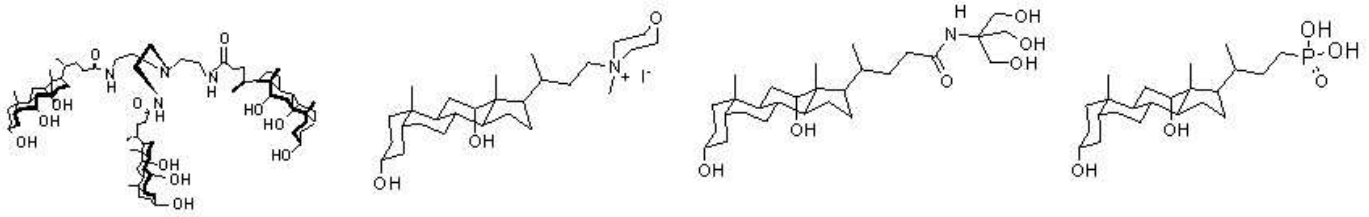
aims of the experiment and scientific background

Polymeric gels are well known. By contrast, thermoreversible gels can be formed from low mass species either in organic or aqueous media. Such gels have been of considerable interest during the past decade because (1) of the challenging fundamental issues related to the self-assembling process giving rise to different morphologies (fibres, ribbons, tubules) and (2) leading to many potential applications (sensors, nanoelectronics, catalysis). Detailed studies of low mass gelators concern mainly organogels[1]. By contrast, the class of molecular hydrogels deserves a special attention due to the importance of aqueous media in biology and nanosciences[2]. One of us (MU) has recently synthesised a series of novel bile acid derivatives, among them tripodal **1** which forms thermoreversible gels in water[3].

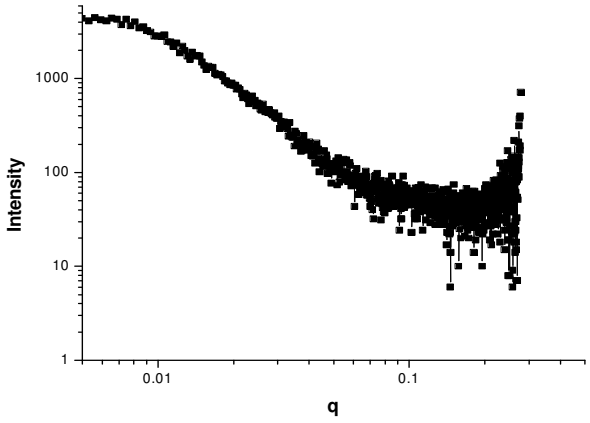


Tripodal gelator (**1**) | Cationic Bile Acid (**2**) | Neutral Bile Acid analog (**3**) | Anionic analog (**4**)

It has also been shown that cationic, neutral and anionic bile salt analogs (**2-4**) form stable hydrogels. As a consequence, we are able to cover the full range of polarities in this class of bile derivatives.

The first objective is to identify the type of 1D aggregates (fibres, tubules, ribbons or helices) forming the self-assembled networks in a variety of these new hydrogels. This step will be done with dilute gels for which the form-factor analysis context is valid in most of the Q-range. The molecular packing of the structures will be approached by the determination of the molecular weight per unit length M_L (requiring low-Q values). From the scattered intensity of concentrated gels we intend to deconvolute or separate contributions from the nodal zones and connected fibres. Such a procedure can be successful only if the Q-range is broad enough (Q_{min} in particular). With compound **2**, the kinetics of formation and thermal stability of the gels are strongly dependent upon the type of counter-ion and in particular iodide strongly enhances the formation of the gel. The high electron density of the counter-ion makes the SAXS technique very appropriate for the localisation of ionic domains in the aggregates. The typical time for equilibration of a gel (less than one hour) makes again ID2 the appropriate instrument for kinetics studies. Exponents for the growth of rod-like species (more or less branched) will be analysed in the context of modified Avrami's and fractal laws. This class of "super-gelators" involves extremely low concentrations (ca.0.1%) that makes an intense synchrotron beam very desirable.

The following figure shows priliminary X-ray scattering data obtained with rotating anode (Cu Kα source) with a 1D detector (1.417 m detector distance, acquistion time ~ 3 hrs) for 1 wt% gel of compound 2 in 0.5 M NaCl aqueous solution



As seen from the above figure, the contrast from the gel is sufficent to be detected. However the statistics is too poor. The Q - range over which data was collected was too much limited. Therefore it would be much desirable to probe the structures at lower q values and high flux ESRF synchroton source.

This proposal concerns the last year of a 3 year-program between France and India (IFCPAR, Indo French Center for the Promotion of Advanced Research, contract 2605-1) and our last chance to have SAXS measurements made on this emerging class of molecular gels. Two post-doctoral fellows from India will be supported by this program to work in TP's lab at Grenoble for one year (starting Sept. 03).

experimental method

The schedule involves gel-like specimens derived from bile analogs **1**, **2**, **3, 4** formed in aqueous media under a variety of conditions (concentration, salt content, type of counter-ion and temperature). We plan to investigate both the kinetics of formation of gels and equilibrated systems. The data analysis will involve classical form-factor models and Debye-Bueche analysis (at least) to complete a more specific modelisation. In total, 35 specimens corresponding to different experimental conditions will be prepared.

The typical average concentration of the samples (ca. 0.5wt %) justifies the use of a high flux source. The nature of the interactions between the aggregates (at the origin of the specific consistency) will be discerned with a screening investigation using 4-6 concentrations for several samples. For this program to be completed, we ask for the ID2 diffractometer (for its brilliance). 9 shifts are necessary in set-up conditions so as to cover the range $0.002Å^{-1}$-$0.5Å^{-1}$.

references

1 D. J. Abdallah and R. G. Weiss, *Adv. Mater.* 12, 1237-1247 (2000).

2 F. M. Menger and K. L. Caran, *J. Am. Chem. Soc.* 122, 11679-11691 (2000).

3 U. Maitra, S. Mukhopadhyay, A. Sarkar, P. Rao, S.S. Indi, *Angew. Chem. Int. Ed.* 40, 2281-2283 (2001).

•

What are the technical reasons which make ESRF necessary for your experiment ? why are other synchrotron radiation sources not appropriate ?

The ID2 high brilliance beamline is appropriate to study such dispersed systems (concentration of the aggregates can be as low as 0.1wt %) in an extended Q-range.

Have you previously done an experiment using synchrotron radiation ?

[x] Yes, at . . ESRF, LURE. . . . . [ ] No.

Have you already used synchrotron radiation for ***this*** project ? [ ] Yes [x] No.

Have you used synchrotron radiation at the ESRF ? [x] Yes [ ] No.

Publications

Please note below the references of all papers published during the past 18 months as a result of measurements which you have done at the ESRF. (If space is insufficient, please attach a list.)

Struth, B., Rieutord, F., Konovalov, O., Brezesinski, G., Grubel, G., Terech, P., Phys. Rev. Lett.,88(2), (2002) using ID10B beam line