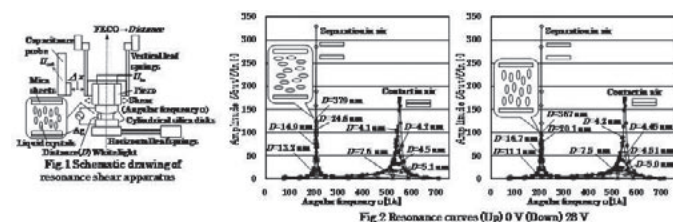


which can monitor the rheological properties of liquids between two surfaces as a function of surface separation distance (D) from  $\mu\text{m}$  to contact with nm resolution. In this study, we investigated the rheological properties of a liquid crystal, 4-cyano-4'-hexylbiphenyl (6CB), under the electric field which induces the orientational change of 6CB. Resonance curves were obtained by measuring the amplitude of shear as a function of angular frequency. Polarizing microscopy confirmed that 6CB was in the planar orientation between mica surfaces without electric field, and in the homeotropic orientation under the electric field (28 V, 1 kHz). The viscosity of 6CB was larger for the case of 0 V than the case of 28 V at 370-14 nm, which agreed with Miesowicz viscosity. Below  $D=14$  nm, the viscosity increased similarly both at 0 V and 28 V, indicating the same orientation of 6CB under confinement.

1) M. Mizukami, K. Kusakabe, and K. Kurihara, Prog. Colloid Polym. Sci., 128, 105, (2004)



Keywords: liquid crystal, orientation, rheology

**P12.06.19**

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**Pressure-induced structural changes of liquid As, Sb, and IV-VI compounds**

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Pressure-induced structural transformations have recently been attracting a lots of attentions. For example, the finding of pressure-induced first-order phase transition in fluid Phosphorous is very interesting in that it showed a possibility of a novel border which separates one fluid phase from another. We investigated the structure of heavier group V elements As and Sb, and IV-VI compounds such as GeS, GeSe, GeTe, PbSe, PbTe, SnSe, SnTe, in liquid phase, by high-temperature high-pressure X-ray diffraction. The intermediate-range structure of liquid As and GeSe was found to change by pressure; we suggest a change from two- to three-dimensional structure. We also found that R2/R1 (the ratio of the second peak position to the first of the pair distribution function) approaches root two with compression. This result show that the bond angle 90 degree is preferred in a certain pressure range. Interestingly this ratio R2/R1 was found to change its pressure dependence when it passes root two. This indicates that further compression causes another structure. For liquid Sb and SnTe, the structure at ambient pressure has been conventionally assigned to a SC-like structure. However we found that the structure is not SC-like in low pressures, and our results suggest a considerable covalency in the bonds. With compression, the structure factor S(Q) showed a similar change to each other for these two liquids, and we found a hump in S(Q) (which is next to the first peak) rapidly and sharply changes at a certain pressure range. The overview of the pressure-induced structural changes for liquid

group-V (and IV-VI compounds) will be given in the presentation, and systematic results and differences from crystalline pressure sequences will be shown.

Keywords: liquid structure, energy-dispersive X-ray diffraction, liquid alloys

**P12.07.20**

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**Low resolution structure of synthetic melanin aggregates in aqueous solutions and organic solvents**

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In an effort to find out details of the melanin fundamental structural unit, a great amount of information has been gathered using several techniques. The local short range order of the melanin molecular clusters has been described as consisting of five to seven 5,6-indolequinone units, arranged in planes which are pi-stacked with a spacing of 0.34 nm. Typical cluster size is 1.5-2.0 nm in lateral dimensions and 1.0 nm; in height. Nonetheless, structural details and dimensions of the aggregates are still not clearly defined and experiments did not answer the key question concerning the identification of the fundamental melanin protomolecule. More recently, small angle scattering of X-rays (SAXS) and neutrons (SANS) were performed. Several authors used these techniques, which are well designed to study macromolecules in solution to find details of melanin-copper ions interaction as well as chemical bleaching effects. A diversity of aggregated structures were proposed for these nanoscaled particles based on size and apparent shape. In this presentation we report the results of SAXS experiments performed with melanin synthesized from L-dopa and L-tyrosine in organic solvents, which were reported to be very effective for thin film formation. Water-based synthetic melanin was also studied for comparison purposes, since molecular aggregation behavior is known to vary with the route used for the synthesis. Reliable data was obtained for the water-based and DMSO dispersions. Data analysis was performed by conventional IFT methods and the overall shape and dimensional parameters of the melanin particles were obtained. Using ab-initio calculations, a low resolution 3D model is proposed for the basic melanin particle in aqueous media and DMSO. Sponsorship: CNPq, LNLS

Keywords: biologically important substances, SAXS, melanine

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**Long period structure in D<sub>2</sub>O/3-methylpyridine induced by adding salt or ionic surfactant**

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The binary mixture of water and 3-methylpyridine, which shows

LCST type phase separation, is known to have a large salt effect. In this study, we selected sodium tetraphenylborate (NaBPh<sub>4</sub>), whose affinities of anion and cation with water are largely different, as a salt because the solvation effect should be intensive and the formation of large clusters is expected theoretically. In cases of the lower amount of NaBPh<sub>4</sub> and water-rich concentration, the mixture becomes colored in blue, and changes to orange with approaching critical temperature. This result suggests that a periodic structure is formed, and its repeat distance increases with increasing temperature. In order to verify the structural formation, we performed SANS measurement at SANS-U in JAEA, Tokai, for the mixtures with 100 mM NaBPh<sub>4</sub>. The results showed that the profiles have a peak around  $Q = 0.1 \text{ \AA}^{-1}$ , and the peak position shifts to lower- $Q$  with increasing temperature. (K. Sadakane et al., J. Phys. Soc. Jpn. 76, 113602 (2007).) Adding ionic surfactant, for example AOT or SDS, also shows the structural formation as the case of NaBPh<sub>4</sub>.

Keywords: solvation effect, critical phenomena, periodic structure

### P12.07.22

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#### Concentration dependence of static and dynamic structure in a spherical microemulsion system

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The concentration dependence of static and dynamic structure in a microemulsion system has been investigated using the contrast variation small-angle neutron scattering (SANS) and neutron spin echo (NSE) techniques. Since structure factor should not depend on the scattering contrast of systems, a relative form factor is defined as the ratio of the scattering intensities for the different scattering contrasts, which is the ratio of the form factors for the different scattering contrasts. This concept allows us to extract concentration dependence of the shape of the unit particles and the interaction between particles [1]. Furthermore, this strategy is extended to the contrast variation NSE data analyses. The shape and structure fluctuations are successfully decoupled using the relative intermediate form factor method in a droplet microemulsion system [2]. The mean radius of the droplets is almost constant below the droplet concentration,  $f$ , of 0.6, while the polydispersity of the system decreases with increasing  $f$ . The frequency and the amplitude of the shape fluctuation mode of the droplets increase with  $f$ . A collision driven enhancement of the shape fluctuation mode in the high droplet concentration is one of the possible explanations of the dynamics. The attractive interaction between droplets decreases with increasing  $f$  below  $f=0.3$ , while it increases with  $f$  above  $f=0.3$ . This suggests that at least two different mechanisms of the change of interaction between droplets exist. Due to the inter-droplet interaction, a clear dynamic slowing down is observed at the length scale corresponding to the inter-droplet distance.

[1] M. Nagao, H. Seto and N. L. Yamada, Phys. Rev. E 75, 061401 (2007).

[2] M. Nagao and H. Seto, submitted to Phys. Rev. E.

Keywords: small-angle neutron scattering, neutron spin echo, microemulsion

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#### Correlation functions of three-phase samples with a film-like or a thread-like phase

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The correlation function of isotropic samples made up of three homogeneous phases is a linear combination of the autocorrelation functions (CF) of the constituting phases. Each of these CFs, referred to as volume CFs (vCF), is the angular average of the overlap volume of a phase with the same phase translated by  $r$ . If the thickness of one phase can be assumed negligible the corresponding CF becomes that of a film or a collection of closed films. The resulting autocorrelation function, referred to as film CF (fCF), has an integral expression that involves the only surface(s). Its expression differs from that of the second derivative of a vCF because its integrand no longer contains the two scalar products between the direction of the translation and the normals to the surface at the points separated by  $r$ . The first important implication of this result is that fCFs go as  $1/r$  as  $r$  goes to zero and, consequently, their contribution to the asymptotic behaviour of small-angle scattering intensities decreases as  $1/q^2$  instead of  $1/q^4$ . The second implication is that the integral expression makes the calculation of the fCF relevant to a monodisperse collection of film-particles shaped as spheres, ellipsoids, cubes or cylinders rather straightforward. In the same way, if one phase extends along a curve and its dimensions transverse to the curve are small, the corresponding limit of the vCF defines the CF of a thread or a collection of threads and its integral expression involves the only curves that define the threads. These CFs go as  $1/r^2$  as  $r$  goes to zero and contribute to the asymptotic scattering intensities with a term decreasing as  $1/q$ .

Keywords: SAS, micelles microemulsions, helical macromolecules

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#### Determination of the contrast mechanism in ultra-small-angle X-ray scattering (USAXS) imaging

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Ultra-Small-Angle X-ray Scattering (USAXS) imaging has been proven useful in studies of metallurgical, biological and polymeric materials. This is a size sensitive imaging technique to directly probe the morphology and three-dimensional arrangements of the small-angle scattering objects, where images acquired at different scattering vectors can reveal different microstructural features within the same sample volume. Until now, the contrast mechanism has not been explained quantitatively. We offer a general treatment of X-ray imaging contrast for USAXS imaging that makes use of phase propagation and dynamic diffraction theory to account quantitatively for the intensity distribution in the detector plane. Simulated results from a model system of micron-sized spherical SiO<sub>2</sub> particles embedded in a polypropylene matrix show good agreement with experimental measurements. Simulations by means of an alternative geometrical ray-tracing method also account for the features in