Colloid Polym Sci 274:732–740 (1996)

ORIGINAL CONTRIBUTION

E.J. Röhm
K.D. Hörner
M. Ballauff

Interactions in mixtures of latex particles and polymers as revealed by turbidimetry

Received: 9 January 1996
Accepted: 6 March 1996

E.J. Röhm · K.D. Hörner
Prof. Dr. M. Ballauff (✉)
Polymer Institut
Universität-TH Karlsruhe
Kaiserstraße 12
76128 Karlsruhe, FRG

Abstract We report a turbidimetric study of the depletion forces between latex particles induced by a dissolved polyelectrolyte. The system consists of a polystyrene latex and potassium polystyrene sulfonate (PSS). Since turbidimetry is practically insensitive to multiple scattering the analysis of the mixtures of the colloid and the dissolved polymer could be extended up to latex concentrations of 50 g/l. The amount of dissolved PSS was varied between 0.025 and 0.2 wt.%. The scattering contribution of the polymer can be neglected in very good approximation and the change in scattering intensity upon addition of PSS can directly be related to the effective attraction of the latex spheres caused by the dissolved polymer. It is demonstrated that a potential based on the volume-exclusion mechanism can describe in good approximation the osmotic compressibility resulting from the turbidimetric analysis.

Key words Depletion forces – latex – polyelectrolyte – turbidity – structure factor

Introduction

For a long time [1] it has been known that non-adsorbing polymers may promote flocculation of colloid particles. Asakura and Oosawa [2] as well as Vrij [3] advanced the hypothesis that the demixing is due to the presence of attractive depletion forces: If the colloid particles get closer than the coil diameter of the dissolved polymer the osmotic pressure in the depleted region between the particles becomes lower than the remainder of the bulk solution. As a consequence, there is a net attractive force between the colloid particles which may lead to creaming and reversible phase separation.

This relatively simple approach which is based on purely hard-sphere interaction of the colloid particles and the polymer coils has turned out to be highly successful in predicting the onset of demixing in many experimental systems [4–11]. Also, first successful attempts to measure directly the depletion forces have been reported [12–14] which corroborate the volume-exclusion mechanism. An exhaustive review over theoretical and experimental studies of the depletion forces and their various implications with regard to colloidal systems has been given by Lekkerkerker and Stroobants [11] and by Poon and Pusey [15].

Recently, a statistical-mechanical theory of the phase equilibrium due to depletion forces has been worked out by Lekkerkerker et al. [16, 17] which has met with gratifying success when compared to experimental phase diagrams. A critical survey over the comparison of this theory with experimental phase diagrams has been given by Poon et al. [18]. The main point of this analysis derives from the fact that the depletion potential is tunable in range and depth [13, 16, 18]. Theory in agreement with experiment demonstrates that if the size of the polymer is small compared to the size of the colloid spheres, depletion interaction will lead to a solid/gas phase equilibrium; for larger size ratios a liquid phase becomes possible.

Another important theoretical contribution was given by Meijer and Frenkel [19, 20]. Based on computer simulations these authors were able to discuss the merits as well as the limits of the treatment of the depletion forces in terms of the volume-exclusion mechanism. In particular, these authors could represent the polymer by a lattice model and not by hard spheres as in previous analytical treatments. Thus, these simulations were able to address the problem of coil deformation at high colloid volume fractions and their influence on the phase behavior.

All theories and simulations discussed so far treat the polymer coils as ideal and do not include the effect of coil–coil interactions. As first shown by Sharma and Walz [21] and later by Mao et al. [22] the mutual exclusion of the small particles representing the polymer coils leads to depletion repulsion as the two large particles first approach; at closer distance the forces switch sign and a significant depletion attraction results. The same effect is predicted when taking into account the polymer–polymer interaction in the vicinity of the Θ-temperature by means of perturbation theory [23]. It must be noted, however, that the calculations presented in ref. [22] refer to a large size ratio of the large and the small spheres. Also, Mao [24] could show that the repulsive barrier will be weakend when the small spheres exhibit a certain size polydispersity.

While the phase diagrams of mixtures of colloid spheres with dissolved polymers seem to be rather well understood (cf. e.g. the discussion in refs. [10, 15, 18]), only a few attempts to assess the depletion forces by scattering methods have been reported up to now [9, 25–28]. On the other hand, static light scattering should be well-suited to study the effect of attractive long-range forces between colloid particles [29]. Under suitable conditions light scattering explores the long-wave part of the structure factor [7, 29] which may be evaluated to yield quantitative information about the effective interaction of particles. Also, scattering methods allow to study the one-phase region thus avoiding all additional complications due to non-equilibrium states (see the discussion of this point in ref. [30]).

A principal difficulty of static light scattering, however, arises from the very strong light scattering of particles of typical colloidal dimensions (ca. 10^2 nm) which leads to the problem of multiple scattering (cf. e.g. the discussion of this problem in ref. [27]) or to the necessity to work with very small particles and/or concentrations [25, 26]. On the other hand, an experimental investigation of the depletion interaction in latex systems requires the change of the volume fraction of the latex particles within a wide range, i.e., up to concentrations where strong scattering of light prevails.

It has been shown [31, 32] that strongly scattering latex systems can be studied by turbidimetry which is practically insensitive towards multiple scattering. Following Vrij and coworkers [33–35] the full analysis of measured turbidity as function of wavelength and latex concentration has been worked out to yield the structure in the region of small angles. In particular, extrapolation of the data to infinite wavelength leads to $S(0)$, the structure factor at vanishing scattering angle [33, 31, 32].

Here, we give a first account of a turbidimetric study of particle interaction in a polystyrene latex when a non-adsorbing polyelectrolyte is added. The soluble polymer used in this study was sodium polystyrene sulfonate (PSS). Anionic polyelectrolytes have the distinct advantage that there will be no adsorption on the negatively charged surface of the latex particles unless the ionic strength is very high [36]. Thus, a number of studies of the flocculation by dissolved polyelectrolytes have appeared recently [28, 37–39] which demonstrate the presence of strong depletion forces in these systems.

Since the scattering intensity due to the latex particles is much larger than the contribution due to the polymer, the resulting turbidity can be directly evaluated to give the structure factor of the latex particles. This in turn may be used to assess the depletion forces operative in presence of dissolved polymer.

Theory

Since the polydispersity of the latex used here is very small, all effects due to polydispersity can safely be dismissed (cf. refs. [31, 32]). For a system of monodisperse spheres the measured turbidity as function of wavelength λ_0 may be rendered as the product of a form contribution $Q(\lambda^2)$ and an integrated structure factor $Z(\lambda^2, c)$ [35, 31, 32]:

$$\tau = K^* c \cdot \left(\frac{n_0 \pi \sigma_L}{\lambda_0}\right)^3 \cdot \frac{16\pi}{3} \cdot Q(\lambda^2) \cdot Z(\lambda^2, c) , \qquad (1)$$

where σ_L is the diameter of the latex particles, n_0 the refractive index of the medium, c denotes the weight concentration and K^* is an optical constant defined by [31]

$$K^* = \frac{3 n_0}{4 \lambda_0 \rho_p} \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 , \qquad (2)$$

with ρ_p being the density of the particles, n_p the refractive index of the latex particles and $m = n_p/n_0$ their relative refractive index. As discussed at length previously [31, 32], the normalized cross-section $Q(\lambda^2)$ accounts for the dependence of the total scattering cross-section on the wavelength. It can be calculated [32] within the frame of the Mie-theory.

The function $Z(\lambda^2, c)$ can be obtained from experimental data by [31, 35] by

$$Z(\lambda^2, c) = \frac{(\tau/c)}{(\tau/c)_{c=0}} , \qquad (3)$$

where $(\tau/c)_0$ is the specific turbidity extrapolated to vanishing concentration. For size parameters $n_0\pi\sigma/\lambda_0$ not too big (see the discussion of this point in refs. [31, 32]) the integrated structure factor may be analyzed by series expansion in powers of $(n_0/\lambda_0)^2$ (cf. Eq. (9) of ref. [1]). For the region of long wavelength the expansion is given by [33, 31]

$$Z(\lambda^2, c) = S(0) + 8\alpha\left(\frac{n_0\pi}{\lambda_0}\right)^2 + O(\lambda^{-4}) , \tag{4}$$

where $S(0)$ is the structure factor $S(q)$ of the system at vanishing scattering angle and α is the first coefficient of the expansion of $S(q)$ in even powers of the scattering vector q. As shown in previous work on a similar latex [32], Eq. (4) may be used to extrapolate $S(0)$ with good accuracy if the turbidity spectra are extending into the near infrared ($1100 \geq \lambda_0 \geq 600$ nm).

The above considerations can be augmented to include polydisperse systems. Here the functions $Q(\lambda^2)$ and $Z(\lambda^2, c)$ are replaced by the respective "measured" quantities $Q_M(\lambda^2)$ and $Z_M(\lambda^2, c)$ [32]. Since the size distribution of the latex used herein is very small, the effect of polydispersity on $Q(\lambda^2)$ and $Z(\lambda^2, c)$ can be dismissed in good approximation [32].

The contribution of the dissolved polymer to the measured scattering intensity can be neglected in excellent approximation since the latex particles have a much higher apparent molar mass. In addition to this the PSS-concentration is also very small (up to 0.2 wt.%). Therefore the integrated structure factor $Z(\lambda^2, c)$ as determined from Eq. (3) refers only to the interaction of the latex particles. In consequence, the structure factor $S(0)$ extrapolated by aid of Eq. (4) gives direct access to the alteration of the interaction of the latex particles when the polyelectrolyte PSS is added.

To account for the depletion forces we use the volume-exclusion potential by Asakura, Oosawa [2] and Vrij (AOV) [3] which has been modified recently by Poon et al. [18] to account for the finite concentration of the colloidal spheres. In addition to this, the electrostatic interaction between the latex spheres is introduced through an effective diameter d of interaction [31]. Since the ionic strength of the system is rather high this approach seems to be permissible (cf. refs. [32, 12, 14]).

The geometry of interaction is depicted in Fig. 1: The latex particles are treated as hard spheres but with an effective diameter d of interaction which exceeds the actual diameter σ_L. The effective volume fraction ϕ_L of the colloid particles is given by $\phi_L = (N/V)(\pi/6)d^3$ with N/V being their number-density. This quantity can be deduced from the turbidimetric study of the pure latex [32].

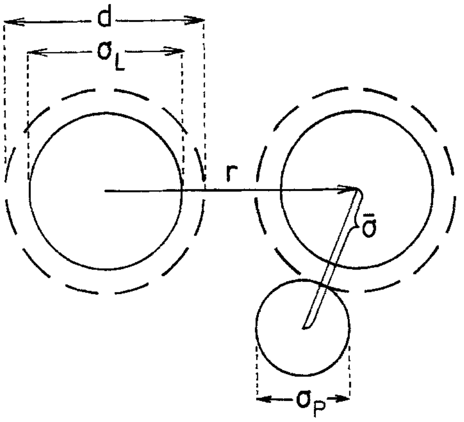


Fig. 1 The volume-exclusion potential of latex spheres in presence of smaller spheres: Definition of parameters. The large spheres symbolize the latex particles whereas the small spheres model the dissolved polyelectrolyte. The distance of closest approach of the large spheres is given by their effective diameter d. The depletion zone in which no dissolved polymer can enter is characterized by $\bar{\sigma} = (d + \sigma_p)/2$ which is the minimum distance of the centers of gravity of the latex particles and the polymer molecules, i.e., the parameter σ_p describes the depletion zone around the latex particles. It does not refer to the polyelectrolyte–polyelectrolyte interaction (cf. text for further explanation)

The interaction between the latex spheres and the polymer coils is introduced in terms of a depleted zone in which the center of gravity of the latter component cannot penetrate. With regard to the colloid spheres the polymer coils therefore may be treated as hard spheres with an effective diameter σ_p. In this context, σ_p is an adjustable parameter. It must be noted, however, that σ_p has been introduced only to describe the depletion zone around the colloid particles and not the interaction between the polymer coils themselves (see below).

With definition of

$$\bar{\sigma} = \frac{1}{2}(d + \sigma_p) \tag{5}$$

the depletion-potential U_{dep} follows as [3]

$$\begin{array}{lll} & = \infty & r < d \\ U_{dep}(r) & = -\Pi^* V_{overlap} & d \leq r \leq 2\bar{\sigma} \\ & = 0 & r > 2\bar{\sigma} . \end{array} \tag{6}$$

The volume of the overlapping depletion zones $V_{overlap}$ is given by [1–3]

$$V_{overlap} = \left(1 - \frac{3}{4}\rho + \frac{1}{16}\rho^3\right)\frac{4\pi}{3}\bar{\sigma}^3 , \tag{7}$$

with $\rho = r/\bar{\sigma}$. Following Poon et al. [18] the osmotic pressure Π^* is calculated from the number density of the polymer molecules in the free volume V_{free} not occupied by the colloid particles or their depletion zones. The ratio α_{free}

of V_{free} to the volume of the system V can be obtained [16] by using the scaled particle theory which gives [16, 18]

$$\alpha_{\mathrm{free}} = \frac{V_{\mathrm{free}}}{V} = (1 - \phi_{\mathrm{L}})\exp[-a\gamma - b\gamma^2 - c\gamma^3] , \tag{8}$$

where $\gamma = \phi_{\mathrm{L}}/(1 - \phi_{\mathrm{L}})$ and $a = 3\xi + 3\xi^2 + \xi^3$, $b = 9\xi^2/2 + 3\xi^3$, $c = 3\xi^3$ with $\xi = \sigma_{\mathrm{p}}/d$. Defining

$$A = \left(1 + \frac{d}{\sigma_{\mathrm{p}}}\right)^3 \tag{9}$$

and ϕ_{p} which is the effective volume fraction of the dissolved polymer in the free volume not occupied by the latex spheres

$$\phi_{\mathrm{p}} = \frac{N}{V\alpha_{\mathrm{free}}} \frac{\pi}{6} \sigma_{\mathrm{p}}^3 , \tag{10}$$

we obtained for the depletion potential

$$\begin{aligned} &= \infty && r < d \\ U_{\mathrm{dep}}(r)/k_{\mathrm{B}}T &= -A\phi_{\mathrm{p}}\left(1 - \frac{3}{4}\rho + \frac{1}{16}\rho^3\right) && d \leq r \leq 2\bar{\sigma} \\ &= 0 && r > 2\bar{\sigma} . \end{aligned} \tag{11}$$

In this expression the interactions between the polymer coils are disregarded (cf. below and refs. [12, 14]).

Since we are only interested in the long-range part of the structure factor, it is expedient to introduce the perturbation by the depletion forces in terms of the random phase approximation (RPA) [40]. Thus, the direct correlation function $c(r)$ of the latex spheres is rendered as

$$c(r) = c_0(r) - \frac{U_{\mathrm{dep}}(r)}{kT} . \tag{12}$$

Here $c_0(r)$ is the direct correlation function of the hard-sphere reference fluid. With aid of the Ornstein–Zernicke equation, the structure factor $S(q)$ follows as [40]

$$S(q)^{-1} = 1 - \frac{N}{V} c(q) . \tag{13}$$

Following the prescription given by Grimson [41], we adopt the WCA-separation [40] of the potential. Therefore $U_{\mathrm{dep}}(r) = U_{\mathrm{dep}}(d)$ for $r < d$ and $U_{\mathrm{dep}}(r) = U_{\mathrm{dep}}(r)$ for $r \geq d$. With Fourier-transformation of Eq. (11), we finally obtain

$$S(0)^{-1} - S_0(0)^{-1} = -8A\phi_{\mathrm{p}}\phi_{\mathrm{L}}\frac{\bar{\sigma}^3}{d^3}\left[1 - \frac{3}{16}\frac{d^4}{\bar{\sigma}^4} + \frac{1}{32}\frac{d^6}{\bar{\sigma}^6}\right] . \tag{14}$$

Treating σ_{p} as an adjustable parameter, Eq. (14) may be compared to experimental values of $S(0)$ as function of latex and PSS concentration.

Equation (14) gives a simple relation between the measured effect of the depletion forces and the decisive parameters ϕ_{L} and ϕ_{p}: For small concentrations, i.e., small ϕ_{L} the free volume of the system coincides in good approximation with the volume of the system and the difference of the reciprocal structure factors (Eq. (14)) should vary linearly with both volume fractions. If ϕ_{L} is raised, V_{free} becomes considerably smaller which leads to an increase of the osmotic pressure of the small spheres. The stronger depletion attraction will lead in turn to a deviation from linearity when the difference of the reciprocal structure factors $S(0)$ is plotted against ϕ_{L}. Because of the neglect of the polymer–polymer interaction in Eq. (14), $S(0)^{-1}$ is predicted to decrease in a linear fashion with an increasing amount of PSS for constant ϕ_{L}. Possible interactions between the polyelectrolyte coils will immediately show up in a non-linearity of this plot.

Experimental

The polystyrene latex used herein was prepared by a conventional batch emulsion polymerization (cf. [32]) of styrene (BASF, destabilized and distilled in vacuo prior to use) at 80 °C using sodium dodecylsulphate (Lancaster) as surfactant and $K_2S_2O_8$ (Fluka; recrystallized twice from water prior to use) as initiator. The stock solution of the latex (20 wt.%) was dialyzed extensively against 0.01 m KCl solution and characterized by dynamic light scattering (hydrodynamic radius: 117 nm). The diameter σ_{L} (turbidity-average diameter; [32]) which follows from the analysis of $Q(\lambda^2)$ was 113 nm. The standard deviation of the size distribution was estimated from small-angle x-ray scattering to 9.8%. The latex was filtered through a membrane filter (1.2 μm, Schleicher & Schuell, cellulose acetate) to avoid disturbance by dust particles and coagulum. A salt concentration of 0.0122 m in the latex after dialysis against 0.01 m KCl solution was calculated according to ref. [42].

Sodium polystyrene sulfonate (Aldrich) with a nominal molar mass of 70 000 g/mol (degree of substitution ca. 87%) has been purified by dialysis against 0.01 m KCl solution for 3 weeks. Latex solutions containing PSS were prepared as follows: First a stock solution of PSS (0.75 wt.%) was added to the stock solution of the polystyrene latex (20 wt.%). The concentration of the PSS-solution was determined using the extinction coefficient supplied by literature ([43]). Dilution was effected by 0.0122 m KCl solution to which the respective amounts of PSS had been added previously. The ionic strength in the dilute solutions is mainly determined by the added diluent and can be regarded as constant throughout the entire series of experiments.

The turbidity was measured for wavelengths between 600 and 1100 nm by a Perkin–Elmer 2S UV/VIS-spectrometer. Details of the measurements and correction of data may be found in ref. [32].

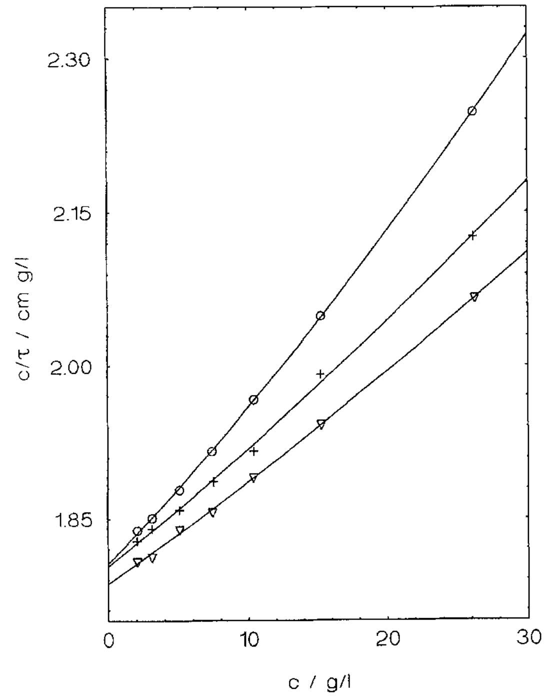
Results and discussion

Specific turbidities at infinite dilution

Application of the above theory requires that the dissolved polymer does not adsorb on the surface of the latex spheres. This can be checked accurately by monitoring the specific turbidities of the latex particles in the dilute regime.

Figure 2 gives as an example the reciprocal specific turbidity τ/c as function of weight concentration c for three concentrations of PSS. The specific turbidities at vanishing concentration are obtained by a second order polynomial fit [32]. For non-adsorbing polymers the intercepts of Fig. 2 should coincide to yield the scattering cross-section of the latex particles. Figure 2 shows that the curves merge approximately at $c = 0$ g/l; the small differences in this limit are within the experimental error [32]. At higher latex concentrations there is a marked difference between the specific turbidities measured as function of the PSS concentration beyond the limits of error thus defined.

Fig. 2 Reciprocal specific turbidity c/τ as function of latex concentration in presence of dissolved PSS measured at 800 nm. o: without PSS; +: 0.15 wt.% PSS; ▽: 0.2 wt.% PSS



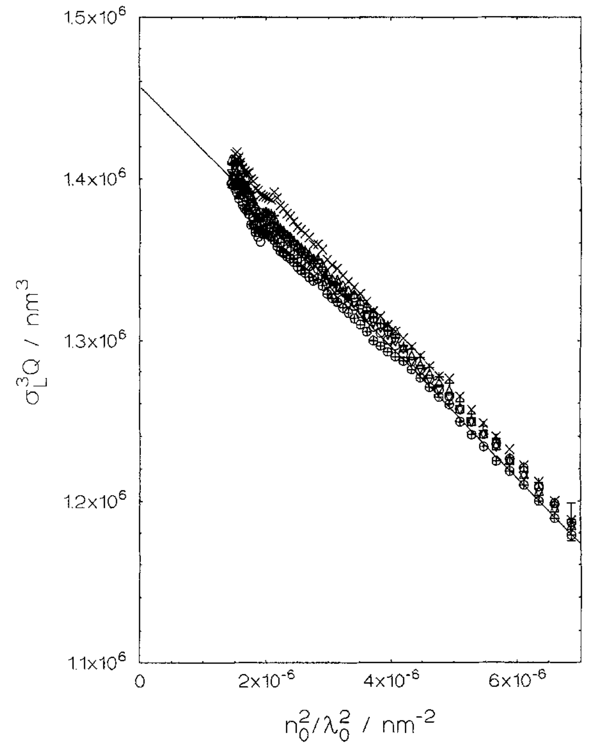


Fig. 3 Dependence of the integrated from factor $Q(\lambda^2)$ scaled by σ_L^3 on $(n_0/\lambda_0)^2$ (Eq. (1); cf. ref. [32]) for various concentrations of PSS: o: without PSS; +: 0.025 wt.% PSS; ▽: 0.05 wt.% PSS; ⊕: 0.1 wt.% PSS; △: 0.15 wt.% PSS; ×: 0.20 wt.% PSS

The specific turbidities at vanishing concentration $(\tau/c)_0$ may be evaluated [31, 32] to yield the normalized measured cross-section $Q_M(\lambda^2)$ and the turbidity-average diameter σ_L of the spheres. As mentioned above, the small nonuniformity of the size distribution of the latex used herein allows to neglect polydispersity. Therefore $Q_M(\lambda^2)$ may be replaced by the respective quantity $Q(\lambda^2)$ calculated for a system of monodisperse spheres [32].

Figure 3 displays the normalized cross-section $Q(\lambda^2)$ scaled by σ_L^3 as function of $(n_0/\lambda_0)^2$ (cf. Fig. 6 in ref. [32]). For this calculation the Cauchy-relations for water and for polystyrene deduced previously have been used [32]. Within the given limits of error (cf. the discussion of Fig. 2) all data fall on a common master curve. The solid line shows $\sigma_L^3 Q(\lambda^2)$ calculated according to ref. [32] for monodisperse polystyrene spheres of 113 nm diameter. It must be noted in this context that the maximum deviations from the master curve occurring for 0.2 wt.% PSS correspond only to a slightly higher diameter ($\Delta\sigma = 0.3$ nm).

Additional experiments using neutral water-soluble polymers show unambiguously that much more marked deviations result when adsorption of the macromolecules on the surfaces of the latex particles occurs followed by the onset of bridging flocculation. In this case the size of the particles and aggregates monitored by $(\frac{\tau}{c})_0$ and by the normalized cross-section $Q(\lambda^2)$ is much larger. The marked increase of the scattering cross-section will manifest itself by a strong upturn in a plot of $\sigma_L^3 Q(\lambda^2)$ at large wavelength, i.e., at small $(n_0/\lambda_0)^2$. From the data displayed in Fig. 3 it is therefore concluded that PSS does not adsorb on the polystyrene particles. The integrated structure factor $Z(\lambda^2, c)$ may therefore be calculated according to Eq. (3) since $Q(\lambda^2)$ does not depend on the concentration of PSS as required for the analysis of particle interaction. In consequence, all alterations of particle interaction can be ascribed to the depletion forces.

Interaction of latex particles mediated through the dissolved polyelectrolyte

Having demonstrated that PSS does not adsorb onto the particle surface, we now discuss the change of the integrated structure factor $Z(\lambda^2, c)$ as calculated from the specific turbidities through Eq. (3). Figure 4a, b show the data obtained for $Z(\lambda^2, c)$ at two different latex concentrations. As in ref. [32] the integrated structure factor is plotted as function of $(n_0/\lambda_0)^2$ as suggested by Eq. (4). The small deviations seen at long wavelengths are due to the absorption of water [32].

From Fig. 2 it was already obvious that even minute weight fractions of PSS in the latex dispersion will lead to strong alterations. The comparison of Fig. 3 with Fig. 4 now unambiguously demonstrates that the decrease of the specific turbidities is solely caused by a change of particle interaction because of the presence of dissolved polymer: The integrated structure factor is shifted in a systematic fashion whereas $Q(\lambda^2)$ remains constant within experimental error.

The dashed lines display a quadratic fit of $Z(\lambda^2, c)$ in powers of $(n_0/\lambda_0)^2$ [32]. The present accuracy of data and the range of wavelengths available in the measurements allow the extrapolation of $Z(\lambda^2, c)$ to infinite wavelength to yield $S(0)$. As discussed previously [32] this procedure allows the accurate determination of $S(0)$ without assuming any particular model of particle interaction.

The solid lines in Fig. 4A, B of the data referring to the latex without added polyelectrolyte (lowermost curves) represent fits by the Percus–Yevick structure factor calculated for a system of monodisperse hard spheres [32]. The effective diameter of interaction derived from these data is given by 130 nm. It denotes the minimum distance of the centers of gravity of the latex spheres as indicated in Fig. 1.

The region of wavelength in which these fits provide a good description of the experimental data are considerably smaller when compared to the same fits in

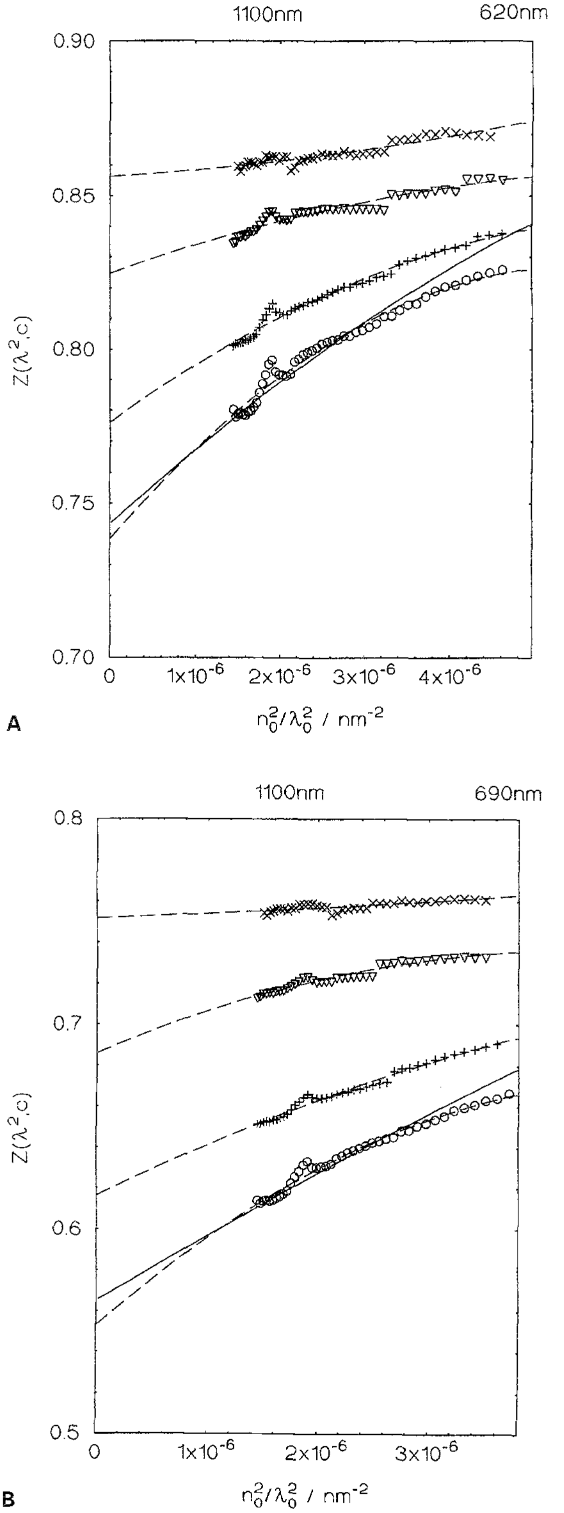


Fig. 4 Integrated structure factor (cf. Eqs. (1), (3) and (4)) as function of $(n_0/\lambda_0)^2$ in presence of dissolved polyelectrolyte PSS. **4A** latex concentration 25 g/l; **4B** latex concentration 50 g/l. ○: without PSS; +: 0.05 wt.% PSS; ▽: 0.15 wt.% PSS; ×: 0.2 wt.% PSS. The dashed lines display second order polynomial fits in powers of $(n_0/\lambda_0)^2$, whereas the solid line gives the fit of the Percus-Yevick structure factor for a system of hard spheres of diameter d

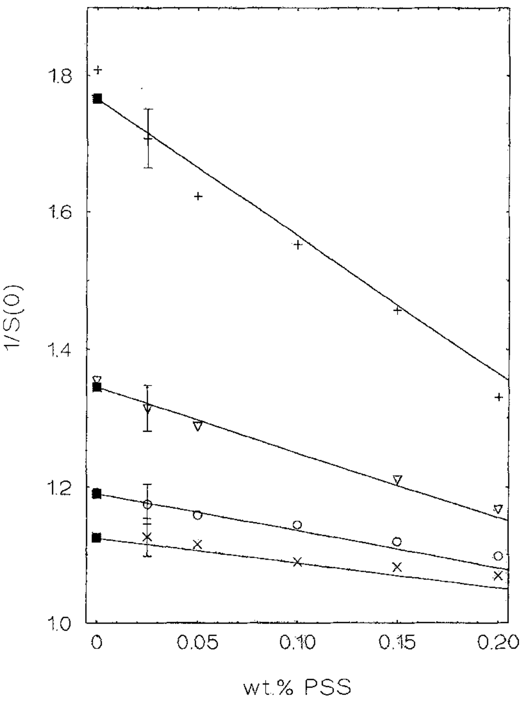


Fig. 5 Comparison of Eq. (14) with experimental data: Dependence of the reciprocal structure factor $S(0)^{-1}$ on the concentration of PSS for different latex concentrations: ×: 10 g/l; ○: 15 g/l; ▽: 25 g/l; +: 50 g/l. The filled squares mark the $S(0)^{-1}$ obtained from the data of the pure latex by the fit of the Percus–Yevick structure factor for a system of hard spheres. (cf. solid lines in Figs. 4a and b)

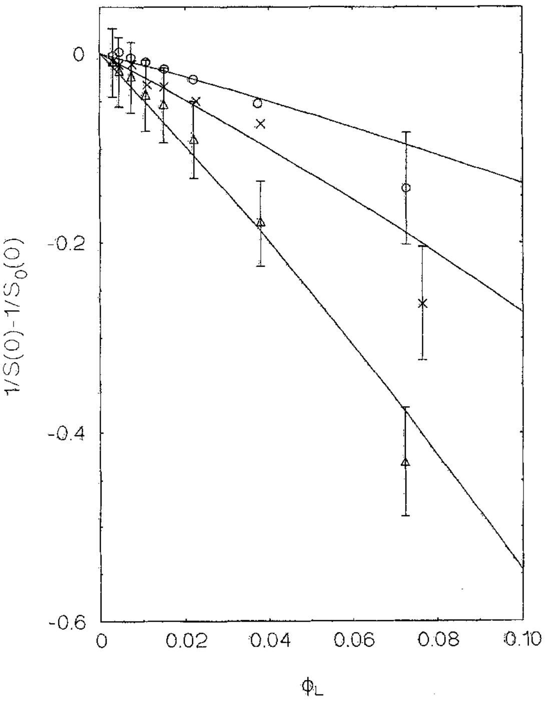


Fig. 6 Comparison of Eq. (14) with experimental data: Dependence of the reciprocal structure factor $S(0)^{-1}$ on the latex concentration for three different PSS-concentrations: ○: 0.05 wt.% PSS; ×: 0.1 wt.% PSS; △: 0.2 wt.% PSS

ref. [32]. One must keep in mind, however, that the latex spheres under consideration here have a greater diameter σ_L and a greater effective diameter of interaction d than the system discussed in ref. [32]. Hence, the integrated structure factor $Z(\lambda^2, c)$ explores a q-range of $S(q)$ extending to higher values of $q \cdot d$. In this region the description of particle interaction in terms of hard spheres is less appropriate, in particular when dealing with higher concentrations.

The $S(0)$ thus obtained may serve for a quantitative test of Eq. (14). Figure 5 displays $S(0)^{-1}$ as a function of the weight concentration of PSS. The linear relationship between $1/S(0)$ and the PSS concentration predicted by Eq. (14) is observed indeed. The straight lines in Fig. 5 have been calculated assuming an effective diameter of interaction $\sigma_p = 16.4$ nm. This diameter would lead to an effective volume fraction of the PSS-polymer of the order of 0.04 at most. If the interaction of the PSS-molecules were characterized by this volume fraction, a small but non-vanishing virial correction of the osmotic pressure of the dissolved polymers would necessarily follow. Figure 5 suggests that this is not the case and the actual effective diameter seems to be smaller than σ_p. Therefore, σ_p must be regarded solely as a characterization of the depletion zone around the latex particles rather than an effective diameter of the PSS-polymer coils in general.

The filled squares shown in Fig. 5 give the $S(0)$ resulting from the fit of the integrated structure factor calculated for a system of monodisperse spheres by use of the Percus–Yevick structure factor (cf. Fig. 4a, b; lowermost curves). Since at lower latex concentrations the hard-sphere model provides a good description, the measured and the hard-sphere $S(0)$ practically coincide. As already discussed above, at higher concentrations the modeling of the interaction of the latex spheres in terms of hard spheres becomes less accurate and the measured $S(0)$ values are higher than expected from Eq. (14). The respective $S(0)$ taken from the fit of the hard sphere model to $Z(\lambda^2, c)$ in absence of PSS (cf. the discussion of Fig. 4a,b) are in full agreement with Eq. (14) as can be seen from Fig. 5; i.e., they correspond to a value of $S(0)$ extrapolated from the data taken at finite PSS-concentration.

A further test of Eq. (14) is given by the relationship of $S(0)$ and the effective volume fraction ϕ_L of the latex. Because $S_0(0)$ depends on ϕ_L, the difference $1/S(0) - 1/S_0(0)$ is plotted in Fig. 6 against the effective volume fraction of the latex. The $S_0(0)$ data have been taken from the fits of the Percus–Yevick structure factor at the respective latex concentrations as discussed above (see discussion of lowermost curves in Fig. 4a and b and the data in Fig. 5 displayed by squares). For a given σ_p Eq. (14) allows to calculate the difference of the reciprocal structure factors without additional adjustable parameters. As seen from Fig. 6, the value of σ_p taken from Fig. 5 provides a good fit of the data, at least in the region of low concentrations. At higher effective volume fractions of the latex theory underestimates the difference between the reciprocal structure factors. It must be noted that the comparison of theory and experiment shown in Fig. 6 is more sensitive to the details of the model since it probes the interaction of the latex particles as well as the interaction of the PSS-coils with the colloid particles at the same time. In view of the simplifications inherent in the description of latex interaction in terms of hard spheres the agreement of theory and experiment displayed in Figs. 5 and 6 can be considered satisfactory. Furthermore, the fits shown in Fig. 5 and 6 are effected through a single adjustable parameter, namely σ_p; all other parameters needed for the calculation have been taken from the description of the pure latex (Fig. 4a,b).

It must be kept in mind, however, that the above comparison of theory and experiment assumes the validity of the purely attractive depletion potential Eq. (11). The interaction between the colloidal spheres has been approximated by a hard-sphere potential and better agreement of theory and experiment may be reached by a refinement of the interaction potential of the latex particles. In addition to this, a part of the discrepancies seen in Fig. 6 might be due to the inherent inconsistencies of the RPA (cf. e.g. the discussion of this point in ref. [40]). Recent work by Kelkar et al. [44] suggests, however, that the RPA seems to be a viable approach for the calculation of the structure factor in colloidal systems.

Conclusion

The analysis of the turbidimetric data has shown that the volume-exclusion potential Eq. (6) provides a good description of the data in the region of low concentrations. Based on the RPA, Eq. (14) allowed to discuss separately the dependence of $S(0)$ on latex concentration as well as on the amount of added PSS. Up to latex concentrations of 2.5 wt.% all data can quantitatively be described by $\sigma_p = 16.4$ nm which is the single adjustable parameter in Eq. (14); the other parameters (d, ϕ_L) can be obtained from the analysis of the latex in absence of dissolved polymer. At higher latex concentrations theory provides only a qualitative description which may be traced back to the various simplifications of the above theoretical treatment. Aside from these problems the present data show, however, that turbidimetry is capable of furnishing quantitative data on the interaction of latex particles in the presence of dissolved polymers.

Acknowledgment Financial support by the Deutsche Forschungsgemeinschaft, by the AIF (project 9749), by the Bayer AG, Geschäftsbereich Kautschuk and by the Bundesministerium für Bildung und Forschung is gratefully acknowledged.

References

1. Bondy C (1939) Trans Faraday Soc 35:1093
2. Asakura S, Oosawa F (1954) J Chem Phys 22:1255; Asakura S, Oosawa F (1958) J Polym Sci 33:183
3. Vrij A (1976) Pure Appl Chem 48:471
4. de Hek H, Vrij A (1981) J Colloid Interf Sci 84:409
5. Sperry PR, Hopfenberg HB, Thomas NL (1981) J Colloid Interf Sci 82:62
6. Sperry PR (1982) J Colloid Interf Sci 87:375
7. Gast AP, Hall CK, Russel WB (1983) J Colloid Interf Sci 96:251
8. Russel WB, Saville DA, Schowalter WR (1989) Colloidal Dispersions, Cambridge University Press, Cambridge
9. Leal Calderon F, Bibette J, Biais J (1993) Europhys Lett 23:653
10. Ilett SM, Orrock A, Poon WCK, Pusey PN (1995) Phys Rev E 51:1344
11. Lekkerkerker HNW, Stroobants A (1994) Il Nuovo Cim 16D:949
12. Richetti P, Kékicheff P (1992) Phys Rev Lett 68:1951
13. Milling A, Biggs S (1995) J Colloid Interf Sci 170:604
14. Mondain-Monval O, Leal-Calderon F, Phillip J, Bibette J (1995) Phys Rev Lett 75:3364
15. Poon WCK, Pusey PN (1995) In: Baus M, Rull LR, Ryckaert JP (eds) Observation, Prediction and Simulation of Phase Transitions in Complex Fluids, Vol 460 of NATO Advanced Study Institute, Series C: Mathematical and Physical Sciences, Kluwer Academic, Dordrecht
16. Lekkerkerker HNW (1990) Colloids Surf 51:419
17. Lekkerkerker HNW, Poon WCK, Pusey PN, Stroobants A, Warren PB (1992) Europhys Lett 20:559
18. Poon WCK, Ilett SM, Pusey PN (1994) Il Nuovo Cim 16D:1127
19. Meijer EJ, Frenkel D (1994) J Chem Phys 100:6873
20. Meijer EJ, Frenkel D (1995) Physica A 213:130
21. Walz JY, Sharma A (1994) J Colloid Interf Sci 168:485
22. Mao Y, Cates ME, Lekkerkerker HNW (1995) Physica A 222:10
23. Warren PB, Ilett SM, Poon WCK (1995) Phys Rev E 52:5205
24. Mao Y (1995) J Phys II (France) 5:1761
25. de Hek H, Vrij A (1982) J Colloid Interf Sci 88:258
26. Tong P, Witten TA, Huang JS, Fetters LJ (1990) J Phys (France) 51:2813
27. Bibette J, Roux D, Pouligny B (1992) J Phys II (France) 2:401
28. Snowden MJ, Williams PA, Garvey MJ, Robb ID (1994) J Colloid Interf Sci 166:160
29. Hunter RJ (1989) Foundations of Colloid Science, Vol II, Clarendon Press, Oxford
30. Pusey PN, Pirie AD, Poon WCK (1993) Physica A 201:322
31. Apfel U, Grunder R, Ballauff M (1994) Colloid Polym Sci 272:820
32. Apfel U, Hörner KD, Ballauff M (1995) Langmuir 11:3401
33. Jansen JW, de Kruif CG, Vrij A (1986) J Colloid Interf Sci 114:492
34. Rouw W, Vrij A, de Kruif CG (1988) Colloids Surf 31:299

35. Penders MGHM, Vrij A (1990) J Chem Phys 93:3704
36. Fleer GJ, Cohen Stuart MA, Scheutjens JMHM, Cosgrove T, Vincent B (1993) Polymers at Interfaces, Chapman & Hall, London
37. Rawson S, Ryan K, Vincent B (1988/89) Colloids Surf 34:89
38. Nashima T, Sudo H, Furusawa K (1992) Colloids Surf 67:95
39. Smith NJ, Williams PA (1995) J Chem Soc Faraday Trans 91:1483
40. Hansen JP, McDonald IR (1986) Theory of Simple Liquids, 2nd edition, Academic Press, London
41. Grimson MJ (1983) J Chem Soc Faraday Trans 2 79:817
42. Brezesinski G (1993) Grenzflächen und Kolloide: Physikalisch Chemische Grundlagen, Spektrum Akademischer Verlag, Heidelberg
43. Reddy J, Marinsky JA (1970) J Phys Chem 74:3884
44. Kelkar VK, Narayanan J, Manohar C (1992) Langmuir 8:2210