responsible for the EM process have been analyzed. The analysis of the obtained results shows that the exchange mechanism is responsible for the EM process in PS.

The difficulties in interpretation of the mechanisms leading to excimer formation, mentioned in the paper, may be in part omitted by investigating rigid diluted solutions, macromolecules of large molecular weights, or block copolymers of the PS–B type, where B is a luminescently inactive polymer of large molecular weight.

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Registry No. PS, 9003-53-6.

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Diffusion of Polystyrene Latex Spheres in Polymer Solutions Studied by Dynamic Light Scattering

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ABSTRACT: The diffusional behavior of latex spheres (radius 720 Å) in both dilute and semidilute solutions of the following linear polymers is reported: (hydroxyethyl)cellulose (HEC), (hydroxypropyl)cellulose (HPC), (carboxymethyl)cellulose (CMC) (pH 4 and 9) at different ionic strengths, and nonionized poly(acrylic acid) (PAA) (pH 3.5). In these systems the scattering is dominated almost entirely by the latex component. In very dilute solutions ($<10^{-3}\%$) of HEC and HPC, the average diffusion coefficient of latex decreases strongly with increasing polymer concentration, and the relative variance shows a concomitant increase. Multiexponential analysis of the time correlation function gave a bimodal fit as the simplest model: (a) fast mode, a polymer concentration-independent D value equal to that of the latex monomer at infinite dilution; (b) slow mode, diffusion coefficient corresponding to aggregate species with apparent radii 2–3 times that of the latex monomer. The aggregation behavior is consistent with a bridging mechanism. In semidilute solutions of nonionized CMC at pH 4 in the salt-free system, latex diffusion follows the theoretically predicted $C^{1/2}$ dependence: $D/D_0 = \exp(-AC^{1/2})$. With HEC and HPC, the adsorptive interactions lead to characteristic deviations from this dependence. Qualitatively similar behavior is observed with CMC in the fully neutralized form (salt free) at pH 9, where electrostatic repulsive forces are operative. In the presence of a low molar mass electrolyte (at pH 9), CMC adsorbs to the individual latex particles and there is a strong positive deviation from the $C^{1/2}$ dependence. The scaling index in $D/D_0 = \exp(-AC^{\delta})$ provides a sensitive index to the interactions in the system.

Introduction

The diffusion of latex spheres in polymer solutions has been the subject of numerous investigations in both the dilute and semidilute regions of polymer concentration. Some recent examples are the studies in ref 1–8, 14, and 30–34. At the dilute end of the scale, dynamic light

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scattering measurements have been used to estimate the apparent hydrodynamic thickness of an adsorbed layer of polymer at the latex surface.[6-8] The thickness is then the difference between the Stokes radius of the bare sphere in the solvent alone and the value for the particle in the polymer solution. It is thus assumed that all effects other than an increased spherical radius are absent. It is implicit that obstruction effects are negligible in the concentration range of polymer used and that the solvent viscosity is the correct term in eq 3 below. Some recent results of Phillies and co-workers,[3-5] however, call into question these assumptions.

In more highly concentrated polymer solutions (semidilute), measurements of the diffusion of latex particles by dynamic light scattering have been used to estimate the validity of various expressions modeling the transport properties of large spheres in the solvent-swollen polymer matrix. There is a very extensive literature dealing with transport phenomena in ternary systems, and no endeavor is made to summarize them here. One may cite as examples the theories of Ogston et al.,[10] Cukier,[11] and, more recently, Altenberger and co-workers[37,38] (see below). The experimental situation, however, is much complicated by effects that are peculiar to the system studied and lead to confusion in interpretation: for example, adsorptive interactions, which may or may not lead to an increased radius or possibly aggregation (flocculation), depending on parameters such as the molar mass of the polymer and its concentration. Electrostatic interactions may also be involved. The character of the polymer is also central (chain length and flexibility) since, for example, Ogston et al.[10] and Altenberger and Tirrell[37] assume fixed rodlike obstacles. Somewhat remarkably, most experimental studies (e.g., ref 1–5) have employed solutions of flexible polymers. The complex interweaving of the various effects makes the interpretation of sphere diffusion in polymer solutions unclear and has stimulated the present investigation. We have taken a broad approach to attempt to elucidate the main features. The present paper describes latex sphere diffusion in (a) dilute polymer solutions ($C \leq 5 \times 10^{-3}\%$ (w/w)) and (b) semidilute polymer solutions ($C > C^*$). The polymers include some inflexible-chain cellulose derivatives: (hydroxyethyl)cellulose (HEC), (hydroxypropyl)cellulose (HPC), and (carboxymethyl)cellulose (CMC). With the latter, the measurements encompass both pH 4, at which both CMC and the latex particles are essentially nonionized, and pH 9, where both are maximally charged. Measurements were also made on the highly flexible polymer poly(acrylic acid) (PAA) at pH 3.5 (nonionized). The latex used is a methacrylic acid modified material with a hydrodynamic radius of 720 Å and high charge ($-40\ \mu C/cm^2$). The measurements are facilitated by the noninterference of the polymer with the scattering behavior since in each case it contributes less than 0.5% to the total scattering over the concentration ranges used.

Materials

Latex was material synthesized by Raisio-National Oy, Raisio, Finland, from butyl acrylate/styrene in the ratio 65:35 with 1% methacrylic acid based on the butyl acrylate/styrene quantity. The charge density was determined as $-40\ \mu C/cm^2$ on the fully neutralized material. The specific charge on the latex spheres was determined conductometrically with a Philips PW 9505 conductivity meter. The solutions were back-titrated with acid following addition of excess NaOH. A similar procedure was used for determining the carboxyl content of the CMC samples. The latex radius was given as 750 Å by the synthesizer and was determined as 720 Å by photon correlation spectroscopy (PCS) measurements. A stock solution of latex was purified by dialysis by using a hollow-fiber dialyzer to remove low molecular contaminants and subsequently titrated to the desired pH with a solution of LiOH.

Polymers. (Hydroxyethyl)cellulose (HEC): fraction C8 from ref 15, $\bar{M}_w = 515\,000$, $[\eta]_{25} = 8.95$ dL g^{-1}, $(S^2)_z^{1/2} = 715$ Å.

(Hydroxypropyl)cellulose (HPC): Klucell, from Hercules Powder Inc., Wilmington, DE. Fraction A: $\bar{M}_w = 8 \times 10^5$, $[\eta]_{25} = 8.8$ dL g^{-1}. Fraction B: $\bar{M}_w = 7.3 \times 10^4$, $[\eta]_{25} = 0.93$ dL g^{-1}.

(Carboxymethyl)cellulose (CMC): from Hercules Powder Inc. Fraction a: CMC 12M8, $\bar{M}_w = 2 \times 10^5$, DS = 1.2. Fraction b: CMC 7HF, $\bar{M}_w = 7 \times 10^5$, DS = 0.7. Fraction c: CMC 7LF, $\bar{M}_w = 9 \times 10^4$, DS = 0.7. Viscosity data on CMC 12M8: pH 9.0, $[\eta]_{25} = 4.38$ (0.05 LiCl); pH 9.0, $[\eta]_{25} = 7.5$ (0.01 LiCl).

Poly(acrylic acid): from BDH Chemicals, Poole, England, $\bar{M}_w = 2.3 \times 10^5$, $[\eta]_{25} = 0.88$ dL g^{-1} (H_2O) at pH 3.5 (acid form). Polymer solutions were made by weight and allowed to reach equilibrium prior to addition of latex suspension. Where Triton-X100 was included, this was added to the latex stock solution (Triton-X100 was obtained from Merck, Darmstadt, FRG). All polymers were initially purified by exhaustive dialysis against distilled water with an approximately 1% solution contained in cellophane tubing bags (Visking, Union Carbide Corp.) and finally recovered by freeze-drying. Where appropriate, the pH of the individual polymer and latex stock solutions was adjusted separately prior to mixing, and the pH of the final solution was then recorded. After standing to attain homogeneity, the solutions were filtered through 0.8-μm Millipore filters into 10-mm precision-bore NMR tubes (Wilmad Glass Co., NJ).

Data Collection and Analysis

All PCS data were obtained in the homodyne mode with full photon-counting detection and a 128-channel Langley–Ford autocorrelator. Incident radiation at 488 nm was from a Coherent Super Graphite 4-W Ar ion laser with a quartz etalon frequency stabilizer in the cavity to ensure single-mode operation and enhance the signal/noise ratio.

All measurements were made at an angle of 90° after it had been ascertained that a linear plot of the average relaxation rate ($\bar{\Gamma}$) vs. the square of the scattering vector (q) was obtained over the range 30–120°.

The quality of the data has been much improved by using an automatic collection procedure whereby approximately 100 runs of length 1 s are accumulated with minimization of the total intensity and added together for each set of measurement parameters. Thus a comparison of the total intensity per second of each run is made with the preceding run. If within ±4% (20), it is accepted; if higher, the run is rejected. If outside this range and lower, all earlier runs are rejected and a new set of runs is accumulated relative to the new intensity standard until at least 60 runs falling within ±4% have been collected.

The above procedure has substantially eliminated any extraneous contributions from dust/particles and yields data with a variance improved by at least an order of magnitude compared with manual operation of the correlator. The statistical base line (i.e., total pulses times the mean number per sampling time) was of the order 2×10^7. Initially, each sum of runs accumulated as described was analyzed with a three-term cumulants fit to assess quality. The correlation function was treated interactively on the same microcomputer used for data collection and reduction. Only runs in which the statistical base line agreed closely with the value from the delayed channels were retained and those with deviant intensity also rejected. The general level of the data precision corresponded to a variance of 2×10^{-7} (i.e., standard deviation of the error 4×10^{-4}).

Data Analysis. As a possible approach to elucidating possible sources of the nonexponentiality revealed by the second cumulant term, $\mu_2/\bar{\Gamma}^2$, the method of discrete multiexponentials has been used. This program is written in Forth for rapidity and compactness and the microcomputer fitted with a math coprocessor for increased speed and accuracy. The time correlation function was analyzed by using a routine based on an equally weighted nonlinear regression procedure with nonnegativity constraint according to the equation

$$g^2(\tau) - 1 = \beta[A_s \exp(-\Gamma_s\tau) + A_f \exp(-\Gamma_f\tau)]^2 \qquad (1)$$

A_s and A_f refer to the relative amplitudes, Γ_s and Γ_f are the corresponding relaxation rates, and β is an instrumental parameter, approximately = 0.65. Comparison of fits was made by using equations of the form of eq 1 with one, two, or three exponential terms, together with or without a base line term. In principle, the routine is capable of handling up to five exponentials.

The quality of the fit was estimated partly on the basis of the Q function:

$$Q = 1 - \frac{\sum_{i=1}^{n-1} \epsilon_i\epsilon_{i+1}/(n-1)}{\sum_{i=1}^{n} \epsilon_i\epsilon_i/n} \qquad (2)$$

If there is no grouping of residuals, ϵ, Q will approximate unity. The present data for latex/dilute polymer solutions ($C < 10^{-3}\%$) could be optimally fit with a two-exponential function without a base line term. Introduction of a third exponential led to a term with almost negligible intensity amplitude, which is a strong indication that the bimodal form correctly describes the distribution. Other possible approaches include the use of programs such as CONTIN[16,17] and the histogram[18-20] method. Although these have the advantage of only requiring the correlation function and the range of possible relaxation times, they are less well able to separate components approaching each other in relaxation rate.

With the present data the relaxation rates of the components differ by a factor of about 3, which provides a congenial condition for their separation (resolution requires that they differ in rate by at least 30%). The latter limit was established by an extensive series of simulated experiments[21] and also the analysis of mixtures of polymer fractions in various proportions. There will, of course, always exist some ambiguity in the interpretation of data derived in this way from the correlation function. An interpretation using two modes, however, yields an alternative viewpoint and allows a potential insight into the dynamics that is impossible by the cumulants approach. Were the relaxation rates more widely separated, it would be possible to separate the components experimentally by varying the sampling time or by using a multi-τ correlator.

Results and Discussion

Latex Diffusion in the Absence of Added Polymer. Diffusion measurements on latex spheres at very low concentrations in water or dilute salt solution provide an unequivocal value for the hydrodynamic radius, $\bar{R}_H$, by means of the Stokes–Einstein equation:

$$\bar{R}_H = k_BT/6\pi\eta_0\bar{D} \qquad (3)$$

Here η_0 is the solvent viscosity, k_B is Boltzmann's constant, T is the absolute temperature, and $\bar{D} = (\Gamma_1/q^2)_{q\rightarrow 0}$ where Γ_1 is the first cumulant of the autocorrelation function. The present measurements were made by PCS on PS latex suspensions in the concentration range close to C_{latex} = 0.001% (volume fraction $\phi = 1 \times 10^{-5}$), where there is no mutual interaction (i.e., zero concentration dependence) and the $\bar{D}$ value corresponds to that for the isolated sphere. For the present latex sample, $\bar{R}_H$ = 720 ± 5 Å, and this figure was determined to be essentially independent of pH over the range pH 4–9 (corresponding to zero and total dissociation of the substituent carboxyl groups, respectively). The normalized second cumulant was in all cases found to be very low (<0.03). $\bar{R}_H$ decreases with increasing concentration of low molar mass electrolyte to a plateau value above about 0.05 M salt as shown in Figure 1. An average value for the decrease in the apparent radius is about 80 Å. If this effect is a real one (and there appears to be uncertainty on this point),[46] a possible explanation could be a deswelling of the latex sphere when the charged sites are screened. It may also be related to the salt, here LiCl. The Li^+ ion in common with divalent ions such as Ca^{2+} and Mg^{2+} is highly solvated.

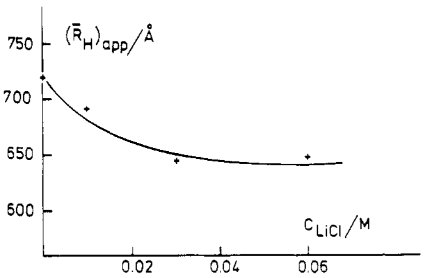

Figure 1. Apparent hydrodynamic radius of polystyrene latex particles at high dilution (C_{latex} = 0.001% (w/w)) as a function of salt concentration. The values of $\bar{R}_H$ have been estimated by eq 3 with the cumulants-evaluated average diffusion coefficient.

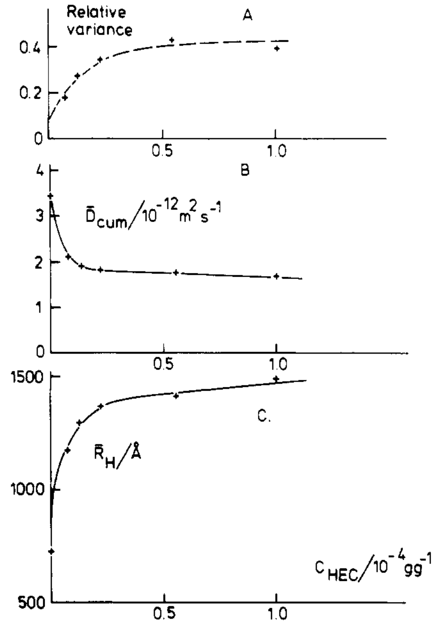

Figure 2. Cumulants-evaluated diffusion coefficient (B) and normalized second cumulant (A) for latex in dilute solutions of (hydroxyethyl)cellulose ($\bar{M}_w = 5.15 \times 10^5$). $\bar{R}_H$ obtained by eq 3. The scattered intensity from the HEC is <0.5% of the total intensity. Latex concentration = 0.001%. Measurements at 25 °C.

Diffusion in Dilute (Hydroxyethyl)cellulose Solutions. PCS measurements were made on dilute suspensions of polystyrene latex particles (0.001%) in dilute HEC ($\bar{M}_w = 5.15 \times 10^5$) solutions in the range up to $5 \times 10^{-3}\%$ HEC. There have been a number of studies of the interaction of latex particles with this polymer, and there is evidence for both adsorption[22] and flocculation.[23] A recent review covering the flocculation aspect of latex/water-soluble cellulose derivatives is given in ref 24. At the concentrations used here the scattering intensity of the HEC is negligible compared to that of the latex (<0.5%).

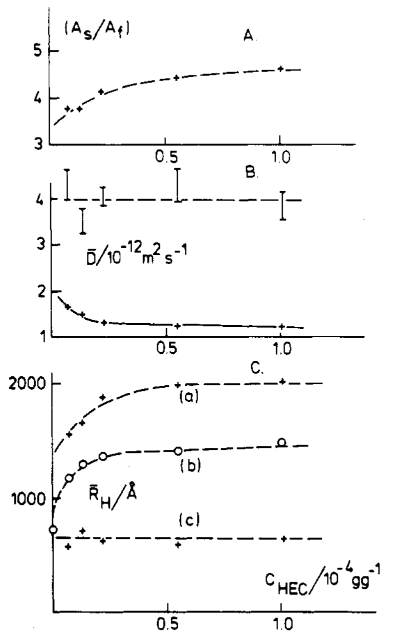

Figure 3. Bimodal fit to the correlation function using eq 1. The diffusion coefficients (B) and radii (C) in Figure 2 correspond to the weighted averages of the values given in the present figure. Panel A shows the ratio of the relative scattering intensities (slow to fast) as a function of HEC concentration.

Some results are shown in Figure 2. The average diffusion coefficient decreases (Figure 2B) sharply and is accompanied by a change in the relative variance (Figure 2A), indicating an increased polydispersity. The apparent hydrodynamic radius has been estimated by the Stokes–Einstein equation, and the values are shown in Figure 2C. The viscosity of water was used in eq 3 since the relative viscosity is close to unity at these concentrations.

The large increase in $\bar{R}_H$ and the variance suggest a bridging mechanism whereby polymer coils form the mediating link between latex spheres. This is supported by the increase in the variance and also the subsequent flocculation which occurs at much higher polymer concentrations. If the polymer were adsorbed as a surface layer on individual latex particles, the relative variance should not increase greatly with polymer concentration.

The cumulants method, however, allows no further progress in describing possible changes in the form of the distribution as suggested by the values of the second cumulant. A bridging mechanism leading in the first case to the formation of dimers, etc., would correspond to a small number of exponential terms in the autocorrelation function obtained in PCS. These are potentially separable by various techniques; see a recent view by Stock and Ray.[25] We use a discrete multiple-exponential nonlinear least-squares algorithm with a nonnegativity constraint to stabilize the solution. The simplest model consistent with the data (using the usual statistical parameters for estimating goodness of fit; see Data Analysis) was a bimodal model according to eq 1. The radius derived from $\bar{D}_{cum}$ will then correspond to the weighted average of the fast and slow components. No base-line term was found to be necessary. The two modes, in the form of the apparent radii from eq 3, are shown in Figure 3C. The fast component corresponds precisely to the value for the latex sphere obtained in the absence of polymer (denoted $R_H{}^m$), while the slow component has a value asymptotically approaching 2000 Å. This result is in line with the bridging model since the radius of a dimer would be about ($2R_H{}^m + R_G$), where R_G is the radius of gyration. There are a number of reports that the hydrodynamic thickness of an adsorbed polymer layer is approximately twice the radius of gyration of the free polymer coil in solution, implying that the polymer coils sit directly at the latex surface in a relaxed conformation. This is a possible deduction from the present cumulant values, $\bar{D}_{cum}$. The radius of gyration of the present HEC is 715 Å and, as shown in Figure 2C, the plateau value of $\bar{R}_H$ is about 1500 Å. We conclude, however, that the bridging model is the more probable since it also provides an explanation for the accompanying large polydispersity increase with concentration. The molecular nature of the binding link is presumably a coupling between the carboxyl groups of the latex and the oxygen in the side chains of the cellulose ethers (bridging is not found with the cellulose derivative (carboxymethyl)cellulose).

The bimodal fit used here is only one (albeit the most simple) of various alternatives having similar statistical significance when employing the usual criteria. However, the observation that one of the relaxations corresponds to the latex particle radius in the absence of polymer gives added weight to the choice. While the slower term may be a heterogeneous mode, use of a six-parameter fit (i.e., three exponentials) gave no significant improvement in the fit.

The present data interpretation may also provide an explanation for the discrepancy observed between small-angle neutron scattering (SANS) results and those from PCS in the latex/poly(ethylene oxide) system by Cosgrove et al.[6] The former technique gave much lower values for the increase in the apparent radius in the presence of PEO. However, SANS cannot give a precise measure of the small amount of polymer participating in the aggregation of latex spheres via bridging, whereas PCS measurements are highly sensitive to a change in the distribution of scattering particles in the size range considered.

The relative scattering intensities derived from eq 1 are shown in Figure 3A. It should be noted that although the scattering mainly reflects the aggregate species, the monomeric latex particles should predominate numerically. The usual interpretation placed on the apparent radius derived by using $\bar{D}_{cum}$ in eq 3 may be dubious if it is determined by the heavy weighting of only a small proportion of the scattering particles. This has serious implications if the PCS results are used to make deductions about the conformation of the polymer at the latex surface. Although the cumulants method is the preferred one for treating molecularly polydisperse systems, it is only readily interpretable if the distribution is unimodal and there is no scattering from dust. When the measurements were extended to higher concentrations (see Figure 4), D/D_0 showed a more gradual decrease, but the variance increased continuously. In none of the systems studied was a discontinuity observed at C^*.

The addition of a nonionic surfactant (Triton-X100) to the latex suspension apparently inhibits the adsorption of HEC to latex[22] as shown in Figure 5. However, the influence of HEC binding is still felt since the relative variance continues to increase with polymer concentration although the effect is less pronounced. The addition of Triton-X100 will be further considered below in connection with the more concentrated systems.

An alternative model used to describe the aggregation of particles in the presence of a polymeric component is that introduced by Asakura and Oosawa.[23,26,27] They considered a volume exclusion potential originating from the depletion of nonadsorbing polymer coils from a portion of the gap between two latex spheres. The low polymer content in this region corresponds to a lower osmotic

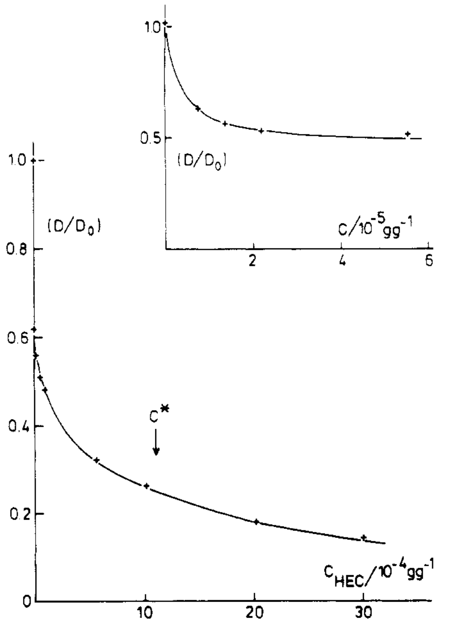

Figure 4. Latex diffusion coefficient in HEC solutions divided by the value in the absence of polymer as a function of HEC concentration over a more extended range of C than shown in Figures 2 and 3. All diffusion coefficients are at a latex concentration of 0.001% and 25 °C.

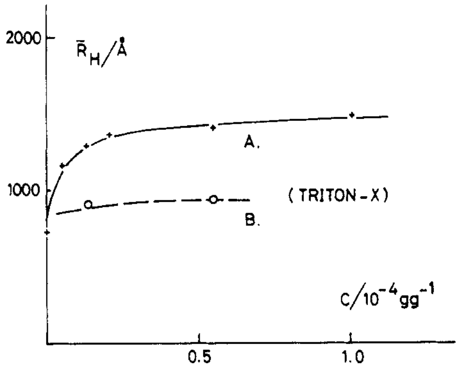

Figure 5. Comparison of latex diffusion coefficients measured in HEC solutions in the absence (A) and presence (B) of a low molecular weight, nonionic surfactant (Triton-X100) at a concentration of 0.15%. The surfactant was added to the latex suspension prior to addition of polymer solution.

pressure than that of the bulk solution and hence a net attractive energy. A recent review covering these aspects is given in the book by Napper.[9]

The possible effect of changing latex concentration in the presence of a constant polymer concentration was examined. Measurements were made in 0.01% HEC and the latex concentration was varied between 0.001 and 0.005%. The change in $\bar{D}_{latex}$ was insignificant.

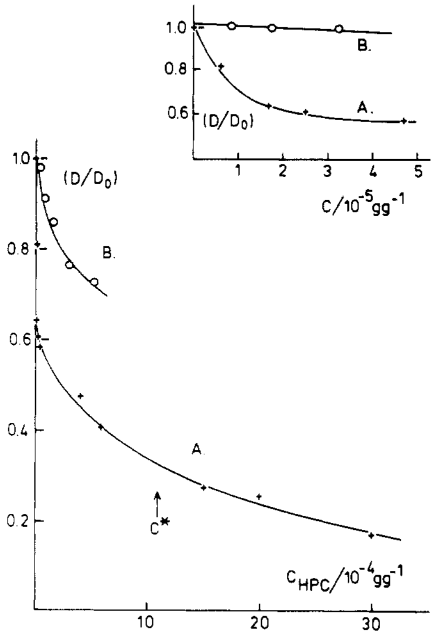

Figure 6. Data for the latex/(hydroxypropyl)cellulose system analogous to those in Figure 4 for HEC. Open circles are for $\bar{M}_w = 7 \times 10^4$ and crosses for $\bar{M}_w = 8 \times 10^5$.

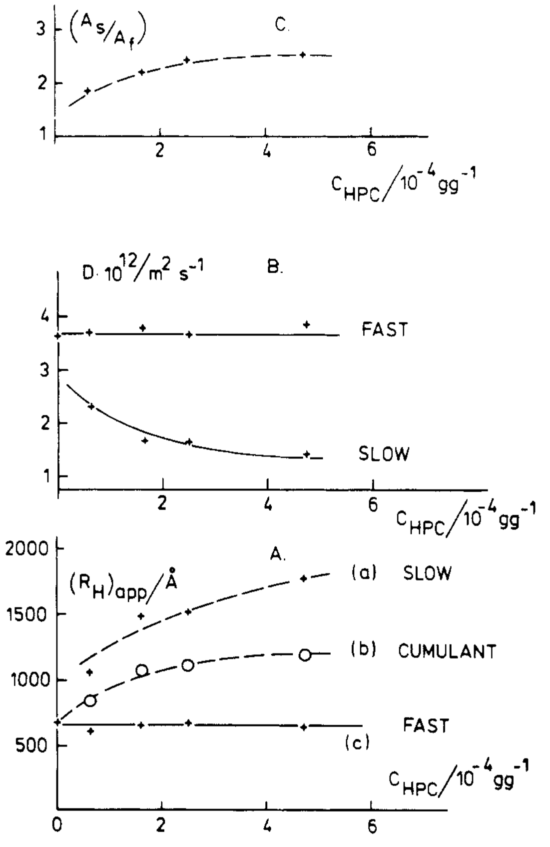

Figure 7. Bimodal fit using eq 1 for the latex/HPC system ($\bar{M}_w = 8 \times 10^5$) similar to the data displayed in Figure 3 for the latex/HEC system.

Diffusion in Dilute (Hydroxypropyl)cellulose Solutions. PCS measurements on latex diffusion in HPC ($\bar{M}_w = 8 \times 10^5$) showed behavior markedly similar to that of HEC in spite of the more hydrophobic character of the substituent. This is illustrated in Figures 6 and 7. The effect of adding a neutral salt is shown in Figure 8 to be negligible although this might have been anticipated owing to the decrease in latex swelling in the presence of salt and possible changes in the degree of solvation at the latex surface. With HPC there is a less pronounced weighting of the slow mode, which suggests that the aggregated latex particles are either smaller or less numerous than is the case in HEC solutions. This difference in behavior should in fact be more pronounced since the HEC sample has a lower molar mass ($\bar{M}_w = 5.15 \times 10^5$). A lower molar mass sample of (hydroxypropyl)cellulose ($\bar{M}_w = 7 \times 10^4$) gives only a very small change in the apparent radius of the latex particle (see Figure 8). Addition of Triton-X100 at a concentration of 0.15% to the latex suspension apparently completely inhibits the adsorption of HPC, the latex radius from eq 3 being some 40 Å larger than the value in the absence of Triton-X100. The latter compound ((*p*-(1,1,3,3-tetramethylbutyl)phenoxy)poly(oxyethylene gly-

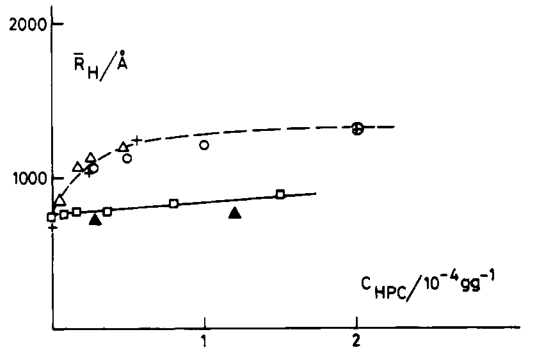

Figure 8. Data for the latex/HPC system ($\bar{M}_w = 8 \times 10^5$) (+) with 0.01 M LiCl, (○) with 0.1 M LiCl, and (△) in the salt-free system. (▲) Data with the addition of the surfactant Triton-X100 to the latex HPC solution (salt-free); (□) data for latex diffusion in HPC of low molar mass ($\bar{M}_w = 7 \times 10^4$) (salt-free). Latex concentration = 0.001%.

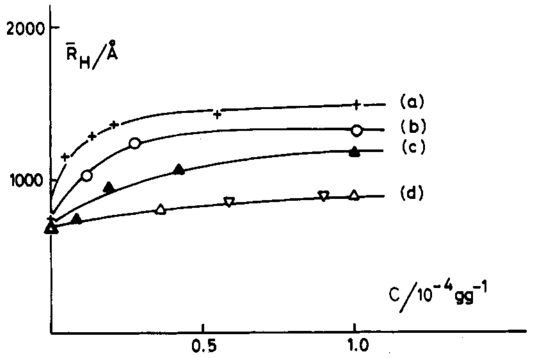

Figure 9. Cumulants-evaluated diffusion coefficient for latex (0.001%) in very dilute solutions of various polymers: (a) (hydroxyethyl)cellulose; (b) (hydroxypropyl)cellulose; (c) (carboxymethyl)cellulose ($\bar{M}_w = 7 \times 10^5$, pH 9); (d) (carboxymethyl)cellulose (salt-free) (▽) $\bar{M}_w = 2 \times 10^5$, pH 4; (△) $\bar{M}_w = 7 \times 10^5$, pH 4.

col)) has an oxyethylene chain length (when fully extended) of about 34 Å[28] and the octylphenyl group is about 10 Å long. This would suggest adsorption of Triton-X100 in an extended configuration.

Intensity light scattering measurements were made on latex suspensions (0.001%) in the presence of HPC as a function of concentration, and the effective molecular weight was determined. The average value was found to increase by about 20%, reaching a plateau value at about 0.05% HPC. A similar change was observed for the latex/HEC system. Since the polymer does not scatter significantly, these results support a bridging mechanism.

Diffusion in Dilute (Carboxymethyl)cellulose Solutions. A comparison of the apparent latex radii derived by eq 3 is shown for the various polymers used in Figure 9. In the nonionized system (pH 4) with CMC, a very small and molecular weight independent increase in $\bar{R}_H$ is found. It will be shown below that there is no evidence for a significant amount of polymer adsorption and that the results are consistent only with the incipient excluded volume effect. This agrees with independent observations[29] on the CMC/latex system. The larger increase in the apparent $\bar{R}_H$ for latex observed with CMC when at pH 9 (latex and CMC fully charged) is most likely an effect on the diffusion deriving from charge interactions. This conclusion is supported by the observation that the addition of Triton-X100 did not significantly change the latex D values determined at pH 9 in CMC. The influence of the ionic strength of the medium was examined. Measurements were made on a solution of CMC at pH 9 ($\bar{M}_w = 2 \times 10^5$) at a concentration of 1 g/L. D_{latex} increased weakly ($D \sim I^{0.13}$) from $D = 2 \times 10^{-12}$ m^2 s^{-1} at zero ionic strength to 2.6×10^{-12} at the plateau value reached at 0.02 M LiCl. Such an increase is anticipated owing in part to latex deswelling as the electrostatic shielding increases. On the other hand, ionic strength has an almost insignificant effect at pH 4, where both latex and CMC are essentially uncharged.

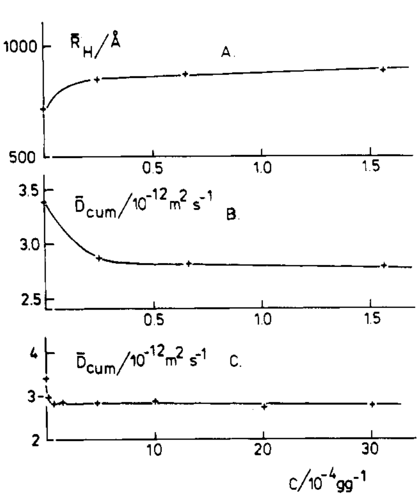

Figure 10. Data for latex diffusion in salt-free poly(acrylic acid) ($\bar{M} = 2.3 \times 10^5$) solutions. (B) Cumulants-evaluated diffusion coefficient at very low polymer concentrations and (C) at higher poly(acrylic acid) concentrations. Panel A shows the apparent radius in the dilute region.

Diffusion in Poly(acrylic acid) Solutions. Measurements of latex particle diffusion were made in solutions of poly(acrylic acid) at pH 3.5 (nonionized) in the low-concentration range. It was found that $\bar{D}$ decreased by a small amount (see Figure 10), indicating an extent of adsorption considerably smaller than with the nonionizable cellulosic polymers but apparently larger than that deduced in solutions of uncharged CMC. At higher concentrations (up to 0.3% PAA but still below the overlap concentration C^*) no further reduction in $\bar{D}$ was observed relative to the $\bar{D}$ value for latex in the absence of polymer.

Diffusion in Polymer Solutions at Concentrations Exceeding Overlap (Semidilute Solutions). In the absence of significant adsorption of a nonionized polymer to the latex particle, any observed decrease in the diffusion coefficient relative to the value in the absence of polymer should reflect the influence of the effective excluded volume on latex translation imposed by the polymer chains. Estimation of an apparent radius for the latex particle by eq 3 then loses its direct relevance. As demonstrated by the results of Phillies et al.,[1-5] the Stokes–Einstein equation must be regarded with circumspection when the "solvent" and solute molecules are of comparable size: neither the macroscopic solution viscosity nor the solvent viscosity is appropriate for describing the reduction in the diffusion coefficient but, instead, some intermediate quantity will be necessary to describe the effective viscous drag on the particle. Thus the Stokes–Einstein equation is not of use here. This conclusion is anticipated from consideration of the limits imposed by the structure of the transient gel. When the polymer solution is semidilute and characterized by a correlation length (ξ) describing the distance between entanglement points which is independent of M and decreases with concentration as $\xi \sim C^{-\nu}$,[36] then scaling in a characteristic manner is anticipated.[12-14] If $R_H \gg \xi$, i.e., the matrix constitutes a continuum relative to the sphere, Langevin and Rondelez[14] proposed that the decrease in D_{sphere} should be mirrored by the increase in the macroscopic viscosity of the solution. When this is so, the sphere radius may be determined from

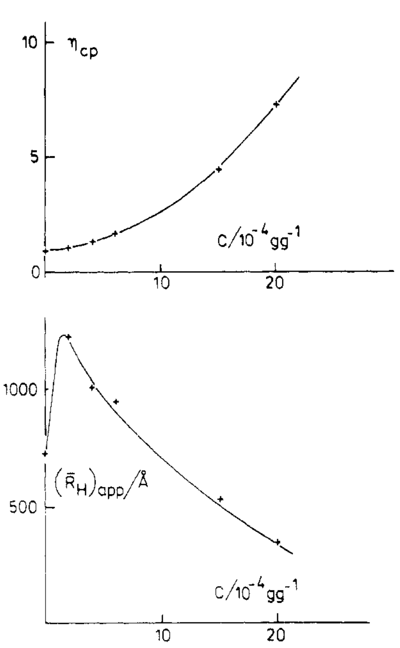

Figure 11. Lower part: Anomalous dependence of the apparent radius, $\bar{R}_H$, for the latex particle in HPC solutions when the bulk viscosity (upper curve) is used in eq 3 to evaluate the radius.

eq 3. If $R_H \ll \xi$, on the other hand, the viscosity of the solvent itself (η_0) should be the relevant variable. Figure 11 shows data for latex in HPC ($\bar{M}_w = 8 \times 10^5$). Apart from the initial increase in R_H due to adsorption of polymer as was shown above, the apparent radius decreases to substantially below the value for the monomeric latex sphere, which is a physically untenable result. Such an observation has been made previously by Phillies and co-workers.[4,5] This suggests that the limiting inequality ($R \gg \xi$)[14] is not realized here, although $R_H > \xi$ certainly applies over the present concentration range. For the HEC fraction used, ξ = 250 Å at C = 0.2% compared with R_H = 720 Å for the latex radius. There is thus an extensive region of relative length over which neither η_0 nor η is appropriate for use in the Stokes–Einstein equation, and this leads to the apparent inconsistencies documented by Phillies. Surprisingly, however, Phillies[4] finds that even when $R \gg \xi$, the bulk viscosity is still unsuitable for the latex/PEO system. These workers used an empirical coefficient (K = ratio between the apparent hydrodynamic radius and the known latex particle radius determined in the solvent alone) to express the mismatch between the viscosity term used in eq 3 (the bulk viscosity) and the viscous drag experienced by the spherical particle. The inadequacy of this approach is also apparent in the investigations of Preston et al.,[30] who present experimental data illustrating the role of the matrix polymer size. They show that for a given diffusant there is a critical molar mass of the dextran matrix polymer above which diffusion becomes independent of the macroscopic viscosity. This observation would explain the very low values of the apparent radius found at high concentrations. Similar behavior is found for latex diffusion in the salt-free CMC system at pH 9 (Figure 12) although the decrease in $\bar{R}_H$ is less pronounced than with HPC. Only in comparison with the system containing 0.05 M salt can a qualitative interpretation be made since it is well-known that adsorptive interactions increase as the ionic strength is raised (see, for example, ref 9) due in part to increased screening of fixed charges as well as possible changes in solvation. Thus, there may be a real increase in $\bar{R}_H$ in 0.05 M salt compared to the decrease in this quantity in the salt-free system.

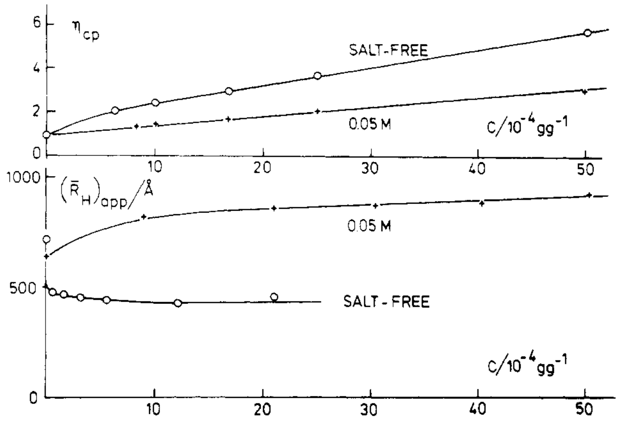

Figure 12. Apparent radius of the latex particle in CMC ($\bar{M}_w$ = 2 × 10^5) solutions at pH 9 with and without the addition of salt (LiCl). The radii were estimated by eq 3 together with the bulk viscosity taken from the upper part of the figure.

Ogston and co-workers[10] have treated the diffusion and sedimentation of large spherical particles in a suspension of rigid random fibers. Although a gel was visualized, the model is equally appropriate to semidilute polymer solutions. The reduction in the random step length through collision with fiber segments was estimated by using a stochastic approach. The final expression may be written in the form

$$D/D_0 = \exp(-AC^{\delta}) \tag{4}$$

where A is a constant determined in part by the radius of the diffusing particle and the exponent $\delta = {}^1/_2$. Cukier[11] has recently derived the same functional dependence by a very different approach, using a hydrodynamic model to describe the screening in semidilute polymer solutions, and derived expressions for the diffusion of Brownian spheres in solutions of both rodlike polymers and coil solutions. The coefficient A, however, is different from that given by Ogston et al.[10]

Altenberger and Tirrell[37] have discussed the self-diffusion of a Brownian particle in a suspension of fixed obstacles modeling a network of entangled polymers. Their expression is

$$D/D_0 = 1 - AC^{1/2} - BC + ... \tag{5}$$

at low concentrations of obstacles. The $C^{1/2}$ dependence is again predicted, where the constant A is directly proportional to the radius of the diffusing particle. Most recently, Altenberger et al.[38] generalized this approach by analysis of the influence of statistical correlations in the gel network and show how an exponent of value ${}^1/_2 \leq \delta \leq 1$ may arise. A number of groups (see also ref 39–42) have deduced a relationship of this fundamental nature, although with differences in the coefficient of the $C^{1/2}$ term. Thus this scaling form appears well established in theory, although experimental support for it is less clear-cut. A number of experimental studies provide some support for the validity of the $C^{1/2}$ dependence. Thus Laurent and co-workers[30,31] found a fit of this type for the diffusion of bovine serum albumin in solutions of the highly extended polymer hyaluronic acid. Jamieson et al.[32] came to the same conclusion for the diffusion of latex spheres of a similar size to the present ones (radius 1100 Å) in semidilute solutions of the stiff-chain polysaccharide xanthan.

Other studies (for example, ref 1–5) suggest that a C^{δ} dependence with ${}^1/_2 \leq \delta \leq 1$ is more appropriate in suspensions of more flexible, or shorter length, chains. As will be emphasized below, the value of δ is highly sensitive to the interactions peculiar to a given system (e.g., adsorption,

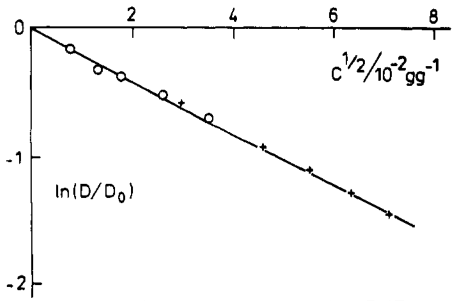

Figure 13. Plot according to the relationship $D/D_0 = \exp(-AC^{1/2})$ for latex diffusion in CMC ($\bar{M}_w = 2 \times 10^5$) solutions at pH 4 in the salt-free system (○) and in 0.05 M LiCl (+). At pH 4 both latex and CMC are essentially uncharged.

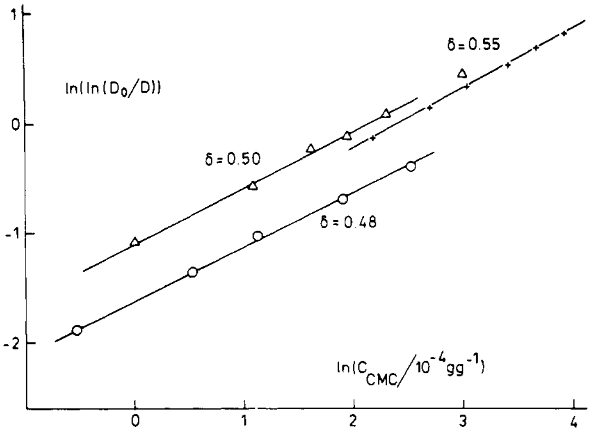

Figure 14. Determination of the exponent in $D/D_0 = \exp(-AC^{\delta})$ for latex diffusion in solutions of CMC of different molar mass at pH 4: (△) $\bar{M}_w = 7 \times 10^5$ (salt free); (○) $\bar{M}_w = 2 \times 10^5$ (salt free); (+) $\bar{M}_w = 2 \times 10^5$ in 0.05 M LiCl. The δ values are indicated.

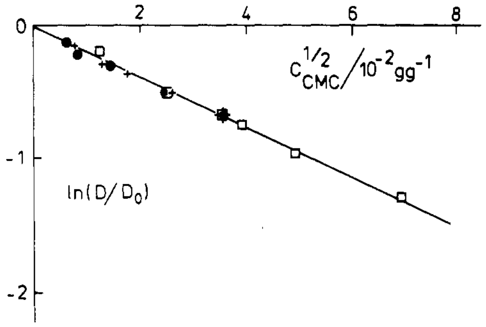

Figure 15. Plot according to $D/D_0 = \exp(-AC^{1/2})$ for latex diffusion in CMC ($M = 2 \times 10^5$) solutions at various charge densities in the absence of salt at pH 9 (□, α = 1.0), pH 7.3 (+, α = 0.47), and pH 4.2 (●, α = 0.05). α is the degree of dissociation.

electrostatic interactions, and also the manner in which these are related to the polymer chain length). Of the present polymer systems, the least complicated appears to be (carboxymethyl)cellulose at pH 4, where both the polymer and the latex are essentially nonionized and adsorptive interactions between them cannot be detected. The inflexible backbone of the cellulosic polymer is also pertinent as regards the rigid-rod model used by Ogston[10] or the fixed-obstacle model of Altenberger and Tirrell.[37] Figure 13 shows the essentially validity of the $C^{1/2}$ dependence, both in the salt-free system and in the presence of salt. Figure 14 depicts the data plotted to yield the exponent δ in eq 4, i.e., using a plot of ln (ln (D_0/D)) vs. ln C. For both molar masses a δ value of about 0.5 is found. Experiments were made to examine the influence of charge density. The $C^{1/2}$ dependence is followed independent of the number of charges on latex and CMC (see Figure 15).

However, in the CMC system at pH 9 it is found that while the lower molar masses yield the anticipated value of δ = 0.5, the highest molar mass (7 × 10^5) leads to a value of δ = 0.3. This difference in behavior is shown clearly in a $C^{1/2}$ plot (Figure 16), where there is a characteristic deviation from the predicted relationship at the highest molar mass. That this is most likely a charge effect is indicated by the absence of a significant change in the latex D values when Triton-X100 is added to the latex suspension at pH 9 prior to addition of CMC solution. The influence of the charges on the components is apparently not felt if the CMC is of low molar mass and the latex size substantially exceeds the coil dimension (correlation length in the network). That the relative size of probe and coil is important is expected since the interactions should change considerably when the coil size approaches the sphere dimension.

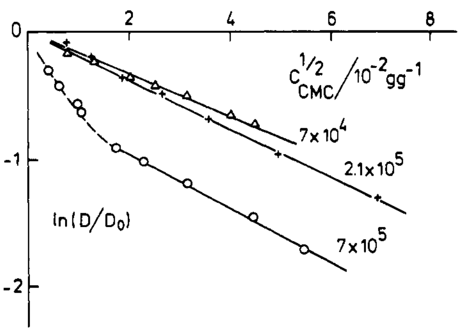

Figure 16. Plots analogous to those in Figure 13 for latex diffusion in solutions of CMC (salt-free) but at pH 9 (full ionization) for different molar mass fractions.

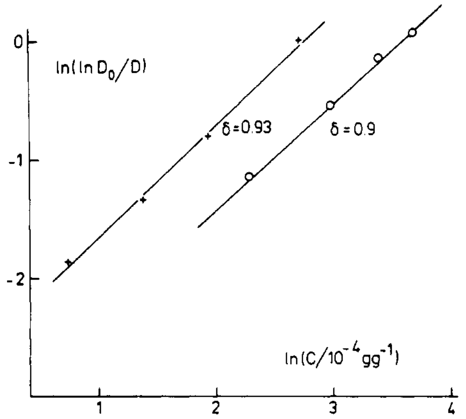

Figure 17. Determination of the exponent in eq 4 for latex diffusion in CMC solutions at pH 9 (full ionization) in the presence of salt (0.01 M LiCl): (+) $\bar{M}_w = 7 \times 10^5$; (○) $\bar{M}_w = 2 \times 10^5$. The δ values are shown.

The addition of salt to the latex/CMC system substantially increases the δ value as shown in Figure 17. Due to electrostatic screening, and possibly an associated decrease in the latex swelling as well as the solvation of both polymer and latex, a significant degree of binding of polymer to the individual latex particles occurs. When this is so, a coupling between matrix and particle motions is expected and hence a larger δ-value. The associated change in D_{latex} due to the larger particle radius may be small if the chains adsorb in a relatively flat configuration.[8,9] (On the other hand, we note that bridging interactions lead to a large change in the diffusion coefficient but this is accompanied by a negligible change in the bulk polymer concentration.) The role of the ionic strength in promoting adsorption between polymer and latex has previously been described; see, for example, the review of Napper.[9] Böhm[43] studied the adsorption of poly(methacrylic acid) to polystyrene latex as a function of surface

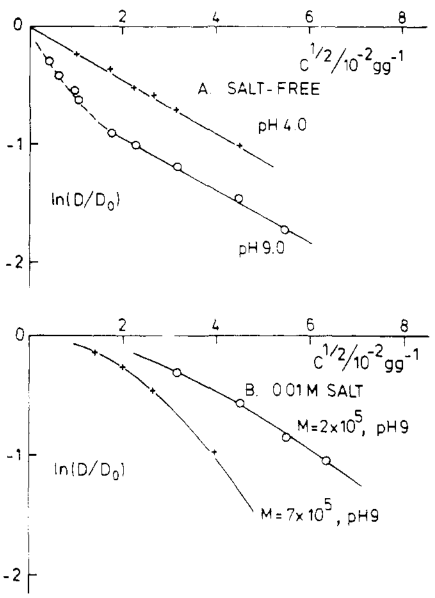

Figure 18. Plots according to $D/D_0 = \exp(-AC^{1/2})$ for latex diffusion in CMC solutions. The upper part (A) shows data in CMC ($\bar{M}_w = 7 \times 10^5$) at pH 4 (nonionized) and when fully ionized (pH 9 under salt-free conditions). The lower part (B) shows data in CMC of different molar mass at pH 9 in the presence of 0.01 M LiCl.

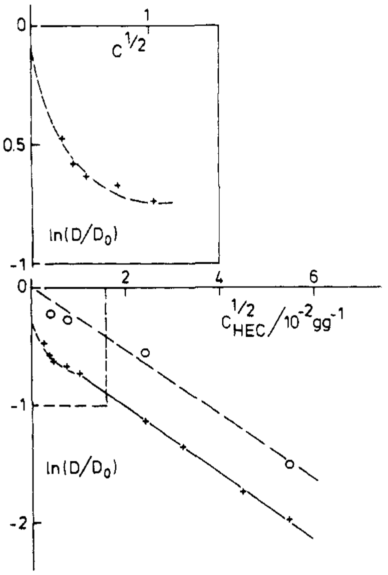

Figure 19. Plots as in Figure 18 but for latex diffusion in (hydroxyethyl)cellulose ($\bar{M}_w = 5.15 \times 10^5$) solutions in the concentration region dilute–semidilute. The insert shows enlarged the region indicated in the main diagram. Points (+) are obtained from the measured values of D. The broken line was obtained by renormalization using the intercept from the linear part of the full line. The open points (O) are for latex diffusion in the presence of 0.15% Triton-X100.

charge density, degree of dissociation (α), and the ionic strength. Adsorption is increased with increased α and also at greater surface charge density. Adsorption was enhanced with increased salt concentration. The charge density on the presently used latex is high (−40 $\mu C/cm^2$), which may account for the negligible adsorption in the salt-free CMC systems. Only in the presence of added electrolyte does adsorption become significant as the repulsive potential is sufficiently reduced.[44]

Figure 19 shows the $C^{1/2}$ plot for the HEC/latex system over an extended range of polymer concentration. Adsorption through bridging causes the initial downward displacement, and thereafter there is an approximately

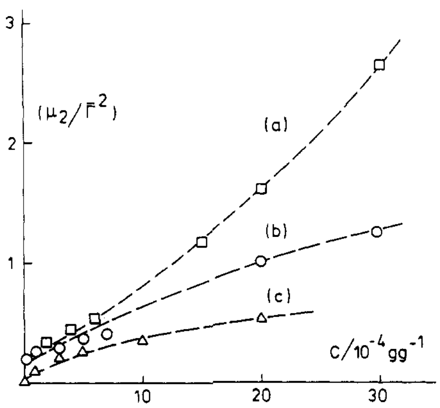

Figure 20. Latex diffusion data. The normalized second cumulant vs. concentration of polymer in the following (salt-free) systems: (a) HEC ($\bar{M}_w = 5.15 \times 10^5$); (b) CMC ($\bar{M}_w = 2 \times 10^5$, data at pH 9); (c) CMC ($\bar{M}_w = 2 \times 10^5$, pH 4).

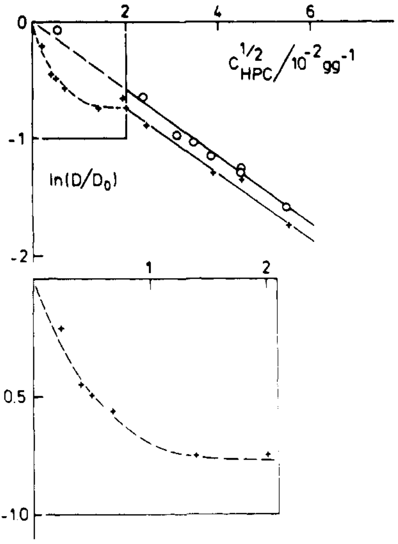

Figure 21. Plot for latex diffusion in (hydroxypropyl)cellulose ($\bar{M}_w = 8 \times 10^5$) solutions analogous to that in Figure 19 for HEC.

parallel shift of the data from the anticipated line passing through the origin. Assuming that bridging has increased the average latex radius, renormalization with a larger D_0 value should, at least in some measure, correct for the influence of aggregate size. The broken line corresponds to a recalculation of the data using a value $D_0 = 2 \times 10^{-12}$ $m^2\ s^{-1}$ obtained from the intercept of the linear portion of the curve on the vertical axis. The open points shown (which agree approximately with this line) are data obtained with the addition of Triton-X100 at a concentration of 0.15%. It may be concluded that the deviation from the $C^{1/2}$ relationship is a result of the aggregation process. Accompanying the strong decrease in the value of D/D_0 as a function of HEC concentration, as was shown in Figure 4, is a simultaneous change in the relative variance reflecting a considerable polydispersity change over the whole range of HEC concentration. This is illustrated in Figure 20. We note that the addition of Triton-X does not imply that the system has necessarily been simplified in the presence of surfactant, since the relative variance remains large, although it is decreased to about half the corresponding value in the absence of Triton-X. Thus there is probably a competitive interaction between the polymer and the surfactant at the latex surface for binding sites.

Figure 21 shows data for latex diffusion in (hydroxypropyl)cellulose solutions. This diagram is similar to that for HEC (Figure 19), and the two lines for D_{latex} in HEC

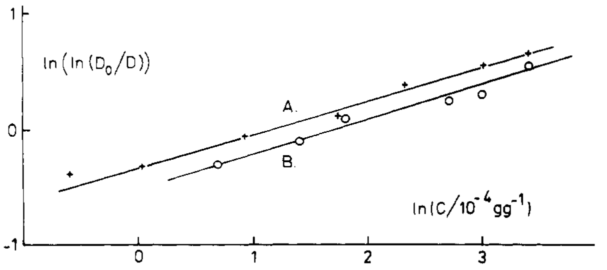

Figure 22. Determination of the exponent in eq 4 by plotting ln (ln (D_0/D)) vs. ln C. Data are for latex diffusion in semidilute solutions of HEC (+) and HPC ($M = 8 \times 10^5$) (O). The slopes are equal to $\delta = 0.3$ in each case.

and HPC in the presence of Triton-X are practically coincident. These data for HEC and HPC yield a δ value of approximately 0.3 (see Figure 22). Thus bridging interactions leading to aggregation and electrostatic interactions (both of which produce significant depression of D_{latex} at extremely low polymer concentrations) will yield a similar qualitative change in the $C^{1/2}$ plot and correspondingly δ values lower than 0.5.

In summary, the value of δ in $D/D_0 = \exp(-AC^\delta)$ will be less than 0.5 if the diffusion coefficient for the sphere is the parameter mainly affected. We also note that large δ values approaching unity are found when the polymer is a flexible one or if of low molar mass (see, for example, the reports on low-M poly(acrylic acid)[2,3] and dextran.[33,34] The lower molecular weight HPC fraction ($M = 7 \times 10^4$) gave $\delta = 0.8$. The present results for latex diffusion in poly(acrylic acid) (nonionized form at pH 3.5) indicate no reduction in D_{latex} over the concentration range up to 0.3% ($C^* = \simeq 1.1\%$ (w/w)). As may be seen in Figures 4 and 6, over this concentration range in the highly extended cellulosic polymers D/D_0 had decreased to about 0.2. Lin and Phillies[2,3] found $\delta = {}^2/_3$ for the diffusion of latex spheres in aqueous solutions of nonionized poly(acrylic acid) where the concentration range was extended up to 10%. The molar mass was similar to that presently used. One may surmise that the relaxation time for the polymer will be insufficiently long for the premise of stationary obstacles since this polymer is highly flexible. For these reasons substantial deviations from the predicted δ value of 0.5 may be anticipated.

A recent paper by Gorti and Ware[45] deals with the self-diffusion of charged latex spheres in sodium poly(styrenesulfonate)solutions using fluorescence photobleaching recovery. The index δ ranged from unity down to 0.5 at high salt and low charge density. The results are in general accord with the present ones for the CMC systems, except that D/D_0 showed a pronounced initial decrease with increasing salt concentration. The factor A in eq 4 is related to the size of the diffusant. We note that A increases with molar mass and a value of $A = 20$ is found for the high molar mass CMC fraction at pH 4 (Figure 13).

Conclusions

In very dilute solutions of water-soluble neutral polymers there is a significant degree of latex–polymer binding. The dominant mechanism appears to be bridging of the latex particles mediated by polymer chains. Multiexponential analysis of the time correlation function yields two modes, the faster of which is approximately equal to the value for the isolated latex sphere. The slower mode is consistent with a particle size of the magnitude dimer/trimer. The number population of the latter is probably low at the dilute end of the polymer concentration scale. Interactions at low polymer concentration carry over to the semidilute region, which complicates comparison with the theoretical predictions for sphere transport in networks. Thus the bridging interactions in HEC (and HPC) lead to pronounced deviations in the $C^{1/2}$ plots and a correspondingly low δ value in $D/D_0 = \exp(-AC^\delta)$. Addition of surfactant (Triton-X) only partly alleviates the situation. The system that apparently most closely meets the assumptions of theory (e.g., neutral, randomly oriented, rodlike obstacles stationary in space) is with nonionized (pH 4) solutions of CMC in suspensions of latex of low effective charge. Here no adsorption could be detected, and the results conform to the predicted $C^{1/2}$ dependence. With high molar mass CMC at pH 9 electrostatic interactions come into play and again produce divergence from the $C^{1/2}$ law. In the presence of salt at pH 9 CMC apparently adsorbs strongly to the individual latex particles, and δ then approaches unity. It may be inferred that the dynamics are then strongly determined by those of the matrix polymer. The index δ provides a sensitive index to the interactions in a particular system.

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Registry No. HEC, 9004-62-0; HPC, 9004-64-2; CMC, 9000-11-7; PAA, 9003-01-4; (butyl acrylate)(styrene)(methacrylic acid) (terpolymer), 25036-16-2.

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Competitive and Displacement Adsorption of Polystyrene and Poly(ethylene oxide)

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ABSTRACT: Competitive and displacement adsorption of polystyrene (PS) and poly(ethylene oxide) (PEO) with narrow molecular weight distributions onto a nonporous silica (Aerosil 130) from carbon tetrachloride solutions at 35 °C was studied by IR and UV spectroscopy. The fraction of silanol groups occupied by styrene or ethylene oxide units was determined from the shift in the IR frequency of the silanol groups. In competitive adsorption, PEO absorbs preferentially over PS, and the preferential adsorption of large molecules over small molecules occurs even in the presence of different species. PS molecules are completely desorbed from the silica surface by addition of PEO (displacer). The degree of displacement of PS by PEO depends on the fraction of styrene units directly attached to the silanol groups as well as on the molecular weights of PS and PEO.

Introduction

Several studies have been reported on competitive and displacement adsorption of different sizes of molecules of a polymer from solution onto a solid.[1-10] Large molecules are in preference to adsorbed small ones, and initially adsorbed small molecules are displaced by larger ones. In an investigation of exchange and competitive adsorption between two chemically different polymers, poly(methyl methacrylate) (PMMA) and polystyrene (PS), it was found that PMMA was preferentially adsorbed, and PS was displaced by PMMA.[11] Similar adsorption studies have been reported[12,13] but they used only one pair of chemically different polymers with polydispersity.

The aim of this paper is to present experimental results on the competitive and displacement adsorption of poly(ethylene oxides) and polystyrenes onto nonporous silica from their carbon tetrachloride solutions at 35 °C. Each sample of both polymers had a narrow molecular weight distribution. Polymer concentrations in solution after adsorption were determined by IR and UV spectroscopy.

Experimental Section

Materials. Samples of PS and PEO were purchased from Toyo Soda Co. Their characteristics from the manufacturer are listed in Table I.

The nonporous Aerosil 130 silica (Degussa AG, West Germany) was used as the adsorbent after being cleaned by the procedure described previously.[10,14,15]

Carbon tetrachloride and dioxane were distilled twice just before use.

Adsorption of Polymers. Adsorption isotherms of the PEO samples were determined at 35 °C in 50-mL stoppered glass centrifuge tubes containing 0.16 g of silica and 20 mL of a CCl_4 solution PEO of known concentration C_0. The tube was agitated in a cabinet controlled at 35 ± 0.1 °C for 24 h. The suspension was then centrifuged, and the bulk concentration C_p of unadsorbed PEO remaining in the supernatant solution was determined from its C-H stretching band in the IR at 2900 cm^{-1}.[16]

Table I
Characteristics of Polystyrenes (PS) and Poly(ethylene oxides) (PEO)

sample	$M_w \times 10^{-3}$	M_w/M_n
PS-102	102	1.02
PS-775	775	1.04
PS-3840	3840	1.04
PEO-39	39	1.07
PEO-86	86	1.02
PEO-252	252	1.04
PEO-660	660	1.04

Competitive adsorption experiments on PS-PEO mixtures (1:1 (w/w)) were performed in the same way. The equilibrium concentration of PEO in the supernatant solution after adsorption was measured by using the IR band of the C-O-C valence vibration at 1107 cm^{-1}.[16] The concentration of PS in the supernatant was determined by evaporating the carbon tetrachloride, drying the residue under vacuum, dissolving it in a definite amount of dioxane, and determining the concentration by UV spectroscopy.

Displacement Adsorption of PS by PEO. PS molecules were adsorbed onto silica (0.16 g) from 20 mL of carbon tetrachloride solution. The PS concentration (0.2 g/100 mL) was chosen to be in the plateau region of PS adsorption isotherms determined previously.[10] After agitation for 24 h at 35 °C and centrifugation, 10 mL of the supernatant solution was withdrawn, and 10 mL of a carbon tetrachloride PEO solution of known concentration was added. The mixture was agitated again for 24 h at 35 °C. After centrifugation, the concentrations of PEO and PS in the supernatant solutions were determined by the spectroscopic procedure described above.

The IR spectra of the sedimented silicas were determined by the method described previously.[10,14,15]

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