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Mesoscopic structures characterized by backscattering of light

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Abstract: In this paper we demonstrate a simple backscattering experiment applied to four different systems forming mesoscopic structures. We observe the transition from crystallized to disordered electrostatically stabilized latex suspensions where the crystal structure is clearly body-centered cubic (bcc). Also, a space-filling face-centered cubic (fcc) arrangement for a sterically stabilized latex is observed. Further, an extension of previous scattering results on an undulation-stabilized lamellar phase (L_α) in a binary non-ionic surfactant-water system is presented. Finally, the application to an electrostatically stabilized gel phase with lamellar ordering (L_β) of relatively stiff membranes below the Krafft-temperature is performed. All these systems are attractive because of the brilliant colors they display upon illumination with white light.

Key words: Light scattering – colloidal crystals – lamellar phase – surfactants – iridescent phases

1. Introduction

Recently, it was observed [1–3] that certain dilute surfactant solutions show iridescent colors when illuminated with white light. The phenomenon was reproduced by several groups [4–8]. Evidently, the effect can be observed with a whole series of ionic and non-ionic as well as binary and multicomponent surfactant systems.

The color effect resembles that seen for deionized suspensions of monodisperse colloidal spheres [9]. The colors observed in both cases are a function of surfactant and latex concentration, respectively, and depend on the angle of observation. Obviously, the iridescence arises from the interference of the light being scattered from periodic colloidal structures having dimensions of the wavelength of visible incident light.

In the present paper a simple experimental technique will be briefly described using a slightly modified UV/VIS-spectrometer to measure the Bragg-reflections. In essence light crystallography on mesoscopic arrays of colloidal structures is performed. The capability of the equipment and its potential use are demonstrated studying several binary surfactant-water systems and suspensions of polymer latices. A schematic illustration of these structures is shown in Fig. 1.

2. Experimental

2.1. The backscattering experiment

The light-scattering studies were performed by modifying a two-beam-UV/VIS spectrometer (UVIKON 860, Kontron) operating in transmission mode. The reference beam was attenuated and the primary beam blocked by a beam stop behind the measuring cell, a quartz cuvette (Hellma), containing the sample. The light-scattering intensity scattered back from the front face of the cell was recorded at a scattering angle of $\Theta = 172 \pm 2°$ using a fiber optic bundle. The back-scattered light is reflected entirely by a prism positioned 30 mm in front of the measuring cell and coupled into the commercial silicone rubber enveloped fiber bundle of 50 cm length. The

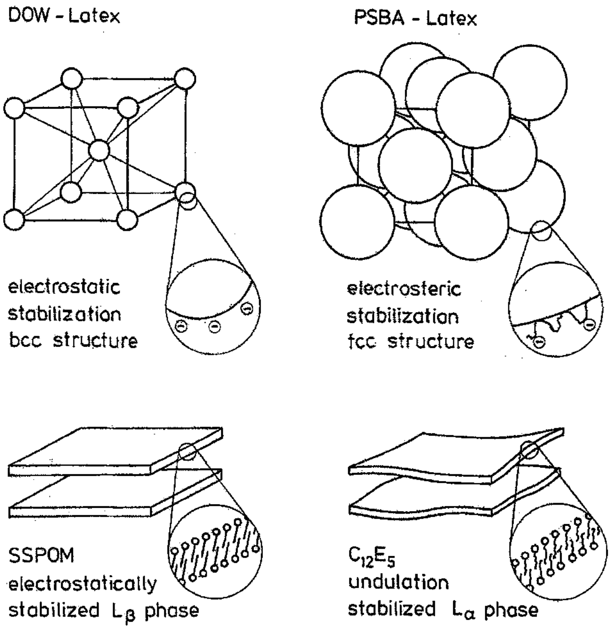

Fig. 1. Schematic representation of the investigated ordered mesoscopic structures for different types of stabilization

optical transmission covered the whole wavelength range of the spectrometer ($180 < \lambda < 900$ nm). A schematic drawing of the experimental set up is shown in Fig. 2. The magnitude of the scattering vector Q for fixed refractive index of the diffracting medium n, scattering angle Θ and the available wave length range λ of the spectrometer is calculated from the Bragg relation:

$$Q = \frac{4\pi n}{\lambda} \sin(\Theta/2) \,. \qquad (1)$$

The Q-vector resolution of the experiment is set by the spectral bandwidth of the spectrometer and the averaging around the mean scattering angle. Both relative errors do not exceed 1%. This fact explains the sharpness of the spectra presented below.

2.2. Preparation of samples

Two different types of polymer latex particles were used for the present backscattering investigations. The first type was a polystyrene (PS) latex with sulfate surface groups, a diameter of 91 nm and a polydispersity (standard deviation of the particle size distribution divided by the mean size) $\sigma = 0.064$ (standard DOW latex), the second one was a specially prepared poly(styrene-butadiene-acrylic acid) latex (PSBA latex, BUNA AG). The PSBA latex is a commercial product and its preparation conditions cannot be given here. The DOW latex is highly charged due to the sulfate groups, whereas the PSBA latex is stabilized by using acrylic acid as comonomer (2% of the total) and thus is a sterically stabilized colloidal system. But because the stabilizing macromolecules are usually charged an additional electrostatic contribution has to be considered. This type of stabilization is therefore sometimes called electrosteric stabilization [10, 11]. The amounts of steric and electrostatic contributions are a function of ionic strength of the dispersion. In aqueous dispersions like ours of about pH = 8 we have to allow for a non-vanishing electrostatic contribution, however, we have no quantitative information about the magnitude of either contribution. The size of

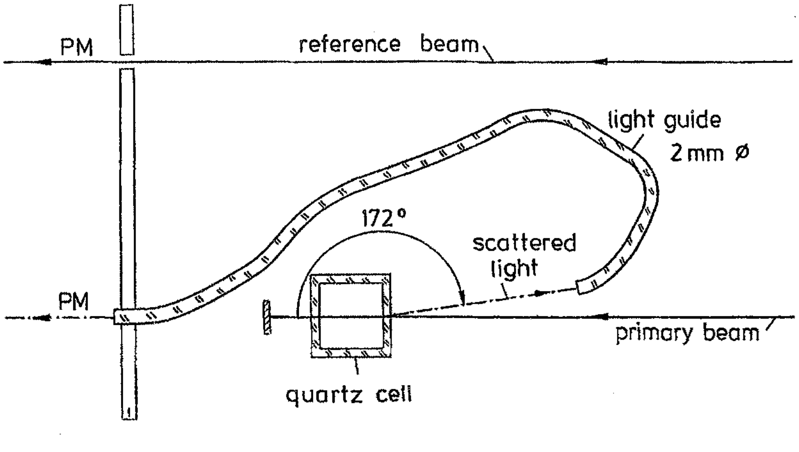

Fig. 2. Modified UV/VIS spectrometer used as experimental tool for measurements of backscattering of light.

the particles was characterized on the one hand by dynamic light scattering (DLS). On strongly diluted dispersions of pH $\cong$ 7 (volume fraction $\cong 10^{-5}$) a particle size and polydispersity of 259 nm and $\sigma = 0.06$, respectively, was obtained. On the other hand, electron microscopy (EM) was used for size characterization. For fixing and staining of the soft particles we used a technique which utilizes the reaction of unsaturated components in the latex particles with osmium tetroxide [12]. For size and polydispersity of these hard particles we obtained the values 241 nm and $\sigma = 0.04$, respectively. The particle size as determined by EM are seen to be slightly smaller than those determined by DLS. This phenomenon can be explained in part by the fact that different moments of the size distribution are probed by the different techniques, but we think it is also a certain indication of the thickness of the surface coating of the particles. More accurate details of the stabilizing layer, in particular its dependence on ionic strength, are lacking at present.

After deionizing the DOW latex by putting a mixed bed ion-exchange resin (Stoess&Co, Eberbach, FRG) into the cuvettes containing the suspension, a crystallization is observed after about 2 days. For latex concentrations in the range of 1% we found polycrystalline samples. Single crystallites of several millimeters developed after several weeks. The PSBA latex was applied in high concentration with water as suspension medium. A polymer content of about 55 wt% was measured gravimetrically. In cuvettes of 10-mm thickness we could not find any macroscopic crystallites in the bulk even after several months. But in 1-mm cuvettes without ion-exchange resin a complete crystallization of the samples starting from the cell walls occurred after a few weeks. Thus, also in this case a polycrystalline sample with crystallites of a size smaller than 1 mm is formed.

We used the alkylpolyethyleneglycolether $C_{12}E_5$, a non-ionic surfactant, from Nikko, Japan, extending previous scattering experiments [7]. The purity was quoted to be better than 99% measured by gas chromatography. The second surfactant used was the ionic Sodium-sulfopropyl-octadecyl-maleate (SSPOM), which was synthesized in our laboratory [13]. For purification it has been at least three times recrystallized from a water-acetone mixture. The purity was checked by thin-layer chromatography, but no impurities were detected, indicating at least 99% purity. For all experiments on aqueous latex dispersions or binary surfactant-water systems doubly quartz-distilled water was used in preparing the samples. The lamellar L_α phase of the $C_{12}E_5$-water system shows the Bragg-peaks due to the high swelling with water thereby reaching spacings up to 300 nm [7]. The L_α phase appears in the phase diagram above 54 °C and extends down to surfactant volume fractions of $\Phi \cong 0.01$. The sample can simply be mixed and heated to 58 °C. While stirring within a few minutes the lamellar state is reached.

The preparation of the iridescent SSPOM samples requires a more sophisticated technique. On the one hand, the samples have to be brought in the hydrated crystalline state where it forms a dense array of alternating rigid lamellae. On the other hand, the individual lamellae have to be dispersed. For that purpose a mixture of water and detergent crystals is slightly warmed up to about 30 °C and strongly shaken up to the complete dissolution of crystals. After cooling down to 17 °C and keeping that temperature a transparent solution, and at higher concentrations (> 2.5 wt%) a clear gel-like solution is formed in less than 1 day, which is optically anisotropic and shows brilliant colors. The reproducibility of the Bragg-peaks of samples prepared in this way is sufficient, but the scatter between different samples somewhat exceeds that of samples in the $C_{12}E_5$-water system. Details on sample preparation, scattering behavior, and microstructure for the SSPOM system will be published elsewhere [14].

For the refractive index n in Eq. (1) we took that of pure water ($n = 1.333$) except for the concentrated PSBA latex. There we took the mean over the volume fractions of latex and water [15] resulting in $n = 1.46$.

3. Results and discussion

In a recent paper of Sirota et al. [16] high-resolution, small-angle, synchrotron x-ray-scattering techniques were used to determine the structure of charged colloidal suspensions over an extended volume fraction range. The authors found a strongly correlated liquid phase and bcc

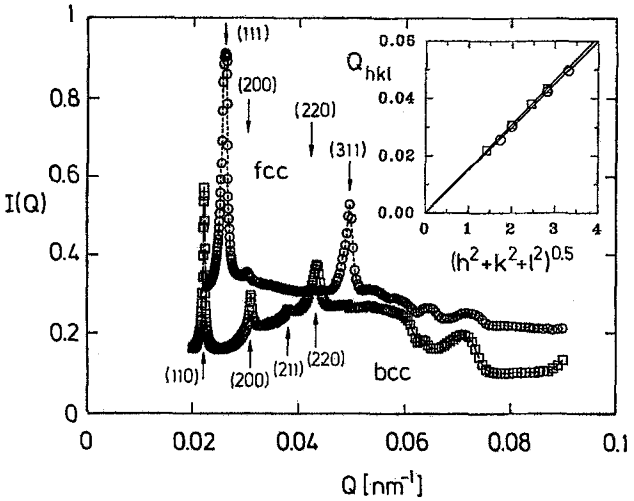

Fig. 3. Typical scattering profiles of intensity I versus scattering vector Q for DOW latex (squares, $\Phi = 0.0087$, 91 nm diameter) and PSBA latex (circles, $\Phi = 0.59$, 259 nm diameter). The inset shows how the Q_{hkl} fit the assumed structures. The arrows indicate the reflections. Intensity in arbitrary units. $T = 20\,^{\circ}\mathrm{C}$.

and fcc solid phases as expected for screened Coulomb systems [17, 18] with rising volume fractions. In Fig. 3 two typical scattering profiles measured for the DOW (squares) and the PSBA latex (circles) with our backscattering equipment are shown. Several sharp Bragg-peaks are evident, but also a broad structured band of diffuse scattering appears. Apart from the smaller available Q range in the light scattering experiment the results are quite comparable to SAXS. The ratios of the first four Bragg-peaks of DOW latex ($\Phi = 0.0087$) correspond with a relative deviation of less than 1% to the theoretically expected ratios of the (110), (200), (211), (220)-reflections of the bcc structure. The corresponding positions calculated from $Q_{\mathrm{hkl}} = 2\pi/a \cdot (h^2 + k^2 + l^2)^{0.5}$ are shown in the inset in Fig. 3, where h, k, l are Miller's indices and a the unit cell size. This fact strongly supports the existence of the bcc lattice for this latex. The result also agrees with the recent experimental phase diagram of Monovoukas and Gast [19] for highly charged polystyrene particles. The volume fraction Φ of the latex calculated from the optically determined lattice constant is about 25% higher than the corresponding value obtained from gravimetric determination of the weight fraction of latex in the starting solution. This difference appears at first sight to be relatively high. Nevertheless, it is of no consequence if only relative changes of quantities are studied. As an illustration, we have measured the Φ-dependence of the Bragg-reflections as discussed below. Very much larger differences between diffraction and gravimetry result, that is, a threefold larger value of concentration from light scattering has been observed with electrostatically stabilized silica and PS suspensions by Kesavamoorthy et al. [20, 21]. These authors attributed the larger particle concentration to the presence of an attractive potential at the container walls due to image charges. This effect should result in a higher concentration of the particles adjacent to the walls. The positions of the first four peaks of the curve of Fig. 3 for the PSBA latex agree with the same accuracy of around 1% with the (111), (200), (220) and (311)-reflections of a fcc lattice. Again, the Q_{hkl}-fit is included in the inset in Fig. 3. Just by accident the unit cell sizes of the two completely different latex crystalline samples are nearly the same. The gravimetrically measured polymer content of the sample amounts to 55%. Using a polymer density of $\rho = 0.93\ \mathrm{gcm}^{-3}$ a volume fraction of $\Phi = 0.59$ is obtained. Comparing this value to that calculated from the optical data, one finds a similar deviation towards higher values as for the DOW latex case, but here the deviation amounts to only 8%. Nevertheless, we have to recognize that an increase of particle concentration near the cuvette wall occurs as suggested already in previous work [20, 21].

The PSBA results are of particular interest in that for highly concentrated latex suspensions with hard-sphere interactions a transition from the crystalline fcc structure to a glassy state should occur for an effective hard-sphere volume fraction [(volume occupied by the composite particles)/(total sample volume)] of around 56% [22–25]. From appearance of Bragg-peaks and the directly observable formation of crystallites in the bulk of sample after some weeks, we conclude, however, that the crystalline state still persists. Pusey et al. [26] have thoroughly studied hard-sphere suspensions at such high particle concentrations. They suggest that close-packed structures may be formed by stacking of hexagonally close-packed layers (hcp) of particles, and they confirm this by light scattering. In general, they observe a random stacking of hcp layers but, if there is enough time for crystallization, fcc structures form. This points to an analogy of our PSBA suspension to a hard-sphere system. Somewhat in contrast is the observation of close-packed structures starting at container walls for systems with soft potentials [20, 27]. According to these investigations, a whole hierarchy of structures from two-dimensional hcp, through random layer up to bcc structures develops during the ordering formation. The terminal state of order depends on volume fraction and ion strength of suspension. For $\Phi > 0.03$ the fcc structure should develop in the bulk. The formation of order in a hard-sphere system with $\Phi \cong 0.56$ cannot be compared strictly with a soft-sphere system of $\Phi \cong 0.03$, although our investigations point out existing similarities in the ordering formation of both systems near the container walls. Because of the lack of optical transparency of the PSBA samples, the incident light does not penetrate very deeply into the cuvettes during the scattering experiment. Thus, we may expect an enhanced contribution to the scattering from regions near the cell walls in spite of fully crystallized samples of 1 mm thickness. Taking these observations together the identified fcc structure of electosterically stabilized PSBA latex is in keeping with the multitude of findings on related colloidal particle systems.

For orientationally invariant materials the intensity of scattered light $I(Q)$ can be written as

$$I(Q) \propto P(Q)S(Q)\,, \qquad (2)$$

where $P(Q)$ is the single-particle form factor and $S(Q)$ the structure factor. Form factors can be estimated experimentally by measurements of $I(Q)$ on dilute suspensions. In Figs. 4a and 4b two approximate structure factors $S(Q)$ are reproduced obtained from the measured scattering profiles of a DOW sample with $\Phi = 0.0053$ utilizing an appropriate form factor. The form factor was estimated to be a smooth function underlying the measured spectrum in the crystalline bcc state at room temperature. It was assumed to be the same for the molten state at $T = 80\,°C$. As expected [28, 29], in the molten sample near the first two sharp peaks of the $S(Q)$ function of the crystalline state two round maxima appear. These maxima are shifted compared to the crystalline state towards smaller Q-values by about 3.5%. This behavior is similar to the general observation in metal systems for which the spacings between the atoms increase by melting.

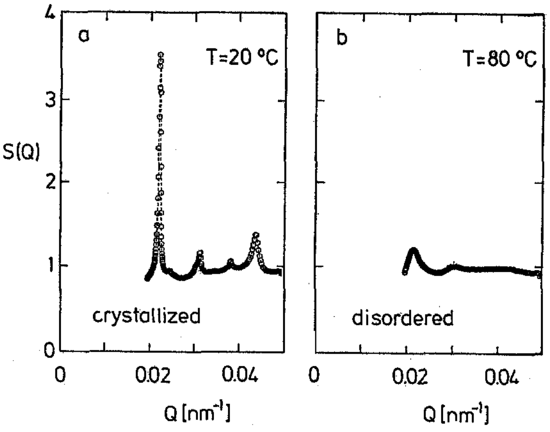

Fig. 4. a) Structure factor $S(Q)$ versus scattering vector Q for crystallized DOW latex ($\Phi = 0.0053$, 91 nm diameter). $T = 20\,°C$. b) Structure factor $S(Q)$ versus scattering vector Q for the same solution as in a), but molten at $T = 80\,°C$.

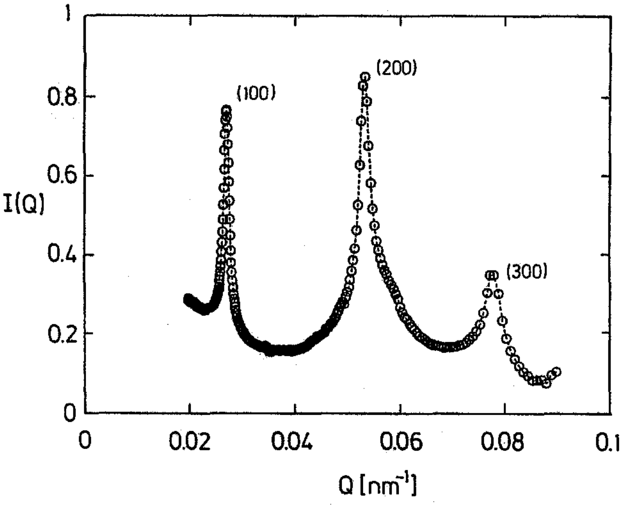

Fig. 5. Scattering spectrum recorded in the gel phase of binary system SSPOM-water at $T = 27\,°C$ (surfactant concentration 0.9 wt%). Intensity in arbitrary units.

We turn now to the dilute membrane dispersion encountered in surfactant solutions. As one example, in Fig. 5 a scattering profile is plotted as obtained from a 0.9 wt% SSPOM-water solution at $T = 27\,°C$. The spectrum shows three well-pronounced peaks with Q-values in the ratios 1, 2, 3.

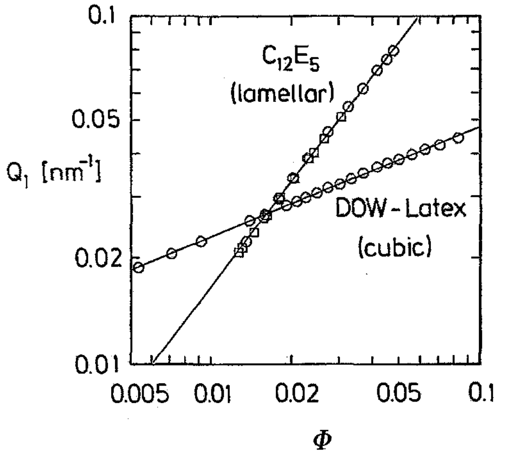

Fig. 6. The scattering vector Q_1 of the first Bragg-peak as a function of volume fraction Φ for the binary $C_{12}E_5$-water system (circles) at $T = 58\,^\circ C$ reproducing previous measurements [7] (squares) and extending them to higher Φ. The variation with Φ for the DOW latex at $T = 20\,^\circ C$ is also included. The lines are least-squares fits to the data points (see Eqs. (3) and (4)).

This peak sequence is typical for a structure of stacked sheets. As will be demonstrated by further studies, including freeze fracture electron microscopy and x-ray scattering [14], the binary system under investigation exists in a supercooled gel state below the Krafft-temperature of about 37 °C, which may be characterized as a stack of relatively stiff electrostatically stabilized surfactant bilayers with intercalated water layers (L_β phase). The order seems to be comparatively high, so that the spectrum exhibits three orders of reflections. The variation of the characteristic length indicated by the spectra will be discussed in a forthcoming publication. Here, we will confine ourselves to the variations of the periodicities of the non-ionic system and contrast it with the cubic DOW-latex system.

In Fig. 6 the measured Φ-dependences of first Bragg-peaks for the $C_{12}E_5$-water system at $T = 58\,^\circ C$, i.e., in the lamellar L_α phase and the DOW latex at room temperature are given. In the log-log representation the data are well-approximated by straight lines. A least squares fit yields for the lamellar phase in the non-ionic surfactant system

$$Q_1 \propto \Phi^{0.994}\,, \tag{3}$$

while for the cubic latex crystals we obtain

$$Q_1 \propto \Phi^{0.324}\,. \tag{4}$$

Considering lamellar liquid crystalline phases, one expects for simple one-dimensional swelling an exponent of unity. For undulating L_α phases as for $C_{12}E_5$ in water, one would predict a systematic deviation from $Q \propto \Phi$ upon dilution [30]. In a preceding publication on the binary $C_{12}E_5$-water system [7] a small, but significant deviation from the ideal one-dimensional swelling was observed. It could be explained by assuming that steric interactions dominate the repulsion between the bilayers and thermal undulations create an area deficit leading to a logarithmic correction term so that $Q_1 \propto \Phi/(1 - kT/4\pi\kappa_0)\ln\Phi)$ where κ_0 is the bending rigidity modulus. The present experimental data (circles) quantitatively support previous measurements (squares) and extend these towards larger Q-values. The swelling behavior observed here is strictly linear within the experiment's limits of error, suggesting an area deficit that is proportional to Φ leading to the same apparent swelling behavior as one would expect for rigid layers. However, quantitative analysis of the proportionality factor in Eq. (3) amounting to $2\pi/\delta$, where δ is the bilayer thickness known from small-angle neutron scattering [31], tells us that about 25% of the total area is lost in undulations.

Also, the Φ-dependence of latex (Eq. (4)) corresponds very well to that expected for a cubic system: $Q_1 \propto \Phi^{1/3}$. Slight deviations towards smaller Q-values occur above $\Phi \cong 0.05$. This may be a result of changing the order in the suspension. A decrease of order in the form of smaller crystallites for increasing concentrations produces larger spacings between the particles and thus smaller Q-values similar as for the case of melting discussed above.

4. Conclusion

The examples presented in this paper demonstrate how the relatively simple experimental tool of backscattering of light in a commercial UV/VIS spectrometer yields structural information on colloidal systems having mesoscopic sizes. Nevertheless, high precision can be achieved. The examples have confirmed previously existing experimental results at the same time, extending our insight into these fascinating, brilliantly appearing, colloidal systems.

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