Small Angle X-ray Scattering
FOX3D CU 12_INF

Application Note n° AN-3D3

Abstract

The study of low contrast sample with small angle X-ray scattering in the lab remains a challenge as it requires highest flux on the sample meaning the highest optical coupling efficiency together with adequate collimation.

In order to demonstrate the performance gain brought by Xenocs FOX3D CU 12_INF optics for this type of application, a comparative testing with two different optics was performed at IFP on their existing SAXS beamline.

Experimental results on a standard HDPE sample and a diluted asphaltene solution in toluene shown a clear performance gain and the access to structural investigation of low contrast samples in the laboratory with this new aspheric single reflection optics.

Fig. 1 : The FOX3D CU 12_INF X-ray multilayer optic.

Application of low divergence SAXS on crude oil research

Data courtesy of Dr Loïc Barré, Institut Français du Pétrole, Rueil Malmaison, France

Introduction

Today, the petroleum industry focuses on heavy crude oils that represent a large part of our resources. Every stage of the heavy crude production process is very difficult mainly because of their high asphaltene content. Asphaltenes are polar and aromatic molecules that aggregate according to mechanisms highly dependent on the chemical and dynamic environment: **concentration, medium, temperature, shear...**

Besides these petroleum industry related characteristics, these molecules present peculiar **surface properties**, i.e. high surface tension or strong emulisifiers. Another similar class of molecule is of our interest usually called asphaltenic "resins" (polar molecules of the crude, soluble in heptane but insoluble in pentane). In the crude, these resins are thought to limit the growth of asphaltenes aggregates. Aggregation affects transport properties, causing high oil viscosity and low diffusion into catalyst network. Asphaltenes are defined as a solubility class (insoluble part of the crude in heptane) and their aggregation process as a function of concentration (see Fig. 2). IFP's investigation focuses on a better comprehension of these aggregation processes in order to better control heavy crude oil properties.

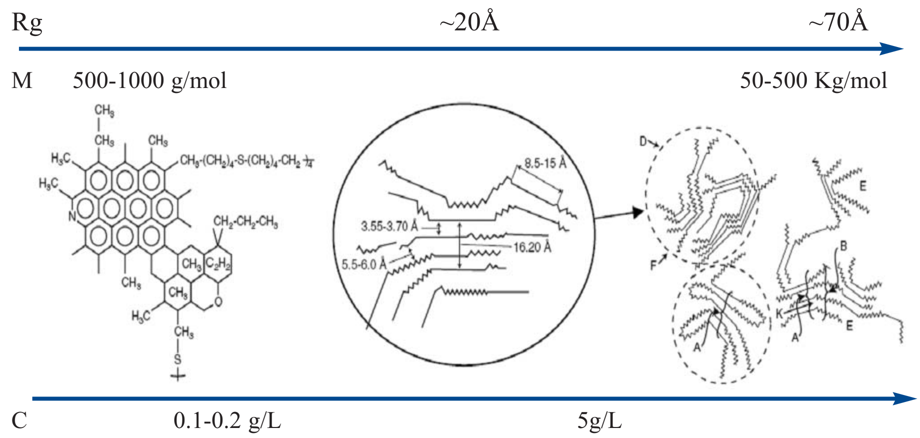

Fig. 2 : Scheme of nanoaggregates made from aromatic stacking surrounded by aliphatic chains, associated to form fractal (named clusters) of radius of gyration around 70Å, however, the association mechanism is not clearly explained.

SAXS is an ideal tool to investigate such interdependencies between structure and properties. In order to track the aggregation mechanisms, useful structure parameters can be determined such as radius of gyration, molecular weight, fractal dimension, form factor, aggregation number and interaction parameters. Unfortunately, asphaltenes offer a low contrast with their solvent and even lower with their crude. Moreover there is a clear challenge approaching low concentrated samples. Indeed, it is of particular interest to investigate low concentrated states in order to capture the form factor of the initial nanoaggregates.

Together with low concentrated samples, smaller particles such as resins offer a low contrast but need to be observed to understand the asphaltene behaviour in the crude. Observing these low scattering samples can only be done by a further improvement of the experimental setup.

Experiment

Since the highest flux is required on the sample, the highest optical coupling efficiency with X-ray generator is required, together with adequate collimation to achieve experimental goals.

In order to achieve the optimum source – optic coupling a FOX3D CU 12_INF was installed on a Rigaku Micromax 007 rotating anode generator. A comparative testing was performed with the previous model of collimating optic from Xenocs product range : FOX2D CU 12_INF. The lower divergence natively delivered by FOX3D full aspheric single reflection mirror offers higher potential for accurate and efficient collimation, with less parasitic from slits and more accurate scattering experiment. The SAXS beamline architecture is described in Figure 3.

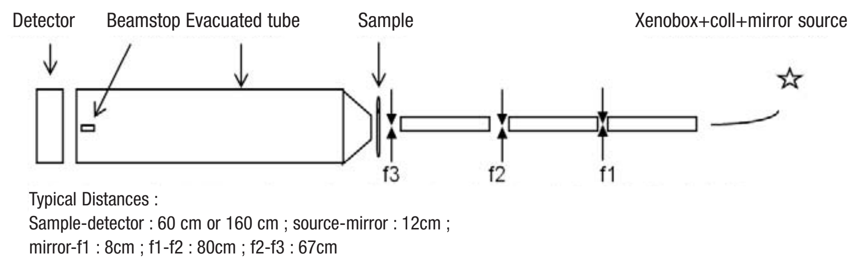

Fig. 3 : Description of the experimental set up based on a MM007 and a Xenocs low divergence mirror.

As described in Table I, various resolution/flux configurations can be achieved with the SAXS beamline depending on slit settings and sample-detector distances. In Table II, flux measurement at f1 and at sample position are listed for the two different optics and in the different slits configurations. Standard operating configurations for IFP are either Low resolution/High Flux or High resolution/Low noise with two different slits settings. The introduction of the FOX3D CU 12_INF enables a third possible configuration with high resolution and higher flux which was not used in this comparative testing.

Table I : Beamline configurations with slits setting and sample to detector distances.

SLIT #	Low resolution	High resolution low noise	High resolution high flux
sample-detector distance	60 cm	160 cm	160 cm
f1	0.6 x 0.6 mm²	0.3 x 0.3 mm²	0.5 x 0.5 mm²
f2	0.4 x 0.4 mm²	0.3 x 0.3 mm²	0.5 x 0.5 mm²
f3	1.2 x 1.2 mm²	0.8 x 0.9 mm²	0.9 x 0.9 mm²

Table II : Measured flux at f1 and at sample position with the different slits configurations.

	Flux at f1 (Mph/s)	Divergence (mrad)	Intensity at sample (Mph/s): Low resolution	Intensity at sample (Mph/s): High resolution low noise	Intensity at sample (Mph/s): High resolution high flux
FOX2D	276	0.8	16.5	3.4	NA
FOX3D	863	0.6	28.4	6.2	29
Gain3D/2D	1.5	-	1.7	1.8	NA

In order to evaluate the performance gain in SAXS application, a test sample made of 1mm high density polyethylene was measured both with FOX2D CU 12_INF and FOX3D CU 12_INF on a 1.6m long SAXS camera collected with High resolution/Low noise slit setting and identical exposure time of 10mn (Fig. 4). On the scattering curves shown below intensities are not corrected from incoming flux and exhibit a 75% increase of scattered intensity. The dotted line is the ratio of FOX3D/FOX2D intensities.

Scattered intensity increase is brought by this enhanced coupling of the FOX3D. Indeed, with such aspheric single reflection optic, the brilliance of the source is better conserved for a given slit setting. This allows for reinforcing data interpretation by a significant increase of the signal to noise ratio. This performance gain opens new possibilities for the exploration of low concentrated samples. As a reason, a similar comparative test was performed on a sample known to be difficult to study since its contrast to XRay is very low, especially in a diluted form. A diluted asphaltene solution in toluene (1.7g/l) was measured with both optics on the same experimental setup with same slit configuration (High resolution/Low noise). The same diluted asphaltenic solution was then measured with the FOX3D in a High Resolution/ High flux configuration with larger slits opening.

Resulting data are plotted in Figure 5. Data were subtracted from pure solvent (toluene). The curves are represented on an absolute intensity scale. The dotted line corresponds to the water scattering level illustrating the intrinsic low scattering power of the sample studied.

The results presented on the same graph demonstrate a clear benefit of the FOX3D for this low diffracting sample for SAXS experiments. In the case of identical slit settings, the higher flux of the FOX3D already allows for a sharper determination of the scattering signal at high q (~0.2Å^{-1}) , even with exposure times as low as 10 minutes. Furthermore, the aspheric single reflection optic offering less aberrations, it is possible to relax the slit settings, offering a much higher flux on the sample, by up to a factor 5, increasing dramatically the signal to noise ratio. The gain at high wave vectors, where most scattering curves are vanishing on high resolution SAXS (long camera setting), is particularly clear on the Figure 4 by comparing the data quality on the FOX3D high resolution/high flux with the regular slits settings employed at the IFP. As a reason, new compromises of flux VS resolution can be achieved.

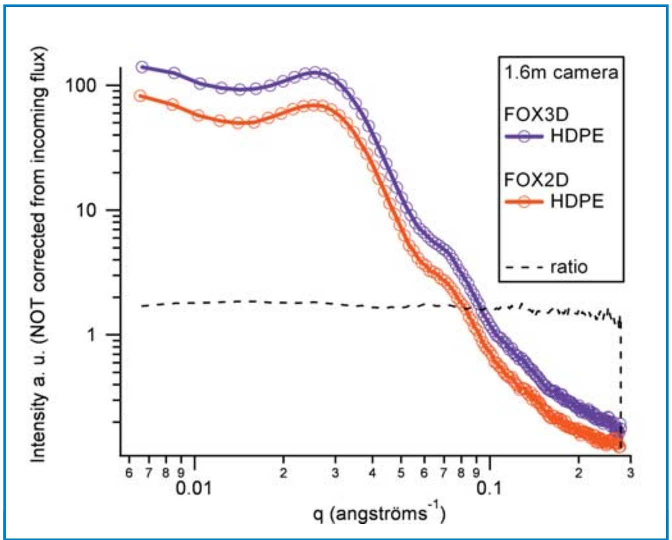

Fig. 4 : Scattering intensities of HDPE 1mm thick sample with FOX2D and FOX3D optics and identical exposure time of 10mn. Data are obviously not corrected by incident flux for sake of comparison.

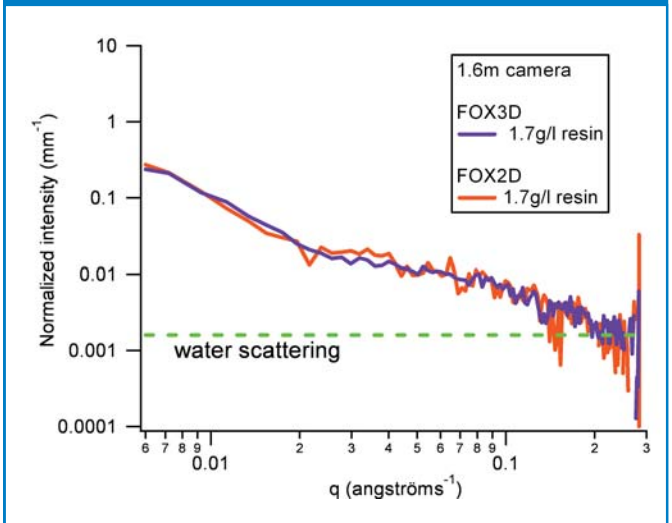

Fig. 5 : Absolute intensity scattering of 1.7g/l resin studied with FOX2D and FOX3D optic. The beam properties of FOX3D allows for high flux slits setting even with a long camera length setting.

Conclusion

We have shown that the new generation of the Xenocs optic FOX3D is successfully used in SAXS application. Indeed, with a purely aspheric single reflection shape, the aberrations are minimised, thus allowing simpler collimation settings. For unchanged slit settings, the flux is almost doubled, but most importantly, new compromises on the flux VS resolution can be adopted. For instance the flux on the sample can be dramatically increased by up to a factor of 5 with little compromise on resolution.

Preservation of the source brilliance by the FOX3D is an asset for the study of low scattering systems since it offers the access to structural investigation of low contrast samples in the laboratory, not possible before within a reasonable experimental time or without use of large facilities as such as synchrotrons.

Finally, such an optical scheme is of the utmost importance for the crude oil investigation in the lab, more particularly since dilution laws and thermal behaviour of asphaltenic resins can be explored down to concentrations within industrial relevance.

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