dead cells.[13] Also, many reports show the particle arrangement in an electric field.[14−21] Colloidal crystals and electrophoretic deposition can give rapid production and larger crystals compared with that obtained from other

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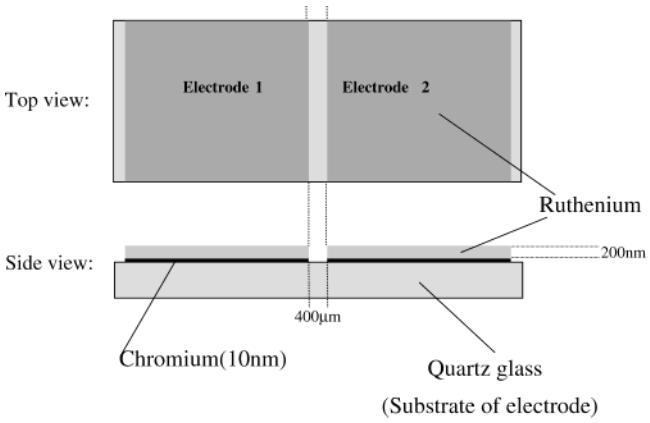

Figure 1. Schematic illustration of the electrodes used in our experimental system.

methods. If this method can be used to arrange particles dispersed in water, we can expect that the method can arrange a large number of fine particles at one time.

We then examine in the present study the effect of alternating electric field under various conditions on the dispersion state and alignment of silica particles with different sizes in water to elucidate the peculiar particle behavior.

2. Experimental Section

Three kinds of monodisperse spherical particles (average diameters of 2.0, 4.9, and 9.9 μm, Shokubai Kasei Ind.) were used as the particle samples.

Figure 1 shows the outline of the electrodes used in this work. These electrodes were prepared by evaporating ruthenium on quartz substrates to give a 200 nm thickness using the lift-off etching method. To avoid the peeling-off of ruthenium, chrome was evaporated on the quartz substrate prior to ruthenium evaporation. The distance between the electrodes was 400 μm.

Sample silica particles were ultrasonically (40 kHz, 10 min) dispersed in distilled water for injection (pH = 5.6, Otsuka Pharm. Co.) at a concentration of 10 mM as silica. A portion (0.05 mL) of the silica dispersion was placed in the gap between the electrodes. After the dispersion was left standing until no particle disturbance was observed in it, the particles were permitted to align on the substrate by applying an alternating potential between the electrodes using a function synthesizer 1915 (NF Electric Instruments). The potential and frequencies were 3.0 V_{rms} and 100−10000 Hz, respectively. The time of potential application was 10 min. Particle behavior was observed with a Nomarski-type differential interference optical microscope and monitored using a CCD camera (CS900, Olympus). The digital image of particle behavior was recorded with a videocassette recorder (WV-DR7, Sony).

The parameters necessary for the evaluation of particle behavior were obtained through measurements using the following instruments. Thus, the specific permittivity of dispersion medium, the viscosity of dispersion medium, the zeta potential of quartz substrate, and the zeta potential of silica particles were respectively measured with an LCR meter (4285A, Hewlett-Packard), a stress control-type rheometer (CSL100, Carri-Med Ltd.), a laser zetameter (ELS-800, Otsuka Electronics), and a zeta potential measured by apparatus for concentrated systems (ESA-9800, Matec Applied Science).

Silanization of the surface of quartz substrate was attempted to prepare a substrate other than quartz substrate. To 300 mL of 1.5 wt % of acetic acid 3 mL of γ-(2-aminoethyl)(aminopropyl)-trimethoxysilane was slowly added dropwise with stirring. After a quartz substrate was immersed in the solution for 18 h, it was taken out of the solution and dried in a dryer (110 °C) for 3 h. Surface modification was checked by measuring the contact angle of water on the surface before and after modification with a goniometer (contact-angle meter, Kyowa Kaimen Kagaku). The contact angle was 13.0° before modification and 78.3° after modification, which indicates a successful silanization of the substrate surface.

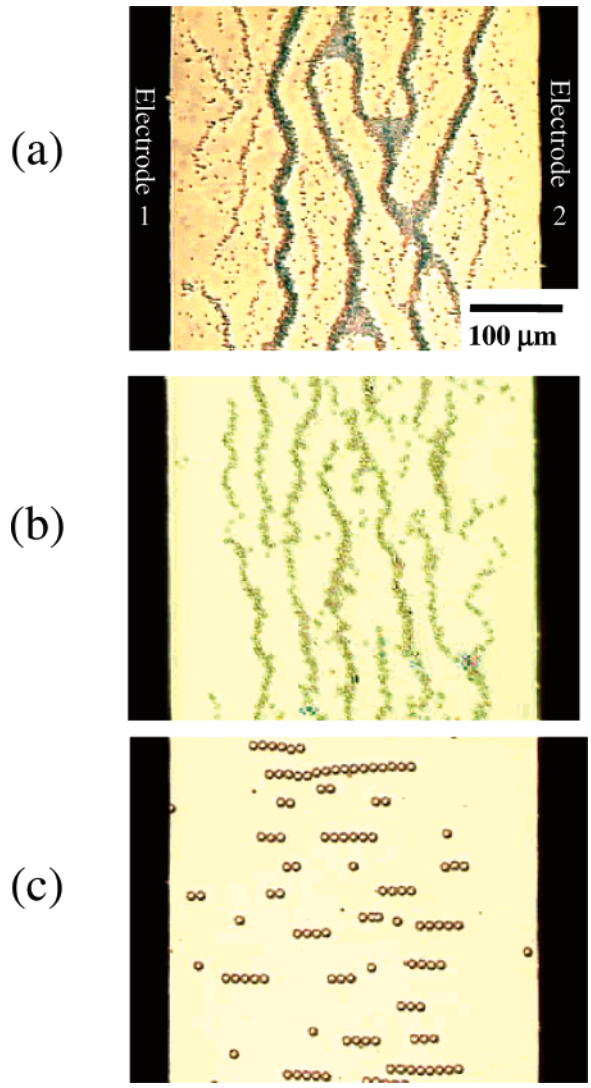

Figure 2. Alignment of silica particles suspended in water between the two flat electrodes. Diameter of silica particles: (a) 2.0; (b) 4.9; (c) 9.9 μm.

3. Results and Discussion

3.1. Peculiar Alignment of Silica Particles. Figure 2 shows the alignment in an alternating electric field (1000 Hz) of silica particles dispersed in aqueous solution. The particles were observed to align perpendicularly to the field when they had relatively small mean sizes of 2.0 and 4.9 μm (parts a and b of Figure 2). Particles with diameters of several micrometers dispersed in water were reported to generally align parallel to the electric field forming strings (Figure 2c) due to their dielectric polarization.[22,23] However no example has so far been reported of particles aligned perpendicularly to the field.

Solid particles dispersed in water are assumed to be subject to two forces that act on the particles to align them parallel and perpendicularly to the field in an applied alternating electric field. Particle alignment depends on the net force acting on the particles. The force causing parallel particle alignment is an electrostatic force due to the electric charges on the particles induced by dielectric polarization and is proportional to the dipole moment of

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the particle. Silica has a specific permittivity of 4.5, an extremely small value, and is a substance hardly polarized. Nevertheless, since the dipole moment of a spherical particle depends on its radius according to eq 1, the moment will be considerably large for particles with large radii[24]

$$\mu = 4\pi R^3 \epsilon_o \epsilon_m \, Re[K_e] \, E_{rms} \tag{1}$$

where μ is the dipole moment of particle, R is the radius of the particle, ϵ_0 is the permittivity (dielectric constant) of vacuum, ϵ_m the relative permittivity (dielectric constant) of dispersion medium, and E_{rms} is the effective field strength. K_e is the Clausius−Mossotti factor given by eq 2. Re[K] is the real part of K_e

$$K_e = \frac{\epsilon'_p{}^* - \epsilon'_m{}^*}{\epsilon'_p{}^* + 2\epsilon'_p{}^*} \tag{2}$$

where $\epsilon'_p{}^*$ and $\epsilon'_m{}^*$ are the complex permittivities of particle and dispersion medium, respectively. The complex permittivity is given by eq 3

$$\epsilon'^* = \epsilon' - j\frac{\sigma}{\omega} \tag{3}$$

where ϵ' is permittivity, $j = \sqrt{-1}$, and σ is the electroconductivity.

As in eq 1, μ is proportional to the cube of particle radius, and hence, large silica particles with a radius of 9.9 μm would be affected by dielectric polarization more than small silica particles with radii of 2.0 and 4.9 μm. Therefore large silica particles align parallel to the field.

3.2. Approach to Elucidation of Perpendicular Particle Alignment. The force causing particles to align perpendicularly to the field is likely to the electroosmotic flow generated in the gap between the electrodes. Here, electroosmotic flow, U, is a flow of solution generated in the vicinity of the charged surface of a solid in the solution. The velocity of the flow can be expressed as

$$U = \left|\frac{\zeta \epsilon_0 \epsilon_m}{\eta}\right| \tag{4}$$

where ζ is the zeta potential of the solid, ϵ_m is the relative permittivity of dispersion medium, ϵ_0 is the permittivity of vacuum, which is 0.0088419 F/cm, and η is the viscosity of the dispersion medium.

According to eq 4, U is proportional to the zeta potential of the solid surface with which dispersion medium is in contact and the relative permittivity of the medium and is inversely proportional to the viscosity of the medium. We then examined the effect of electroosmotic flow on the perpendicular alignment of silica particles using various dispersion media with different values of ϵ_m and η while changing ζ. Experiments similar to those in Figure 2 were conducted first using aqueous media with added sodium chloride at various concentrations (Figure 3).

Small silica particles (2.0 μm) were found again to align forming three to four stripes perpendicularly to the field between the electrodes at 0 mM sodium chloride and 1000 Hz (Figure 3a). With an increase in the salt concentration to 0.25 mM, the number of stripes increased to five to six (Figure 3b) and remained unchanged until the salt concentration reached 0.75 mM. The particles changed the direction of their alignment to that parallel to the field (Figure 3c) with further increase in the salt concentration to 1.0 mM. Although perpendicular alignment was also observed for silica particles (4.9 μm) at 0 mM sodium chloride, the particles aligned parallel to the field at a salt concentration of 0.25 mM (Figure 4). Since the absolute value of the zeta potential of colloid particles decreases with increasing salt concentration, the electroosmotic flow also decreases according to eq 4. Then, the contribution of dielectric polarization to the driving force of particle alignment becomes much larger than that of electroosmosis at increased salt concentrations. This would cause silica particles to align parallel to the field. These findings suggest that particle alignment between the electrodes depends strongly on the relative contributions of electroosmosis and dielectric polarization.

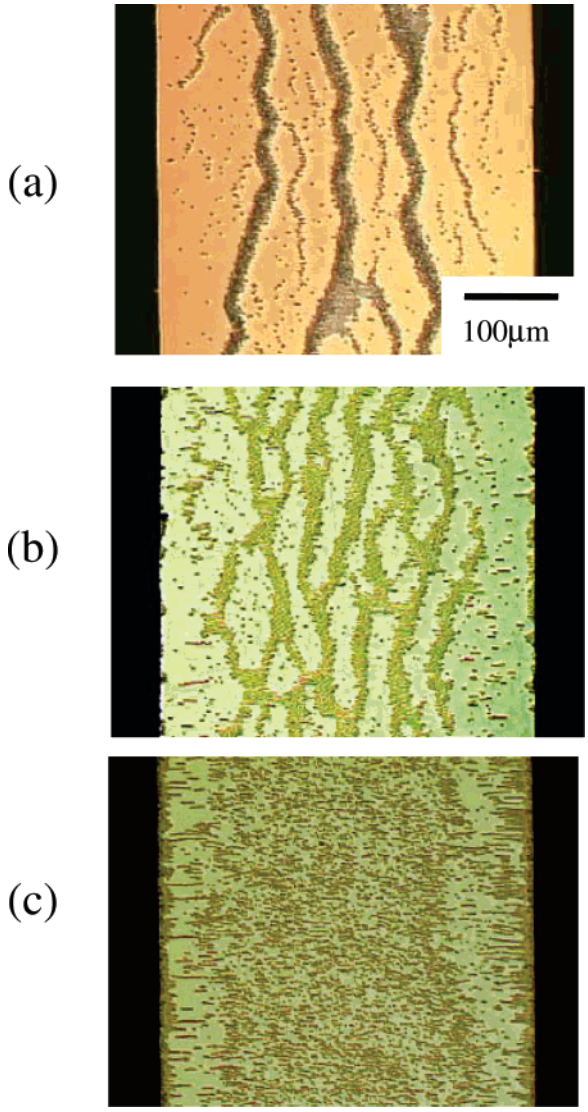

Figure 3. Alignment of silica particles with diameter of 2.0 μm suspended in salt solutions between the two flat electrodes. Salt concentration: (a) 0; (b) 0.25; (c) 1.0 mM.

Next, we studied the effect of salt concentration on the parameters of electroosmosis. Table 1 gives the values of the dielectric constant and viscosity of medium measured at various salt concentrations and Table 2 lists the values of the zeta potentials of substrate (electrode) surface and silica particles at different salt concentrations. As seen from Tables 1 and 2, the dielectric constant and viscosity of dispersion medium showed insignificant changes with salt concentration while the absolute value of zeta potential decreased. Since $Re[K_e]$ in eq 1 can be approximated by a constant of $-1/2$ when the electrocon-

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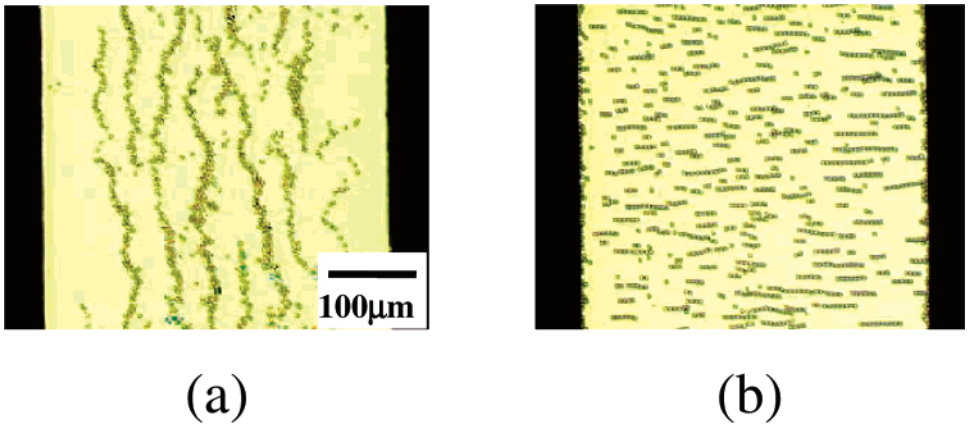

Figure 4. Alignment of silica particles with diameter of 4.9 μm suspended in salt solutions between the two flat electroded. Salt concentration: (a) 0; (b) 0.25 mM.

Table 1. Relative Permittivity ϵ_m and Viscosity η of Disperse Medium Containing NaCl Solutions

NaCl/mM	ϵ_m	η/cP	(ϵ_m/η)/cP^{-1}
0	72.9	1.08	67.3
0.250	71.8	1.10	65.0
0.500	71.1	1.11	63.8
1.00	69.9	1.12	62.4

Table 2. ζ-Potential of Quartz Plate or Silica Particles with Diameter of 2 mm Containing NaCl Solutions

NaCl/mM	quartz plate/mV	silica/mV
0	−79.3	−73.8
0.250	−77.5	
0.500	−66.2	
1.00	−61.9	−46.6

ductivity of particles is appreciably lower than that of dispersion medium as in the present case,[25] the dipole moment of particles at constant radius and applied potential is proportional to the dielectric constant of dispersion medium alone. Hence, the observed change in the direction of particle alignment in water from perpendicular to parallel would be caused by the suppression of electroosmotic flow with dielectric polarization unchanged at increased salt concentrations.

Experiments similar to those in Figure 2 were also performed using mixed solvents of water and ethanol as the dispersion medium. Figure 5 shows typical silica particle alignments in the mixed dispersion medium. Small silica particles (2.0 μm) were observed to align perpendicularly to the field at ethanol concentrations up to 30 wt % and almost disperse at 40 wt % or higher. When a frequency of 1000 Hz was used, the particles aligned forming four to five stripes, the number of which was somewhat larger than that in the absence of ethanol, at 10 wt % ethanol concentration (Figure 5a) and the number of stripes increased to eight to nine at 30 wt % ethanol concentration (Figure 5b), whereas no particle alignment was observed and all particles were dispersed at 50 wt % ethanol concentration (Figure 5c). The feature of silica particle alignment in this mixed solvent means that the packing of particles in each string becomes sparser as ethanol concentration rises even when perpendicular particle alignment is observed. As seen in Table 3, with increase in ethanol concentration, η increased while ϵ_m and ϵ_m/η, which is proportional to electroosmotic flow, decreased. Electroosmotic flow is then suppressed more with increasing ethanol concentration, thereby gradually

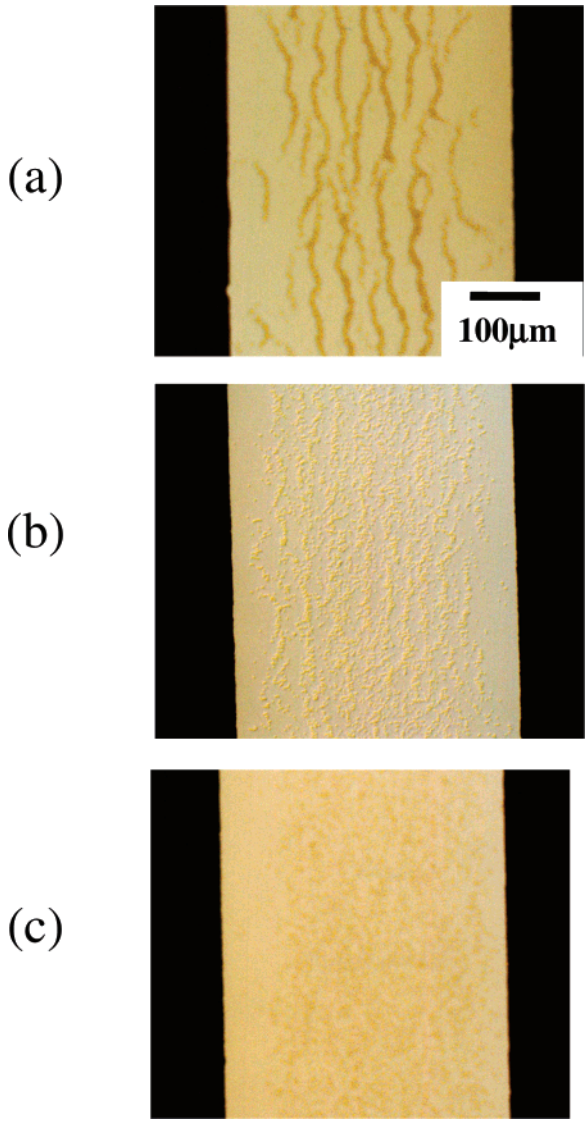

Figure 5. Alignment of silica particles with diameter of 2.0 μm suspended in aqueous ethanol solutions between the two flat electrodes. Ethanol concentration: (a) 10; (b) 30; (c) 50 wt %.

preventing perpendicular particle alignment. The reason no parallel particle alignment was observed in the mixed solvent would be a decrease in dielectric polarization produced by the decrease in ϵ_m with increasing ethanol concentration. The packing of particles aligned perpen-

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Table 3. Relative Permittivity ϵ_m and Viscosity η of Disperse Medium Containing EtOH with Various Concentrations

EtOH/wt %	ϵ_m	η/cP	(ϵ_m/η)/cP^{-1}
0	72.9	1.08	67.3
10	67.3	1.51	44.7
30	57.0	2.33	24.4
50	45.6	2.54	17.9

dicularly in each string is closely related to the electrostatic attraction between the particles and the action of dielectric polarization. Especially in this case, the packing is denser as this action becomes stronger. Hence, the observed sparse particle packing in each string at high ethanol concentrations would be brought about by a decrease in the dielectric polarization.

These findings demonstrate that perpendicular particle alignment is produced mainly by electroosmotic flow since the alignment was observed to disappear when the flow decreased and that both of the forces to cause particles to align parallel and perpendicularly to the field act in the alternating electric field and particle alignment depends on the competition of these two forces.

3.3. Effect of Frequency on Silica Particle Alignment. The relationship between the frequency of applied alternating electric field and silica particle alignment was examined (Figure 6). The figure shows that small silica particles (2.0 μm) cannot align and remain dispersed in the high-frequency range (a), whereas they start to align perpendicularly to the field forming stripes at about 7000 Hz (b) when the frequency is scanned toward the lower frequency side and the number of stripes reduces to six to seven at 3000 Hz (c), three to four at 1000 Hz (d), and one at 100 Hz (f). A similar trend was found for large silica particles (4.9 μm). Thus, the particles exhibited no

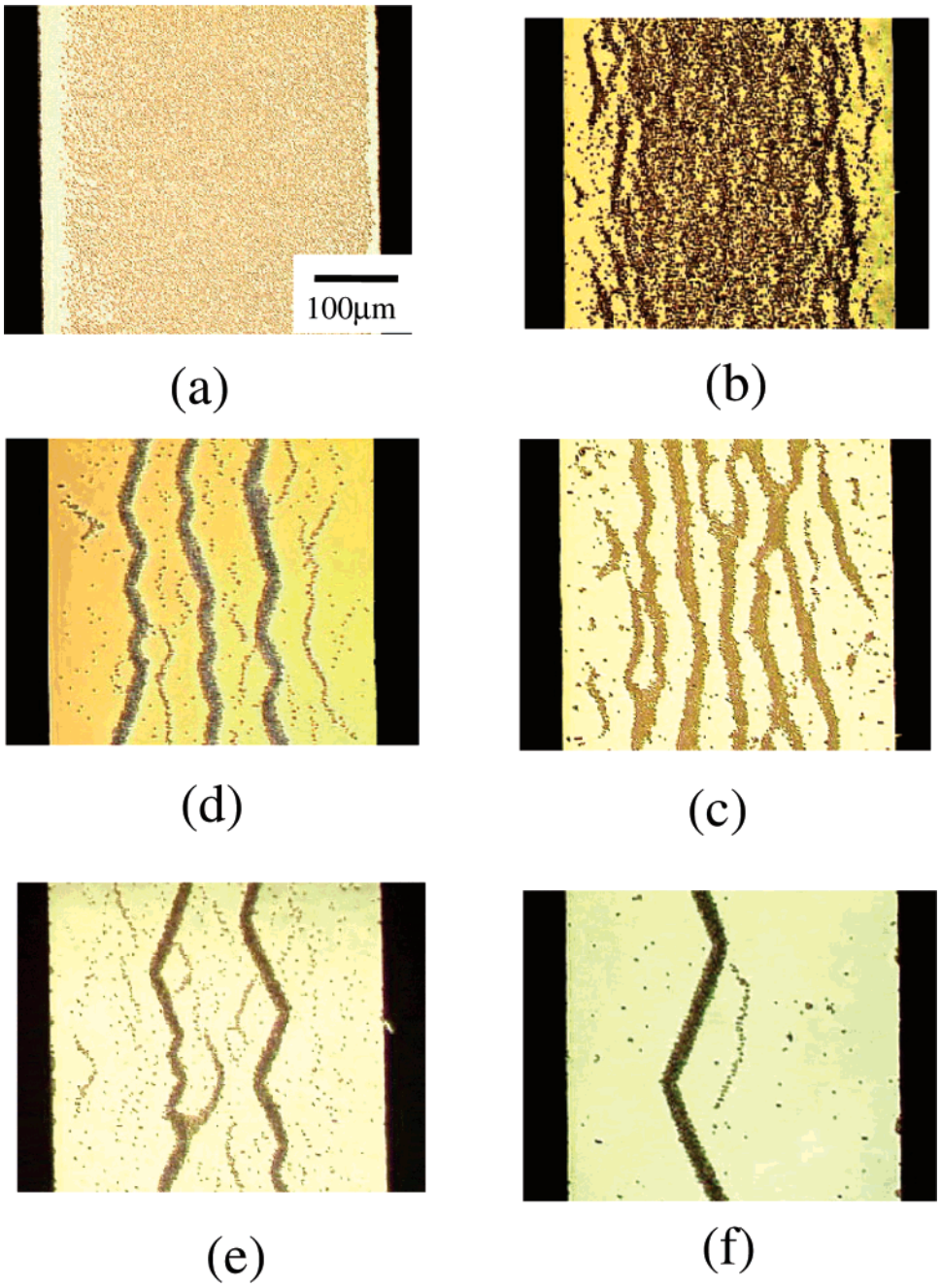

Figure 6. Frequency dependence of the number of stripes formed by silica particles with diameter of 2.0 μm suspended in water between the two flat electrodes. Frequency: (a) 10000; (b) 7000; (c) 3000; (d) 1000; (e) 200; (f) 100 Hz (3 V_{rms} ac 10 min after dispersion).

Table 4. Correlation between Frequency and Line Number

	100 Hz	200 Hz	400 Hz	600 Hz	1000 Hz	2000 Hz	3000 Hz	5000 Hz	6000 Hz	7000 Hz
2.0 μm	1	1−2	1−2	1−2	3−4	5−6	6−7	6−7	8−9	−13
4.9 μm	1	1−2	2−3	3−4	5−6	5	5			

alignment and remained dispersed at frequencies above a certain value and the number of stripes decreased with decreasing frequency in the frequency range where stripelike particle alignment was observed. Table 4 shows the relationship between frequency and the number of stripes.

The experimental results shown in Figure 6 and Table 4 clearly indicate that the number of stripes decreases and the distance between stripes widens as the frequency decreases. This would be related to the fact that since electroosmotic flow vibrates laterally in the alternating electric field in accordance with field alternation the width of the vibration in a cycle widens with decreasing frequency.

4. Conclusion

A peculiar phenomenon in which silica particles align perpendicularly to the field forming stripes was found when the behavior of the particles in aqueous solution between the electrodes was examined in an alternating electric field. The number of stripes changed with the frequency of alternating potential. The perpendicular silica particle alignment was suggested to be caused by electroosmotic flow generated around the particles. Alignment of solid particles dispersed in water was also suggested to be controllable by changing the balance between electroosmotic flow and dielectric polarization.

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