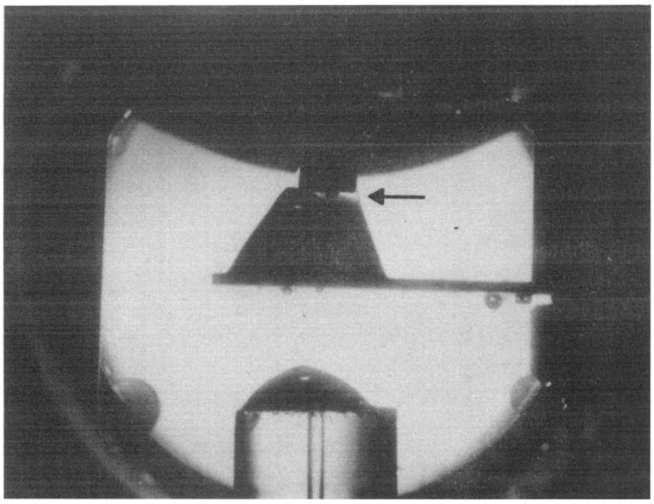

Figure 3 Movement of dispersion/monomer boundary (indicated by arrow) towards the electrode tip on application of +1.5 V to the electrode tip

was observed as demonstrated by comparing *Figures 2* and *3*. It should be noted that the left hand side of the dispersion/monomer boundary in the conical monomer drop shown in *Figures 2* and *3* is obscured by a vapour-bubble of VCM.

The polarity of the applied field and the direction of movement of the dispersion/monomer boundary showed that the PVC particles carried a negative charge. However, uncertainty in the magnitude of the electric field between the electrodes meant that no quantitative estimate of the electrophoretic mobility of the PVC particles in monomer could be made.

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Electrophoresis of poly(vinyl chloride) dispersed in vinyl chloride monomer

Introduction

Bulk poly(vinyl chloride) (PVC) formed by initiation in liquid vinyl chloride monomer (VCM) appears to consist of aggregates of small polymer particles. The size of the aggregates and constituent particles greatly affects the porosity of the bulk material and so knowledge and control of the stage in the polymerization at which aggregation occurs is important. It has been suggested that the polymer particles, before aggregation, might be electrically charged[1] and that the colloidal stability of these so-called primary particles might be affected by the magnitude of particle charge in a manner predicted by colloidal stability theory. We describe here an examination of the electrophoresis of PVC primary particles dispersed in liquid VCM.

Experimental

We have constructed an electrophoresis cell which can withstand the pressures of about 10 atm necessary to liquefy VCM at temperatures up to 350K. The cell, shown in *Figure 1*, is constructed of quartz. Pt wire electrodes are inserted through glass/metal seals. The lower tube, in which particle electrophoresis was examined, is a cylindrical capillary of 2.6 mm internal diameter. The front and back external faces are ground flat to reduce optical distortion. The two larger diameter electrode compartments joined to the lower tube are also connected by an upper cross tube. Each electrode compartment is fitted with a side arm to which ball valves can be attached and through which the cell can be filled or emptied.

Using apparatus described elsewhere[2] approximately 5 cm^3 of VCM was polymerized to about 4% conversion in a pressure test tube and a small sample of this dispersion was added to about 6 cm^3 of VCM in the electrophoresis cell. This reduction of the initial particle concentration by a factor of about 100 was necessary to give a low enough particle concentration in the electrophoresis cell for examination by ultramicroscopy.

Particle electrophoresis was observed using an electrophoresis apparatus (Rank Bros., Cambridge) in which the quartz cell was positioned vertically in a thermostat bath. On application of a potential gradient of about 16 V/cm, the particle velocity was determined by noting the time taken for particles to travel a given distance as indicated by a calibrated graticule in one microscope eyepiece.

The observed velocity, ν_{obs}, for particle electrophoresis in a circular cross section capillary is given by:

$$\nu_{obs} = \nu_e + \nu_{eo}(2(r/a)^2 - 1)$$

where ν_e is the electrophoretic velocity, ν_{eo} the electro-osmotic velocity, r the distance from the centre of the cell to the point of observation and a the internal radius of the capillary. A plot of ν_{obs} against $(r/a)^2$ should be linear for electrophoresis about the axis of the capillary and at the stationary levels ν_{obs} is equal to ν_{eo} when $(r/a)^2$ is equal to 0.5. An optical correction is necessary for locating a given level within the cell because of curvature of the inner wall of the capillary. The usual correction for a Mattson type cell[3] has been used[4].

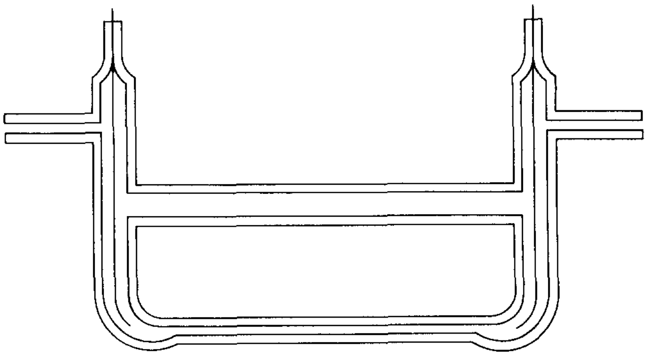

Figure 1 Electrophoresis cell

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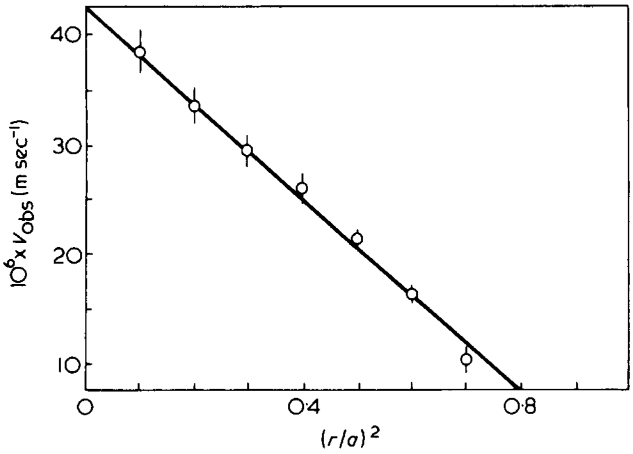

Figure 2 v_{obs} *versus* $(r/a)^2$ for PVC particles dispersed in VCM

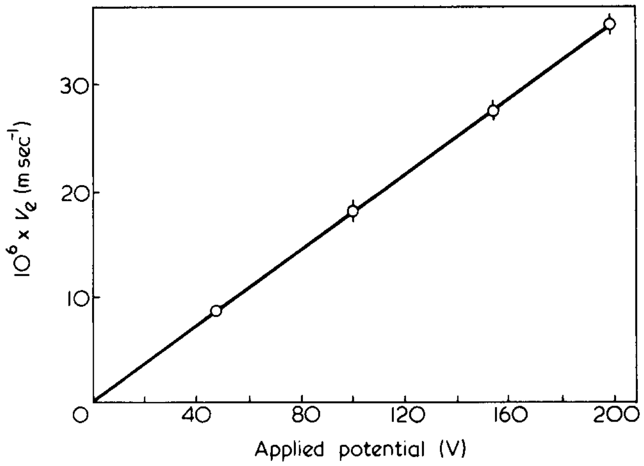

Figure 3 v_e *versus* applied potential for PVC particles dispersed in VCM

Results

Confirmation of reliable electrophoresis. Our first aim was to confirm that reliable observation of electrophoresis of PVC in VCM was possible. The criteria described by van der Minne and Hermanie[5] for the successful observation of electrophoresis have been achieved for our system using the quartz electrophoresis cell. A graph of v_{obs} against $(r/a)^2$ is fitted by a straight line as shown in *Figure 2.*

Particle velocity at a fixed depth in the cell should be proportional to the applied potential gradient. The effective interelectrode distance for our cell was 9.15 cm and results for electrophoretic velocity at the stationary level in the cell as a function of applied potential are shown in *Figure 3.* As indicated in *Figure 3,* the linear relation required by the criteria of van der Minne and Hermanie was achieved.

Zeta potential of primary PVC particles

The electrophoretic mobility, u, is the electrophoretic velocity under unit potential gradient and is related to the zeta potential, ζ, for sytems containing small particles surrounded by thick electrical double layers by the Huckel equation[6]:

$$\zeta = \frac{1.5u\eta}{\epsilon_0 \epsilon_r}$$

where η is the dispersion medium viscosity, ϵ_0 the permittivity of free space, 8.854×10^{-12} J^{-1} C^2 m^{-1} and ϵ_r the relative permittivity of VCM. AT 293K we have taken the values of η and ϵ_r to be 1.90×10^{-4} Nm^{-2} sec and 4.68[7], respectively.

We have polymerized dry VCM for periods ranging from 3 to 20 min at 343K using dicetylperoxydicarbonate initiator at a concentration of 0.050% w/v. The PVC particles referred to in *Figure 2* were produced by polymerization for 4 min. The measured electrophoretic mobility of -1.2×10^{-8} m^2 V^{-1} sec^{-1} corresponds to a zeta potential of -83 mV. Using a typical primary particle radius of 1.5×10^{-7} m, obtained from scanning electron microscopy, the total particle charge was -6.5×10^{-18}C or 41 elementary charges per particle assuming the particles to be spherical. This is a surface charge of -2.4×10^{-5}C m^{-2}.

Further investigations of the variation of zeta potential with the extent of polymerization, nature of initiator and additives are in progress.

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The origin of charge on nascent poly(vinyl chloride) particles in monomer

In the early stages of suspension polymerization of vinyl chloride monomer (VCM), primary particles are formed in VCM from the precipitated polymer. These primary particles (radius ~0.15 μm) are highly monodisperse and colloidally stable when first formed. It has been demonstrated that these particles carry a negative charge[1] and ζ potentials of

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