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Dielectric Properties of Electrorheological Fluids Containing Zeolite Particles

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Abstract. — Relationships between electrorheological (ER) effects and dielectric properties of suspensions are investigated from measurements of ER and dielectric properties of suspensions containing particles of type A zeolite such as 3A, 4A and 5A. In each suspension containing zeolite 3A or 4A particles, the ER effect is recognized, i.e., an increase in the apparent viscosity is observed when an electric field is applied, and the dielectric property is characterized by a dielectric dispersion in audio frequency region. On the other hand, the suspension containing zeolite 5A particles does not show a distinct ER effect and has a low dielectric constant without dielectric dispersion above 1 Hz. These results indicate that relaxation time of the induced polarization is associated with the ER effect; for the appearance of the ER effect the relaxation time should be shorter than a characteristic time. It is suggested that the characteristic time is associated with an angular velocity of rotating particles under a steady shear flow and also that the relaxation time of the polarization is mainly determined by the electric conductivity of the particle.

1. Introduction

The discovery of the ER effect was made by Winslow [1] in suspensions consisting of water-adsorbed particles such as hydrated SiO2, Fe3O4 and Zn(OH)2 in electrically non conducting liquids; apparent viscosities of such suspensions were observed to increase under applications of electric field of a few kV mm⁻¹. Such an increase in the viscosity has been interpreted as a result of following structure formations in the suspension. When an electric field is applied to the quiescent suspension, the constituent particles are arranged to form chain and/or column structures along the electric field. These structures are distorted if a shear strain is applied perpendicular to the electric field and the energy dissipated in this process results in the increase in the viscosity. The suspensions having such properties are called ER fluids or ER suspensions and the details of such fluids are described in some review articles [2,3].

In an early stage of the studies, it had been suggested that adsorbed water is necessary for the appearance of the ER effect, since an electric double layer around the particle was considered to play an essential role for the ER effect [4]. Later in the second half of the 1980's the ER effects
were observed even in anhydrous suspensions containing dehydrated organic semiconductors [5] or zeolite particles [6], which made various applications using the ER suspension more realistic and also made fundamental researches in this field more extensive.

The origin of the structure formation has been suggested to be interactions between the electrical polarizations induced on the interface between the particle and the liquid [2, 7, 8]. Some works, therefore, have been performed on the dielectric properties of ER fluids [4, 9–11], but the relationship between the ER effect and the interfacial polarization is not well understood. In some systems, e.g., TiO$_2$ dispersed system, the ER effect cannot be explained even qualitatively in the framework of the conventional theory of the interfacial polarization [10].

In the present study, dielectric properties of the anhydrous suspensions containing type A zeolite particles are explored and relationships between the ER effect and the dielectric properties of the system are studied. As is well known dehydrated zeolite has a composition of M$_x$Al$_y$Si$_z$O$_d$ and has a variety of structures depending on the Si/Al ratio; there exist open structures composed of aluminosilicate networks with various sizes and shapes of channels and cavities [12]. In these networks various species of metal ions (M) are incorporated to accomplish an electrical neutrality of the crystal and some of zeolites are known as ionic conductors with metal ions showing diffusional motions through the channels and the cavities in the network [13]. The type A zeolite is specified by Si/Al ratio of unity and its general composition of dehydrated form is M$_x$Al$_{12}$Si$_{12}$O$_{48}$. According to the species of the metal (M) ions contained in the aluminosilicate network, various type A zeolites are synthesized; e.g. 4A, 3A, and 5A zeolites contain Na, K and Na, and Ca and Na ions, respectively. Since these incorporated ions show diffusional motions characteristic to the respective zeolites, different ER effects are observed in the suspensions containing these zeolite particles [6,10].

In the course of our studies on the ER effect of the suspensions including zeolite particles, we became aware that suspensions containing zeolite 3A or 4A particles showed ER effects whereas no ER effect was observed in a suspension containing zeolite 5A particles. Such results motivated us to examine the dielectric properties of these suspensions, since some difference in the properties of the polarization induced on the interface was expected to reflect the difference in the ER effects. Our results indicate that suspensions in which the relaxation times of the interfacial polarization are shorter than a characteristic time show the ER effect. Factors associated with the characteristic time and origins of the relaxation time of the induced polarization are discussed.

2. Experimental

2.1. MATERIALS — Particles of type A zeolites of 3A, 4A and 5A, the formula of which are K$_9$Na$_3$Al$_{12}$Si$_{12}$O$_{48}$, Na$_{12}$Al$_{12}$Si$_{12}$O$_{48}$, and Ca$_{24}$Si$_{12}$Al$_{12}$Si$_{12}$O$_{48}$, respectively, were obtained from Sigma Chemical Corporation. These particles have some facets with the average grain size of 6 μm. Zeolites 3A and 5A were dehydrated by keeping the materials at 773 K for more than 6 hours and zeolite 4A at 873 K under 10$^{-6}$ torr for more than two days. Anhydrous suspensions of about 20 vol% were prepared by dispersing the zeolite particles in 50 cS silicone oil T5F451-50 (Toshiba Silicone Co., Ltd., Japan) dehydrated by pellet-type molecular sieves 4A. In order to get well-dispersed suspensions, the suspensions were stirred by adding zirconia balls in the vessels. The effect of zirconia impurity, which is contaminated in the stirring process, on the ER and the dielectric properties is considered to be negligible, since the amount is a few orders of magnitude less than those of the zeolite particles. In the following sections of this article, the suspensions consisting of type A zeolites and silicone oil are abbreviated for instance in the case of zeolite 4A as 4A suspension.
2.2. APPARATUS. — The electrorheological properties of the suspensions were measured in the region of shear rate from 6.59 to 659 s⁻¹ using a homemade concentric cylindrical viscometer. In order to generate an electric field perpendicular to the flow, the inner and the outer cylinders were electrically insulated to make possible the applications of high voltages at the 1 mm gap between these cylinders.

For applications of the high voltages, a DC power source HPR-15P (Matsusada Precision Co., Ltd., Japan) and a variable frequency AC power source CVFT1-50HVP2 (Tokyo Seiden Co., Ltd., Japan) were used. When DC fields were applied, the particles adhered especially on the surface of the inner cylinders (positive electrode) owing to an electrophoresis of the particle, resulting in irreversible changes of the rheological properties of the suspensions. The measurements, therefore, were preferentially carried out under AC fields. Frequency dependence of the ER effects under applications of AC electric fields was measured except for a region centered around 50 Hz, since in this region a forced vibrations occurred in the viscometer to make the measurements impossible. The magnitudes of the AC fields are represented in r.m.s.

The dielectric constants were measured by an impedance analyzer 4192A (Hewlett Packard Co., USA) or a method using a lock-in amplifier [14]. When the 4192A is used, the measurements of dielectric constants below 100 Hz become impossible owing to the large impedance in this frequency region. In such cases, a lock-in amplifier 5610B (NF Electronic instruments, Japan) was used to obtain the data of the dielectric constants.

For temperature measurements of the suspensions, e.m.f from a chromel-constantan thermocouple attached to the outer cylinder was monitored using a digital voltmeter KP (Chino Corporation, Japan). In the case of the measurements of dielectric constants, the temperature of the suspensions was controlled within 0.1 K.

3. Results

3.1. ER EFFECTS. — Rheological properties of the 4A suspension at 300 K are given in Figure 1. Under no electric field the suspension behaves as a Newtonian fluid, which is evidenced by the linear increase of the shear stress with the increase of the shear rate. When an AC field of 2 kV mm⁻¹ is applied to the suspension, the shear stress increases with some amounts over the measured shear rate region as a characteristic of a Bingham fluid, indicating
Fig. 2. — Yield stress $\Delta \sigma$ at 659 s$^{-1}$ as a function of magnitudes of AC fields (100 Hz) for the 4A suspension at 300 K. $\Delta \sigma$ is almost proportional to square of the electric field, which is confirmed by the solid line of $\Delta \sigma \propto E^2$.

Fig. 3. — Rheological properties (shear stress $\sigma$ vs. shear rate $\dot{\gamma}$) of the 5A suspension at 300 K.

the appearance of the ER effect in this suspension. Such an increase in the shear stress is called yield stress and is a characteristic property of the ER suspensions. The increase in the yield stress with lowering the shear rate, which has been reported in some articles [15,16], is observed also in this suspension. The ER effect is also confirmed under applications of DC electric field, but the adhesion of the particles on the wall of the cylinders makes it difficult to get qualified results.

Figure 2 shows an electric field dependence of the yield stress ($\Delta \sigma$) at a shear rate of 659 s$^{-1}$. The amount of $\Delta \sigma$ is almost proportional to square of the electric field as expected from theoretical results [2,7], which shows that an interaction between induced dipoles is the origin of the yield stress and this interaction results in the square law dependence of the yield stress against the electric field. Similar ER effects are also observed in other suspensions containing particles of 3A zeolite or other types of zeolites such as F, Y and X.

In Figure 3, the electric field dependence of the rheological properties of the 5A suspension at 300 K is depicted. As obvious from this figure, a distinct ER effect is not observed in this suspension under the application of the AC field of 2 kV mm$^{-1}$, which is also confirmed under a DC field up to 5 kV mm$^{-1}$. However, when the suspension is heated up to 385 K, a small
ER effect is observed under 2 kV mm$^{-1}$ AC field with a yield stress less than 10 Pa.

3.2. DIELECTRIC PROPERTIES. — Results of the frequency dependence of the dielectric constants in the 4A suspension are given with real and imaginary parts in Figures 4 and 5, respectively. Similarly to the dielectric spectrum in polar liquids, dielectric dispersions are observed, suggesting that there is some mechanism responsible for a generation of a polarization in this suspension. The relaxation times $\tau$ of the polarization at 300, 325 and 350 K, which are obtained from a relationship $\tau = 1/(2\pi f_{\text{max}})$ with $f_{\text{max}}$ being the frequencies at the maxima in the respective imaginary parts of the dielectric constants, are $2.0 \times 10^2 \mu$s, 2.1 $\mu$s, and 3.6 $\mu$s, respectively. Supposing that the relaxation time is governed by the Arrhenius process, the activation energy for the motion of the polarization is determined as 70 kJ mol$^{-1}$. Such a dielectric dispersion is also observed in other suspensions which show the ER effects; e.g., the 3A suspension has a dielectric dispersion with longer relaxation times than those in the 4A suspension; 4.2 ms, 0.80 ms, and 0.13 ms at 300, 325, and 350 K, respectively, and the activation energy of 60 kJ mol$^{-1}$.

Figures 6 and 7 are real and imaginary parts of the dielectric constants in the 5A suspension, respectively. Contrary to the case of the 4A suspension, below 350 K any dielectric dispersion is not observed in the frequency region of 1 Hz to 100 kHz. At 375 K, however, an indication of a dielectric dispersion below 1 Hz is recognized. These results suggest that the relaxation...
Fig. 6. — Frequency dependence of the real part of the dielectric constant for the 5A suspension.

Fig. 7 — Frequency dependence of the imaginary part of the dielectric constant for the 5A suspension. The increase of $\varepsilon''$ at lower frequencies is due to DC conductivity.

time of the polarization in this suspension is longer than 1 s even at 375 K. The increase in the imaginary part of the dielectric constant at lower frequencies is due to a DC conductivity ($\sigma_{dc}$), which contributes to $\varepsilon''$ as proportional to $\sigma_{dc}/\omega$.

4. Discussion

4.1. Origin of the Dielectric Dispersion. — Which mechanism is responsible for the dielectric dispersion in the 4A suspension? The measurements of the dielectric constants of zeolite 4A itself has been made for a powder compacted pellet [17]; dielectric dispersions are observed, although they are not clear compared with those of the present 4A suspension, with the activation energy of 48 kJ mol$^{-1}$ and the dielectric constant (real part) of about 20 at 363.2 K in the frequency region less than 100 kHz. These results suggest that the observed dielectric dispersions (Figs. 4 and 5) are not due to the 4A particle itself but to an interfacial polarization which is caused by a mismatch of the dielectric constant and electrical conductivity between the particle and the liquid.

When spherical particles (diameter $a$, real part of the dielectric constant $\varepsilon_p$ and conductivity $\sigma_p$) are dispersed in a liquid (real part of a dielectric constant $\varepsilon_l$ and conductivity $\sigma_l$), the interfacial polarization induced by the electric field (E) is proportional to $\varepsilon_l a^3[\varepsilon_p - \varepsilon_l]/(\varepsilon_p + 2\varepsilon_l)E$. 
The frequency dependence of the complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ associated with such a Maxwell-Wagner type polarization is expressed by the following well-known equations when $\sigma_p \gg \sigma_l$ [18]:

\[
\varepsilon^* = \frac{\varepsilon_\infty}{1 + \frac{k}{1 + i\omega\tau}}
\]

\[
\varepsilon_\infty = \varepsilon_l\left[1 + \frac{3\nu(\varepsilon_p - \varepsilon_l)}{2\varepsilon_p + \varepsilon_l}\right]
\]

\[
k = \frac{9\nu\varepsilon_l}{2\varepsilon_l + \varepsilon_p}
\]

\[
\tau = \frac{2\varepsilon_l + \varepsilon_p}{4\pi\sigma_p}
\]

where $\omega$ is an angular frequency of the electric field, $\tau$ the relaxation time of the polarization, $\varepsilon_\infty$ a dielectric constant at $\omega \gg \tau^{-1}$, and $\nu$ the volume fraction of the particles. Although there are some developed expressions for the interfacial polarization [19, 20], equation (1) is a prototype and enough to understand the mechanism qualitatively.

Using the data of the conductivity [21] and the dielectric constant [17] of zeolite 4A and the dielectric constant of the silicone oil, which are $2.0 \times 10^{-8}$ Scm$^{-1}$, $\sim 20$, and $\sim 2$, respectively, the relaxation time of the polarization in the 4A suspension can be calculated from equation (4) to be about $1.0 \times 10^{2}$ ms at 300 K. This is almost consistent with the relaxation time $2.0 \times 10^{2}$ $\mu$s obtained from the dielectric dispersion in this suspension, which confirms that the interfacial polarization is responsible for the dielectric dispersion.

For zeolite 5A, measurements of the dielectric constants and the electrical conductivity have not been reported. Only the data for Ca-substituted zeolite Ca$_1$Na$_{10}$Al$_{12}$Si$_{12}$O$_{48}$ are available; the electrical conductivity of this material at 614.4 K is estimated to be $1.8 \times 10^{-6}$ S cm$^{-1}$ indirectly from the increase of the $\varepsilon''$ at low frequency region [17]. Such a low electrical conductivity is also expected for zeolite 5A with a result of longer relaxation time of the polarization in this suspension as expected from equation (4), making the observation of a dielectric dispersion impossible in the measured frequency region. The indication of a dielectric dispersion below 1 Hz when heated up to 375 K is interpreted as the result of an increase of electrical conductivity of the 5A particle at higher temperatures.

The difference in the dielectric property among these zeolite suspensions can be interpreted from the distinct diffusional motions of the metal ions in respective zeolites. In type A zeolite the metal ions are accommodated in three sites, $\alpha$, $\beta$ and $\gamma$, in the aluminosilicate network. Of these ions the metal ions in the $\gamma$ site are suggested to be mobile to make some of zeolites ionic conductors [17, 22, 23]. Such a $\gamma$ site ion is present in 3A and 4A zeolites whereas this ion is lacking in 5A zeolite [12, 22], which would be responsible for the dielectric properties of these suspensions.

4.2. RELAXATION TIME OF THE POLARIZATION AND ER EFFECT. — The results of the ER effects and the dielectric properties suggest that the relaxation times of the polarization are reflected in the appearance of the ER effect. It is generally accepted that the ER effect occurs as a result of the dipole-dipole interaction between the polarizations induced at each particle, indicating that the polarizations should survive for the appearance of the ER effect. When the frequency of an applied AC field becomes higher than the relaxation rate of the polarization, the polarization cannot follow the AC field with, as a result, the reduction of the polarization and hence a decrease in the ER effect. Such an effect is observed at 300 K in our measurement of the ER effect as a function of the frequency of the AC fields (Fig. 8); the ER effect becomes
smaller at frequencies higher than 40 Hz. Above 300 K the decrease of the ER effect was recognized to occur at higher frequencies compared with the result at 300 K. These results are consistently interpreted by comparison with the dielectric properties of this suspension (Figs. 4 and 5).

Under a steady shear flow particles in a suspension also feel an AC field even under a DC field, since some motions of the particles are excited owing to an exertion of a viscous torque on the particles. The frequencies of the AC field which the particles feel are characterized by the motions of the particles, and are specified by a characteristic time $\tau_c$. Similarly to the case of the above-mentioned frequency dependence of the ER effect, the ER effect under such motions is expected to appear if the relaxation time $\tau$ of the polarization is shorter than the characteristic time $\tau_c$.

The motions of particles under a steady shear flow have been theoretically examined by Jeffrey [24] with a result that under a steady shear flow a forced rotation of the particles occurs owing to a viscous torque exerted on the particle and the angular velocity $\omega_r$ of the rotation is equal to (shear rate)/2 when the particles are spherical and the particle-particle interactions are absent. This is experimentally confirmed by Block et al. [25] from the measurements of dielectric constants of a dilute suspension under a shear flow. It may, thus, be possible as a first approximation to consider that the characteristic time $\tau_c$ is given by the inverse of $\omega_r$, indicating that for the appearance of the ER effect a condition of $\tau < 2/\dot{\gamma}$ should be satisfied between the relaxation time $\tau$ and the shear rate $\dot{\gamma}$.

Our rheological measurements are performed under the shear rate up to 659 s$^{-1}$, which indicates that for the appearance of the ER effect the relaxation time of the polarization should be in the region of $\tau < 3$ ms. This condition is fulfilled in the case of the 4A suspension while is not in the case of the 5A suspension, which might reflect in the results of the ER effects of these suspensions at 300 K. The small ER effect observed at 385 K in the 5A suspension can also be interpreted; the relaxation time becomes shorter at high temperature, although it is not short enough for a full induction of the polarization, to give rise to the ER effect.

In the above discussion, the effects of the electric field on the rotational motion of the particle are not considered. Some theoretical works on a dilute suspension suggest that an electric field exerts a torque on the polarizable particle to suppress the rotational motion of the particle [26–29], which is experimentally observed from our recent measurement of an

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**Fig. 8.** Yield stress at 300 K as a function of the frequency of the applied AC field (2 kV mm$^{-1}$ in r.m.s.) for the 4A suspension. Decrease in the yield stress above 40 Hz is observed, which can be interpreted from the dielectric properties of this suspension (Figs. 4 and 5).
electrorheological resonance in a dilute suspension containing TiO₂ particles [30]. In addition particle-particle interactions originating from a dipolar interaction would also contribute to suppress the rotational motion. These effects would make the angular velocity of the rotation lower compared with that in the absence of the electric field, leading to the characteristic time \( \tau_e \) longer than \( 2/\gamma \). For further understandings of the relationship between the ER effect and the dielectric properties, these contributions should also be taken into account. The study of the ER effect has just begun and there are many factors to be unveiled. The present result is a step towards a thorough clarification of this effect.

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References

    As the dielectric constants at 300 K is not reported, the value at 363.2 K, which can be estimated from the Cole-Cole plot, is used to calculate the correlation time at 300 K by assuming that the temperature dependence of the dielectric constant is small.

In a dilute suspension containing TiO$_2$ particles, a peak in shear stress is observed when the shear stress is measured as a function of the frequency of the applied AC field. This is caused by matching of the angular velocity of the rotating particle with the frequency of the AC field and we call this phenomenon an ER resonance.