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ORIGINAL CONTRIBUTION

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Interaction of blockcopolymer micelles as probed by small-angle neutron and by small-angle X-ray scattering

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Abstract The analysis of the interaction of micelles formed by a blockcopolymer is given by means of small-angle X-ray (SAXS) and small-angle neutron scattering (SANS). The blockcopolymer consists of poly(styrene) and poly(ethylene oxide) (molecular weight of each block: 1000 g/mol) and forms well-defined micelles (weight-association number: 400, weight-average diameter: 15.4 nm) in water. The internal structure has been studied previously (Macromolecules 29:4006 (1996)) by SAXS. There it has been shown that the micelles are spherical objects. The structure factor $S(q)$ as a function of the scattering vector q ($q = (4\pi/\lambda)\sin(\theta/2)$; λ: wavelength of the radiation in the medium; θ: scattering angle) can be extracted from both sets of small-angle scattering data (SANS: $q \leq 0.4\ \text{nm}^{-1}$; SAXS: $q \leq 0.6\ \text{nm}^{-1}$). It is shown that particle interaction in the present system can be described by assuming soft interaction which is modeled by a square-step potential.

Key words Micelles – blockcopolymers – SAXS – SANS – structure factor

Introduction

When blockcopolymers are mixed with solvents which dissolve only one block but constitute a poor or a nonsolvent for the other block, self-association may occur which leads to the formation of micellar structures [1–5]. The insoluble part will tend to form a dense core whereas the soluble part forms the corona. Scattering methods [6–8] as small-angle neutron scattering (SANS) or small-angle X-ray scattering (SAXS) provide excellent tools for studying the structure of micelles (see, e.g., refs. [9–14] and additional references gathered in [3–5]). A further point studied by small-angle scattering is the interaction between the micelles and ordering phenomena occurring at higher concentrations [15–22].

In principle, scattering methods are capable of scrutinizing particle interaction to detect the softness of the pair potential [23, 24] or possible attraction between the particles [25–27]. Such an investigation of particle interaction requires the micelles to remain stable to up elevated concentrations; no alteration of shape or transition to a lamellar phase must occur. On the other hand, the scattering intensity of the micelles must be measured down to low concentrations to allow the evaluation of the form factor of the objects. Often both requirements provide insurmountable difficulties so that scattering intensities are only available in a certain range of concentrations.

Another problem is related to the shape to the micelles. In many cases studied so far, a strictly spherical structure of the micelles has been presumed when comparing the measured structure factor to theoretical models as furnished by integral equation theories [28]. It is evident that an elongated shape of the micelles would profoundly disturb such an analysis. Therefore this point must be clarified carefully prior to addressing the problem of particle interaction.

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As shown by a recent study [12], micelles formed by poly(styrene)-poly(ethylene oxide) blockcopolymers (molecular weight of each block: 1000 g/mol) in aqueous solution present aggregates stable up to 25 wt.%. The SAXS-study of the micelles was conducted using contrast variation [6–8, 29–32]. These SAXS-data demonstrated that the micelles deriving from this particular blockcopolymer exhibit a spherical shape with a stable, frozen-in core. In addition to this, the micelles turned out to be stable in a wide range of concentrations and the polydispersity deduced from the scattering data was found to be rather small. It is thus evident that these micelles meet all requirements for a meaningful study of particle interaction by scattering methods.

The present study aims at the investigation of the interaction of the micelles by measuring the structure factor [28] by SAXS and SANS. The structure factor will be analyzed to assess the softness of the pair potential. The combination of this study with the results of the previous investigation [12] therefore gives a complete set of data for this particular micellar system.

Theoretical background

The scattering intensity as a function of the scattering vector $q (q = (4\pi/\lambda)\sin(\theta/2)$; λ: wavelength of the radiation in the medium; θ: scattering angle) for an ensemble of interacting monodisperse particles can be split into a form factor $P(q)$ and a structure factor $S(q)$ by [8, 12]

$$\begin{aligned} I(q) &= N V_p^2 (\bar{\rho} - \rho_m)^2 P(q) S(q) \\ &= \phi \cdot V_p (\bar{\rho} - \rho_m)^2 P(q) S(q) , \end{aligned} \tag{1}$$

where N is the number of particles per unit volume, V_p is the volume of the particles, $P(q)$ is the form factor normalized to unity at $q = 0$ and ϕ is the volume fraction of the particles. The quantity $S(q)$ denotes the structure factor of the system, ρ_m is the scattering length density of the medium and $\bar{\rho}$ is the average scattering length density of the particles defined by

$$\bar{\rho} = V_p^{-1} \int_V \rho(\mathbf{r}) \mathrm{d}V \tag{2}$$

with $\rho(\mathbf{r})$ being the local scattering length density inside the particles. All SAXS-intensities have been multiplied by the Thomson-factor r_0 [6–8] to ensure comparison with data deriving from SANS experiments.

In order to determine $P(q)$, the scattering intensities must be extrapolated to vanishing volume fraction. For small volume fractions, we have (cf. refs. [7, 8])

$$\frac{1}{S(q)} = 1 + 2B_{\mathrm{app}} \cdot \phi , \tag{3}$$

where the apparent second virial coefficient B_{app} is a function of the effective pair potential as well as of q (cf. ref. [12]). Equation (3) in combination with Eq. (1) allows to obtain $I(q)/\phi$ at infinite dilution for the entire range of scattering vectors [12].

In first approximation the interaction of the micelles can be treated in terms of a purely hard-sphere potential and $S(q)$ is given by the respective expression derived by the Percus–Yevick theory [33]. Within this approach, micellar interaction is described through an effective diameter d_{eff} of interaction together with an effective volume fraction ϕ_{eff}. The latter quantity can be derived from experimental data in different ways: in the region of smallest angles, $S(q)$ is expected to vary as [33, 34]

$$S(q) = S(0) + \alpha q^2 + \cdots \tag{4}$$

which allows the extrapolation of $S(0)$ from experimental data. Within the framework of a perturbative approach according to Weeks, Chandler and Anderson (WCA; [33]) the experimental $S(0)$ can be equated to the respective $S_{\mathrm{HS}}(0)$ value furnished by the Percus–Yevick theory. For hard spheres $S_{\mathrm{HS}}(0)$ is solely a function of an effective volume fraction ϕ_{eff} and this procedure leads directly to d_{eff} for a given particle number density N ($\phi_{\mathrm{eff}} = N(\pi/6)d_{\mathrm{eff}}^3$; cf. also ref. [34]). In case of soft repulsion the description of $S(q)$ in terms of $S_{\mathrm{HS}}(q)$ is expected to work less satisfactorily with increasing q. General arguments [23] show that in this case the coefficient α obtained experimentally is greater than α obtained from the Percus–Yevick theory.

Another approach consists of comparing the experimental $S(q)$ in the entire range of q with $S_{\mathrm{HS}}(q)$ calculated from the Percus–Yevick theory for a properly chosen effective volume fraction ϕ_{eff}. A valid criterion for an appropriate choice of d_{eff} is given by the location of the maximum of $S(q)$ to be reproduced by $S_{\mathrm{HS}}(q)$. The effect of the finite width of the size distribution can be taken into account by using the expression for $S(q)$ furnished by van Beurten and Vrij [35] for a system of polydisperse hard spheres. Both approaches define criteria for the choice of the effective volume fraction ϕ_{eff} and the effective diameter d_{eff} of interaction. These data may be compared to the actual volume fraction ϕ and to the structural data of the micelles [12].

The model of hard sphere interaction will not lead to a valid description of the structure factor of the entire range of q-vectors and the interaction of spherical micelles should be modeled in terms of the steric interaction of two spherical brushes [18, 19, 24]. For the present system, however, we believe that this approach is not justified because the corona is not well defined but there is a rather broad transition from the hydrophobic core to the hydrophilic shell (cf. the discussion of the radial structure in ref. [12] and below). In addition to this, the chains of the corona are short and the prerequisites of the models treating steric interaction between spherical brushes are not given for the present system.

We therefore model the soft repulsion by the simplest model possible which is given by a square-step potential defined through

$$U(r) = \begin{cases} \infty & r < d_{SS} , \\ \varepsilon & d_{SS} < r \leq \lambda d_{SS} , \\ 0 & r > \lambda d_{SS} , \end{cases} \qquad (5)$$

where λ and ε correspond to the width and the height of the soft repulsive barrier, respectively. The diameter d_{SS} is the hard-core diameter of the particles. Hence, the comparison with experimental data requires the fit of three adjustable parameters.

For the calculation of $S(q)$ from this potential for a system of monodisperse spheres we have used the theory of Sharma and Sharma [25]. Within this approach the structure factor $S_{SS}(q)$ may be calculated by using Eq. (5) of ref. [25] and the following equation [26]:

$$S_{SS}(0) = \left[\frac{(1 + 2\phi_{SS})^2}{(1 - \phi_{SS})^4} + \frac{8\varepsilon\phi_{SS}}{k_B T}(\lambda^3 - 1) \right]^{-1} , \qquad (6)$$

where $\phi_{SS} = N(\pi/6)d_{SS}^3$ is an effective volume fraction which may be compared to ϕ_{eff} as defined above. (Note the different definition of the sign of ε as compared to ref. [26].)

The theory of Sharma and Sharma is based on the random-phase approximation [33] and is expected to work best at low q and low concentrations. To assess its validity for the present comparison of theory and experiment which comprises higher q and concentrations, $S(q)$ can be checked by using the invariant [6, 7]. Porod [29] has shown that for a two-phase system with sharp interfaces the invariant is given by

$$Q = \int_0^\infty I(q) q^2 \, dq = 2\pi^2 \phi(1 - \phi)(\rho_1 - \rho_2)^2 , \qquad (7)$$

where ρ_1 and ρ_2 denote the scattering length densities of the two phases. This relation is valid for both particulate and non-particulate systems which consist of two homogeneous phases. Therefore Eq. (7) must hold whatever the interaction of the particles might be. In consequence, Eq. (7) provides a check for theoretical structure factors. Thus, calculations have been performed for the structure factor provided by the theory of Sharma and Sharma [25]. Here a system of homogeneous spheres (d_{SS}: 13.4 nm) has been assumed interacting through a potential Eq. (5) where $\varepsilon/k_B T$ was taken to be 1.0 and $\lambda = 1.15$.

These data have been chosen to ensure a meaningful comparison with the experimental results obtained from the system under consideration here. The scattering intensity for such a system follows from Eq. (1) using the form factor $P(q)$ of homogeneous spheres [7]. Numerical integration of $I(q)q^2$ allows to determine Q which can be compared subsequently to the condition (7). By these calculations it could be shown that the structure factor supplied by the theory of Sharma and Sharma is valid up to a volume fraction of ca. 0.2; i.e., the criterion is fulfilled within the limits imposed by the numerical integration. At higher volume fractions there are small deviations but it must be taken into account that the Percus–Yevick theory on which the Sharma–Sharma approach is based is thermodynamically not fully consistent [28]. For the comparison of theory and experiment the Sharma–Sharma theory is sufficiently accurate with the exception of the highest concentration under consideration here. There only qualitative conclusions can be drawn.

Effect of polydispersivity on $S(q)$

All theoretical results discussed so far have been derived for a system of monodisperse particles. In case of polydispersivity, Klein and coworkers (see ref. [28] and further citations given there) have shown that $S(q)$ can be replaced by a "measured structure factor" $S_M(q)$ which embodies the effect of the size distribution on the scattering intensity at finite concentration. For broader distributions, $S_M(q)$ contains at low q a non-negligible incoherent contribution solely due to polydispersity. An expression of $S_M(q)$ for a polydisperse system of hard spheres has been derived by Beurten and Vrij [35] which will be used further below for a comparison with experimental data. It must be kept in mind, however, that the standard deviation of the present system is rather small (10.9%) and the effect of polydispersivity is still low enough to allow for a meaningful comparison of theory and experiment.

Experimental

Materials

The blockcopolymer SE10 consisting of a short poly(styrene) and a short poly(ethylene oxide) block (molecular weight of each block = 1000 g/mol) was supplied by the Goldschmidt AG and used as received. Solutions of the blockcopolymer in H_2O or in mixtures of H_2O and D_2O were prepared as described previously [12]. The partial specific volumes of all solutions were determined using a Paar DMA-60 apparatus.

SAXS-measurements

All SAXS-data were obtained using a Kratky-Kompakt-Kamera equipped by a position-sensitive counter. Details of the measurements and the subsequent treatment of the data have been given elsewhere [12].

SANS-measurements

Small-angle neutron scattering have been performed at the D11 instrument of the Institut Laue-Langevin (ILL) in Grenoble using a wavelength of 0.6 nm. To achieve maximum contrast we chose D_2O as a solvent. The range of momentum transfer was $0.0325 \leq q \leq 0.38\ \mathrm{nm}^{-1}$ by using three different positions of the detector (2.5, 10 and 20 m). All data have been treated using the standard software supplied by the ILL. The data obtained from a 1 mm standard water sample at a detector distance of 2.5 m served for the calibration to obtain absolute intensities. Data deriving from measurements taken at different positions of the detector were normalized by using appropriate shift factors determined from measurements of a Teflon-probe. The present investigation focuses mainly on particle interaction and the q-range has been restricted to lower values. Therefore no corrections for the incoherent background had to be applied.

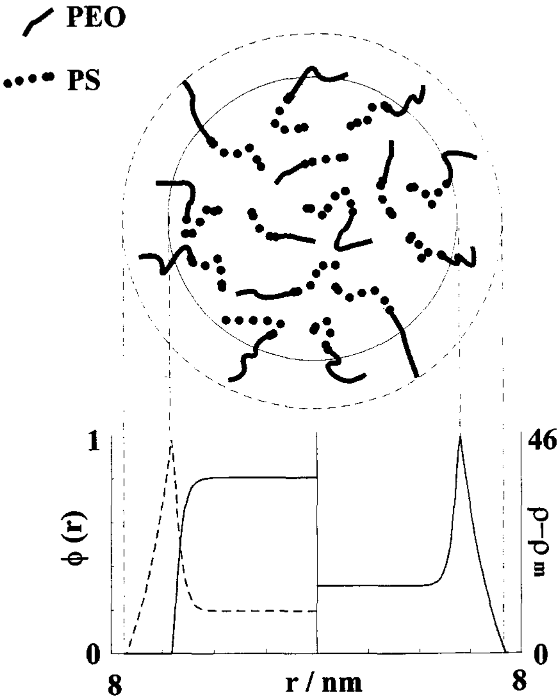


Fig. 1 Model of the radial structure of the micelles (upper part) and the excess electron density in water (right-hand side) according to ref. [12]. The curve on the left-hand side of the lower part shows the volume fraction of the unpolar component poly(styrene) (solid line) and of the polar component poly(ethylene oxide) (dashed line)

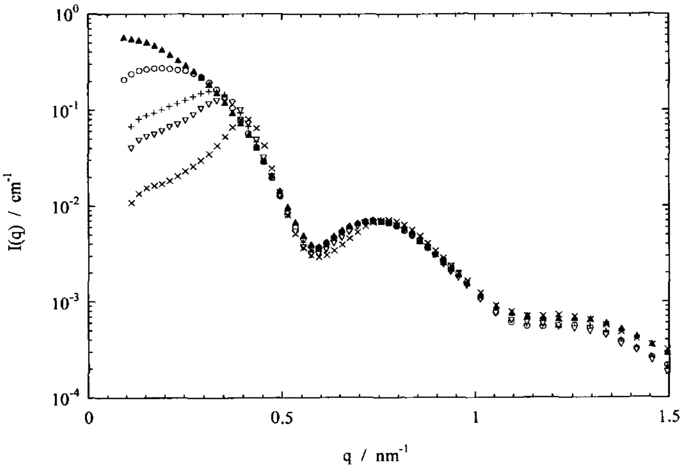


Fig. 2 Influence of concentration of the blockcopolymer on the scattering intensity as measured by SAXS: absolute scattering intensities normalized to the volume fraction ϕ of the micelles as a function of scattering vector q. ▲: extrapolated to $\phi = 0$ according to Eq. (3); ○: $\phi = 0.074$; +: $\phi = 0.154$; ▽: $\phi = 0.188$; ×: $\phi = 0.252$

Results and discussion

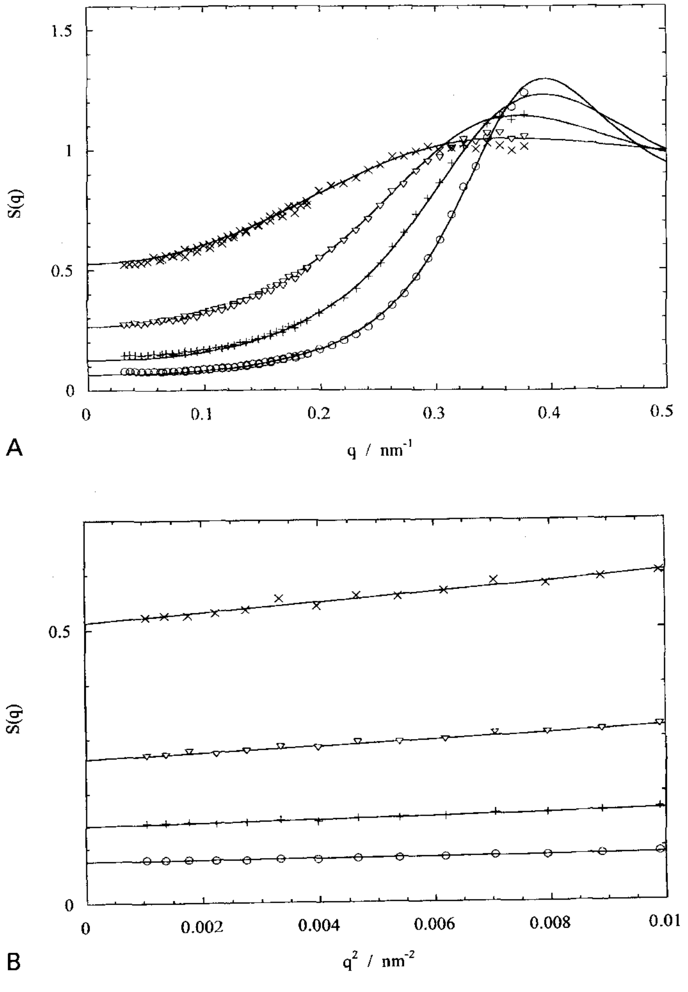
For comparison with the previous result deriving from SAXS, Fig. 1 displays the structural model describing the radial density of poly(styrene) and poly(ethylene oxide) within the micelle. The micelles consist of a core (radius = 5.9 nm) which embodies the polystyrene blocks and an appreciable amount (ca. 30%) of the poly(ethylene) segments. There is a non-negligible transition zone whereas the corona of the micelles consists of the poly(ethylene oxide) chains dispersed in water. The entire weight-average radius is given by 15.4 nm. The weight-average aggregation number is 400. In particular, the data demonstrate unambiguously that the micelles under consideration here exhibit a spherical shape [12]. Thus, the analysis of the structure factor $S(q)$ may proceed along the lines elaborated for systems of spherical particles.

A already mentioned in the Introduction, a necessary prerequisite for a comparison of the experimental $S(q)$ with theoretical models is the stability of the micelles against coagulation and against a change of shape at elevated concentrations. This is the case as is directly evident from the experimental scattering data measured by SAXS at higher concentrations. Fig. 2 gives the desmeared scattering intensities normalized to the volume fraction ϕ of the micelles as a function of q. The scattering contribution due to the density fluctuations within the micelles has been subtracted as described in ref. [12]. The data displayed in

Fig. 2 show that all scattering curves normalized to ϕ merge for $q > 0.6\ \mathrm{nm}^{-1}$ within the given limits of error. Small discrepancies at highest scattering angles are due to the finite accuracy of the experimental data in this range and are of no concern in this context. This result demonstrates that the form factor $P(q)$ of the micelles is not affected by raising the concentration. Therefore $S(q)$ can be extracted from the scattering data by division of $I(q)$ through the normalized scattering intensity [cf. Eq. (1)] at vanishing concentration (cf. ref. [12]).

Fig. 3A displays the measured structure factor as obtained by SANS whereas Fig. 3B shows the SANS-data in the region of smallest angles as plotted according to Eq. (4). The SANS-data are mainly suited to explore the region of smallest scattering angles. It is evident that the low q-range allows the extrapolation of $S_M(0)$ to good accuracy. The effective volume fractions ϕ_{eff} have been calculated from $S(0)$ by application of the Percus–Yevick structure factor of a system of monodisperse spheres. The resulting effective diameters d_{eff} of interaction are gathered in Table 1.

Fig. 3 Structure factor $S(q)$ as obtained by SANS at different volume fractions ϕ. (A) $S(q)$ as a function of q together with the best fit (solid line) obtained from the Sharma–Sharma $S(q)$ [25] with $d = 15.3$ nm, $\varepsilon/k_BT = 1.0$, $\lambda = 1.15$. The volume fractions ϕ are: ×: $\phi = 0.045$; ▽: $\phi = 0.09$; +: $\phi = 0.134$; ○: $\phi = 0.179$. (B) Fit of the same data by Eq. (4). The data of $S(0)$ derived from this fit have been presented in Table 1



The variation of $S(0)$ with the concentration of the micelles can consistently be explained by assuming an effective diameter d_{eff} of 16.1 ± 0.1 nm. The coefficient α is higher than the respective value furnished by the Percus–Yevick theory for a system of monodisperse hard spheres as expected [23]. Any disturbance by attractive interaction between the micelles or by association of the micelles would show up in this angular region by an increase of the scattering intensity with decreasing q. The data displayed in Fig. 3A show that this can be ruled out. Therefore the micellar solutions under consideration here can be treated as a system of well-defined stable particles exhibiting only repulsive interaction.

The respective structure factors as obtained by SAXS are displayed in Fig. 4. Here the q-range does not extend to the low q-values as in case of SANS but these data allow the discussion of $S(q)$ up to $q \cong 0.6\ \mathrm{nm}^{-1}$. The experimental error can be estimated from repetitive measurements marked by different symbols in Figs. 4a–c. The comparison of repetitive measurements show that the data for $q > 0.5\ \mathrm{nm}^{-1}$ are less accurate than around the first maximum of $S(q)$ but still allow a comparison with theoretical models.

The long dashed lines in Figs. 4C and 4D display the best fit of the experimental $S(q)$ by assuming hard sphere interaction in a system of monodisperse particles. It is evident that $S_{\mathrm{HS}}(q)$ does not provide a valid description for

Table 1 Parameters characterizing the interaction of the micelles as obtained by SANS

ϕ[a]	$S(0)$[b]	$\alpha_s[\mathrm{nm}^2]$[b]	ϕ_{eff}[c]	d_{eff}[d]	ϕ_{SS}[e]
0.009	0.875	4.61	0.017	16.1	–
0.045	0.517	8.21	0.084	16.1	0.08
0.09	0.265	5.21	0.170	16.2	0.16
0.134	0.140	2.72	0.251	16.1	0.237
0.179	0.074	1.36	0.329	16.0	0.317

[a] Determined from the volume V_p of the micelles in water and their number-density (calculated from the weight-average association number; cf. ref. [12]).

[b] Determined from the SANS-data by extrapolation according to Eq. (4); see Fig. 3b.

[c] Determined from $S(0)$.

[d] Calculated from ϕ_{eff}.

[e] Determined from d_{SS} and the experimental number density N of the micelles.

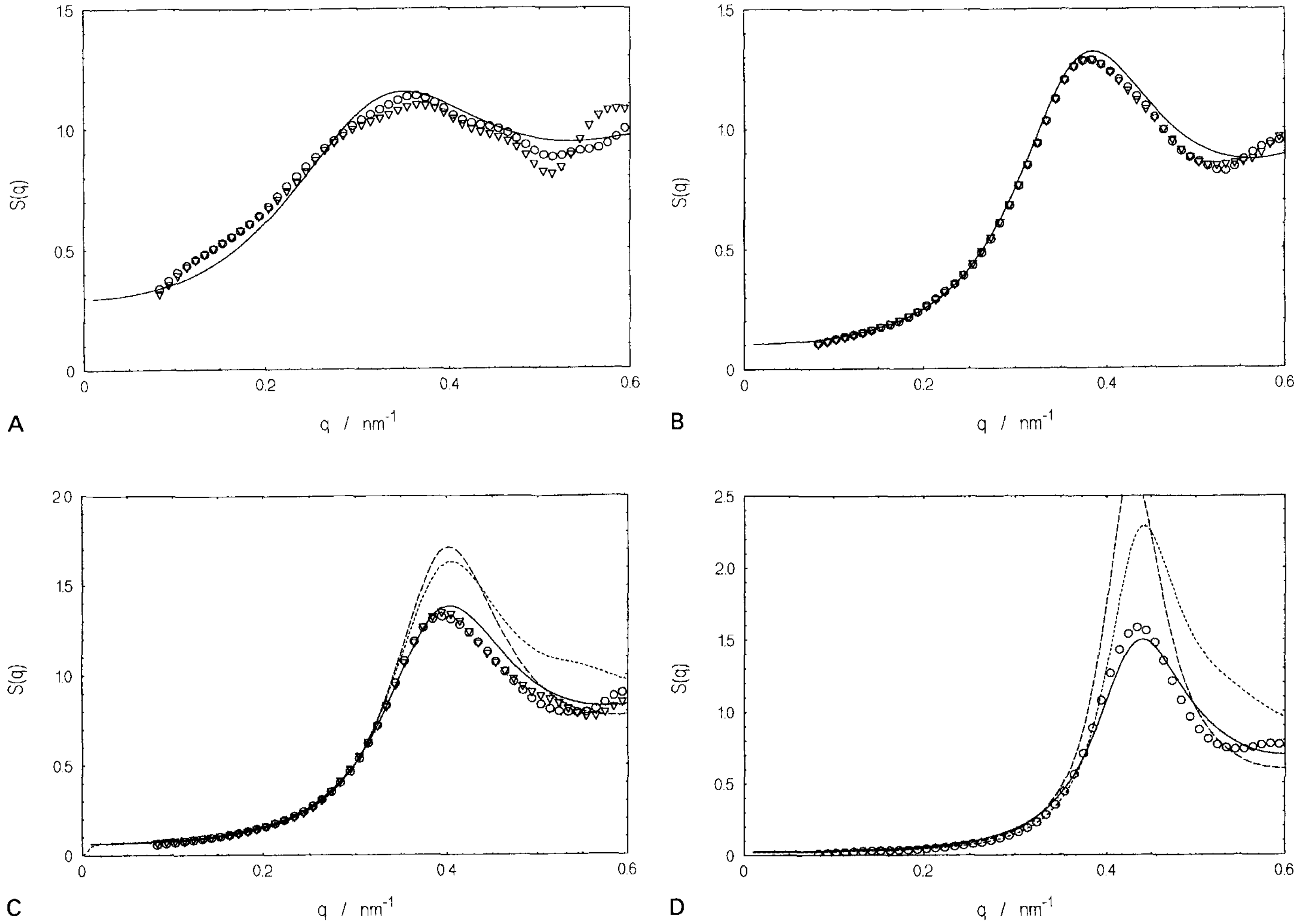


Fig. 4 Comparison of the structure factor obtained by SAXS and the theoretical $S(q)$ obtained from the Sharma–Sharma theory (solid lines; $d = 15.3$ nm, $\varepsilon/k_BT = 1.0$, $\lambda = 1.15$; cf. also Fig. 3 and the respective discussion in the text). Parameter of the different experimental data is the volume fraction ϕ. Triangles mark repetitive measurements of the data. (A) $\phi = 0.074$; (B) $\phi = 0.154$; (C) $\phi = 0.188$; (D) $\phi = 0.252$. The long dashed line in Fig. 4C and 4D show the best fit of the experimental data obtained by the Percus–Yevick $S_{HS}(q)$ for a system of monodisperse spheres ($\phi_{eff} = 0.463$) whereas the short dashed lines display the best fit obtained by the Percus–Yevick structure factor calculated for a polydisperse system (cf. ref. [35]) with a Gaussian size distribution ($\phi_{eff} = 0.470$, standard deviation of size distribution = 10.9%; taken from ref. [12])

the entire q-range under consideration here; only at lowest angles a satisfactory fit can be achieved. The fit is particularly poor around the first maximum of $S(q)$ which is sensitive towards the finer details of the repulsive interaction. Therefore the present data cannot be explained solely in terms of hard sphere interaction but the effect of soft repulsion must be taken into account. Hence, the ϕ_{eff} given in Table 2 have been derived by only taking into account the low-angle part of the experimental $S(q)$-data.

It must be kept in mind that the above comparison of theory and experiments neglects polydispersity. To discuss this point in further detail, a comparison of the exterimental $S(q)$ with $S_{HS}(q)$ deriving from monodisperse as well as polydisperse systems may be helpful. Figs. 4C and 4D display the best fit of the experimental $S(q)$ with the polydisperse Percus–Yevick $S_{HS}(q)$ (short-dashed lines; calculated according to ref. [35]). Although satisfactory agreement may again be achieved for small q, the maximum of $S(q)$ is largely overestimated by the Percus–Yevick structure factor, regardless of whether polydispersivity is taken into account or not. It is therefore obvious that the hard-sphere model cannot describe the interaction of the micelles under consideration here.

The solid lines in Figs. 3A (SANS) and 4A–D (SAXS) give the best fits which can be achieved in terms of the Sharma–Sharma $S(q)$ [25] by a single set of adjustable

Table 2 Parameters characterizing the interaction of the micelles as obtained by SAXS

$\phi^{a)}$	$\phi_{eff}{}^{b)}$	$d_{eff}{}^{b)}$	$\phi_{SS}{}^{c)}$
0.074	0.128	16.5	0.130
0.154	0.282	16.1	0.272
0.188	0.346	16.1	0.332
0.252	0.463	16.0	(0.446)

[a] Determined from the density of the micelles in water (cf. ref. [12]).
[b] Determined from $S(0)$ using the Percus-Yevick structure factor for a system of monodisperse spheres.
[c] Determined from d_{SS} and the experimental number density N of the micelles.

parameters given by $\varepsilon/k_BT = 1$ and $\lambda = 1.15$. The number density N has been calculated from the volume fraction of the micelles (cf. Tables 1 and 2) and the volume $V_p(= 1060\ \text{nm}^3)$ as determined in ref. [12]. The parameters ε, λ, and the diameter d_{SS} have been chosen by a trial and error procedure. Criteria for the choice of the present set were the optimal description of $S(q)$ as well as the constancy of all three parameters for all concentrations investigated herein. The error in ε and λ can be estimated to be of the order of 20% whereas d_{SS} is afflicted by an error of approximately 10%. The effective volume fractions ϕ_{SS} following from this fit are gathered in Tables 1 and 2.

Fig. 3A and Fig. 4A–D demonstrate that a semi-quantitative fit may be achieved throughout the q-range in which $S(q)$ deviates significantly from unity. There are small deviations of theory and experiment around the second minimum of $S(q)$ ($q > 0.5\ \text{nm}^{-1}$) which may be ascribed to the inconsistencies of the present theoretical approach based on the Percus–Yevick theory (cf. ref. [28] for this point). The differences are small, however, when compared to the finite accuracy of the experimental determination of $S(q)$ and do not afflict the main conclusions from this study.

The effective diameter d_{SS} amounts to 15.3 nm which lies in the range expected from the structural model. The parameters ε/k_BT $(= 1.0)$ and $\lambda(= 1.15)$ give a measure of soft repulsion and are also compatible with the model shown in Fig. 1 [12]: The effective diameter $d_{SS} = 15.3$ nm is the minimum distance beyond which two micelles cannot approach each other. This compares favorable with the outer diameter of the micelles of 15.4 nm (cf. Fig. 1). When comparing these values it must be kept in mind, however, that the polydispersivity of micellar sizes will be weighted stronger when considering $S(q)$: As already discussed in ref. [12] the interaction of the micelles will be sensitive towards the longer chains located in the corona which hardly contribute to the excess electron density of the particles. Thus, the particles start to interact already at a distance of approximately $d_{SS} \cdot \lambda = 17.6$ nm and exhibit a harsh repulsion when the coronas strongly overlap at a diameter of 15.3 nm.

As expected, the volume fractions ϕ_{SS} are smaller than the volume fractions ϕ_{eff} stemming from a fit of the hard-sphere model. The latter approach embodies a part of the effect of soft repulsion and thus d_{eff} $(= 16.1$ nm) and ϕ_{eff} must be slightly larger than d_{SS} $(= 15.3$ nm) and ϕ_{SS}, respectively (cf. Tables 1 and 2).

Conclusion

The experimental structure factor $S(q)$ of the micelles under consideration here can be described quantitatively by the structure factor $S(q)$ based on the potential of Eq. (5) which has been calculated by the Sharma–Sharma-theory [25]. Only at small q the data can be modeled in terms of hard-sphere interaction; the $S(q)$ furnished by the Percus–Yevick theory for hard spheres overestimates the height of the first maximum of $S(q)$ considerably. Taking into account the effect of polydispersivity [35] does not improve the agreement of theory and experiment around the first maximum of $S(q)$. Thus, hard sphere interaction can be ruled out for the present system. The micelles exhibit a softly repulsive interaction described by the potential of Eq. (5) with $\varepsilon/k_BT = 1$ and $\lambda = 1.15$. The finer details of repulsion, however, cannot be determined from the present experimental data. This shows that the potential of Eq. (5) embodies the maximum knowledge to be gained from the present data of $S(q)$.

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