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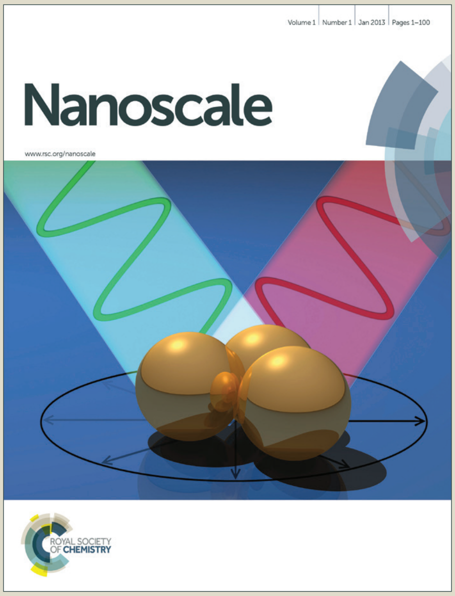

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# Graphene oxide hydration and solvation: in-situ neutron reflectivity study.

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ABSTRACT: Graphene oxide membranes were recently suggested for applications in separation of ethanol from water using vapor permeation method. Using isotope contrast, neutron reflectivity was applied to evaluate amounts of solvents intercalated into a membrane from pure and binary vapors to evaluate selectivity of the membrane permeation. Particularly the effect of $D_2O$, ethanol and $D_2O$/ethanol vapours on graphene oxide (GO) thin films (~25 nm) was studied.. The interlayer spacing of GO and amount of intercalated solvents were evaluated simultaneously as a function of vapour exposure duration. The significant difference in neutron scattering length density between $D_2O$ and ethanol allows distinguishing insertion of each component of the binary mixture into the GO structure. Amount of intercalated solvent at saturation corresponds to 1.4 molecules per formula unit for pure $D_2O$ (~1.4 monolayers) and 0.45 molecules per formula unit (one monolayer) for pure ethanol. This amount is in addition to $H_2O$ absorbed at ambient humidity. Exposure of GO film to ethanol/ $D_2O$ vapours results in intercalation of GO with both solvents even for high ethanol concentration. Mixed $D_2O$/ethanol layer inserted into GO structure is water enriched compared to composition of vapours due to slower ethanol diffusion into GO interlayers.

## 1. Introduction.

Graphite oxides can be dispersed to give single-layered graphene oxide (GO) sheets in polar solvents.[1] Single-layered GO can then be deposited from solution into multilayered papers[2], thin films or membranes.[3-7] Interest to GO membranes has revived recently due to their ability for rapid water permeation, while being impermeable by dry gases.[1, 7] The GO membranes have also been shown to be not permeable by pure ethanol,[7] which is not trivial property taking into account that precursor graphite oxide can be intercalated with several ethanol monolayers.[8, 9] Thin GO films demonstrated promise for application [10]. Just 2-3 layers thick GO membranes have been reported recently also to exhibit extraordinary gas separation properties.[11] Permeation of the membranes by several gases could be controlled using humidity-dependent variation of distance between GO layers.[12] Surprisingly, little is known about hydration and especially solvation of graphene oxide membranes or thin films.

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 particular synthesis method (e.g. methods by Brodie[16], Hummers[17], including strong difference in hydration/solvation.[8, 9, 18-20] Graphite oxide hydration and solvation by polar solvents (e.g. alcohols) results in expansion of inter-layer distance.[1, 21-23] Hydration of GO is rapid in liquid solvents[24-27] whereas similar hydration degree is achieved only after hours of exposure to saturated vapour.[14, 22, 28]

Understanding the GO structure under hydration and solvation conditions is extremely important for prediction and understanding of the membrane properties, as the solvent travels through a "labyrinth path" of interlayers.[1, 7, 29] However, even hydration of precursor graphite oxides is still rather poorly understood, despite very strong recent efforts.[14, 22, 24, 30] Recently, we demonstrated that results obtained on precursor powders cannot be directly applied to GO membranes; membrane structure seem to hinder intercalation of alcohols.[31]

The degree of the GO hydration/solvation is typically evaluated by diffraction methods using variations in the inter-layer distance of GO structure. However, solvents are inserted into multi-layered GO structures in disordered state whereas state and thus exact amount of intercalated solvents cannot be determined by these methods. Interestingly, the d(001) of hydrated graphite oxide is known to change *gradually* with temperature variation[27]; under humidity variations[23] and is not linearly proportional to the amount of adsorbed water.[32]

Neutron scattering in general is a powerful tool for studies of solvents in intercalation materials.[33] However, so far only hydration of pristine graphite oxides (and only Brodie type) has been studied using neutron scattering.[22, 23] Compared to the scattering method used in refs 12b,c, the advantage of Neutron Reflectivity (NR) is that it allows simultaneous determination of the GO unit cell volume and its chemical composition.[34] Using isotopic contrast, this method allows to distinguishes $D_2O$ and ethanol insertion into the GO structure and simultaneously gives quantitative information about volume density of intercalated molecules of each type.

Therefore, we can use NR to explain and to predict properties of GO membranes towards separation of binary vapour mixture of water and ethanol. The study by Nair et al [7] revealed that GO membranes are easily permeated by pure water vapours but not by pure ethanol. Therefore, they suggested that GO membranes can possibly be used for purification of ethanol using selective vapour permeation of water vapours. It has to be noted that composition of binary water/ethanol vapours which pass through GO membranes was not determined in this study.[7]

Here we report first NR study of graphene oxide thin film deposited on Si wafer and exposed to $D_2O$, ethanol and $D_2O$/ethanol vapours. We demonstrate that NR can be used for time-dependent quantification of solvent amounts intercalated into GO structure and thus to predict and quantify selectivity in permeation of solvent vapors trough layered membranes.

## 2. Experimental.

Thin films were prepared using Hummers graphite oxide with C/O=2.47 as a precursor (ACS Materials, USA). The powder was sonicated in water for 12 hours yielding solution with concentration 1 mg/ml and diluted with ethanol (75% volume). The water/ethanol dispersion was then deposited as a thin film onto the cleaned surface

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of Si plate using spin-coating and dried over period of 5 weeks at ambient conditions. Resulting films are almost transparent with very slightly brownish color. Detailed characterization of the precursor graphite oxide powder and membranes deposited after sonication/precipitation procedure is available elsewhere[9,15] Neutron reflectivity experiments were performed in a specially designed humidity cell at the reflectometer Super-Adam at the Institute Laue-Langevin[35], Grenoble, France[35] using a monochromatic beam with wavelength $\lambda$ = 4.41 Å. X-ray reflectivity measurements were performed at the ID10 beamline of the European Synchrotron Radiation Facility (ESRF),[37] Grenoble, France, using photons with $\lambda$ =0.654 Å. The GO film was exposed to ethanol, $D_2O$ and ethanol/$D_2O$ vapors for several hours, vapor exposure periods were separated by periods of air drying. $D_2O$ with purity 99.9 atom % D (Sigma-Aldrich) and ethanol with purity ≥99.9% (G CHROMASOLV® , Sigma Aldrich) were used for these experiments. The film was air dried between exposures to vapours.

Raman spectra were recorded from GO film using Renishaw spectrometer equipped with 633 nm laser.

### 3. Results and discussion.

The thickness of as-deposited film was determined by model fitting using the least-squares method[36] as 26.7 nm (at ambient humidity). This corresponds to 32 GO monolayers assuming an interlayer distance 8.3 Å found from position of (001) Bragg peak (recorded using X-ray reflectivity, see **Figure 1**).

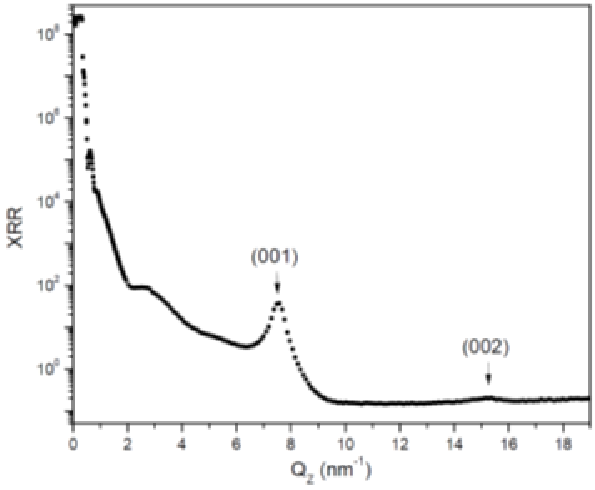

***Figure 1*** X-ray reflectivity pattern recorded on dry pristine GO film.

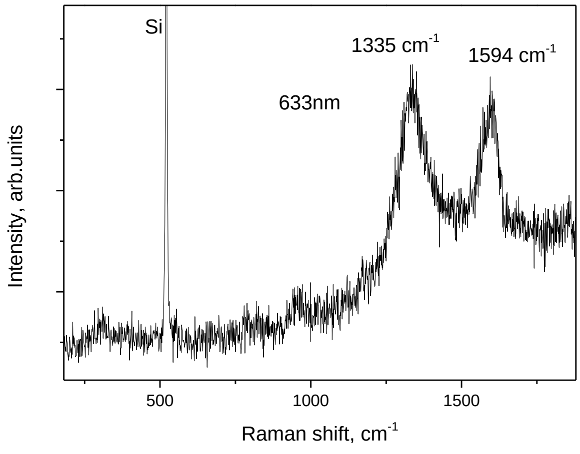

***Figure 2.*** Raman spectrum of GO film deposited on Si plate.

The pristine GO film was also characterized by Raman spectroscopy, **Figure 2.** The spectrum shown in this figure is typical for Hummers graphite oxide showing two broad asymmetric peaks from G and D modes.

Examples of NR data collected from the pristine film and for the same film under ethanol and $D_2O$ vapours as well as fitting results are shown in **Figure 3.**

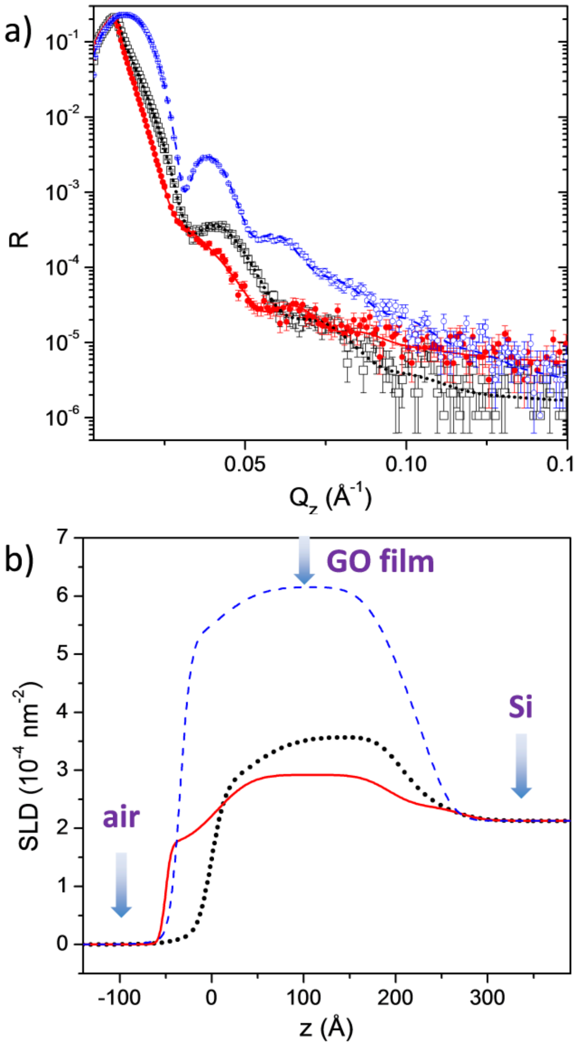

***Figure 3.*** a) Examples of the neutron reflectivity data (circles) and corresponding fit lines obtained from original dry film (black), film in ethanol vapor (red) and in heavy water vapor (blue). b) Model scattering length density profiles used to fit experimental curves. Thickness of dry film 26.7 nm and d-spacing 8.3 Å implies that the sample consists of 32 GO monolayers. Zero of x-axis corresponds to the level of the top surface of pristine GO film.

Reflectometry methods provide structural information about thin films including film thickness, roughness and scattering length density (SLD). Note that bulk samples of GO are not suitable for NR method, only films with thickness up to few hundred nm can be studied. Neutron SLD is calculated as $B/V$, where V is volume of the unit cell and $B=\sum b_i$ is total neutron scattering length (NSL) of all elements in this cell (Table S1 in SI). Individual NSL $b_i$ is a unique quantity for every chemical element and its isotopes.[34] Therefore, experimentally obtained SLD can be used for quantitative determination of the chemical composition of a sample film.

Results of experiment are summarized in **Figure 4** which shows d-spacing (a) and SLD (b) for the GO films as a function of time and vapor composition in the following sequence: exposure of

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GO film to ethanol vapour, air drying, exposure to $D_2O$ vapour, air drying, exposure to 1:1 ethanol/$D_2O$ vapour, air drying, 10:1 ethanol/$D_2O$ and final air drying. The total film thickness was used to extract d-spacing of the GO.

The number of solvent molecules intercalated into the GO structure per formula unit (taken as $C_2O_{0.76}H_{0.24}$) calculated using d-spacing and SLD values is shown in **Figure 4c** (see SI for details of calculations). Altogether **Figure 4** shows time dependence for inter-layer distance and number of solvent molecules inserted into the GO film not only during the exposure to pure $D_2O$ and ethanol but also during exposure to binary vapours. In the latter case amount of each solvent can be estimated separately.

Below we discuss first some general results extracted from analysis of **Figure 4** followed by detailed quantitative analysis of GO film intercalation with pure and mixed solvents.

Analysis of inter-layer distance changes (**Figure 4a**) shows several remarkable results:

1) Intercalation of GO film with $D_2O$ and ethanol occurs relatively slowly, with saturation achieved after 4-5 hours, while de-intercalation of solvents upon air drying is completed within one hour.

2) The film thickness increases gradually upon exposure to solvent vapours. No clear steps in film thickness correlated with size of solvent monolayer are observed.

Inhomogeneous oxidation of graphene oxide flakes on nanometer scale contributes to existence of domains which are more easily or less easily solvated/hydrated thus providing different interlayer distance within one interlayer and increased disorder in the mutual alignment of GO flakes. Our recent study demonstrated that averaged thickness of single GO layer shifts gradually upon changes of humidity due to inhomogeneous hydration on microscopic nanometer scale.[37]

3) The GO film returns to its initial state when solvent vapours are removed even after several cycles of exposure to $D_2O$ and ethanol. The “ground state” (d=8.3 Å) corresponds to formula unit $C_2O_{0.8}\,H_{0.24}+0.85H_2O$; the water in the ground state is due to exposure of films to ambient humidity. The SLD of the ground state cannot be ascribed to the presence of -OH groups in the GO. The amount of “ground state” $H_2O$ is in good agreement with previously reported amounts of water adsorbed by GO at ambient humidity[14] and d-spacing measured for our films. It should be noted that chemical composition of the “ground state” is a reference which does not affect our experiments aimed on quantitative estimations of $D_2O$ or ethanol added by exposure of films to vapours.

4) The maximal values of d-spacing obtained in water (11.2Å), ethanol (11.5Å) and water/ethanol mixtures (11.9Å for 1:1 mixture and 9.9Å for 10:1 ethanol/$D_2O$ mixture) are in good agreement with data obtained previously using X-ray diffraction on free standing micrometer thick membranes immersed in liquid solvents.[17]

5) The lattice expansion in ethanol/$D_2O$ 1:1 mixture is higher compared to pure water and looks more similar to pure ethanol

6) For ethanol/$D_2O$ 10:1 mixture the lattice expansion is significantly smaller compared to pure ethanol and water.

Variations of d-spacing provide important insight into the kinetics of intercalation but allow only very rough estimation of the amount of intercalated solvents even for pure solvents. For example, insertion of diluted solvent layer may result in the same lattice change as for close packed solvent layer. In case of binary solvents the same lattice expansion can also be explained by intercalation of two solvents but in different amounts/proportions. In contrast, NR allows to determine exactly which solvent intercalates GO and in case when mixed layer is intercalated and to provide quantitative estimation for proportion between amounts of intercalated solvents.

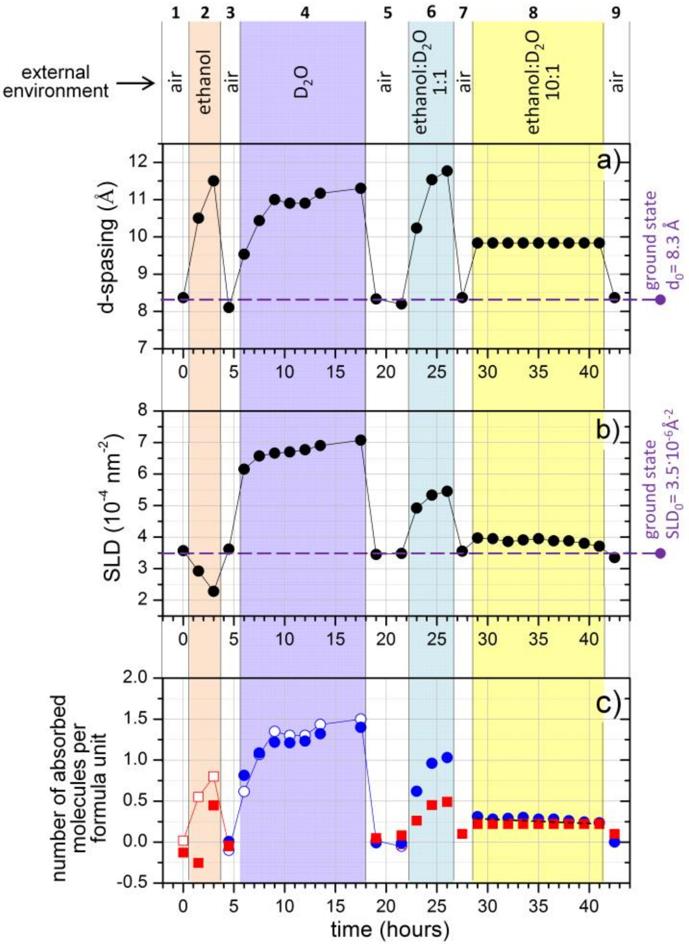

***Figure 4.*** Evaluation of the parameters of the GO film at different external conditions presented in chronological order. a) d-spacing determined using measurements of the film thickness by NR; b) SLD; c) number of adsorbed molecules of D2O (blue circles) and ethanol (red squires) per GO formula unit calculated from change of d-spacings (open symbols) and SLD variation (filled symbols). The time periods marked by numbers and different colors correspond to following the conditions: 2- exposure to ethanol vapor, 4- $D_2O$ exposure, 6- ethanol/$D_2O$ mixture 1:1, 8- ethanol/$D_2O$ mixture 10:1. Periods 1,3,5,7,9 (white) correspond to solvent free drying conditions

The SLD values are shown in **Figure 4b**, these values are used for calculation of amount and composition of solvents intercalated into GO film (**Figure 4C**). Note that negative shift of SLD values is observed for ethanol whereas for $D_2O$ it is positive (see **Figure 4b and Table S1**) which allows easily distinguishing intercalation of ethanol and $D_2O$. Below the **Figure 4** is analysed in more details following sequence of vapour exposure periods from sector 1 to 9.

Quantitative evaluation of ethanol intercalation into GO lattice (**Figure 4a-c,** sector 2**)** shows that expansion of GO lattice starts *before* any significant change of SLD. This could be explained if very small amount of ethanol intercalated into the GO structure results in a large increase of interlayer distance, thus ethanol molecules serving as “pillars”. Most likely, ethanol inserts only into edge regions of GO interlayer on the initial stages of solvation but this results in “lifting” whole sheet. The change of d-spacing (~3.5Å) is in good agreement with insertion of one solvent monolayer. The thickness of ethanol monolayer in GO (~4Å) is known thanks to phase transitions connected to insertion of ethanol

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monolayer.[8, 21] The SLD values show that about 0.45 molecules per formula unit are inserted into GO lattice at saturation point, compared to about 0.5 molecules/unit cell required for formation of close packed layer of ethanol molecules.

Exposure of GO film to $D_2O$ vapour results in insertion of ~1.4 molecules per formula unit. This amount correlates well with lattice expansion (~3Å) assuming thickness of $D_2O$ monolayer ~2Å (**Figure 4,** sector 4). The thickness of water monolayer in various layered hydrophilic systems is known to be in the range 2-3Å.[38] Unlike alcohols, water insertion into GO structure always results in *gradual* changes of interlayer distance. The only step-like change of hydration degree in GO (with d-spacing change of ~2Å) was observed for samples immersed in liquid water at the point of bulk water media solidification and this change was interpreted as de-insertion of water monolayer.[25] Here we assume the lateral density of intercalated monolayer of water equal to 1 water molecule per 1 GO formula unit (or per two C atoms). This observation agrees with the construction of the sample "ground state" where 0.85 adsorbed molecule of $H_2O$ increases d-spacing compared to vacuum dried membranes by ~1.8 Å[31] which is about 0.9 of size of water molecule.

Exposure of GO film to 1:1 $D_2O$/ethanol vapour clearly results in intercalation of both solvents (**Figure 4C**, sector 6) according to SLD data. However, the inter-layer distance remains almost the same as in pure ethanol. Absence of inter-layer distance change can be rationalized assuming that ethanol forms diluted monolayer with less than 0.45 molecule per unit cell and the spaces between ethanol molecules are sufficient to accommodate additional amount of water. Alternatively, water and ethanol could form nm size clusters of pure solvents, ethanol clusters serving as "pillars" which hold inter-layer distance.

Exposure of GO films to strongly concentrated ethanol vapours (10:1 ethanol/$D_2O$ ratio) results in d-spacing smaller compared to that for pure ethanol (sector 8, **Figure 4c**). The same result was observed previously by XRD on HGO membranes immersed in liquid solvent.[31] Increase of d-spacing compared to the ground state corresponds to 0.75 $D_2O$, while increase of SLD corresponds to much smaller value 0.25 $D_2O$ molecule per HGO formula unit. Therefore we have to conclude that both water and ethanol are inserted. The composition of solvent absorbed by GO film (0.79:1) is drastically smaller compared to 10:1 ethanol/$D_2O$ vapours composition. Thus the solution which passes through the GO membrane should be enriched with water but selectivity is limited, moreover it decreases with time. The SLD slightly decreases with time indicating that ratio ethanol/$D_2O$ inside the sample slowly increases from 0.79 to 0.94 while the d-spacing changes in the first hour of exposure and remains constant over 13 hours while. This result is in agreement with slow kinetic observed for insertion of pure ethanol (sector 2).

It can be concluded that exposed to 10:1 mixture the GO film is penetrated by $D_2O$ more rapidly, while ethanol diffuses through interlayers much slower, note that saturation was not achieved in our experiments even after 13 hours. Most likely, $D_2O$ and ethanol form one mixed monolayer in the GO structure. Composition of this layer for first point of sector 8, (**Figure 4C**) corresponds to insertion of 0.25 molecules of ethanol and 0.4 molecules of $D_2O$ per GO formula unit.

The smaller value of inter-layer distance for GO film in 10:1 ethanol/$D_2O$ vapour (compared to values for pure ethanol and pure water) indicates that ethanol and $D_2O$ can be again rationalized if we suggest that various regions of GO interlayers are solvated/hydrated inhomogeneously on nm scale. Some regions can be free from both water and ethanol (and exhibit smaller local d-spacings) while the averaging with ethanol and water rich regions will provide smaller values. This phenomenon can be considered as analogue of interstratification within one single inter-layer and named e.g. as intrastratification. The interstratification is also plausible explanation if some layers (e.g. blocked by ethanol molecules at the entrance point) are filled by solvents to smaller degree.

Simultaneous adsorption of ethanol and water from binary mixtures is not a trivial result. It was reported previously that µm thick Hummers GO membranes are permeated only by water and not by pure ethanol. The study by Nair et al also speculated that only water penetrates through Hummers GO membranes if exposed also to mixture water/ethanol vapours.[7]

Results presented here provide direct evidence for absence of highly selective intercalation of GO membranes by either water or ethanol. Exposed to 10:1 ethanol/$D_2O$ vapour the GO film is intercalated by ~10-13 times water enriched solution but anyway far from anything required for water/ethanol separation applications. It can also be predicted that pure ethanol will penetrate through the membranes, but with very slow kinetics compared to water (**Figure 4**). Applied to GO vapour permeation it can be expected that both water and ethanol penetrate trough membranes when 10:1 ethanol/water feed solution is used, but the penetration will slow down with time due to increase in ethanol concentration in the GO lattice.

This result is in agreement with previous experiment performed with GO membranes immersed in mixed water/ethanol liquid solvents which also demonstrated absence of strong selectivity.[31] Most recent report also demonstrated that propanol (another alcohol molecule) permeates trough GO membranes together with water[29] in agreement with our findings.

In summary, it is demonstrated that neutron reflectivity offers unique possibilities for *in-situ* insight into kinetics and microscopic processes of the membrane solvation/hydration. Quantitative evaluation of solvent amounts intercalated into the GO structure from binary mixtures provides key information for prediction of the membrane separation properties. This was demonstrated in our study using example of water/ethanol system. Exposure of Hummers GO membrane film to vapours of pure solvents results in insertion of additional (over "ground state") ~1.5 monolayers of $D_2O$ or one ethanol monolayer at saturation point. When the film exposed to mixed $D_2O$/ethanol vapours, both solvents are inserted into GO lattice but water penetrates faster. Slower diffusion of ethanol into GO lattice results in certain selectivity of water intercalation from highly concentrated 10:1 ethanol/$D_2O$ vapours. However, the selectivity of water absorption observed in our experiments is not high (0.79:1 ethanol/water after 1 hour) which makes GO membrane unlikely for application in water/ethanol separation using vapour permeation method, in contrast to suggestions by Nair et al [7]

Results presented in our study also provide experimental background for understanding fundamental intercalation and permeation properties of thin graphene oxide membranes exposed to solvent vapours, e.g. in humidity controlled gas separation experiments [12].

**Supporting Information.** Neutron scattering lengths of relevant atoms and molecules, list of involved parameters and equations, details of qualitative data treatment leading to construction of Fig.4.

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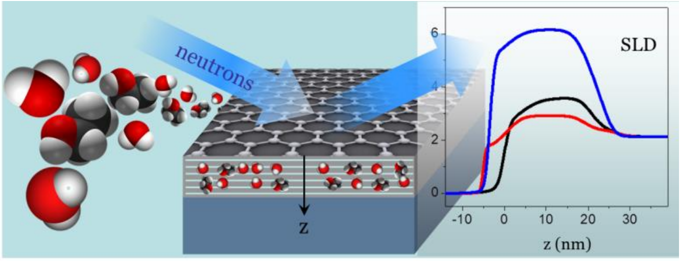

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