Dielectrophoretic and electrophoretic force analysis of colloidal fullerenes in a nematic liquid-crystal medium

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This research focuses on the electrorotation motion of fullerene suspended in liquid crystal host medium, which are investigated in the homogeneously aligned nematic liquid crystal cells driven by in-plane field. We investigated the effect of electrophoretic and dielectrophoretic forces and related parameters of the colloidal fullerenes in liquid crystals. The electrophoretic mobility, zeta potential, and critical voltage have been evaluated. Fullerenes suspended in liquid crystal medium migrated toward the positive electrode, but were pulled back in the opposite direction when the polarity was reversed especially at low frequency range (<5 Hz). At higher electric field and higher frequency ranges, the net displacement of fullerenes has been observed. We demonstrate that the dielectrophoretic force dominated the motion in the colloidal fullerenes by a proper analysis of different electrophoretic parameters. In addition, the electrodynamics of fullerenes was explained by applying the theory of the dielectrophoresis and Schwarz’s formula. We propose a model to estimate the density of fullerenes suspended in liquid crystal medium.

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I. INTRODUCTION

Different forces such as interparticle forces [1–7], optical trapping [8,9], and electrokinetic forces [10–16] of the colloidal suspension have triggered tremendous motivation among scientists to explore the possibilities of using them in biotechnology and genetic engineering [17], nanotechnology [18–20], display devices [21]. Among them electric field induced controlled forces of the colloidal particle have attracted considerable scientific and technological interest especially in an electronic-paper-like display in which modulated light can be realized by utilizing the motion of such nanoparticles [22–26]. Electric field induced force on the colloidal particle can cause the fractal formation, chaining, net- or matrixlike structure or translation motion in the dielectric host medium. However, an electric field induced dynamics of nanoparticles in liquid crystal (LC) host medium are rarely reported [27–33]. Liao et al. [32] reported electrorotation (Quincke rotation) and electrotranslation of microscopic cylindrical and spherical inclusions dispersed in LCs. They showed that when the applied dc electric field increased above the threshold field, the cylinders start to rotate about their symmetry axis, and it triggers an additional translational motion at higher fields. Some of the controlled force studies have been carried out on the laser trapping of colloidal particles in liquid crystal medium [8,9]. Recently, we have reported the translational motion of aggregated carbon nanotubes (CNTs) suspended in LC medium, in which the CNTs deform the LC director due to its translational motion [29–33] under ac electric field.

Further electric field induced motion in the colloidal suspension is in general explained either by dielectrophoretic (DEP) or by electrophoretic (EP) force. The DEP force is defined as a force invoked by the dipole layer that is formed at the interface of two inhomogeneous materials, for instance, colloidal particles with no permanent charges in dielectric solvent. The induced motion is determined by the dielectric properties of the guest and host dielectric medium, whereas in electrophoresis the motion of the particle is determined by the magnitude and polarity of net electric charge. The DEP force was studied in early work of Pohl [12] in the 1950s and a comprehensive review has been presented by Buke [13]. In an electrophoretic force particles migrate in response to an applied voltage across electrodes, and the response of the material is sensitive to the sign of the applied voltage. Charged pigment particles move toward one electrode by electrophoretic forces. There are two different effects associated with DEP forces: positive and negative DEP force. Positive DEP force occurs when the particles are more polarized than the medium, whereas the polarized particles move forward to the maximum field gradient. The reverse is true for negative DEP force.

There are very few reports [23,24,33] in which both DEP and EP forces have been taken into account in order to explain an electric field induced motion of suspended particles in the host dielectric medium. Previously in an electronic-paper-like display, in which charged pigment particles move toward one electrode, only electrophoretic force was believed to be present. The presence of both dielectrophoresis and electrophoresis in electronic displays was first noted by Bert and Smet, who showed that the DEP force play the important role in electrophoretic display. Therefore, the qualitative studies of both EP and DEP forces are very much important in order to explain the theoretical calculation and
respective parameters. In this paper we explained effects of DEP and EP forces and related parameters such as electrophoretic mobility, zeta potential, and critical electric field in the colloidal suspension of fullerenes and liquid crystals. We also proposed a model to estimate the density of fullerenes suspended in the LC medium.

II. EXPERIMENT

Fullerene of 1 wt % was dispersed in nematic LC medium. The interdigitated opaque electrodes made from aluminum have been separated at a distance of 30 μm with an electrode width of 10 μm. For a cell fabrication, a homogenous alignment layer (AL-16139) from Japan Synthetic Rubber Co.; was first spin-coated to a thickness of 800 Å on an electrode-patterned glass substrate. A rubbing process to an in-plane field direction was then performed on the substrate to align the nematic LC to minimize flow motion effect of LC on C60. The same alignment layer was coated on another glass substrate without an electrode, and the similar rubbing process was then performed in antiparallel direction to the first one. The cell was assembled to give a cell gap (d) of 10 μm, where the plastic balls were used to maintain the cell gap. Superfluorinated LC mixtures purchased from Merck Co. (dielectric anisotropy Δε=+7.4 at 1 kHz, birefringence Δn=0.088 at λ=589 nm, flow viscosity η =18 mm²/s at 20 °C) was filled at room temperature by the capillary action. The fabricated test cells were observed under optical polarizing microscopy (Nikon DXM1200) by applying a sine wave voltage of different fields and frequencies. The velocity (v) of the fullerenes was determined by monitoring the fullerenes’ motion and textures at the rate of 30 frames/s.

III. RESULTS AND DISCUSSION

For convenience, we have divided the results and discussion into two subsections. In Sec. III A, we evaluate different electrophoretic parameters and show that the dielectrophoretic force is dominated in the colloidal suspensions. In Sec III B, the translational motion of suspended fullerenes with varying electric field and frequency is discussed by applying the theory of dielectrophoresis and Schwarz’s formula and a model is proposed to estimate the density of fullerenes, suspended in the LC medium.

A. Electrophoretic parameters

Figure 1 shows optical micrographs of the dispersed fullerenes in the LC medium. In the absence of an external electric field, the C60 cluster inside the LC medium appears in a form of black domains. At low frequencies (1–5 Hz), C60 clusters translate between electrodes and migrate toward the positive electrode during the positive half cycle of the applied sine wave and bounce back in the next half cycle (see Fig. 1). We calculated the different electrophoretic parameters by applying the formulas used by Comiskey et al. [21]. The Reynolds number is given by Re=ρrvη−1, where ρ is the internal fluid density, r is the particle radius, η is the internal fluid viscosity and v is the velocity of the suspended fullerenes. For present system we have ρ =1.0714 ×10³ kg/m³, r =2.23×10⁻⁶ m, and η =19.3 ×10⁻³ kgm⁻¹s⁻¹ at room temperature (20 °C). Variation of Re with applying electric field is shown in Fig. 2. Clearly, as shown in Fig. 2, the values of Re are of the order of 10⁻⁵ and far less than 1, which justifies the Stokes law and hence, it is safe to presume a laminar flow. The transient time to establish the laminar flow can be estimated from Navier Stokes equation, τ s=(1/9)ρv⁴η⁻¹=123 ns. Thus for a time scale of interest, an electrophoretic mobility (μ) in a laminar flow regime can be expressed as

$$μ = \frac{v}{E_p} = \frac{ε χ}{6πη} = \frac{q}{12πνη}$$ (1)

where $E_p$ is the peak value of an applied ac electric field (E), χ is the zeta potential, ε is the dielectric constant of the internal fluid and q is the charge per particle.

Variation of electrophoretic mobility with electric field is given in Fig. 3. It is evident from Fig. 3 that the mobility of the C60 clusters increases linearly with electric field. Using the calculated mobility from Fig. 3, we evaluated the $χ$ potential at different electric fields as plotted in Fig. 4. The evaluated $χ$ potentials increase with increase in electric field, which shows that an electric field effect has positive impact in order to avoid the agglomeration. However, the evaluated $χ$ potentials are five to six times higher [21–25] and well above than the usual values.
Bert and Smet [23,24], also reported high values of \( \zeta \) potential and found that it was due to the presence of the dielectrophoretic force. They reported that the contribution of dielectrophoretic force was 90% for the 1 V of \( \zeta \) potential. This is because Eq. (1) can only be applied for the electrophoretic part of the velocity. The dielectrophoretic part of the velocity should be taken out to estimate the exact value of \( \zeta \) potential. The high values of \( \zeta \) potential showed that the velocity of C\(_{60}\) clusters in LC medium is dominated more strongly by the dielectrophoretic force than by electrophoretic force in the present case. In fact the total velocity comes from total force on the suspended particles, which has both electrophoretic and a dielectrophoretic part. We believe that the dominant part of the velocity and, therefore, the force has a dielectrophoretic origin due to anomalously very high value of \( \zeta \) potential.

The actual distribution of the velocity over the electrophoretic part and the dielectrophoretic part should be in general different for every colloidal suspension, depending upon the types of host and guest materials. For the charge per particle, we find equally unrealistic high values, which also indicate presence of strong dielectrophoretic force in the present colloidal suspension. (See Fig. 4). The value of \( q \) reported by Comiskey et al. [21] is 16 e\(^-\), however in our case it is 1161 e\(^-\) at an electric field of 0.20 V/\( \mu \)m.

When the effect of quadrupole and higher order multipoles are ignored, electric force acting on the particle in an external electric field can be expressed as [33–37].

\[
F = -qE + \rho(\nabla E),
\]

where \( \rho \) is the dipole moment on the fullerenes and \( \nabla E \) is the gradient of electric field. The first term describes the Coulombic interaction between the net charge \( q \) of the particle and an electrical field \( E \) and embodies all electrophoretic phenomena. This vanishes in the absence of net charge on the particle. The additional force terms arise from the interaction of dielectric polarization components induced in the particle by an electric field with spatial inhomogeneities in that field. This dielectrophoretic force term only vanishes if the field is spatially homogeneous (\( \nabla E = 0 \)). Hence, in order to apply the dielectrophoretic force, the applied electric field must be inhomogeneous. In their case [23,24], pigments were subjected to homogeneous electric field and the presence of charged particles inside the pixel made the total electric field nonuniform. However, in our case the applied field itself is nonhomogeneous, causing strong dielectrophoretic force on the suspended particles because of the use of the interdigitated electrode only at bottom substrate [30]. The distance between the bottom and top of the substrates is much larger than the height of the bottom interdigitated electrodes, developing the strong nonuniform electric field in the cell. Hence, the electrophoretic force can be assumed to be very small when compared to dielectrophoretic force for C\(_{60}\) clusters and LCs colloidal suspension.

**B. Dielectrophoresis and numerical simulations**

The use of dielectrophoresis is fast becoming a proven technique for manipulating particles and macromolecules in microfluidic systems. When the colloidal suspension of C\(_{60}\) clusters and LC is placed in nonuniform electric field, the net force acting on the C\(_{60}\) clusters in host LC medium can be calculated by the following general dielectrophoretic force (\( F_{DEP} \)) [10,13]

\[
\vec{F}_{DEP} = \Gamma \varepsilon_0 \text{Re}(K(e_2^* e_1^*)) \vec{V} E^2,
\]

where \( \Gamma \) is a geometrical factor, \( e_2^* \) and \( e_1^* \) are complex dielectric permittivities of the colloidal particles and the host dielectric medium, respectively. \( K(e_2, e_1) \) represents the complex polarization factor (for spherical objects this is known as Clausius-Mossotti function). \( E \) denotes an applied ac field. For a radius \( r \) of polarizable particle, the geometrical factor \( \Gamma \) is given by

\[
\Gamma = 2\pi r^3.
\]

The complex polarization factor is given by

\[
K(e_2, e_1) = \frac{e_2^* - e_1^*}{e_2 + 2e_1^*},
\]

where \( e^* = e - \frac{\omega}{\omega_0^2} j \) and \( \omega \) and \( \omega_0 \) stand for the conductivity and electric field frequency, respectively. Therefore, \( \text{Re}(K(e_2^*, e_1^*)) \) can be expressed as

\[
\text{Re}(K(e_2^*, e_1^*)) = \frac{\omega^2(e_2 - e_1)(e_2 + 2e_1^*) + (\sigma_2 - \sigma_1)(\sigma_2 + 2\sigma_1)}{\omega^2(e_2 + 2e_1^*)^2 + (\sigma_2 + 2\sigma_1)^2}.
\]

Equation (6) reveals a strong correlation between \( \text{Re}(K(e_2^*, e_1^*)) \) and electric field frequency. As a result when ac electric field is employed, both the magnitude and sign of
the force can be manipulated by means of a frequency change. This feature makes ac fields preferable for DEP than dc fields. For low and high frequency limit, the Eq. (6) can be written as

\[
\text{Re}[K(\omega)] = \frac{\sigma_2 - \sigma_1}{\sigma_2 + 2\sigma_1} \quad (\omega \to 0),
\]

\[
\text{Re}[K(\omega)] = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} \quad (\omega \to \infty).
\]

The formulation of expression of the DEP force in Eq. (3) did not include the effect of local electric fields developed by the other neighboring dipoles, and is based on the point dipole model. However, in the present case, particle occupies a finite space and affects the strength of the local electric field. To account for the size effect [38] and the local electric field due to the induced dipole moment, a heuristic scaling factor \(\alpha\) is introduced in Eq. (3)

\[
\vec{F}_{\text{DEP}} = 4\pi r^3 \varepsilon_1 \text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)] \vec{E}^2.
\]

Considering the one dimensional translation motion of colloidal particles in LC medium along \(x\) axis and applied electric field as a sinusoidal wave, the instantaneous force at a time \(t\) can be written as

\[
\vec{F}_{\text{DEP}} = 4\pi r^3 \varepsilon_1 \text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)] \frac{d}{dx} E_p^2 \sin^2(\omega t).
\]

The velocity (\(v\)) and displacement (\(x\)) of colloidal particles as a function of time can be obtained [27] from Eq. (10)

\[
v = \left( E_p - E_{cr} \right) \frac{4\pi r^3 \varepsilon_1 \text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)]}{m} \sin(\omega t),
\]

\[
x = \frac{2\left( E_p - E_{cr} \right)}{\omega} \sqrt{\frac{4\pi r^3 \varepsilon_1 \text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)]}{m} \sin^2 \left( \frac{\omega t}{2} \right)},
\]

where \(E_{cr}\) is the critical electric field [27] at which the colloidal particles start motion. For \(\omega t\) is an odd multiple of \(\pi\), the displacement of the suspended particles in LC medium will be maximum (\(x_{\text{max}}\)). Therefore, amplitude (Ampl) i.e., maximum displacement of the translational motion of the C\(_{60}\)s in LC medium can be written as

\[
\text{Ampl} = \frac{2\left( E_p - E_{cr} \right) \sqrt{4\pi r^3 \varepsilon_1 \text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)]}}{m}.
\]

where \(m = (4/3)\pi r^3 \rho\) is the mass of the suspended fullerenes and \(\rho\) is the corresponding mass density. \(\omega = 2\pi f\), where \(f\) is the applied frequency. Therefore, Eq. (13) can also be expressed as

\[
\text{Ampl} = \frac{\left( E_p - E_{cr} \right)}{\pi f} \sqrt{\frac{3\alpha \varepsilon_m \text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)]}{\rho}}.
\]

In low frequency region (<10 Hz), the dielectric permittivity of the LCs increases with decrease in the frequency due to the contribution of electrode polarization capacitance of LC cell and dielectric permittivity of LCs can be expressed as [39]

\[
\varepsilon_m = \varepsilon_{\infty} + \frac{A_1}{f^m},
\]

where \(\varepsilon_{\infty}\) is relative permittivity in the high frequency limit and the second term of Eq. (15) represents the contribution of electrode polarization capacitance at low frequencies [39]. From Eqs. (14) and (15), the amplitude of the translational motion of suspended C\(_{60}\) clusters in LC medium can be expressed as

\[
\text{Ampl} = \frac{(E_p - E_{cr})}{\pi f} \sqrt{\frac{3\alpha \varepsilon_m \text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)]}{\rho}}.
\]

Figure 5 shows the variation of \(\text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)]\) with ac frequency. The conductivity of the fullerenes (~10\(^{-4}\) S m\(^{-1}\)) [40] was much higher than that of the LC host medium (~10\(^{-9}\) S m\(^{-1}\)). The dielectric permittivities of the C\(_{60}\) and LC were 4.4\times8.85\times10\(^{-6}\) and 6.07\times8.85\times10\(^{-6}\) kg \(\mu\)m \(s^{-2}\) \(V^{-2}\), respectively. The value of \(\text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)]\) was found to be \(-0.14\) and +0.99 for the present C\(_{60}\) clusters and LC colloidal suspension. When the Clausius-Mossotti factor (\(\text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)]\)) is less than zero, negative DEP occurs.

We measured the amplitude of translational motion with change in frequency and electric fields. Figure 6 shows the variation of amplitude of translational motion with increasing frequency at a certain applied electric field of 0.38 V/\(\mu\)m. Initially an electric field with frequency 1 Hz was applied between electrodes. It is apparent from Fig. 6 that amplitude of oscillation motion decreases with increasing frequency and it becomes zero at a frequency of ~5 Hz. The experimental curve of Fig. 6 has been fitted to Eq. (15) to estimate the density of suspended C\(_{60}\) clusters. From Fig. 5, \(\text{Re}[K(\varepsilon_2^*, \varepsilon_1^*)]\) can be assumed to be equal to 1, the evaluated fitted parameters are listed in Table I. From fitting, \(\rho\) is found to be 1.6\times10\(^{-15}\) kg/\(\mu\)m\(^3\). The density of fullerenes reported in the other literature [40] is 1.65\times10\(^{-15}\) kg/\(\mu\)m\(^3\) and hence, the density for fullerene clusters estimated by DEP force is quite reasonable. Figure 7 shows the variation
FIG. 6. Variation of amplitude of translational motion of C$_{60}$ clusters in LC medium with frequency in homogeneous aligned cell driven by in-plane field at a field strength of 0.39 V/µm. Circles represent the experimental data whereas continuous line on the circles is the best fitting according to Eq. (16).

of amplitude of translational motion with electric field at a certain applied frequency of 1 Hz. The amplitude of translational motion decreases linearly with decrease in applied electric fields. However, it deviates from its linear decrease near the critical electric field at which C$_{60}$ clusters start the translational motion. In Fig. 7, there would not be any low frequency effect as it is plotted at particular frequency. Therefore Eq. (14) was fitted to the linear part of experimental curve of Fig. 7 in order to estimate the density of C$_{60}$ clusters. The estimated fitted parameters are listed in Table II. From fitting, the estimated density of C$_{60}$ clusters was found to be 1.5 × 10$^{-15}$ kg/µm$^3$, which is almost equal to the value estimated from Fig. 6. The estimated critical electric field ($E_{cr}$) was found to be 0.24 V/µm, which is in good agreement with the extrapolated value of Fig. 7 at abscissa. The C$_{60}$ clusters did not move appreciably for the applied electric field of less than 0.24 V/µm and measured amplitude of translation motion was of the order of ~1.0 µm. We could measure the amplitude of translation motion with the uncertainty of ~100%, below the applied electric field of 0.24 V/µm. Therefore, the estimated electric field of 0.24 V/µm can be considered as a critical electric field.

As mentioned earlier, for the frequency range of 1–5 Hz, the C$_{60}$ clusters tend to move toward the region where electric field intensity is high. At a frequency of 5 Hz, the amplitude of translational motion of C$_{60}$ clusters almost becomes zero. The DEP also provides an explanation for the zero amplitude of translational motion at a frequency of 5 Hz. Hopper and Novotny [41] first reported on the need of a delay time in the theoretical model of electronic paper image displays. Schwarz’s formula gives a value for the delay time needed to induce a dipole from a particle at rest [42,43],

$$\tau = \frac{r^2e}{2\mu kT}. \quad (17)$$
e is the elementary charge, $k$ is the Boltzmann constant and $T$ is the temperature. This delay time gives an approach for the minimum time that a field has to be applied in a certain direction to fully induce a dipole in that direction. If the period of the applied field is lower than the delay time needed to induce the dipole, the dipole cannot follow the field. The presence of this dipole moment is necessary for dielectrophoretic force to act on the particle. The calculated value of delay time at an electric field of 0.38 V/µm was found to be 0.19 s, which corresponds to the electric field frequency of 5.3 Hz. Therefore, the calculated frequency of 5.3 Hz from Eq. (17) is in good agreement with experimental results shown in Fig. 6, in which the amplitude of translational motion becomes zero at a frequency of ~5 Hz.

At higher frequency of greater than 60 Hz and electric field of greater than 5 V/µm, the net displacement of the C$_{60}$ clusters was observed rather than any translational motion i.e., clusters travel in particular direction in a presence of electric field without any translation motion. At higher frequency, the period of the applied electric field will be shorter than the delay time needed to induce the dipole and the dipole will not be fully formed. If the maximum dipole switching speed exceeds the external field, the dipole will not switch completely when the field switches, resulting in a net dipole-moment and therefore, a net force in one direction [26,27]. The details of the physical mechanism of the field-induced net-movement of suspended particles, at higher field and higher frequency will be the subject of future studies.

IV. CONCLUSIONS

In summary, we investigated the effect of electrophoretic and the dielectrophoretic force and the related parameters of the colloidal fullerenes in LC. We demonstrated that the dielectrophoretic force on the suspended fullerenes in the LC

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<th>$E_{cr}$ (V/µm)</th>
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<th>$A_1$</th>
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<td>0.14</td>
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medium play a major role under applied electric field. The electrophoretic mobility and zeta potentials increase with increasing electric field. Fullerenes suspended in the LC medium moved toward the positive electrode, and were pulled back in the opposite direction when the polarity was reversed especially at the low frequency (~5 Hz), which was found to be in good agreement with the frequency estimated by the Schwarz’s formula. The amplitude of this translational motion decreases with increasing frequency, whereas it increases with electric fields. We proposed a model to estimate the density of fullerenes suspended in the LC medium. The density of fullerene agglomerates was found to be ~1.6 ×10^{-15} \text{kg/\mu m}^3. The electric field induced dynamics behavior of C_{60} clusters in LC medium suggests that C_{60} can be one of the future candidates for electronic-paper-like displays.

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[40] http://www.creative-science.org.uk/propc60.html