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ORIGINAL CONTRIBUTION

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Adsorption of polyethylene oxide on surface modified silica – stability of bare and covered particles in suspension

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Abstract The adsorption of polyethylene oxide (PEO) on modified colloidal silica and the stability of the aqueous suspension was investigated. With octanol some silanol groups at the silica surface were replaced by octylgroups. The size of the modified silica particles and the charge and chemical groups on the surface were charaterized by ultracentrifugation, photon correlation spectrometry, polyelectrolyte titration and IR spectrometry. The adsorbed amounts of polyethylene oxides of different molar mass were determined on the modified silica in water. With photon correlation spectrometry (PCS) the hydrodynamic layer thickness of the PEO layers on the particles were measured. The dependences of the layer thicknesses on molar mass of the PEO, polymer concentration and adsorption time were determined. The aggregation of the suspended PEO coated and uncoated modified silica particles was examined with PCS by the time dependence of the diffusion coefficient at different salt concentrations. The influence of molar mass and concentration of PEO as well as of the age of the dispersion was explored. The measured dependences are discussed and compared with the behavior of unmodified silica- and latex-particles.

Key words Surface modified silica – photon correlation spectrometry – adsorption of PEO – stabilization – flocculation

Introduction

The regulation of the aggregation and stability behavior of dispersions is of high technological and scientific interest [1, 2]. The stability of colloidal suspension can be influenced by adsorbed polymer and polyelectrolyte and by addition of electrolyte [3–5]. Increasing electrolyte concentration reduces the thickness of the electric double layer and leads to coagulation. The influence of neutral polymer depends on the conformation of the adsorbed macromolecules, stabilization or flocculation may occur. Different methods exist to characterize layer specifications like adsorption isotherm by measuring the excess concentration in solution, hydrodynamic layer thickness (by sedimentation [6], photon correlation spectrometry, PCS [7]), bound fraction (by NMR [8], IR [9] ESR [10] microcalorimetry [11]) and volume fraction profile (by SANS [12]). With these measurements can be examined how parameters like surface charge density, surface chemistry, electrolyte concentration, molar mass and adsorption time influence the adsorption of the polymer and its conformation. The adsorbed amount depends strongly on the size and number of the loops. The hydrodynamic layer thickness is a measure of the tail length. But their is no direct method to analyze the distribution in trains, loops and tails of the adsorbed polymer.

On the other hand, the influence of the system parameters on stability of the suspensions can be observed with different methods like sedimentation rate [13] and volume

[14], raster electron microscopy [15], particle counting [16, 17], turbidity [14] and PCS [18, 19], the method used in this paper.

Experimental

Colloidal silica particles

The silica particles were prepared according to the method of Stöber et al. [20] by hydrolysis of ortho silica acid with ammonium–water solution in ethanol. The detailed description of the preparation is given in [21]. To modify the silanol surface groups by octylgroups, the particles were treated with a high excess of boiling octanol for 8 h. Then they were washed three times with hexane and dried at 0.5 mbar. The samples are redispersed in water by stirring for 48 h and finally dispersed by ultrasonication. At the resulting pH = 5.8 all measurements were accomplished. The modification of the silica surface is not stable in acid and basic medium.

Polyethylene oxides

The polyethylene oxides (PEO) were produced by Polymer Laboratories Ltd. (Shrewsbury, UK). Seven PEO-samples of molar masses between 2.0×10^4 and 9.0×10^5 are used. They have narrow distributions in molar mass ($M_W/M_N < 1.1$).

Adsorbed amount

Aqueous solutions of PEO are added under stirring to suspensions of silica. The covered silica particles were separated from the solution after 1 h by centrifugation (ca. 2000 g). Then the polymer concentration in the solution was determined by the turbidity after addition of tannin [22].

Photon correlation spectrometry (PCS)

PCS measurements were accomplished with an autocorrelator (Malvern Instruments, Spring Lane, Worchestershire, England) equipped with an argon ion laser (Model 2016, Spectra Physics) with 514.4 nm wavelength.

Experimental results

Characterization of the colloidal particles

The diameters of the modified and in comparison of unmodified silica and of latex particles [23] and their distribution parameters obtained by different methods are shown in Table 1.

Table 1 Diameters of modified and unmodified silica and latex

		Modified silica	Unmodified silica	Latex
PCS	D_0	2.98×10^{-12} m^2/s	3.36×10^{-12} m^2/s	2.2×10^{-12} m^2/s
	d_0	164 nm	146 nm	222 nm
	p	13%	11%	3%
EM	d	141 nm	136 nm	222 nm
	σ	10%	11%	9.3%
UC	S	$8743 \times 10^{-13} S$	$6166 \times 10^{-13} S$	1450×10^{-13} S
	d	115 nm	97 nm	216 nm

D_0 = diffusion coefficient extrapolated to the angel of 0°, d = diameter, p = polydispersity (second moment), σ = standard deviation, S = sedimentation coeffcient.

The standard Dow-latex is nearly monodispers. The distribution of the diameters of modified silica is larger than of unmodified silica. The larger distribution can be seen in the angle dependence of the D-values from PCS as well as in the second moments p. Possible reasons could be, that hydrophobic modified silica can not be fully redispersed or that during the reaction of the silanol surface groups with the octanol a bridging between some silica particle occurs as described in the literature [24].

According to [25–27] 4–5 SiOH/nm^2 are at the surface of the unmodified silica. IR-measurements show that 1.1 octyl groups/nm^2 exist on the modified silica particles. So nearly a fourth of the silanol groups at the surface is modified.

The surface charge density is obtained by adsorption of positively charged polyelectrolyte poly(diallyl-dimethyl-ammoniumchloride)s (P-DADMAC) on the negatively charged particles. The adsorbed amount is determined from the depletion in solution by polyelectrolyte titration [28, 29] after removing the particles by centrifugation. The surface charge densities, 3.1 μC/cm^2 on modified silica and 3.9 μC/cm^2 on unmodified silica in neutral medium [30], are calculated from the adsorbed amount. Charge density and number of silanol groups decrease with modification of the silica surface by the same value. The surface charge density of the silica depends strongly on the pH of the medium because the charge is produced by protonated silanol groups.

The charge density of latex of 5.3 μC/cm^2 is caused by the sulphonate groups of the initiator molecules at the surface and does not depend on the pH of the medium.

Zeta potential measurements show that at plateau adsorption the negative charge of the particles is overcompensated to positive charge. The zero point of charge is located at nearly 80% of adsorbed plateau amount of P-DADMAC.

Adsorption of polyethylene oxides

Adsorption isotherms

For the adsorption of PEO on modified silica the following results had been achieved. The plots of the adsorbed amount against the concentration of polymer in the solution show high affinity isotherms (Fig. 1). The adsorbed plateau amounts A_∞ depend on the molar mass M of the polymer (Fig. 2), as described by the Eq. (1).

$$A_\infty = 2.5 \times 10^{-4} \times M^{0.11}. \qquad (1)$$

The adsorbed amounts are constant at adsorption times between 10 min and 48 h.

According to the adsorption theory of Scheutjens and Fleer [31, 32] for neutral polymers, the adsorbed amount should increase if the solvent gets worse. If the salt concentration is increased water becomes a worse solvent for PEO. An increase of the adsorbed amount could not be found with modified silica and PEO in water at salt concentrations up to 0.008 mol/l. At higher salt concentrations the dispersion is no longer stable and the determination of the adsorbed amount is accompanied by a large error [33, 34].

The adsorption of PEO on unmodified silica [35] and on latex [23] show high affinity isotherms too. But the adsorbed plateau amount and the dependence on the molar mass differ strongly from modified silica (Fig. 2). The adsorbed amounts are lower and the molar mass dependence is less on unmodified silica. The silica surface and the PEO are interacting by hydrogen bridges of the surface silanol groups with the oxygen of the polyether. The octylgroups make parts of the surface hydrophobic. At this places the formation of loops becomes stimulated. In the loops the largest part of the adsorbed amount is located. An increase of the loops cause an increase of the adsorbed amount. The stronger dependence of the adsorbed amount on molar mass at modified silica can also be explained by the better formation of loops. The larger adsorbed amount and the stronger dependence on molar mass of PEO on latex can be refered to hydrophobic interactions. No competition of water and PEO segments exists on the latex surface.

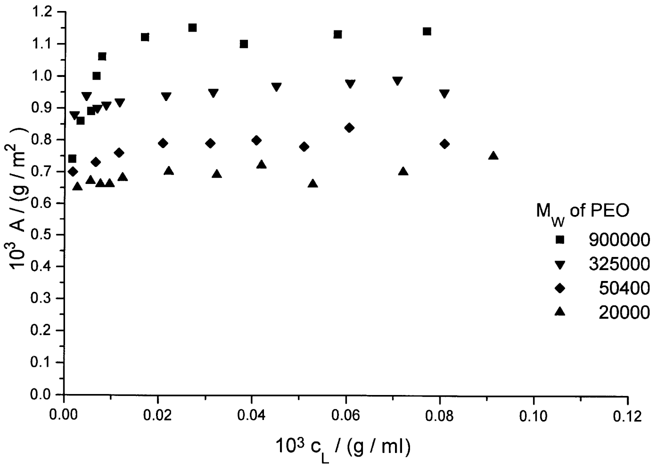
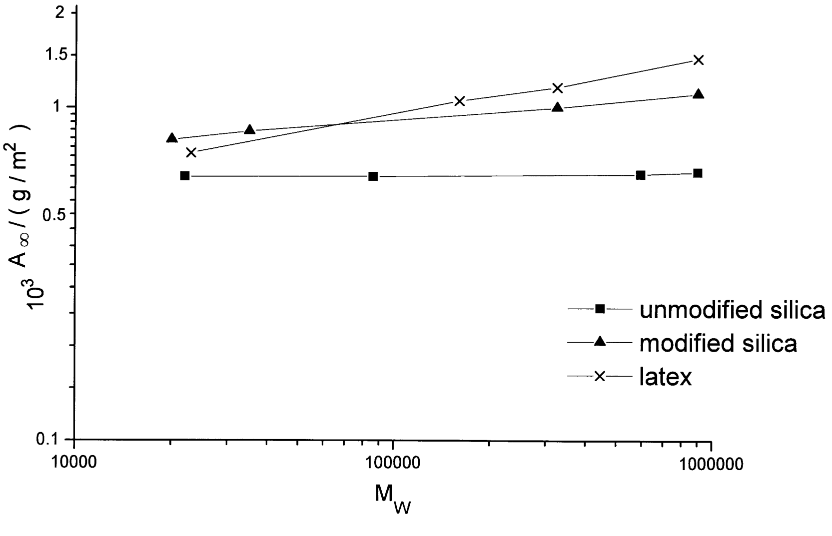


Fig. 1 Adsorption isotherms of PEO M_W 20 000, 50 400, 325 000 and 900 000 on modified silica; $c_{\text{silica}} = 5 \times 10^{-4}$ g/ml

Adsorbed polymer layers

Adsorbed polymer layers increase the friction coefficients and decrease the diffusion coefficients of the particles. The

Fig. 2 Dependence of the adsorbed amounts in the plateau A_∞ on the molar mass M_W of PEO on unmodified silica, modified silica and latex; $c_{\text{silica}} = 5 \times 10^{-4}$ g/ml, $c_{\text{latex}} = 1.5 \times 10^{-3}$ g/ml



hydrodynamic effective radii r of spherical particles can be calculated with the Stokes–Einstein equation (2) from the diffusion coefficient D.

$$D = \frac{k_B T}{6\pi\eta r} , \tag{2}$$

where η is the dynamic viscosity, k_B the Boltzmann constant, T the temperature.

The difference in the determined effective radii r with and without the adsorbed polymer layer corresponds to the hydrodynamic thickness d of the layer.

The layer thickness d of PEO on modified silica increase with increasing polymer concentration. In Fig. 3 the layer thickness still increase at polymer concentrations in excess to the plateau adsorption nearly up to a concentration which corresponds to twice the plateau value. After that value, the increase becomes lower, but a small increase is still existing. With increasing molar mass of PEO the thickness d of the layer increases (Fig. 4) according to Eq. (3).

$$d \propto M^{0.54} . \tag{3}$$

To compare the layer thicknesses of particles with different radii, the layer thickness has to be corrected, because the available angular segment volume for an adsorbed macromolecule increases with increasing surface curvature. Assuming an identical volume for an adsorbed macromolecule the thickness becomes smaller with increasing curvature with respect to the flat surface. In Eq. (4), developed by Garvey [36], this correction is formulated:

$$\delta = \frac{4\pi}{3} \frac{(r+d)^3 - r^3}{4\pi r^2} , \tag{4}$$

where δ is the thickness on a flat surface; d the measured thickness, r the radii of the particle.

The dependence of the layer thickness on molar mass of PEO is identical at modified and unmodified silica [35] if the layer thickness is corrected for a flat surface (Fig. 4). Because the layer thickness depends on the length of the tails can be concluded that the tails are not influenced by the hydrophobic parts of the surface.

The corrected layer thickness on latex [23] differ strongly from the values on silica. Different adsorption mechanisms seems to influence the length of the tails.

On all three substrates the layer thickness increase strongly when the plateau of the adsorption is reached. This is explicitly shown for PEO 900 000 in Fig. 5.

On modified silica the PEO layer thickness is independent of the addition sequence of polymer and modified silica suspension. The layer thickness is also not affected by stepwise polymer addition in comparison to addition in one step.

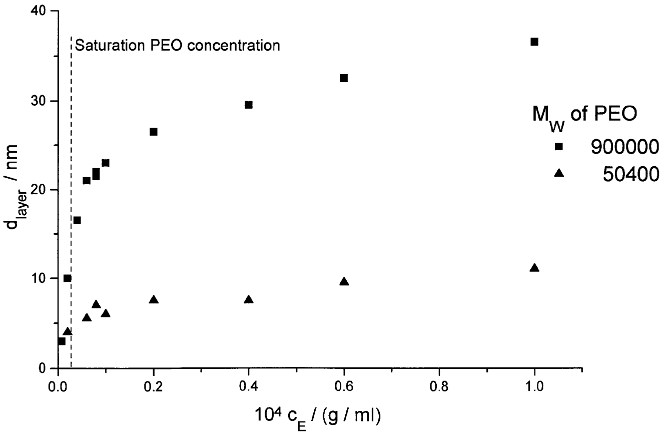


Fig. 3 Dependence of the hydrodynamic layer thickness d on the concentration c_E of PEO M_W 50 400, 900 000 in the solution; $c_{silica} = 5 \times 10^{-5}$ g/ml

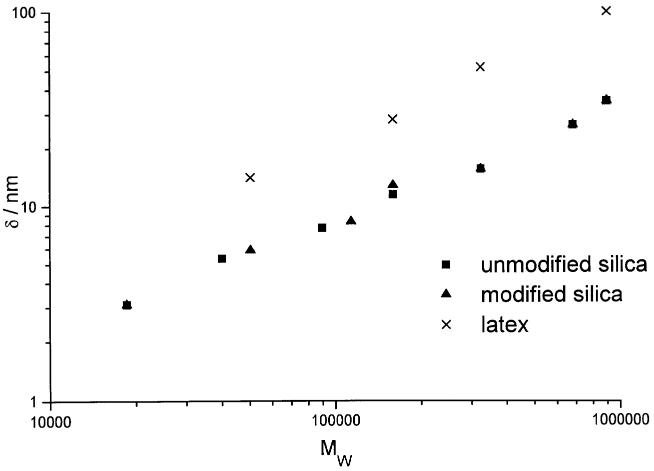


Fig. 4 Dependence of the corrected hydrodynamic layer thickness δ on the molar mass M_W of PEO on unmodified silica, modified silica and latex; $c_{silica} = c_{latex} = 5 \times 10^{-5}$ g/ml

It is possible to displace PEO of low molar mass by PEO of high molar mass. If PEO 900 000 is added to silica fully covered by PEO 50 400 the layer thickness increase within 10 min. Nearly, the same layer thickness is reached as with direct addition of PEO of high molar mass.

The time dependence of the PEO layer thickness on unmodified and modified silica and latex was examined. In contrast to the adsorbed amount the layer thickness of some systems depend on the adsorption time. On modified silica the layer is built up in 5 min. After this time the thickness is reduced in some systems in days. The higher the molar mass of the polymer, the stronger the dependence of the layer thickness (Fig. 6) on time.

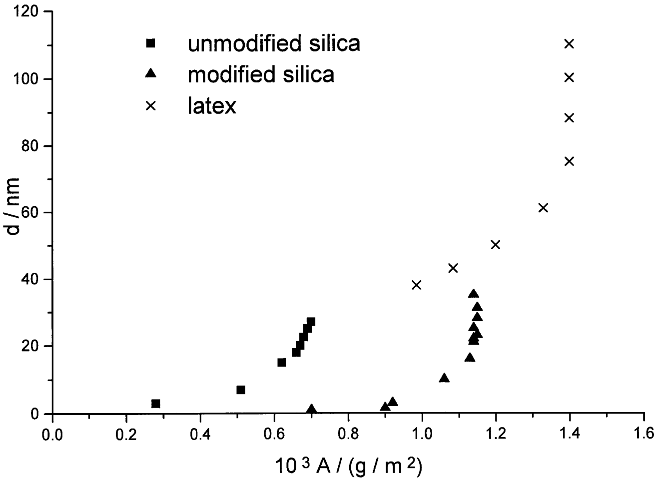


Fig. 5 Dependence of the hydrodynamic layer thickness *d* on the adsorbed amount *A* of PEO M_W 900 000 on unmodified silica, modified silica and latex; $c_{silica} = 5 \times 10^{-4}$ g/ml, $c_{latex} = 5 \times 10^{-5}$ g/ml

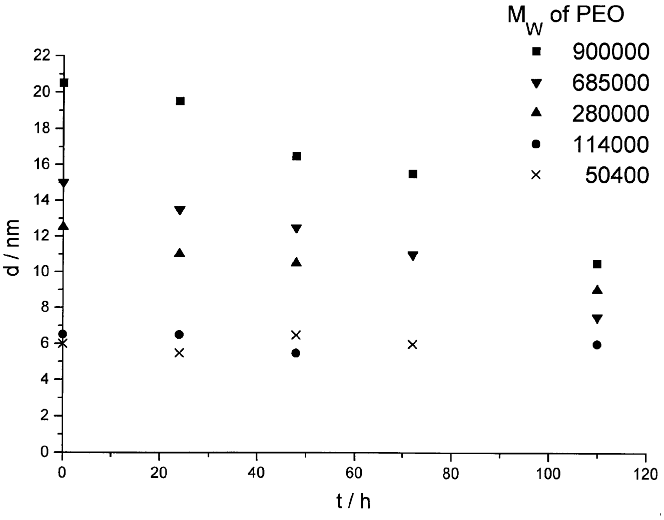


Fig. 6 Dependence of the hydrodynamic layer thickness *d* of PEO M_W 50 400, 114 000, 280 000, 685 000, 900 000 on the time *t*, modified silica; $c_E/c_\infty = 8$; $c_{silica} = 5 \times 10^{-5}$ g/ml

The reduction of the layer thickness with time depends also on the excess of polymer in the solution. The layer thickness nearly do not decrease with time at a molar mass of 50 400, but decrease in 4 days by 10 nm from 20.5 nm to 10.5 nm at a molar mass of 900 000, if the polymer concentration of PEO 900 000 is 8 times the plateau concentration. At lower excess polymer concentration the decrease is lower. Surprisingly, at higher polymer concentration the layer thickness stay constant with time (Fig. 7). So a critical polymer concentration exists for the transition from time-dependent to time-independent layer thickness.

The dependence of the adsorbed layer thickness with time can also be observed on unmodified silica. The decrease of the layer thickness is more or less identically to modified silica.

At latex no reduction of the adsorbed layer thickness is observed within 6 days.

The are two possible reasons for the decrease of the polymer layer thickness. From literature [37] is known that polyethylene oxide is decomposed in water solution by sunlight. The reduction of the molar mass reduces the layer thickness. If an old PEO-solution is added to the silica suspension the measured layer thickness is lower than for a new PEO-solution. The layer thickness is reduced by 1.5 nm if the PEO 900 000 solution is stored 10 days in darkness and in daylight by 4 nm (Fig. 8). The decomposition reaction is catalyzed by acid [38]. The acidic silanol groups may be able to catalyze the decomposition. So only at modified and unmodified silica but not on latex the reduction of the layer thickness could be observed.

But an explanation fails why their is an upper critical polymer concentration upon which no decrease of the PEO layer thickness occurs and under which the reduction is faster when more excess polymer is added. The rate of decomposition should be larger in present of daylight, like for pure PEO solution. But the reduction of the layer thickness is not influenced by daylight (Fig. 8).

The other possible reason for the reduction of the layer thickness is a reorganisation of the polymer layer. Their are some references in the literature [39–41] that polymer layers change their conformation in several hours. Also the existent time-dependence flocculation by bridging is a hint for a change of the layer structure in a period of hours.

But none of both explanations for the reduction of the layer thickness can be ensured.

Stability of particles without adsorbed PEO layer

Aggregation of suspended particles can be proved by measuring the diffusions coefficient at a certain time after salt addition. The rate constant *k* of aggregation can be determined from the time dependence of the diffusion coefficients [19]. The modified silica suspension is stable in pure water for more than 10 days. The diffusion coefficient and its dependence from scattering angle do not change in this time, no aggregation can be observed. At small salt concentrations $0 < c_{NaCl} < 0.003$ mol/l the diffusion coefficients of modified silica show a small increase with increasing ionic strength of the dispersion. This was also observed for unmodified silica [35] and latex [23] (Fig. 9).

Fig. 7 Dependence of the hydrodynamic layer thickness *d* of PEO M_W 900 000 at different excess concentrations c_E/c_∞ on the time *t*, modified silica; $c_{silica} = 5 \times 10^{-5}$ g/ml

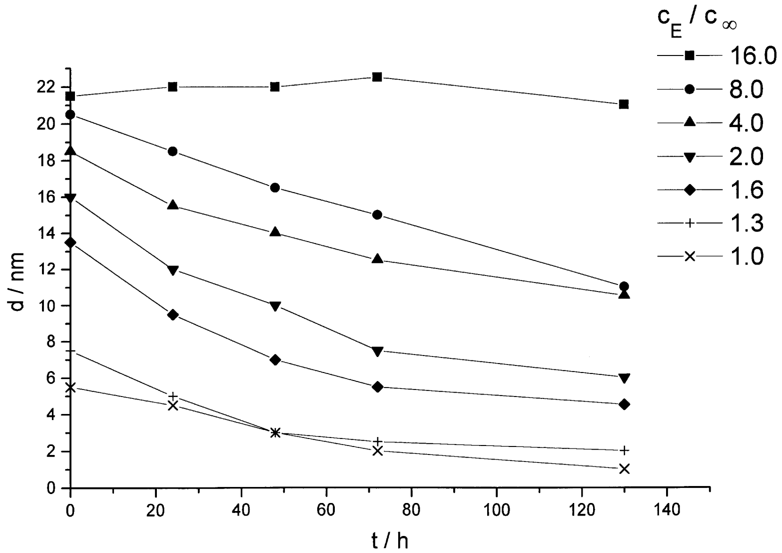
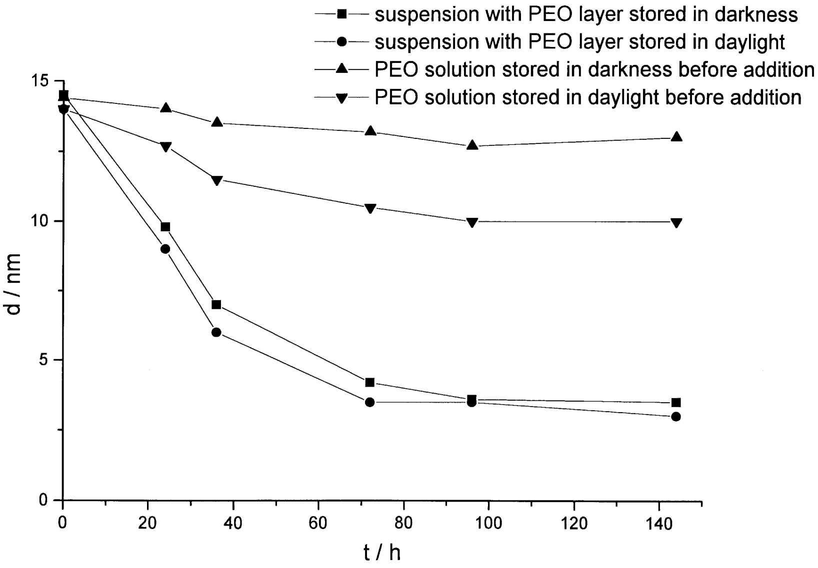


Fig. 8 Dependence of the hydrodynamic layer thickness *d* of PEO M_W 900 000 on the store time t in darkness or light of the suspension or the solution; $c_E/c_\infty = 8$; $c_{silica} = 5 \times 10^{-5}$ g/ml



The increase was related to an electrolyte friction effect [42, 43].

At salt concentration $c_{NaCl} > 0.008$ mol/l the dispersion of modified silica is no longer stable. The diffusion coefficient of the particles measured 40 min after salt addition decreases with increasing ionic strength from 3.68×10^{-12} to 3.21×10^{-13} $m^2 s^{-1}$ at $c_{silica} = 5 \times 10^{-5}$ g/ml (Fig. 9). At a salt concentrations larger than $c_{NaCl} = 0.03$ mol/l no further decrease occurs. At this ionic strength also the rate constant of aggregation increases from zero to 5×10^{-18} $m^3 s^{-1}$ particle^{-1}. This is near to the value 6.2×10^{-18} $m^3 s^{-1}$ particle^{-1} of Smoluchowski [44, 45] for diffusion controlled fast aggregation.

The critical salt concentrations for coagulation are for unmodified silica $c_{NaCl} = 0.02$ mol/l [21] and for latex $c_{NaCl} = 0.4$ mol/l [46] (Fig. 9). At the same particle concentration of unmodified, modified silica and latex nearly the same diffusion coefficients are reached after 40 min above the critical salt concentration. The rate constants *k* are the same also.

The different critical salt concentrations can be attributed to the different surface charges because of the

Fig. 9 Dependence of the diffusion coefficient D_{90} on $-\log c_{\mathrm{NaCl}}$ after $t = 40$ min for bare particles of unmodified silica, modified silica and latex; $c_{\mathrm{silica}} = c_{\mathrm{latex}} = 5 \times 10^{-5}$ g/ml

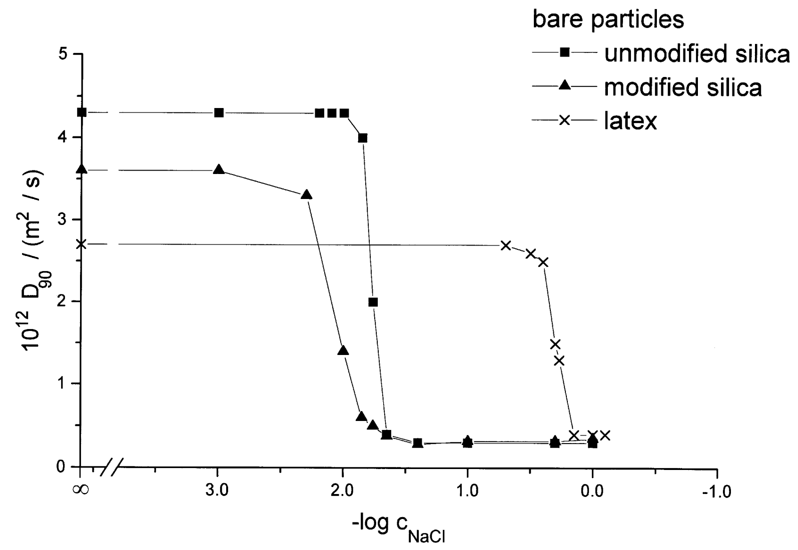
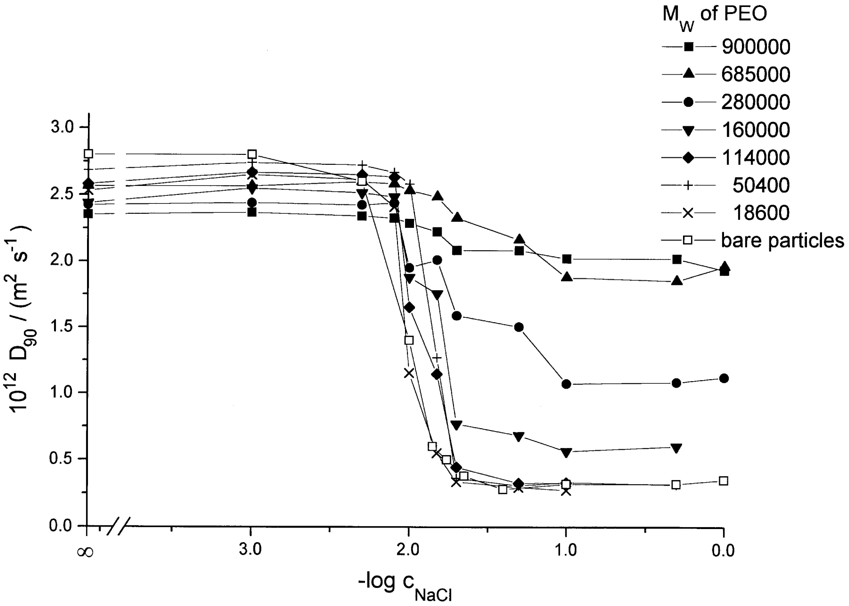


Fig. 10 Dependence of the diffusion coefficient D_{90} on $-\log c_{\mathrm{NaCl}}$ after $t = 40$ min for modified silica bare and covered with PEO M_{W} 18 600, 50 400, 114 000, 160 000, 280 000, 685 000, 900 000; $c_{\mathrm{silica}} = 5 \times 10^{-5}$ g/ml



influence on the electrostatic double layer and the electrostatic repulsion of the particles. Unmodified silica has a little higher surface charge density than modified silica and need so a slightly higher salt concentration density than modified silica to become unstable. Latex has an essentially higher surface charge and need distinctly more salt for destabilization.

Stability of particles with adsorbed PEO layer

Coating of particles with polymer influences the stability. This was examined for modified silica with polyethylene oxide adsorption layers.

At a salt concentration of about 0.01 mol/l the modified silica bare and with adsorbed PEO layers begin to aggregate (Fig. 10). For the aggregation measurements of the particles with PEO-adsorption layers the PEO concentration was selected 8 times the PEO concentration which corresponds to the adsorbed plateau amount. The diffusion coefficient after 40 min increases with molar mass and consequently with layer thickness of the PEO. The rate constant of the flocculation decreases with increasing molar mass of the PEO. With PEO 900 000 the flocculation is very slow. But experiments about long time show that modified silica coated with PEO 900 000 aggregate already. The diffusion coefficient decreases continually over many hours.

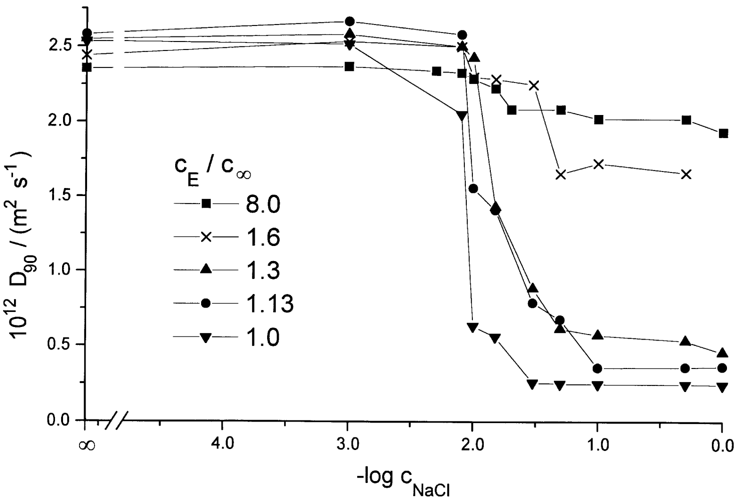


Fig. 11 Dependence of the diffusion coefficient D_{90} on $-\log c_{\mathrm{NaCl}}$ after $t = 40$ min for modified silica at different polymer excess c_E/c_∞ with PEO M_W 900 000; $c_{\mathrm{silica}} = 5 \times 10^{-5}$ g/ml

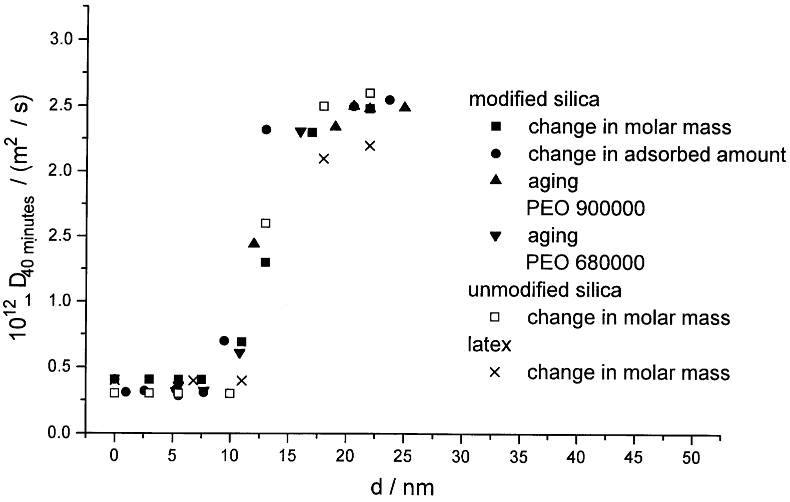


Fig. 12 Dependence of the diffusion coefficient D_{90} after $t = 40$ min on the hydrodynamic layer thickness d by different ways to get the thickness: change in the molar mass, change in adsorbed amount, aging of the suspension and different surfaces, unmodified silica, modified silica and latex; $c_{\mathrm{silica}} = 5 \times 10^{-5}$ g/ml, $c_{\mathrm{NaCl}} = 0.1$ mol/l, $c_{\mathrm{latex}} = 5 \times 10^{-5}$ g/ml, $c_{\mathrm{NaCl}} = 1$ mol/l

Also, the excess of polymer in the dispersion in relation to the PEO concentration which corresponds to the adsorbed plateau amount influence the flocculation kinetics. At low molar mass there is no change of the diffusion coefficients after 40 min and of the rate constant of aggregation with the PEO excess. At a salt concentration of 0.03 mol/l a diffusion coefficient of 3.2×10^{-13} m^2 s^{-1} at $c_{\mathrm{silica}} = 5 \times 10^{-5}$ g/mL and a rate constant k of 5×10^{-18} m^3 s^{-1} particle^{-1} independent of the polymer concentration is reached.

With PEO 900 000 the diffusion coefficient and the rate constant depend extremely on polymer concentration. The diffusion coefficient after 40 min increases with increasing surplus of the polymer (Fig. 11). The corresponding rate constants k decrease at a salt concentration of 0.1 mol/l from 5×10^{-18} to 6×10^{-21} m^3 s^{-1} particle^{-1} at an increase of the polymer concentration between one and 1.6 times the PEO concentration which corresponds to the adsorbed plateau amount.

The aggregation of silica coated with polymer of high molar mass becomes faster, when the layer thickness decreases with time at increasing age of the suspension. The rate constant k of silica coated with PEO 685 000 at a salt concentration of 0.1 mol/l increases from 1.2×10^{-20} m^3 s^{-1} particle^{-1} at the first day to 2.7×10^{-18} m^3 s^{-1} particle^{-1} at the fifth day.

The kinetics of flocculation is extremely influenced by the thickness of the PEO layer. The stability of the dispersion increases distinctly between 10 and 15 nm independent from the way to get this hydrodynamic layer thickness (Fig. 12).

The same dependence can be observed on unmodified silica [21] and on latex [44]. The stability of these suspensions with adsorbed PEO layers depends in the same

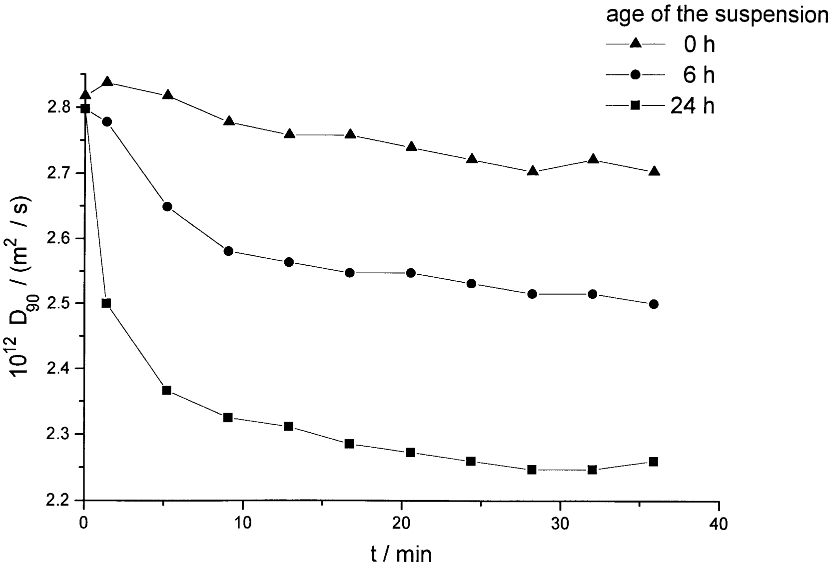


Fig. 13 Dependence of the diffusion coefficient D_{90} on the time after salt addition $c_{NaCl} = 0.001$ mol/l for modified silica at different aging times of the suspension; $c_{silica} = 5 \times 10^{-5}$ g/ml and partly covered with PEO M_W 900 000 $c_{PEO} = 6 \times 10^{-7}$ g/ml

characteristic way on molar mass and polymer concentration. Latex will be stabilized by lower molar masses then silica because of higher layer thickness on latex of the corresponding molar mass of PEO.

Independent from substrate the three examined suspensions, modified silica, unmodified silica, and latex become stabilized by PEO at the same hydrodynamic layer thickness (Fig. 12). The hydrodynamic layer thicknesses and the lengths of the tails, respectively, are decisive for the sterical stabilization of colloid suspensions by polymers.

At low coverage modified silica with adsorbed PEO layer of high molar mass aggregates already at low salt concentration $c_{NaCl} = 0.001$ mol/l. The flocculation is very fast at the beginning and becomes slow after 10 min (Fig. 13). But aggregation is not observed at increasing adsorption time (Fig. 13) and with PEO of low molar mass. With bare silica or at full coverage no aggregation is existent at this salt concentration. Also unmodified silica or latex do not show aggregation at this salt concentration and low coverage. The explanation for this behavior may be a bridge flocculation between two partially coated modified silica particles. This process becomes favored if the tails are long enough with PEO of high molar mass.

In the first adsorption period immediately after the addition of the polymer conformation equilibrium is not established, long tails still exist and favor bridging. The equilibration process, leading to short tails in the PEO-layer at low coverage seems to be retarded by the existence of the hydrophobic surface groups on the modified silica, so the chance for bridging becomes increased.

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