8426 *Macromolecules* **1995,** *28,* 8426–8428

Communications to the Editor

Complex Formation between Poly(dimethyldiallylammonium chloride) and Carboxylated Starburst Dendrimers

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Received February 27, 1995

Polyelectrolytes interact strongly with oppositely charged colloid particles. This phenomenon takes many forms: colloid flocculation in water treatment and paper-making,[1] stabilization of colloidal suspensions,[2] association of DNA with basic proteins,[3] and complexation of proteins with synthetic polyelectrolytes.[4] The consequences of these interactions are similarly varied; they may lead to precipitation, coacervation, or the formation of soluble complexes.

The commonality among these diverse systems is the strong Coulomb interaction between the polyion and the colloidal surface. Thus, the key parameters should be the polyelectrolyte linear charge density (ξ), the colloid surface charge density (σ), and the ionic strength (I)—or the related Debye length κ^{-1}. Theoretical treatments have been offered for a rather similar problem, the binding of a polyelectrolyte to an oppositely charged *planar* surface,[5–10] and these show how the magnitude of the interaction increases with ξ, σ, and κ^{-1}. All of these treatments find phase transition behavior, generally expressed as a critical temperature at which, for a given set of conditions (corresponding to a set of ξ, σ, and κ), a bound polymer state appears. The temperature appears in these formulations through a Boltzmann term and is not a particularly meaningful parameter, as these treatments neglect temperature-induced changes in ion solvation and water structure, which may in fact be dominant. More usefully, these analyses predict that a polyelectrolyte of charge density ξ in a medium of some given ionic strength will not electrostatically adsorb onto a surface until that surface's charge density exceeds some critical value. In general, all of these formulations lead to expressions of the form

$$\sigma_{\mathrm{crit}}(\xi)^{a} \sim \kappa^{b} \qquad (1)$$

and differ primarily in the scaling terms.

There seems to be little experimental confirmation of this phase transition behavior. We have found that polyelectrolytes bind to oppositely charged micelles only when the micelle charge density exceeds some critical value,[11] and this transition, observed by turbidimetry, dynamic light scattering, or electrophoretic light scattering, is quite abrupt for most combinations of polyelectrolytes and micelles. These systems include polycations with nonionic/anionic mixed micelles,[12] polyanions with nonionic/cationic mixed micelles,[13] and polyanions with cationic micelles whose surface charge can be modulated via pH.[14] In those cases where it is possible to measure micelle surface charge density, the data appear to conform closely to eq 1 with $b = 1$, although the value of a is less well established. However, the micelles in question range from small (6 nm diameter) spheres to large (20–200 nm) ellipsoids or cylinders, whereas the treatments of refs 5–10 are for planar surfaces. On the other hand, a recent modification for spherical and cylindrical surfaces did not lead to substantial change in the theoretical result.[15] A second problem that arises in comparing observations on micelles to any model reflects the dynamic nature of micelles; i.e., restructuring of the surfactant assembly upon polymer binding cannot be disregarded. For that reason, verification of eq 1 with well-defined particles of variable surface charge density is an ongoing objective.

Large spherical or rodlike colloids such as micelles provide systems in which progressive deviations away from the theoretically modeled planar charge surfaces may be experimentally accessed. At the other geometric extreme are the well-established theoretical treatments for polyelectrolytes interacting with small ions, which are typically treated as point charges. The formalism, assumptions, and results are of course quite different for the two cases; in fact, the use of the term "binding" in the context of both small ion–polyelectrolyte interactions and polyelectrolyte–surface interactions is to some extent superficial and misleading. Nevertheless, one may visualize the interaction of polyelectrolytes with oppositely charged colloids whose sizes progress continuously from dimensions nearly as small as those usually ascribed to large multivalent ions to large particles with negligible surface curvature. One extreme corresponds to particles legitimately treated as discrete charges, the other to colloids conventionally treated as surfaces with continuous charge distribution. It is interesting to examine the intermediate particle size range in which one or both approaches may fail.

In this communication we describe preliminary results on complex formation between a cationic polyelectrolyte, poly(dimethyldiallylammonium chloride) (PDMDAAC), and carboxylated dendrimers (CD).[16] Dendrimers are compact, spherical macroions, whose distal functional groups can be synthetically varied, and have most frequently been studied as amine- or carboxyl-terminated macroions. The surface charge density of CD's can be readily varied via the pH; due to the congested state of the distal functional groups, dendrimer expansion upon ionization is rather limited for the "higher generation" compounds. In addition to allowing us to vary colloid surface charge density, these compounds facilitate an examination of the effect of colloid diameter, i.e., surface curvature, on the binding to polyelectrolytes. Turbidimetry is the primary technique used here to detect complex formation, but we have also employed quasi-elastic light scattering and electrophoretic light scattering to confirm the absence

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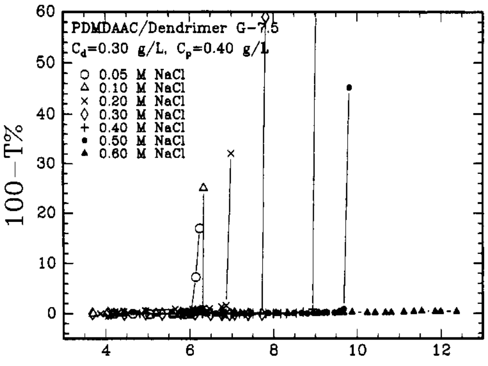

Figure 1. Turbidity of PDMDAAC/G7.5 solution as a function of pH. The concentrations for PDMDAAC (C_p) and the dendrimer (C_d) are 0.40 and 0.30 g/L, respectively.

of complex formation below the critical pH determined turbidimetrically.

Experimental Section. Carboxylated dendrimers were synthesized in a stepwise manner starting from the trifunctional core ammonia by the reiteration of two reactions (Michael addition of methylacrylate followed by amidation of the methyl ester with ethylenediamine). Consequently, the molecular size grows in three dimensions with each additional reaction step (called a "generation"). As a final step, the methyl ester was hydrolyzed in the presence of Na_2CO_3 to generate the sodium carboxylate salt. Two generations, denoted "G7.5(NH_3)" and "G0.5(NH_3)" were used in this study. Purification and isolation of PDMDAAC were carried out in the laboratory of H. Dautzenberg, MPI—Colloid & Interface Science, Teltow, Germany. The polymer was synthesized by free-radical polymerization in aqueous solution to a conversion of 12% using a cationic azo initiator, ultrafiltered through a 30K nominal molecular weight cutoff membrane, and freeze-dried. M_w and M_n were 256K and 170K by light scattering and osmometry, respectively.

Turbidity, reported as 100 − %T, was measured using a Brinkmann PC800 probe colorimeter. Quasi-elastic light scattering (QELS) measurements (reported as apparent hydrodynamic radii, R_h) were carried out with a Brookhaven Instruments system equipped with a 72-channel digital correlator (BI-2030AT) and an Omnichrome air-cooled 200 mW Ar ion laser operating at $\lambda_0 = 488$ nm. Electrophoretic light scattering (ELS) was performed with a DELSA 440 apparatus from Coulter Instrument Co., using a constant current of 4−7 mA. All measurements were carried out at dendrimer concentration of 0.30 g/L and polymer concentration of 0.40 g/L. More details about turbidimetry, QELS, and ELS of such systems can be found elsewhere.[12]

Results and Discussion. Figure 1 shows the turbidity of PDMDAAC/G7.5(NH_3) as a function of pH for varying ionic strengths. Solutions are optically clear up to the point of phase separation, which we designate as pH_ϕ. Since PDMDAAC has no titratable groups, pH_ϕ corresponds to a critical degree of ionization of dendrimer carboxylate groups. To verify that no interaction between dendrimer and polycation takes place prior to pH_ϕ, we carried out limited quasi-elastic and electrophoretic light scattering measurements. The results, shown in Table 1, reveal that at conditions just short of phase separation (e.g., pH 5.89 and $I = 0.10$ M for G7.5), the apparent Stokes radius and the electrophoretic mobility of PDMDAAC are identical in the presence and absence of dendrimer. Evidently, the contribution of free dendrimer to the scattering intensity is negligible at these concentrations. Thus, pH_ϕ corresponds to a microscopic phase boundary, beyond which a bound state appears.

Table 1. Characteristics of Dendrimers, PDMDAAC, and PDMDAAC/Dendrimer Mixtures (0.10 M NaCl)

sample	$M_w \times 10^{-3}$	R_h (nm)[a]	no. of charge groups	U (10^4 cm^2 V^{-1} s^{-1})[b]
CSD G7.5(NH_3)	160	6.0[c]	(−) 768	
CSD G0.5(NH_3)	0.92	0.9[c]	(−) 6	
PDMDAAC	256	15	(+) 1610	2.4
PDMDAAC/G0.5, pH 5.84		14		2.4
PDMDAAC/G0.5, pH 10.73		15		2.4
PDMDAAC/G7.5, pH 5.89		15		2.4

[a] Estimated relative uncertainty ±5%. [b] Estimated relative uncertainty ±10%. [c] From ref 16.

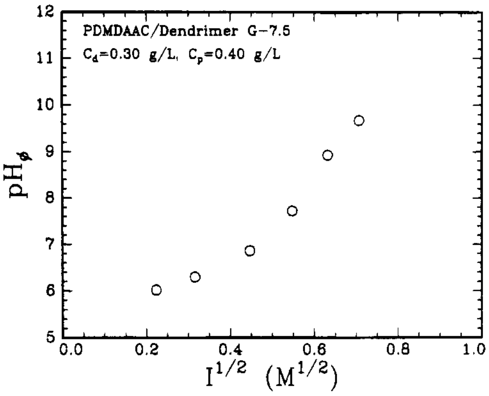

Figure 2. Phase bondary (pH_ϕ vs $I^{1/2}$) for PDMDAAC/G7.5 solution based on the results presented in Figure 1.

It is apparent that polyion binding occurs when the surface charge density σ of G7.5 exceeds some critical value. The electrostatic nature of this interaction is also expressed in the ionic strength dependence of pH_ϕ, shown in Figure 2. This phase boundary may be a reflection of eq 1, but the dependence of σ on pH has not yet been determined. It is likely, however, that carboxylate ionization is nearly complete by pH 10, for which the critical ionic strength is about 0.5 M. Thus, upon further increase of I to 0.60 M, the screening of intermacroionic Coulomb forces suppresses complexation of fully ionized dendrimer, and further increase in pH, even above 12, has no effect.

Figure 3 shows that PDMDAAC does not phase separate with G0.5, regardless of I or pH. The mobility and QELS results in Table 1 suggest that no complexation occurs in these optically clear solutions, since binding of dendrimer to PDMDAAC would be expected to affect U or R_h, even if complexes remained soluble. It is not known at present whether the absence of interaction between PDMDAAC and G0.5 is a consequence of (1) the latter's low net charge (−6 at high pH), (2) its low surface charge density (the mean distance between carboxylate groups decreases with increasing generation number), or (3) its high surface curvature (which reduces the number of polymer configurations which allow the cationic residues proximity with dendrimer carboxylate groups, thus making the binding entropy more unfavorable). In this regard, a comment by Turro et al.[17] is particularly germane: based on photophysical data, they concluded that whereas generations between 3.5 and 9.5 behave as if they had

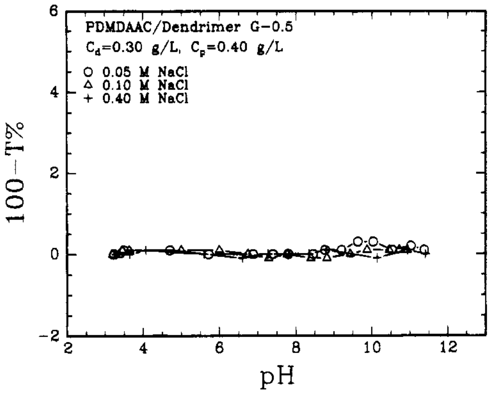

Figure 3. Turbidity of PDMDAAC/G0.5 solution as a function of pH. The concentrations for PDMDAAC (C_p) and the dendrimer (C_d) are 0.40 and 0.30 g/L, respectively.

"closed Stern layer structures", lower generations behave as "simple electrolyte anions". These observations are consistent with the present findings.

The determination of σ_{crit}(pH) and its dependence on ionic strength and generation number will be the subject of a future report, which will also examine the effect of polycation charge density and molecular weight, and the influence—if any—of polymer:dendrimer stoichiometry.

Acknowledgment. This work was supported by Grant DMR9311433 from the National Science Foundation, jointly funded by the Divisions of Materials Research and Chemical Transport Systems. We thank Dr. W. Jaeger of the Fraunhofer Institute for Applied Polymer Research and Dr. H. Dautzenberg of the Max Planck Institute for Colloid and Surface Chemistry, both in Teltow, Germany, for providing the PDMDAAC sample. D.T. acknowledges support from the U.S. Army Chemical Research Development and Engineering Center.

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MA950252Y