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## Evidence for hydrophobic attraction between latex particles in aqueous systems as investigated by turbidimetry

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**Abstract** We report the evidence for attractive interaction of latex particles which are covered by poly(ethylene oxide) chains. These particles are suspended in aqueous solutions of ammonium sulfate. The interaction is probed by measurements of the turbidity of the suspensions up to 70 g/l. Turbidity is insensitive to multiple scattering and allows the static structure factor,  $S(q)$  [ $q = (4\pi n_0/\lambda_0)\sin(\theta/2)$ , where  $\theta$  is the scattering angle,  $n_0$  is the refractive index of the medium and  $\lambda_0$  is the wavelength in vacuo], to be determined at small  $q$

values. The analysis of  $S(q)$  at small  $q$  values yields information about possible attraction of the particles. The analysis of the turbidity data furthermore shows that no aggregation took place in these systems. A weak but long-range attractive interaction was found at ammonium sulfate concentrations of 0.01 and 0.1 M. The relation of this attractive force to hydrophobic forces is discussed.

**Key words** Turbidity · Light scattering · Hydrophobic attraction · Structure factor · HMSA

### Introduction

Colloidal particles may be stabilized against coagulation by attaching linear polymer chains to their surface [1, 2]. If the dispersion medium is a good solvent for the chains attached to the surface, strong steric repulsion will result upon approaching these particles [2]. If, on the other hand, the dispersion medium is a poor solvent for the tethered chains, an attractive force may arise which has the same range as the dimensions of the surface chains. Within the frame of classical theory, the stability of such particles is determined by the balance of the steric repulsion and the attraction due to the van der Waals forces between the particles [1, 2].

Poly(ethylene oxide) (PEO) chains have often been used for the stabilization of colloidal particles [1, 2]. Steric stabilization provides the colloidal stability for a great manifold of association colloids composed of amphiphilic molecules in which the hydrophilic part consists of PEO chains. Direct measurements of the forces between mica surfaces covered by a nonionic

surfactant having PEO chains, however, showed that an attractive minimum of the force–distance curve may appear at higher temperatures [2, 3]. Hence, attraction can occur even when the suspension medium is a good solvent for the polymers attached to the surface. In general, it is believed that such surfaces may become more hydrophobic with increasing temperature and the resulting attraction can be classified as a hydrophobic force [2]. These hydrophobic forces, the origins of which are not exactly known, have been the subject of a number of recent investigations. A detailed discussion of recent work on this subject has been given by Vinogradova and coworkers [4, 5].

Up to now, most of the work devoted to attraction between hydrophobic surfaces has been carried out using the surface force apparatus [2]. Evidently, hydrophobic attraction should also be detectable in suspensions of colloidal particles with suitably modified surfaces. Zhu and coworkers [6–8] have invoked hydrophobic forces to explain the attraction between particles covered by PEO and by poly(*N*-isopropylacrylamide) chains. These

workers studied the coagulation of these particles dispersed in salt solutions. The attraction between the particles was assessed by a discussion of the fractal dimensions of the resulting aggregates. The results reported in Refs. [6–8] clearly point to specific effects of the different ions added to the solutions.

In addition to this, there is growing evidence for short-range attractive forces between globular proteins in solution if a sufficient amount of salt is added. A survey of current literature on this problem may be found in a recent review by Piazza [9]. It is thus evident that hydrophilic surfaces and/or hydrophilic particles may exhibit hydrophobic attraction if enough salt is added to the solution or if raising the temperature of the system changes the hydrophilicity. The strength and the range of attractive interaction, however, are still a matter of debate.

In many cases attractive forces operative in colloidal systems are assessed from the threshold of coagulation and from the analysis of the fractal structures obtained by flocculation of the dispersion [1, 6–8]. Strong attractive interaction, however, leads to nonequilibrium structures and the equilibrium pair potential may be derived from these results only in a quantitative manner. Here we present a study of attractive forces between well-defined latex particles induced by high salt concentrations in equilibrium, i.e., in suspensions which are still stable against flocculation. The system used here consists of well-defined polystyrene latex particles coated by a thin layer of PEO chains. These particles, the synthesis and the characterization of which have recently been reported [10], can be dispersed in aqueous salt solutions with defined ionic strength. The strength of interaction is probed by static light scattering in the one-phase region, i.e., under conditions under which the suspension is still stable. Static light scattering allows the structure factor,  $S(q)$  [ $q = (4\pi n_0/\lambda_0)\sin(\theta/2)$ , where  $\theta$  is the scattering angle,  $n_0$  is the refractive index of the medium and  $\lambda_0$  is the wavelength in vacuo], to be obtained, which in turn may be evaluated to yield information about the interaction potential of the particles [11]. If the measurements are done at sufficiently low  $q$  values,  $S(q)$  may give information about weak attractive forces, which is difficult to obtain by other experimental techniques [12].

The particles investigated here meet all the requirements necessary for an investigation of attractive interaction by scattering methods:

1. Small-angle X-ray scattering (SAXS) showed that the surface layer of PEO chains has a thickness of about 3 nm [10]; hence, the range of layer–layer interaction is well defined.
2. The size distribution of the particles is found by SAXS and transmission electron microscopy to be narrow (standard deviation: about 9% [10]); therefore, strong effects of polydispersity on the measured

structure factor which may obscure the effect of particle interaction [11] are not to be expected.

3. By virtue of their synthesis these particles bear no chemically fixed surface charge. These particles are solely sterically stabilized and complications caused by the presence of a high number of surface charges are not to be expected.

Up to now, these latex particles have been studied in salt solutions of low ionic strength (0.001–0.005 M monovalent salt) [10, 13]. Turbidimetric studies have demonstrated that under these conditions preferential adsorption of anions takes place [13]. At low salt concentration (0.001 M) the electrostatic repulsion caused by these adsorbed charges can be derived directly from turbidimetric data. Raising the salt concentration to 0.005 M leads to an effective screening of these charges. Here turbidimetric measurements revealed that under these conditions the particles interact as hard spheres and that stabilization is solely provided by the PEO surface layer [10]. The hard-sphere radius found by turbidimetry pointed to a thickness of the surface layer of 2–3 nm, in good agreement with SAXS data [10].

As an investigative tool we use turbidimetry. Previous studies [12, 14–17] have shown that turbidimetry is capable of exploring the static scattering intensity in the region of smallest scattering vectors. These data, in turn, yield the structure factor. Turbidimetry is not disturbed by multiple light scattering and, hence, allows the interaction of particles in concentrated dispersions [14–17] to be explored.

## Theory

The investigation of attractive forces between dispersed latex particles presented here rests on the analysis of  $S(q)$  in the region of low  $q$  values.  $S(q)$  is defined through the ratio of the scattering intensity,  $I(q)$ , for an interacting system and the scattering intensity,  $I_0(q)$ , of the noninteracting system, where the latter quantity is accessible through extrapolation to vanishing concentration [11]. Careful measurements of  $S(q)$  obtained from a narrowly dispersed system of spheres with diameter  $\sigma$  may, in principle, furnish the following information. In the region of the first maximum of  $S(q)$  where  $q \approx 1/\sigma$  the steepness of the mutual repulsion of the particles may be obtained. If  $q \ll 1/\sigma$ , that is at much lower scattering angles,  $S(q)$  is mainly sensitive to mutual attractive forces between the particles [11, 12]. This is immediately evident when considering that attractive interaction between particles in suspension will lead to transient clusters of the particles. The size of such clusters far exceeds  $\sigma$  and their detection necessitates a  $q$  range in which  $q \ll 1/\sigma$ . Hence, for particles having diameters of 100 nm the  $q$  range of light scattering as furnished by the turbidimetric method

[14–17] is necessary to pursue the problem of hydrophobic attraction.

It is evident that the  $q$  range furnished by most scattering experiments is too small to obtain experimentally the entire range of  $S(q)$ , i.e., from  $q=0$  to a  $q$  range in which  $S(q) \approx 1$ . Hence, the analysis of the experimental structure factor proceeds through a comparison with values calculated for a given interaction potential,  $U(r)$ . It is therefore clear that  $U(r)$  cannot be extracted in a unique fashion from given data of  $S(q)$ . The advantage of scattering methods, however, lies in the fact that even minute tendencies for clustering of particles may be detected. Hence, even weak attraction which does not lead to phase separation is easy to detect and to quantify by light scattering.

The method used here consists of two parts. First,  $S(q)$  has to be calculated for a suitable interaction potential,  $U(r)$ . In the second step,  $S(q)$  is compared to experimental data and the parameters of  $U(r)$  are changed until agreement between theory and experiment is reached. The discussion of this problem in Ref. [12] shows that the information to be gained from  $S(q)$  at low  $q$  values may be related to the zeroth and the second moment of the attractive part of  $U(r)$ . The procedure applied here allows the range and the depth of the effective pair potential operative between the latex particles to be determined. No statement can be made from these data about the exact form of  $U(r)$ , of course. The details of this procedure and the determination of  $S(q)$  from turbidimetric data have recently been delineated in detail in Ref. [12]; therefore, a summary of the pertinent expressions will suffice here.

We consider a system of monodisperse spheres with diameter  $\sigma$  interacting through a square-well potential,  $U(r)$ :

$$\begin{aligned} U(r) &= \infty & r < \sigma, \\ U(r) &= -\varepsilon & \sigma \leq r \leq \lambda_{\text{sq}}\sigma, \\ U(r) &= 0 & r > \lambda_{\text{sq}}\sigma, \end{aligned} \quad (1)$$

where  $\varepsilon$  denotes the depth of the well and  $\lambda_{\text{sq}}$  determines the range of attractive interaction. The choice of this potential is derived from its simplicity. In the absence of further information on the possible attractive potential it therefore seems to be a good choice to model the data. Given this potential,  $S(q)$  of the suspension can be calculated with the aid of the HMSA integral equation theory [18]. The choice of the HMSA theory is derived from the fact that it may be considered as a virtually exact solution of the problem throughout the range of volume fractions,  $\phi$ , of the spheres.

Previous work on hydrophobic interaction [19, 20] suggests that an interaction potential exhibiting an exponential seems to be appropriate to describe hydrophobic attraction:

$$\begin{aligned} U(r) &= -\varepsilon \exp\left(-\frac{r}{D_0}\right), \\ \varepsilon &= \frac{\sigma C D_0}{4}, \end{aligned} \quad (2)$$

where  $D_0$  is the decay length of the interaction. The hydrophobic interaction constant,  $C$ , provides a measure of the strength of the interaction. This potential is used here to compare our data to the results of Refs. [19, 20]. In order to compare the  $S(q)$  related to Eq. (2) to experimental data, the random-phase approximation (RPA) is used. The RPA provides a convenient access to  $S(q)$  for arbitrary interaction potentials without recourse to integral equation theories. It has been demonstrated in Ref. [12] that the RPA may fail at higher volume fractions. For the small attractive forces under consideration here the error induced by the RPA is expected to be negligible, however.

To assess the range of attractive forces in more detail the sticky-sphere potential,  $U_{\text{st}}(r)$ , may be used as well in a comparison of theory and experiment.  $U_{\text{st}}(r)$  is given by [21]

$$\frac{U_{\text{st}}(r)}{kT} = \begin{cases} \infty & r < \sigma \\ \ln \left[ \frac{12\tau_{\text{st}}(r_{\text{st}} - \sigma)}{r_{\text{st}}} \right] & \sigma < r < r_{\text{st}} \\ 0 & r > r_{\text{st}} \end{cases} \quad (3)$$

where the stickiness parameter,  $\tau_{\text{st}}$ , defines the strength of the attractive interaction. This potential was chosen since it may be used for the description of short-range attractive interaction. In the limit of a vanishing range of interaction,  $\Delta = (r_{\text{st}} - \sigma)/r_{\text{st}}$ , this potential leads to the analytic expression for  $S(q)$  given in Ref. [21].

For a given  $S(q)$  (cf. Eqs. 1, 2, 3), the turbidity may be calculated through

$$\tau = 2\pi \int_0^\pi I_0(q) S(q) \sin \theta \, d\theta, \quad (4)$$

where  $I_0(q)$  is the intensity referring to a non-interacting system. The specific turbidity,  $\tau/c_L$ , may be factored as well into an integrated form factor,  $Q(\lambda^2)$ , and an integrated structure factor,  $Z(\lambda^2, c)$ , according to

$$\frac{\tau}{c_L} = K^* \left( \frac{n_0 \pi \sigma}{\lambda_0} \right)^3 \frac{16\pi}{3} Q(\lambda^2) Z(\lambda^2, c_L), \quad (5)$$

where  $c_L$  denotes the weight concentration of the latex and  $n_0$  is the refractive index of the medium.  $K^*$  is an optical constant given by

$$K^* = \frac{3n_0}{4\lambda_0 \rho_L} \left( \frac{m^2 - 1}{m^2 + 2} \right)^2. \quad (6)$$

Here  $\rho_L$  is the density of the particles,  $n_L$  the refractive index of the latex particles and  $m = n_L/n_0$  their relative

refractive index. The quantity  $Z(\lambda^2, c)$  can, therefore, be derived from the specific turbidities,  $\tau/c_L$ , through

$$Z(\lambda^2, c_L) = \frac{\left(\frac{\tau}{c_L}\right)}{\left(\frac{\tau}{c_L}\right)_0}, \quad (7)$$

with  $(\tau/c_L)_0$  being the specific turbidity extrapolated to vanishing latex concentration,  $c_L$ .

Given these definitions the analysis of the suspension proceeds along the lines given in Ref. [12]: The latex particles are dispersed in salt solutions of defined ionic strength and the turbidity is measured for small concentrations up to  $c_L = 70$  g/l. The optimal range of wavelengths in which all data were taken is  $600 \text{ nm} \leq \lambda \leq 1100 \text{ nm}$  [14–16]. Data of  $\tau$  taken at small  $c_L$  serve for the extrapolation of  $(\tau/c_L)_0$ , which in turn leads to  $Z(\lambda^2, c)$  according to Eqs. (5) and (7). These experimental data are compared to calculated values of  $Z(\lambda^2, c)$  (see the discussion of Fig. 2 in Ref. [12]). The parameters of the potentials (Eqs. 1–3) are subsequently changed and the entire calculation is repeated until the measured and calculated  $Z(\lambda^2, c)$  coincide throughout the entire range of wavelengths.

The importance of attractive interaction for the present system may furthermore be judged by comparing the measured  $Z(\lambda^2, c)$  to the integrated structure factor calculated for a system of hard spheres. This calculation is easily done by use of the structure factor of a system of hard spheres furnished by the Percus–Yevick theory [22]. If no attraction is operative between the particles, the hard-sphere diameter necessary for this fit should coincide with the value derived from the radial structure of the particles obtained by SAXS. A larger effective diameter points to additional repulsive forces between the particles as effected through electrostatic repulsion. A smaller diameter, however, immediately demonstrates that the hard-sphere potential is not applicable and that attractive forces are operative in the system [14–16].

## Experimental

Two latexes were used throughout this investigation: System 1 had a number-average diameter,  $\sigma_N$ , of 87.0 nm ( $\sigma_w/\sigma_N = 1.02$ ;  $\sigma_w$ : weight-average diameter) and system 2 had a  $\sigma_N$  of 112.0 nm ( $\sigma_w/\sigma_N = 1.01$ ). Both values were determined by SAXS using the equipment and the method reported in Ref. [23]. SAXS also verified the core–shell structure expected from the synthesis of the particles according to the method described in Ref. [10]. Dynamic light scattering (Peters ALV 5000) gave hydrodynamic radii which indicated a polymeric shell of approximately 5-nm thickness when compared to the core diameters obtained from SAXS.

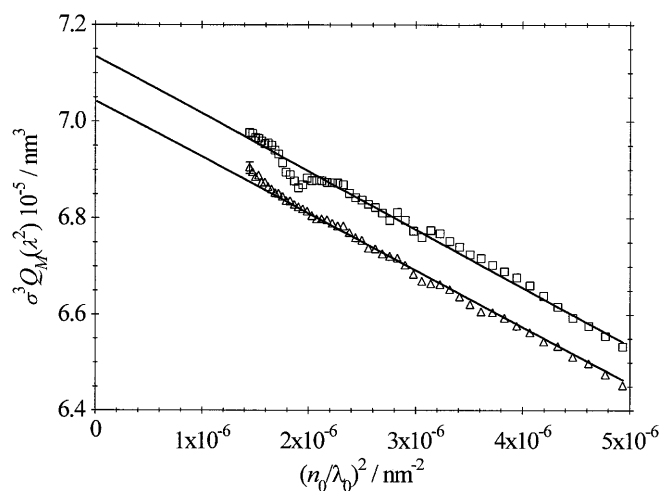
Purification was achieved through extensive dialysis against pure water. The conductometric titration gave a very low surface charge ( $0.3 \mu\text{C}/\text{cm}^2$  [10]). Hence, chemically bound surface charges are not expected to play a significant role. The concentration of  $(\text{NH}_4)_2\text{SO}_4$  was adjusted through addition of salt or by dilution

with salt solution of given concentration. The turbidity of all the suspensions was determined at 25 °C through careful measurements of the extinction using a Perkin Elmer Lambda 2S photometer in the range  $600 \text{ nm} \leq \lambda \leq 1100 \text{ nm}$ . The length of the optical path was varied as a function of  $\lambda$  to keep the extinction in the optimal range (0.15–1.5 [15, 16]) throughout all concentrations. All the solutions were filtered through a  $0.45\text{-}\mu\text{m}$  filter (Roth, Germany).

## Results and discussion

A meaningful analysis of the turbidimetric data requires the system to be stable for a prolonged time. Moreover, addition of  $(\text{NH}_4)_2\text{SO}_4$  should not change the structure of the particles. Both points were verified for both systems by the determination of the integrated form factor,  $Q(\lambda^2)$ , according to Eq. (3). The result obtained for system 1 ( $\sigma_N$ : 87.0 nm;  $\sigma_w/\sigma_N = 1.02$ ; determined by SAXS [10]) in the presence of 0.01 and 0.1 M ammonium sulfate is displayed in Fig. 1. The shift of the curves amounts to a difference in diameters of 0.4 nm, which is within the limits of error. The average diameter of the particles of system 1 is 89.2 nm, which practically coincides with  $\sigma_w$  furnished by SAXS (89 nm). The good reproducibility of the measurements furthermore underscores that the latex is still stable against coagulation.

Additional measurements of the hydrodynamic radius,  $R_H$ , by dynamic light scattering in the dilute regime corroborated this finding: The values of  $R_H$  measured in 0.01 and 0.1 M ammonium sulfate solution agreed with the data obtained by the same method at much lower



**Fig. 1** Determination of the diameter of system 1 by turbidimetry. Integrated form factor,  $Q(\lambda^2)$  (Eq. 3), scaled by the cube of the radius of the particles,  $\sigma^3$ , as a function of the reciprocal quadratic wavelength in the medium. The *squares* refer to measurements in 0.01 M ammonium sulfate solutions, whereas the *triangles* refer to 0.1 M ammonium sulfate. The *solid lines* give the best fits of the total cross section calculated by Mie's theory [14, 16]

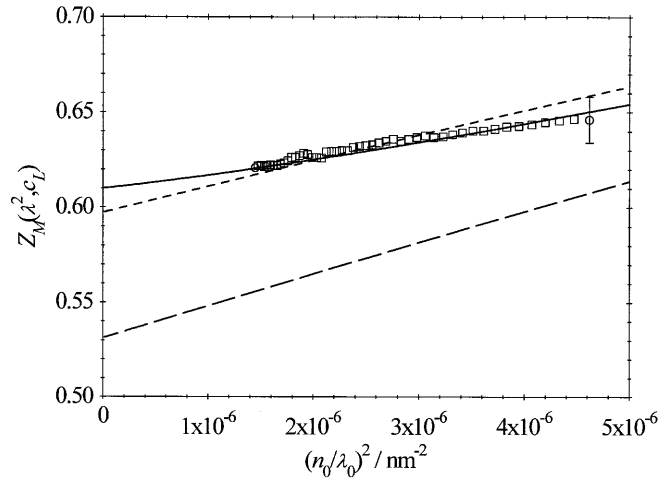
ionic strength [10, 13]. This shows that the latex is stable under these conditions; no drastic change in the PEO layer took place. Only at much higher salt concentration (1 M) was  $R_H$  found to increase with time, indicating slow coagulation of the particles.

$Z(\lambda^2, c)$  measured for system 1 is displayed in Fig. 2. Very similar results were obtained for system 2. The concentration of  $(\text{NH}_4)_2\text{SO}_4$  was 0.01 and 0.1 M in these measurements. All attempts to describe these data and the data obtained for higher salt concentrations by the hard-sphere model failed. The solid lines in Fig. 2 display the best fits of the data by a square-well potential (Eq. 1). For this fit the outer radius, which includes the PEO layer, was taken from the SAXS data [10]. For system 1, the radius is 46.5 nm, whereas for system 2 a value of 59 nm is given. The range parameter,  $\lambda_{\text{sq}}$ , as well as the depth,  $\varepsilon$ , are varied until optimal agreement of the measured and the calculated  $Z(\lambda^2, c)$  is achieved.

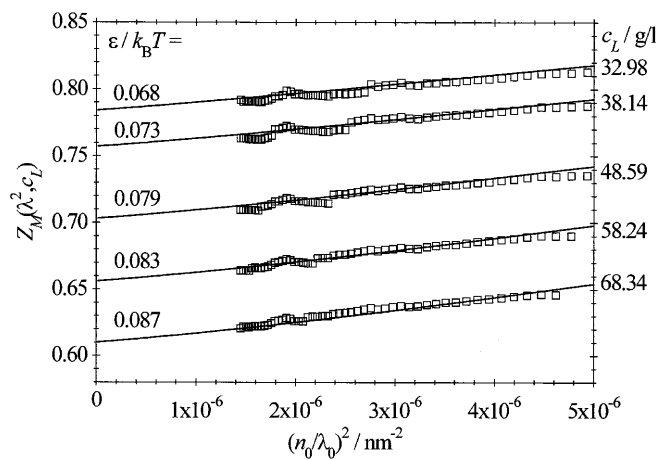
A comparison of  $Z(\lambda^2, c)$  measured at an ammonium sulfate concentration of 0.01 M for system 1 with data calculated for different interaction potentials is displayed in Fig. 3. The short-dashed line gives the best fit by the sticky-sphere model (Eq. 3), which clearly can be ruled out for the present system. Despite the problem of determining  $U(r)$  from static scattering experiments, this comparison clearly shows that the attractive interaction investigated here must have an appreciable spatial range. The long-dashed line displays  $Z(\lambda^2, c)$  calculated from the outer radius as determined by SAXS. Pure hard-sphere repulsion is seen to lead to erroneous results.

It turned out that the data of system 1 can be described by  $\lambda_{\text{sq}} = 1.6 \pm 0.2$  (solid lines in Figs. 2, 3), whereas system 2 required a slightly smaller value, namely  $\lambda_{\text{sq}} = 1.48 \pm 0.5$ . Given the different diameter

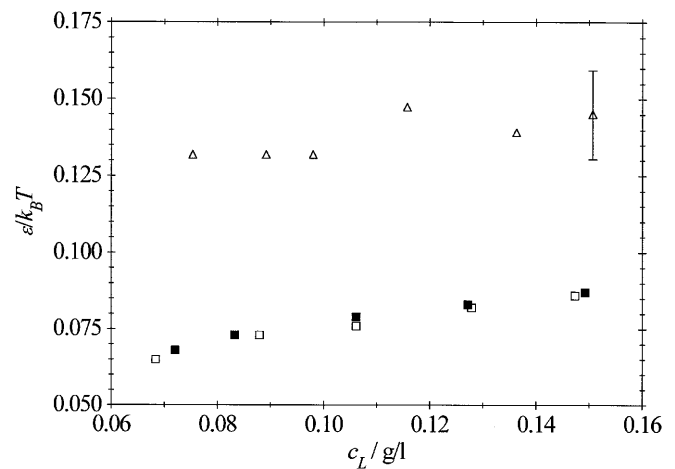
of the two latexes the range of attractive interaction remains approximately the same (about 55 nm).  $\varepsilon$  is displayed in Fig. 4 for both systems. There is a slight increase in  $\varepsilon$  with latex concentration, which is hardly outside the present limits of error. Also, the larger particles of system 2 require a considerably higher  $\varepsilon$ .  $\varepsilon$  is found to be independent of salt concentration in case of system 1, i.e., 0.01 as well as 0.1 M ammonium sulfate solution led to the same  $\varepsilon$ .



**Fig. 3** Comparison of different interaction potentials.  $Z(\lambda^2, c)$  (Eq. 5) as a function of the reciprocal quadratic wavelength in the medium for the smaller latex with  $c_L = 68.34$  g/l (see Fig. 2). The solid line displays the fit by the square-well potential discussed in conjunction with Fig. 2. The short-dashed line gives the best fit of  $Z(\lambda^2, c)$  by use of the Baxter potential, Eq. (6). The long-dashed line refers to the  $Z(\lambda^2, c)$  calculated for a system of hard spheres. For this calculation the radius of the particles determined by small-angle X-ray scattering was used



**Fig. 2** Determination of the particle interaction in system 1 by turbidimetry. Integrated structure factor,  $Z(\lambda^2, c)$  (Eq. 5), as a function of the reciprocal quadratic wavelength in the medium for the smaller latex studied here. The latex concentrations,  $c_L$ , are indicated in the graph. The solid lines refer to the best fit of a square-well potential (Eq. 1) with  $\lambda_{\text{sq}} = 1.6$  and the values of  $\varepsilon$  indicated in the graph



**Fig. 4** Depths,  $\varepsilon$ , of the square-well potential as determined from the fits shown in Fig. 2 as a function of  $c_L$ . Squares: system 1, open squares: 0.01 M ammonium sulfate, filled squares: 0.1 M ammonium sulfate. Triangles: system 2 measured in 0.01 M ammonium sulfate solution

As expected from the considerations and model calculations in Ref. [12] Eq. (2) also provides a fit of the present data of  $Z(\lambda^2, c)$  if  $\varepsilon$  and  $D_0$  are taken as adjustable parameters. The decay length,  $D_0$ , is found to be approximately 40 nm, whereas the overall strength of interaction,  $\varepsilon$ , is of the order of  $kT$ . Evidently the fit of the data in terms of Eq. (2), which assumes an exponential decay of the attractive interaction, leads to a higher  $\varepsilon$ . The approximate range of interaction remains the same, however.

All the results demonstrate that the PEO-covered polystyrene particles immersed in ammonium sulfate solutions interact through an effective-pair potential that may be described by Eq. (1). There is a weak but long-ranged attraction in solutions of 0.01 and 0.1 M ammonium sulfate, which is absent at lower ionic strength. It must be reiterated, however, that the present analysis gives only an overall estimate of the strength and range of the attractive force; there is no information about the exact dependence of the potential on distance. There is no doubt, however, that this weak attraction, which is not present at low salt concentrations [10, 13], arises through addition of sufficient amounts of ammonium sulfate to these latex particles. Similar effects have been observed upon addition of sodium phosphate.

Having clearly established the presence of attractive forces between the latex particles in solutions of sufficient salt concentration, it remains to discuss possible origins of this force: It is clear that this attraction cannot be traced to the direct interaction of the polymeric layer on the surface of the particles or to bridging by long macromolecules. The method of synthesis together with the previous analyses of these particles described in Refs. [10, 13] easily rules out such possible ambiguities. Furthermore, the strength of the interaction observed here is too large to be traced back to the van der Waals interaction of the particles. Here the expression furnished by Vold [24] was used to estimate the interaction potential of two core-shell particles investigated here.

This comparison demonstrates that neither the range nor the strength of  $U(r)$  observed here can be reproduced by van der Waals attraction. In particular, van der Waals attraction would not undergo any drastic change upon adding salt to the solution.

From the comparison of theory and experiment it becomes evident that the origin of the attractive interaction can be traced back neither to steric forces nor to van der Waals attraction. By comparing our system to the latexes studied previously by other authors [6–9] we assign the attraction we deduce from our data to hydrophobic forces. Since there is no accepted theoretical model for these forces, a comprehensive comparison of our data with theory is not possible so far. From the literature it is evident, however, that only hydrophobic forces may be invoked to explain the strength and the range of attraction deduced from our experimental findings.

It remains to compare the strength of the attractive force with available data from the literature. From the fits of Eq. (2) to experimental data the strength of  $U(r)$  at contact can be converted in a hydrophobic interaction constant,  $C$ , of about  $5 \times 10^{-3} \text{ mJ/m}^2$ . Experimental data on the force laws between various hydrophobic surfaces in aqueous solutions lead to  $C$  typically of the order of  $10\text{--}100 \text{ mJ/m}^2$  according to hydrophobicity [2, 19]. From the results of coagulation experiments of aqueous suspensions of methylated silica particles  $C$  values of about  $1 \text{ mJ/m}^2$  have been estimated [20]. The hydrophobic interaction constants deduced here are clearly lower than those published so far. It must be kept in mind, however, that the dispersions investigated here are stable, whereas other investigations observed coagulation. In view of this fact the range of  $C$  we observe here seems to be reasonable.

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