Experimental report

01/02/2021

Proposal: 7-05-499 **Council:** 10/2018

Title: Neutron reflectivity study of size-dependent sorption of molecules bygraphene oxide multilayers.

Research area: Chemistry

This proposal is a resubmission of 9-10-1549

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Samples: Graphene Oxide

Instrument	Requested days	Allocated days	From	To
SUPERADAM	7	4	06/02/2020	10/02/2020

Abstract:

The project suggests to study sorption of molecules with different size by graphene oxide films (GO) exposed to solutions in polar solvents (D2O or d-ethanol). Experiments will be performed using solid-liquid interface cell available at SUPERADAM and designed for Si blocks 50x50x10 mm size. Neutron reflectivity method allows to evaluate swelling of GO films (change in the film thickness) in polar solvent and, simultaneously, composition of sorbed solution. If the size of dissolved molecule exceeds size of "pore" formed by graphene oxide layers in solvent-swelled state, it is expected that only pure solvent will be adsorbed by the film. Smaller molecules are expected to penetrate into inter-layer space of GO structure in either hydrated (solvated) or de-hydrated (de-solvated) state. Using deuterium substituted solvent and organic molecules with different sizes (mostly sugars) we expect to find experimentally the "cut off" size of molecules which defines permeation/not permeation condition for GO membranes.

Experimental report for proposal 7-05-499 details

Title **Neutron reflectivity study of size-dependent sorption of molecules by graphene oxide multilayers.**

Total 7 days were allocated for the experiment and 4 days were used in 2020 (06/02/2020 To 10/02/2020). Therefor this report is preliminary. Experiments were performed according to the plan and included neutron reflectivity tests for sorption of various molecules by Graphene Oxide (GO) thin films. Experiments were performed with thin films exposed to ethanol solution of three dyes (Methylene Blue, Crystal Violet and Rose Bengal) to evaluate change in film thickness and change in composition of films due to sorption. This part of experiment was completed successfully, data processed and prepared for publication.

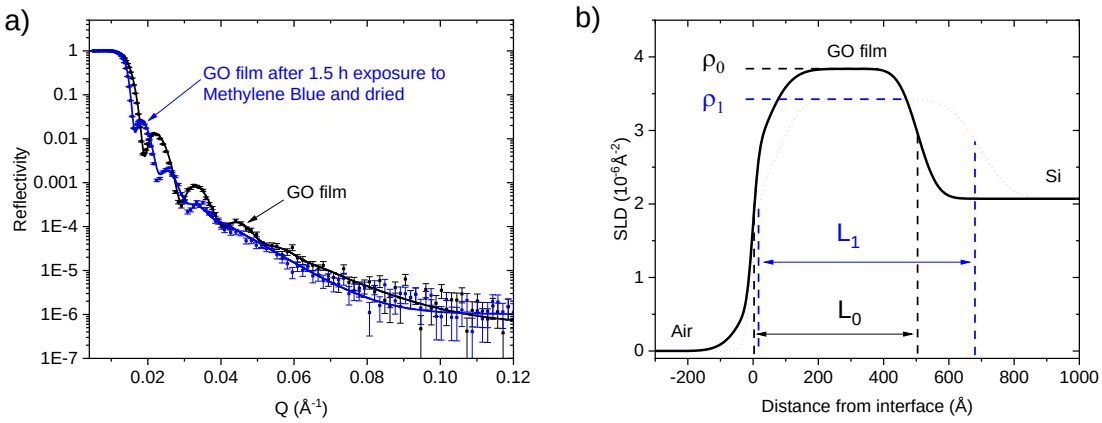

Figure 1. a) Neutron reflectivity data (including error bars) obtained from GO film in ambient conditions before and after MB sorption b) Scattering length density profile of the GO film before and after MB sorption obtained as result of the modelling (fitting) of experimental data.

Example of the processed data is shown in **Figure 1**. Sorption of methylene blue is evident from the increase of film thickness and change in composition. Quantitative evaluation of sorption was done using fitting of NR curves and analysis of data. The results were also verified by XRD after experiments at ILL. The sorption of MB by thin GO films is found to be significantly stronger compared to sorption of Crystal Violet (CV) and Rose Bengal (RB). This effect is attributed to the difference in the geometrical shape of planar MB and essentially non-flat CV and RB molecules. Graphite oxides and re-stacked multilayered GO are found to exhibit different Methylene Blue (MB) sorption. Structural characterization demonstrates that MB sorption by precursor graphite oxide and thin spin-coated films of GO is significantly stronger compared to free-standing μm thick membranes prepared by vacuum filtration. Intercalation of GO membranes and thin films by dyes provides explicit evidence for penetration of these molecules into GO interlayers. It is not hydration or solvation diameter but the exact geometrical shape of molecules that need to be taken into account considering size effects for penetration of molecules between GO layers in membrane applications.

Experiments were also performed with direct in situ testing of sorption I liquid cell. However, the GO films showed some issues with stability in liquid and insufficient quality of reflectivity oscillations for confident interpretation of the data. The remaining days will be used for testing sorption from solutions in different solvents and in different experimental setup in order to find experimental conditions which allow high quality of data to be recorded in situ in liquid solvent.