Measurements of Cluster Size Distribution for Latex Particles Flocculating in the Presence of Flexible Water-Soluble Polymers

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ABSTRACT: The size distribution of latex particles flocculating in the presence of poly(4-vinylpyridine) was measured by using an automatic particle counter. The distribution and its time evolution were determined as a function of the polymer concentration and the pH of the aqueous suspension. The cluster size distributions $c(g,t)$ are well described at large time by the form $c(g,t) = t^{-2w}\Psi(gt^{-w})$, where the function Ψ does not depend explicitely on time. The first moment of the distribution scales like t^{-w}. The scaling exponent w depends on the polymer concentration. At the polymer concentration where the flocculation efficiency is maximum, w is equal to unity. This simple behavior is interpreted on the basis of generalized Smoluchowski kinetic equations. However, for small and large polymer concentrations, w becomes negative. This point is explained by taking into account the probability of efficient collisions between g and n-fold clusters when electrostatic repulsions and polymer–polymer repulsions are dominant at respectively small and large polymer concentrations.

Introduction

It is well-known that polymers act as efficient flocculants for aqueous dispersions of colloidal particles. Progress in understanding the mode of association of colloids by polymers has been made in the light of recent theories on the structure of flexible polymers at a solid–liquid interface. Adsorbed polymers are viewed as a succession of monomer trains in the attraction zone of the surface with loops which may extend into the solution phase over distances of several hundred angstroms. The flexible loops of one colloid may therefore establish bridges with another colloid. The requisite condition for bridging is that the repulsive free energy, when the loop layers do interpenetrate, is not large, compared to the thermal energy (the repulsive forces originate from the reduction of the number of conformations available to a flexible loop in a good solvent). Bridging is therefore possible only at a low surface monomer density, whereas at high polymer concentrations, stabilization is generally the rule. A vast body of data has been accumulated on the role of thermodynamics and conformations in stabilization and (or) destabilization of polymer/colloid suspensions. For current theories and references, the reader is referred to comprehensive reviews and articles.[1-4] It is true, however, that the structure of a colloidal suspensions in the presence of polymer is a consequence of a complex dynamic evolution. In the present paper, we want to emphasize these dynamical aspects which so far have received little attention. To illustrate this, let us imagine that a large amount of polymer has been added to a suspension so that stabilization of primary particles against flocculation is expected. Nevertheless, the coating of colloids by polymer needs a certain time, because adsorption proceeds at a finite rate.[5,6] When the adsorption rate is not large compared to the time interval characterizing the colloid collisions, then association through polymer bridging occurs in the initial time period. In the final situation, clusters of n primary particles connected by polymer chains and unassociated primary particles protected by a dense polymer layer coexist. In short, flocculation and stabilization are both operative on time scales which depend on polymer and colloid concentrations. This complex interplay of polymer/colloid and colloid/colloid encounters usually results in a flocculation efficiency which as a function of polymer concentration displays a broad variation around a maximum.

In this paper, we present data on the kinetic evolution of the size distribution $c(g,t)$, which gives the number of aggregates containing g associated primary particles at time t. Results are reported for latex particles flocculating in the presence of poly(4-vinylpyridine). The distributions are interpreted by using dynamic scaling arguments in the context of the generalized Smoluchowski kinetic equations. The scaling exponents are interpreted on the basis of the foregoing discussion.

Experimental Section

Materials. (a) Latex Particles. Latex of spherical shape and narrow size distribution was kindly provided through the courtesy of Dr. C. Pichot of the Laboratoire des Matériaux Organiques (Lyon). The latex particles were polymerized under emulsifier-free conditions by using potassium persulfate as free radical initiator.[7] They were converted to the Na^+ form by ion exchange. Dimensions were the following: $\bar{D}_v$ = 840 nm (diameter obtained from quasi-elastic light scattering); $\bar{D}_n$ = 860 nm and $\bar{D}_w$ = 866 nm (both from microscopic determination). The latex as provided differed in the nature of the surface charged chemical groups.

(i) Latex LPS(a). The origin of the charge at the surface of the latex comes from the sulfate surface groups SO_4^-. However, during the polymerization, oxydation of SO_4^- occurs, and during aging, hydrolysis of SO_4^- occurs as well, so that the surface of the latex bears carboxylate COO^- and hydroxyls OH groups. The electrophoretic mobility of the latex was measured in the presence of 10^{-2} M NaCl electrolyte with a Rank Brother Mark II apparatus. In Figure 1, one observes a strong variation of the electrophoretic mobility U vs pH, which indicates the presence of COO^- surface groups.

(ii) Latex LPS(b) was obtained after hydrolysis of latex LPS(a) at 90 °C during 7 days. The electrophoretic mobility (cf. Figure 1) increases steeply around pH 4.

The flocculation experiments were performed at pH 3.5 and pH 3, 2.5 for respectively latex LPS(a) and LPS(b). At these pHs, both latices are negatively charged.

(b) Polymer. Poly(4-vinylpyridine) (P4VP) of average molecular weight $M_w = 3.4 \times 10^5$ was prepared by free-radical polymerization in methanol, using α,α'-azobis(isobutyronitrile) as a free radical initiator. Purification proceeded through precipitation of the reaction mixtures in water. The polymer after redissolution in a 1:1 dioxane/water mixture was freeze-dried and used without fractionation.

Methods. (a) Flocculation Experiments. The latex suspension was ultrasonicated prior to use; flocculation was started by adding to a polymer solution (5 cm^3), adjusted to a fixed pH, a latex suspension (20 cm^3) at identical pH, so that the final composition in latex was 1.6×10^{-2} wt %. As soon as the latex suspension was added to the polymer solution in a 30-cm^3 measuring cylinder, the cylinder was closed and its content mixed by gentle inversion, repeated several times. The dispersion was then allowed to stand at a temperature of 18 °C. A number of

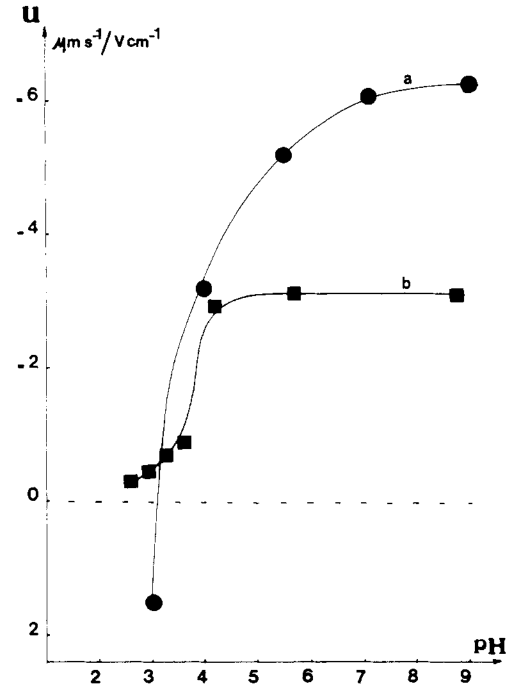

Figure 1. Electrophoretic mobility at latex LPS(a) and LPS(b) as a function of pH.

Table I
Polymer Concentration C_p and pH Used in Flocculation Experiments with 1.6×10^{-4} g of Latex per mL of Suspension

latex type	pH	10^4C_p, g/g^a			
LPS(a)	3.5	5.0	10	12.5	17.5
LPS(b)	3.0	0.7	1.4	3.5	4.9
		7.0	9.0	12	14
LPS(b)	2.5	0.3	0.7	2.1	3.5
		4.9	9.0	12	14

[a] The concentration is expressed in grams of polymer per grams of latex.

runs, differing in polymer concentration and pH, with fixed latex concentration of 1.6×10^{-2} wt %, are reported in Table I.

(b) Size Distribution Determination. Small samples of approximately 1 mL of suspension were removed at intervals with a 3-mm-bore needle at a slow rate corresponding to a shear of 10 s^{-1}, diluted 10^2 times with a 0.15 M NaCl aqueous solution, and analyzed by the Coulter technique to obtain the size distribution $c(g,t)$ of aggregates comprising a number g of associated primary particle at time t. The 16-channel TA II Coulter with a variable-threshold adapter and an orifice of 50 μm gives an experimentally observed distribution of pulse heights stored within each channel. The amplitude of the voltage change produced by the passage of a cluster through the pore is proportional to the number of particles in the cluster. All technical information concerning the determination of the curve $c(g,t)$ from the pulse distribution are presented in a recent paper.[8] Two points need some additional comments: in all out experiments, latex was allowed to flocculate in the presence of polymer without added electrolyte. Nevertheless, analysis was done on a sample diluted 100-fold in 0.15 M NaCl aqueous solution (electrolyte is needed to increase the conductivity of the pore liquid). Modification of the aggregation number in the presence of electrolyte is unlikely for at least two reasons. First, electrostatic repulsions among primary particles in a floc are screened in the presence of salt; second, the solvent quality for P4VP decreases in the presence of salt. Both effects should enhance the floc stability. The shear rate in the needled was 10 s^{-1}. The influence of the shear rate was tested in performing the sampling in a systematic way at lower shear rates. Since no difference in the cumulative distribution function could be detected at lower shear rates, the possibility of damage to the aggregates and/or shear induced coagulation was excluded, and all sampling was done at a shear rate of 10 s^{-1}.

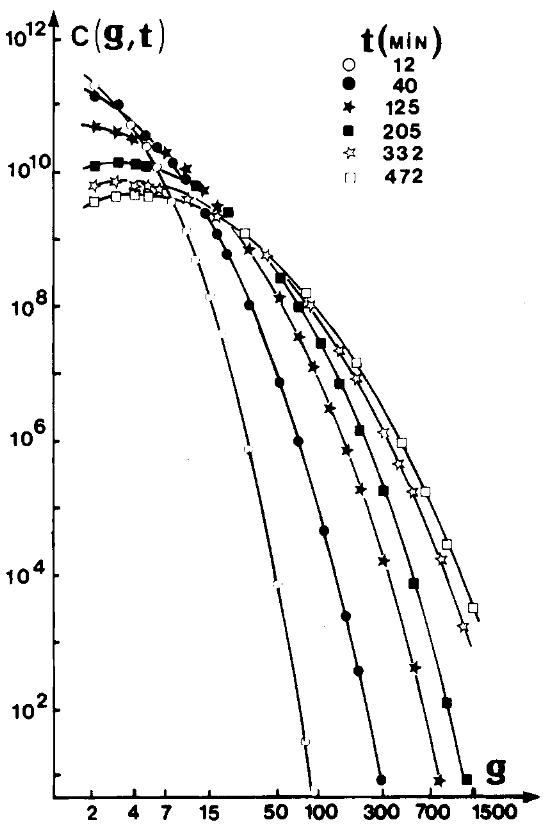

Figure 2. Particles size distribution for LPS(a), pH 3.5, at different times.

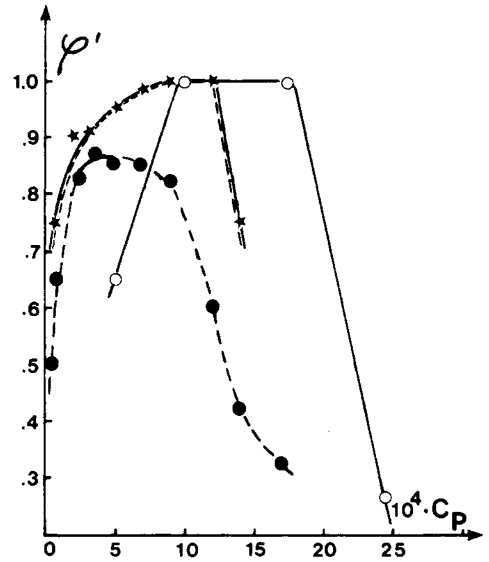

Figure 3. Volume fraction Φ' of associated particles as a function of polymer concentration at a flocculation time of 400 min: (○) LPS(a) at pH 3.5; (★) LPS(b) at pH 3.0; (●) LPS(b) at pH 2.5.

Results

Typical curves showing the time evolution of the distribution function $c(g,t)$ for latex LPS(a) at pH 3.5 and polymer concentration $C_p = 1.25 \times 10^{-3}$ are reported in Figure 2. Here, $c(g,t)$ is the number of clusters, comprising g associated primary particles, per gram of total colloid. The time interval is 12–470 min. The distribution broadens with time and a maximum appears at large time. After 472 min, the number of 2-fold particles has decreased from 1.7×10^{11} (recorded at 12 min) to 3.6×10^9. The large decrease in the concentration of small clusters increases their mean-free path and hence their association rate with clusters of any size is reduced. On the other hand, the large clusters have a reduced Brownian mobility and their contribution to the aggregation process is not rate controlling. At large time, the total number of clusters does therefore not change much with time. In Figure 3 is reported the fraction Φ' of flocculated latex as a function of polymer concentration for different systems and at a time of 400 min. Φ' is defined as follow:

$$\Phi' = \sum_{g=2}^{\infty} gc(g,t) / \sum_{g=1}^{\infty} gc(g,t)$$

All curves in Figure 3 display the typical shape of flocculation efficiency with polymer concentration which is usually recorded in the case of macroscopic phase separation by mass determination of sediment or by the determination of the optical density of the supernatant.[9-11] In each case, the maximum is broad; $\Phi'_{\max} = 1$ for latex LPS(a) and LPS(b) for polymer concentrations in the range $(10-17) \times 10^{-4}$ g/g and $(9-12) \times 10^{-4}$ g/g at pH 3.5 and 3.0, respectively. For PS(b), $\Phi'_{\max}$ is approximately 0.86 at pH 2.5 for that situation 14% primary unassociated particles are still present in the suspension.

Theory

The analysis of the time evolution of colloids flocculating through Brownian collisions in the presence of "excess" electrolyte (which ensures a regime of strong aggregation) was made several years ago by Friedlander and Lushnikov.[12-14] Smoluchowski's kinetic equations were used in their integro-differential form:

$$\partial c(g,t)/\partial t = \int_0^g K(g-n,n)c(g-n,t)c(n,t)\,\mathrm{d}n - 2c(g,t)\int_0^\infty c(n,t)K(g,n)\,\mathrm{d}n \quad (1)$$

The right-hand side first term represents the increase in g-fold particules due to collision between $g - n$ and n-fold particles, while the second term represents the decrease of g-fold particles due to collisions between g-fold and any sized particles. The kernel $K(g,n)$ is the collision frequency. It has been shown that eq 1 is invariant under the following scaling transformation:

$$c\left(\frac{g}{g_0},t\right) = g_0^{\,2}c(g,g_0^{\,1-\lambda}t) \quad (2)$$

provided that K is a homogeneous function of degree λ; then $c(g,t)$ can be represented in terms of a universal time invariant function:

$$c(g,t) = t^{-2/(1-\lambda)}\psi[gt^{-1/(1-\lambda)}] \quad (3)$$

$$N(t) \sim t^{-1/(1-\lambda)} \quad (4)$$

$N(t)$ is the moment of order zero of the distribution, i.e.

$$N(t) = \int_0^\infty c(g,t)\,\mathrm{d}g \quad (5)$$

Equation 1 has also been solved numerically, and it was shown that eq 3, the "self-preserving" spectrum, applies well after a sufficiently long time lag.[14,15] Equations 3 and 4 were also derived on the bases on Monte Carlo simulations,[16-18] and the long-time behavior of $c(g,t)$ was found to scale like

$$c(g,t) \sim t^{-w}g^{-\tau}f(g/t^z) \quad (6)$$

For diffusion coefficients of the form $D_g \sim g^\gamma$ with $\gamma < 0$, τ is zero[19] and the forms (3) and (6) are therefore similar with $w = 2z$ and $w = 2(1-\lambda)^{-1}$. By simulations, it was also shown, that the mean field eq 1, in which concentration fluctuations are neglected, as well as eq 7, is appropriate.[20]

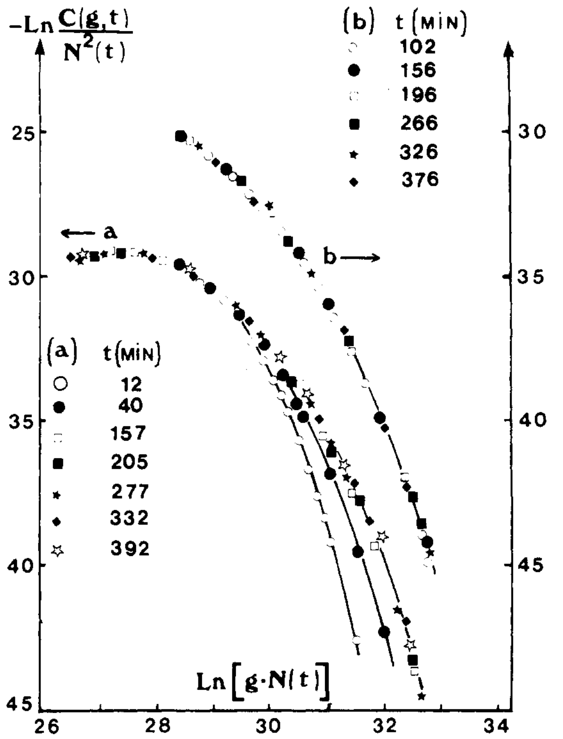

Figure 4. Size distribution represented according to eq 3 and 4 for LPS(a), pH 3.5: (a) $C_p = 12.5 \times 10^{-4}$ g; (b) $C_p = 5 \times 10^{-4}$ g.

The scaling theory was derived to explain the coagulation kinetics of Brownian particles in the presence of electrolyte; it is a priori not obvious that this theory can as well explain the flocculation kinetics of Brownian particles occurring through the presence of polymers. It appears, however, that the shapes of our experimental distribution and the shapes of the distributions derived numerically for Brownian coagulation in the presence of electrolytes are strikingly similar[15] (compare Figure 2 here and Figure 5 of ref 15) and an attempt to apply the theory to our results seems reasonable.

In Figures 4–6, we show ln $[c(g,t)/N^2(t)]$ as a function of ln $[gN(t)]$ for the different situations investigated. All data, after a certain time period, fall on a single curve as predicted by the theory. The dependence of ln $[N(t)]$ on ln t is represented in Figures 7–9. After a time period which is of the order of 30 min for LPS(a) and somewhat larger for LPS(b) at pH 3 and 2.5, the data can be fitted by straight lines. The linear regime appears at the time at which the asymptotic size distribution in terms of the reduced variable $gN(t)$ applies. At small time, the size distribution cannot be represented by a continuous function, nor can Smoluchowski's equation be expressed by the integro-differential form (1); therefore, the scaling argument (2) is not valid at small time.

Discussion

In Table II, we have reported the values of λ calculated from the slope of the straight lines at large time in Figures 7–9 using eq 4. The volume fractions Φ' taken from the data of Figure 2 are reported in the third column; when Φ' is near or equal to unity, which is for a polymer concentration corresponding to a maximum flocculation efficiency, λ becomes zero (a difference of ±5% is not significant on account of the experimental precision). In the following we shall discuss this remarkable result.

The collision frequency $K(g,n)$ can be expressed as

$$K(g,n) = \frac{kT}{3\eta}(R_g + R_n)(D_g + D_n) \quad (7)$$

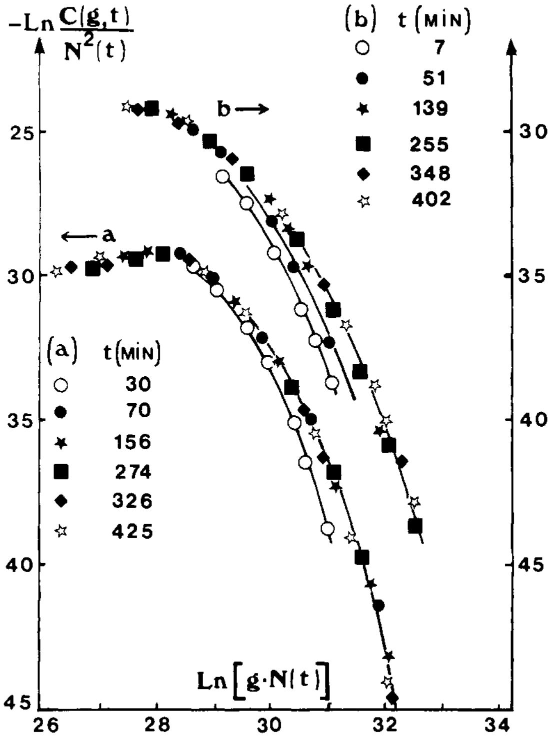

Figure 5. Size distribution represented according to eq 3 and 4 for LPS(b), pH 3: (a) $C_p = 9 \times 10^{-4}$ g; (b) $C_p = 1.4 \times 10^{-4}$ g.

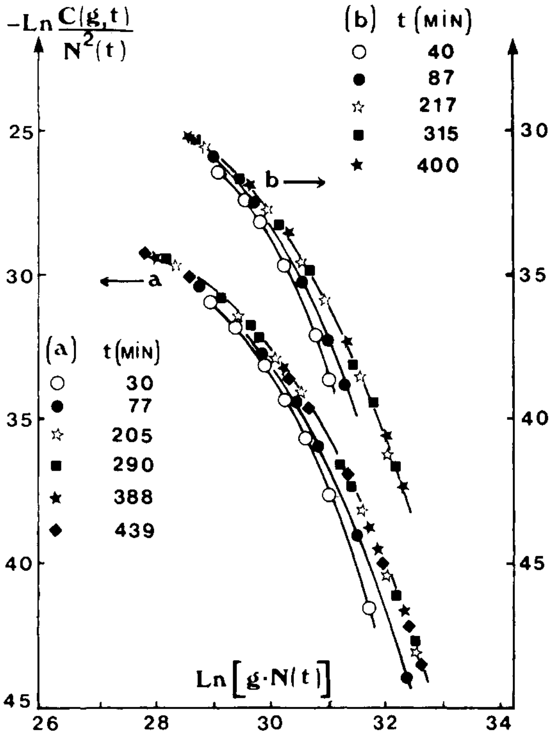

Figure 6. Size distribution represented according to eq 3 and 4 for LPS(b), pH 2.5: (a) $C_p = 3.5 \times 10^{-4}$ g; (b) $C_p = 12 \times 10^{-4}$ g.

R_g, R_n and D_g, D_n are respectively the radius of gyration and the diffusion coefficients of clusters composed of g and n primary particules; η is the solvent viscosity. If R_η scales like a power ν of g, i.e., $R_g \sim g^\nu$ (for large clusters, $\nu = 1/D$, D being the Hausdorf dimension of clusters which have a fractal self-similar geometry. From Monte Carlo simulations, D was found equal to 1.75–1.80 for three-dimensional cluster–cluster aggregations[21,22]). If furthermore $D_g \sim g^\gamma$, then

$$\lambda = \nu + \gamma \qquad (8)$$

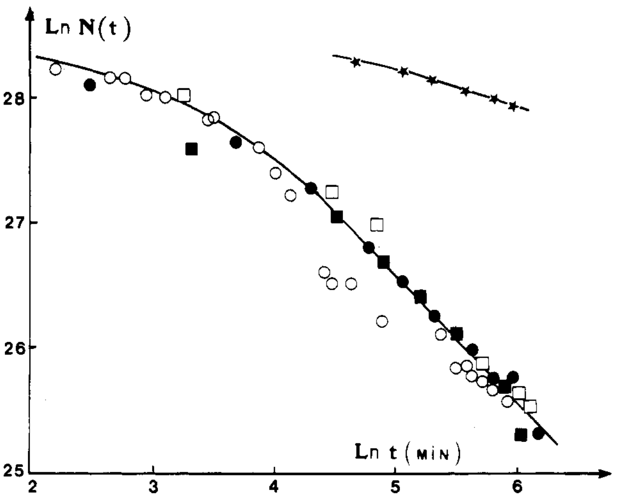

Figure 7. Total number of clusters represented as a function of time t for LPS(a) at pH 3.5 and different polymer concentrations: (★) $C_p = 5 \times 10^{-4}$ g; (□), (●), (■) polymer concentrations 10^{-3} g, 12.5×10^{-4} g, and 17.5×10^{-4} g, respectively; (○) flocculation of LPS(a) in the presence of 0.15 M NaCl at pH 3.5.

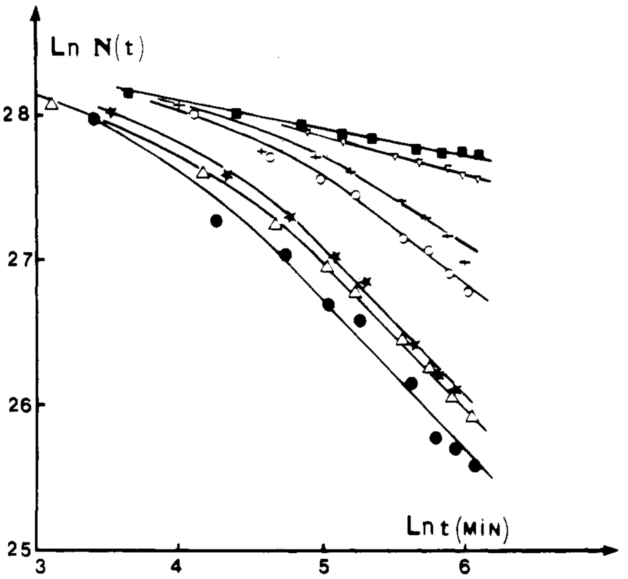

Figure 8. Total number of clusters represented as a function of time t for LPS(b) at pH 3.0 and different polymer concentrations: (▽), (+), (○), (△), (●), (★), (■) polymer concentrations 0.7×10^{-4} g, 3.5×10^{-4} g, 4.9×10^{-4} g, 7×10^{-4} g, 9×10^{-4} g, 12×10^{-4} g, and 14×10^{-4} g, respectively.

Table II
Exponents Characterizing the Cluster Size Distributions

colloid	10^4C_p, g	Φ′	−λ
LPS(a), pH 3.5	5	0.65	4.5
	10	~1	~0
	12.5	~1	~0
	17.5	~1	~0
LPS(b), pH 3.0	0.7	0.75	2.8
	3.5	0.91	0.58
	4.9	0.95	0.33
	7.0	0.99	~0
	9.0	~1	~0
	12	~1	~0
	14	0.75	4.26
LPS(b), pH 2.5	0.3	0.50	3.5
	0.7	0.65	2.5
	2.1	0.83	1.0
	3.5	0.87	0.88
	4.9	0.85	1.0
	9.0	0.82	1.0
	12	0.60	2.6
	14	0.40	5.7

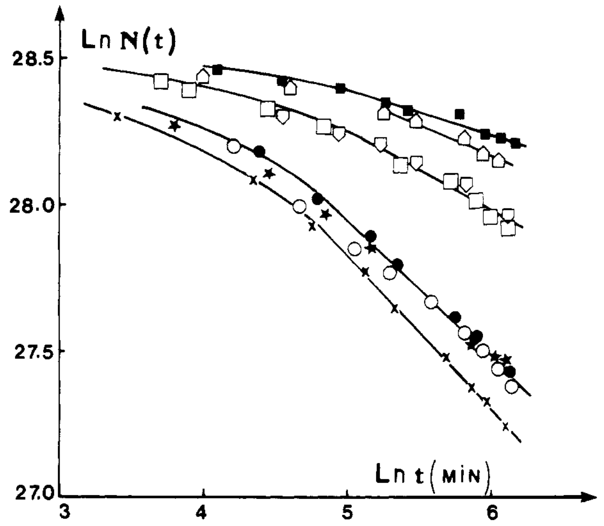

Figure 9. Total number of clusters represented as a function of time t for LPS(b) at pH 2.5 and different polymer concentrations: (⬠), (⭔), (★), (×), (○), (●), (□), (■) polymer concentrations 0.3×10^{-4} g, 0.7×10^{-4} g, 2.1×10^{-4} g, 3.5×10^{-4} g, 12×10^{-4} g, and 14×10^{-4} g, respectively.

If $\nu = -\gamma$, the diffusion coefficient is inversely proportional to the radius of the particle and $\lambda = 0$. This simple behavior was indeed found previously for the coagulation of latex PS(a) by addition of electrolyte.[8] The variation of $N(t)$ with time of latex LPS(a) flocculated at pH 3.5 by the addition of 0.15 M NaCl are reported in Figure 7. In the limit of experimental precision, the time evolution of $N(t)$ is seen to be identical in the presence of polymer at a concentration corresponding to $\Phi' = 1$ and in the presence of electrolyte. This property is explained on the basis of electrophoretic measurements (not reported here) of latex particles LPS(a) as a function of polymer concentration. The mobility was found to be zero at $C_p = 10^{-4}$ g, which signifies that the colloid plus adsorbed polymer complex is electroneutral and the flocculation for that specific situation is induced by charge neutralization and/or mosaic interaction[9,10] (at pH 3.5, P4VP has approximately 10% of its pyridinium group in the NH^+ form; ion pairing between NH^+ and COO^- or SO_4^- groups is expected[23]). If for polymer concentrations corresponding to a maximum flocculation efficiency a classical DLVO-type mechanism can be invoked in the case of LPS(a) at pH 3.5, it should not be so at higher polymer concentration. Indeed, for $C_p > 1.7 \times 10^{-3}$ g, the electrophoretic mobility becomes negative, which in turn signifies that the net charge of the latex + polymer complex has a positive sign. Clearly, when the adsorption amount exceeds the amount which corresponds to a stoichiometric ion-pairing, large positively charged polymer loops do develop at the colloid surface. Flocculation is then induced by the classical bridging mechanism and at still higher polymer concentrations, the steric stabilization effect sets in with a concomitant decrease in flocculation efficiency as seen in Figure 2. The relation $D_g \simeq R_g^{-1}$ is specific to a process, which we would qualify as "normal". To explain the negative values of λ for $\Phi' < 1$, we must reconsider the significance of eq 7.

(i) Contrary to the exponent ν, the exponent γ could approach its asymptotic limit only at a large g value;[24] so that for sizes below that g value, γ would be a function of the particles sizes and $D_g + D_n$ should be expressed as

$$D_g + D_n \sim g^{\gamma(g)} + n^{\gamma(n)} \tag{9}$$

However, from the data reported in Figure 3 we infer that at any time, a large amount of small particles are still present in the suspension (approximately 38% of particles are of dimension $g < 15$, at $t = 470$ min). Since λ is zero, we must conclude that the Stokes radius is inversely proportional to the radius of gyration even for very small association numbers.

(ii) For $\Phi' < 1$, the structure of the polymer surface layer is in fact not well adapted for "easy" colloid–colloid binding. This can be understood in the following way: when two colloids approach each other, the probability of binding is proportional to a Boltzmann factor:

$$p \sim \int_0^L \exp[-(\Delta G_e(x) + \Delta G_p(x))/kT]\, dx \tag{10}$$

$\Delta G_e(x)$ is the electrostatic free-energy of two charged colloids at distance x, whereas $\Delta G_p(x)$ represents the free-energy of polymer–polymer interactions when two polymer diffuse layers interpenetrate; binding is expected for $x < L$, L being the polymer diffuse layer thickness. At low polymer concentrations, the polymer adopts a flat conformation, and consequently $\Delta G_p \ll kT$; we have, however, also $L \ll \kappa^{-1}$ (κ^{-1} being the electrical double layer thickness); therefore, $\Delta G_e \gg kT$. On the other hand, at large polymer concentrations, $\Delta G_p \gg kT$. For both situations, we expect $p \ll 1$; there is, however, an intermediate concentration with an optimum layer thickness L which corresponds to a maximum in flocculation. Correcting $K(g,n)$ for $\Phi' < 1$ by an appropriate probability factor $p(g,n)$ we obtain

$$K(g,n) \sim (g^\nu + n^\nu)(g^\gamma + n^\gamma)p(g,n) \tag{11}$$

To keep $K(g,n)$ a homogeneous function, $p(g,n)$ should be of the form $(gn)^\alpha$ or $(g^\alpha)(n)^{\alpha'}$, with $\alpha < 0$ or $\alpha + \alpha' < 0$. This form implies that the binding probability decreases with the association degree. To progress further, we should consider various models which are in the line of a size-dependent sticking probability. Recently preliminary results on computer simulations on cluster–cluster aggregation by polymers were published by Jullien et al.[25] The model was restricted to two dimensions and excluded-volume effects were ignored. A fractal dimension of $D \simeq 1.7$ was found in the presence of polymer, but the authors have not computed the size distribution, nor its kinetic evolution. Needless to say that any realistic modeling requires a great number of parameters. Most of them are at present the stage not included in the theory. For instance, in addition to excluded-volume effects the effect of structural rearrangements which might be particularly important in the presence of polymers must be considered.

Conclusion

The present experiments provide a detailed measurements of the cluster size distribution of colloids in the presence of polymers. The results were discussed in terms of an asymptotic distribution function of reduced variables. All results could be described in terms of one scaling exponent which has a simple interpretation at maximum flocculation. In the regime of low and large polymer concentration where respectively electrostatic repulsions among colloids and polymer–polymer interactions are particularly important, the parameter λ is concentration dependent. Further experimental data on diffusivity and cluster dimensions are necessary to explain via realistic aggregation models this behavior.

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Quantitative Prediction of α in the Scaling Law for Self-Diffusion†

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ABSTRACT: The Kirkwood–Riseman picture of interacting polymer beads is used to calculate the parameter α of the universal scaling law $D_s = D_0 \exp(\alpha c^{\upsilon})$ for polymer self-diffusion. The previously predicted (Phillies, G. D. J. *Macromolecules* 1987, *20*, 558) behavior $\alpha \sim M^{-1}$, M being the polymer molecular weight, is confirmed. In contrast to previous work, the numerical prefactor of α is here obtained. For $M = 1.0 \times 10^6$ polystyrene in a good solvent, $\alpha = -2$, within calculational uncertainty of the experimental $\alpha = -0.7$ for this M. An extension of the universal scaling law to rotational diffusion is presented.

Introduction

The dependence of the self-diffusion coefficient D_s of random-coil polymers in good solvents upon polymer molecular weight M and concentration c has for the past decade been a topic of intense experimental and theoretial investigation.[1,2] Motivated by my laboratory's experimental studies[3] on the diffusion of spherical probe particles through polymer and protein solutions, I recently advanced a simple scaling law[4]

$$D_s = D_0 \exp(\alpha c^{\upsilon}) \qquad (1)$$

for D_s. Comparison[4] of the scaling law with the entirety of the then-available literature found eq 1 to be valid in every case, including good solvent systems of long polymers at semidilute and dilute concentrations, short polymers ($M <$ the critical molecular weight M_e for entanglement) at all concentrations, protein solutions, and polymers in θ solvents. For random-coil polymers in good solvents, D_0, α, and υ were all found to have simple correlations with M. More recently, a derivation of eq 1, based on the dominance of hydrodynamic forces over polymer entanglements, was obtained.[5] The derivation predicted the functional form of eq 1, numerical values for υ, and the M dependence of α, all of which were in good agreement with experiment.

A significant limitation of ref 5 is that it did not predict the numerical value of α, only its M dependence. This limitation is here removed, using a bead-spring picture of polymer chains to compute α. In a natural extension, the model is used to treat the rotational diffusion coefficient D_r of interacting polymer coils, including relations between D_r, c, and M.

Computation of α for Translational Diffusion

In this paper we discuss treatment of polymer chains in good solvents, using a refinement of the general dynamic model of Kirkwood and Riseman.[6] In this model, a polymer chain is represented as a sequence of N beads of radius a_0, the beads being separated by rigid or semirigid couplings ("springs"), which constrain the probable equilibrium configurations of the polymer beads. Bead–bead interactions include the following: (i) the rigid couplings (bonds) between adjoining monomers; (ii) hard-core "excluded volume" interactions, which prevent the beads from overlapping, thereby ensuring that chains cannot come closer to each other than a distance $2\alpha_0$ (in the original paper of Kirkwood and Riseman,[6] which only required $\langle r_{ij}^{-n} \rangle$ for $n = 1$, excluded volume interactions were not critical; with $n > 1$ (as arises here) such interactions will need to be treated explicitly); (iii) hydrodynamic interactions, which describe the wake set up by a polymer molecule acted on by an external force, and also the correlations between the random Brownian forces on different polymer beads. A moving bead, with velocity $\mathbf{v}_r$ relative to the solvent, applies a force $6\pi\eta\alpha\mathbf{v}_r$ on the solvent. The response of the solvent—a hydrodynamic interaction between a pair of beads—can be described by the Rotne–Prager hydrodynamic interaction tensor[7]

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