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## Electric Birefringence and Electrophoretic Light Scattering for Colloid Stability Characterisation\*

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The effect of an electric field on a dilute suspension of asymmetric colloidal particles is to impose rotational order which can be detected as an induced birefringence in the sol. Furthermore, if the particles are charged, such rotation is followed by electrophoretic translation. In a single apparatus, pulsed electric fields have been applied to sols of the rod-like clay mineral attapulgite, and both the transient induced birefringence and the variation in the fluctuations of the scattered light have been measured. Experiments involving the addition of CTAB surfactant, resulted in the measurement of the electrical polarisability anisotropy, electrophoretic mobility, translatory and rotary diffusion coefficients as the inherent negative surface charge of the mineral particles was swept through the zero point of charge and into a positive condition. The accompanying changes in sol stability and flocculation were monitored in terms of these parameters.

### INTRODUCTION

Electro-optical methods have been gaining increasing popularity for the characterisation of colloidal dispersions<sup>1</sup>. The majority of colloidal particles are geometrically anisodiametric, optically anisotropic and are either or both anisotropic electrically or contain surface charge. They are thus influenced by an applied electric field and any change in their distributional order within the sol can be detected by one or more optical properties. This paper is concerned with two electro-optical methods, namely electric birefringence and electrophoretic scattering, for the characterisation of the electrical, geometrical and optical properties of colloids in suspension.

The first mentioned of these methods has been developed for two purposes, namely the estimation of particle size and size distributions for colloidal sols and for the evaluation of the electrical polarisability ( $\alpha$ ) of the dispersed particles. In fact, the anisotropy ( $\Delta\alpha$ ) of the polarisability associated with the two principal particle axes for particles with cylindrical symmetry is determined. During recent years there has been an increasing number of dielectric and electro-optical studies on colloids which indicate that in aqueous

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media the polarisability is of interfacial origin<sup>2-4</sup> and is thus related to the charge double-layer characteristics. If so,  $\Delta\alpha$  may be of significance in our future understanding of colloidal stability.

Whereas fluctuation light scattering<sup>5,6</sup> has enjoyed extensive popularity for the evaluation of the translatory diffusion coefficient ( $D_t$ ) of particles in suspension, the recent method of electrophoretic light scattering<sup>7</sup> has produced a rapid means of measuring the electrophoretic mobility ( $u$ ) in dilute sols. Such a parameter relates closely to the surface charge density<sup>8</sup> at the particle-liquid interface and so is itself an important experimental parameter for the characterisation of colloid double layers and sol stability.

In this work a single apparatus has been used to measure all of the foregoing parameters and their properties for aqueous sols of the rod-like mineral attapulgite. Each of the parameters  $\Delta\alpha$ ,  $u$ ,  $D_t$  and  $D_r$  — the rotary diffusion coefficient — have been enumerated. Furthermore, to demonstrate the close interrelation between the parameters  $\Delta\alpha$ ,  $u$  and the stability of the sol, these parameters have been recorded as the attapulgite suspensions were subjected to the cationic surfactant cetyltrimethylammonium bromide (CTAB), whose increasing presence in the sol influenced, neutralised and finally dominated the inherent negative surface charge of the mineral particles. The variations of the electrooptical parameters show them to be useful indicators of the dispersion stability. The study also indicates that the apparatus is of potential utility as a rapid means of studying colloid double-layer properties.

#### APPARATUS AND THEORY

Fluctuation light scattering in the absence of electric fields has been measured using the photon correlation procedure.<sup>5</sup> A He—Cd ( $\lambda = 442$  nm) laser and polariser system provided a well collimated and polarised blue light beam which was incident on an optical cell holding the sol under test. This cell was of cylindrical form and held 1 ml of fluid. It was centred in a black cylindrical vat, designed to hold a refractive index compensating liquid. Light scattered at any angle  $\theta$  to the forward direction of the incident beam was collected by a detector which could be rotated concentrically about the cell centre. This limb held various selectable optical components. For scattering experiments, an aperture of 0.5 mm width and 1 mm height was followed by a lens which focussed the light to a slit aperture of 0.25 mm width at the photocathode of a photon-counting tube. The electrical output from the phototube passed directly to a discriminating circuit and a digital autocorrelator which gave an output in real time of the correlation function  $C(\tau)$ . As the light scattered from the sol exhibited rapid fluctuations in intensity due to chaotic Brownian motion of the scattering elements, structure existed in the temporal intensity fluctuations. Measuring with the so-called homodyne detection procedure,<sup>6</sup>  $C(\tau)$  had the form

$$C(\tau) = A \exp(-2 \Gamma K^2 \tau) + 1 \quad (1)$$

Here  $\tau$  was the correlation delay time,  $A$  an optical constant and  $K = (4\pi/\lambda) \sin \theta/2$ . The parameter  $\Gamma$  varied with  $\theta$  and  $\tau$ . Under the conditions of  $\theta \rightarrow 0$  and  $\tau \rightarrow 0$ ,  $\Gamma$  became equal to the  $Z$  average of  $D_t$  for rigid particles.

For the electrophoretic measurements a different cell design was used. This was only some 2 mm thick and held a pair of thin stainless steel electrodes which were mounted vertically with a separation of 1.6 mm. The sol volume was only 0.1 ml and the electric field ( $E$ ) was applied in a horizontal direction. A pulse generator supplied voltages of up to 15 V for durations of 200 ms across the electrodes. Alternate pulses were of reversed polarity to reduce heating and electrode polarisation phenomena. Application of the pulse was accompanied by initial particle orientation followed by translation. Care was taken to ensure that some 20 ms dead time was allowed at the beginning of each pulse prior to the correlator accumulating

data, to ensure that translational electrophoresis alone was recorded. For these electrophoresis measurements, a sample of the incident light was needed to mix optically with the scattered beam. This is the so-called heterodyne detection method. It is readily achieved by slightly scoring the inside front face of the cell so that the detector receives simultaneously light from the incident beam and the scattering volume. In such cases the time dependent part of the heterodyne term of the auto-correlation function then has the form<sup>6,7</sup>

$$C(\tau) = A' \exp(-\Gamma K^2 \tau) \cos\{K \cdot v \tau\} \quad (2)$$

where  $A'$  is a variant of the constant  $A$ . It is the cosine modulation of  $C(\tau)$  that leads to the electrophoretic velocity  $v$  and hence  $u$ . The period of the oscillation in  $C(\tau)$  is given by

$$T_0 = \lambda / (u E \sin \Theta) \quad (3)$$

Hence  $u$  is evaluated.

Electric birefringence was readily measured by recording the light transmitted through a system consisting of the birefringent medium placed between a pair of 'crossed' polarising devices<sup>9</sup>. In the current apparatus this was readily achieved by rotating the detection limb to the  $\Theta = 0$  position and placing an analysing prism in the beam. For refinement, a quarter-wave plate was also placed in this detection limb. The electric field had to be applied across the sample at  $45^\circ$  azimuth to the polarisation state of the incident beam, whilst the quarter-wave plate was set in parallel azimuth to the polariser. The analyser was either crossed or slightly offset from the crossed position. This offsetting increased the sensitivity and enabled the sign of the birefringence to be determined. A special cell was used of some 3 ml capacity and 4.5 cm length. A pair of horizontal steel electrodes were spaced some 2 mm apart either side of the light beam. An applied electric voltage provided a field across the sample. Under the influence of the field the initial random orientational array of the suspended particles underwent orientational order as the field interacted with any permanent ( $\mu$ ) or induced dipole moment. The induced dipole moment arose from  $\Delta\alpha$ . Using pulsed electric fields the recorded birefringence was transient in nature. Following the field application, the particles orientated and the birefringence built up in a steady manner to an equilibrium state. Termination of the pulse was accompanied by a field-free relaxation process back to the pre-field condition. The birefringence was related directly to the transmitted light intensity. This was recorded on an auxiliary photomultiplier operating in the analogue mode and positioned at the end of a fibre-optic light guide which sampled the transmitted light directly. The output of this photomultiplier was fed to a transient digitiser and recorder from whence it was either displayed on an oscilloscope or passed to a microcomputer for data analysis.

Any measured birefringence ( $\Delta n$ ) depends upon the inherent anisotropy ( $\Delta g$ ) in the optical anisotropy per unit volume ( $g$ ) associated with a colloid structure. It also depends on the degree of orientation of the particles. Hence

$$\Delta n = \frac{2\pi c}{n} \cdot \Delta g \cdot \bar{\Phi} \quad (4)$$

where  $c$  is the concentration of the sol having an average refractive index  $n$ . At very high field strengths, when full particle orientation is encountered,  $\bar{\Phi} = 1$ . If low intensity *alternating* fields are used (so that permanent dipoles cannot contribute to the orientation) then  $\bar{\Phi}$  has the form

$$\bar{\Phi} = \frac{1}{15} \cdot \frac{\Delta\alpha}{kT} \cdot E^2 \quad (5)$$

This equation indicates the so-called Kerr law region where  $\Delta n$  is proportional to the mean-squared value ( $E^2$ ) of the applied electric field. The birefringence indicated in equations (4) and (5) is the equilibrium value obtained.

Following the termination of the pulse, a monodisperse sol would exhibit a single exponential decay in the birefringence according to the equation<sup>10</sup>

$$\Delta n_t = \Delta n_0 \exp(-6 D_r t) \quad (6)$$

where  $\Delta n_0$  is the birefringence given by equation (4) at the beginning of the decay for which  $t = 0$ . With a polydisperse sample a multiexponential decay process is encountered. Recently we have developed in this laboratory<sup>11,12</sup> a means of analysing initial slopes of such transient decay processes under various field conditions so as to enable the distribution of particle sizes to be estimated. A commonly encountered distribution for colloidal particles in suspension is the log-normal function. For rigid rod particles of length  $l$  this can be described by the function<sup>13</sup>

$$f(l) = \frac{1}{\sigma \sqrt{2\pi}} \cdot \frac{1}{l} \cdot \exp \left[ - \left\{ \frac{\ln(l/m)}{\sqrt{2}\sigma} \right\}^2 \right] \quad (7)$$

where  $m$  represents the median of the distribution and  $\sigma$  characterises its width. In principle the two parameters  $m$  and  $\sigma$  require only two specific experimental data for the characterisation of  $f(l)$ . These data come from the initial slope of the logarithm of the birefringence decay under high and low field conditions. In principle, the larger the electric field applied, the more complete is the contribution to the observed birefringence from all particles present. With low fields, the larger particles predominantly contribute. Hence the decay under various field conditions is weighted by the polydispersity of the sample. For rigid rods, as used in this study, we define the average rotary diffusion coefficients obtained under high field ( $D_{E\infty}$ ) and low field but high frequency ( $D_{f\infty}$ ) conditions where<sup>11</sup>

$$(D_{E\infty}) = \frac{3kT}{\pi\eta} \cdot \ln(2r - 0.5) \cdot \frac{1}{m^3} \cdot \exp \frac{3\sigma^2}{2} \quad (8)$$

and

$$(D_{f\infty}) = \frac{3kT}{\pi\eta} \cdot \ln(2r - 0.5) \cdot \frac{1}{m^3} \cdot \exp - \frac{9\sigma^2}{2} \quad (9)$$

with  $r$  the axial ratio and  $\eta$  the medium viscosity. It can be seen that the ratio  $D_{E\infty} : D_{f\infty}$  equals  $\exp(6\sigma^2)$ . Once  $\sigma$  has been evaluated, either equation (8) or (9) can be used to determine  $m$ .

Furthermore, from equation (4) the pre-decay birefringence for high fields with  $\Phi = 1$  enables  $\Delta g$  to be determined, whilst the pre-decay value of  $\Delta n$  under low field conditions enables  $\Delta \alpha$  to be determined. Hence from two such transients  $\Delta \alpha$ ,  $\Delta g$ ,  $m$  and  $\sigma$  can all be evaluated for a single sample.

#### RESULTS AND DISCUSSION

All measurements were made on suspensions of approximately  $1 \times 10^{-5}$  g ml<sup>-1</sup> concentration. These were prepared by dispersing the original clay, which was of Spanish origin, in freshly double-distilled water and subjecting it to a high speed blender. The material was then sonicated and left to stand for several hours at an elevated temperature of 55 °C. The stock solution was formed by centrifuging off any coarse dust particles and subsequently diluting as required. Electron micrographs taken of the stock sol indicated the regular needle-like nature of the particles.

In the absence of electric fields, photon correlation spectroscopic data were recorded over the angular range  $10^\circ < \Theta < 30^\circ$ . Variation in the correlation function is shown in Figure 1a, from the initial slope of which a value of  $D_t = 7 (\pm 1) \times 10^{-3}$  m<sup>2</sup> s<sup>-1</sup> was obtained. From the Perrin<sup>14</sup> equation

$$D_t = \frac{kT}{3\pi\eta} \cdot \frac{1}{l} \cdot \ln^{-1}(2r) \quad (10)$$

and assuming the attapulgite needles to be of 30 nm diameter, then the  $l$ ,

corresponding to a Z average  $D_t$ , was of  $3.2 \mu\text{m}$  value. Oscillations in the correlation function in the presence of electric fields were recorded as shown in Figure 1b. A linear graph with values of  $T_0$  versus the applied voltage  $V$  yielded a straight line from which  $u = 2.0 (\pm 0.1) \times 10^{-8} \text{ m s}^{-1} \text{ V}^{-1}$  was obtained.

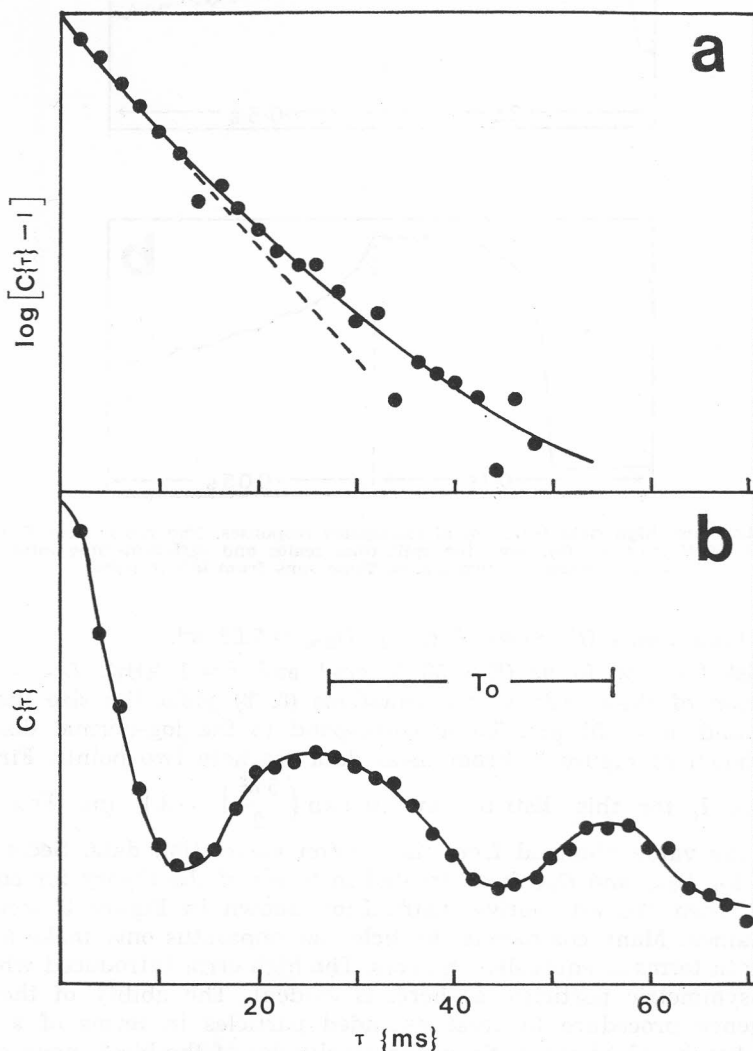


Figure 1: (a) Correlation function for attapulgite sol,  $\theta = 20^\circ$ . The initial slope is highlighted. (b) Oscillations in this function (period  $T_0$ ) in the presence of a 10 V electric potential with  $\theta = 70^\circ$ .

Typical electric birefringence transients are shown in Figure 2. Note the variable time scales and the fact that the high field transients give rise to the much faster decay processes as the smaller particles contribute to a greater degree. From the initial slopes of these decay curves under the conditions indicated, the following data were obtained.

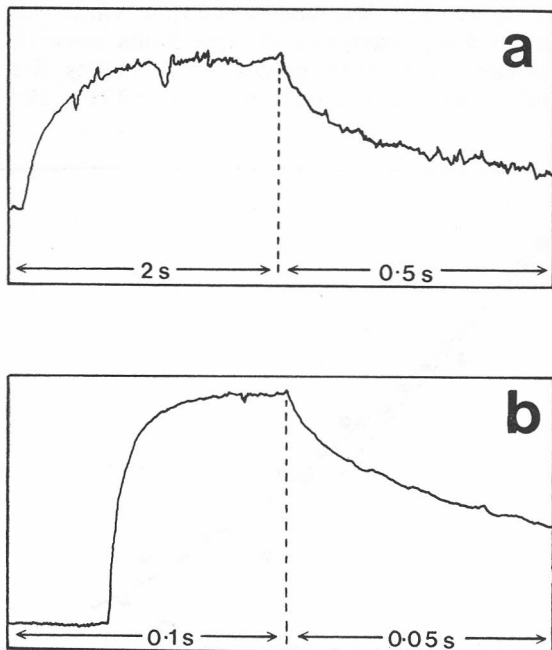


Figure 2: Low and high field transient birefringence responses. The *r.m.s.* field  $E = 46 \text{ V cm}^{-1}$  for (a) and  $800 \text{ V cm}^{-1}$  for (b). Note the split time scales and different time intervals within and between the two traces. Time runs from left to right.

For high fields ( $E > 600 \text{ V cm}^{-1}$ ),  $D_{E\infty} = 7.02 \text{ s}^{-1}$ .

Whilst for low fields ( $E < 50 \text{ V cm}^{-1}$  and  $f = 1 \text{ kHz}$ ),  $D_{f\infty} = 1.37 \text{ s}^{-1}$ . Substitution of these values into equations (8, 9) yield the size parameters  $\sigma = 0.53$  and  $m = 1.51 \mu\text{m}$ . These correspond to the log-normal distribution curves shown in Figure 3. From these data we note two points. Firstly, the Z average  $l_z$  for this distribution  $= m \exp\left(\frac{5\sigma^2}{2}\right) = 3.1 \mu\text{m}$ . This is very close to the value obtained from the photon correlation data. Secondly, had the data for  $D_{E\infty}$  and  $D_{f\infty}$  been treated in terms of the theory for equivalent spheres<sup>12</sup>, then the alternative distribution shown in Figure 3 would have been obtained. Many commercial particle size apparatus only make allowance for sizing in terms of equivalent spheres. The high error introduced when using highly asymmetric particles, as here, is evident. The ability of the electric birefringence procedure to treat extended particles in terms of a realistic model is hereby highlighted. From the amplitudes of the birefringence responses, the polarisability factors were determined as follows

$$\Delta g \approx 4 \times 10^{-3}, \text{ and}$$

$$\Delta \alpha = 21 \times 10^{-29} \text{ F m}^2 \text{ were obtained.}$$

The effect of adding the surfactant on the various parameters  $\Delta\alpha$ ,  $u$ ,  $D_r$  and  $D_t$  was measured in an extensive series of experiments. The relative

changes in each of these parameters is indicated in Figure 4. The results have been normalised to a set clay concentration of  $1 \times 10^{-5} \text{ g ml}^{-1}$ . Throughout the region indicated by the bar, flocculation was evident. This is the region where the surface charge of the clay particles is neutralised in the presence

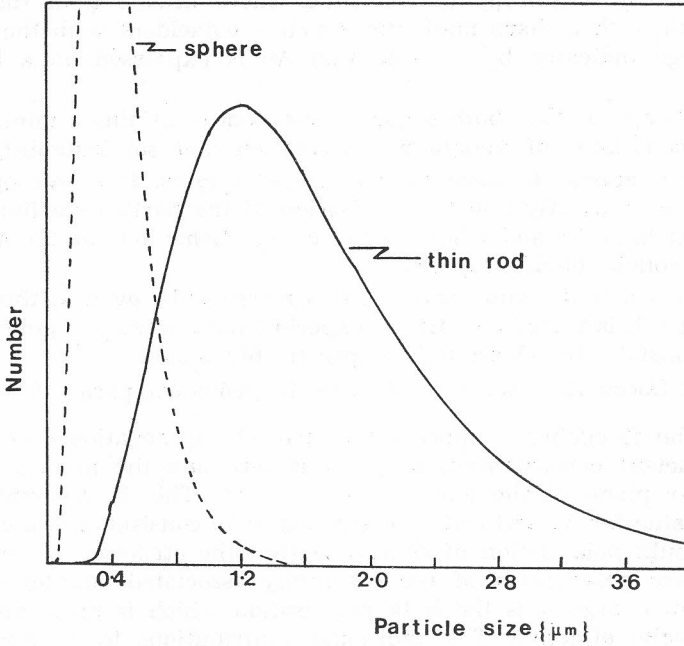


Figure 3: Log-normal distribution of particle sizes based on the birefringence theory. Full line for thin rods of 30 nm diameter;  $\sigma = 0.53$  and  $m = 1.51$ . The distribution for equivalent spheres is shown as the broken line.

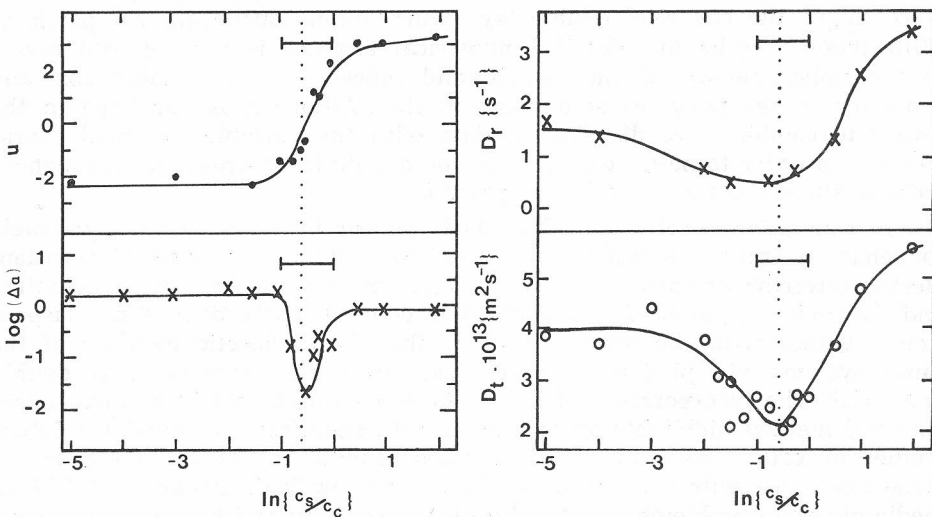


Figure 4: Variation of the electrical parameters ( $u$ ,  $\Delta\alpha$ ) and geometrically related diffusion coefficients ( $D_r$ ,  $D_t$ ) with relative surfactant-to-clay concentrations ( $c_s/c_c$ ).

of the surfactant and the sol becomes unstable. It can be readily detected by eye. From these curves we note a number of interesting factors.

- (i) The electrophoretic mobility passes through a zero value and is approximately symmetric in its behaviour about this point. The change in the polarisability anisotropy ( $\Delta\alpha$ ) is much more drastic than that in  $u$ . It passes through a sharp minimum which is coincident with the zero point of charge indicated by  $u$ . Note that  $\Delta\alpha$  is expressed on a logarithmic scale.
- (ii) It would appear that both  $u$  goes to zero and  $\alpha$  attains a minimum value under conditions of maximum flocculation and sol instability.
- (iii)  $\Delta\alpha$  and  $u$  appear to have closely related origins. It is our opinion that  $\Delta\alpha$  is predominantly due to polarisation of the particle-medium interface and that both  $\Delta\alpha$  and  $u$  reflect the charge behaviour at the shear plane of the colloid double layer<sup>15</sup>.
- (iv)  $\Delta\alpha$  retains a finite value and hence is measurable, even at the zero point of charge. It is therefore a useful experimental parameter under conditions of sol instability where  $u$  is impracticably small.
- (v) Particle flocculation is also evident in the geometric parameters  $D_r$  and  $D_t$ .

From the foregoing it appears that particle aggregation occurs with an added surfactant concentration where  $u$  is zero and the net charge density at the shear plane of the double layer is zero. This is accompanied by a minimum value for  $\Delta\alpha$  and can be explained if  $\Delta\alpha$  consists of two components, namely, a bulk polarisation of charges within the structure of the material, and a surface polarisation of the externally associated counterions. At the zero point of charge it is the bulk polarisation which is predominantly (but not exclusively) effective. The additional contributions to  $\Delta\alpha$  for surfactant concentrations removed from the zero point of charge would appear to be related to the double layer properties. It would thus appear that analysis of the combination of  $u$  and  $\Delta\alpha$  should be of use in quantifying the characteristics of the electrical double layer surrounding such colloidal particles. With these experiments, detailed numerical analysis is not relevant owing to the polydispersity of the sample and indeed of the variable size and geometry of the particles accompanying flocculation. It is our hope in the future to combine size distribution data with the variable electrical characteristics in order to better characterise the double layer properties throughout various stages in the flocculation process.

In conclusion, electro-optical methods appear to be particularly valuable for characterising the stability of colloidal systems. The use of transient electric birefringence measurements to determine particle size, size distribution and the surface polarisability anisotropy of colloidal particles in dilute suspension, together with the measurement of the electrophoretic mobility of the same systems via photon correlation spectroscopic procedures, is doubly beneficial. The incorporation of both sets of measurements in a single experimental method highlights an apparatus with significant potential for future studies of colloid sol stability. The major limitations to the methods are those associated with the necessity of studying low ionic strength ( $< 10^{-2}$  M) media owing to problems associated with conductivity and heating phenomena at higher strengths.



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## SAŽETAK

**Električki dvolom i elektroforetsko raspršenje svjetla kao karakterizacija koloidne stabilnosti**

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Električno polje prouzrokuje rotacijski red i svojstvo dvoloma u razrijeđenim suspenzijama asimetričnih koloidnih čestica. Rotacija električki nabijenih čestica popraćena je elektroforetskom translacijom. Pulsno električno polje primjenjeno je na sol štapićastih čestica glinenog minerala atapulgita. Mjerena je promjena u fluktuaciji rasutog svjetla i inducirana dvolomnost. Dodatak CTAB mijenja površinski naboj preko nule sve do pozitivnih vrijednosti. Istražen je utjecaj CTAB na anizotropiju, električnu polarizabilnost, elektroforetsku pokretljivost te translacijski i rotacijski koeficijent difuzije. Ti parametri omogućili su i praćenje promjene stabilnosti i flokulacije koloidnih sustava.