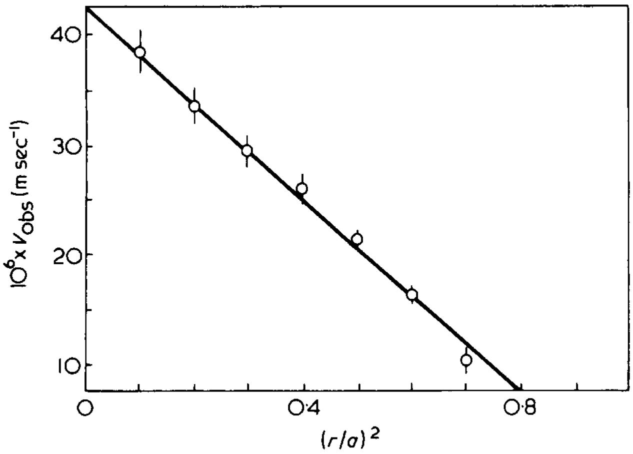

Figure 2 v_{obs} *versus* $(r/a)^2$ for PVC particles dispersed in VCM

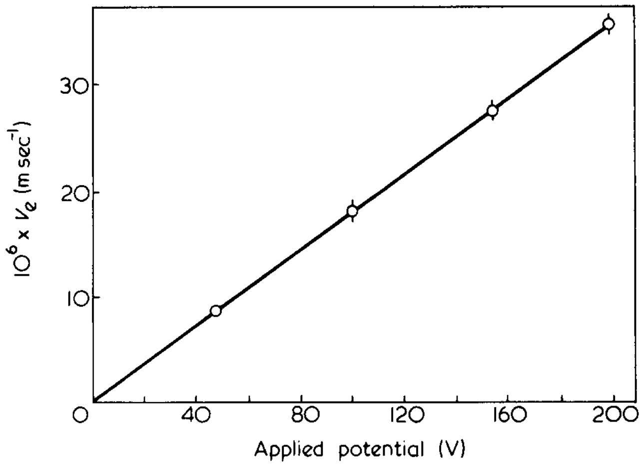

Figure 3 v_e *versus* applied potential for PVC particles dispersed in VCM

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 ν_{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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between −50 and −100 mV have been measured[2]. Depending on the colloidal stability of primary PVC particles in VCM with increasing conversion, various particulate structures within the suspension polymer are obtained which to some extent determine the internal porosity of the fully polymerized material[3]. It is hoped that an examination of the electrophoretic behaviour of primary particles under different polymerization conditions will lead to a better understanding of structure formation, and perhaps eventually to the optimization of polymer porosity. Since this involves the surface charge of the primary particles, a mechanism for the nature and origin of the surface charge of PVC particles in VCM is proposed and compared with other well-characterized colloidal systems.

The origin of the surface charge of aqueous dispersions of polymers, prepared from non-ionizable monomers in the absence of emulsifiers, is usually attributed to the incorporation of initiator radicals at the ends of polymer chains[4]. Hence aqueous dispersion polymerization of styrene using persulphate as initiator results in negatively charged particles due to the presence of sulphate groups[4], whereas amidine groups are responsible for the positive charge on particles prepared using azobisisobutyramidine hydrochloride[5]. However, VCM was initiated using dicetyl peroxydicarbonate which, when incorporated in the polymer results in non-ionic end-groups. Hence it is unlikely that decomposition products contribute to the surface charge at the PVC/VCM interface.

The presence of negative charge on a non-ionizable surface has been ascribed to either the preferential adsorption of anions or the preferential desorption of cations. For example, measurements of the ζ-potential of purified oil droplets dispersed in water showed that the surface of the droplets was negatively charged[6] and this was attributed to the preferential adsorption of hydroxyl ions from the aqueous phase. However, Davies and Rideal[7] prefer to explain the negative charge in terms of a selective desorption of hydrated protons from the interface.

VCM can be classed as a dipolar aprotic solvent which nevertheless can dissolve a finite but small quantity of water. At 20°C the saturation water content of VCM as measured by the du Pont 510 moisture analyser was 1150 ± 30 ppm (5.8×10^{-2} mol/dm^3). Despite the low dielectric constant of VCM (5.7 at 20°C when saturated with water) the conductivity of a sample of dried VCM was found to increase on the addition of small quantities of water, and this was attributed to the dissociation of water in VCM. It has been shown[8] that in the initial stages of VCM polymerization hydrochloric acid is generated by reaction with oxygen present in the system. VCM readily reacts with oxygen in the presence of radicals to form vinyl chloride peroxide which subsequently decomposes to give hydrochloric acid as one of the products. After all the oxygen has been used up, the number of ionizable species in the system will remain constant and the ionic species likely to be present in VCM at this stage are Cl^-, OH^- and H_3O^+ ions.

The PVC molecules contain polarizable C—Cl bonds which may interact with ionic species in the monomer. However, assuming a random orientation of dipoles at the PVC/VCM interface, the effect of ion-dipole interactions would not give rise to a net surface charge.

The possibility of ionization of adsorbed water or hydrochloric acid molecules or the adsorption of ions from the bulk of the monomer was considered in terms of the adsorption potential of the various ions at the PVC/VCM interface. Neglecting ion–dipole interactions, contributions to the adsorption potential arise from an image potential energy and a dispersion interaction energy. Calculations showed that the adsorption potentials of OH^- and Cl^- ions are attractive whereas the adsorption potential of H_3O^+ ions results in a net repulsive interaction, thus making hydrated protons good leaving groups from the interfacial region. The adsorption potential of chloride ions was found to be highest on account of their large polarizability and poor solvation.

It is of interest to comment on the number of charges required to produce stable PVC particles in VCM. Assuming that the counterions in VCM form an electrical double layer around the particles, the Debye–Hückel approximation of the Gouy theory relates the charge density at the plane of shear (σ_{ps}) to the ζ potential of a spherical particle of radius a:

$$\sigma_{ps} = \frac{\epsilon\epsilon_0\zeta}{a}(1 + \kappa a) \tag{1}$$

In the PVC/VCM system, $\kappa a \ll 1$ so that equation (1) approximates to:

$$\sigma_{ps} = \frac{\epsilon\epsilon_0\zeta}{a} \tag{2}$$

For particles having a radius of 0.15 μm, the ζ-potential was found to be[2] −83 mV, so that equation (2) gives $\sigma_{ps} = -2.4 \times 10^{-5}$ C/m^2, corresponding to 41 elementary charges per particle.

In *Table 1* the number of charges at the plane of shear per PVC particle is compared with the number of surface charges per particle obtained by titration for typical anionogenic polymer latexes of similar particle size. *Table 1* also shows the Lifshitz–Hamaker constants (A_L) for these systems. The value for PVC particles in monomer was calculated assuming that the polymer was swollen 33% v/v by monomer[11]. The Lifshitz–Hamaker constants for all three systems are of the same order of magnitude and this implies that their attractive interactions are similar.

The data in *Table 1* demonstrate that colloid stability in the PVC/VCM system is obtained with a much smaller charge density (about 1/100th) than is needed for aqueous latexes. The reason for this difference is found in the different nature of the dependence of the particle/particle interaction energy on particle separation. The potential energy against distance of separation curves for PVC particles in VCM and polystyrene particles in an aqueous medium are shown in *Figure 1* (curves A and B, respectively). The electrostatic and attractive contributions to the total potential energy of interaction between particles were calculated using simplified expressions. For both systems, the same ζ-potential (−80 mV) and particle radius (0.15 μm) were used, and the dispersion

Table 1 Number of charges per particle and Lifshitz–Hamaker constants for different polymer latex systems

Latex system	Charges/particle at plane of shear	Charges/particle at surface	A_L (10^{-21}J)
PVC/VCM	41	–	5.0
PTFE/water	–	5.7×10^3 (ref 9)	3.6 (ref 10)
Polystyrene/ water	–	7.1×10^4 (ref 4)	9.0 (ref 10)

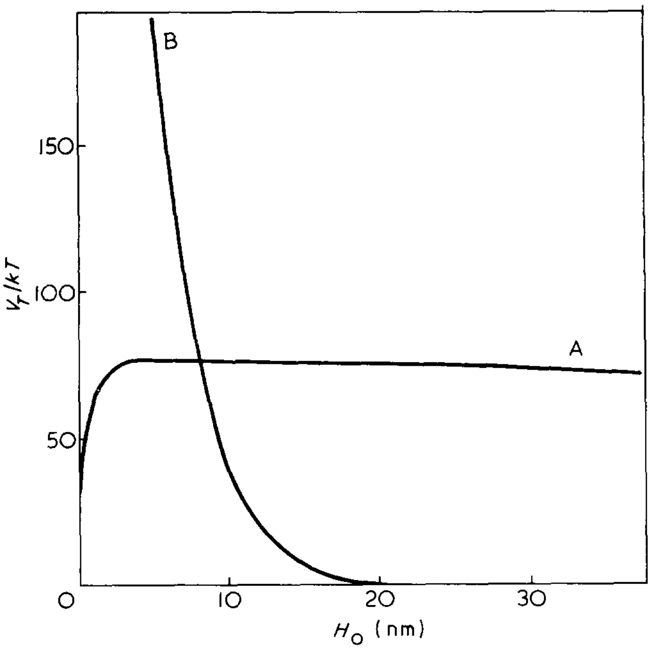

Figure 1 Diagram of total potential energy (V_T) against distance of particle separation (H_0) for spherical particles of radius 0.15 μm and ζ potential –80 mV. (A) PVC particles in VCM; (B) polystyrene particles in 10^{-2} mol/dm^3 1:1 electrolyte solution

medium for polystyrene particles was taken as a solution of 10^{-2} mol/dm^3 1:1 electrolyte. From *Figure 1* the potential energy maximum of curve A is much smaller than curve B. This reflects the lower dielectric constant of VCM compared with an aqueous solution. However, after the maximum in potential energy, the electrostatic contribution to the potential energy of curve B decays much more rapidly with increasing particle separation than curve A as a result of the much thinner electrical double layer surrounding particles in an aqueous medium ($1/\kappa = 3$ nm) compared with VCM ($1/\kappa > 10$ μm).

In conclusion, we suggest that the charge at the PVC surface probably results from a preferential desorption of hydrated protons from the PVC/VCM interface and that the stability of PVC particles in VCM at much lower surface charge density than for aqueous polymer latexes is the result of extended electrical double layers around the particles.

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