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Interaction of (Carboxymethyl)cellulose with Latex Spheres Studied by Dynamic Light Scattering

Wyn Brown* and Roger Rymdén

Institute of Physical Chemistry, University of Uppsala, S-751 21 Uppsala, Sweden.

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ABSTRACT: The apparent thickness of an adsorbed layer (δ_H) of the weak polyelectrolyte (carboxymethyl)cellulose (CMC) on polystyrene latex particles (Dow) of low surface charge has been estimated by using quasielastic light scattering (QELS) under a variety of conditions, e.g., pH, ionic strength, molecular weight, particle size. δ_H is smaller at low pH (CMC noncharged) and also in the presence of a simple 1:1 electrolyte compared to pH 9 where the CMC is fully charged. It is concluded that the polymer adopts a flat conformation at the interface, but less so at the higher pH. δ_H depends on the CMC molecular weight. When a highly carboxylated latex was used, δ_H was insignificant, indicating the absence of adsorption. When the diffusion of carboxylated latex was measured at high CMC concentrations the data show a rapid increase in the relative variance, suggesting incipient aggregation. The fast mode in a bimodal fit corresponds to the monomeric latex while the slow approximates that for CMC in solution in the absence of latex. This suggests immobilization of some of the latex in the transient network. The aggregated latex dominates the scattering behavior. The complex interactions in aqueous latex/polymer systems preclude analysis of sphere self-diffusion in polymer networks. Comparison with data for nonpolyelectrolytes suggests that these aspects generally pervade such systems.

Introduction

A previous paper[1] described QELS measurements on carboxylated latex particles in solutions of high molecular weight cellulose derivatives [(hydroxyethyl)cellulose (HEC) and (hydroxypropyl)cellulose (HPC)]. Bridging interactions between latex particles mediated by HEC or HPC dominated the concentration dependence for latex diffusion in both dilute and semidilute ranges of polymer concentration. It had originally been hoped that these semistiff polymers would better approximate the theoretical models[2-4] used for sphere self-diffusion in ternary systems than the flexible chains which have been the usual substrates.

The present paper is directed toward a more detailed examination of the interactions between latex particles (low and high surface charge) and the weak polyelectrolyte (carboxymethyl)cellulose (CMC). The earlier report[1] included data on CMC of low molecular weights and the interactions were found to be small in comparison to those between HEC or HPC and the latex. The present approach is limited to measuring the apparent thickness of the polymer layer at the latex interface. Equilibrium measurements of the amount adsorbed are difficult to perform in this system with the required accuracy owing to the small quantities involved (a few milligrams of polymer per gram of latex) although such data would simplify interpretation.

There is extensive literature on the adsorption of polymers from solution and also the role of polymers in the stabilization of colloidal dispersions. Recent reviews include those in ref 6, 7, and 9. References 8 and 16 deal with the use of QELS in the estimation of adsorbed layer thickness in the latex/poly(ethylene oxide) (PEO) system, which, as will be seen below, is comparatively well-behaved.

The transport of charged latex spheres in polymer solutions [PEO and poly(acrylic acid)] has been investigated over broad intervals in concentration by Phillies et al.,[10-13] although the role of adsorption was not explored in any detail. Focus was instead placed on the gross aspects of transport—for example, the marked divergences from the Stokes–Einstein equation and the possible usefulness of a stretched exponential form to describe latex transport. The literature tends to be confusing since those addressing the transport problem often choose to neglect adsorption effects which, as will be shown below, may exert a dominant influence on the concentration dependence. At the same time, studies of layer thickness often consider superficially that the hydrodynamic interactions will be adequately described by including the macroscopic viscosity in the Stokes–Einstein equation. This is also shown below not to be justifiable and probably is not so in most aqueous ternary systems.

Experimental Section

Materials. Dow polystyrene latex samples have been used having the nominal diameters 0.109, 0.22, and 0.399 μm and a surface charge of $-2.5\ \mu C/cm^2$. A recent brochure[14] gives details. These materials were purified by dialysis of a stock suspension and subsequently titrated to the desired pH with LiOH solution (used as the electrolyte in a parallel investigation by NMR[15] of latex–ion binding).

All measurements have been made at a fixed latex concentration of 1×10^{-5} g g^{-1} and at 25 °C. The carboxylated latex was synthesized from butyl acrylate/styrene in the ratio 65:35 with 1% methacrylic acid based on the former materials. This material was described in detail in the previous paper.[1]

The **(carboxymethyl)cellulose** (CMC) was obtained from Hercules Powder Inc.: CMC 7HF ($\bar{M}_w = 7 \times 10^5$, DS = 0.70); CMC 12M8 ($\bar{M}_w = 2 \times 10^5$, DS = 1.2); CMC 7LF ($\bar{M}_w = 9 \times 10^4$, DS = 0.7).

Poly(acrylic acid) ($\bar{M}_w = 2.3 \times 10^5$) was obtained from BDH Chemicals, Poole, England.

The preparation of the solutions and the prior treatment of the polymer solutions by exhaustive dialysis to remove low molecular weight tails was described in the previous paper.[1]

Data Collection and Analysis. QELS data were taken up with the previously described[1] apparatus and technique. All measurements were thus made in the homodyne mode at an angle of 90° after it had first been established that a linear plot passing through the origin of the average relaxation rate (Γ) versus the square of the scattering vector ($\mathbf{q}$) was obtained over the angular range 30°–120°, thus confirming diffusive motion. The data were always first processed by using second- and third-order cumulant fits and this was then followed by sequential fits to one-, two-, and three-exponential functions by using a discrete multiexponential analysis with an equally weighted nonlinear regression procedure with a nonnegativity constraint.

Macroscopic shear viscosities were measured on the salt-free CMC ($M_w = 7 \times 10^5$) solutions at pH's 3.5, 5.5, and 8.8, by using a Bohlin VOR rheometer at a shear rate of 23 s^{-1} and at 25 °C.

Results and Discussion

Polystyrene Latex (Low Charge Density) in CMC Solutions. QELS measurements may be used[1,8,16] to es-

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timate the apparent thickness (δ_H) of an adsorbed layer of a polymer at the latex/solvent interface. δ_H is evaluated as the difference between the Stokes' radius of the sphere in the solvent alone and the dimension in the presence of polymer. This necessitates working in a range of polymer concentration where hydrodynamic interactions between the latex particles themselves and between latex and polymer may be neglected. (Extensive investigations by Phillies et al.[10-13,21] in aqueous systems have established that the hydrodynamic radius of the particle cannot be evaluated in a straightforward manner simply by introducing the macroscopic viscosity of the solution in the Stokes–Einstein equation.) At very low polymer concentrations it may be possible to interpret D/D_0 versus C_{polymer} curves as binding isotherms.[19] However, this leads to ambiguities since the apparent thickness of the adsorbed layer may not correlate with the amount of adsorbed material. In the case of polyelectrolytes, for example, the conformation of the bound polymer is expected to be sensitive to the pH of the medium. When the polymer is a neutral, low molecular weight, flexible one, however, and the concentration is below that corresponding to coil overlap, the plateau region may be observed[16,17] over extended ranges of concentration.

QELS measurements have the advantage that precise measurements can be made at very low particle concentrations and lead to the self-diffusion coefficient which is uncomplicated by thermodynamic terms. This interpretation presupposes that the scattering derives only from the latex entity, which is approximately true in the present system where, over the considered concentration range, CMC contributes less than 1% of the total scattered intensity. Evaluation of an unambiguous value of the apparent radius also requires that the correlation function approximates a single exponential or that the second cumulant is small (≤ 0.05) if a cumulants analysis is used. In the recently investigated latex/HEC system[1] the relative variance was not small even at extreme dilutions and the correlation function could be optimally fit by using a bimodal expression, indicating a bridging mechanism.[7]

Figure 1 illustrates data for the diffusion of a polystyrene latex in a CMC solution of high molecular weight at pH 9 where the CMC is fully charged. The data are presented in the form of the diffusion coefficients without normalizing with the macroscopic solution viscosity since the accumulated evidence shows that the Stokes–Einstein equation is in general not applicable in aqueous latex/polymer systems (see below). Up to a CMC concentration $C \cong 3 \times 10^{-5}$ g g^{-1}, the relative variance is small and approximately equal to the value for the latex in water, which justifies the use of a single-exponential approximation. The reduced diffusion coefficient passes through a plateau region (insert) between 5×10^{-6} g g^{-1} and 2×10^{-5} g g^{-1} and this corresponds to an apparent hydrodynamic radius, R_H = 705 Å and thus an increment in the particle radius of δ_H = 160 Å. We note that at these extremely low concentrations, at which the solution viscosity is approximated by that of the pure solvent, the above reservations regarding the use of the Stokes–Einstein equation will not apply.

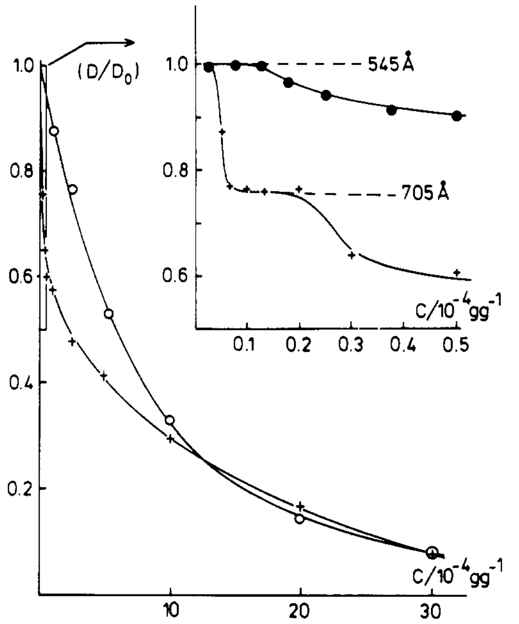

Figure 1. Dow latex (ϕ = 0.109 μm). Reduced latex diffusion coefficient as a function of concentration of CMC ($\bar{M}_w = 7 \times 10^5$) in the salt-free (+) and in 0.01 M LiCl solutions (○) at pH 9 where CMC is fully charged. The insert shows the low concentration range ($C \leq 5 \times 10^{-5}$ g g^{-1}) for the salt-free system (+) and the effect of adding a surfactant (Triton X100) at 0.15% (●).

These data suggest that rather precise estimates of the thickness of the polymer layer at the latex surface may be obtained. As the concentration is further increased beyond the plateau region, there is a monotonic decrease in D_{latex} as the hydrodynamic interactions become increasingly felt. Theoretical treatments of the self-diffusion of Brownian particles in polymer systems have utilized a variety of models and recent examples are given in ref 2–4. It may be noted that reports[13,19] dealing with latex particle diffusion in polyelectrolyte solutions at low ionic strength observed a monotonic decrease in D/D_0 rather than a plateau region. Evidence supporting the interpretation of the plateau region as an adsorption effect is obtained by addition of the short-chain surfactant Triton X100 to the latex suspension prior to mixing with polymer solution (insert, Figure 1). It was previously shown that this surfactant effectively inhibits the binding of cellulosic polymers to latex particles[5,1] and this observation also applies in the latex/poly(ethylene oxide) system.[21] Previous workers[8,16,17] have concluded that the thickness of the adsorbed layer of a neutral polymer approximately equals twice the radius of gyration of the polymer coil (R_g) as determined in dilute solution. This is clearly not the case in the present polyelectrolyte system. Although R_g data are not available for CMC at zero ionic strength at pH 9 where the coil is maximally extended, $R_g \cong 1700$ Å for a CMC fraction ($\bar{M}_w = 7.5 \times 10^5$) in 0.005 M NaCl solution.[22] The comparatively small δ_H values indicate that CMC adsorbs in a flat conformation when fully charged. This is in agreement with predictions.

Recent theoretical approaches to the adsorption of polyelectrolytes are those in ref 27–29. When the adsorbate is charged and the ionic strength is low, they show that thin layers of adsorbate are formed; i.e., the formation of loops and tails is supressed in contradistinction to the case with neutral polymers. This has received experimental support—see, for example, the results of Horn[30] for polyethylenimines on PS latex and Williams et al.[31] for CMC on $BaSO_4$. Cosgrove et al.[20] have recently reported results for the poly(styrenesulfonate)(NaPSS)/PS latex system with latex particles of low charge but in solutions of high ionic strength. They also concluded that adsorption was in a flat conformation ($\delta_H \ll 2R_g$). Measurements were also made to determine the effect of changing the latex concentration. The CMC ($\bar{M}_w = 7 \times 10^5$) concentration was 1.5×10^{-5} g g^{-1} and the latex (ϕ = 0.109 μm) concentration varied over the range 2×10^{-7} to 2×10^{-5} g g^{-1}. D_{latex} was found to be independent of the latex concentration. Fig-

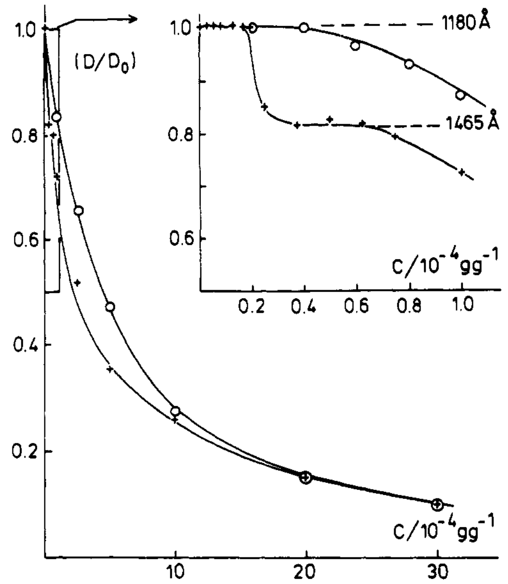

Figure 2. Dow latex (ϕ = 0.22 μm). Plot analogous to Figure 1. The insert shows the low concentration range ($C \leqslant 1 \times 10^{-4}$ g g^{-1}) in the salt-free (+) and in 0.01 M LiCl (O) solutions at pH 9.

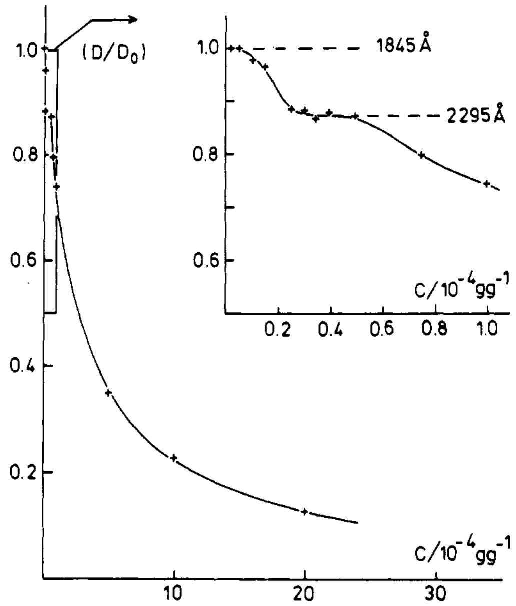

Figure 3. Dow latex (ϕ = 0.399 μm). Reduced diffusion coefficients in the salt-free system as a function of CMC ($\bar{M}_w = 7 \times 10^5$) concentration. The insert shows the low concentration region ($C \leqslant 1 \times 10^{-4}$ g g^{-1}).

ures 2 and 3 show analogous data to those of Figure 1 but refer to latex particles of larger diameter. Data are included in Figures 1 and 2 to allow the influence of salt content to be compared. Figure 2 (insert) indicates that a flatter adsorbed layer, alternatively less binding, is the case at an ionic strength of I = 0.01 M. One explanation of these results would be that there is a change in the conformation of the bound polymer from looped to flat when salt is present and the persistence length shorter.

The dependence of the increment δ_H on the latex particle diameter is shown in Figure 4A. Garvey et al.[17] have found a similar increase in the latex/poly(vinyl alcohol) system as have Ullmann et al. in the poly(ethylene oxide)/latex system.[21]

This effect is, however, not readily understood. Our tentative explanation for the monotonic increase in δ_H is that there is a coupling between the dynamics of the latex and polymer. There is direct evidence for this (see Figure 9) and indirect evidence for such an effect may be found in the data of Phillies et al.[12] who noted that the dependence of D_{latex} on C_{polymer} and particle radius become very strong in the entangled regime with very great departures from the Stokes–Einstein equation. Such anomalies are apparently not found[34] in nonaqueous systems for which $D\eta$ is constant over wide ranges of C_{polymer} and polymer molecular weight, η being the macroscopic solution viscosity. One would anticipate that such a coupling would become more pronounced with large particle sizes and lead to artificially low diffusion coefficients and large apparent δ_H values. We also note that Gorti and Ware[19] observe bimodal decays in the NaPSS/serum albumin system, and they interpret the slow mode as reflecting BSA adsorbed to the NaPSS.

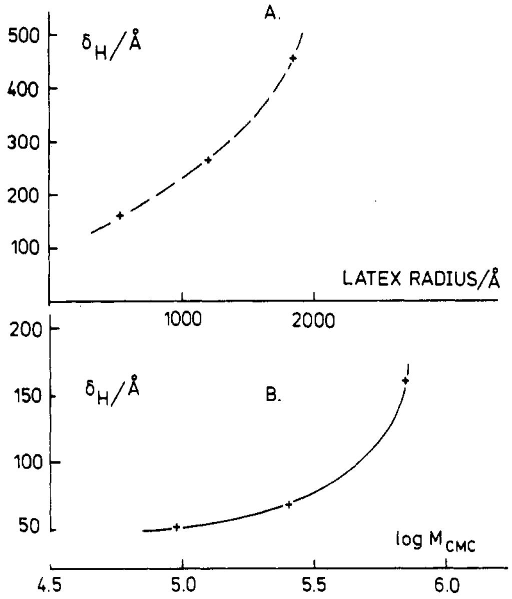

Figure 4. (A) Hydrodynamic thickness, δ_H, of the CMC ($\bar{M}_w$ = 7 × 10^5) layer as a function of the radius of the polystyrene latex spheres. Data for the salt-free systems at pH 9. (B) δ_H as a function of the molecular weight of the CMC fraction. Polystyrene latex (ϕ = 0.109 μm), salt-free systems at pH 9.

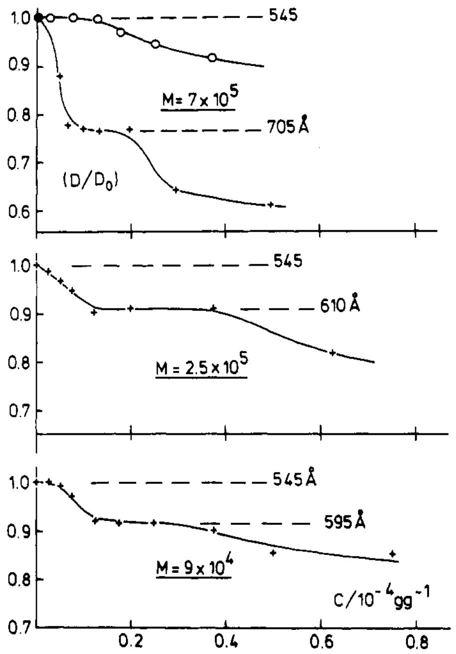

Figure 5. Dow latex (ϕ = 0.109 μm). Reduced diffusion coefficients vs CMC concentration for three molecular weights as indicated (salt-free systems at pH 9). The open circles denote the system containing Triton X100.

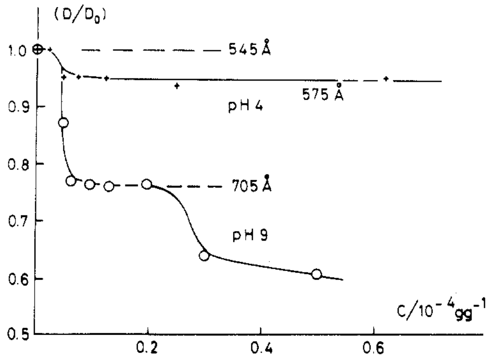

Figure 6. Dow latex (ϕ = 0.109 μm). The influence of pH change in the low concentration range for CMC ($\bar{M}_w = 7 \times 10^5$) at pH 4 (CMC uncharged) and pH 9 (CMC fully charged).

The increment δ_H is shown as a function of the CMC molecular weight in Figure 4B, where δ_H has been derived from the data in Figure 5. Theory[27-29] predicts that adsorption should be independent of M for polyelectrolytes, as distinct from neutral polymers. These data thus suggest that tails/loops are present at the highest molecular weight. However, a strong increase in the amount adsorbed with increasing M is an indication of entropy-steered, weak adsorbent–adsorbate interactions as pointed out by Papenhuijzen[33] who experimentally observed a pronounced molecular weight dependence in such systems.

It is usually anticipated that adsorption will decrease as the degree of dissociation, α, of the polyelectrolyte groups increases. Figure 6 shows that at pH 4 (CMC uncharged) where the polymer should behave as a neutral polymer, δ_H is small in comparison with the value at pH 9. One way of rationalizing these results is by postulating a change in the conformation of the bound polymer from flat to looped when the pH changes from 4 to 9. This interpretation is consistent with the influence of a neutral salt as shown in Figure 2.

At higher ionic strengths one anticipates increased adsorption as the charged sites are increasingly screened—see, for example, the results of Böhm[24] for poly(methacrylic acid) adsorbing to PS latex particles. Measurements have been made on a similar latex (ϕ = 0.109 μm) in CMC ($\bar{M} = 7 \times 10^5$) at pH 9 in 0.1 and 0.5 M LiCl. In 0.1 M electrolyte, δ_H = 170 Å, which agrees approximately with the value found in the salt-free system (Figure 1) but is considerably larger than the δ_H value in 0.01 M LiCl. This arises because the average diffusion coefficient decreases when destabilization of the latex suspension sets in. In 0.5 M salt there is good evidence for aggregation/incipient flocculation. The relative variance increases strongly and the correlation functions may be well fit by using a bimodal expression—see below. The faster mode is consistent with latex dimers and the slower with a 6-mer or larger. Such destabilization at high ionic strength is expected.

We note here that measurements were also made of the latex diffusion coefficient in salt solutions over the ionic strength range $0.001 \leq I \leq 0.1$ in the absence of CMC. No appreciable effect of ionic strength on D_{latex} was observed. This result contrasts with the behavior of the carboxylated latex sample where the apparent radius decreases significantly[1] over the same range of ionic strength.

Carboxylated Latex Diffusion in CMC. Figure 7 shows data for a highly carboxylated latex (charge, −40 μC/cm^2) diffusing in CMC ($\bar{M} = 7 \times 10^5$) at pH 9. This latex is identical with the sample previously used in the study[1] of latex interactions with (hydroxyethyl)cellulose (HEC) and (hydroxypropyl)cellulose (HPC). In this system there is no indication of the plateau at low C_{polymer} which was assumed to represent adsorption effects in the previous section. D/D_0 decreases monotonically with increasing C_{polymer}. There is a pronounced sensitivity to the presence of salt, see insert, which however, diminishes with increasing C_{polymer}. The addition of Triton X100 had no significant influence on the data in the salt-free system, in contrast to the low-charge PS/latex systems (Figure 1). We note that the overlap concentration in the salt-free system will be almost immeasurably low, whereas it is approximately 5×10^{-4} g g^{-1} in the 0.01 M salt system. We conclude that the sensitivity of latex diffusion to salt at low C_{polymer} mostly reflects the limited mobility of the particle in the transient network.

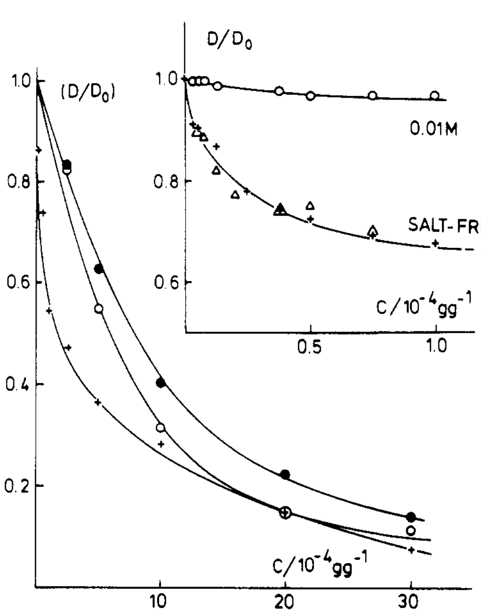

Figure 7. Carboxylated latex (ϕ = 0.134 μm). Data analogous to Figure 1; salt free (+), 0.01 M LiCl (○), 0.05 M LiCl (●) all at pH 9. The insert shows the low concentration CMC range: diffusion in 0.01 M LiCl (○), the salt-free system (+) and in the presence of Triton X100 (△).

At higher concentrations of CMC (i.e. $\geq 5 \times 10^{-4}$ g g^{-1}) the relative variance increases strongly with C_{polymer} as shown in the upper part of Figure 8A. Such a change reflects a departure from a single-exponential decay and may derive from a broad distribution of decay times (polydispersity) or participation of a small number of discrete relaxational modes. We note that a good fit may be obtained by using a bimodal expression and such fits are depicted in the lower part of the figure for data at pH 4 and in Figure 8B at pH 9. In both cases the data for the fast mode extrapolate to the D value for the monomeric latex particle at $C = 0$ (i.e., a sphere radius of 720 Å).

At pH 4 the radius obtained by using the Stokes–Einstein equation with D_{slow} is 1410 Å. The relative intensity of the slow component is shown in the insert and demonstrates the domination of the scattering behavior by the aggregate species. Although this would fit with a bridging mechanism[7] as found for HEC and HPC, this mechanism is deemed unlikely with the CMC/latex system since adsorption appears to be insignificant with these carboxylated particles. At pH 9 the tendency to aggregation is more pronounced than at pH 4 since the slow mode now corresponds to considerably larger particles as is seen from the intercept in Figure 8B.

Measurements of the diffusion of CMC itself ($\bar{M}_w = 7 \times 10^5$) in aqueous solution were carried out over the same concentration interval. Although the scattering intensity was very low, it was possible at full laser power to make measurements of acceptable precision. These data are

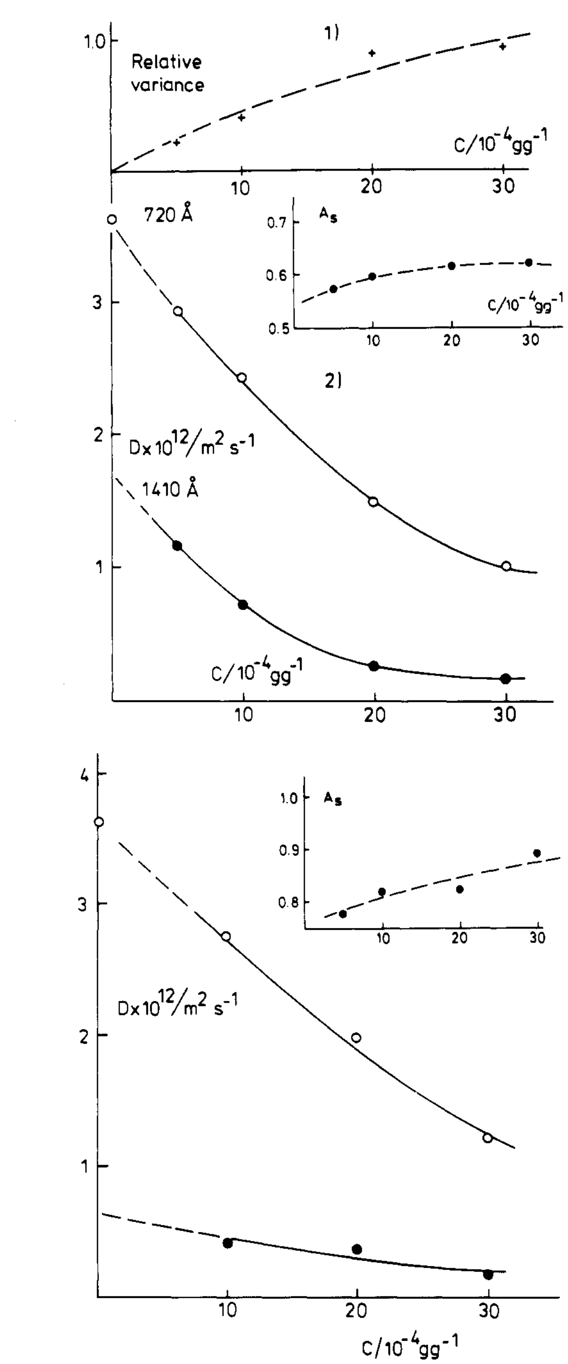

Figure 8. (A, top) Carboxylated latex (ϕ = 0.134 μm). (1) Dependence of the relative variance (cumulants analysis) vs concentration of CMC ($\bar{M}_w$ = 7 × 10^5). Data at pH 4 in the salt-free system. (2) Results of a bimodal fit. The fast mode (○) extrapolates to the diffusion coefficient of the single latex particle at C = 0. Corresponding dimensions are obtained by using the Stokes–Einstein equation and are indicated. The insert shows the dependence of the relative intensity (A_s) of the slower mode on the CMC concentration. (B, bottom) Carboxylated latex (ϕ = 0.134 μm). Data analogous to those in Figure 8A, but at pH 9 in the salt-free system: Fast mode (○); slow mode (●).

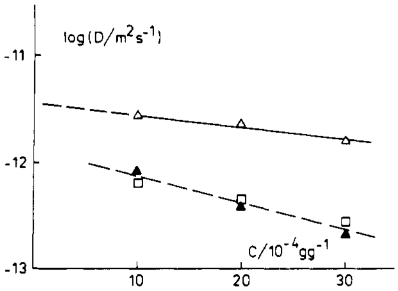

Figure 9. Carboxylated latex (ϕ = 0.134 μm). Comparison of the latex diffusion data for the bimodal fit taken from Figure 8A (fast mode (△); slow mode (▲)) with diffusion coefficients for CMC (□) in solution in the absence of latex at the same concentrations.

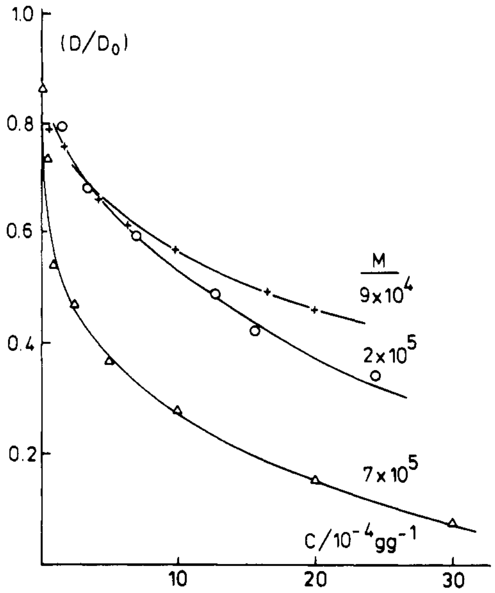

Figure 10. Carboxylated latex (ϕ = 0.134 μm). Reduced diffusion coefficients vs CMC concentration for polymers of three different molecular weights (salt-free systems at pH 9).

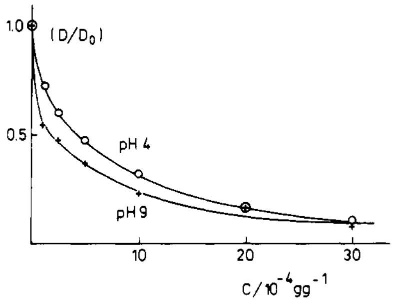

Figure 11. Carboxylated latex (ϕ = 0.134 μm). Data for the reduced diffusion coefficient vs CMC ($\bar{M}_w$ = 7 × 10^5) concentration. Data in the salt-free systems at pH 4 (CMC, acid form), and pH 9 (CMC, fully neutralized).

included in Figure 9 with those for the bimodal fit for the latex/CMC data. The slow latex mode corresponds to the CMC diffusion, with the same concentration dependence. This observation strongly suggests that some of the latex particles are immobilized in the semidilute polymer network, effectively labeling it ($C^* \cong 5 \times 10^{-4}$ g g^{-1} using the definition $C^* = 1/[\eta]$, where $[\eta]$ is the intrinsic viscosity). It is noted that Gorti and Ware[19] also found a bimodal decay time spectrum (in the bovine serum albumin/sodium poly(styrene sulfonate) system) and interpreted the slow mode as a coupling of the motions of these components. Adsorption is presumably not a necessary feature, for such a coupling, since it would suffice to have highly dipolar components in close proximity in the congested network.

Figure 10 illustrates the concentration dependence of D/D_0 for three molecular weights of CMC in the salt-free system at pH 9. These data may be seen in conjunction with those at pH 4 in Figure 11. The differences are small with the highest molecular weight, since C^* is exceeded over most of the concentration range at both pH values. The nonapplicability of the Stokes–Einstein equation referred to earlier may be exemplified with these data at pH 9. The hydrodynamic radius of the latex at infinite dilu-

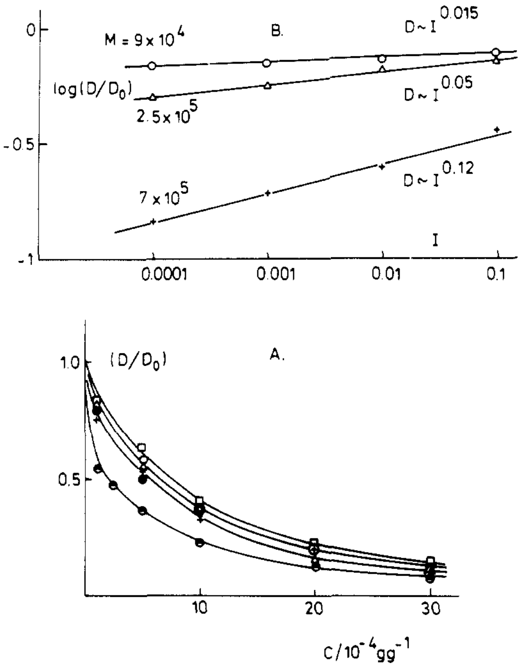

Figure 12. Carboxylated latex (ϕ = 0.134 μm). (A) Reduced diffusion coefficient vs CMC ($\bar{M}_w = 7 \times 10^5$) concentration at different ionic strengths: I = 0 (◓); 0.001 (+); 0.005 (○); 0.01 (△); 0.05 (□); 0.10 (●). (B) log–log diagram of the reduced diffusion coefficient vs ionic strength for CMC of different molecular weights as shown. Data are at pH 9 and a CMC concentration of 1×10^{-3} g g^{-1}.

tion is 720 Å, while the apparent radius calculated by using the macroscopic viscosity and the average diffusion coefficient at $C = 2 \times 10^{-3}$ g g^{-1} is 220 Å. This figure is more in agreement with the expected correlation length for the CMC network, cf. also ref 1. Figure 12A shows that a significant salt effect exists on the self-diffusion coefficient of the carboxylated latex in CMC solutions. Figure 12B depicts the dependence of the ratio D/D_0 on the ionic strength of the medium in a log–log diagram for three different molecular weights of CMC. The exponent in $D \sim I^{\alpha}$ is small at each molecular weight and of the same magnitude as found by Gorti and Ware[19] for latex diffusion in NaPSS solutions. We note that Phillies et al.[13] report a much stronger dependence on ionic strength for a carboxylated latex in poly(acrylic acid) solutions. To examine to what extent the semistiff character of a cellulosic polyelectrolyte changes the transport behavior in comparison with a flexible chain, we have made complementary measurements on the carboxylated latex suspended in poly(acrylic acid) ($\bar{M}_w = 2.3 \times 10^5$).

Figure 13 summarizes the results. At pH 3.5 where the polymer is in the noncharged form, D/D_0 falls initially to a plateau value corresponding to a hydrodynamic radius increment of 150 Å. This is proportionally much greater than with CMC (Figure 5) for which δ_H = 65 Å with $\bar{M}_w = 2.5 \times 10^5$ at pH 9. One expects this behavior for a neutral flexible polymer where loops and tails characterize the conformation of the bound polymer. No further decrease in D/D_0 is observed at pH 3.5 up to a concentration of 3×10^{-3} g g^{-1}, the highest examined. At pH 9 where the poly(acrylic acid) is fully charged, no adsorption plateau was found, as was also the case with CMC at pH 9 when the same carboxylated latex was used as the probe particle (Figure 7). The values of D are substantially greater at pH 3.5 compared to those at pH 9. This is because $C < C^*$ at pH 3.5 over the whole concentration region examined ($C^* \cong 8.8 \times 10^{-3}$ g g^{-1}) whereas at pH 9 $C > C^*$ at all concentrations used. We recall that this apparent effect

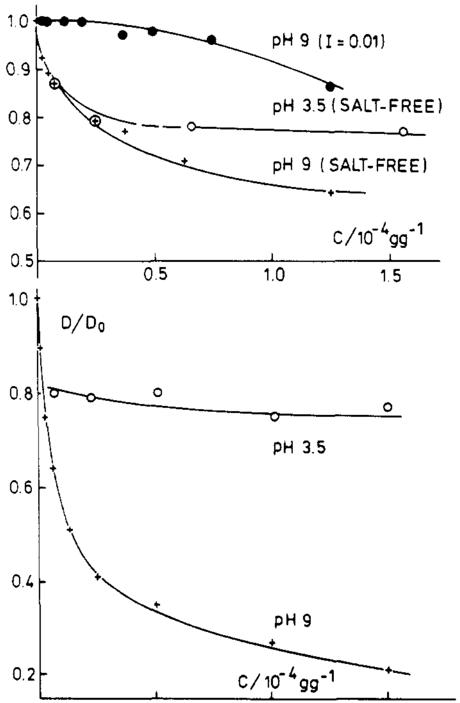

Figure 13. Carboxylated latex (ϕ = 0.134 μm). Reduced diffusion coefficient vs concentration of poly(acrylic acid) ($\bar{M}_w = 2.3 \times 10^5$) at pH 3.5 (uncharged polymer) and pH 9 (fully charged) in the salt-free systems. The upper part of the diagram shows the dilute region enlarged. Also included are data at an ionic strength of 0.01 at pH 9.

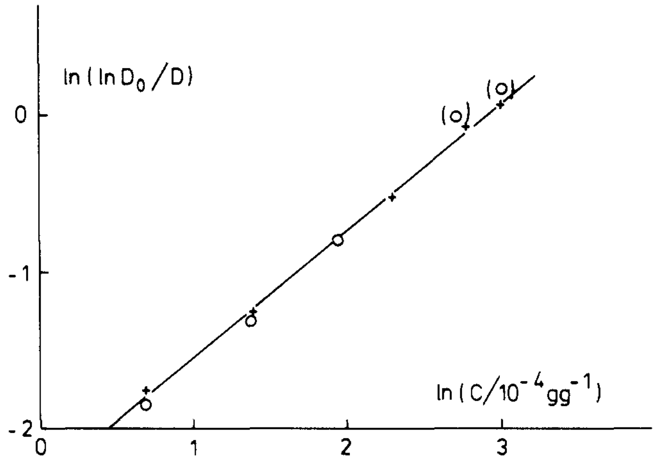

Figure 14. Carboxylated latex (ϕ = 0.134 μm). Determination of the exponent in $D/D_0 = \exp(-AC^{\nu})$ for latex diffusion in solutions of CMC ($\bar{M}_w = 7 \times 10^5$) in 0.01 M LiCl (+) and in the same solvent but including 0.15% Triton X100 (○). The exponent $\nu = 0.8_1$. All data are at pH 9 and 25 °C.

of pH is not observed with the CMC system since $C > C^*$ is valid at both pH values at the concentrations used (Figure 11).

A stretched exponential form, $D/D_0 = \exp(-AC^{\delta})$, has been extensively used[10–13] by Phillies' group to describe the dependence of latex particle self-diffusion on polymer concentration. For comparison, some of the present data are plotted in Figure 14 and yield the exponent δ = 0.81. This value falls in the expected interval 0.5–1 and is in approximate agreement with theory[25,26] for solutions of polyelectrolytes relating the correlation length (ζ) to concentration: $\zeta \sim C^{-0.75}$. However, the expectation from these theories is also that a dependence on particle radius will be found whereas the experiments suggest that D/D_0 is independent of the sphere radius. Points are also included in Figure 14 for parallel measurements made in the presence of Triton X100 to check whether adsorption effects are present. This was not found to be the case.

Conclusions

QELS measurements can provide further insight into the interactions between latex particles and polymers in solution. At very low concentrations of the polymer, the self-diffusion of latex particles of low surface charge in solutions of the polyelectrolyte CMC indicates significant adsorption, where this is reflected in the incremental thickness due to the layer of bound polymer. Although data for the absolute adsorbed quantity of polymer are not available, the magnitude of δ_H suggests a flat profile for the bound layer in contrast to flexible polymers which are characterized by a bound layer thickness of about $2R_g$. A highly carboxylated latex showed no tendency to adsorption to the same CMC fraction. The strong interactions between the components lead to interpretative problems; for example, the anomalous dependence of δ_H on particle radius is probably an artifact deriving from a coupling of the motions of particle and polymer and which is accentuated with increasing radius.

In the higher concentration range of polymer, the relative variance increases strongly, suggesting incipient aggregation. A bimodal fit to the QELS correlation function yielded a fast mode corresponding to the monomeric latex particle. The slower mode indicates dimers at pH 4 and larger aggregates at pH 9. Parallel measurements on the CMC solutions in the absence of latex strongly suggest that some latex particles are immobilized in the transient network (almost all measurements refer to the overlap region for CMC at both pH values). The contributions of adsorptive interactions and also the coupling of the decay processes in the network of these semistiff chains precludes a meaningful testing of theoretical expressions[2-4,25,26] which have been advanced for sphere transport in polymer solutions.

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Registry No. Triton X100, 9002-93-1; CMC, 9004-32-4; LiCl, 7447-41-8; (butyl acrylate)(styrene)(methacrylic acid) (copolymer), 25036-16-2; poly(acrylic acid), 9003-01-4; polystyrene, 9003-53-6.

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