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Swelling of Thin Graphene Oxide Films Studied by *in-situ* Neutron Reflectivity

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ABSTRACT

Permeation of multilayered graphene oxide (GO) membranes by polar solvents is known to correlate with their swelling properties and amount of sorbed solvent. However, quantitative estimation of sorption using standard (e.g. gravimetric) methods is technically challenging for few nanometers thick GO membranes/films exposed to solvent vapors. Neutron reflectivity (NR) was used here to evaluate amount of solvents intercalated into film which consists of only ~35 layers of GO. Analysis of NR data recorded from GO film exposed to vapors of polar solvents provide information about change of film thickness due to swelling, amount of intercalated solvent and selectivity in sorption of solvents from binary mixtures. Quantitative study of GO film sorption was performed for D₂O, d-methanol, ethanol, dimethyl sulfoxide (DMSO),

acetonitrile, dimethylformamide (DMF) and acetone. Using isotopic contrast we estimated selectivity in sorption of ethanol/d-methanol mixtures by the GO film. Estimation of sorption selectivity was also performed for D₂O/dimethylformamide, D₂O/dimethyl sulfoxide and D₂O/acetonitrile binary mixtures. Sorption of polar solvents was compared for thin GO film, micrometer thick free standing GO membranes and graphite oxide powders.

1 INTRODUCTION

Graphite oxides are hydrophilic layered materials which can easily be dispersed in polar solvents thus producing solutions with few mg/ml concentration of single-layered graphene oxide (GO).¹ Single-layered GO can then be deposited from solution to form multilayered assemblies which are named after expected applications and thickness as papers², thin films or membranes.³⁻⁷

Membranes properties of micrometer thick free standing or supported GO laminates have been rather actively studied in recent years both for permeation of liquid solvents and solutions and permeation of vapors (pervaporation).^{1, 7} Membrane tests were demonstrated to be successful also for relatively thin GO laminates with thickness of only 4-300 nm.⁸⁻⁹ Very thin (~1 nm) GO films have been reported recently also to exhibit extraordinary gas separation properties.¹⁰ Permeation of the membranes by several gases could be controlled using humidity-dependent variation of distance between GO layers.¹¹ The vapor permeation properties of GO membranes are defined by their ability to swell in polar solvents which results in expansion of inter-layer distance and formation of a labyrinth path of interconnected „channels“.^{1, 7, 12} Therefore,

understanding of GO films/membranes swelling and quantitative estimation of solvent sorption are important parameters which allow to understand permeation mechanism.

GO is material with somewhat uncertain structure due to variable oxidation degree and disorder in attachment of various functional groups.¹³⁻¹⁵ Many properties of GO are dependent on synthesis method including strong difference in hydration/solvation.¹⁶⁻²⁰ Graphite oxide's swelling in polar solvents was studied in details over past years, both in liquid solvents and saturated vapors.^{1, 14, 21-27} In particular, our recent study provides quantitative estimation of GO sorption for several polar solvents, both at ambient temperature (using saturation by solvent vapour) and near the temperature point of solvent melting (sorption of liquid solvent).²⁸

One of the surprising properties of μm thick GO membranes revealed in our recent studies is that they swell significantly differently in many polar solvents as compared to precursor graphite oxides.²⁸⁻³⁰ This effect was attributed to different geometry of individual GO sheets packing in the membranes prepared by vacuum filtration and effect of edge enveloping. In particular, membrane swelling is significantly smaller in alcohols and several other polar solvents²⁹ while for several solvents the swelling of GO membranes and their precursor graphite oxides seem to be similar.³⁰ However, it remains to be unknown if the swelling of GO membranes depends on thickness of films or on deposition method (e.g. vacuum filtration¹² or drop casting⁷).

Drop casting⁷ and spin coating³¹ are methods which are most commonly used for preparation of rather thin 1-50 nm films of GO while vacuum filtration provides films of several micrometer thickness.²⁹⁻³⁰ It cannot be ruled out that swelling of spin coated GO films consisting of few layers will be different compared to thick films which are composed by thousands of densely

packed layers. However, direct evaluation of the sorption using e.g. simple gravimetric measurements is extremely difficult or impossible for thin films due to their negligibly small absolute weight and weight change due to swelling.

The GO hydration/solvation is typically evaluated by diffraction methods using variations in $d(001)$ which corresponds to the averaged distance between GO layers. However, solvents are inserted into multi-layered GO structures in disordered state and the exact amount of intercalated solvents cannot be determined by diffraction methods. Interestingly, the $d(001)$ of hydrated graphite oxide is known to change *gradually* with temperature variation²⁶; under humidity variations²² and is not linearly proportional to the amount of adsorbed water.³² It is important to emphasize that diffraction methods provide averaged value of interlayer distance while effects of interstratification and intrastratification³³ must be taken into account to explain gradual changes of lattice spacing. Moreover, expansion of GO lattice cannot directly be used for quantitative estimation of solvent sorption since the structure of intercalated solvent is unknown. The same lattice expansion could, in principle, be achieved for different amount of sorbed solvent.

Recently we demonstrated that neutron scattering can be used as a powerful tool for studies of solvent sorption by thin GO films.³¹ Neutron Reflectivity (NR) provides simultaneous determination of the GO unit cell volume and its chemical composition.³⁴ Therefore, exact amount of solvent sorbed by GO thin film can be evaluated. Using isotopic contrast, this method allowed also to distinguish D₂O and ethanol insertion into the GO structure providing information about selectivity in vapour sorption. Our experiments demonstrated that solvent sorbed by GO films is enriched by ethanol compared to the composition of vapour³¹ which is in

agreement with experimental observations of selectivity of ethanol permeation through GO membranes exposed to water/ethanol vapors.^{7, 35} However, many other polar solvents and their binary mixtures are of interest for possible membrane applications of GO thin films

Here we demonstrate that neutron scattering can be used for quantitative evaluation of sorption by thin (~25 nm) graphene oxide film deposited on Si wafer and exposed to vapors of several polar solvents and their binary mixtures. The sorption of polar solvents by thin GO films is found to be smaller compared to sorption by precursor graphite oxide powder samples and more similar to the sorption by micrometer thick membranes. Selectivity of sorption by GO film was estimated for several binary mixtures: d-methanol/ethanol, D₂O/acetonitrile, D₂O/DMSO, D₂O/DMF and D₂O/acetone. The data collected using neutron reflectivity can be used to predict and to quantify selectivity in permeation of solvent vapors through multilayered GO membranes.

2 EXPERIMENTAL

Thin films were prepared using Hummers graphite oxide precursor synthesized using slightly modified Hummers procedure, see details elsewhere.³⁶ The graphite oxide powder was sonicated in ethanol/water (90-95% ethanol by volume) for 12 hours yielding solution with concentration 1 mg/ml. The dispersion was then deposited as a thin film onto the cleaned surface of Si plate using spin-coating and dried at ambient conditions. Resulting films are almost transparent with very slightly brownish color. It is believed that the GO flakes of micrometer size are closely packed in the GO films forming dense layered material.¹¹ High flexibility and strong hydrophilic nature of GO prevents formation of voids as a significant fraction of total film volume.³³ The

surface of GO film was characterized using SEM (see Figure 1S) which demonstrated relatively smooth surface with few wrinkles in the regions of flakes overlap. Note that the size of GO flakes is in scale of few micrometers and total area of wrinkles is negligibly small compared to the area of flat regions. Note that even if some voids are present in the structure of GO films, SLD of air is usually considered to be zero due to the low density of gas compared to the density of solids. Therefore, no contribution from voids is expected in NR scans.

Micrometer-thick free standing GO membranes were prepared using water dispersions by vacuum filtration and used for experiments with sorption of solvent vapors as described below. The membrane was cut on pieces and used for experiments with vapor sorption. The C/O ratio of 2.47 was determined by XPS using piece of this membrane.

The sorption of polar solvents by free standing membranes was studied using gravimetric method. Rubotherm microbalance system with magnetic suspension was used for direct weight measurements of membrane sample (~26 mg) exposed to vapors of polar solvents inside of the sealed measurement cell at ambient temperature conditions (~23°C). The balance provides ± 0.01 mg weight precision and “zero point” calibration every 2 minutes to allow continuous monitoring of the weight change over prolonged periods of time. The *in situ* method allows to observe increase of the sample weight while the liquid solvent evaporates from the vial placed at the bottom of the cell. The sorption test was stopped at the moment when the weight of sample achieved saturation, the cell was open and weight decrease due to the solvent evaporation monitored until the equilibrium with room conditions achieved. Separate test experiment was

performed using humidity sensor/data logger to verify the kinetic of water evaporation and saturation of vapor pressure inside of the cell.

X-ray reflectivity measurements at ambient conditions were performed at the ID10 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble, France, using photons with $\lambda=0.654\text{\AA}$. Neutron reflectivity experiments were performed in a specially designed humidity cell at the reflectometer Super-Adam at the Institute Laue-Langevin (ILL), Grenoble, France using a monochromatic beam with wavelength $\lambda=5.19\text{\AA}$.

The humidity cell was loaded with several ml of liquid solvent which evaporated under the sealed aluminum jar until saturation is achieved. The rate of humidity change and response of GO film inside of the cell was verified in a separate experiment which demonstrated that vapor pressure saturation is achieved inside of the cell after several hours. Separate test was performed using humidity data logger to verify how quickly the evaporation of solvent provides saturation of vapor inside of the experimental cell. The cell was closed at 26°C and 55% ambient humidity and the humidity close to saturation point (92%) was achieved after two hours. Further exposure up to four hours provided increase up to 96% humidity level (see SI file for details).

The GO film was exposed to ethanol, D₂O and ethanol/D₂O vapors for 3-6 hours, vapor exposure periods were separated by periods of air drying. D₂O with purity 99.9 atom % D (Sigma-Aldrich) and ethanol with purity $\geq 99.5\%$ (Solveco, Sweden), DMSO $\geq 99.9\%$ (Sigma Aldrich), Acetone, $\geq 99.5\%$ (Sigma Aldrich), Acetonitrile $\geq 99.9\%$ (Sigma Aldrich), Dimethylformamide (DMF) 99% (Alfa Aesar), d₆-ethanol $\geq 99.5\%$ (Sigma Aldrich) were used for these experiments. The film was air dried between exposures to solvent vapors.

Typically, the NR measurements were repeated until no further changes in the shape of NR curves observed. This time is individual for each solvent depending on vapor pressure at ambient conditions, typically 2-4 hours. However, for DMSO the saturation point was not achieved and experiment stopped after several hours due to the time limitations of NR.

Two key parameters characterizing the GO film at each state in the NR measurements – Scattering Length Density (SLD) ρ and film thickness L – were obtained by fitting experimental data using Motofit software.³⁷ Simple calculations allowing to retrieve amount of intercalated molecules from values of ρ and L parameters can be found in SI.

The number of solvent molecules intercalated into the GO structure per formula unit was calculated assuming composition $C_2O_{0.76}H_{0.24}$. This formula corresponds to the C/O ratio provided by XPS while the amount of hydrogen was added according to the most common structural model of GO.

3 RESULTS

3.1 AMBIENT STATE OF GO FILM AND EXPERIMENT TIME LINE

The GO film was first characterized at ambient conditions. The thickness of as-deposited film was determined by NR as $L_0=25\text{nm}$ (at ambient humidity 55%). This corresponds to 31.5 GO monolayers based on interlayer distance $d_0=7.93\text{\AA}$ found from position of (001) Bragg peak as determined by XRD test. In agreement with our earlier studies, the film also contains some water due to exposure to ambient humidity. It follows from discrepancy between expected and experimental values of Neutron Scattering Length (NSL) B_0 which is defined as $B_0= \rho_0V= \rho_0d_0S_h$, where V is volume of unit GO cell and S_h is area of carbon hexagon. Value of B_0

corresponding to the GO formula unit $C_2O_{0.8}H_{0.24}$ is expected to be $1.704 \cdot 10^{-4} \text{Å}$ which is too high comparing to the experimental value $1.56 \cdot 10^{-4} \text{Å}$. The difference of $0.198 \cdot 10^{-4} \text{Å}$ between expected and experimental B_0 values should be assigned to light water (with $B=0.1675 \cdot 10^{-4} \text{Å}$ per molecule) in quantity $(1.704-1.56) / 0.1675 = 0.86$ molecules per GO unit cell. Therefore, the ambient composition of studied GO film is described by following formula $C_2O_{0.8}H_{0.24}+(H_2O)_{0.86}$. The composition of film was also verified at the conditions of lower humidity using separate experiment with silica gel desiccator loaded inside of measurement cell. The amount of water in the GO film was found to decrease down to 0.27 molecules per formula unit at 6.1% relative humidity at $23^{\circ}C$ (see SI file). That is in reasonable agreement with literature data for the amount for residual water in graphite oxide structure. Note that complete removal of residual water from the graphite oxides is considered to be very difficult and may take up to several weeks under conditions of exposure to humidity lowered by desiccator.^{28,38}

In general, if a film with SLD, NSL and thickness equal to ρ_0 , B_0 and L_0 respectively gets intercalated or releases N molecules with NSL equal B_s (specific for every chemical element and its isotopes; see³⁹ and Table S1) the SLD and thickness will be changed to new values ρ_1 and L_1 , the number N can be found as

$$N = \left(\frac{V_1 \rho_1}{V_0 \rho_0} - 1 \right) \frac{B_0}{B_s} = \left(\frac{L_1 \rho_1}{L_0 \rho_0} - 1 \right) \frac{B_0}{B_s}$$

This is valid only in case of uniaxial expansion/shrinking of the sample unit cell when relative change of its volume can be substituted by a change of its “height” or, consequently, by the change of total film thickness L . This is exactly the case of GO films which consist of 2D sheets

oriented parallel to the substrate and the only parameter which is changed as a result of swelling is increase/decrease of inter-layer distance.²⁵ Isotopic sensitivity of neutron scattering is widely used for unambiguous distinguishing between different molecules or atoms in complex structures.

Experiments with pure solvents demonstrated that changes in the shape of NR curve correlate with increase of vapor pressure inside of the cell. The humidity (vapor pressure) increases inside of the cell slowly over the period of 2-3 hours and decreases rather quickly (within few minutes time) when the cell is opened and beakers with solvent are removed. As verified in experiments with water vapors, the films respond rapidly to the change of humidity (or solvent vapor pressure for other solvents) due to the solvent evaporation. The rate of humidity increase in the closed cell was verified using humidity data logger. The stabilization of humidity level was observed after ~ 2hours, (see SI file). Note that the vapor pressure for most of the studied solvents is higher compared to water (except for DMSO). Nevertheless, we always performed several NR scans in order to detect the moment when the vapor pressure inside of the cell get stabilized (3-6 scans typically). The Figure 2S in SI shows two examples of NR measurements with d-methanol and D₂O which demonstrated that nearly identical shape of NR scans was achieved already for scans 2-3 and 3-4 respectively. Note that solvent desorption was typically much faster and did not required more than two scans to observe return to the pristine film state.

The solvent sorption results in increase of GO film thickness due to swelling effect and change of its scattering length density (SLD) value which could be either positive or negative depending

on NSL values of the sorbed molecules (see **Figure 1** and supporting information for details of calculations).

Figure 1 shows effects of intercalation of d-methanol (with positive B) and ethanol (with negative B) into GO film as an example of real data obtained in the present study.

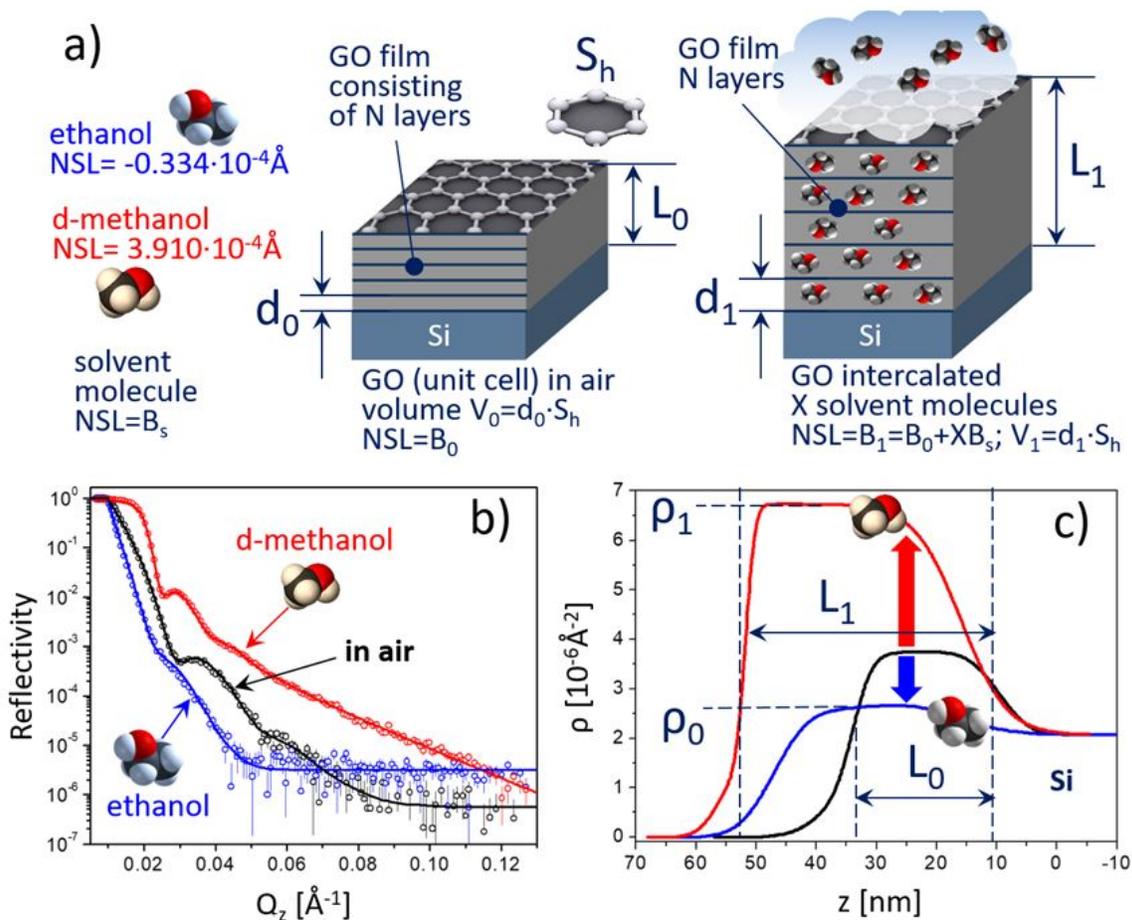


Figure 1. Using neutron reflectivity of GO film for evaluation of selectivity in sorption from binary vapor mixture. a) Examples of neutron scattering length (NSL) values for ethanol and d-methanol) and schematic presentation of how intercalation affects main parameters of GO film – thickness (L) and NSL. b) Reflectivity plot: black – GO film in air, red – GO film intercalated

ethanol, green – GO film intercalated d-methanol; solid lines represent best fit model curves. c) Modeled scattering length density profiles obtained from the fit: black – GO film in air, red – GO film intercalated ethanol, green – GO film intercalated d-methanol.

The film was then exposed to vapors of solvents and binary solvent mixtures with air drying intermissions. Complete scheme of the experiment is shown in the **SI (Table 1S)**. The time line includes sorption tests with several pure solvents and tests with binary mixtures of several solvents. Therefore, the first part of results describes selectivity in sorption of mixed vapors and second part summarizes sorption of pure solvents by GO films compared to the sorption by micrometer thick membranes and graphite oxide powders.

3.2 SELECTIVITY IN SORPTION OF MIXED SOLVENTS.

3.2.1 Ethanol/d-methanol system.

The experiment was aimed on evaluation of selectivity in sorption of d-methanol/ethanol vapors by Si supported GO film. The NSL values of d-methanol and ethanol are relatively high and opposite in signs providing strong isotopic contrast (see **Figure 1**). This system is also of high application value. For example, highly selective methanol sorption would be important for purification of ethanol. In this case only methanol would be expected to pass through the GO membrane. Note that sorption of methanol and deuterium substituted methanol are assumed to be identical.

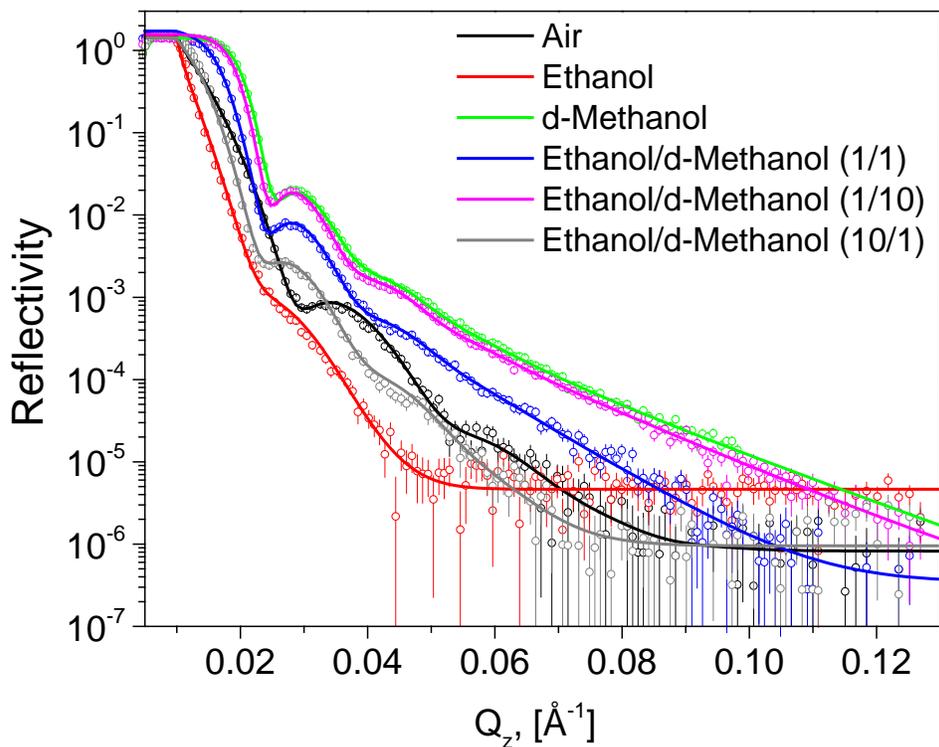


Figure 2. NR scans recorded from GO film on air, in ethanol, d-methanol and ethanol/d-methanol mixed vapors. The composition of feed solvent mixtures (1/1; 1/10 and 10/1) was used. Note that scans used in this figure are last from the time series shown in Figure 3 and correspond to the environment with saturated vapor inside of the cell.

NR data collected from the pristine film and for the same film under vapors of ethanol/d-methanol mixed in different proportions are shown in **Figure 2** and analysis of these data summarized in **Figure 3**.

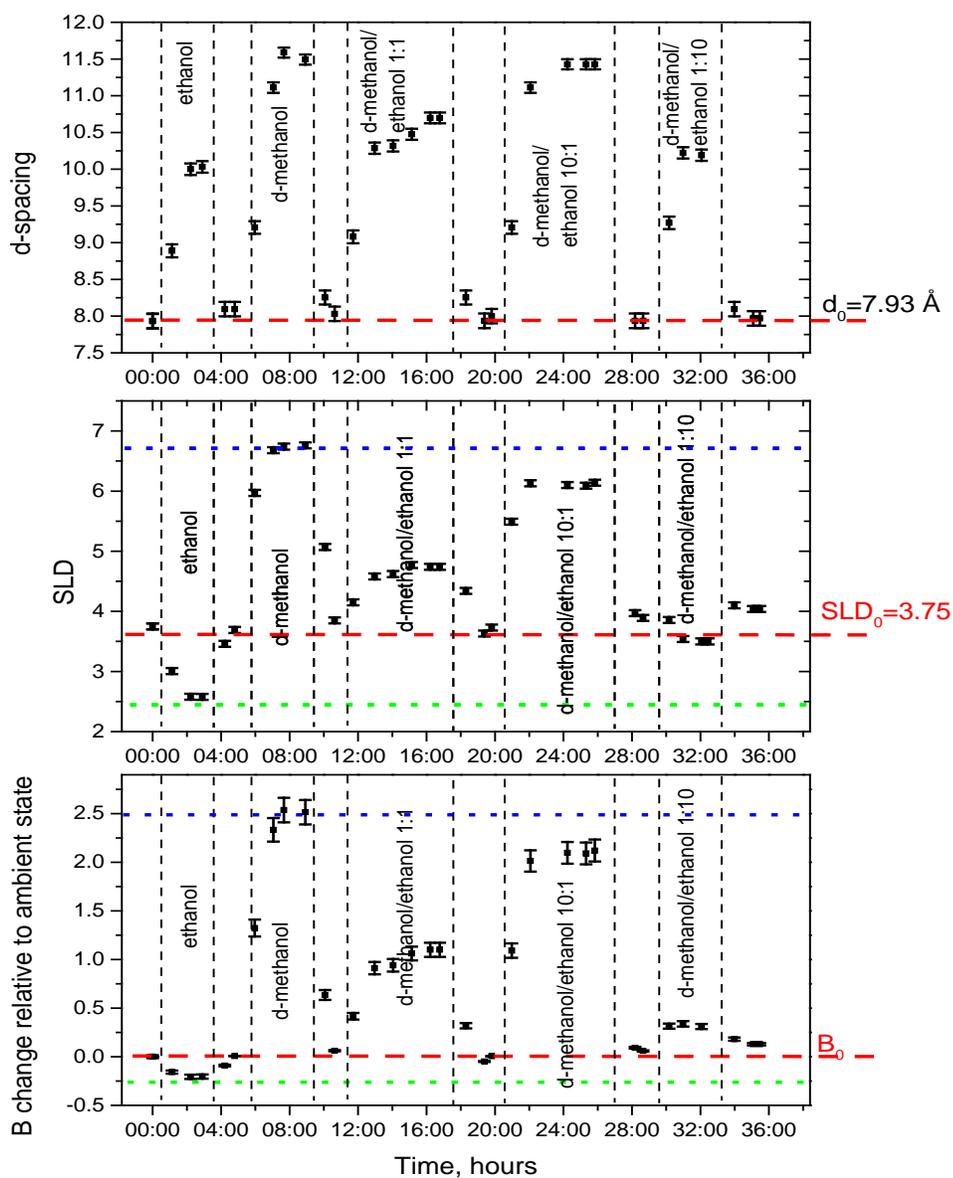


Figure 3. Time line of GO film sorption experiment for d-methanol/ethanol system step by step:

- 1) pristine ai-exposed; 2) exposed to ethanol vapor; 3) air dried; 4) d-methanol; 5) air-dried; 6) d-methanol/ethanol in 1:1; 7) air-dried; 8) d-methanol/ethanol in 10:1; 9) air-dried; 10) d-

methanol/ethanol in 1:10, 11) air dried. The d-spacing was calculated assuming change of film thickness and 31.5 layers of GO (top panel), SLD (middle panel) and change of B value (total NSL of unit cell) relative to ambient state (bottom panel).

Fitting of NR curves provided us with film thickness and SLD value as a function of time and exposure to vapors of various composition. The total film thickness was used to extract d-spacing of the GO and SLD values were used for calculation of amount and composition of sorbed solvent. The **Figure 3** shows times line of experiment and most important parameters which characterize swelling of GO films in solvent vapors: d-spacing calculated using thickness of films and two parameters which characterize sample composition (SLD and ΔB). The time line of this experiment shows that thickness and composition of film are stabilized (come to saturation) after certain period of time, typically after 2-3 hours (See also Figure 3Sa in SI). Blue (d-methanol) and green (ethanol) lines show positions of these parameters in case if perfect selectivity would be observed. As shown in **Figure 3**, exposure of film to alcohol vapors results in reversible sorption. The film thickness was increasing due to sorption of vapors but once the film is exposed to air the film returned back to the “ambient” state which is indicative of complete desorption of alcohols. Interestingly, there is no indication for substitution of water trapped in the film at ambient humidity with solvent sorbed from vapor.

According to the results of NR experiments (**Table 3**) the composition of sorbed solvent mixture remains almost the same as composition of d-methanol/ethanol mixture in the *liquid* phase for 1:1 and 10:1 provided by source. That is despite the fact that vapor phase is significantly enriched by d-methanol thanks to its higher vapor pressure. For example, d-

methanol/ethanol 1:1 volumetric composition of liquid corresponds to 2.4:1 composition of vapor while the composition of sorbed mixture is close to 1:1. The difference between composition of vapor and sorbed solvent mixture could be considered as a sign of sorption selectivity. However, the selectivity is nearly absent if we suggest that solvent vapors condense on the surface or between the layers of GO film and solvents are intercalated in liquid-like state. In this case the molar ratio of solvent source 1.13:1 must be compared to sorbed solvent composition of 1:1.11, thus providing nearly negligible selectivity in the sorption from d-methanol/ethanol mixture. Only when mixture with significant excess of methanol (10:1 volumetric and 10:0.86 molar) is used as a feed, some selectivity becomes obvious. The amount of d-methanol sorbed by film is found to increase by ~4 times relative to the composition of liquid mixture.

Results shown in the **Figures 2,3** and **Table 3** allow to predict properties of GO membranes in pervaporation experiments with methanol/ethanol mixtures. It can be expected that for ethanol enriched mixtures the methanol will evaporate through the membrane faster than ethanol providing certain purification of ethanol inside of the volume sealed with the membrane. However, the selectivity in sorption of ethanol is not that high to be directly useful for practical applications. Nevertheless, it is quite possible that modification of film deposition methods could improve selectivity.

Table 3. Sorption of ethanol, d-methanol and ethanol/d-methanol mixtures by GO film.

Mixture №	Solvents	Feed Solvent				N of mol/f.u. sorbed	Sorbed amount (mol/mol)
		Liquid (volume fraction)	Liquid g/g	mol/mol	Vapor composition mass% 23°C		
1	Ethanol	1	1	1	32	0.30	1.11
	D-Methanol	1	0.89	1.13	68	0.27	1
2	Ethanol	1	0.87	1.11	4	0.06	1.09
	D-Methanol	10	10	10	96	0.55	10
3	Ethanol	10	10	10	82	0.35	10
	D-Methanol	1	1.1	0.86	18	0.12	3.58

For example, high pressure deposition of GO films was found previously to improve significantly selectivity in separation of water from ethanol.³⁵

Finally, it can be noted that GO film thickness change due to sorption of ethanol and methanol is almost identical. Therefore, in absence of NR data, it would be impossible to estimate selectivity in sorption of these solvents from binary mixtures using e.g. only XRD. Below we discuss several other systems tested for selectivity of sorption by GO films showing examples of systems which are both suitable and difficult for analysis with NR method.

3.3.2 DMSO/D₂O system.

This system provides stronger challenges for interpretation of NR data. The NSL signs for D₂O and DMSO are opposite but sorption for one of solvents is very difficult to detect.

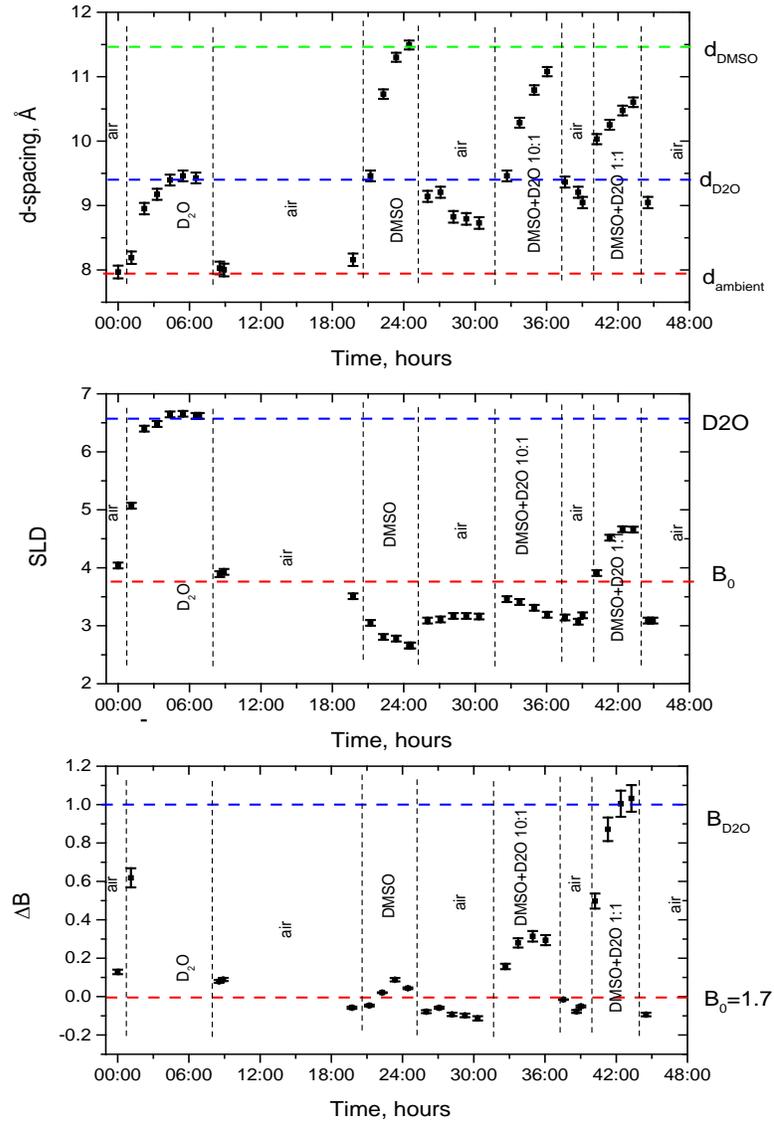


Figure 4. Time line of GO film sorption experiment for D₂O/DMSO system: d-spacing calculated from thickness change (top), SLD (middle) and change of B value relative to ambient

state (bottom). The film was exposed to D₂O, DMSO, DMSO/D₂O in 10:1 and 1:1 ratios. The film was air dried between exposures to vapors.

The NSL value of DMSO is low ($B = -0.0492$) which results in unacceptable errors in quantitative estimation of sorption. Assuming the error in experimental evaluation of $\Delta B = \pm 0.05$, the error in estimation of DMSO sorption will be as high as ± 1 mol p.f.u. Second problem is too slow increase of vapor pressure reflected in absence of saturation within reasonable scale of NR experiments. Finally the partial irreversibility of the sorption was revealed in our experiments. Therefore, the selectivity in sorption of DMSO and D₂O can only be roughly estimated by using difference in d-spacing. The DMSO sorption is obvious from strong increase of film thickness. There is also relatively strong difference between d-values calculated for pure D₂O and DMSO. According to the data shown in **Figure 3** the d-spacing for 1:1 solvent mixture is 10.6 Å which is almost exactly the average value between d-spacing of GO film in pure D₂O (9.5 Å) and DMSO vapors (11.5 Å). Thus it can be assumed that the GO sorption selectivity is absent or insignificant for this solvent mixture. That is despite the fact that vapor pressure of DMSO (0.056 kPa at 20°C) is about two orders of magnitude lower compared to D₂O (2.34 kPa). It can be concluded that the composition of sorbed solvent mixture corresponds roughly to condensation of vapors into liquid state in GO film.

3.3.3 Acetonitrile/D₂O and DMF/D₂O systems and Acetone/D₂O.

Three binary systems which include D₂O as one of solvents were analyzed for sorption selectivity using the same GO film.

Table 4. Sorption data for acetone/D₂O, acetonitrile/D₂O and DMF/D₂O systems. Compositions of feed solvent mixtures and compositions of solvents adsorbed by GO film according to analysis of NR results.

Mixture №	Solvents	Feed Solvent				Solvent intercalated	
		Liquid (vol.)	Liquid (g/g)	Liquid (mol/mol)	Vapor composition, mol/mol) 23° C	N of mol/ f.u.	Ratio, (mol/mol)
Acetone/D ₂ O							
1	Acetone	1	1	1	0.91	0.46	2.38
	D ₂ O	1	1.43	4.17	0.09	0.56	1
2	Acetone	10	10	10	0.96	0.67	10
	D ₂ O	1	1.43	4.17	0.04	0.29	1.49
Acetonitrile/D ₂ O							
1	acetonitrile	1	1	1	1	0.38	1
	D ₂ O	1	1.41	2.88	1.56	0.50	1.31
2	acetonitrile	10	10	10	10	0.21	10
	D ₂ O	1	1.41	2.88	1.5	0.40	20
DMF/D ₂ O							
1	DMF	1	1	1	N/A	0.21	1
	D ₂ O	1	1.17	0.427	N/A	0.59	2.8
2	DMF	10	10	10	N/A	0.52	10
	D ₂ O	1	1.17	0.43	N/A	0.13	2.5

The results of these experiments are summarized in the **Table 4** which shows compositions of liquid solvent loaded into the cell, compositions of solvent vapors and composition of solvent mixture sorbed by GO. Similar for all three systems, the solvent mixture sorbed by the GO film showed enrichment with D₂O. Below the results obtained for these systems are discussed in more details.

Acetonitrile/D₂O

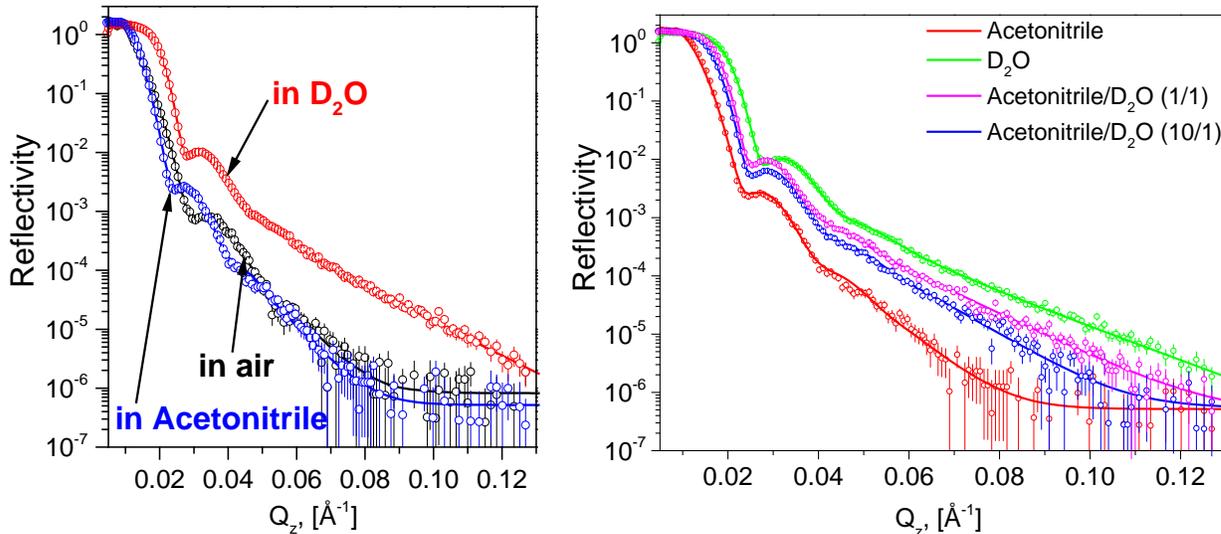


Figure 5. NR scans recorded from GO film: a) on air, in D₂O vapor and in acetonitrile vapor. b) in acetonitrile/D₂O mixed vapors, 1/1 and 10/1 by volume of liquid vapor feed. The scans shown here are last from the time series which mean they are recorded at the conditions close to vapor saturation.

This system provides example of mixture with two solvents with positive sign of NSL values (1.1446 for acetonitrile and 1.9150 for D₂O). Sorption of these solvents by GO films is hardly distinguishable by simple comparing of d-spacings (10.4Å and 9.5Å for acetonitrile and D₂O respectively, **Figure 5**). According to the NR data shown in the **Table 4**, the film exhibits strong sorption selectivity for that binary mixture. The GO film exposed to vapor of acetonitrile rich

feed solution with 10:1 volumetric and 10:0.69 mol/mol composition provides significant enrichment with D₂O (by factor of ~7) for the intercalated solvent. Note that composition of vapors in this binary system is similar to the composition of liquid mixture. The sorption of acetonitrile is reversible as it is obvious from the data shown in **Figure 5**. Similar results were obtained for other two studied solvent/D₂O systems.

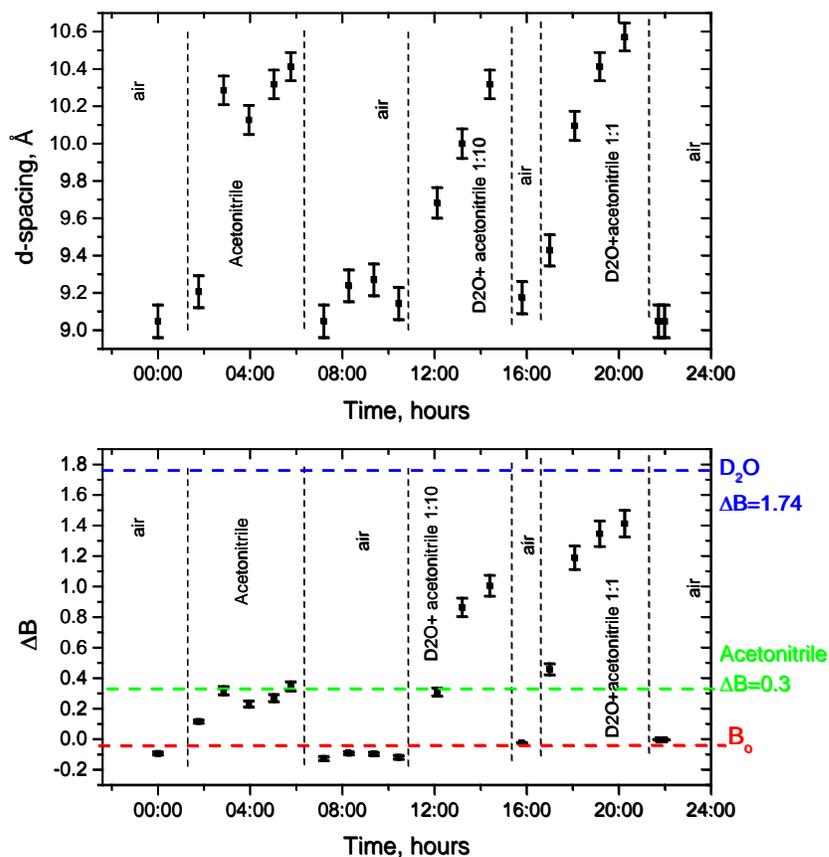


Figure 6. Time line of GO film sorption experiment for acetonitrile/D₂O system: d-spacing calculated from thickness change (top) and change of B value (total NSL of unit cell) relative to ambient state (bottom). The film was exposed to D₂O, acetonitrile, acetonitrile/D₂O in 10:1 and

1:1 ratios. The film was air dried between exposures to vapors. Blue dashed line shows expected ΔB value for sorption of pure D₂O and green line for pure acetonitrile.

Selectivity in DMF /D₂O sorption.

The following sequence was used in this experiment: exposure of GO film to ethanol vapour, air drying, exposure to d-methanol vapour, air drying, exposure to 1:1 ethanol/d-methanol vapour, air drying, 10:1 ethanol/d-methanol, air drying, 1:10 ethanol/d-methanol and final air drying. Results of the experiment which show d-spacing, SLD and change of B value (total NSL of unit cell) relative to ambient state (bottom) for the GO film as a function of time and vapor composition are provided in SI file. The DMF/D₂O system is yet another example when d-spacings of solvent exposed film are rather similar (11.7Å and 9.5Å respectively), NSL values of solvents are both positive but the difference between them is sufficiently large (see **Table 4**) to allow selectivity estimation. Once again the solvent mixture sorbed by GO film is enriched with D₂O relative to the feed composition increasing approximately by factor of two for both DMF/D₂O feed compositions (1:1 and 10:1).

Selectivity in acetone /D₂O sorption.

The acetone /D₂O is an example of yet another system where NSL values are positive for both solvents. The GO film swelling in pure vapors of these two solvents results in similar d-spacing values (9.5Å for D₂O and 10.4Å for acetone, see SI for details). Therefore, selectivity of sorption from binary mixture cannot be distinguished using e.g. XRD or only change of film thickness.

However, the difference in NSL values of acetone and D₂O is relatively strong which allows estimation of selectivity.

This system provides example of relatively high selectivity, see **Table 4**. The feed composition of 10:1 acetone /D₂O mixture in volumetric units corresponds to 2.42:1 mol/mol composition of liquid phase. The acetone/D₂O ratio of 6.7:1 mol/mol is found for the solvent mixtures absorbed by the GO film, thus exhibiting increase in the concentration of D₂O by factor of 2.8. Therefore, it can be expected that pervaporation of acetone rich mixtures with D₂O will result in faster permeation of D₂O. Note that d-spacing and inter-layer distance of GO calculated for the film exposed to pure acetone vapor is almost the same as d-spacing for feed mixtures with D₂O.

3.2 SORPTION OF PURE SOLVENTS

One of the main objectives of this study was to evaluate possible difference between solvents sorption by GO films, micrometer thick free standing GO membranes and graphite oxide powders. The sorption data calculated for GO film using analysis of NR curves for seven tested solvents are summarized in the **Table 5** (extended version of this table is also available in SI). The amount of sorbed solvent is provided as a number of molecules per formula unit. This value is re-calculated into weight ratios g(solvent)/g(GO) using water free formula C₂O_{0.8}H_{0.24} in order to compare with literature data on sorption of solvents by graphite oxide powders. The value of sorption is also calculated in g(solvent)/g(GO_a) for ambient composition of film assuming C₂O_{0.8}H_{0.24}+(H₂O)_{0.86} formula.

It is important to note that the error in estimation of sorption values is specific for each solvent and depends mostly on the absolute value of the solvent NSL. Rather good precision of sorption data is found for solvents with high NSL (e.g. d-methanol or D₂O), while for solvents with low absolute value of NSL the errors are relatively large (e.g. for ethanol). The amount of DMSO solvent could not be determined reliably due to rather low value of NSL which results in unacceptably high error for sorption results. In case of DMSO the sorption can be detected only by the increase of film thickness and d-spacing.

The thickness data obtained in our experiments with thin GO film are compared to d(001) obtained using XRD for powder samples of precursor graphite oxides and micrometer-thick membranes prepared by vacuum filtration.³⁰ The quantitative sorption data are available mostly for sorption by graphite oxide while for free standing membranes the literature provided sorption value only for water.²⁸ Quantitative sorption data for GO membrane samples exposed vapors of polar solvents have not yet being reported in literature to our knowledge. Therefore, we performed own analysis of solvent sorption using in situ gravimetric measurements of free standing micrometer thick GO membrane sample exposed to vapors of several polar solvents (**Table 5**). Example of gravimetric curves recorded for sorption and desorption of solvent is provided in SI file. The sorption of solvents follows increase of vapor pressure in the closed measurement cell. Once the film or membrane is exposed to air, it results also in rapid and reversible desorption for most of tested solvents except DMSO which has relatively low vapor pressure at ambient temperature.

The data shown in the **Table 5** allow to evaluate some trends in sorption of several polar solvents. First of all, lattice expansion due to vapor driven swelling of GO film is similar to the one reported for free standing micrometer thick membranes and lower compared to powders. Note that literature data are provided only for samples immersed in excess of liquid solvent, not at saturated vapor.

The vapor sorption values obtained in our experiments with free standing thick membranes are in good agreement with earlier reported sorption data obtained on powders. Remarkably, the sorption values demonstrated by Si supported thin GO film are higher compared to the sorption by powders for alcohols and DMF. Almost the same sorption is observed for the film and membrane in acetonitrile vapors while for D₂O the sorption is smaller compared to the sorption of water by the membrane. In other hand, the sorption of water calculated relative to the water free GO films state (0.49g/g) is in rather good agreement with data reported for GO membrane in the ref²⁸ (0.49g/g).

The data shown in the **Table 5** are based on assumption that the water adsorbed by GO film due to ambient humidity is not substituted by the solvent adsorbed from vapor. It is not unexpected effect considering that the solvent which evaporates inside of the experimental cell is added to air. In fact, experiments performed without vacuum removal needs to be considered as a sorption of binary water/solvent mixture. Experiments with careful vacuum drying of the films are required in future to verify exact sorption values by GO films for pure vapors. However, our results are of higher practical importance for various applications since most of the GO

membrane experiments reported in literature were performed with samples exposed to ambient humidity.

Table 5. Summary of NR results for GO film exposed to vapors of several solvents showing average inter-layer distance compared to literature d(001) data obtained by XRD for HGO powders and membranes (ref³⁰); solvent sorption in number of molecules per formula unit (N) and in g/g relative to the composition of ambient state (Molar mass=52.5) and relative to water free state (M=37). The data from ref.²⁸ were obtained using isopiestic method and powder HGO dried prior to sorption measurements. Data marked by * were recorded for non-deuterated solvents (H₂O and methanol) sorption was measured in the ref ²⁸ for powder and membrane (*) samples. The data obtained in our experiments solvent vapor experiments with micrometer thick membranes are provided as a reference.

Solvent	d, (Å)	d(001), (Å) Membr Ref ³⁰	d(001),(Å) Powd., Ref. ³⁰	N mol/f.u	g _s /g _{Goa} (ambient)	g _s /g _{GO} (dry)	Sorption by reference materials, g/g	
							Powder ²⁸	Membr.
Ethanol	10.0±0.1	11.1	15.5	0.61	0.53	0.76	0.36	0.47
d-methanol	11.6±0.1	10.6	13.1	0.65	0.38	0.56	0.48*	0.29
D ₂ O	9.5±0.1	12.3	12.7	0.91	0.35	0.49	0.75* (0.49*)	0.69
DMSO	11.5±0.1	18.6	19.8	N/A	N/A	N/A	0.78	0.76
Acetonitrile	10.4±0.1	9.0	14.0	0.30	0.23	0.33	0.34	0.25
DMF	11.7±0.1	13.8	17.7	0.53	0.71	1.04	0.63	0.57
Acetone	10.4±0.1	8.7	12.5	0.73	0.81	1.14	N/A	0.17

The water substitution effect would also be detectable for some binary mixtures where isotopic contrast is high. So far, all results obtained for GO films with polar solvents could be completely described without substitution effects. Therefore, we assume that the solvent adsorbed from the vapor is added over the water sorbed by the GO film at ambient humidity. It is found also that

once the film is exposed to air, the sorbed solvent evaporates and the film returns into ambient state both in terms of thickness and composition.

Our experiments confirmed reversible sorption for all tested solvents except DMSO. Incomplete reversibility of DMSO sorption by our GO film is evident from analysis of film thickness. The film thickness of air exposed film ($d=11.5\text{\AA}$) have not returned back to original ambient state. The d-spacing calculated for the film after exposure to DMSO and air drying had increased from 7.93\AA (initial state) to 9.22\AA . The ambient d-value was recovered only after exposure of film to acetone vapors on the last step of experiment. Note also that swelling of powder GO in liquid DMSO reported earlier resulted in much stronger swelling but with relatively slow kinetics.³⁰ Since the film was slightly modified by irreversible sorption of DMSO, the absolute values measured for sorption of acetonitrile and DMF (**Table 2**) must be considered with some caution.

The data shown in the **Table 5** indicate that spin-coating method provided films with sorption properties comparable to those obtained by vacuum filtration but with some important deviations. The multilayered structure of GO films with thickness of only ~ 30 layers seems to be comparable to the structure of micrometer-thick membranes with hundreds and thousands of individual GO layers. Somewhat higher sorption observed for GO film in several solvents could possibly be explained by less dense packing of GO flakes achieved by spin coating compared to the membranes obtained by vacuum filtration.

In general, the data shown in the **Table 2** prove that NR can be used as a powerful method for estimation of solvent sorption even for rather thin GO films composed by few tens of layers.

However, it has to be noted that using NR for measurements of absolute values of sorption are meaningful and reliable only for solvents with relatively high absolute magnitude values of NSL. In some cases (e.g. DMSO) it also becomes complicated due to partly irreversible trapping of solvent by GO film. Therefore, possible chemical modification of GO by certain solvents must be taken into account for membrane applications whereas it is rarely verified in the past literature reports.

The relatively large errors in estimated values of solvent sorption for solvents with small modulus of NSL do not necessary affect errors of sorption selectivity in the systems with binary mixtures. In case if relative amount of solvents sorbed by GO film is estimated, it is not the absolute value of NSL but the difference between individual NSL values of solvents in the binary mixture which is of importance for precision of measurements. The error in estimation of selectivity will be smaller for solvents with larger difference in NSL even if one of them has low absolute value. Below we demonstrate that on several examples.

4 DISCUSSION

Our earlier study of vapor sorption properties by thin GO film were performed using only one system with binary mixtures of D₂O and ethanol in different proportions. This system exhibited certain selectivity toward enrichment of sorbed solution with D₂O. For example, feed solvent with molar composition ethanol/D₂O 10:3.23 mol/mol (corresponds to 10:1 in volumetric proportion) provided 10:5.49 mol/mol composition of sorbed solution, thus exhibiting enrichment by factor of 1.7. The D₂O enrichment was expected considering earlier vapor

permeation experiments reported e.g. in ref³⁵ where selective permeation of water was observed for micrometer thick films. New experiments presented here confirmed selectivity of D₂O sorption by GO films exposed to several other solvent/D₂O binary mixtures. Even for the systems where vapor pressure of second solvent is significantly higher the composition of sorbed mixture is found to shift towards enrichment with D₂O.

The strongest selectivity is found for the systems with 10:1 volumetric feed solution composed by acetonitrile/D₂O (factor of 6.9 for feed composition 10:0.427 mol/mol), DMF/D₂O (factor of 5 for feed composition 10:0.427 mol/mol), acetone/D₂O (factor of 2.8 for feed composition 10:0.427 mol/mol).

The selectivity in D₂O sorption is even stronger for the studied here D₂O/solvent systems compared to previously reported ethanol/D₂O. According to literature reports micrometer thick GO membranes prepared by vacuum filtration are reported to show significant selectivity in permeation of water when water/ethanol feed mixture is used.^{7, 35} Similar correlation can possibly be expected between sorption properties of drop casted or spin coated thin films and pervaporation by micrometer thick membranes. Therefore, we suggest that micrometer thick membranes in pervaporation setup will be permeating D₂O with high selectivity allowing to eliminate contaminations of acetonitrile, acetone and DMF. None of these systems was studied so far for pervaporation using micrometer thick membranes to our knowledge.

GO multilayered materials were also proposed as a protective barrier and ideally as a clothing which allows water vapor to escape from protected environment and at the same time prevent organic solvents from penetration.⁴⁰ However, these reports were mostly about mixtures of water

with non-polar solvents (e.g. benzene) which are known not to cause swelling of GO materials. Our results provide a promise for preparation of protective and water permeable coatings or clothing which could prevent permeation of hazardous polar solvent vapors as well.

Significant selectivity in the sorption of d-methanol from ethanol/d-methanol 10:1 (volumetric) mixture was also observed. The methanol concentration in the sorbed mixture increased by factor 3.2 (mol/mol) compared to composition of feed mixture. Considering similar chemistry of alcohols-GO intercalation the smaller size of methanol molecule could be a possible reason for selectivity. Therefore, it can be predicted that micrometer thick membranes exposed to ethanol contaminated with methanol impurity could be purified using pervaporation through the GO membrane.

It should be noted that rather thin films studied in our NR experiments demonstrate lower selectivity compared to micrometer thick membranes typically studied for permeation. Very recent studies of rather thin free standing membranes with similar thickness (but prepared using vacuum filtration) demonstrated presence of “pin holes” between GO flakes due to their irregular size and overlap extending to tens of nanometers.⁴¹ While the abundance and depth of these pin holes should be strongly dependent on the film deposition conditions, the holes are expected to affect swelling properties of thin films to much larger extent compared to micrometer thick membranes composed by thousands of layers. Note that authors of ref⁴¹ had to increase the thickness of their membranes up to 70 nm in order to record XRD of GO multilayers first immersed and then exposed to vapors of several polar solvents. The advantage of NR method used in our experiments is that we were able not only to measure increase of film thickness

(recalculated into the change of d-spacing) but also to estimate quantitatively the sorption of solvents. XRD method does not provide this possibility and would not take into account the solvent which fills pores and pinholes of the sample.

The exact values of d-spacings are not provided in the ref⁴¹ but even approximate reading from their figures demonstrates that some significant differences are observed. The difference can be assigned to variations in deposition condition, conditions of XRD pattern recording or to chemical modification of membranes unintentionally introduced by authors of ref.⁴¹ by addition of surfactant to prevent dissolving samples in water.

The possibility of irreversible sorption of polar solvents by GO is also evident from our experiments with DMSO sorption. Unlike other tested solvents, the sorption of DMSO was only partially reversible, while the DMSO-modified films was still capable to sorb reversibly other solvent vapors (acetonitrile and DMF) while exposure of the film to acetone resulted in the removal of DMSO impurity.

In summary, NR method was used to study swelling of thin (~31 layer) film of GO exposed to vapors of several polar solvents and their binary mixtures. Quantitative evaluation of change in film thickness and solvent sorption values are reported for D₂O, d-methanol, ethanol, acetonitrile, DMF and acetone. The swelling of GO film was compared to swelling of micrometer thick free standing GO membrane and graphite oxide powders revealing some significant differences. The GO film exposed to binary mixture of D₂O with acetonitrile, DMF and acetone (10:1 volumetric) demonstrates selectivity which results in a sorption of D₂O-enriched solution. The composition of adsorbed solvent mixture for 1:1 composition shows

correlation with initial composition of liquid binary mixture but not with composition of solvent mixture vapor produced by evaporation of feed. This effect can be explained if solvent vapors condense into liquid-like phase when adsorbed by GO film. Since it is known that permeation of GO films occurs through the labyrinth path of interlayers, the study of GO film swelling in several polar solvents allows to predict selectivity in permeation of micrometer thick membranes exposed to vapors of binary solvent mixture. The GO films with highly selective water permeation which simultaneously cannot be penetrated by hazardous polar solvent impurities, can be proposed as “breathable” protective shields for bio environments or for preparation of protective clothing.

ASSOCIATED CONTENT

Supporting information.

Details of model and calculations used for analysis of NR data and table 1S listing NSL for all involved atoms and molecules. Figure 1S showing SEM image of GO film. Neutron reflectivity data: full time line of experiment including all solvents (Table 1S), NR data for experiment with decreased humidity (Figure 2S and Table 2S), time series of NR data recorded in d-methanol and D₂O (Figure 3S), NR scans showing swelling of GO film in D₂O and acetonitrile vapors (Figure 4S), in D₂O and DMF vapors (Figure 5S and 6S), in D₂O and acetone vapors (Figure 7S and 8S). Humidity increase inside of the experimental cell recorded using data logger (Figure 9S). Example of gravimetric sorption experiment data for micrometer thick free standing membrane in acetone vapor (Figure 10S).

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