

The effect of electric fields on nonaqueous dispersions

R. H. Ottewill¹), A. R. Rennie²) and A. Schofield¹)

¹) School of Chemistry, University of Bristol, UK

²) Institut Laue Langevin, Grenoble, France

Abstract: Small angle neutron scattering has been used to investigate the structure of poly(methylmethacrylate) dispersions in dodecane in the presence of an electric field. In dodecane alone field effects were not observed. In the presence of calcium octanoate, however, the particles apparently become charged and increased ordering was observed. The effect of an electric field on the latter dispersions produced anisotropy of structure which suggested that the particles were forming loose "strings of beads" in the direction of the applied field.

Key words: Neutron scattering; polymer lattices; nonaqueous dispersions; electric fields; microstructure

Introduction

The effects of electric fields on nonaqueous dispersions have been rather sparsely studied in comparison to studies carried out on aqueous systems. However, the availability of monodisperse spherical polymer particles at high volume fractions in media of low relative permittivity [1,2] has provided excellent systems for fundamental studies [3,4]. Moreover, the development of small angle neutron scattering has provided a means of studying the structure of concentrated colloidal systems in applied fields and has already been used to examine systems of this type under shear fields [5,9].

In this communication we provide a brief report on the use of small angle neutron scattering to investigate the effect of applied electric fields on the microstructure of dispersions of poly(methylmethacrylate) particles stabilised by poly(12-hydroxystearic acid) in a hydrocarbon medium. In the first instance the particles were examined in dodecane alone and then in dodecane with the addition of small amounts of calcium octanoate to provide some conductance to the dispersion medium.

Experimental

Materials

Dodecane was B.D.H. material.

NUOSYN CALCIUM 10% was obtained from Durham Chemicals Limited, Birtley, Chester-le-Street, Co. Durham, UK. According to the manufacturers this is a solution of calcium iso-octanoates in a hydrocarbon medium. It is reported in this communication as calcium octanoate.

The polymer latex, SPSO90, was prepared by the dispersion polymerisation technique previously described [2]. The number average particle diameter determined by electron microscopy was 0.20 μm and the weight average diameter determined by small angle neutron scattering was 0.22 μm [5].

Small angle neutron scattering

The small angle scattering measurements were carried out using the neutron diffractometer D11, at the Institut Laue Langevin, Grenoble [10], with a sample-detector distance of 35.7 m and a neutron beam wavelength of 0.80 nm. For elastic scattering measurements, the magnitude of the scattering vector, Q , is defined by,

$$Q = 4\pi \sin(\theta/2)/\lambda$$

with θ = the angle between the incident and the scattered beams.

The measurements were carried out in an optical-standard quartz cell with a pathlength of 1mm. Bright platinum rods were inserted into the cell at a separation distance of 6 mm. An A.C. field of frequency 50Hz was applied across the electrodes. The applied voltage was varied from zero to 1800V. The experimental arrangement is illustrated schematically in Fig. 1. The neutron beam, of diameter 4mm, passed between the electrodes in a direction perpendicular to the applied electric field.

The scattered neutrons were measured using a two-dimensional detector, a square matrix of 64 \times 64 elements.

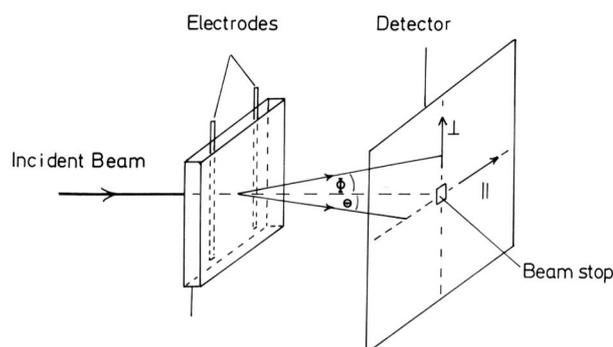


Fig. 1. Experimental arrangement used for examining the small angle neutron scattering from a polymer colloid dispersion during the application of an electric field

This allowed either two-dimensional contour plots to be obtained showing lines of equal intensity or three-dimensional plots showing intensity across the detector. For isotropic two-dimensional patterns the intensities can readily be radially averaged to give one-dimensional plots of intensity, $I(Q)$, against Q . Anisotropy if the sample can be clearly recognised in a contour plot. In this case in order to obtain plots of $I(Q)$ against Q the averaging procedure can be restricted to small sectors, for example, parallel ($0 \pm 15^\circ$) and perpendicular ($90 \pm 15^\circ$) to the direction of the applied field [11].

Results

Intensity measurements without an electric field

The intensity of scattering at a particular value of Q is, for spherical particles, given by [3,4],

$$I(Q) = A\phi V_p P(Q)S(Q)$$

Where for spheres of the core-shell type A contains instrumental constants, and terms in coherent scattering length density described elsewhere, [3], V_p = the particle volume, ϕ = volume fraction of the particles, $P(Q)$ = the particle shape factor and $S(Q)$ = the structure factor.

Figure 2 shows a curve for a 40% w/w dispersion of the latex SPSO90 in dodecane. This shows a broad peak consistent with short-range interactions of the hard sphere type examined in earlier work on polymethylmethacrylate latices [3-5]. The addition of calcium octanoate to the sample caused a substantial change in the form of the curve. As can be seen from Fig. 2, the broad peak of the original latex became very much narrower and sharper. Since the basic latex was the same in both cases, i.e. $P(Q)$ was the same,

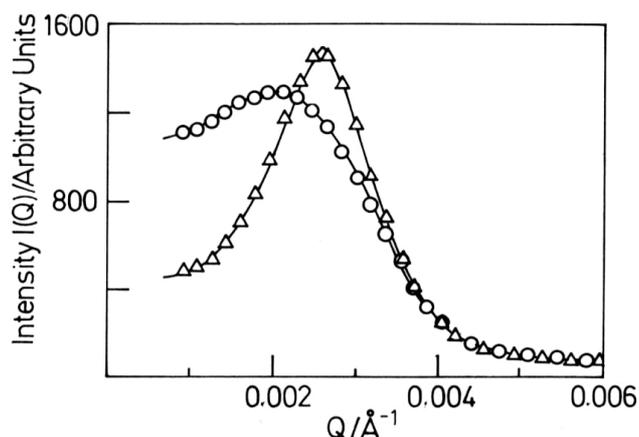


Fig. 2. Intensity, $I(Q)$, against scattering vector Q , for a 40% w/w poly(methylmethacrylate) latex dispersion: -O-, in dodecane; -Δ-, in dodecane containing 0.1% calcium octanoate

and the samples were essentially in the same medium, A also remained constant. Thus the changes in the scattering curve were attributed to changes in $S(Q)$. The changes in shape indicated an increase in interaction between the particles with the implication that this arose because the addition of calcium octanoate caused the particles to acquire a weak electrical charge. This led to the form of the interaction changing from that between sterically stabilised particles, a short-range repulsion, to that between electrically charged particles, a long-range repulsion. In the latter case the system becomes more ordered at the same volume fraction, and hence the peak in $I(Q)$ against Q becomes more clearly defined. Electrophoresis measurements on dilute dispersions confirmed that in the presence of calcium octanoate the particles had a positive mobility.

The effect of an electric field

Calcium octanoate absent

Figure 3 shows the 2-dimensional contour plots obtained using an 18% w/w dispersion of poly(methylmethacrylate) particles in dodecane alone. The pattern obtained from latex in the absence of the field is shown in Fig. 3a, and that with a field strength of 3800 V cm^{-1} applied is shown in fig. 3b. No discernable change in the pattern was observed on the application of the field.

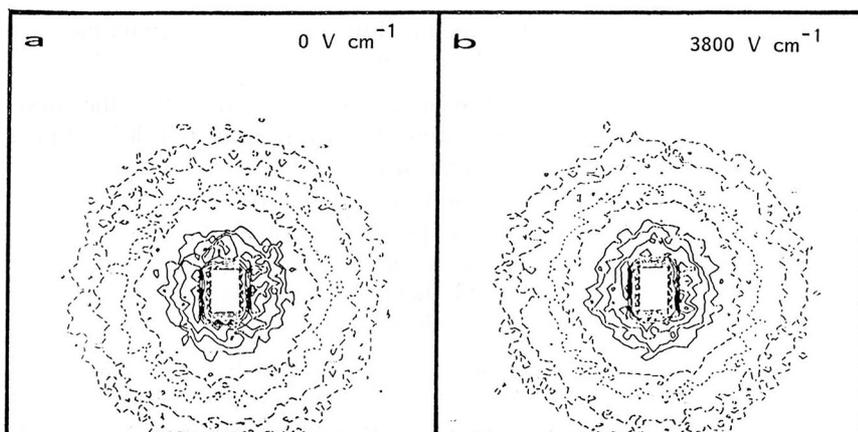


Fig. 3. Contour plots of constant intensity, $I(Q)$, lines against Q for an 18% w/w poly (methylmethacrylate) dispersion in dodecane in the absence and presence of an electric field

Calcium octanoate present

Figure 4 shows the 2-dimensional pattern obtained using a 10% w/w dispersion of polymethylmethacrylate) containing 0.025% calcium octanoate. Figure 4a shows the absence of an applied field. The contours are symmetrical showing that the sample is behaving

as an isotropic dispersion with the peak in the structure factor showing up as a well-defined ring. Figures 4b, 4c and 4d illustrate the contour plots obtained at field strengths of 900, 1800 and 3800 $V\ cm^{-1}$. The anisotropy of the sample increases as the field strength increases and is most marked in Fig. 4d the system at the highest field strength.

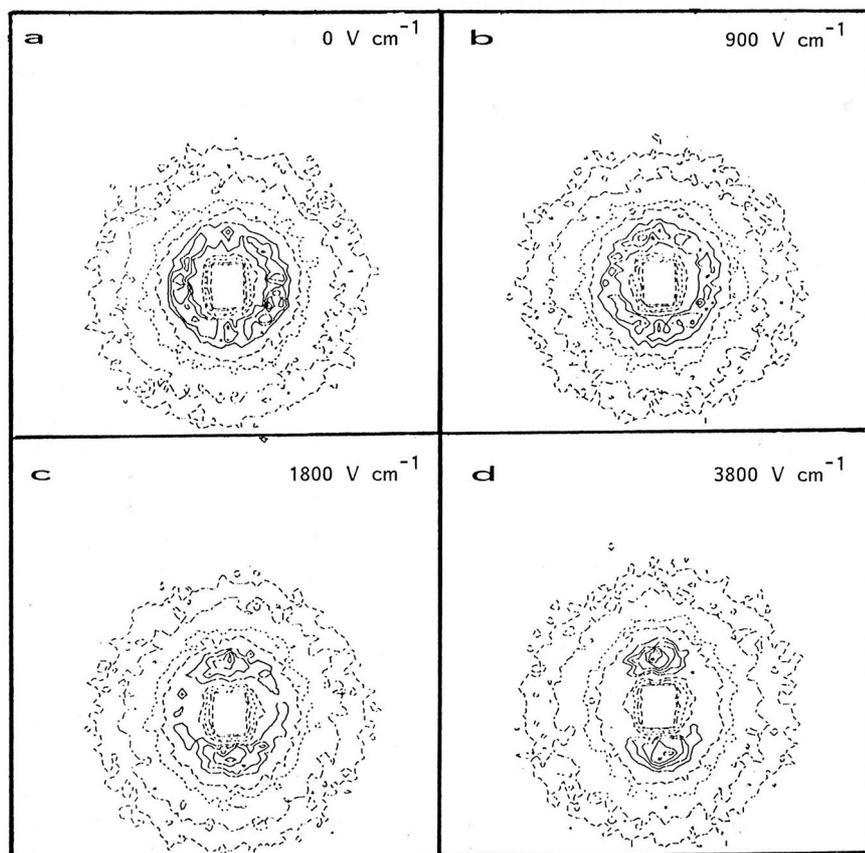


Fig. 4. Contour plots of constant intensity, $I(Q)$, lines against Q for a 10% w/w poly(methylmethacrylate) dispersion in dodecane containing 0.025% calcium octanoate at various applied field strengths

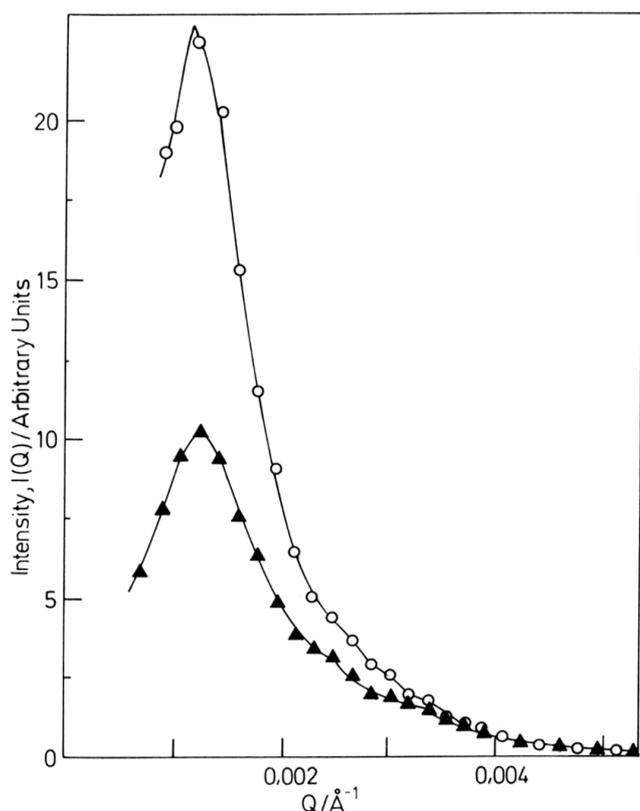


Fig. 5. Intensity, $I(Q)$, against scattering vector, Q , for a 10% w/w poly(methylmethacrylate) dispersion in dodecane containing 0.025% calcium octanoate at a field strength of 3800 V cm^{-1} . $-O-$, perpendicular to the applied field; $-\blacktriangle-$, parallel to the applied field

Using the information obtained on the 2-dimensional detector, radial averages were taken in sectors at $0^\circ \pm 15^\circ$ and $90^\circ \pm 15^\circ$. This gave $I(Q)$ against Q plots for the sample in directions parallel and perpendicular to the applied electric field. These are illustrated in Fig. 5. In the direction of the field the intensity has been reduced in comparison to that in the absence of the field. The peak in intensity is very well defined suggesting a significant peak in the curve of $S(Q)$ against Q thus indicating strong interaction between the particles. In a direction perpendicular to the applied electric field the intensity has markedly increased compared to that in the absence of the field. The peak is still present, although less well defined, and has moved marginally to a lower Q value.

Discussion

Three separate pieces of evidence suggest that particles of poly(methylmethacrylate) stabilised by poly(12-hydroxystearic acid) become electrically charged in the presence of low concentrations of cal-

cium octanoate in a low relative permittivity medium, dodecane. These are:

- i) the formation of a well-defined peak in the curves of $I(Q)$ against Q indicating a well-defined peak in $S(Q)$ against Q .
- ii) the development of a positive electrophoretic mobility in the presence of calcium octanoate.
- iii) the development of anisotropy, as detected by small angle neutron scattering in the presence of an applied electric field.

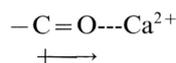
The calcium octanoate used in these experiments has a similarity to the calcium diisopropyl salicylate used in earlier work by van der Minnie and Hermanie [12-14]. Since the conductivity of the dodecane increases on the addition of calcium octanoate [15] weak dissociation appears to occur to give,



and possibly



Since the Oct^- ion is essentially oleophilic, it appears likely that this will remain in the dodecane whilst the Ca^{2+} or CaOct^+ associates with the dipole on the ester groups of the poly(12-hydroxystearic acid), leading to a positive charge on the particles by ion-dipole association, viz:



Only a small number of charges would be needed to produce a positive charge on the particles.

The results shown in Fig. 2 for a 40% w/w dispersion suggest that in the absence of added calcium octanoate the interaction between the particles is relatively short range consistent with the hard sphere behaviour observed in earlier work [3]. Addition of calcium octanoate in small quantities causes the peak in $I(Q)$ against Q to sharpen considerably suggesting much stronger interaction and short range ordering of the particles, due to electrostatic interactions. The fact that the latter are of long range is substantiated by experiments on the 10% w/w dispersion where a well-defined peak is found with calcium octanoate present (Fig. 4a), but is essentially absent for the dispersion without calcium octanoate. On the application of the electric field an interesting effect occurs in that the intensity increases in the direction perpendicular to the field and decreases in the direction parallel

to the field. This shows clearly with a field of 3800 V cm^{-1} as illustrated in Fig. 5. In the direction of the field the peak is very sharp. It is somewhat less so in the perpendicular direction and has moved slightly to a lower Q value. The complete interpretation of these results requires further analysis and separation of the curves into interactions ($S(Q)$) and form factors ($P(Q)$). A possible interpretation of the results is that the dipoles formed by the charges on the particles line up in the electric field and cause a preferential alignment in the direction of the field which causes increased interaction in that direction without essentially changing the number concentration, hence sharpening $S(Q)$. In view of the sensitivity of the $I(Q)$ against Q curves to the rapid falling off of $P(Q)$ with Q this could lead to a major drop in intensity. Similarly, a weaker interaction in the perpendicular direction at the same number concentration would diminish the structure and hence give an increase in intensity.

A measurement of electrophoretic mobility on a very dilute dispersion in the presence of calcium octanoate gave a value of $0.1 \mu\text{m cm V}^{-1}$ and hence the time for the particle to travel one particle radius ($0.1\mu\text{m}$) in a field of 3800 V cm^{-1} can be calculated to be 0.3 msec. A similar calculation for the particle to diffuse translationally one radius gives the time as 0.7 msec. Hence the ratio;

$$\frac{\text{time to travel one radius in the electric field}}{\text{time to diffuse one radius}}$$

gives a value of 0.43. This rather simplistic calculation would suggest that appreciable Brownian motion of the particles is still occurring even in the presence of the electric field of 3800 V cm^{-1} . This would suggest that the average number concentrations in the directions parallel and perpendicular to the field are probably not appreciably different, although the particle-particle interactions, as suggested above, are significantly different.

Acknowledgements

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Authors' address

Prof. Dr. R. H. Ottewill
School of Chemistry
University of Bristol
Cantock's Close
Bristol, BS8 1TS, England