SCATTERING TECHNIQUES AS STRUCTURAL INVESTIGATION TOOLS OF COLLOIDAL AGGREGATES IN ORGANIC MEDIA

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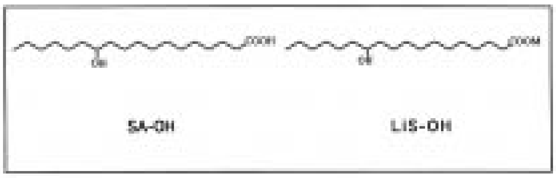
Colloids, such as those found in oil industry [1], are complex systems exhibiting specific viscoelastic properties. Among these industrial materials, lubricating greases are of special interest as they provide a good illustration of the important contribution of the scattering techniques to the structural investigation of self-assembling systems. They can be composed of numerous components and additives to meet specific needs (e.g. extreme pressure, anti-corrosion). However, greases made up of saponified fatty acids in mineral oils can be modeled with extremely simple binary systems thus favoring the analysis of the structural and mechanical properties within the appropriate fundamental context.

A number of commercial lubricating greases contain lithium 12-hydroxy stearate (abbreviated as LiS-OH). Corresponding model systems are LiS-OH in organic liquids such as decalin, dodecane, nitrobenzene, etc. The self-association reactions of the LiS-OH molecules under appropriate thermodynamic conditions (concentration, temperature) give rise to colloidal aggregates. If the LiS-OH concentration is increased, the aggregates overlap to form three-dimensional networks. This structure provides specific mechanical properties which are the basis of the well-known industrial applications. These materials display all mechanical and thermal properties of rigid physical gels which constitute the reference background [2]. The fatty acid derivative (12-hydroxy stearic acid, SA-OH) also gives organogels but which exhibit a lower thermal stability in various aromatic and alkanic solvents; and can be used to complete the investigation of the mechanisms which govern the growth of the heterogeneous materials [3].



Formulae

Gelator molecules: SA-OH and Li-SA (where the metallic atom M is lithium).

It is interesting to note that the formation of physical organogels from low-molecular weight derivatives is not a rare phenomenon since approximately twelve families of chemical compounds exhibiting this property have been discovered [4] and [5]. The isolated gelator molecules can be considered as "monomeric" species that associate into "equilibrium aggregates" so as to minimise the resulting free energy. The self-aggregation process results from thermal reactions using specific chemical interactions (H-bonding, organometallic coordination bonding, donor-acceptor, electron transfers) between the gelators. Unidirectional aggregates (fibers, ribbons, rods, semi-rigid threads) are formed which entangle in more or less organised junction zones of the gel network. Electron microscopy techniques have been historically used for the initial structural characterisation of lubricating greases [6]. This technique cannot give the genuine structural organisation of the networks since the procedures are frequently very aggressive with respect to the brittle and fragile three dimensional architectures. In contrast, scattering techniques using intense synchrotron sources are able to probe the structures of very dilute and dispersed materials without modification of their native constitution (hydrogenated solvents, oils, etc.) and

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morphology. In particular, small angle scattering of X-ray or neutron radiation beams (SAXS and SANS, respectively) can provide information on long correlation distances typical of colloidal systems (1000 Å < d < 20 Å). In addition, selective deuteration of the gelators, use of deuterated solvents, and comparison between X-ray and neutron scatterings can provide useful contrast variation opportunities. The angular intensity distribution of X-rays or neutrons scattered within small angles constitutes the scattering curve typical of the sample. It consists of an interference pattern whose reverse Fourier transform delivers real-space structural information [7] and [8]. The long-range fluctuations depend upon the contrast of the particles in the medium and, consequently, any change in the constitution of the system (solvent or gelator composition) can lead to a variation of the scattering level in a fashion related to the morphology, internal homogeneity and composition of the aggregates. SAXS and SANS have proved to be very efficient in characterising colloidal aggregates [9].

Figure 1 illustrates the amount of information which can be gained using SANS on model materials (SA-OH in benzene and LiS-OH in nitrobenzene) mimicking the lubricating greases. The appropriate data treatment [3] gives evidence for the unidirectionality of the aggregates and the characteristics of their cross-section (shape, dimensions, homogeneity, polydispersity, nature of the interfaces with solvent). In benzene, long and rigid fibres are formed with well-defined square cross-sections (ca. 215 Å side [3]). Scattering experiments at larger angles are used to access crystallographic information related to the internal ordering of the fibres and junction zones in the network. Fibres are fused into crystalline microdomains constituting the extended nodes of the network in which molecules pack in a monoclinic form. "Head to head" contacts between the carboxylate groups and growth of multiple hydrogen sequences along with the fibre axis are ubiquitous features of these gels (see Figure 2). In these organogels, a random long-range organisation coexists with ordered ones either unidirectionally extended along with the fibre axis or with a variable symmetry in the junction zones (cylindrical-like or lamellar-like, depending on the solvent type and concentration). The structural organisation is consistent with the rheological behaviour of the LiS-OH and SA-OH organogels or greases that behave as viscoelastic solids exhibiting important yield stress values [10].

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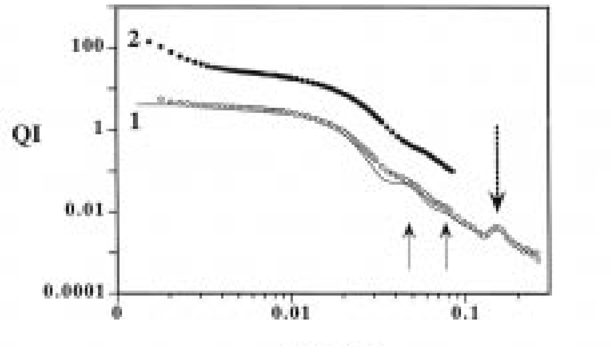

Figure 1
Neutron cross-section scattering curves QI vs Q appropriate for rod-like scatterers. Q is the momentum transfer defined as $Q = 4\ \pi/\lambda\ \sin\ \theta$ for elastic scattering where λ is the radiation wavelength and θ half the scattering angle.

1: SA-OH, concentration C = 2.5% wt in benzene. Two arrows indicate two of the form-factor oscillations characterising the relative monodispersity of the cross-sections. A dashed arrow points to a first Bragg peak ($Q \approx 0.149$ Å^{-1}) due to ordered regions of the network (see text). The full line is a theoretical adjustment for long fibers with a square cross-section (side = 215 Å).

2: LiS-OH, C = 2.1% wt in nitrobenzene.

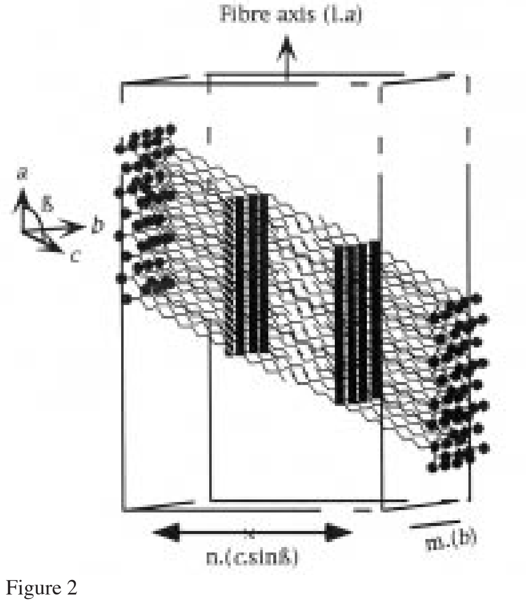

Figure 2
Structural model of fibrillar or ribbon-like aggregates of SA-OH in organic solvents. The crystallographic axis and the fibre geometry are indicated. The dimensions are proportional to the crystallographic cell parameters, as shown ($P2_1$ monoclinic symmetry). The thick lines are the H-bond sequences connecting the hydroxyl groups at C_{12} and the grey spheres are carboxylic end groups [3].

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