A method is developed, based on transient electric birefringence, for evaluating the length \( l \) dependence of the ionic component of the anisotropy of the electrical polarisability \( \Delta \alpha \), for polydisperse, dilute suspensions of rod-like particles. Two average values of the rotary diffusion coefficient, obtained from the birefringence decay under specific experimental conditions, are combined with an average translational diffusion coefficient, from photon correlation data, to generate the best log-normal function to fit the particle size distribution and to estimate the length dependence of \( \Delta \alpha \). These factors are employed to analyse the field dependence of the birefringence and to obtain the size independent part of \( \Delta \alpha \). Illustrative data are given for aqueous suspensions of sepiolite. A value of \( \Delta \alpha \) proportional to \( l^{1.8} \) was obtained.

INTRODUCTION

In aqueous or ionic media the predominant contribution to \( \Delta \alpha \) (the anisotropy of the electrical polarisability) for large colloidal particles is generally believed to arise from interfacial polarisation (1). Thus \( \Delta \alpha \) should provide a useful parameter for characterising particle surfaces, investigating particle electrical double layer structures, studying surface interactions and monitoring the stability of colloidal suspensions. An important problem in electro-optics is the determination of the dependence of \( \Delta \alpha \) on particle size. Most practical systems studied are polydisperse in particle size. The measured electrical parameters are then average values which depend on the mean particle size and the breadth of the particle size distribution. The interpretation of these averages...
to yield reduced or size independent parameters, characteristic of the material or particle-medium interface, requires knowledge of the dependence of the electrical parameters on particle size. Further, knowledge of the dependence of $\Delta \alpha$ on particle size is essential for testing theoretical models for $\Delta \alpha$.

Theoretical analyses for rod-shaped particles predict a dependence of $\alpha$ on length ($\ell$) of the form $\ell^\gamma$ with $\gamma$ ranging from 1 to 3 (2-8). The value of $\gamma$ depends on particle size and whether tightly bound or diffuse ions dominate the polarisation process. The extent of interaction between the ions is also of importance. As far as the authors are aware, there have been only two experimental determinations of $\gamma$. Käss and Brückner (9) have determined $\gamma = 2$ for platelets (bentonite, kaolinite) and $\gamma = 1$ for rods (halloysite) using electric birefringence studies on fractionated suspensions. Takashima (10) has found $\gamma = 2.2$ for sonicated DNA samples using dielectric studies. The latter results are well approximated by the model of Dukhin and Shilov (8) invoking polarisation of the diffuse double layer.

In this report we describe a practical method for evaluating $\gamma$ for polydisperse suspensions which eliminates the need to fractionate the sample. Measurements are made of two averages of the rotary diffusion coefficient $\langle D_R \rangle$ under different experimental conditions using electric birefringence. When combined with a measured average $\langle D_T \rangle$ of the translational diffusion coefficient from photon correlation data, one can determine $\gamma$, generate a particle size distribution in terms of a simple two parameter function, and evaluate a reduced value of $\Delta \alpha$. The method has been tested by measurements on aqueous suspensions of the clay mineral sepiolite.

**METHOD**

For suspensions of particles $\Delta \alpha$ may be determined by electric birefringence measurements (11).

**Monodisperse Suspensions**

Consider a suspension of particles subjected to a burst of alternating electric field, with the pulse length of sufficient length for the induced birefringence to reach an equilibrium value $\Delta n(o)$. The decay following termination of the pulse is given by (11).

$$\Delta n(t) = \Delta n(o) \cdot \exp (-6D_R t)$$  \hspace{1cm} (1)