	Experiment title: GISAXS Study of the Structure and State of Ion Aggregation in the Surface Layer of Nafion Exposed to Water Vapor	**Experiment number**: SI-1692
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Shifts: 12	**Local contact(s)**: Dr. Amarjeet Singh	*Received at ESRF:*

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Report:

The bulk scattering of Nafion is well known, perhaps the most complete curves were reported by Gebel and Diat and is shown in Fig. 1 [1]. Schmidt-Rohr and Chen [2] has concluded recently that the bulk scattering of Nafion is best explained by assuming a 2D morphology, in which water and hydrated ionic groups form long channels stabilized by long crystallites of the matrix (Fig. 2). The most characteristic feature in scattering of Nafion and similar materials is the ionomer peak observed at q~0.1 Å^{-1} that is assigned to hydrated ionic aggreagates of a typical size of a few nm that varies with hydration.
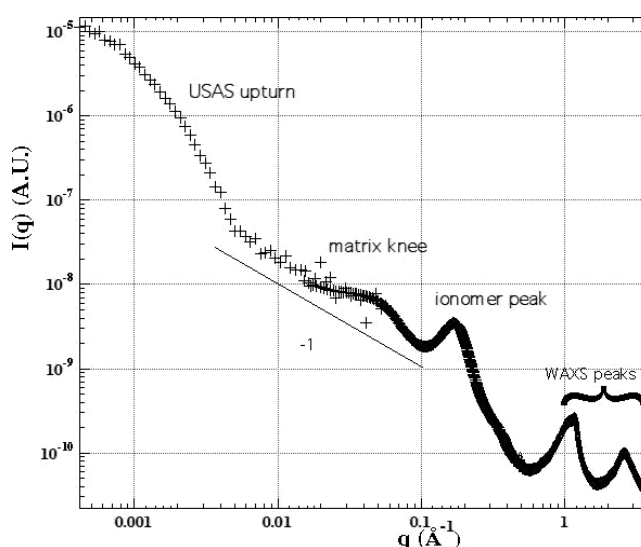

Fig. 1. A typical SAXS spectrum of a hydrated Nafion, after Gebel and Diat [1].
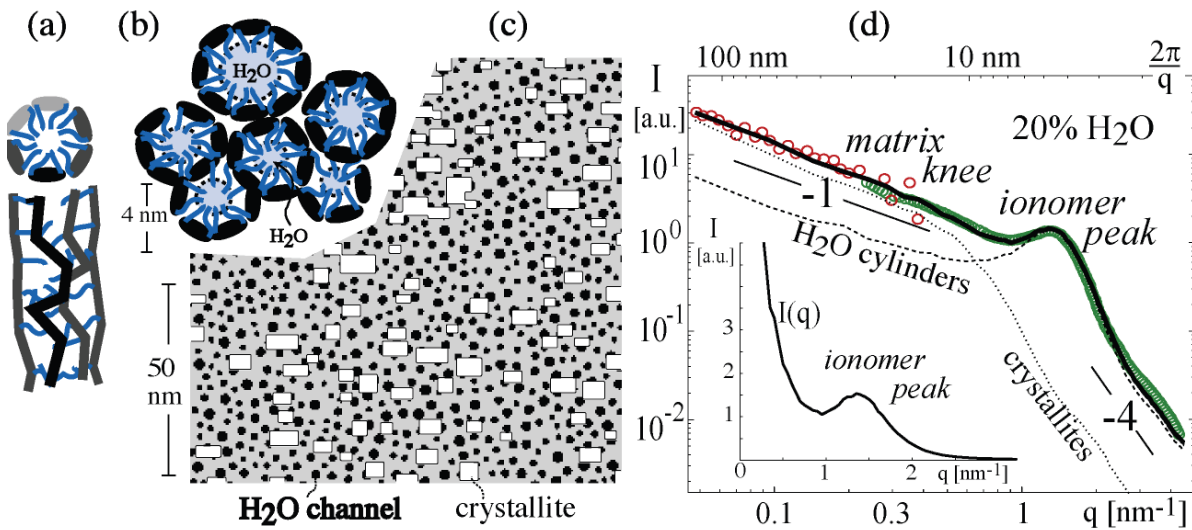
Fig. 2. The anisotropic bulk structure of hydrated Nafion comprising elongated channels stabilized by long matrix crystallites: (a) shape of aggregates, (b) aggregate packing, (c) suggested bulk morphology, (c) scattering curve in Fig. 1 as superposition of scattering by aligned water channels and crystallites. After Schmidt-Rohr and Chen [2].

Despite presence of crystallites that mechnically stabilize the material at the macroscopic scale, the immediate vicinity of aggregates and the microscopic matrix-water interface should be able to relax and should then be nearly liquid-like at long timescales required to establish swelling equilibrium. In particular, this means, as our analysis shows [3], that the requirement of of force balance at 3-phase contact lines will make the external surface of the polymer adopt different configurations subject to whether it is exposed to liquid or vapor. In vapor a thin hydrophobic layer ("crust") is expected to form or "spead" on the surface and the ionic aggreagates will then be "buried" under the surface. However, unlike free spreading of an oil on water surface, the covalent bonds between the ionic groups and matrix will lead to formation of an array of closely packed inverted micells with a hydrophilic core (the aggregate) and a hydrophobic shell, similar to ones in Fig. 2a, on the Nafion surface. The external medium will then be faced with a layer of hydrophobic material of a thickness commensurable with the shell thickness, i.e., about the radius of the micelle. The presence of a hydrophobic layer depleted of ionic aggregates on the Nafion surface exposed to vapor indeed confirmed by some data, such as contact angle and AFM [4]. On the other hand, in water or aqueous solution the polymer will tend to expose the ionic groups and "bury" the hydro phobic matrix under the surface, i.e., form normal-type micelles on the surface. The consequence of this effect is that it should exert different pressures on the inner bulk [3], which will result in different hydration in two conditions – the effect known as Schroeder's paradox – important, for instance, in designing and running membrane fuel cells.

The purpose of the experiment was to examine the surface layer of Nafion exposed to vapor using GISAXS and verify absense or reduced content of ionic aggreagtes. Two kinds of Nafion samples were used: genuine Nafion -117 membranes and a layer of Nafion about 100 nm thick spin-coated onto a Si wafer. The reason for preparing spin-coated samples was the significant large-(~μm) and small-(~nm) scale roughness of Nafion membranes and their tendency to curle, which makes it difficult to align the sample for GISAXS or reflectivity measurements. The use of a clamp to pull the membrane taut allowed for some improvement and

one successful set of measurements was obtained with a membrane sample, yet the residual curling and the micrometer-scale roughness of membranes made spin-coated samples the preferred option for these exploratory experiments.

  The samples (in H or Na form) were prequilibrated in a closed evacuated disiccator containing a saturated solution of a salt providing an appropriate humidity and quickly transferred to the experimental enviromental chamber with Kapton windows mounted in the hutch, in which the sample was mounted and temperature 30 C and desired humidity were maintained (Fig. 3). Before measurements at least 0.5 h was allowed for sample re-equilibration. In the course of experiment we found a noticeable damage by X-ray beam, seen as traces on the sample surface (Fig. 3a). Therefore, to minimize possible artifacts due to radiation damage in subsequent experiments the sample was moved across the beam after each scan.
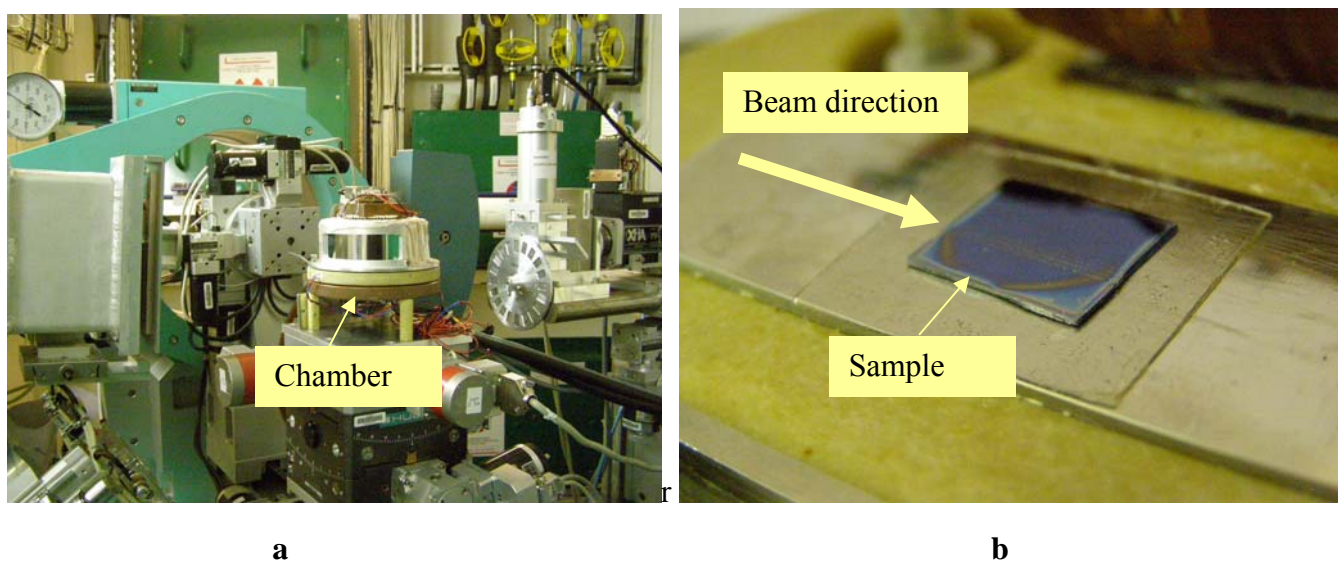

a **b**

Fig. 3. The experimental setup: (a) the environmental chamber and (b) a sample (Si wafer spin-coated with Nafion) with signs of radiation damage.

Typical plots of measured intensity I scattered parallel to the surface (integrated over PSD and normalized to the monitor intensity and filter) vs. scattering wavenumber Q_{xy} are shown in Fig. 4a. The different curves were obtained at differnet incident angles (α_i), both below and above the critical angle $\alpha_c \approx 0.21°$. The value of the critical angle was assessed using an X-ray reflectivity scan (not shown) and the electrone density calcuated from this value closely correspond to the one estimated from the known chemical composition and density of the perfluorinated Nafion matrix.

The ionomer peak sitting on top of a featureless diffuse scatteing background is well observed in all spectra in Fig. 4a as a shoulder at $Q_{xy} \sim 0.1$ Å^{-1}. Its relative intensity is nearly constant above and near the critical angle, however it clearly decreases when α_i decreases below α_c. Since the background scattering decays with Q_{xy} with an exponent close to 1 (see. Fig. 2 and [2]), the ionomer peak can be made more clearly seen when IQ_{xy} instead of I is plotted vs. Q_{xy}, as shown in Fig. 4b. The attennution of the ionomer peak with decreasing α_i below α_c seeems to agree with the existence of a surface layer depleted of aggregates. The minimal

pentration depth of X-rays calculated from the value of α_c is about 30 Å, which is commensurable with the size of an aggregate hence with the expected thickness of the hydrophobic surface layer. The scattering at low subcritical incidence angles is then supposed to come mostly from the surface layer that does not contain aggregates hence should not produce an ionomer peak, a peak of lower intensity still coming from the attenuated evanescent wave reaching the underlying bulk. Similar considerations may apply to the WAXS peak assigned to the bulk crystallinity, which is attenuated at the lowest α_i as well (but for some reason not at intermediate angle $\alpha_i = 0.21°$) and might indicate reduced degree of crystallinity of the surface layer.

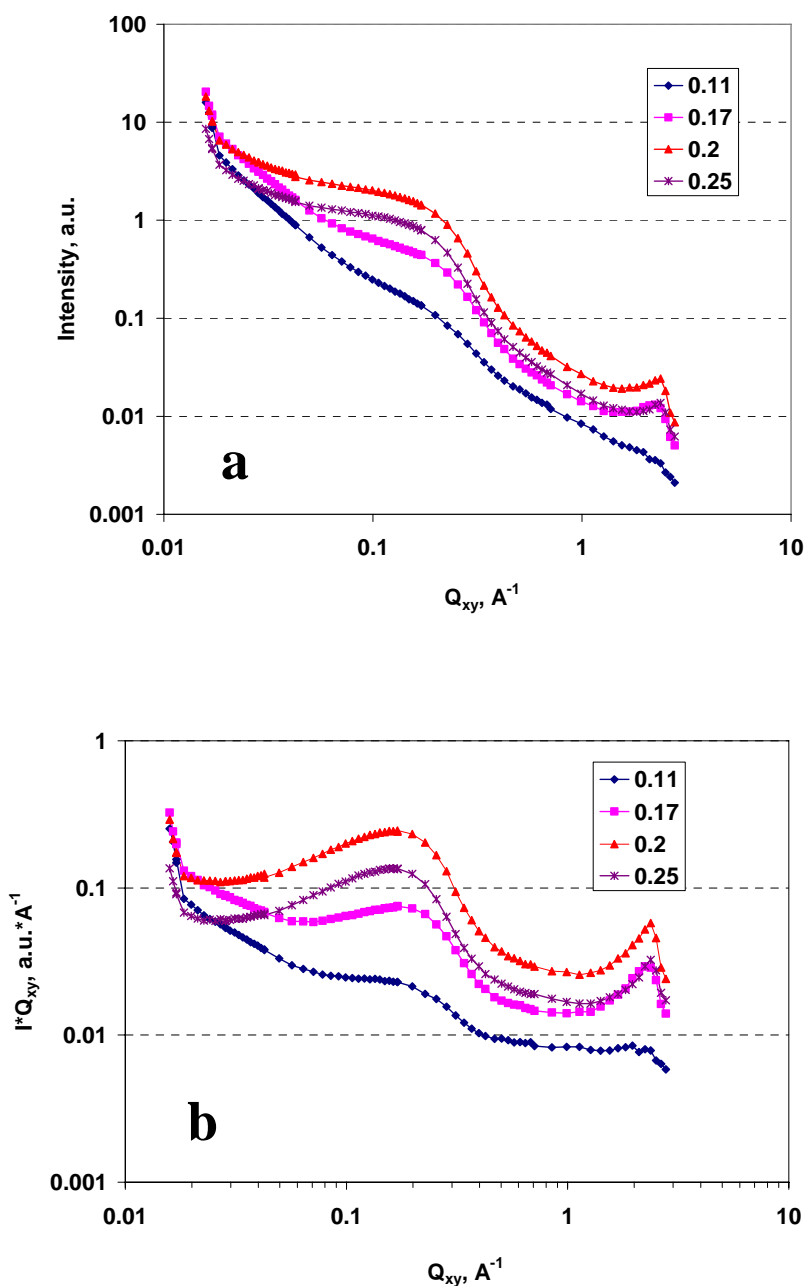*Fig. 4. Intensity scattered along the surface vs. Q_{xy} for several incident angles (a) I vs. Q_{xy}, (b) IQ_{xy} vs. Q_{xy}. The sample was a Si wafer spin-coated with Nafion, relative humidity 84%, temperature 30° The incident angles corresponding to each curve are in degrees.*

A more detailed picture may be obtained from 2D scattering intensity maps shown in Fig. 5 for the same sample and the same incidence angles as in Fig. 4. For technical reasons (due to problems with the data reduction software, to be fixed) they plot the intensity data versus PSD channel number and scattering angle δ rather than, respectively, Q_z and Q_{xy}, yet the axes are appropriately scaled to cover nearly the same Q-range up to about 0.3-0.5 Å^{-1} on both axes in order to facilitate comparison of the ionomer peak in both directions. Inessential to the analysis is the distortions (Yoneda) in the z-direction below $Q_z \sim Q_c$ (corresponding to α_c) in the bottom part of the maps.
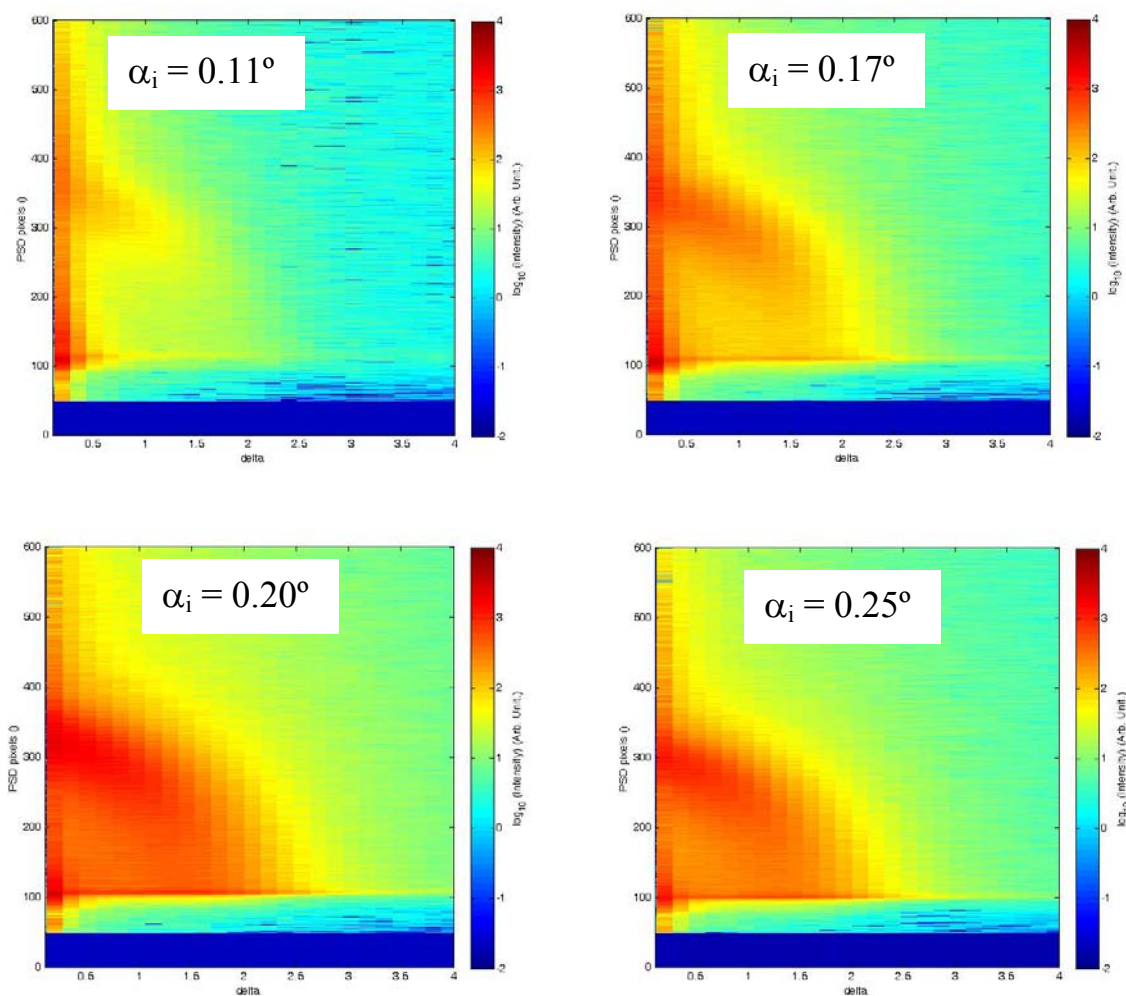

Fig. 5. 2D scattering intensity maps (row data) for the curves shown in Fig. 4.

Although anisotropy may be observed for all incidence angles, it is seen that near and above the critical angle the anisotropy is less significant, as expected for bulk-like scattering. However it is greatly enhanced at lower angles. At the lowest angle $\alpha_i = 0.11°$ the ionomer peak in the direction normal to the surface is much more pronounced that parallel to the surface approaching the characteristic pattern of Bragg sheets (layered structure parallel to the surface). This may emphasize the confining and aligning effect of the polymer-vapor surface on the inverted micelle structure and packing in the surface region in the normal direction. The ionomer peak in the z-direction may then be interpreted simply as the thickness of the micelle shells, i.e., of the hydrophobic surface "crust". However, absence of such effect in lateral directions and reduced content of

aggregates in the crust make the ionomer peak disappear in x- and y-directions when the penetration depth goes to minimum, as indeed observed. We may then conclude that the results seem to agree well with previously assumed physical structure of the Nafion surface in vapor .

The noteworthy point is that the first experiments, in which the sample was not consistently moved after each scan, showed somewhat more isotropic patterns, which could be a result of the beam gradually "eating out" the surface layer and "digging" deeper into the bulk without letting sufficient time for the polymer structure to re-arrange. Nevertheless, attenuation of the ionomer peak with decreasing α_i was observed in these experiments as well. Similar results were obtained for Nafion 117 membranes, the only notable diference being a less regular backround scattering, which may result from the more irregular surface morphology and poor flatness of the membrane. These points are to be checked in future experiments.

In conclusion, the reported first experiments seem to conform to the proposed picture. In the future, apart from clarifying questionable points with the current setup, it will be highly intersting to attempt similar experiments under water (necessary facilities are available at ID10B). In the latter case, the expected surface structure should be principally different; for instance, surface layer should contain as many aggregates as the bulk and no attenuation of the ionomer peak should be observed.

References

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4. Zawodzinski, T.A., Gottesfeld, S., Stoichet, S., McCarthy, T.J. *J. Appl. Electrochem.*, **1993**, *23*, 86; McLean, R.S., Doule, M., Sauer, B.B., *Macromolecules*, **2000**, *33*, 6541.