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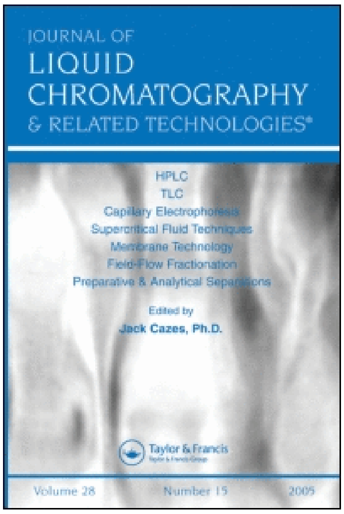

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AN INVESTIGATION OF THE APPLICABILITY OF UNIVERSAL PARTICLE-SIZE CALIBRATION IN THE SIZE-EXCLUSION CHROMATOGRAPHY OF POLYMER LATICES USING POROUS GLASS PACKINGS

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ABSTRACT

Two series of polymer latices, one of pure polystyrene, the other being coated with polymethylmethacrylate, were prepared using seeded emulsion polymerisation techniques. They were characterised by transmission electron microscopy and found to have narrow particle-size distributions with diameters, $\overline{D_0}$ in the range 57.7 to 207.1 nm. They were chromatographed on an SEC instrument equipped with columns packed with porous glasses. Aqueous chromatographic eluants included sodium dodecylsulphate or sodium dodecylbenzene sulphonate surfactants plus sodium nitrate added to vary the ionic strength between 4.44 and 150 mmol dm^{-3}. At ionic strengths below and including 62.5 mmol dm^{-3} the data for the two latex types fell on common plots of log $\overline{D_0}$ against elution volume indicating the validity of universal calibration. Variation of the surfactant type in the eluant and a comparison of dialysed against undialysed latices showed no significant effect on latex retention volumes. Anomalous behaviour, which was attributed to adsorption effects, was, however, observed at higher ionic strengths.

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INTRODUCTION

Until recently, chromatographic techniques, including size-exclusion chromatography (SEC) have been concerned with the separation of matter at the molecular level. The chromatographic separation of aqueous colloidal suspensions was first reported by Krebs and Wunderlich in 1971 (1), using porous silica-glass packings. The mechanism of separation in such systems is differential-pore permeation according to size, as is the case in conventional SEC, whereby large colloidal particles migrate through the columns more quickly than, and elute ahead of, small ones. Small demonstrated in 1974 (2) that size separation in such systems could be achieved by passage through columns packed with non-porous spherical beads which were considerably larger than the suspended particles. The mechanism for hydrodynamic chromatography (HDC), a term coined by Small, was actually proposed in 1969 before the technique was first applied, by Di Marzio and Guttman (3,4). Their "separation by flow" mechanism was first proposed to explain the phenomena occurring in conventional SEC, but was rejected since it could not explain, for example, separations observed during static-mixing experiments. In essence, a parabolic flow profile is proposed to exist in the interstices between the packing particles, with zero velocity at the walls tending towards a maximum at the centre of the flow channels. Large particles are more excluded by their physical size from the walls than small ones and so experience faster-flowing streams of eluant. They therefore elute ahead of the small ones, much as in SEC.

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Since the mid-seventies considerably more effort has been expended in the development of HDC than SEC for latex particle-size analysis. This is partly because HDC was conceived and developed in an industrial environment at Dow Chemical (5), where the relatively short-term objective of reducing the time involved in measuring colloidal sizes was desired. Another reason is that the low diffusion coefficients of polymer latices give rise to very large axial dispersion contributions to peak broadening when porous packings are used, which was perceived as a severely limiting factor. In any event, the HDC technique was patented by Dow in 1975 and licensed to the Micromeritics Instrument Corp. for commercial exploitation in 1977. Subsequent development has yielded instrumentation capable of performing particle size and distribution analyses within 10 minutes (5).

Many interesting studies using porous packings have, however, appeared in the literature, coming from predominantly academic environments. Adherents to

SEC will often cite the much greater peak separation of this technique over HDC as an overriding advantage. As an example we refer to an HDC system employed by Silebi (6) in which a typical peak retention volume V_{pk}, for a latex was approx. 60 cm^3, whilst the peak separation between a latex of diameter 380Å and one of diameter 3570Å was around 1.5 cm^3 for most eluants. For comparison, we refer to an SEC system previously employed by one of the authors (7-9). Here, latex retention volumes varied between 95 and 120 cm^3 (depending strongly on particle size and eluant ionic strength) with a peak separation between a latex of approx. 300Å diameter and another of approx. 900Å diameter being some 20 cm^3 when the ionic strength was 107 mmol dm^{-3}.

For further details concerning the mechanisms of both HDC and SEC as well as examples of specific applications, the reader is referred to two useful recent review articles (10,11).

Before tackling the specific problem addressed in this paper it is first instructive to examine certain phenomena, common to both SEC and HDC, which need to be carefully considered if the chromatographic data is to be properly interpreted. It was recognised from the outset (1,2) and has since been observed many times (10) that in order for latex particles to elute at all from the packed columns, a small amount of ionic surfactant at around the critical micelle concentration (CMC) needs to be incorporated in the aqueous eluant. Furthermore, the addition of simple electrolyte to the eluant drastically affects the latex retention volumes. In the absence of surfactant the latex particles do not elute, presumably due to adsorption of the relatively large hydrophobic latices onto the surface of the packing materials which in their untreated state are also hydrophobic. When anionic surfactant is present, as is the case in all hitherto published work, it imparts electrostatic colloidal stability to the latex by adsorption at the surface, as well as conferring a similar charge to the packing surface, again by adsorption. Repulsive electrical double layers are hereby set up. This mechanism is illustrated in Fig. 1. Other contributions to the negatively-charged surfaces come from the dissociation of silanol groups in the case of glass packings and from ionic initiator residues at individual polymer chain ends (e.g. SO_4^{2-}) which are known to reside primarily at latex particle surfaces rather than being randomly embedded in the body of the particles (12). According to DLVO theory (13,14) we can assign to each double layer a certain thickness, $1/\kappa$, which varies according the the well-known equation

$$\kappa = (8\pi nz^2e^2/\varepsilon kT)^{1/2} \qquad (1)$$

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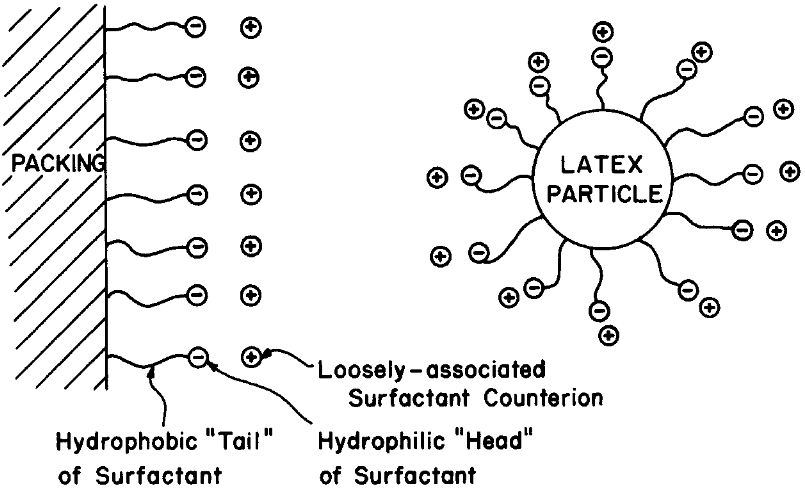

Figure 1. Illustration of Adsorption of Surfactant and Setting up of Double Layers Between Packings and Particles.

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where n and z are respectively the valency and charge of the ionic species present in the "ionic atmosphere" surrounding the particles, ε is the dielectric constant of the medium, k is the Boltzmann constant and T the temperature. This equation applies to to similarly-sized, similarly-charged spheres. We see that the double-layer (DL) thickness is thus a direct function of the inverse square root of the ionic strength, $I^{-1/2}$, of the medium surrounding the particles. This thickness is defined as the distance r at which the electrical potential, $\psi(r)$, falls to 1/e times the surface potential, ψ_0, i.e. when $1/\kappa = r$,

$$\psi(r)/\psi_0(r) = 1/e \tag{2}$$

The situation in SEC and HDC is best visualised as an interaction between a wall (the packing material) and a charged sphere (the latex particle) (7,8). The form of the D-L interaction potential energy, U(r), for such a system was first formulated by Bell, et al. (15), as follows

$$U(r) = \varepsilon a_2 (kT/e)\, \psi_{0,1}\, \psi_{0,2} \exp(-\kappa r) \tag{3}$$

Here a_2 is the radius of the sphere, $\psi_{0,2}$ its surface potential and $\psi_{0,1}$ is the surface potential of the wall. Essentially, then, the repulsive interaction energy between two surfaces is a function of their surface potentials, the DLVO double-layer thickness (hence the ionic strength of the medium), the distance between them and the radius of the sphere. The values of $\psi_{0,1}$ and $\psi_{0,2}$ are strongly dependent on the surface chemistry of respectively the packing and the latices. Considering the latter, contributions to $\psi_{0,2}$ arise from a number of sources. We have already briefly mentioned ionic initiator residues and the adsorption of ionic surfactant. The chemical nature of the latex plays an important role in the adsorption process. The area occupied by each surfactant molecule has been shown to increase as the surface becomes more hydrophilic (16,17). Since each surfactant molecule contributes a single charge to the total surface charge, $\psi_{0,2}$ then decreases with increasing latex hydrophilicity. The effect of such interactions on chromatographic behaviour can be visualised with reference to figure 2. The particle is excluded from the packing pore (or the wall in the case of HDC) due to its own naked or "core" radius, r_e with a further contribution δ from the two DLs on packing and sphere. The total "effective" radius, r_e is then the sum of the two contributions:

$$r_e = r_c + \delta \qquad (4)$$

At low ionic strength, r_e is relatively large and the particle therefore elutes more quickly than is the case at high ionic strength. In a study involving the SEC of seven narrow particle-size distribution polystyrene latices by Styring et al. (7,8), it was predicted by application of equations 3 and 4 and successfully shown that latex retention volumes decrease linearly with $I^{-1/2}$, keeping other factors constant, provided the sole parameter determining separation is r_e. The core radius alone affects separation only when δ is zero, i.e. when $I \to \infty$. This condition cannot, of course, be examined experimentally (the latices all adsorbed to the columns at $I > 110$ mmol dm^{-3}), but was approached by extrapolation of data obtained at finite values of I to $I = \infty$. The retention volumes of the seven latices thus obtained by extrapolation were then compared with those of linear polystyrene standards eluted from the same column set in tetrahydrofuran (THF) eluant (7,9) on an hydrodynamic-volume basis (18). The coincidence of the log $[\eta]M$ versus retention volume calibration curves thus obtained was felt to be indicative of the correctness of the procedure for extrapolating the latex data to $I = \infty$.

An interesting question now arises from the foregoing. If we accept the premise that the retention volume of a given latex particle at any value of I is dependent on r_e, not solely on r_c and hence the latex surface potential, then how do we set about calibrating an instrument which we intend to use for colloids of varying chemical types, hence $\psi_{0,2}$ values?

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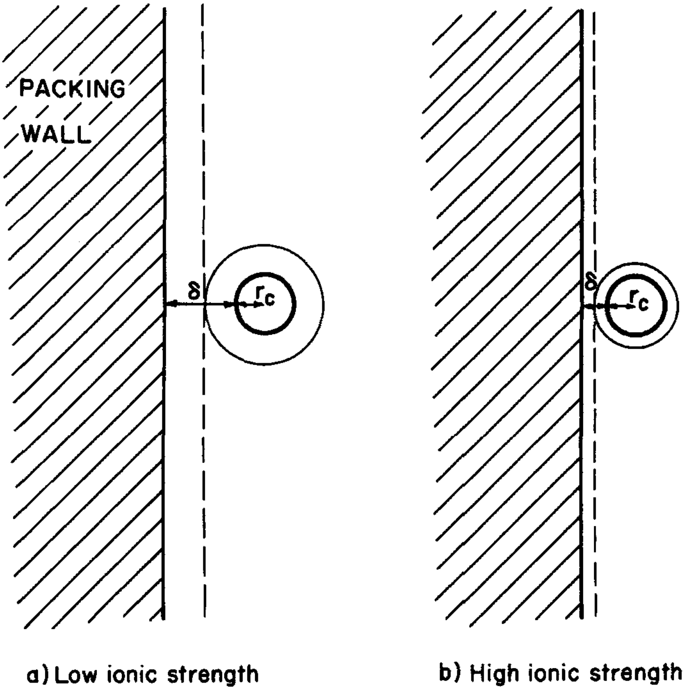

a) Low ionic strength b) High ionic strength

Figure 2. Variation in Double-Layer Thickness and its Effect on Effective Particle Radius.

A rigorous method would be to take a set of (say polystyrene) particle standards, chromatograph them at various values of I then extrapolate to $I = \infty$ ($I^{-1/2} = 0$) to establish the true log r_c vs. retention volume calibration. Any unknown species would then also have to be chromatographed over a range of I and the data similarly extrapolated in order to find its r_c from the calibration curve. This is obviously a very time-consuming procedure; quite unacceptable for most industrial applications.

Before examining this issue more deeply it is instructive to review the methodology applied to calibration in HDC. This technique has been quantified in terms of a capillary-bed model for the flow-separation process. Instead of elution volume, the experimental quantity of interest has by convention become the separation factor, R_F which is the ratio of the rate of transport of the colloidal particle through the column to that of the eluant. The eluant velocity is assumed to be equal to that of a low-molecular-weight "marker" species, commonly a dichromate salt. We then have

$$R_F = <v_p>/<v_m> \tag{5}$$

where $<v_p>$ is the average velocity of the particle and $<v_m>$ is that of the marker. This is determined experimentally from the ratio of retention volumes of the marker and particle;

$$R_F(\text{expt}) = V_m/V_p \tag{6}$$

Using the capillary-bed model the velocity of a spherical species travelling down the column is given by (19-22)

$$<V_p> = \frac{\int_0^{R_o-R_p} v_p(r)\exp(-\phi/kT)r\,dr}{\int_0^{R_o-R_p} \exp(-\phi/kT)r\,dr} \tag{7}$$

Here R_o and R_p are respectively the radii of capillary and particle. The eluant velocity is obtained by setting $R_p = 0$ (19). ϕ is the total interaction energy between particle and wall comprising contributions in this case not only from DL repulsions but also relatively short-range Van der Waals attractions (19,21). The exponential term is the effective probability that a particle will occupy a given flow streamline at a distance r from the wall. The particle streamline velocity, $v_p(r)$ is given by

$$v_p(r) = v_o[1-(r/R_o)^2] - \gamma v_o(R_p/R_o)^2 \tag{8}$$

where v_o is the average eluant velocity and γ is the wall-effect parameter which may be calculated from the expressions obtained by Goldman et al. (22). By judicious choice of material constants (such as the Hamaker constants and surface potentials) the model was shown to give good agreement (19,21) with the experimental data of Small (2). This is illustrated in Fig. 3. The decrease in R_F with increasing I is well accounted for. At high I there is evidence of adsorption ($R_F<1.0$) arising from the shrinkage of the repulsive DLs to such an extent that their effects begin to be outweighed by the attractive Van der Waals forces.

Further model calculations by Nagy et al. (23) indicate that at very low values of I, R_F becomes independent of particle chemistry which suggests that universal particle-size calibration should be valid. This proposition was tested by chromatographing a series of seven Dow polystyrene latex standards (presumably characterised by electron microscopy) on an HDC instrument using Aerosol MA surfactant with a value of I = 1.29 mmol dm^{-3} to establish a calibration. A poly(vinylchloride)

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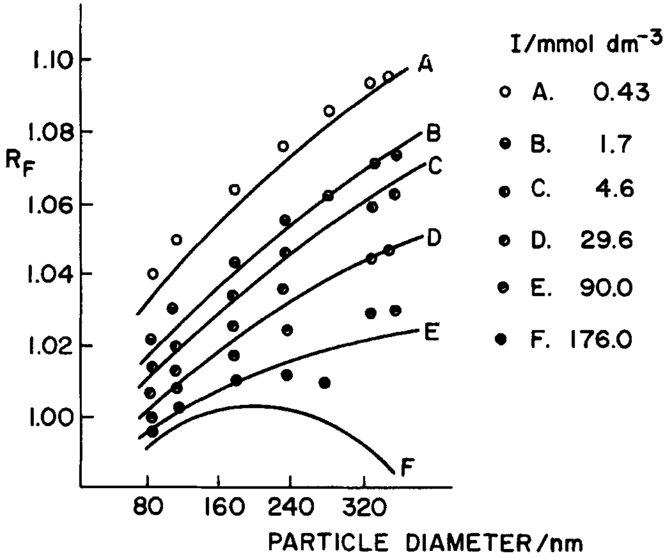

Figure 3. Comparison of the Experimental Data of Small (2) with Model of McHugh et al.(19,22).

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(PVC) and three poly(co-styrenedivinylbenzene) (PSB) latices, when chromatographed under the same conditions, were found to conform closely to the same calibration curve, although the method of independent characterisation of the PVC and PSB latices was not disclosed. A further evaluation of universal calibration was carried out by Nagy (24) in which an HDC instrument was calibrated once again using polystyrene standards (Dow) and a colloidal silica (Du Pont, Ludox) with $I = 5 \times 10^{-4}$M. On this occasion various vinyl acetate, vinyl acetate-ethylene, ethylene-vinylchloride and vinyl acetate-acrylic latices were analysed on the HDC and separately using a Joyce-Loebl disc centrifuge. The values of $\overline{D_n}$ obtained using this latter technique were found to be consistently smaller than the average particle size determined from HDC by between 0.8 and 14.2%; on average 7.5%. The $\overline{D_w}$ values obtained from the Joyce-Loebl were somewhat in excess of the HDC averages by between 3 and 105%, on average 33%. Based on the findings of these two studies (23,24), and arguments presented above concerning the nature of DL repulsions in the systems being examined, the question of the validity of universal particle-size calibration in HDC and SEC is still open to debate. It is the purpose of this work to shed further light on this matter.

In the present study, it was decided to use an SEC instrument rather than an HDC since it was felt that its superior peak separation would permit observation of subtle variations in retention volumes more readily.

For a proper study of the applicability of universal calibration it was felt desirable to have two series of monodispersed, well-characterised latices having different surface chemistry yet falling in the same particle-diameter range. In this manner a calibration established for one latex type could be directly compared with another without the need for extrapolation.

As is common practice in SEC/HDC it was decided to use narrow-distribution polystyrene latices as one series of calibration standards owing to their relative ease of preparation and of characterisation. We employed a recipe based on the conventional emulsion polymerisation procedure of Woods et al. (25) to produce a narrow-distribution polystyrene "seed" latex. Successive seedings according to the method described by Dodge et al. (26) were made in order to obtain additional polystyrene latices in a convenient range of particle diameters. Such seedings are not limited strictly to the production of larger homopolymer particles as outlined above. The technique may be employed using different overcoating monomers to obtain latices having core-shell morphologies and so different surface chemistry from the core seed as was required in our study. This and other methods of preparing latices having controlled surface-charge densities are described by Hearn et al. (27-29). In particular we utilised a seeded growth method based on that described in reference 28 to produce narrow-distribution latices overcoated with PMMA.

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A large number of techniques are available for determination of latex particle sizes (27). Average diameters may be measured by light scattering, ultracentrifugation, small-angle X-ray scattering, photon-correlation spectroscopy and for particles larger than 1 μm in diameter, optical microscopy and the Coulter counter. Electron microscopy, both in transmission (TEM) and scanning (SEM) modes can be used to obtain not only average diameters but in addition size distributions as well as providing a direct visual assessment of particle shapes, information which is not available from other techniques. Of particular use in our application is the ability of TEM to indicate the presence of a fraction of small particles resulting from secondary particle nucleation (30). This is a common occurrence in seeded emulsion polymerisations (26) if too much surfactant is present in the reaction mixture.

Disadvantages of the technique have been well documented and include possible aggregation of the dispersions during sample drying and possible swelling or shrinkage on exposure to the intense electron beam under reduced pressure (31-33). Such effects are generally negligible in the case of hard glassy polymer latices such as polystyrenes. However, in the case of soft, film-forming latices, steps need to be taken to ensure that electron-beam damage does not lead to inaccurate particle-size determinations. Strictly speaking, PMMA is not a soft polymer. It has a glass-transition temperature, T_g, of around 110°C. It does, however, degrade easily in an electron beam, which is one reason for its use in lithography (chip manufacture). It should therefore be treated in the same manner as truly "soft" polymers as regards its characterisation by electron microscopy. Soft latices may be hardened by staining with bromine or osmium tetroxide (34). Alternatively, they could be replicated (35) or shadowed using a suitable heavy metal (36). Another method is to adsorb a known quantity of styrene monomer into the soft latex and expose the sample to γ-rays, thereby cross-linking and hardening the particles (37). Heavy-metal shadowing was the method of choice in our work.

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Apart from variations in latex chemical type, other factors influencing the surface charge densities on latex and packing may be readily varied. One of these is the type of surfactant employed in the eluant. It is well known that different surfactants occupy different surface areas per molecule on any given latex (38-41) and presumably likewise on packings. Further, especially in the case of latices prepared in industrial environments, the emulsifier used in the polymerisation process is frequently different from that used in the chromatographic eluant. In addition, residual impurities in the latex solution such as excess initiator might have some effect on elution parameters. This could be tested, as was done in the present work, by cleaning samples of the latices of interest and comparing their chomatographic behaviour with the untreated equivalents. Of the various methods available for cleaning latices (27), dialysis (42), our method of choice, is experimentally the simplest and is usually quite effective in removing the major portion of impurities. Briefly, the latex solution is enclosed in Visking dialysis tubing and immersed in a large excess of deionised or distilled water with frequent changes of water. The process is complete once the conductivity of dialysate equals that of the deionised water employed. It is a slow process, relying on the impurity-concentration gradient across the membrane, becoming increasingly slow as the impurity concentration is reduced. Three to four weeks are usually necessary for maximum purity to be achieved.

In summary the major objectives of this work were

a) To prepare and characterise by some absolute method, two series of polymer latex standards of differing chemical type and hence different surface potentials.

b) To chromatograph these latices at varying ionic strengths both in their "raw" state and with slight surface modifications (through dialysis and change of surfactant).

c) To construct appropriate calibration curves from the data and thereby examine the assertion that universal particle-diameter calibration is valid.

EXPERIMENTAL, RESULTS AND DISCUSSION

Preparation and Characterisation of Narrow-Particle-Size-Distribution Polystyrene Latex Standards

Six polystyrene latices, designated L1 to L6, were prepared. The smallest of these, L1, was used as a seed for all the other latices, including those overcoated with PMMA (see subsequent section). A modification of the method of Woods et al. (25), using Aerosol MA-80 surfactant instead of mixed anionic and nonionic surfactants, which has been shown to yield a nearly monodisperse latex of approximately 60 nm diameter (8), was employed to make L1. This and all other polystyrene latex reactions were carried out in a Chemineer (Dayton, Ohio) pilot-scale reactor of 8 litres capacity. All interior reactor parts such as the stirrer and dip tubes were made of stainless steel. The polymerisation temperature was maintained at 90°C by means of a thermostatted steam/water jacket. The ingredients were 3500 cm^3 of deionised water, 135 cm^3 of MA-80 surfactant (Cyanamid Corp.), 1800 cm^3 of styrene monomer (Aldrich Chemical Corp), with an initiator solution comprising 21.0 g of potassium persulphate and 4.0 g of sodium hydrogen carbonate (both from BDH Chemical Co.) dissolved in a further 600 cm^3 of deionised water. All chemicals were used as received from the suppliers. After addition of the initiator solution to the monomer/emulsifier/water mixture, which had been stirred and purged at ambient temperatures with nitrogen gas overnight, the reaction was allowed to proceed for 90 minutes whereupon complete conversion was judged to have been achieved by the near disappearance of the styrene odour. The reaction mixture was quickly cooled to room temperature before the latex solution was collected and filtered through a bed of glass wool packed in a cylindrical glass column. The solids content was determined by evaporation of the water from two carefully-weighed latex samples on aluminium

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trays in a vacuum oven at 50°C. The solids-content analysis, when taken together with measured particle size, can serve as a check on the degree of conversion of monomer to polymer-in-latex. Similar analyses were performed on all latices prepared in this study and are discussed in due course.

Characterisation of this and the five other polystyrene latices was carried out by TEM using a Philips Model TEM 300 apparatus operating at 60 kV. Barely-turbid (approx. 0.01% solids) latex samples were pipetted onto Formvar/carbon-coated copper grids and allowed to dry under ambient conditions before being introduced into the microscope which was calibrated for each magnification employed using a diffraction-grating replica. Photographs of representative portions of the grid were taken for particle-size analysis. It was desired that around 300 or more latex particles per sample could be counted in order to obtain an accurate particle size and distribution in each case. Table 1 gives characterisation data for all the polystyrene latices examined here.

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Having satisfied ourselves that L1 was sufficiently monodisperse for the current purposes, a portion of the latex was taken as a seed to be grown to successively larger diameters to produce the range of calibration standards required for our study. This was done according to the method of Dodge et al. (26). An approximate doubling of latex volume, i.e. a diameter increase by a factor of $\sqrt[3]{2} = 1.259$ at each seeding was considered desirable. The basic procedure at each stage was to stir the seed latex together with the additional water, monomer and emulsifier at room temperature for

TABLE 1

Characterisation Data for the Polystyrene Latices used in This Study

Sample	$\overline{D}_n$/nm	$\overline{D}_w$/nm	$\overline{D}_o$/nm*	SD/nm**	n***
L1	57.2	58.2	57.7	4.2	407
L2	64.3	65.9	65.1	6.4	497
L3	83.3	84.6	83.9	6.6	520
L4	99.8	101.9	100.9	8.6	446
L5	146.5	146.9	146.7	4.4	310
L6	180.2	182.3	181.2	11.4	323

* $\overline{D}_o = (\overline{D}_w \overline{D}_n)^{1/2}$

** SD = standard deviation in sizing data

*** n = number of particles per sample counted in determining particle-size data.

TABLE 2

Recipes Employed in Preparation of Seeded Polystyrene Latices L2 to L6

Latex	Amount (type) of seed/cm^3	Styrene /cm^3	MA-80 /cm^3	Deionised water/cm^3	$K_2S_2O_8$/$NaHCO_3$ (/g) in water (/cm^3)
L2	2000 (L1)	590	60	1000	7.07/1.00 (330)
L3	2000 (L2)	600	30	1000	7.02/1.00 (400)
L4	2000 (L3)	600	25	1000	7.04/1.00 (400)
L5	2000 (L4)	600	20	1000	7.05/1.07 (400)
L6	2000 (L5)	600	15	1000	7.09/1.14 (400)

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4 hours under a purging atmosphere of nitrogen gas. The temperature was then increased to 60°C and the initiator solution added. One hour was generally sufficient for maximum conversion to be achieved. Table 2 gives details of the individual recipes employed for L2 to L6. Plate 1 is an electron micrograph of latex L3 and is typical of the whole series L1 to L6. Further seedings to produce yet larger monodisperse particles were attempted but problems with secondary particle nucleation, often a problem with seed polymerisations when surfactant is present, were observed when the next largest latex, L7, was prepared using L6 as a seed. The problem was exacerbated when yet larger latices were made using the now bimodal seed latices. This is clearly shown in plate 2, an electron micrograph of latex L8 prepared from L7. The presence of small particles is indicative of a "crop" of new latex.

Table 3 gives the solids content of each latex determined by gravimetry together with the theoretical value calculated from the known amount of monomer, initiator, surfactant (which is 80% solids, according to the manufacturer) and seed latex charged to the reactor each time. Clearly the two sets of figures are in close agreement, which indicates that on or near total conversion of monomer to polymer was achieved in each case. The slight decrease in total solids in descending the table is reflective of loss of a small amount of polymer by coagulation (filtered out) in each case. The third column in this table gives the theoretical diameter of the latex particle after each seeding, assuming perfect sphericity and monodispersity of the particles. The calculations were made according to the following equation:

$$D' = D\left(\frac{m_s + m_m}{m_s}\right)^{1/3} \qquad (9)$$

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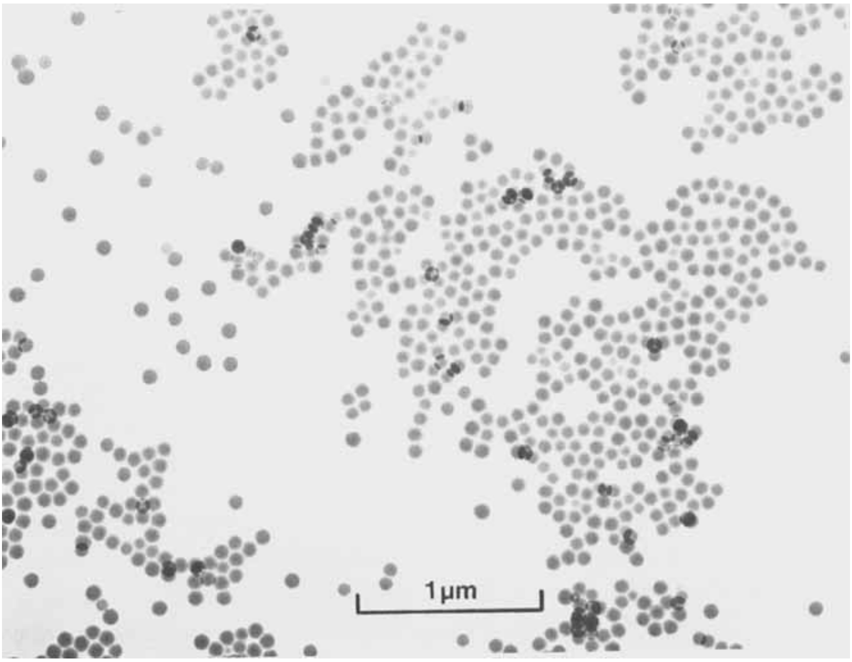

PLATE 1. Transmission Electron Micrograph of Seeded Polystyrene Latex L3.

TABLE 3

Theoretical and Actual Solids Contents and Particle Diameters for the Polystyrene Latices

Sample	% Solids by Weight calculated	% Solids by Weight by gravimetry	D/nm calculated	$\overline{D_0}$/nm by TEM
L1	30.01	29.05	-	57.7
L2	29.90	30.45	72.1	65.1
L3	29.79	28.50	80.95	83.9
L4	28.75	26.80	105.5	100.9
L5	27.65	26.0	127.8	146.7
L6	27.18	26.35	186.9	181.2

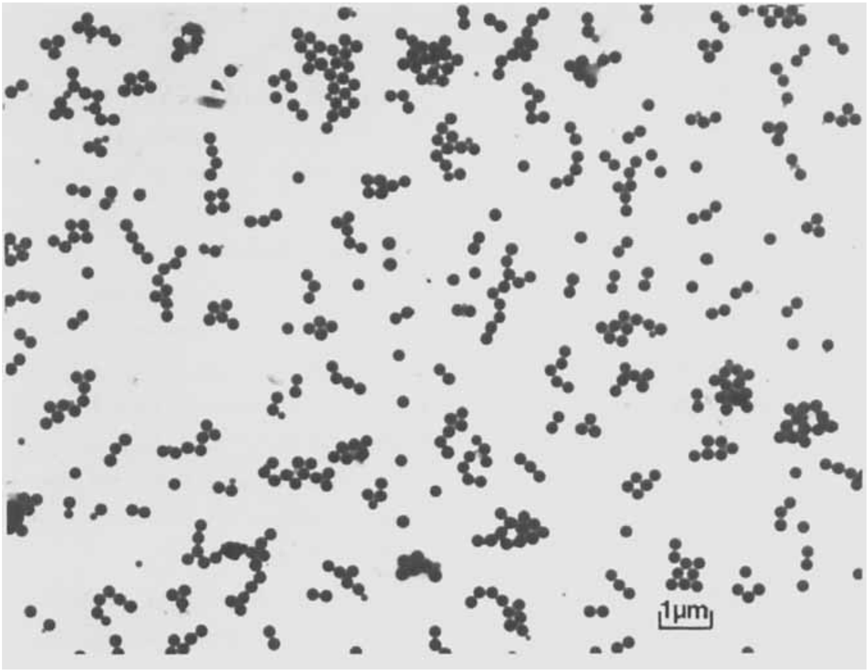

PLATE 2. Transmission Electron Micrograph of Seeded Polystyrene Latex L8.

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Here D' is the diameter of the latex particle after reaction and D is that of the starting seed (taken as $\overline{D}_0$ measured by TEM). m_s is the total mass of latex solids based on the gravimetric determinations (taken here as polystyrene plus initiator less the contribution from the surfactant solids) and m_m is the mass of monomer added during the reaction. The values of $\overline{D}_0$ actually obtained are given for direct comparison in the fourth column. With the exception of L2 and L5 the calculated and actual diameters are in good agreement, given that the error of the TEM technique is accepted as being ±5% (8). This indicates that not only was the monomer totally converted to polymer, but also that it was all incorporated within the latex particles themselves. In the case of the exceptions (L2 and L5) repeat TEM measurements were made, and the particle diameters were found to be within 5% of the original determinations. The larger deviations in these cases may be a result of the simplistic assumptions made in performing the diameter calculations.

Preparation and Characterisation of Narrow-Particle-Size-Distribution PMMA-Coated Latices

Five PMMA-coated latices, designated M1 to M5, were prepared. The polystyrene seed, L1, was used as the starting material. Consequently each latex had a polystyrene core with successively thicker PMMA shells. The recipes employed, based on the method described by Chainey et al., (28) are outlined for each latex in Table 4. These preparations were carried out in a scaled-down Chemineer reactor of 5 litres capacity. The procedure in each case was to charge the ingredients, apart from the initiator solution, to the reactor and stir with a slow nitrogen-gas purge at room temperature for 30 minutes. The temperature was then brought to 80°C and the initiator solution added. The reaction time thereafter was between 3 and 4 hours, depending on when the odour of MMA monomer (Rohm and Haas Corp., used as received) was judged to have disappeared. The reactor contents were once again cooled to room temperature before collection of the latex solution followed by filtration.

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It was noticed that significantly more solids were removed from the PMMA-coated latex solutions than was the case for the polystyrenes. This may have been due to some specific surface interaction between the PMMA and the glass wool fibres since very little coagulum was noticeable in the latex solutions, nor was any more polymer deposited in the reactor than during the preparation of the polystyrene latices. As is indicated in Table 5, more than two-thirds of the total solids were removed by filtration from latex M3.

The first attempt at particle-size characterisation of these latices by TEM was exactly as for the polystyrene latices. Plates 3 and 4 show respectively the micro-

TABLE 4

Recipes Employed in Preparation of Core-Shell Latices M1 to M5

Latex	Amount(type) of seed/cm^3	MMA Monomer /cm^3	Deionised water/cm^3	$K_2S_2O_8$ (/g) in water(/cm^3)
M1	500 (L1)	135	750	1.06 (100)
M2	800 (M1)	150	550	1.01 (100)
M3	700 (M2)	150	550	1.03 (100)
M4	600 (M3)	120	750	1.30 (100)
M5	800 (M4)	120	550	0.99 (100)

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TABLE 5

Characterisation Data for the PMMA-Coated Latices

A	B	C	D	E	F	G
Sample	$\overline{D}_0$*/nm (n/sample)	$\overline{D}_0$**/nm	SD** /nm		% solids by weight	
				before filtration	after filtration	theoretical
M1	66.6 (512)	71.1	6.3	–	17.86	18.51
M2	76.0 (425)	78.4	5.9	18.25	17.45	18.21
M3	102.4 (378)	104.4	6.5	20.24	6.36	18.09
M4	126.6 (441)	155.4	10.0	–	9.30	11.37
M5	174.0 (496)	207.1	12.9	–	10.03	12.06

* Refers to untreated latices

** Refers to shadowed latices. True standard deviations for the uncoated particles will be slightly smaller than the values quoted in column D.

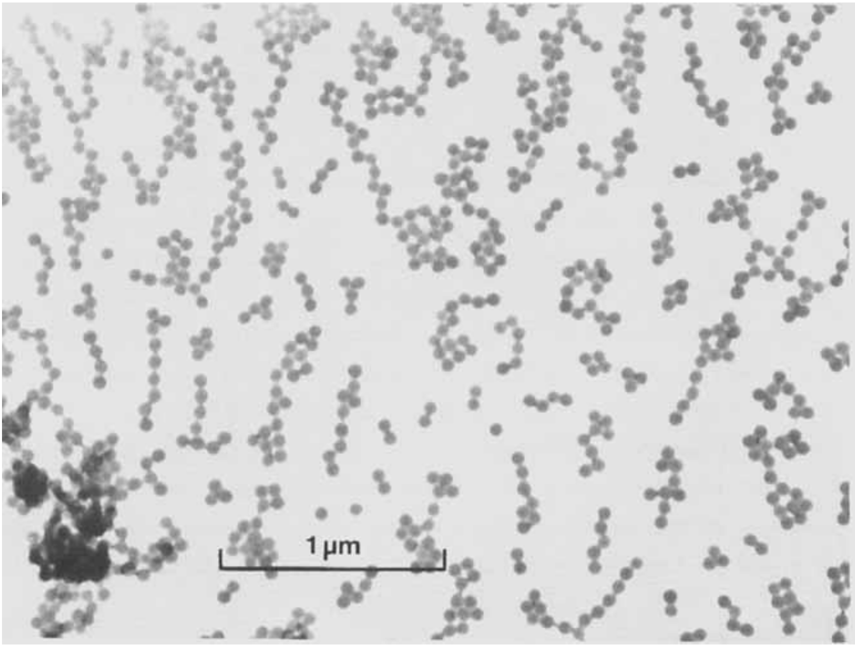

PLATE 3. Transmission Electron Micrograph of Seeded, PMMA-Coated Latex M1, without Pt/C Deposition.

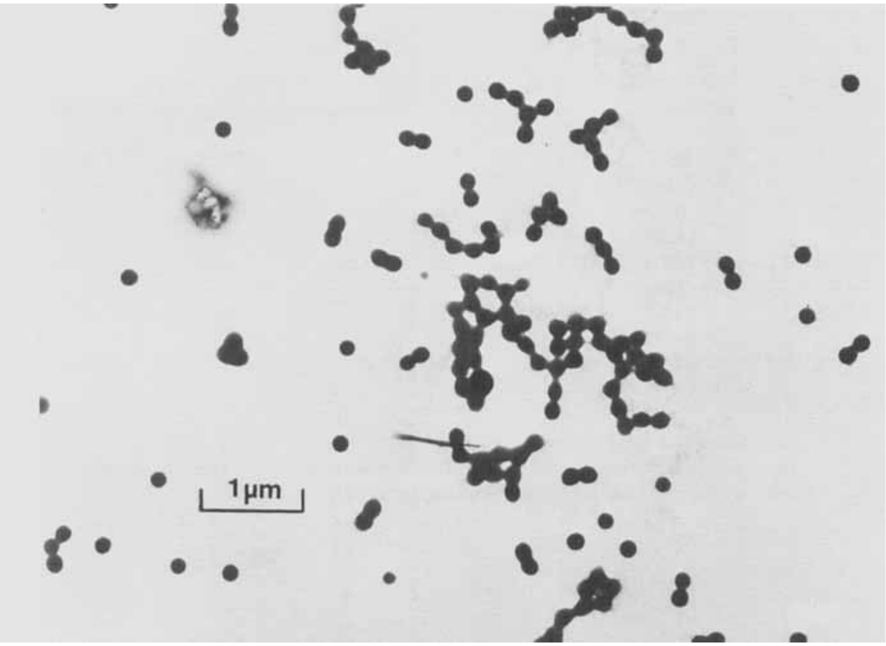

PLATE 4. Transmission Electron Micrograph of Seeded, PMMA-Coated Latex M5, without Pt/C Deposition.

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graphs obtained for latices M1 and M5. The data thus obtained are shown in column B of Table 5. It was noticed, however, that some of the individual latex particles, particularly in the case of the two larger samples M4 and M5, appeared to be somewhat distorted from true sphericity, e.g. compare Plate 4 (M1) with Plate 5 (M5). It was thought that this may have been due to electron-beam damage in the microscope which, if it were to happen at all, should become more prevalent for a greater thickness of the PMMA shell. Further evidence indicating possible inaccuracy of these preliminary characterisations came from some of the chromatographic data, which is discussed in the next section. In addition, some discrepancies were found in the diameters predicted for these latices, assuming 100% incorporation of monomer into latex, and those obtained by electron microscopy (compare columns A and B in Table 6).

These calculations were based on the observed latex solids contents from gravimetry (column F in Table 5) and were performed according to the following

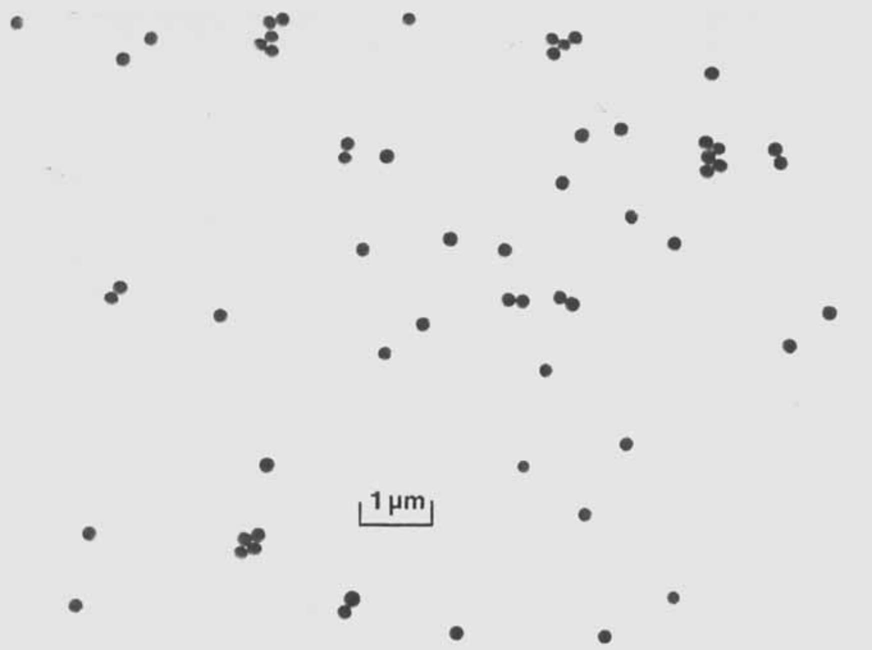

PLATE 5. Transmission Electron Micrograph of Seeded, PMMA-Coated Latex L5, Shadowed with Pt/C.

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TABLE 6

Comparison of Predicted and Observed Particle Diameters for M1 to M5

Sample	A $\overline{D}_0$/nm* observed	B D/nm calculated	C $\overline{D}_0$/nm** observed	D D/nm calculated
M1	66.6	70.35	71.1	70.35
M2	76.0	83.2	78.4	88.9
M3	102.4	98.2	104.4	101.3
M4	126.6	173.7	155.4	177.1
M5	174.0	173.4	207.1	212.8

N.B. Starting seed (L1) diameter $\overline{D}_0$ = 57.7 mm
* Data for untreated latices
** Data for shadowed latices

equation, which is a modification of equation 9 accounting for the differences in the bulk densities of polystyrene and PMMA:

$$D' = D\left(\frac{m_s/\rho_s + m_m/\rho_{PMMA}}{m_s/\rho_s} \right)^{1/3} \tag{10}$$

Here ρ_s is the average density of the composite seed particle and ρ_{PMMA} is the density of bulk PMMA (1.188 gcm^{-3} from Polymer Handbook and the density of the pure polystyrene initial seed was taken as 1.06 $g\,cm^{-3}$ from the same source). Even allowing for the simplistic method of calculation, the difference between the predicted and observed values for latex M4 seemed extraordinarily large and might be accounted for if some of the PMMA coating was burned off in the microscope. In order to examine this assertion it was decided to use heavy-metal shadowing as a means of circumventing possible beam damage. Samples of the five PMMA-coated latices were made up for the TEM as described previously, together with a repeat of L1. All six grids were placed adjacent to one another in an Edwards model EI2E vacuum evaporator equipped with a Pt/C electrode in order to vapour deposit a Pt/C coating on the specimens at an angle of approx. 45° to the plane of the grids. Electron micrographs were then obtained as before in a Philips TEM 300. Since all the samples were treated in this fashion simultaneously, it was assumed that their coating thicknesses were identical. This being the case, the actual coating thickness was calculated from the micrograph obtained from latex L1. The "true" particle diameter was known to be 57.7 nm from the prior TEM determination (see Table 1). The total diameter of the shadowed particle was found to be 71.3 nm, yielding a coating thickness of 13.6 nm. This coating thickness was subtracted from the measured diameters of the shadowed M-series latices to yield the values of $\overline{D_0}$ shown in column C of Table 5 and column C of Table 6. The difference in observed diameters is small for the three smaller latices, but is rather substantial for the two larger ones having the thicker PMMA coatings, as suspected. Further, somewhat better agreement between the calculated and observed latex-diameter values is obtained when we use the data for the coated latices (compare columns C and D in Table 6) than when we use the uncoated-latex data. The electron micrograph for shadowed latex M5 is shown in Plate 5. Comparison with the uncoated equivalent (Plate 4) shows that the former is rather more spherical. The standard deviations of the particle sizes are indicative that the M-series latices have similarly narrow distributions to the L series.

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Dialysis of Latices

Small samples, approx. 20 cm^3, of each latex were dialysed against deionised water in Visking dialysis membrane bags. The Visking tubing was conditioned in boiling water before use. All eleven samples, L1 to L6 and M1 to M5, were placed in a covered 10-litre plastic bucket which was filled to capacity with deionised water. The dialysate was completely changed daily over a period of 4 weeks. The dialysis was not followed quantitatively but certain simple visual inspections indicated satisfactory progress. For example, just prior to the daily change of dialysate, the solution in the bucket was vigorously agitated with a stainless-steel paddle. Throughout the first three weeks of the process, this agitation produced a foam on the surface, presumably due to surfactant still dialysing out from the samples. By the beginning of the fourth week, no more foam was observed, indicating that the majority of the surfactant had dialysed out. At the end of the fourth week when the latex solutions were removed from the dialysis bags it was noticed that despite considerable dilution (migration of water into the dialysis bags during the process by osmosis) the solutions were considerably more viscous than at the start, especially in the case of the polystyrene latices. This observation is consistent with all the extraneous electrolyte having dialysed out of the samples, permitting the so-called electroviscous effects to come into the operation. The primary electroviscous effect (43) arises from the deformation of the electrical double layers around each latex particle under flow, a process which results in the dissipation of energy and hence an increase in viscosity. The secondary electroviscous effect (44) occurs at relatively high colloid concentrations when the double layers around individual particles can interact with one another, again causing an increase in latex-solution viscosity. It has been shown (45) that even extremely low electrolyte concentrations cause sufficient double-layer shrinkage to counteract the electroviscous effects, thus lowering viscosities.

SEC

The apparatus used is shown schematically in Figure 4. The eluant reservoir was a 4-litre Pyrex Ehrlenmeyer flask. The degasser was an Erma model ERC-3110. The pump was a Waters Associates model 6000 of dual reciprocating-piston design with a pulse dampener inserted immediately thereafter (simply a long coil of narrow-diameter tubing). The injection valve was a Rheodyne model 7010, equipped with a

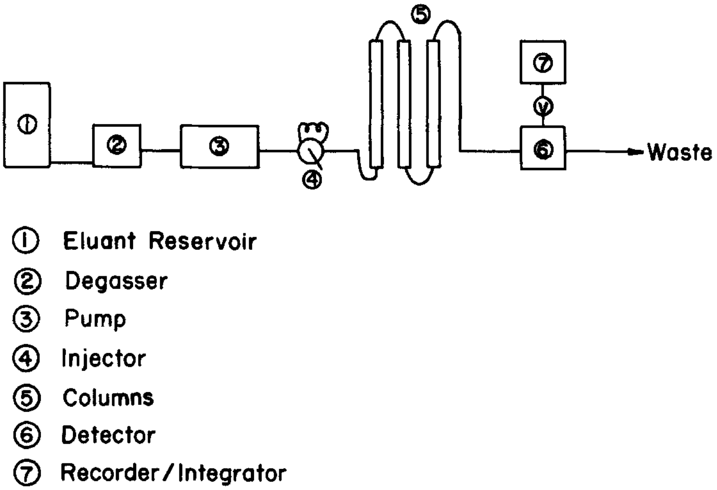

Figure 4. Schematic Diagram of SEC Apparatus.

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10 µl sample loop. The chromatographic columns were each 1 metre long with 6 mm internal diameter. The three were packed using a dry-packing technique with porous glasses of respective nominal average pore diameters 50, 300 and 500 nm. The former two glasses were borosilicates of the series CPG-10, mesh size 200-400, manufactured by Electro-Nucleonics Inc., New Jersey. The 500 nm glass was a silica-based Fractosil of mesh size 120-230 and manufactured by E. Merck, Darmstadt, F.R.G. All glasses were supplied by BDH Limited. Column plate counts, given in Table 7, were typical of these types of packing material.

TABLE 7

Plate Counts for Chromatography Columns

	Column Packing	Plates per metre
1)	CPG-10, 50 nm porosity, 200-400 mesh size	1250
2)	CPG-10, 300 nm porosity, 200-400 mesh size	2100
3)	Fractosil, 500 nm porosity, 120-230 mesh size.	460

The detector was a Beckman model 160 UV absorption detector. UV detectors are considerably more sensitive than differential refractometers which are frequently used in conventional SEC. This sensitivity permits the injection of small, relatively dilute latex samples, thereby reducing problems due to clogging of columns and filters. The recorder was a Spectra Physics model SP4200 computing integrator, which continuously recorded the chromatograms, as would a conventional strip-chart recorder, and stored the peak heights in 15-second intervals. Samples were filtered through a Millipore Millex PF cellulose acetate filter of 0.8 µm pore size prior to injection into the sample loop. The eluant flow rate was 2.0 cm^3 per minute and was checked periodically for constancy. The total column volume, V_t, was determined as 120.0 cm^3 from the peak retention volume, V_{pk}, of a dilute acetone solution. Numerous eluants were examined in this study, all based on deionised water with added anionic surfactant (Ultrawet-K, sodium dodecylbenzene sulphonate from Koch-Light; sodium dodecylsulphate, SDS from BDH), and various concentrations of added electrolyte, $NaNO_3$ from BDH. Latex samples of approx. 0.5% solids content were made up in the desired eluant for injection into the instrument. All runs were made at ambient temperature, 23-26°C.

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Several series of chromatographic experiments were made in order to examine systematically the effect of a single experimental variable. To avoid confusion it is convenient to examine each set of runs in turn. Unless otherwise stated the undialysed latices were exclusively used.

a) SDS Surfactant at 0.5 g dm^{-3}; Varying Ionic Strength

Eluants at four ionic strengths between 4.44 and 27.8 mmol dm^{-3} (added $NaNO_3$) were examined using SDS as the adsorption-preventing surfactant. It was intended to go much higher in ionic strength, but at 27.8 mmol dm^{-3} the SDS was observed to "salt out", i.e. was not completely dissolved when added to the 27.8 mmol salt solution. By contrast, complete dissolution was observed at the three lower ionic strengths. It is noteworthy that unlike Nagy et al. (23,24), we chose not to include the contribution of the ionic surfactant itself to the total ionic strength of the eluant. They decided to use Stigter and Mysel's (46) value of the charge, Q, on an SDS micelle, 23, and calculate therefrom a contribution to I. However, the variation of Q with the ionic strength of the medium was not accounted for (Stigter and Mysels reported a variation in Q from 23 to 47 as the concentration of NaCl was increased from zero to 0.1 mol dm^{-3}). Besides, anionic micelles in general display behaviour which is far different from that of ideal electrolytes (46). Their relatively large size (approx. 24Å for an SDS micelle in 0.1 molar NaCl (47)) means that they cannot be considered as point charges in the way that simple electrolytes are assumed to be when ionic-strength calculations are made. Further, anionic micelles are not the only large charged species migrating down the SEC column during the experiment. The latex particles themselves, as we have discussed in the introduction, carry many surface charges. Since they are an order of magnitude larger than micelles, their contribution to I would be difficult to quantify, even if we had a good estimate of Q. A further problem with the latices is that at the start of the SEC process the latex solution has a relatively high concentration when it is first injected, becoming progressively diluted as it migrates down the column. Ionic strength contributions from the latex therefore decrease in some fashion throughout the course of an experiment. Until a satisfactory theory is developed for the ionic strength of large charged particles in solution we find it convenient to calculate I as being the sum of contributions from simple electrolyte(s) added to the solution

$$I = 1/2 \sum_{i} c_i Q_i^2 \tag{11}$$

where c_i is the total bulk concentration of ionic species and Q_i its corresponding charge, the summation being made over all ionic species present.

Typical latex chromatograms are shown in Figure 5, a) for latex L1 and b) for latex M2 in 10.0 mmolar eluant. The results of the four sets of runs at varying ionic strength, I, are given in Table 8, expressed in terms of latex peak retention volumes.

The PMMA-coated latices were not chromatographed at the highest ionic strength since it was anticipated that problems within the columns, e.g. plugging due to salting out of surfactant, might occur. It is clear from Table 8 that a systematic increase in V_{pk} with ionic strength occurs for both latex types, which is in accordance with previous findings as pointed out in the introductory remarks. We now turn our attention to the log $\overline{D}_0$ versus V_{pk} calibration curves shown in Figure 6. These are constructed from the particle diameters calculated from the TEM results discussed earlier, using the values obtained for the shadowed PMMA-coated latices, together with the values of V_{pk} given in Table 8. It is clear that within the bounds of experimental error (error bars; ±5% in $\overline{D}_0$ by TEM and ±0.2 cm^3 in V_{pk} determined from reproducibilities, discussed later) both L- and M-series latices fall on a common straight line at each ionic strength. This indicates the validity of universal particle-size calibration, at least for this particular set of experimental conditions.

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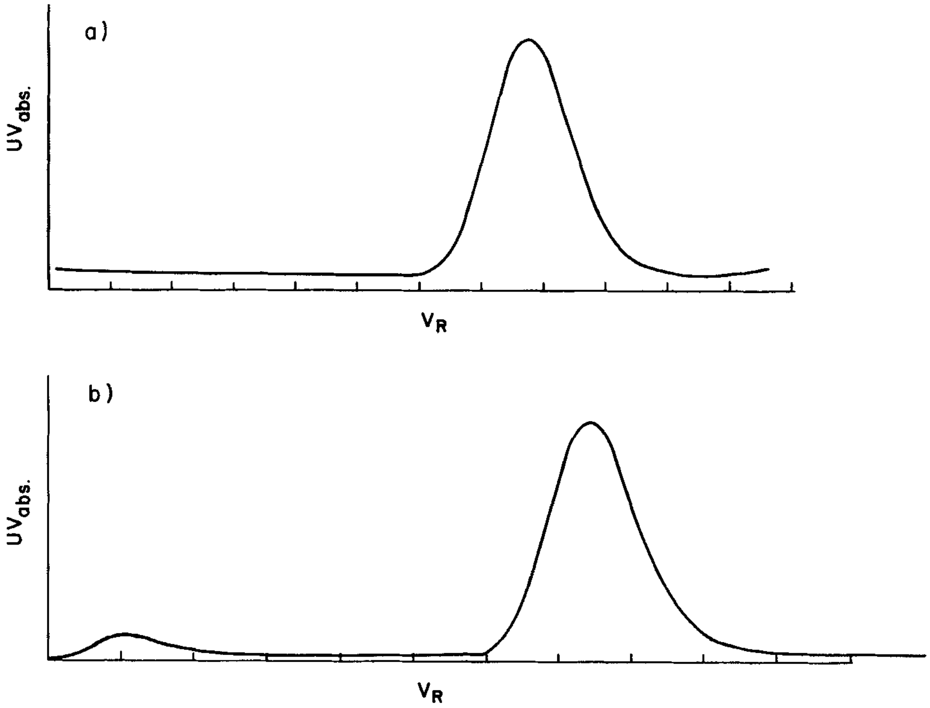

Figure 5. Chromatograms Obtained in 10 mmolar Eluant with SDS Surfactant. a) Latex LI b) Latex M2.

TABLE 8

Results of Chromatographic Runs using SDS as Surfactant at Varying Ionic Strengths

Latex	V_{pk}/cm^3			
	I = 4.44 mmol dm^{-3}	I = 10.0 mmol dm^{-3}	I = 15.60 mmol dm^{-3}	I = 27.80 mmol dm^{-3}
L1	76.4	78.2	78.8	80.8
L2	74.8	76.5	77.4	79.4
L3	72.4	73.6	74.8	77.2
L4	70.5	72.0	72.6	75.0
L5	68.5	69.6	70.5	72.4
L6	66.5	67.6	68.0	70.0
M1	75.5	–	77.2	–
M2	73.5	74.4	75.2	–
M3	71.0	71.6	72.6	–
M4	67.5	68.0	68.8	–
M5	–	66.0	66.8	–

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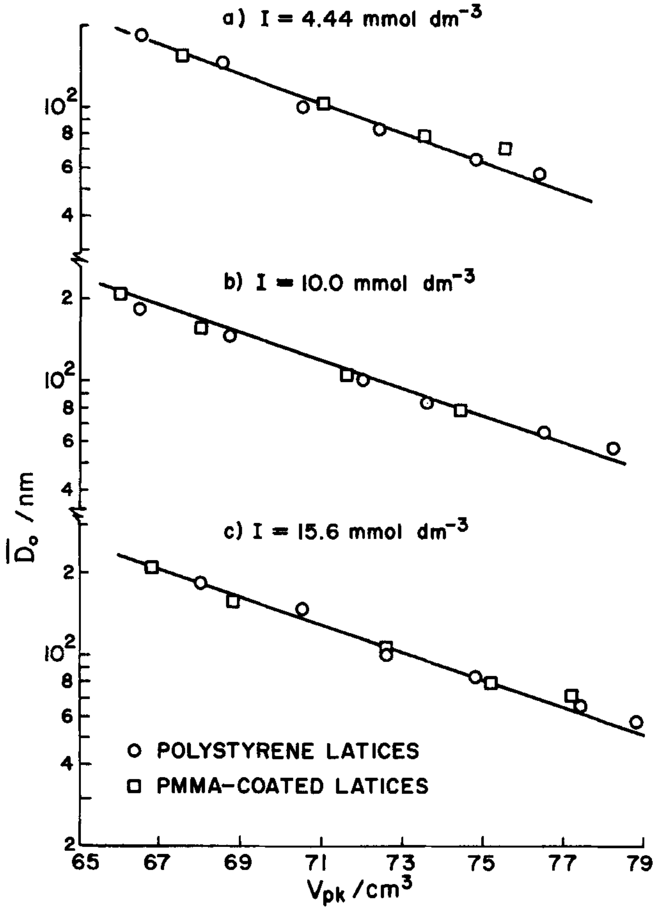

Figure 6. Calibrations Established in Eluants of Three Different Ionic Strengths Using SDS Surfactant.

Figure 7 shows the log $\overline{D}_0$ vs V_{pk} plot obtained at $I = 15.6$ mmol dm^{-3} using the values of $\overline{D}_0$ for the PMMA-coated latices obtained from TEM on the unshadowed samples (Table 5, Column B). Good agreement between the polystyrenes and the PMMA-coated latices is observed at the smaller particle diameters ($\overline{D}_0 \leq 100$ nm). Considerable deviation from the polystyrene curve is observed for the two larger samples M4 and M5. Two straight lines of best fit are drawn separately through both data sets to emphasise this point. This serves to illustrate the importance of obtaining

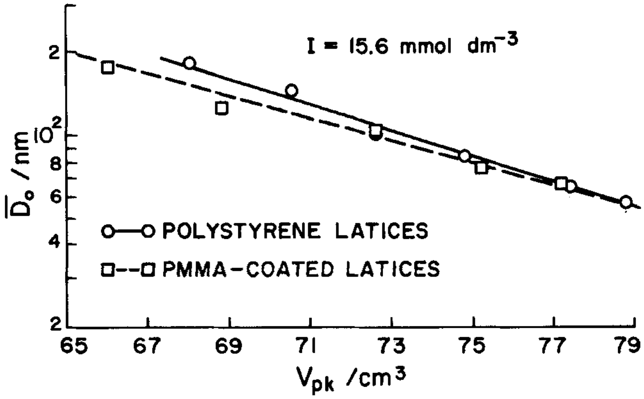

Figure 7. Calibration Established Using Electron Microscopy Data for Uncoated PMMA Latices.

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truly reliable characterisation data for the polymer standards if one is to properly pursue an investigation of this nature. This apparent deviation of M4 and M5 from "universal" behaviour may be attributed to electron-beam damage sustained by these samples in the TEM instrument, causing their observed diameters to be somewhat smaller than is actually the case.

b. The Effect of Changing Surfactant at Constant I

The observation of salting out of SDS at I = 27.8 mmol dm^{-3} made this a convenient point to change surfactant to Ultrawet-K (at a concentration of 0.4 g dm^{-3}), which has superior electrolyte tolerance (8). Table 9 shows the two sets of L-series latex elution volumes at I = 27.8 mmol dm^{-3}, one determined using SDS surfactant, the other using Ultrawet-K. We see that changing surfactant has no significant effect.

All subsequent data were obtained using an eluant containing Ultrawet-K at 0.4 g dm^{-3}.

c. Reproducibility of Results

Repeat runs of two latices, L3 and M3, were made to examine the reproducibility of elution volumes. The value of I chosen was 62.5 mmol dm^{-3}. For L3 successive values of V_{pk} were 78.1, 78.2 and 78.3 cm^3. For M3 the values were 75.2 and 75.6 cm^3. This indicates an experimental error in measurement of V_{pk} of ± 0.2 cm^3.

TABLE 9

The Effect of Varying Surfactant Type on Polystyrene Latex Elution Volumes at $I = 27.8$ mmol dm^{-3}

Latex	V_{pk}/cm^3 Using SDS Surfactant	Using Ultrawet-K Surfactant
L1	80.8	81.2
L2	79.4	79.6
L3	77.2	77.2
L4	75.0	75.5
L5	72.4	72.4
L6	70.0	69.6

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d. Ultrawet-K at 0.4 g dm^{-3} Varying Ionic Strength

These experiments were carried out in the same manner as those described in section a. Table 10 shows the actual values of I examined and the V_{pk} values obtained.

Once again an increase in V_{pk} with I is observed, except in the case of the M series where increasing I from 27.8 to 40.0 mmol dm^{-3} yields little discernible effect. Although we do not plot the data here, the interested reader can easily verify that once again the data for both L- and M-series latices give common plots of log D_0 vs. V_{pk} at each value of I, showing that universal particle-diameter calibration is experimentally valid at these higher ionic strengths up to 62.5 mmol dm^{-3}.

It is interesting that the four smallest polystyrene latices, L1 to L4, did not elute at the highest value of I examined here, presumably due to adsorption as has been previously reported for high-ionic-strength eluants (2,8). That this observation was not an artefact was verified by a repeat run. The two larger polystyrene latices and all the PMMA-coated samples eluted, as expected, slightly later than at the next-lowest ionic strength.

It was hypothesised from this observation that the adsorption of polystyrene latex onto the glass packing, all other things being equal, might be a function of particle size, as well as ionic strength. In the next set of experiments, I was lowered to some level intermediate between 62.5 mmol dm^{-3} (where all the latices had previously eluted) and 111 mmol dm^{-3} and then raised in small increments towards 111 mmol dm^{-3}. The results for $I = 75$ and 85 mmol dm^{-3} are given in Table 11.

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TABLE 10

Results of Chromatographic Runs using Ultrawet-K as Surfactant at Varying Ionic Strengths

Latex	V_{pk}/cm^3			
	$I = 27.8$ mmol dm^{-3}	$I = 40.0$ mmol dm^{-3}	$I = 62.5$ mmol dm^{-3}	$I = 111$ mmol dm^{-3}
L1	81.2	81.5	81.7	-
L2	79.6	79.7	80.5	-
L3	77.2	77.4	78.2	-
L4	75.5	75.5	76.0	-
L5	72.4	73.0	74.0	74.3
L6	69.6	70.4	70.9	71.6
M1	79.6	79.6	80.8	81.5
M2	77.6	77.6	78.8	79.7
M3	74.5	75.0	75.8	76.5
M4	70.5	70.6	71.6	72.2
M5	67.6	67.5	68.4	69.4

TABLE 11

Chromatographic Runs using Ultrawet-K Surfactant at $I = 75$ and 85 mmol dm^{-3}; Polystyrene Latices Only

Latex	V_{pk}/cm^3	
	$I = 75.0$ mmol dm^{-3}	$I = 85.0$ mmol dm^{-3}
L1	82.2	82.4
L2	81.0	81.0
L3	78.4	78.4
L4	75.8	76.3
L5	73.7	-
L6	70.9	-

The SEC system was found to run normally through the first set of runs, with a measured back pressure of approx. 500 psi (pressure-gauge reading on Waters M-6000 pump). However, part way through the second set (I = 85 mmol dm^{-3}) during the elution of latex L5, a sudden large increase in back pressure to 2000 psi was observed, whereupon the pump fail-safe mechanism came into operation and caused it to cut out. With the fail-safe device inoperative, a back pressure of 4000 psi was registered and several leaks appeared in the SEC-system plumbing. The cause was traced to both the inlet and outlet frits on the column packed with 50 nm CPG-10 porous borosilicate glass, on which had deposited a solid white layer which looked like polymer, but did not dissolve in tetrahydrofuran (THF). The frits were duly replaced but approx. 1500 psi back pressure was still registered. On close examination the packing bed at the two ends of the 50 nm column appeared somewhat discoloured. The texture of the first 5 cm of the packing removed from each end of this column was hard and blocky instead of the friable small granules which one normally observes. The 5 cm gaps at each end of the column were replaced by fresh CPG-10 of the same specification as the original. Owing to the leaks which had previously developed at high pressure, some new interconnecting tubing for the apparatus was necessary, although care was taken to ensure that the tubing lengths matched as closely as possible to the original. However, some changes in the column performance were expected and indeed observed. Table 12 shows the latex retention volumes obtained on the "new" column set at I = 27.8 mmol dm^{-3} compared with the data previously obtained for identical chromatographic conditions on the "old" column set. A systematic increase in retention volumes, on average 1.43 cm^{3}, was observed on the "new" column set.

Having repacked the 50 nm-porosity columns and having obtained normal chromatographic peaks at I = 27.8 mmol dm^{-3}, it was decided to continue the investigation into the behaviour of the polystyrenes at high I which had been interrupted at I = 85 mmol dm^{-3} by equipment failure. The results are given in Table 13.

The most remarkable feature was the lack of adsorption which had been observed to occur in the case of latices L1 to L4 in replicate runs on the "old" column set at I = 111.0 mmol dm^{-3}. Even when I was raised to 150.0 mmol dm^{-3}, all the latices eluted. This behaviour was rather peculiar, since the only difference between the old and the new column set was some new plumbing and renewal of approx. 10% of the 50 nm-porosity column packing bed. Perhaps there had been some interaction

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TABLE 12

Comparison of Elution Volumes of Latices on "Old" and "New" Column Sets. $I = 27.8$ mmol dm^{-3}

Latex	V_{pk}/cm^3 "Old"	"New"	Difference/cm^3
L1	81.2	82.1	+0.9
L2	79.6	80.8	+0.8
L3	77.2	79.1	+1.8
L4	75.5	76.8	+1.3
L5	72.4	74.4	+2.0
L6	69.6	71.6	+2.0
M1	79.6	79.8	+0.2
M2	77.6	79.1	+1.5
M3	74.5	76.3	+1.8
M4	70.5	71.5	+1.0
M5	67.6	70.0	+2.4
			+1.43 Average

TABLE 13

Chromatography of Polystyrene Latices at High Ionic Strengths

			V_{pk}/cm^3		
Latex	$I = 95.0$ mmol dm^{-3}	$I = 102.5$ mmol dm^{-3}	$I = 107.0$ mmol dm^{-3}	$I = 111.0$ mmol dm^{-3}	$I = 150.0$ mmol dm^{-3}
L1	84.5	85.0	85.0	84.8	85.0
L2	83.1	83.0	83.0	83.0	83.6
L3	80.7	81.0	81.0	81.0	82.0
L4	78.8	79.0	78.8	79.0	80.2
L5	76.5	76.5	76.8	76.8	78.6
L6	73.2	73.8	74.2	74.2	76.4

between the four smaller polystyrenes and the deteriorating packing material at the 50 nm-porosity column ends.

e. A Comparison of the Elution of Dialysed and Undialysed Latices

(New column set)

The dialysed and undialysed latices were chromatographed together at three ionic strengths and the results are shown in Table 14.

Without exception, the retention volumes of the polystyrenes are identical within experimental error, whether dialysed or not. Some differences occur between the dialysed and undialysed PMMA-coated samples at low I (27.8 mmol dm^{-3}), particularly for the larger latices M4 and M5 where the difference in retention volumes is 1.0 cm^3, larger for dialysed M4, but smaller for dialysed M5. At intermediate I, no significant differences in V_{pk} were observed. At high I, considerable differences were observed for the three smaller latices, particularly for M1 where the undialysed sample elutes 3.2 cm^3 ahead of the dialysed one. However, when performing chromatography on the M-series latices at this high ionic strength, sample concentrations had to be drastically increased (by a factor of approximately 3) in order to obtain discernible peaks and even then those peaks were much diminished in area compared with those from equivalent latices at lower I. This is clearly shown

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TABLE 14

Comparison of the Elution of Dialysed and Undialysed Latices

Latex	V_{pk}/cm^3 I = 27.8 mmol dm^{-3} Dialysed	 Undialysed	 I = 40.0 mmol dm^{-3} Dialysed	 Undialysed	 I = 150.0 mmol dm^{-3} Dialysed	 Undialysed
L1	82.2	82.1	83.6	83.6	85.0	85.0
L2	80.8	80.8	82.4	82.4	82.5	83.6
L3	79.0	79.1	80.4	80.4	82.0	82.0
L4	76.8	76.8	78.2	78.2	80.0	80.2
L5	74.5	74.4	76.0	76.0	78.8	78.6
L6	71.7	71.6	73.6	73.4	76.5	76.4
M1	81.1	80.5	81.6	81.6	78.8	83.0
M2	79.0	79.1	80.6	80.2	80.8	82.0
M3	76.1	76.3	77.4	77.8	79.6	78.8
M4	72.5	71.5	74.0	73.5	76.0	75.8
M5	69.0	70.0	72.0	71.6	73.6	73.2

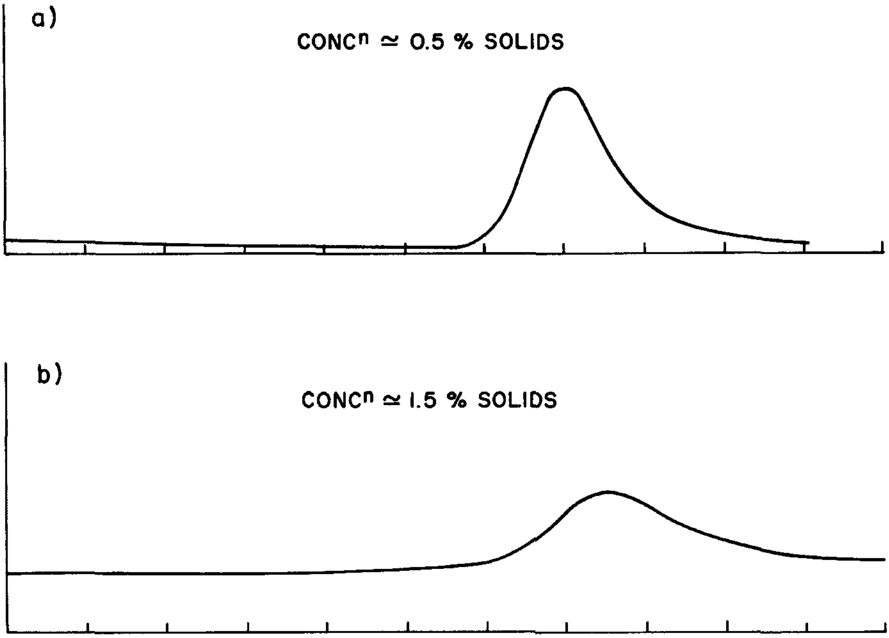

Figure 8. Comparison of Elution of Latex M4 at
a) I = 27.8 mmol dm^{-3} and
b) I = 150 mmol dm^{-3} .
using Ultrawet K Surfactant.

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in Figure 8. This is evidence of adsorption of the PMMA-coated latices at this high ionic strength. No great confidence should therefore be placed on the values of V_{pk} obtained for these latices under such conditions. It suffices to say that reliable chromatographic data may be obtained at lower ionic strength in such instances.

The polystyrene latices, by contrast, eluted as normal (i.e. with undiminished peak areas) at I = 150 mmol dm^{-3}.

The overall conclusions from this section of the work are that dialysis caused no effect on polystyrene latex retention volumes over a wide range of I. The behaviour of the PMMA-coated latices was less certain, but in general at low I the same conclusion can be made. At I = 150 mmol dm^{-3}, however, clear evidence of adsorption was obtained. The differences in retention volumes between dialysed and undialysed samples were likely much more affected by this than by any differences arising from the dialysis process.

SUMMARY

We have carried out a study concerning the validity of universal particle-size calibration in the aqueous SEC of latices. The study was stimulated by the findings of earlier workers in this field who had shown that the ionic strength of the eluant plays a significant role in latex retention volumes in both SEC and HDC. This is through its influence on the interactions between packings and latex particles arising from variations in the thicknesses of the repulsive electrical double layers known to exist in the systems. It was hypothesised that factors independent of particle size influencing these double-layer interactions might thereby have some effect on the retention volumes of latices in SEC. Notwithstanding these considerations, some previous results obtained from HDC systems were argued to show that universal calibration was valid at very low ionic strengths. We felt a need to extend this type of study to SEC, which is known to have inherently superior peak separation to HDC and thereby may show better any subtle difference in retention volumes arising from the effects described above. Several variables have been examined in eluants covering a wide range of ionic strengths. Two series of narrow-particle-size-distribution latices were prepared by seeded emulsion polymerisation techniques, one being pure polystyrene and the second was polystyrene coated with varying thicknesses of PMMA. This was to examine the effect of latex chemical type on elution in SEC. The latices were characterised by TEM. The procedure was straightforward for the polystyrenes, but the PMMA-coated latices, particularly the larger ones, underwent electron-beam damage in their untreated state. Vapour deposition of a known amount of Pt/C was used to circumvent this difficulty.

Other variables included, never heretofore systematically examined, were the type of surfactant in the eluant and the effect of dialysis, i.e., the effect of small amounts of surfactant residual from the polymerisation process involved in preparing the latices (Aerosol MA-80). Within experimental error, at ionic strengths at and below 62.5 mmol dm^{-3}, universal particle-size calibration was experimentally valid in all cases. However, some interesting anomalous behaviour was observed at high ionic strengths ($\geq$111.0 mmol dm^{-3}). Using the original column set, the four smaller polystyrene latices were observed to adsorb totally on the column packings at $I = 111.0$ mmol dm^{-3}, yet the two larger ones and all the PMMA-coated samples eluted as normal. Then, using a slightly modified column set, all of the polystyrene latices were observed to elute normally at up to and including $I = 150$ mmol dm^{-3}.

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At this high ionic strength, however, evidence of adsorption of the PMMA-coated latices was observed. Adsorption is generally believed to occur when the balance of colloidal forces between the double-layer repulsions and the Van der Waals and other attractions between packings and particles begin to tip in favour of the latter. The critical ionic strength, analogous to the critical value for colloidal agglomeration in DLVO theory, is known to depend on the specific nature of the latex, as seems to be borne out by our findings.

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