

Small-Angle Scattering Functions of Micelles

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ABSTRACT

Models for small-angle scattering of spherical micelles are briefly reviewed, considering both the intra-molecular form factor and the inter-molecular structure factor. Recent examples from the literature, where such approaches have been used to extract information on micellar structure and ordering, are then discussed. A particular emphasis is on micelles formed by block copolymers in solution.

1. Introduction

Micelles are stable aggregates formed by the self-assembly of amphiphiles or copolymers. They exist in thermodynamic equilibrium with unassociated molecules above the critical micelle concentration (at a fixed temperature) or critical micelle temperature (at a fixed concentration). They can adopt a variety of shapes - the most common being spherical, although if the packing of the molecules favours it, anisotropic ellipsoidal, worm-like or rod-like micelles are possible.

The present review is focussed on the analysis of the structure in solutions of spherical micelles via small-angle scattering methods. Although the examples we present are primarily for micelles of block copolymers, the models described can be applied in many cases to other systems such as microemulsion droplets.

Small-angle scattering methods are well suited to investigate the structure of micelles because their size is typically ~5-100 nm, which leads to scattering at small angles. Both Small-Angle X-ray Scattering (SAXS) and Small-Angle Neutron Scattering (SANS) techniques may be employed. X-ray scattering has the advantage that it can be performed in the lab, whereas neutron scattering requires access to central facilities. However, in neutron scattering it is possible to probe details of micellar structure by contrast variation experiments, using mixtures of selectively deuterated amphiphiles or solvents [1]. In very dilute solution, it is possible to measure only intra-micellar scattering, the so-called form factor.

However, in most cases the inter-micellar scattering contributes to the scattering, especially at low wave vector q , and increasingly as concentration is increased.

A number of reviews of scattering from micellar systems have appeared recently. Pedersen has presented useful compendia of form factors and structure factors for particulate systems, including micelles [2]. The focus of the latter article was on free-form fitting methods to determine intra-micellar structure. The present review, where the emphasis is on modelling the form factor and structure factor (it is particularly difficult to obtain these together by free-form techniques), complements nicely ref [2]. Scattering studies on block copolymer micelles have been mentioned as part of a review of scattering from polymer systems [3].

2. General Theory

The small angle scattering intensity $I(q)$ of an isotropic solution of polydisperse spherical micelles can be written within the "decoupling approximation" as [4]:

$$I(q) = n_p \bar{P}(q) S'(q) \quad (1)$$

where n_p is the average number density of micelles and $\bar{P}(q)$ is the average of the form factor $P(q,R)$ over the distribution $f(R)$ of micellar radius:

$$\bar{P}(q) = \int_0^\infty P(q,R) f(R) dR \quad (2)$$

$S'(q)$ in Eq. 1 is the effective structure factor, given

$$\text{by: } S'(q) = 1 + \beta(q)[S(q) - 1] \quad (3)$$

where $S(q)$ is the structure factor of the system and $\beta(q)$ is defined by

$$\beta(q) = \langle F(q, R) \rangle^2 / \bar{P}(q) .$$

$F(q, R)$ is the amplitude factor [4,5], which is related to the form factor through:

$$P(q, R) = F(q, R)^2 \quad (4)$$

An alternative model for the scattering from polydisperse spherical particles was proposed by Pedersen [5]. In contrast to the decoupling approximation, where the positions of particles are independent of their size, the particle position is completely correlated to its size, i.e. the system is approximated as a series of subsystems in which the particles are monodisperse. The corresponding expression for the scattered intensity in this so-called monodisperse approximation is:

$$I(q) = n_p \int_0^\infty P(q, R) S(q, R_{eff}) f(R) dR \quad (5)$$

where R_{eff} is the effective radius of interaction between the micelles. R_{eff} is a function of R , and therefore is included in the integral in Eq. 5.

Pedersen has shown that the local monodisperse approximation works better than the decoupling approximation for high volume fractions and large polydispersity, in that it is able to reproduce average micellar radii and size distributions when fitting simulated data for spherical particles such as micelles [5].

In a very dilute system only the form factor needs to be considered. Intermolecular interferences are manifested by the increasing contribution of the structure factor as concentration is increased.

Here, we review recent attempts to model small angle scattering data from micellar systems. First we give expressions for model form factors and structure factors and then discuss their application to micellar systems, taking examples from the recent literature.

2a. Form Factors

The simplest model for scattering from a spherical micelle is based on a uniform sphere (radius R_o and

volume V_o) with excess electron density $\Delta\rho$. The corresponding well-known equation for the form factor was derived by Lord Rayleigh [6]:

$$P(q) = (\Delta\rho)^2 V_o^2 \left[3 \frac{\sin(qR_o) - qR_o \cos(qR_o)}{(qR_o)^3} \right]^2 \quad (6)$$

Generalizing to the case of a micelle with a uniform core of radius R_c and shell of thickness R_s (with different density) leads to a core-shell model, the corresponding form factor being [7]:

$$P(q) = \left[\frac{4}{3} \pi (\rho_s - \rho_m) (R_s + R_c)^3 F(q, (R_s + R_c)) + \frac{4}{3} \pi (\rho_c - \rho_s) R_c^3 F(q, R_c) \right]^2 \quad (7)$$

where $F(q, R_i) = 3 \{ [\sin(qR_i) - (qR_i) \cos(qR_i)] / (qR_i)^3 \}$ is the amplitude factor for a sphere of radius R_i , ρ_i is the scattering length density, and $i=c, s, m$ label core, shell and solvent medium respectively.

Other models consider that the core scattering amplitude is that of a homogeneous sphere, but the density profile of the shell is a function of the radial distance r , for example the density profile of the shell is given by [8]:

$$n(r) = r^{-x} / (1 + \exp[(r - R_M) / \sigma_F]) \quad (8)$$

where the Fermi function exhibits a smooth density decay up to $R_M = R_c + R_s$ (here again R_c refers to the micellar core radius and R_s to the width of the shell), σ_F being the width of the Fermi function. For $x \sim 4/3$ a density profile similar to that for a star-like polymer [9] is obtained.

A related model is the so-called "cap and gown" model, with uniform core (cap) and a shell with a decaying density profile (gown) of width σ , described by [10]:

$$n(r) = k \exp(-r^2 / \sigma^2) \quad (9)$$

where k is a constant proportional to the excess scattering length density. This model is also known as a box Gaussian model [11].

Recently, Pedersen and Gerstenberg introduced a new model for the form factor of block copolymer micelles, which also considers a homogeneous spherical micelle core, but with attached Gaussian

chains. The Pedersen and Gerstenberg (PG) monodisperse micellar form factor is written [12,13]:

$$P(q) = N^2 \Delta\rho_c^2 P_c(q, R_c) + N \Delta\rho_s^2 P_s(q, R_g) + N(N-1) \Delta\rho_s^2 S_{cs}(q) + 2N^2 \Delta\rho_s \Delta\rho_c S_{cs}(q) \quad (10)$$

where the subscripts c and s refer to uniform spherical micelle cores (radius R_c) and attached Gaussian chains (R_g : radius of gyration of the Gaussian chain), and N is the micelle association number. $\Delta\rho_x$ is the total excess scattering density of a chain in the core ($x=c$) or in the corona ($x=s$). The term $P_c(q, R_c)$ in Eq. 10 is the normalised self-correlation term for a uniform sphere and $P_s(q, R_g)$ is the self-correlation term for Gaussian chains. $S_{cs}(q)$ corresponds to the interference cross term between the sphere and the Gaussian chain starting at the surface of the sphere and $S_{ss}(q)$ is the interference term between the Gaussian chains attached to the surface of a sphere. Data from Monte Carlo simulations of an individual block copolymer micelle consisting of a hard core with attached semiflexible chains have recently been analysed and fitted with box-Gaussian profiles for the corona radial density, and profiles derived from a maximum entropy distribution [11].

It should be mentioned that Eq. 10 reduces to the Gaussian star form factor in the limit of $R_c=0$ [13]. The Gaussian star form factor, which describes the scattering profile of highly dilute solutions of star-like micelles with only one level of electronic density, is given by [14]:

$$P(q) = \frac{2}{fV^4} [v^2 - (1 - \exp(-v^2))] + \frac{f-1}{2} [1 - \exp(-v^2)]^2 \quad (11)$$

$$\text{where } v = \sqrt{\frac{f}{3f-2}} q R_G,$$

f is the number of arms and R_G is the radius of gyration of the whole star, which is related to that of one arm, $R_{G,arm}$, by [15]

$$R_G^2 = \frac{(3f-2)}{f} R_{G,arm}^2.$$

Within the Gaussian approximation, the radius of the Gaussian star, R_{star} , can be estimated by $R_{star} = R_G$, since for a Gaussian chain the radius of the chain can be taken as the radius of gyration.

Finally, Pedersen has also recently developed another model for $P(q)$, which is based on Monte

Carlo results, and corresponds to micelles with a spherical core and self avoiding chains [16]. This model relies on the detailed modelling of the corona density profile which is then used to model the form factor. Within this model $P(q)$ is given by [16]:

$$P(q) = N^2 \beta_c^2 F_c(q) + N \beta_s^2 F_s(q) + 2N^2 \beta_c \beta_s S'_{cs}(q) + N(N - F'_s(q=0)) \beta_s^2 S'_{ss}(q) \quad (12)$$

where $F'_s(q)$ in Eq. 12 is the effective-single chain form factor of self avoiding chains [17]. Both $S'_{cs}(q)$, which is the interference cross term between the sphere and the chains in the corona, and $S_{cc}(q)$, which corresponds to the interference term between chains in the corona, in Eq. 12 are expressed as a function of $A_s(q)$, which is the Fourier transform of the configurationally averaged radial density distribution $\rho_s(r)$ of the chains in the corona [16].

As an alternative to model fitting, so-called "free form" methods are frequently used to analyse small angle scattering data in the absence of structure factor effects. For a brief discussion of these methods, the reader is referred to a recent review [18]. Briefly, $P(q)$ is fitted to obtain the pair distance distribution function $p(r)$, which is represented by a set of basis functions such as splines. The excess scattering density can then be obtained from $p(r)$ by the so-called square-root deconvolution method. The first "free-form" method, the indirect Fourier transformation (IFT), was introduced by Glatter [19] and other methods, which essentially give the same result as Glatter's IFT method, have also been described [20-22].

2b. Structure Factors

Liquid theory gives methods by which the structure factor $S(q)$ of a system of interacting particles can be determined for a given interparticle interaction potential. For example, it is well known that the most accurate approximation for $S(q)$ able to describe a system of interacting hard spheres is that obtained by Percus and Yevick (PY) [23].

It should be mentioned that the analytical expressions for structure factors found in the literature are limited to interacting spherical or weakly anisotropic particles [24-26]. Hayter and coworkers gave the analytical solution of the structure factor for a system of particles interacting via a repulsive screened Coulomb potential [24,25].

The repulsive potential is represented by a Yukawa potential, which has a 'soft' tail at large separations of the particles. The repulsive potential becomes hard sphere-like at short distances between them. This formalism uses the mean spherical approximation as closure for the pair distribution function, and leads to the same result as PY when the micellar surface charge is zero.

In some micellar systems there is an effective intermicellar attraction that has the form of surface adhesion, in addition to the excluded volume effect represented by the finite size hard core. This interaction has been described by Baxter in his sticky hard sphere model (SHSM), within which the PY approximation is used to solve the Ornstein-Zernike (OZ) equation analytically to first order for an adhesive hard sphere potential [26].

In all of the structure factors mentioned above it is assumed that the interaction between the micelles is dominated by the shape of the micelles as a whole and not the characteristics of the molecules that make the micelles. But in the case of some polymeric systems this approximation breaks down because not only the interaction potential between micelles, but also the surface density of the polymer chains themselves, influence $S(q)$. For example, in contrast to star-like polymers, a thin polymer layer tethered to a large spherical micellar core has highly extended chains resembling a polymer brush. A theoretical investigation of the transition between the polymer brush profile and the star-like density profile was undertaken some years ago by Lin and Gast [27-29]. The work focused on polymeric chains tethered to a surface in a curvature regime between the limiting cases of a star polymer and a planar interface, i.e. polymer micelles mimicking polymer brushes. Each tethered polymer was described as a freely jointed chain with n statistical segments of length b . The chains were modelled as random walks within a mean field potential. In contrast to star polymers or planar polymer brushes mentioned above, the total interaction potential depended upon the polymer segment distribution and was determined numerically from self-consistent field (SCF) calculations. In this model the radial distribution function is calculated from the interaction potential using integral equations from liquid theory and the OZ equation is solved within the Rogers-Young closure, which is a hybrid approach mixing the PY and Hypernetted Chain (HNC) approximations. The calculations were used to model the structure factor

of PS-PI micelles in decane [27-29]. The regime of intermediate surface coverage (between mushrooms and brushes), applicable to block copolymer micelles, was also examined in the Monte Carlo simulations of Svaneborg and Pedersen [11].

3. Recent Applications

The modelling of small-angle scattering data is a useful tool for the analysis of the structure in solutions of spherical micelles. For example, the phase behaviour of a Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide) (PEO₂₅-PPO₄₀-PEO₂₅, the subscripts denote the number of repeats) triblock copolymer in aqueous solution has been studied by SANS, and the structural properties have been determined by fitting the SANS curves with the form factor of a homogeneous sphere in combination with a hard sphere potential of interaction [30]. Another recent SANS study on tertiary amine methacrylate-based diblock copolymer micelles modelled the micelle structure using a core-shell form factor and a polydisperse hard sphere structure factor [31].

In addition to its use to describe interactions between polymeric micelles, the hard sphere structure factor has been used to fit SAXS data obtained for solutions of zwitterionic lipid micelles in the study of the liquid-solid phase transition [32]. The uniform sphere micellar form factor has also been used for other lyotropic systems. For example, the influence of urea on Aerosol-OT/n-hexane/water reversed micelles has been probed by SAXS [33]. In this case, the percolation process occurring in the system was analysed using the structure factor for the SHSM model for the attractive interaction.

The core-shell micellar form factor was used to fit SANS data from reverse micelles of PEO_y-PPO_z-PEO_y, where $y=10, 13, 19, 27$ and $x=23, 30, 43, 61$. The reversed micelles were formed by controlled addition of oil to the block copolymer/water solutions [34]. Scattering curves from reversed micelles formed by the surfactant perfluoroalkylpoly(ethylene oxide) in supercritical carbon dioxide have also been successfully modelled with a core-shell model [35]. This model has further been used to fit SANS data for polystyrene-poly(ethylene oxide) (PS-PEO) micelles, while a repulsive screened Coulomb potential was used to describe the corresponding structure factor [36]. For the PEO_y-

PPO_z-PEO_y micelles ($x, y = 23, 34$ and $26, 40$ respectively), the unimer-to-micelle transition region was also studied by modelling SANS curves with a core-shell micellar form factor [37,38]. More recently, the core-shell form factor has also been used to model SANS data from poly(lactic acid)-poly(ethylene glycol) micelles in H₂O/D₂O mixtures [39].

The core-shell model was applied to describe the form factor in a SANS study of the percolation process in PEO₁₉-PPO₄₃-PEO₁₉ micelles in aqueous solution, where micellar interactions were described by the SHSM model for the attractive interaction potential [40]. The same authors improved the quality of model fits to SANS data from a related block copolymer solution that exhibits a percolation transition due to intermicellar interactions, by fitting the 'cap-and-gown' form factor to scattering curves from micelles of PEO₁₃-PPO₃₀-PEO₁₃ [10,41,42].

A systematic study of the influence of the length of the soluble PEO block on the structural micellar properties was undertaken for poly(ethylene-co-propylene)-PEO micelles modelling SANS curves using Eq. 7 to describe the density profile of the shell [8,43]. A density profile with a power-law derived from scaling theory for star-like polymers has been used in the shell component of the form factor of spherical polymer brushes [44].

The form factor of block copolymer micelles in water has successfully been described by the PG model, for a number of systems, including PS₁₀-PEO₆₈ [45], PEO₂₅-PPO₄₀-PEO₂₅, PS-polyisoprene (PI) [12,13] PEO_m-PBO_n (PBO=poly(butylene oxide), $m, n = 86, 10$ and $87, 18$ respectively) [46-48]. In particular, this form factor was used in combination with the hard sphere structure factor to study the liquid-solid phase transition observed in aqueous micellar solutions of diblocks PEO₈₆PBO₁₀ and PEO₈₇PBO₁₈. Representative fits are shown in Figure 1.

SANS studies have been performed on more complex micellar structures, such as onion-type block copolymer micelles, prepared from PS-P2VP (P2VP=poly(2-vinylpyridine)) combined with P2VP-PEO to produce a PS-P2VP-PEO three-shell structure with a PS core and PEO corona [49]. Despite the complexity of the onion micelles the scattering data could be fitted using simple models

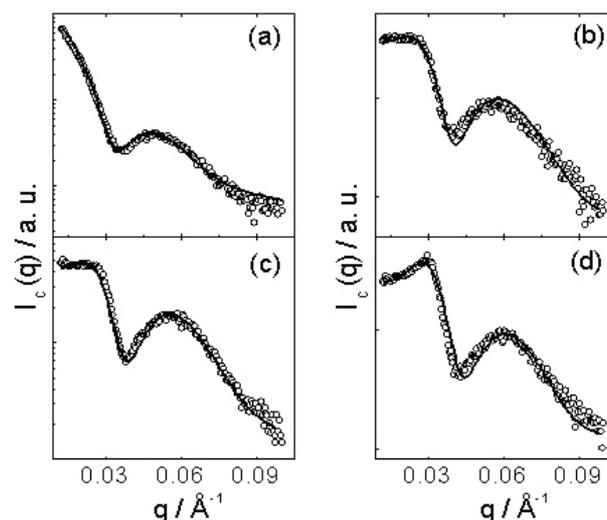


Figure 1. SAXS data and fits using the hard sphere model in combination with the PG model (solid line) for PEO₈₇PBO₁₈ at 70° C for: (a) 2, (b) 10, (c) 11 and (d) 12 wt % PEO₈₇PBO₁₈. (Figure extracted from reference [47])

for the form factor: either that for polydisperse uniform spheres (so-called "bare core" approximation) or the PG model. These models have been used to analyse SANS data from a variety of multi-shell block copolymer nanoparticles, for example three-layer nanoparticles prepared by gamma-radiation-induced polymerization of methyl methacrylate (MMA) around the PS core of PS-poly(methacrylic acid) micelles in aqueous solution [50,51]. The distributions of MMA before polymerization and the structure of nanoparticles containing polymerized MMA were elucidated by modelling the scattering data using the bare-core approximation for a two-component core and also considering a hard micellar core with attached Gaussian chains. The structure of micelles of an ABC triblock, poly(2-ethylhexyl acrylate)-block-poly(methyl methacrylate)-block-poly(acrylic acid) (PEHA-PMMA-PAAc), in H₂O/ D₂O mixtures have been studied via SANS using contrast variation by a selective swelling of PEHA blocks with *d*-cyclohexane [52]. Modelling of the scattering curves with the bare-core approximation showed that the three blocks are segregated in a micelle, PEHA forming the inner and PMMA the outer layer of the core. Solutions in D₂O of other charged micelles, formed by PMMA-PAAc copolymers neutralized to various degrees with Li, Na, or K counterions, were studied by SANS [53]. The bare-core approximation for the form factor was used to study the influence of degree of neutralization on the solubilization of organic substances, such as chloroform or chlorobenzene, in the PMMA core.

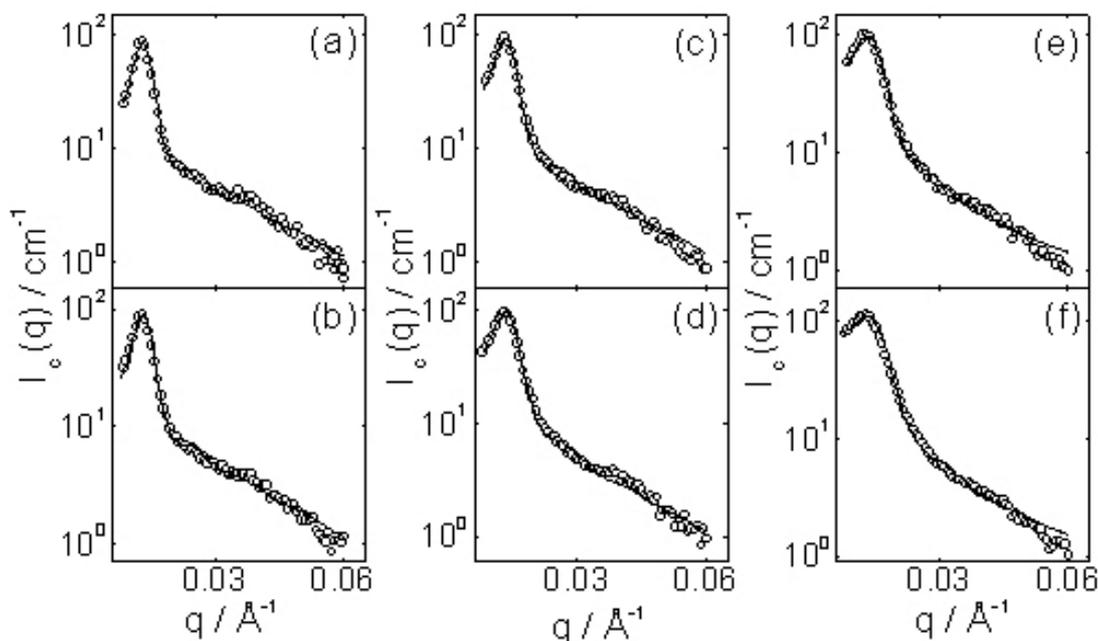
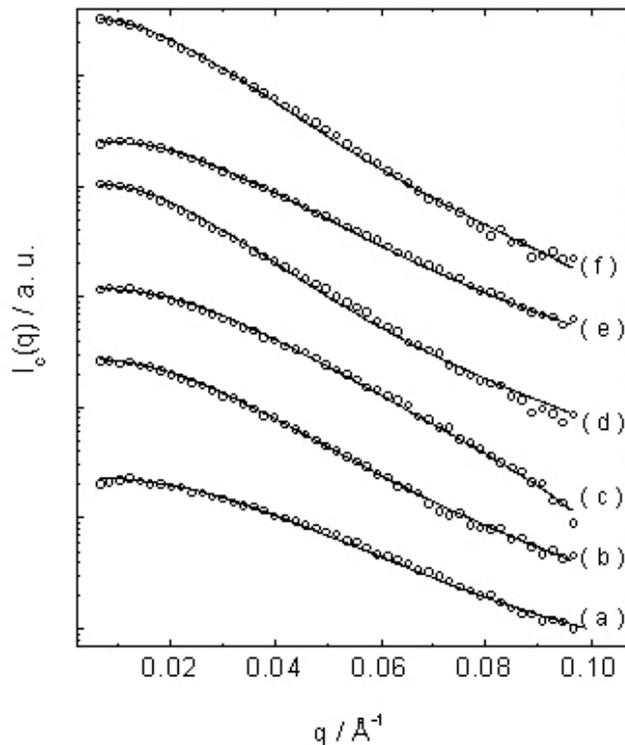


Figure 2. SANS data and fits using the hard sphere model in combination with the form factor with self avoiding chains (solid line) at 45 °C for: (a) 3 and (b) 3.6 wt % PEO₃₉₈PBO₁₉. (Figure extracted from reference [54])

Figure 3. SAXS data and fits using the hard sphere model in combination with the form factor for Gaussian stars (solid line) for 2 wt % MMA₁₀-b-DMAEMA₁₀-b-HEGMA₁₀ at (a) 25 and (b) 66 °C, for 2 wt % MMA₁₀-b-HEGMA₁₀-b-DMAEMA₁₀ at (c) 25 and (d) 66 °C and for 2 wt % DMAEMA₁₀-b-HEGMA₁₀-b-MMA₁₀ at (e) 25 and (f) 66 °C (DMAEMA: 2-(dimethylamino)ethyl methacrylate; HEGMA: hexa(ethylene glycol)methacrylate; MMA: methyl methacrylate; the subscripts are the number-average block lengths in repeat units) The SAXS patterns have been shifted by multiplying by an arbitrary constant. (Figure extracted from reference [58])



The form factor of highly swollen block copolymer micelles, including PS-PI and PEO₃₉₈PBO₁₉ systems [16,54], has been successfully described by the model reported by Pedersen for micelles with a spherical core and self avoiding chains [16] Representative fits showing the results obtained using this form factor in combination with the hard sphere structure factor to study the liquid phase of PEO₃₉₈PBO₁₉ aqueous micellar solutions, are shown in Figure 2 [54].

A systematic structural investigation of star polymers in solution by SANS has been undertaken on a series of PI or polybutadiene star polymers using the Gaussian star model to fit the scattering curves [55].

In a SANS study of the dilute solution behaviour of a series of star-branched PEO molecules, the modelling of the scattering curves using the Gaussian star model has also been reported [56]. Recently, the Gaussian star model has been successfully used in SAXS studies of ABC starblock copolymers, in order to provide a alternative simplified picture of the system (representatives fittings are shown in Figure 3) [57].

4. Conclusions

Analysis of small-angle scattering data from micellar solutions consisting of lyotropic or polymeric materials has been discussed. The most common analytical expressions for model form factors and structure factors for spherical micelles have been presented.

Despite the alternative 'free-form' methods often used to interpret small-angle scattering data from micellar systems [18], modelling is still an important procedure for analysing small angle scattering data, in particular because it can account for the structure factor contribution and because it facilitates comparison with theoretical density profiles or structure factors. It is expected that during the next few years computer simulations and integral equation theories will play an increasing role in data analysis, supplementing existing analytical and numerical methods.

References

- [1] Hamley, I. W. *Introduction to Soft Matter*; John Wiley: Chichester, 2000.
- [2] Pedersen, J. S. (1997) Analysis of small-angle scattering data from colloids and polymer solutions: modeling and least-squares fitting. *Advances in Colloid and Interface Science* **70**, 171-210.
- [3] Fairclough, J. P. A.; Hamley, I. W.; Terrill, N. (1999) Application of scattering techniques to polymers, block copolymers and micellar systems. *Radiation Physics and Chemistry* **56**, 159-173.
- [4] Kotlarchyk, M.; Chen, S.-H. (1983) Analysis of small-angle scattering spectra from polydisperse interacting colloids. *Journal of Chemical Physics* **79**, 2461-2469.
- [5] Pedersen, J. S. (1994) Determination of size distributions from small-angle scattering data for systems with effective hard-sphere potential. *Journal of Applied Crystallography* **27**, 595-608.
- [6] Rayleigh, Lord (1911) *Proceedings of the Royal Society (London)* **A-84**, 25.
- [7] Cabane, B. *Colloides et Interfaces: Les Ulis*, France, 1984.
- [8] Willner, L.; Poppe, A.; Allgaier, J.; Monkenbusch, M.; Lindner, P.; Richter, D. (2000) Micellization of amphiphilic diblock copolymers: Corona shape and mean-field to scaling crossover. *Europhysics Letters* **51**, 628-634.
- [9] Halperin, A. (1987) Polymeric micelles: A star model. *Macromolecules* **20**, 2943-2943.
- [10] Lobry, L.; Micali, N.; Mallamace, F.; Liao, C.; Chen, S.-H. (1999) Interaction and percolation in the L64 triblock copolymer micellar system. *Physical Review E* **60**, 7076-7087.
- [11] Svaneborg, C.; Pedersen, J. S. (2002) Form factors of block copolymer micelles with excluded-volume interactions of the corona chains determined by Monte Carlo simulations. *Macromolecules* **35**, 1028-1037.
- [12] Pedersen, J. S.; Gerstenberg, M. C. (1996) Scattering form factor of block copolymer micelles. *Macromolecules* **29**, 1363-1365.
- [13] Pedersen, J. S. (2001) Structure factor effects in small-angle scattering from block copolymer micelles and star polymers. *Journal of Chemical Physics* **114**, 2839-2846.
- [14] Benoit, H. (1953) On the effect of branching and polydispersity on the angular distribution of the light scattered by Gaussian chains. *Journal of Polymer Science* **11**, 507.
- [15] Zimm, B. H.; Stockmayer, W. H. (1949) The dimensions of chain molecules containing branches and rings. *Journal of Chemical Physics* **17**, 1301.
- [16] Pedersen, J. S.; Svaneborg, C.; Almdal, K.; Hamley, I. W.; Young, R. N. (2002) A small-angle neutron and X-ray contrast variation scattering study of the structure of block copolymers micelles: corona shape and excluded volume interactions. *Macromolecules*, submitted.
- [17] Pedersen, J. S.; Schurtenberger, P. (1996) Scattering functions of semiflexible polymers with and without excluded volume effects. *Macromolecules* **29**, 7602-7612.
- [18] Pedersen, J. S. (1999) Analysis of small-angle scattering data from micelles and microemulsions: free-form approaches and model fitting. *Current Opinion in Colloid and Interface Science* **4**, 190-196.
- [19] Glatter, O. (1977) A new method for the evaluation of small-angle scattering data. *Journal of Applied Crystallography* **10**, 415-421.
- [20] Svergun, D. I.; Semenyuk, A. V.; Fejgin, L. A. (1988) Small-angle-scattering data treatment by the regularization technique. *Acta Crystallographica* **A44**, 244-250.
- [21] Hansen, S.; Pedersen, J. S. (1991) A comparison of three different methods for analyzing small-angle scattering data. *Journal of Applied Crystallography* **24**, 541-548.
- [22] Svergun, D. I.; Pedersen, J. S. (1994) Propagating errors in small-angle scattering data treatment. *Journal of Applied Crystallography* **27**, 241-248.
- [23] Percus, J. K.; Yevick, G. J. (1958) Analysis of classical statistical mechanics by means of collective coordinates. *Physical Review* **110**, 1-13.
- [24] Hayter, J. B.; Penfold, J. (1981) An analytical structure factor for macroion solutions. *Molecular Physics* **42**, 109-118.
- [25] Hansen, J. P.; Hayter, J. B. (1982) Rescaled MSA structure factor for macroion solutions. *Molecular Physics* **6**, 651-656.
- [26] Baxter, R. J. (1968) Percus-Yevick equation for hard spheres with surface adhesion. *Journal of Chemical Physics* **49**, 2770-2774.
- [27] Lin, E. K.; Gast, A. P. (1996) Self consistent field calculations of interactions between chains tethered to spherical interfaces. *Macromolecules* **29**, 390-397.
- [28] Gast, A. P. (1996) Structure, interactions and dynamics in tethered chain systems. *Langmuir* **12**, 4060-4067.
- [29] Lin, E. K.; Gast, A. P. (1996) Semicrystalline diblock

- copolymer platelets in dilute solution. *Macromolecules* **29**, 4432-4441.
- [30] Mortensen, K.; Pedersen, J. S. (1993) Structural study on the micelle formation of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer in aqueous solution. *Macromolecules* **26**, 805-812.
- [31] Bütün, V.; Armes, S. P.; Billingham, N. C.; Tuzar, Z.; Rankin, A.; Eastoe, J.; Heenan, R. K. (2001) The remarkable "flip-flop" self-assembly of a diblock copolymer in aqueous solution. *Macromolecules* **34**, 1503-1511.
- [32] Castelletto, V.; Itri, R.; Amaral, L. Q. (1997) Micellar aggregates near the isotropic-cubic liquid crystal phase transition. *Journal of Chemical Physics* **107**, 638-644.
- [33] Itri, R.; Amaral, C. L. C.; Politi, M. J. (1999) Interactive forces on Aerosol-OT/n-hexane/water/urea reversed micelles by small angle X-ray scattering. *Journal of Chemical Physics* **111**, 7668-7674.
- [34] Svensson, B.; Olsson, U.; Alexandridis, P.; Mortensen, K. (1999) A SANS investigation of reverse (water-in-oil) micelles of amphiphilic block copolymers. *Macromolecules* **32**, 6725-6733.
- [35] Fulton, J. L.; Pfund, D. M.; McClain, J. B.; Romack, T. J.; Maury, E. E.; Combes, J. R.; Samulski, E. T.; DeSimone, J. M.; Capel, M. (1995) Aggregation of amphiphilic molecules in supercritical carbon dioxide: A small-angle X-ray scattering study. *Langmuir* **11**, 4241-4249.
- [36] Brown, G. J.; Richards, R. W.; Heenan, R. K. (2001) Organisation and interactions in aqueous dispersions of polystyrene-polyethylene oxide block copolymer micelles. *Polymer* **42**, 7663-7673.
- [37] Goldmints, I.; von Gottberg, F. K.; Smith, K. A.; Hatton, T. A. (1997) Small-angle neutron scattering study of PEO-PPO-PEO micelle structure in the unimer-to-micelle transition region. *Langmuir* **13**, 3659-3664.
- [38] Goldmints, I.; Yu, G.-E.; Booth, C.; Smith, K. A.; Hatton, T. A. (1999) Structure of (deuterated PEO)-(PPO)-(deuterated PEO) block copolymer micelles as determined by small angle neutron scattering. *Langmuir* **15**, 1651-1656.
- [39] Heenan, R. K.; Eastoe, J. (2000) Droplet interfacial structure studied by SANS contrast variations. *Journal of Applied Crystallography* **33**, 749-752.
- [40] Liu, Y. C.; Chen, S. H.; Huang, J. S. (1996) Relationship between the microstructure and rheology of micellar solutions formed by a triblock copolymer surfactant. *Physical Review E* **54**, 1698-1708.
- [41] Liu, Y.; Chen, S.-H.; Huang, J. S. (1998) Small-angle neutron scattering analysis of the structure and interaction of triblock copolymer micelles in aqueous solution. *Macromolecules* **31**, 2236-2244.
- [42] Chen, S.-H.; Liao, C.; Fratini, E.; Baglioni, P.; Mallamace, F. (2001) Interaction, critical, percolation and kinetic glass transitions in pluronic L-64 micellar solutions. *Colloids and Surfaces A* **183-185**, 95-111.
- [43] Poppe, A.; Willner, L.; Allgaier, J.; Stellbrink, J.; Richter, D. (1997) Structural investigation of micelles formed by an amphiphilic PEP-PEO block copolymer in water. *Macromolecules* **30**, 7462-7471.
- [44] Förster, S.; Wenz, E.; Lindner, P. (1996) Density profile of spherical polymer brushes. *Physical Review Letters* **77**, 95-98.
- [45] Mortensen, K.; Brown, W.; Almdal, K.; Alami, E.; Jada, A. (1997) Structure of PS-PEO diblock copolymers in solution and the bulk state probed using dynamic light-scattering and small-angle neutron scattering and dynamic mechanical measurements. *Langmuir* **13**, 3635-3645.
- [46] Castelletto, V.; Caillet, C.; Hamley, I. W.; Yang, Z. (2002) The liquid-solid transition in a model hard sphere system of diblock copolymer micelles. *Physical Review E* **65**, 050601(R).
- [47] Castelletto, V.; Caillet, C.; Fundin, J.; Hamley, I. W.; Yang, Z.; Kellarakis, A. (2002) The liquid-solid transition in a micellar solution of a diblock copolymer in water. *Journal of Chemical Physics* **116**, 10947-10958.
- [48] Derici, L.; Ledger, S.; Mai, S.-M.; Booth, C.; Hamley, I. W.; Pedersen, J. S. (1999) Micelles and gels of oxyethylene-oxybutylene diblock copolymers in aqueous solution: The effect of oxyethylene-block length. *Physical Chemistry, Chemical Physics* **1**, 2773-2785.
- [49] Pleštil, J.; Křoz, J.; Tuzar, Z.; Prochazka, K.; Melnichenko, Y.; Wignall, G.; Talingting, M.; Munk, P.; Webber, S. (2001) Small-angle neutron scattering study of onion-type micelles. *Macromolecular Chemistry and Physics* **202**, 553-563.
- [50] Pleštil, J.; Pospíšil, H.; Kadlec, P.; Tuzar, Z.; Křoz, J.; Gordeliev, V. (2001) SANS study of multilayer nanoparticles based on block copolymer micelles. *Polymer* **42**, 2941-2946.
- [51] Pleštil, J.; Pospíšil, H.; Křoz, J.; Kadlec, P.; Tuzar, Z.; Cubitt, R. (2001) Characterization of nanoparticles based on block copolymer micelles. *Langmuir* **17**, 6699-6704.
- [52] Křoz, J.; Masaø, B.; Pleštil, J.; Tuzar, Z.; Pospíšil, H.; Doskočilová, D. (1998) Three-layer micelles of an ABC block copolymer: NMR, SANS, and LS study of a poly(2-ethylhexylacrylate)-block-poly(methylmethacrylate)-block poly(acrylic acid) copolymer in D₂O. *Macromolecules* **31**, 41-51.
- [53] Křoz, J.; Masaø, B.; Pospíšil, H.; Pleštil, J.; Tuzar, Z.; Kiselev, M. (1996) NMR and SANS study of poly(methyl methacrylate)-block-poly(acrylic acid) micelles and their solubilization interactions with organic solubilizers in D₂O. *Macromolecules* **29**, 7853-7858.
- [54] Castelletto, V.; Hamley, I. W.; Pedersen, J. S. (2002) A SANS investigation of the structure of highly swollen block copolymer micelles. *Journal of Chemical Physics* **117**, 8124-8129.
- [55] Willner, L.; Jucknischke, O.; Richter, D.; Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; Fetters, L. J.; Huang, J. S.; Lin, M. Y.; Hadjichristidis, N. (1994) Structural investigation of star polymers in solution by small angle neutron scattering. *Macromolecules* **27**, 3821-3829.
- [56] Boothroyd, A. T.; Squires, G. L.; Fetters, L. J.; Rennie, A. R.; Horton, J. C.; de Vallera, A. M. B. G. (1989) Small-angle neutron scattering from star-branched polymers in dilute solution. *Macromolecules* **22**, 3130-3137.
- [57] Castelletto, V.; Hamley, I. W.; Triftaridou, A. I.; Patrickios, C. S.; Staurouli, N.; Tsitsilianis, N. (2002) A SAXS investigation of ABC triblock star polymers. *Journal of Macromolecular Sciences: Physics*, in press.