Colloid Polym Sci 273:1071–1079 (1995)
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ORIGINAL CONTRIBUTION

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Coagulation and flocculation measurements by photon correlation spectroscopy – colloidal SiO_2 bare and covered by polyethylene oxide

Received: 23 February 1995
Accepted: 7 July 1995

Dedicated to Prof. Dr. Joachim Klein on the occasion of his 60th birthday

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Abstract With photon correlation spectrometry (PCS) the diffusion coefficients, average diameters and polydispersities of colloidal particles can be determined in dilute aqueous suspensions. In this study PCS is used to follow the coagulation and flocculation of silica particles. Electrolyte solution added to suspensions of bare particles and of particles covered with adsorbed polyethylene oxide layers induces aggregation. The rate constants of aggregation are evaluated by the second-order Smoluchowski theory with the assumptions of spherical aggregated particles and volume proportional light-scattering amplitude. Adsorbed PEO layers of molar mass lower than $M_w = 160\,000$ decrease the critical flocculation concentration and the flocculation states and rate constants for bare and covered particles are the same at high electrolyte concentrations. Polymer layers of high molar mass ($M_w = 325\,000, 900\,000$) reduce at full coverage the rate constants and stabilize the suspensions even at high electrolyte concentrations. At low coverage adsorption of high molar mass polymers results in the same values as of low molar mass PEO. The correlation between rate constants and hydrodynamic PEO layer thicknesses demonstrates the steric influence of the tails of the adsorbed macromolecules on stability and flocculation.

Key words Photon correlation spectrometry – colloidal silica – polyethylene oxide adsorption – flocculation – stabilization

Introduction

The regulation of the stability of dispersed particles by adsorbed polymer and polyelectrolyte layers is of high scientific and technological significance [1]. The influence of the adsorbed macromolecules upon stabilization and flocculation depends mainly on their conformation in the adsorbed state. The segment density profile and especially the extension of the adsorbed layer into the solution plays a decisive role for steric stabilization. The effective hydrodynamic layer thickness is markedly influenced by the outer segments of the segment density profile. Therefore, the most promising methods to obtain informations on those layer extensions are hydrodynamic methods like diffusion, sedimentation, and electrophoresis. By photon correlation spectrometry (PCS) the diffusion coefficients of the colloidal particles suspended in water can be measured. The effective hydrodynamic particle diameters are obtained by the Stokes–Einstein equation. From the diameters of bare and polymer covered particles the hydrodynamic layer thicknesses can be calculated [2–4, 6].

In this article, we demonstrate that PCS is also suited to follow the aggregation of blanc and polymer-covered particles in suspension. The term coagulation is used for aggregation without polymer, flocculation designates the

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aggregation in presence of adsorbed polymer layers. State and kinetics of aggregation can be characterized by the time-dependent average diffusion coefficient and its distribution. The silica particles are well characterized, polar, negatively charged colloids with low polydispersity in particle size distribution, which can be used as model systems for the flocculation by uncharged polyethylene oxide, PEO, soluble in water and organic solvents. Especially, correlations to the extensively studied adsorption behavior can be achieved. PEO is used as stabilizer and flocculant in many industrial applications [40].

Experimental

Colloidal silica particles

Precipitated amorphous silica particles were prepared according to the method of Stöber et al. [5] by hydrolysis of ortho silic acid with ammonia-water solutions in ethanol. The diameters of the relatively spherical particles can be regulated by ammonia concentration and by temperature. After precipitation the particles were purified by twice centrifugation, washing and boiling in doubly distilled water in order to extract residues of organic ester and alcohol. Finally, they were dried at 150 °C. The samples are redispersed in water by ultrasonic treatment. The flocculation measurements reported in this article were carried out at pH ~ 6.3 with silica samples characterized in Table 1 [3].

Polyethylene oxides

The polyethylene oxides (PEO) were produced by Toyo Soda (Polymer Laboratories, Ltd. Shrewsbury, U.K.). They have narrow distributions in molar mass ($M_w/M_n < 1.1$) and are identical with those used in ref. [2]. Five PEO-samples in the range $2.7\ 10^4 < M_w < 9\ 10^5$ were selected for the flocculation measurements.

Table 1 Characterization of the silica samples

	Si 119	Si 138	Si 209
PCS:			
D_{90} [m^2/s]	$5.41\ 10^{-12}$	$4.33\ 10^{-12}$	$2.41\ 10^{-12}$
D_0 [m^2/s]	$4.13\ 10^{-12}$	$3.55\ 10^{-12}$	$2.34\ 10^{-12}$
d_{90} [nm]	90.7	113.3	203.6
d_0 [nm]	118.7	138.2	209.0
σ^2 [%]	20.8	11.4	3.8

D_{90}, D_0 = Diffusion coefficient at 90° and extrapolated to 0°, d_{90}, d_0 = Particle diameters calculated with Stokes–Einstein, σ^2 = Normalized variance of the D-distribution.

Earlier measurements

Depletion experiments have been accomplished to measure the amounts of the polymer adsorbed from solution [6]. Hydrodynamic thicknesses have been obtained from PCS and sedimentation measurements [2–4]. Orthokinetic flocculation of pyrogenic and precipitated silica with PEO has already been measured with a laser photo sedimentometer and by rheometry [6–9].

Photon correlation spectrometry (PCS)

The PCS-measurements were performed at 25 °C using an autocorrelator 4700 (Fa. Malvern Instruments, Spring Lane, Worchestershire, England) with an Argon-ion-laser (Model 2016, Spectra Physics, 2 Watt) at 514.4 nm. The PEO- and NaCl-solutions and the silica dispersions were prepared with bidistilled and thoroughly filtered water (Sterivex GS, 0.22 μm filter unit, Fa. Millipore). The adsorption process occurs undisturbed by flocculation when aqueous solutions of different PEO concentrations are added to the silica/water suspensions. After an adequate equilibration time the hydrodynamic diameters of the bare and PEO-covered silica samples are measured by PCS. Subsequent addition of NaCl-solution starts the flocculation process.

Theoretical Background

The auto correlation functions $g^2(K, \tau^*)$ were measured at different aggregation times and evaluated by the moment method of Koppel [10, 11]:

$$g^1(K,\tau^*) = \int_0^\infty B(\Gamma)\, e^{-\Gamma\tau^*} d\Gamma;$$

$$g^2(K,\tau^*) = 1 + \gamma |g^1(K,\tau^*)|^2 \tag{1}$$

$$\ln((g^2(K,\tau^*) - 1)^{1/2}) = \ln(\gamma^{1/2}) - \bar{\Gamma}\tau^* + \mu_2\tau^{*2}/2! - \mu_3\tau^{*3}/3! + \cdots \tag{2}$$

$B(\Gamma)$ = scattering contribution of particles with line width Γ, τ^* = correlation time, γ = fitting parameter, $K = (4\pi n \sin(\theta/2))/\lambda_0$, λ_0 = wave length in vacuum, θ = scattering angle, n = refractive index, $\Gamma = D\ K^2$ = line width, $\bar{\Gamma} = -\bar{D}K^2$, $\bar{\Gamma}$ = average line width.

The moments are defined by

$$\bar{\Gamma} = \int_0^\infty B(\Gamma)\, d\Gamma \tag{3}$$

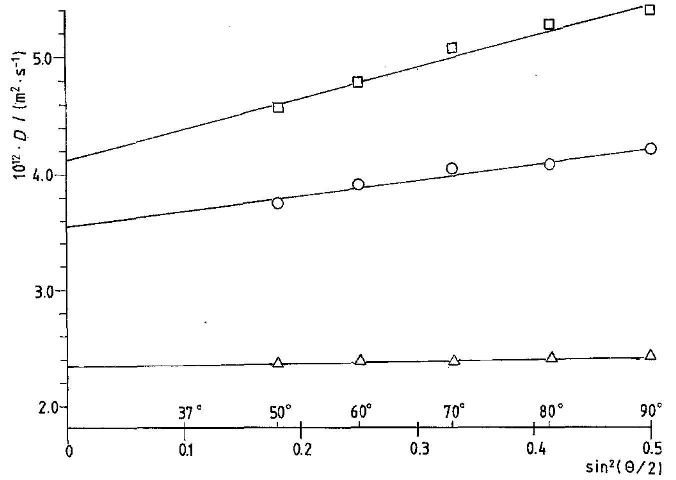

Fig. 1 Dependence of the diffusion coefficient, D, on scattering angle, Θ; H_2O, $T = 25\,°C$; $c_{Si} = 2\,10^{-5}$ g cm^{-3}; □ silica 119, ○ silica 138, △ silica 209

$$\mu_i = \int_0^\infty B(\Gamma)\,(\Gamma - \bar{\Gamma})^i\,d\Gamma \quad \text{for } i = 2, 3, \cdots \tag{4}$$

$$\mu_2/\bar{\Gamma}^2 = (\overline{D^2} - (\bar{D})^2)/(\bar{D})^2 = \sigma^2. \tag{5}$$

The first moment $\bar{\Gamma}$ (Eq. (3)) corresponds to the average diffusion coefficient $\bar{D}$, the second moment, μ_2, (Eq. (5)) to the polydispersity of the sample (normalized variance σ^2).

For large particles of a polydisperse sample the angular dependence of the scattering function $P(K, m)$ has to be considered and scattering contributions of all particle sizes have to be summarized, and for $\bar{D}$ results:

$$\bar{D} = \frac{\int_0^\infty N m^2\ P(K, m)\,D\,dD}{\int_0^\infty N m^2\ P(K, m)\,dD}\,. \tag{6}$$

The correlation function and the average diffusion coefficient become angle dependent. With $\bar{D} = k_B T/(6\pi\eta\bar{a})$ the average radii $\bar{a} = a_{6,\,5}$ (sixth over fifth moment) of spherical particles are calculated. In Fig. 1 the angle dependence of the diffusion-coefficients of different sized silica particles is demonstrated. The increasing angle dependence of the D-values with decreasing particle size is produced by the larger size distribution of the small particles. This conclusion is confirmed by the corresponding increase of the polydispersity of the samples (normalized variance σ^2 in Table 1). Influences of particle interactions can be excluded because the measured diffusion coefficients are independent of the particle concentration up to 10^{-3} g cm^{-3} [3].

Kinetics of aggregation

From the time dependence of the average diffusion coefficient the rate constant of coagulation or flocculation has to be determined. Based on the Smoluchowski theory [12, 13] for rapid aggregation and on a paper of Pusey [14] about the influence of polydispersity on the average diffusion coefficient, Versmold and Härtl [15] developed an evaluation procedure assuming the existence of spherical particles for the whole aggregation process. This is a valid approximation in the beginning of aggregation.

The average diffusion coefficient from PCS is defined [14] as:

$$\bar{D}(t) = \frac{\sum_p n_p(t) f_p^2 D_p}{\sum_p n_p(t) f_p^2} \tag{7}$$

$n_p(t), f_p, D_p$ = Number, scattering amplitude, diffusion coefficient of particles of aggregation p.

With V_1 = volume of the original particle, V_p = volume of species p, a_p = radius of species p and $f_p \sim V_p \sim pV_1 \sim a_p^3$, $D_p = k_B T/(6\pi\eta a_p)$ results:

$$\bar{D}(t) = \frac{k_B\,T\,\overline{a^5}(t)}{6\pi\eta\,\overline{a^6}(t)} = \bar{D}_0 \frac{\overline{p^{5/3}}(t)}{\overline{p^{6/3}}(t)}\,. \tag{8}$$

The corresponding moments of p can be calculated from

$$\overline{p^{n/3}}(t) = \sum_{p=1}^{r} p^{n/3} n_p(t)/n_0 \quad \text{within } n = 5, 6 \tag{9}$$

and from the equation of Smoluchowski [12, 13] with $t' = t/\tau$

$$n_p(t') = n_0 t'^{(p-1)} (1 + t')^{-(p+1)} \quad p = 1, 2, 3, \ldots, r \tag{10}$$

and introduced in Eq. (8).

A suitable half-time τ is assumed and the calculated theoretical average diffusion coefficients $\bar{D}$ are compared with the measured values. The curves are fitted by an iteration procedure. From the iterated optimal τ value the rate constant k of the second order aggregation process is obtained with $k = 1/\tau n_0$ (n_0 = particle concentration [particle m^{-3}] at the beginning). An example of a good quality fit is demonstrated in Fig. 2, showing the measured and calculated quotients D_{rel} of the average diffusion coefficients in dependence of flocculation time t.

Experimental results

State of aggregation

The measured diffusion coefficients after an aggregation time of 40 min were selected in order to compare the state

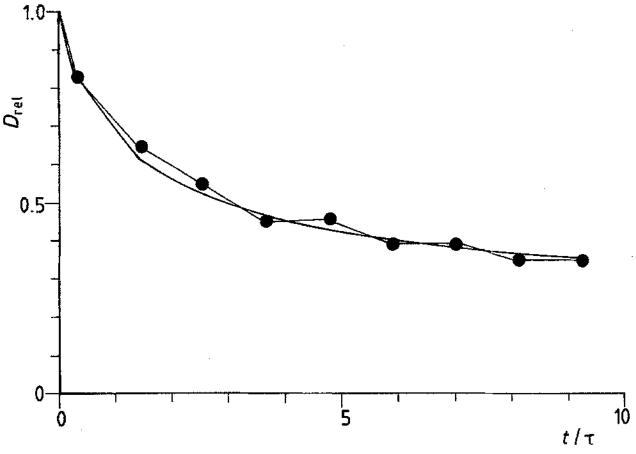

Fig. 2 Dependence of the relative diffusion coefficient, D_{rel}, on relative time, t/τ; silica 138, $c_{Si} = 2\,10^{-6}$ g/cm^3, 0.1 n NaCl, ● measured values, —— theoretical fitted curve, $\tau = 208$ sec, $k = 4.1\,10^{-18}$ m^3 (s particle)$^{-1}$

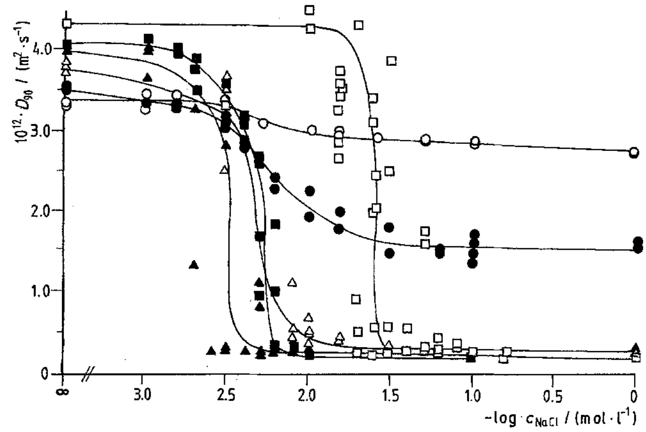

Fig. 3 Dependence of the diffusion coefficient, D_{90}, on c_{NaCl} after $t = 40$ min; silica 138 bare and covered with PEO of different molar mass at full coverage $A = A_\infty$; $c_{Si} = 1\,10^{-4}$ g/cm^3, $T = 25\,°C$; silica bare □; silica covered with PEO 27250 ■, PEO 50400 ▲, PEO 160000 △, PEO 325000 ●, PEO 900000 ○

of flocculation under different conditions (concentrations of silica, polymer and salt, molar mass of PEO).

At electrolyte concentrations $c_{NaCl} > 10^{-2}$ mol/l and at pH < 3.5 the silica dispersions become unstable and aggregation occurs. Under comparatively stable conditions near the critical values in the transition region between fast and slow aggregation the aggregation extends over 40 min and higher aggregates are already formed.

In Fig. 3 the diffusion coefficients D_{90} measured at 90° are plotted versus $\log c_{NaCl}$ for silica 138 bare and covered with PEO of different molar masses. The adsorbed amounts and the thicknesses of the layer correspond to the plateau region of the isotherms reported in [2, 3, 6]. The critical coagulation and flocculation concentrations of NaCl are demonstrated by the steep transitions from high to low diffusion coefficients.

In Fig. 4 the D-values of the flocculated silica particles covered with relative adsorbed amounts of 80%, $A = 0.8\,A_\infty$, are compared with the values at full coverage A_∞.

Kinetics of aggregation

As described in the theoretical part the half time values τ and the rate constants k of coagulation and flocculation are determined from the time dependence of the decreasing average diffusion coefficient D. Examples of some of the rate constants k for different concentrations of bare silica at two NaCl-concentrations are given in Table 2.

The theoretical value for the fast coagulation $k = 4\,k_B T/3\eta = 6.16\,10^{-18}$ [m^3 (s particle)$^{-1}$] ($T = 25\,°C$, $k_B = 1.38\,10^{-23}$, η = viscosity of water at 25 °C) is nearly approached at high salt concentration. Measured and fitted time dependences are compared for bare silica in Fig. 2 and for silica covered with PEO 160 000 in Fig. 5. The fit becomes better with decreasing silica concentrations because of excluded interparticle interactions.

In Fig. 6 the rate constants k are plotted versus $\log c_{NaCl}$ for silica 138 bare and covered with PEO of different molar masses. The adsorbed amounts and the thicknesses of the layer correspond to the plateau region of the isotherms reported in [2, 3, 6]. Addition of PEO-polymers of low molar mass $M_W < 160\,000$ results in distinct decrease of the critical flocculation concentration c_{NaCl} in comparison to the critical coagulation value for bare silica. In Fig. 7 the k-values of silica particles covered with relative adsorbed amounts of 80% ($A = 0.8\,A_\infty$) are compared

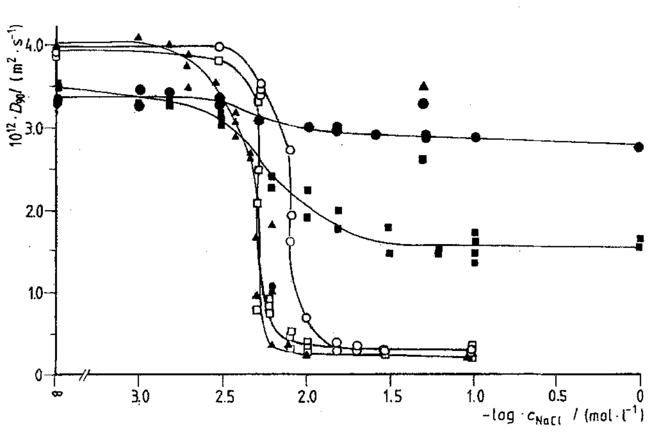

Fig. 4 Dependence of the diffusion coefficient, D_{90}, on c_{NaCl} after $t = 40$ min; silica 138 covered with PEO at different adsorbed amounts A; $c_{Si} = 1\,10^{-4}$ g/cm^3, $T = 25\,°C$; $A = A_\infty$: ▲ PEO 27 250, ■ PEO 325 000, ● PEO 900 000; $A = 0.8\,A_\infty$: □ PEO 325 000, ○ PEO 900 000

Table 2 Rate constants, *k*, of coagulation and flocculation in dependence of the silica concentration

Bare silica

c_{Si} (g/ml)	particle conc. [cm^{-3}]	10^{18} k [$m^3 s^{-1}$ particle^{-1}] C_{NaCl} = 0.1 mol/l	C_{NaCl} = 0.04 mol/l
$1\ 10^{-4}$	$5.8\ 10^{10}$	4.6	1.5
$5\ 10^{-5}$	$2.9\ 10^{10}$	2.4	2.1
$1\ 10^{-5}$	$5.8\ 10^{9}$	5.0	1.2
$5\ 10^{-6}$	$2.9\ 10^{9}$	4–6	
$2\ 10^{-6}$	$1.2\ 10^{9}$	4–5	

Silica covered with PEO 160 000

c_{Si} (g/ml)	particle conc. [cm^{-3}]	10^{18} k [$m^3 s^{-1}$ particle^{-1}] C_{NaCl} = 0.1 mol/l	C_{NaCl} = 0.03 mol/l
$1\ 10^{-4}$	$5.8\ 10^{10}$	0.17	0.13
$5\ 10^{-5}$	$2.9\ 10^{10}$	0.17	0.09
$1\ 10^{-5}$	$5.8\ 10^{9}$	0.13	0.12

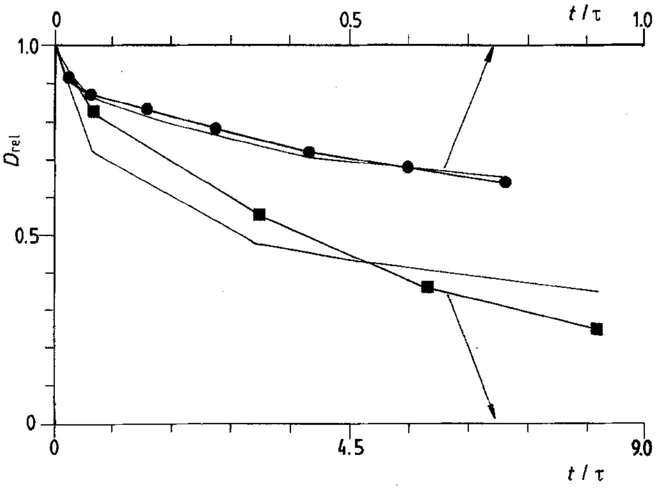

Fig. 5 Dependence of the relative diffusion coefficient, D_{rel}, on relative time, t/τ; silica 138 covered with PEO 160 000, $c_{NaCl} = 0, 1$ n, $A = A_\infty$ symbols measured values, —— theoretical fitted curve; ● $c_{Si} = 1\ 10^{-5}$ g/cm^3, $\tau = 1540$ s, $k = 1.1\ 10^{-19}$ m^3 (s particle)$^{-1}$ ■ $c_{Si} = 1\ 10^{-4}$ g/cm^3, $\tau = 99$ s, $k = 1.7\ 10^{-19}$ m^3 (s particle)$^{-1}$

with values at full coverage A_∞. At high salt concentration the flocculation rate becomes essentially higher at small coverage and the *k*-values correspond to those of bare particles and of particles covered with PEO of low molar mass. The *k*-values for bare and PEO 160 000-covered particles are independent of the particle concentration ($1\ 10^{-5} < c_{silica} < 1\ 10^{-4}$ g cm^{-3}).

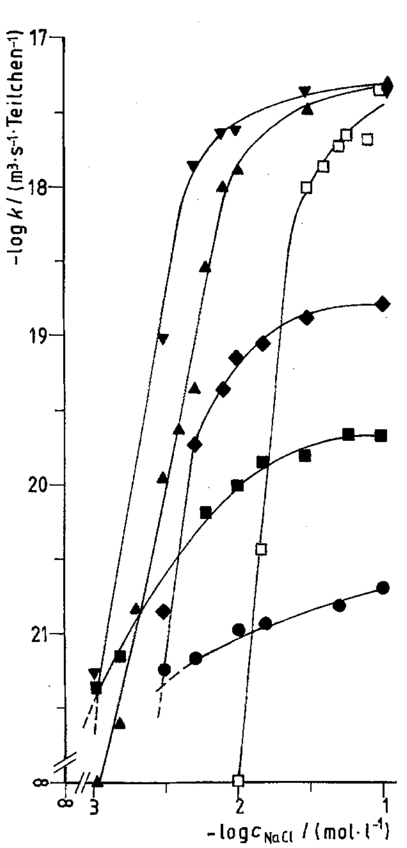

Fig. 6 Double logarithmic plot of the rate constants, *k*, versus c_{NaCl}; silica 138 bare and covered with PEO of different molar mass at full coverage $A = A_\infty$, $c_{Si} = 1\ 10^{-4}$ g/cm^3, $T = 25$ °C, silica bare □; silica covered with PEO 27 250 ▲, PEO 50 400 ▼, PEO 160 000 ◆, PEO 325 000 ■, PEO 900 000 ●

Problems of evaluation

Generally, the fitting procedure is more exact for larger half-time values. Therefore, measurements at small particle concentrations and low flocculation rates are more reliable.

At $1\ 10^{-4}$ [g cm^{-3}] = $5.8\ 10^{10}$ [particles cm^{-3}] the coagulation is very fast, the half-time value drops below the time of the first measurement (60 s). Correspondingly, the time resolution of the PCS-measurements becomes insufficient to follow the stadium of the beginning aggregation and the error of the evaluated *k*-values is about 50%. The lowest particle concentration measurable with reasonable accuracy by our PCS apparatus is $2\ 10^{-6}$ [g cm^{-3}] = $1.2\ 10^9$ [particles cm^{-3}]. In this case the distance of the particles becomes 100 times the diameter and interparticular interactions are excluded.

Systems with PEO 27 250 and 50 400 at low NaCl-concentrations remain stationary. No higher aggregates are formed after the first period of flocculation. This

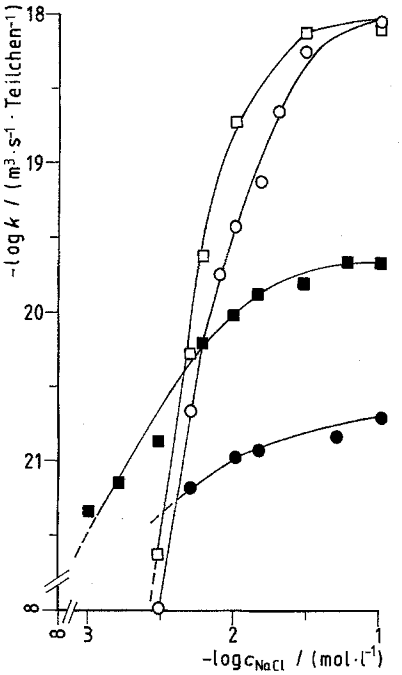

Fig. 7 Double logarithmic plot of the rate constants, k, versus c_{NaCl}; silica 138 covered with PEO at different adsorbed amounts A; $c_{\mathrm{Si}} = 1\,10^{-4}$ g/cm³, $T = 25\,°\mathrm{C}$; $A = A_\infty$: PEO 325 000 ■, PEO 900 000 ●; $A = 0.8\,A_\infty$: PEO 325 000 □, PEO 900 000 ○

behavior can be described by the Smoluchowski kinetics introducing a maximal number of particles in the aggregate.

Flocculation measurements in the literature

The second-order kinetics and the approach of the rate constants of coagulation at high salt concentration to the theoretical Smoluchowski value $6.2\,10^{-8}$ [m³(s particle)$^{-1}$] are in agreement with results on latices obtained by other authors [16–19]. But also deviations from second-order kinetics are found [20]. In some published results the coagulation rate reaches only values of 40 to 90% of the theoretical value [16–19].

Hydrodynamic and steric interactions, viscous effects [17, 22, 23], repulsive potentials [24, 25] or the reversibility of aggregation [26, 27] are supposed to be the reason for the disagreement and are introduced in the theoretical derivations. PCS coagulation measurements on bare precipitated silica particles [28] in the concentration range between 10^{12} and 10^{19} [particles cm^{-3}] are also reported. Decreasing particle radii from 515 and 45 nm result in decreasing rate constants $3.2\,10^{-18}$ to $1.7\,10^{-24}$ [m³(s particle)$^{-1}$] distinctly lower than our k-values. With $\mathrm{SiO_2}$ of nearly the same diameter $d_{\mathrm{PCS}} = 101$ nm a rate constant of $k = 2.8\,10^{-20}$ [m³ (s particle)$^{-1}$] was obtained at the concentration of $1.9\,10^{11}$ [particles cm^{-3}] in $\mathrm{H_2O}$ at 20 °C. This is in contrast to our essentially higher value of $k = 5,38\,10^{-18}$ [m³ (s particle)$^{-1}$]. The difference from the Smoluchowski value is explained by hydration forces which increase the stability [28]. Coagulation results with latices demonstrate that the Smoluchowski theory is only applicable at particle concentrations $< 10^8$ [particles cm^{-3}] [21].

Discussion

The actual object of this study was not to examine the kinetic aggregation models but rather to test the photon correlation spectrometry for its potential to measure the kinetics of the aggregation process, especially in presence of adsorbed polymer layers. The influences of coverage, molar mass of the polymer, ionic strength and silica particle concentration are investigated. The validity of the Stokes law, the proportionality of the scattering light amplitude to the particle volume of aggregated particles and the presumed spherical shape are assumptions which restrict the evaluation in a strict sense to the beginning period of aggregation. During the aggregation process the initially relative monodisperse silica particles become larger and more polydisperse. The second moment (Eq. (5)) of the correlation function, representing the polydispersity of the particle distribution, increases. Double, triple and multiple aggregates deviating from spherical shape are formed. No experimental details on the size distribution and on the structure of the aggregates are found in the literature. An evaluation based on the dependency of the second moment on time to obtain the kinetics of aggregation was not possible because of the scatter of the measured P_2 values. After undisturbed adsorption of the PEO polymers, the electrolyte solution is added in one step during 1s. This guarantees that the following flocculation process is perikinetic without shear stress. The layer thicknesses measured before flocculation agree with PCS results in former extensive measurements [2, 3, 6] .

The subsequent characteristic dependences are obtained from the state of flocculation given by the diffusion coefficient after 40 min of aggregation and by the rate constant of flocculation derived from the time dependence of the diffusion coefficients.

– The critical coagulation and flocculation concentrations of NaCl are demonstrated by the steep transitions from high to low diffusion coefficients at increasing electrolyte concentration after 40 min flocculation time.

– Addition of PEO-polymers of low molar mass $M_{\mathrm{W}} \leq 160\,000$ results in distinct decrease of the critical flocculation concentration in comparison to the critical coagulation value for bare silica. With this low molar mass PEO the very small diffusion coefficients of the flocculated particles at high salt concentrations equal the values of the coagulated bare particles (Fig. 3).

– At adsorption of PEO of the higher molar masses 325 000 and 900 000 an essentially smaller decrease of the diffusion coefficients of the particles is observed in Fig. 3. Stabilization with considerable smaller aggregation is accomplished.

– The D-values of the flocculated silica particles covered with smaller adsorbed amounts $A = 0.8\ A_\infty$ correspond at high salt concentration to those of bare particles and of particles covered with PEO of small molar mass (Fig. 4). The stabilizing effect diminishes and flocculation becomes more efficient at small coverage.

– The rate constants k for silica 138 bare and covered with PEO 160 000 (Table 2) are independent of the silica concentration between 5.8 10^9 and 5.8 10^{10} [particles cm^{-3}], confirming the validity of the second order flocculation kinetics.

From the flocculation rate constants of polymer covered particles (Figs. 6, 7) the following conclusions can be drawn:

– Addition of PEO-polymers induces already at small salt concentrations of $c < 0.003$ mol/l a distinct increase of the flocculation rate in comparison to the bare silica.

– At high salt concentration the adsorption of low molar mass PEO results in the same rate constants as for bare particles.

– Adsorption of polyethylene oxides of the higher molar masses 160 000, 325 000 and 900 000 results in distinctly smaller rate constants in comparison to the bare particles. Thus, the stabilizing effect on the flocculation state shown before is also demonstrated in the considerable smaller aggregation rates (Fig. 6).

– Silica particles covered with relative adsorbed amounts of 80% ($A = 0.8A_\infty$) demonstrate essentially higher flocculation rates than at full coverage, A_∞, and the k-values approach those of bare particles and of the particles covered with PEO of small molar masses 27 250 and 50 400 (Fig. 7).

Two possible flocculation mechanisms [30–32] can be discussed to explain the measured dependences: (1) The bridging of particles by simultaneous adsorption of macromolecules on at least two particles. In this case a conformation change of the adsorbed macromolecules is necessary after the change of the ionic strength by addition of electrolyte. (2) The flocculation by contact of adsorbed polymer layers at instable interaction conditions with a Flory Huggins parameter $\chi > 0.5$. The change in interaction from soluble $\chi < 0.5$ to insoluble conditions would be accomplished by the change of the ionic strength.

In the theory [31] an interpenetration domain and an interpenetration plus compression domain are differentiated. The free energy of interpenetration is calculated by the Flory–Krigbaum theory for coils in solution introducing the Flory–Huggins interaction parameter χ. Dependences of the χ-parameter on ionic strength are frequently observed with solutions in the literature. Osmotic and elastic repulsions of the PEO layers of large thickness with long tails and loops prevent the approach of the particles and the irreversible aggregation in the first minimum at reduction of the electrostatic double layer. A weak aggregation in the second minimum with loose aggregates seems to be demonstrated by the small decrease of the diffusion coefficients of particles covered with PEO of very high molar mass.

Particles covered with layers of small thickness by low molar mass polymer or by high molar mass polymer at small coverage possess no steric stabilization by elastic and osmotic repulsion. With decreasing double layer repulsion by salt addition the approach of the particles and the formation of large aggregates is possible. According to the DLVO-theory London-dispersion forces are responsible for the behavior of bare and polymer covered particles with dense layers. Calculations of London forces in presence of thick loose polymer layers show that these interactions become very small [31].

In a kinetic model of flocculation [32, 33] the following steps are of decisive influence: mixing of polymer and dispersion, collision of polymer and particle leading to the first adhering, conformation change of the adsorbed macromolecule on the surface, collision of covered particles followed by bridging of already adsorbed macromolecules. Dependent on the rate determining step, equilibrium or non equilibrium flocculation occurs. If the conformation change is fast, in comparison to the first adhering, equilibrium flocculation, in the opposite case non equilibrium flocculation takes place. Equilibrium flocculation should follow the second order Smoluchowski kinetics [32].

Flocculation is also treated theoretically as combined effect, coagulation of uncovered sites, weak aggregation of covered sites and bridging between covered and uncovered sites [34]. The optimum of the calculated collision efficiency factor deviates from the coverage 0.5 postulated earlier [35]. With the same assumptions an increase in stability in comparison to the bare particles is theoretically shown for polymer induced flocculation at high coverages [36]. A faster adsorption rate than the collision frequency leads to a significant error.

Other authors [37] interpret the flocculation results of PEO-covered silica particles by (1) bridging flocculation under non-equilibrium conditions and by (2) the formation of loose aggregates by small long-range interactions.

In the equilibrium state at small coverage the macromolecules are adsorbed as flat lying chains. At high coverage the adsorbed macromolecules are provided with long tails, extending far into the solution [2–4, 6]. Increasing salt addition reduces the thickness of the repulsing electrostatic double layer and enables the approach of the adsorbed layers. Because of the availability of free surface sites, bridging is possible at partial coverage without change in conformation opposed to full coverage. A particularity of our results is that the maximal aggregation number to achieve optimal fitting is smaller than 5 for the flocculation of particles covered with thin layers of PEO 27250 and 50400 at low salt concentration. The aggregation stops and no higher aggregates are formed. This is not explainable by irreversible aggregation, and it seems to be an indication for a reversible aggregation process. The repulsion by the electrostatic double layers seems high enough to avoid the transition from the secondary into the primary minimum. Only a small number of publications is involved with reversible aggregation. Polystyrene latices of large size demonstrate reversibility at high salt concentration in contrast to small latices [38]. The repulsive potential [24] has been calculated. Copolymers of acrylamide and vinylimidazol show reversible flocculation of silica by change of pH [39].

The influence of a distinct steric effect on state and kinetics of flocculation by PEO of high molar mass can be demonstrated clearly by the plot of the rate constants k in dependence of the hydrodynamic PEO layer thicknesses [2, 3, 6] (Fig. 8).

Up to critical layer thicknesses of 5 nm, the k-values increase with c_{NaCl} (k [m^3 (particle $s)^{-1}$] = 4.4 10^{-20} for 0.005 n, 1.34 10^{-18} for 0.01 n, 4.8 10^{-18} for 0.1 n). At $c_{\mathrm{NaCl}} = 0.1$ n no change of the k value is seen with increasing thickness d. Below 5 nm PEO layer thickness the range of the double layer is larger and their influence is dominant. A steric stabilization by layers lower than 5 nm is not possible.

For layer thicknesses larger than 5 nm the PEO-layer becomes stabilizing because of repulsive osmotic and elastic interactions. A decrease of the flocculation rate constant k with d is observed and given by $k = k_0 \exp(-\beta d)$, $\beta = 0.28\ \mathrm{nm}^{-1}$ for all salt concentrations c_S. Increase of the electrolyte concentration results in a small increase of the k-values.

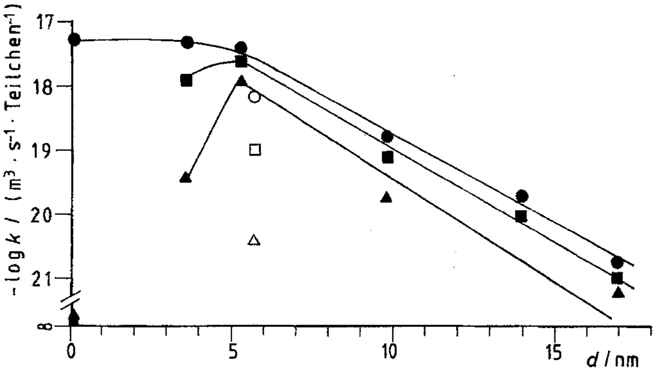

Fig. 8 Logarithmic plot of the rate constants, k, versus the hydrodynamic thicknesses, d; silica 138 covered with PEO of different molar mass; $T = 25\,^{\circ}\mathrm{C}$; $c_{\mathrm{Si}} = 1\ 10^{-4}\ \mathrm{g/cm^3}$; ●,○, $c_{\mathrm{NaCl}} = 0.1$ n; ■,□ 0.01 n; ▲,△ 0.005 n; ●,■,▲ $A = A_\infty$; ○,□,△ $A = 0.8\ A_\infty$

The results of the state and kinetics of flocculation show that the hydrodynamic thickness, determined by the tails of the adsorbed macromolecules, is decisive for the perikinetic flocculation of the silica particles.

At low particle coverage the hydrodynamic thicknesses of the high molar masses are nearly the same as those of low molar masses, but the conformation, the segmental distribution in the layer is different. Some tails are still existing for long chains. These tails give rise to a certain steric stabilization. The influence of the electrolyte is not as effective as with the low molar mass polymer. Lower rate constants of flocculation are obtained for high molar mass PEO at the same electrolyte concentration and layer thickness (Fig. 8).

Acknowledgements The authors are indebted to the Arbeitsgemeinschaft Industrieller Fördervereinigungen and the Deutsche Forschungsgemeinschaft for financial support.

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