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Swollen Structures of Brodie Graphite Oxide as Solid Solvates.

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ABSTRACT

Swelling of Brodie graphite oxide (B-GO) was studied for the series of normal alcohols from methanol to 1-nonanol. Isopiestic, XRD, TG and DSC data demonstrated that sorption of polar liquids into GO lamellas formed the set of regular swollen structures, simple binary “solid solvates”, characterized by the distance between the GO planes and the value of sorption. Temperature - composition behavior of the swollen structures was adequately described by conventional binary phase diagrams. Phase transformation of the low temperature swollen structure of B-GO with 1-nonanol gave the clear example of incongruent melting transition typical for the binary solvates. Discreet set of the inter-plane distances observed by XRD and the step-wise equilibrium desorption pointed to layered arrangement of solvent molecules in the swollen structures. The swollen structures with one to five parallel layers were observed for the series of normal alcohols with B-GO. The average volume of one layer, $0.36 \pm 0.06 \text{ cm}^3 \text{ g}^{-1}$ B-GO, was almost the same for rather different organic liquids and was possibly restricted by the internal geometry of B-GO. This internal volume available for the sorption of the first layer was reasonably estimated from geometrical parameters of B-GO.

INTRODUCTION

Swelling of graphite oxide (GO) powders in polar liquids is a significant phenomenon from both a theoretical and a practical viewpoint. Practical interest is associated mainly with possible separation/filtration of liquids and storage of gases by means of thin, tunable and mechanically strong GO layered structures, respectively, membranes ¹⁻⁶ and pillared frameworks ^{7,8}. First studies of GO membranes were performed already in 1960s ⁹. R.Nair et al. ¹⁰ have demonstrated

that properties of GO membranes may be tuned by swelling in water. Water rapidly permeates through graphene oxide membranes. The most likely explanation for this is swelling of structure. Surprisingly some other polar liquids known to induce swelling of graphite oxides demonstrate nearly complete absence of permeation across graphene oxide membranes¹⁰. Swelling is a combination of two processes namely sorption of liquids into the inter-plane space of GO and of simultaneous increase of inter-plane distances. The latter process is well documented by X-ray diffraction (XRD)¹⁰⁻¹⁶ while quantitative data on sorption of polar liquids are limited^{17, 18}. Relatively more sorption data at ambient temperature is available for water¹⁷⁻²¹. Sorption typically decreased with the increase of temperature leading to the decrease of inter-plane distances, which sometimes was considered as pseudonegative thermal expansion²². The structures formed by the interaction of GO with polar liquids (swollen structures, SwSt) are defined by temperature, external pressure and are different for different types of polar liquids and GO (Brodie GO (B-GO) vs more common Hummers GO (H-GO)). The difference in properties of B-GO and H-GO swollen structures may be caused by the difference in the number and type of oxygen containing groups on graphene planes.²³⁻²⁵

Extensive characterization of these materials provides evidence that SwSt of B-GO are more regular compared to H-GO^{23,24}. The former were similar to the binary phases with fixed composition while the latter with the solid solutions in the two component systems¹⁸. Brodie graphene oxide is also known to exhibit much better mechanical properties both for individual flakes and for multilayered membranes²⁴. Reversible phase transformations of SwSt were found on heating/cooling in the systems of B-GO with methanol, acetonitrile and several other polar liquids²⁶⁻²⁸. These transformations were interpreted as incongruent melting of SwSt of B-GO with partial release of the sorbed liquid¹⁸. As predicted by thermodynamic equations the same transformations were observed while changing of pressure at constant temperature²⁸. Such transformations were never observed for SwSt of H-GO. It is not clear to which extent the properties of BGO and HGO powders can be applied to multilayered membranes. GO membranes prepared from Brodie graphite demonstrate absence of phase transitions and nearly flat temperature dependence of inter-layer distance.²⁹

SwSt of B-GO with normal alcohols were extensively studied by XRD already in 1960s¹⁴⁻¹⁶. These early papers claimed formation of two types of structures, namely of α - and β -phases with the sorbed molecules oriented respectively parallel and in stand up orientation relative the GO planes. SwSt of B-GO were examined along the series of normal alcohols from methanol to 1-octadecanol and the change from α - to β -phase were reported to occur when moving along the series from 1-propanol to 1-butanol. The results obtained in¹⁴⁻¹⁶ were based solely on the XRD measurements mostly made at ambient temperature. The amount of polar liquid incorporated into

the structures was not known. It was demonstrated recently²⁸ that the B-GO immersed in liquid 1-octanol forms swelled structure with four solvent layers parallel to the graphene oxide planes. Successive layer by layer removal of 1-octanol was observed with XRD in process of solvent evaporation under vacuum conditions. Moreover, reversible insertion of additional fifth solvent layer into the structure was explicitly demonstrated for B-GO immersed in octanol upon cooling and pressure increase²⁸.

In this paper we provide consistent use of thermodynamic approach to follow changes in the SwSt of B-GO along the series of normal alcohols (1-ROH) from methanol to 1-nonanol using primarily sorption/desorption and also XRD data. B-GO was specially chosen as it was reported to form more regular structures compared to other forms of GO. It was demonstrated that normal alcohols in the methanol- 1-nonanol set intercalate into B-GO forming several SwSt which may be considered as binary phases in the two-component systems B-GO – (1 – ROH) and as the simple solid solvates of B-GO. We prepared sketches of typical binary phase diagrams to account for observed transformations of SwSt with temperature and with change of composition. Discussing the internal arrangement of the SwSt the concept of “liquid layer” in the inter-plane space of B-GO was carefully examined. Averaged sorption capacity and the size of such a “layer” were estimated. These parameters were correlated with the geometry and chemical formula of B-GO.

EXPERIMENTAL SECTION

Materials.

B-GO samples were synthesized according to the procedure described elsewhere³⁰. The details of current procedure used in our lab are given in³¹. Here we used Brodie oxidation materials with one step oxidation and two step oxidation, (see Supplementary Information (SI) file for details). Note that the difference between Step 1 and Step 2 Brodie oxides (BGO1 and BGO2, respectively) is relatively small. For example, nearly identical phase transitions were found for BGO1 and BGO2 upon cooling in methanol.²⁴. The synthesized samples were dried to a constant mass under vacuum (10^{-4} bar, 12 hours) and/or in the desiccators with P_2O_5 for 3-5 days. The averaged C/O ratio as measured by XPS after drying was 2.7 ± 0.2 for 5 samples used (see SI file). Chemical formula of B-GO may be written as $CO_{0.37}H_x$. The value of “ $x=0.12$ ” was taken from ref.²³. In²³ the formula of B-GO was $CO_{0.38}H_{0.12}$ according to elemental analysis. The molecular mass of B-GO used in this study was estimated as 18 g mol^{-1} . Organic liquids $CH_3-(CH_2)_n-OH$ ($n=0$ to $n=8$) and CF_3CH_2OH , CH_3CH_2CN , were specially re-distilled before use. The resulting purity was $>99\%$ according to DSC.

Methods.

Sorption measurements at $T=298\pm1$ K were performed by isopiestic method. Equilibration of GO with organic liquids vapors occurred within the desiccators and persisted until the mass of GO saturated with organic liquids became constant (5-10 days, 30 days for 1-octanol). Each saturated sample was checked by DSC for the absence of the excess of free organic liquid. DSC was also employed for detecting of phase transformations in the swollen structures. DSC-30 TA from Mettler was used for measurements. The quantitative measurements rely on heating traces with the scanning rates 2 and 5K/min. Isothermal desorption of organic liquids from the B-GO saturated samples were studied using thermogravimetric (TG) analysis. The isothermal traces were taken using TG-50 Mettler Termobalances. The initial samples consisted of the saturated swollen B-GO and the excess of the organic liquid. This excessive, non-intercalated amount was essentially pure organic liquid as B-GO is insoluble in none of the liquids used. The samples were put into the cylindrical quartz pans ($d=0.7$ cm). Organic vapors evaporated through the small orifice ($d=0.03$ cm) on the top. The flow of dry nitrogen passed above the orifice. In this way the conditions close to the Knudsen cell experiment were reproduced.

X-ray diffraction (XRD) measurements were performed with Panalytical X'Pert Diffractometer with $\text{CuK}\alpha$ radiation. Several experiments were also performed using synchrotron radiation $\lambda=0.46794$ Å at ID22 beamline, ESRF, France. Heating/cooling of samples in sealed glass capillaries was performed using Oxford Cryosystems CryoStream system. Two sets of XRD measurements were performed. “Equilibrium measurements” were carried out in the closed cell containing B-GO and the excess of the polar liquid. Such experiment provides temperature dependences of XRD patterns of the swollen structures in equilibrium with the sorbed liquid. “Non-equilibrium” measurements were performed in the open cells while vacuum drying of the swollen structures at ambient or elevated temperatures. These experiments provide XRD patterns of the whole set of the swollen structures formed in the system.

RESULTS and DISCUSSION

“Three-step” desorption.

Fig.1 presents the TG data for isothermal desorption in the system B-GO – 1-heptanol. The initial sample was B-GO in the state of saturated swelling with the excess amount of liquid 1-heptanol. As seen from the Fig.1 there are three steps of the process with different, but constant in time, desorption rates. The conditions of TG desorption were close to the vapor-solid phase equilibrium (see section SI for discussion). It may be assumed that a number of equilibrium swollen structures of B-GO with 1-heptanol, namely (I), (II) and (III), are formed and three two-phase regions occurred in the system (see section **Phase diagrams of the systems BGO-normal**

alcohols for discussion). Similar equilibrium three-step desorption was observed for SwSt of B-GO with normal hexanol, pentanol and butanol (see SI). For 1-octanol and 1-nonanol such TG isothermal runs had been impossible to carry out due to the low desorption rates in the temperature interval of these experiments. Raising of temperature above 370 K results in degradation of B-GO.

Fig.1. Isothermal desorption ($T=368$ K) in the system B-GO (8.7 mg) – 1-heptanol (21.2 mg). Black line – mass of the system vs time, blue line – rate of desorption vs time, red line – rate of desorption of pure 1-heptanol at $T = 368$ K, taken from independent run. Roman numbers denote swollen structures in equilibrium (see Fig.8a and section **Phase diagrams of the systems BGO-normal alcohols** for discussion). Gray circles correspond to the compositions of the swollen structures (III) and (II).

Non-equilibrium and equilibrium XRD.

Fig. 2a shows XRD patterns recorded in process of vacuum drying of B-GO sample initially immersed in liquid 1- heptanol with little excess. The evaporation occurred from the open surface under non-equilibrium conditions. 1- heptanol evaporates rather slowly at room temperature. Therefore, vacuum and heating up to 333K was used to accelerate the solvent

removal. The initial pattern recorded in the presence of liquid 1-heptanol showed reflections from only one swollen structure, SwSt (III). The pattern recorded after 85 mins of vacuum drying showed three sets of (00 ℓ) reflections (see Fig.2a) which correspond to three different SwSt, namely (III), (II) and (I). Three sets of reflections were observed simultaneously. No intermediate reflections were detected. Solvent free structure was not recovered even after 145 min of vacuum exposure and increase of temperature up to 333 K. The intensity of XRD peaks from SwSt (I) and (II) become stronger in process of solvent desorption while the peak from SwSt (III) phase almost completely disappeared in the last scan. The Figure 2b shows that the difference between values of d(001) recorded in all XRD patterns in process of desorption remains to be the same (~ 2.5 - 3.5 Å) and corresponds to the size of one 1-heptanol layer in the swelled B-GO structures (see section **Layers of organic liquids within the inter-plane space of B-GO**). This result is in good agreement with our previously published study of the B-GO – 1-octanol vacuum drying which started from swelled phase (IV) immersed in the excess of liquid and resulted in appearance of SwSt (III), (II) and I structures²⁷.

Fig. 2. Vacuum drying from the open surface in the system BGO–1-heptanol ($\text{CuK}\alpha$ -radiation). Nonequilibrium conditions. a) Selected XRD patterns recorded in process of vacuum drying. “145 min” pattern was recorded at $T = 333$ K, other two at ambient temperature. b) $d(001)$ value for three swollen structures (I), (II), (III) revealed by XRD in process of non- equilibrium solvent evaporation, $T = 298 - 333$ K.

Similar experiments were performed also with other alcohols starting from 1-butanol to 1-nonanol. Note that smaller alcohol molecules evaporate too rapidly in the scale of our experiments which required at least 5-20 minutes for single scan. The data for the non-equilibrium vacuum drying are summarized in Fig.3 that show inter-plane distances in distinct structures at ambient temperature. For 1-octanol and 1-nonanol in addition to SwSt (I)-(III) swollen structures (IV) were observed at the beginning of the experiments (see ref.²⁸ and section **Phase diagrams of the systems BGO-normal alcohols**).

Fig. 3. The set of the inter-plane distances in the swollen structures (I),(II), (III) and (IV) of B-GO with normal alcohols identified in process of slow solvent evaporation under vacuum conditions or under vacuum at elevated temperatures. Non-equilibrium conditions. Data points for B-GO in 1-octanol are from Ref. ²⁸.

As it seen from Fig. 3 three similar SwSt of B-GO, namely, (I), (II) and (III), were formed for the whole series of normal alcohols. The inter-plane distances in (I) and (II) are practically the same for the whole series while for SwSt (III) the distance increases from 16,5 Å to 19,5 Å from 1-butanol to 1-nonanol, respectively.

Fig.4 presents $d(001)$ inter-plane distances vs temperature dependences for the swollen structures in equilibrium with 1- ROH from 1-butanol to 1-heptanol in the range from the melting point of the alcohol up to the ambient temperature. These data were recorded in the closed cell in excess of liquid solvent and no possibility of the solvent desorption from the system. Under such conditions in all cases except 1-heptanol only one set of (00l) reflections was detected. corresponding to one SwSt in equilibrium with the liquid alcohol. Comparing Fig.3 and 4 one may conclude that the swollen structures in equilibrium with 1-butanol, 1-pentanol and, 1-hexanol are SwSt (III).

Fig.4. Inter-plane distances vs temperature in the swollen structures in equilibrium with the pure 1-R-OH. All temperatures are above the melting points of the corresponding alcohols.

Fig.5a presents XRD patterns recorded in the system B-GO – 1-hexanol. One and the same set of peaks were observed at different temperatures.

Figure 5. a) XRD patterns recorded from BGO immersed in excess of 1-hexanol in process of equilibrium cooling , b) XRD patterns recorded during cooling from BGO immersed in 1-heptanol BGO-heptanol shows two sets of (00ℓ) -reflections at 240K and below corresponding to the swollen structures (IV) and (III). ($\lambda=0.46794\text{\AA}$).

Fig.5b shows XRD patterns recorded in the system B-GO – 1-heptanol in process of cooling. The patterns recorded at temperatures below 260K show formation of a new swollen structure SwSt (IV) with the inter-plane distance $d(001) = 22,6\text{ \AA}$ (see Fig.5b). XRD pattern recorded at 240 K showed two sets of (00ℓ) reflections. In addition to SwSt (IV) weaker reflections of SwSt (III) were still present indicating that the transformation of SwSt (III) into SwSt (IV) was not completed. Note that the 1-heptanol was still in liquid state at the moment of SwSt (IV) phase formation (260K). Solidification of 1-heptanol was detected only at 220K thanks to appearance of multiple additional reflections from frozen solvent. SwSt (IV) was also detected in the systems of B-GO with 1-octanol²⁸ and 1-nonanol (see section **Reversible phase transition in the system BGO- 1- nonanol**). In the latter two systems in equilibrium with 1-ROH at low temperatures or high pressures²⁸ further swelling led to formation of SwSt(V). Fig. 6 summarizes all swollen structures formed in equilibrium with the pure 1-ROH under various conditions.

Fig.6. Inter-layer distance $d(001)$, in the SwSt B-GO in equilibrium with the excess of liquid 1-ROH alcohols. Circles – swollen structures formed at ambient temperature; Triangles – structures observed at low temperature, Squares – structures at high pressure ²⁷.

Reversible phase transition in the system BGO- 1- nonanol.

This system presents the clear example of a reversible first order phase transition between two SwSt with different composition. In the DSC heating trace (Fig.7a) there are two well-resolved peaks. The one at $T=268$ K corresponds to melting of pure 1-nonanol, while peak at higher temperature relates to decomposition (incongruent melting) of SwSt (V) with the formation of SwSt (IV):

Fig. 7. The system B-GO – 1-nonanol. (a) DSC trace for the sample with the mass ratio (1-nonanol: B-GO = 3.1). Peaks at 268, 284 K are melting of free 1-nonanol and incongruent melting of the SwSt (V), respectively; (b) Temperature dependence of c-unit cell parameter of B-GO immersed in 1-nonanol in process of heating. Abrupt change of the c-unit cell parameter occurs at the temperature of incongruent melting. (c) The set of the inter-plane distances in the swollen structures (I),(II), (III) and (IV) of B-GO with 1- nonanol identified in process of non-equilibrium vacuum drying at elevated temperatures. First two points (in the circle) were recorded in solvent immersed state without vacuum.

The processes in Fig. 7a,b are reversible on cooling. Compositions of both swollen structures (V) and (IV) were calculated using the squares of the two DSC peaks and the know masses of 1-nonanol and B-GO in the samples. The calculation method is described in Supplementary Information. The abrupt change of the c – unit cell parameter (Fig.7b) occurred at the temperature of incongruent melting indicated by the peak in the DSC traces (see also XRD patterns in Fig.8S in the Supporting Information)). Fig. 7c presents the XRD data obtained in process of non – equilibrium vacuum drying in the system B-GO – 1-nonanol. Under non-

equilibrium conditions d(001) reflections from SwSt (I)-(III) were soon appeared. The d(001) reflection from SwSt (IV) was detected in the initial moment of vacuum drying at room temperature when small amount of liquid 1-nonanol was still in the system. Comparison of Fig.7b and 7c shows that SwSt (IV) is the swollen structure in equilibrium with 1-nonanol at room temperature. In Table 1 the thermodynamic parameters of incongruent melting (1) are compared with the same values for melting of 1-nonanol. Also in the Table 1 are corresponding data for incongruent melting of B-GO – methanol swollen structure ^{27,32} and melting of methanol ³³. For normal alcohols from 1-propanol to 1-heptanol the incongruent melting transition was not observed.

As seen in the Table 1 temperatures of melting of 1-nonanol and incongruent melting of SwSt (V) are close, while for methanol the temperature difference between this transitions is about 130 degrees . Also enthalpy of incongruent melting constitutes almost 70% of the melting enthalpy for 1-nonanol and only 37% for methanol. According to ref.^{18,21} sorbed alcohols do not melt/freeze within the swollen structure. One may reasonably assume however, that with the increase of the inter-plane distance the enthalpy of incongruent melting will become closer to the melting enthalpy (see section **Layers of organic liquids within the inter-plane space of B-GO** for discussion).

Table 1. Thermodynamic parameters of incongruent melting in B-GO- 1-ROH and of melting of 1 – ROH.

Phase transition	T,K	ΔH_{in} kJ mol ^{-1a}	ΔS_{in} J mol ^{-1 K^{-1*}}
Reaction (1)	284±1	17.6	62.1
1- nonanol, melting	268±1	24,7	92.4
Reaction (1) ^b	285±1	1.2	4,2
Metanol, melting ^c	157	3.2	18.3

^a mol of 1-ROH,

^b The incongruent melting reaction is B-GO (CH₃OH)_{0.30} → B-GO (CH₃OH)_{0.17}+(CH₃OH)_{0.13} data from ref.²⁷;

^c data from ref.³³.

Equilibrium sorption into B-GO.

The values of sorption of normal alcohols into BGO are listed in Table 2. The data at ambient temperature were obtained using isopiestic method. For 1-butanol -1 heptanol these sorptions determine compositions of SwSt (III). Third column of Table 2 presents the same compositions

measured by TG although these data correspond to the higher temperatures of TG isothermal desorption and are less accurate. For 1-octanol the swollen structure in equilibrium with the vapor in the isopiestic experiment is SwSt (IV). Isopiestic measurements for 1-nonanol failed due to the low vapor pressure of this alcohol. Sorption for 1-nonanol was calculated from the DSC data and corresponds to SwSt (IV).

Table 2. Specific sorption of normal alcohols into B-GO.

System	Sorption, T=298K, g g ⁻¹ B-GO ^a	Sorption g g ⁻¹ B-GO ^b (T,K)	d(001), T=298K
B-GO- methanol	0.31 ^{d,e}		8.97 ^f
B-GO-propanol	0.37 ^e		8.9 ^e
B-GO-1-butanol	0.64	0.63 (335)	16.5
B-GO-1-pentanol	0.67	0.73 (343)	18.0
B-GO-1-hexanol	0.84	0.78 (353)	18.5
B-GO-1-heptanol	0.75	0.85 (368)	19.0
B-GO-1-octanol	0.88		23.3
B-GO-1-nonanol	1.16 ^c		25.5

^a Isopiestic data, ± 0.02 ; for 1-heptanol and 1-octanol ± 0.05 ; ^b TG data ± 0.1 ^c DSC data ± 0.15 ^d Data from ref [18] ^e Data from ref ¹⁷; ^f Data from ref. ²³.

The swollen structures SwSt (III) which are in equilibrium with the pure liquid alcohols at T = 298 K may be considered as solid solvates B-GO*(1-ROH)_n, where n = 0.14 $\pm$ 0.02 for 1-ROH from 1-butanol to 1-heptanol. The calculated compositions are based on the data from Table 2. Molecular mass of B-GO was taken to be 18 (see “Materials”) . The structure of such simple solvates may be adequately characterized by inter-plane distance d(001) and doesn't require XRD single crystal analysis.

Phase diagrams of the systems BGO-normal alcohols.

The TG, XRD and DSC data presented above may be adequately explained based on the routine phase diagrams (see Fig.8) of the binary systems B-GO – 1 - ROH. Swollen structures, although not entirely homogeneous, may be thought of as binary phases in these systems. Let us look at

the systems of B-GO with 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol first. The sketch of the phase diagram is presented in Fig.8a. Three swollen structures, (I), (II) and (III) are formed in these systems. Their existence was first confirmed in the non-equilibrium vacuum XRD experiments (see Fig.2,3) where all three swollen structures were observed simultaneously. They are characterized by the three inter-plane distances, $d(001)$ recorded in process of solvent desorption at ambient and elevated temperatures under non-equilibrium conditions. The traces of isothermal TG (see Fig.1 and Fig.2Sa,b,c in SI) note moving of the figurative point along the composition axes of the phase diagram towards compositions with the lower amount of 1-ROH in the course of equilibrium desorption (see dash line in Fig.8a). The constant rates of desorption corresponding to the three two-phase regions of the diagram, respectively, (III) + pure 1-ROH; (III)+(II) and (II)+(I), are consecutively observed (see portions of the TG trace parallel to the time axis in Fig.1). The rate of desorption in every region has to be proportional to the equilibrium partial pressure of the desorbed alcohol. Abrupt changes of the rates of desorption occurred while going from one two phase region to the other and crossing the composition of SwSt (III) and SwSt (II) (see Fig.1, Fig.2S and Fig.8a). Equilibrium XRD (fig.4, Fig.5a) corresponds to the phase region ((III) + pure 1-ROH) and detected the temperature independent inter-plane distance in SwSt (III), since (III) according to the phase diagram is the phase in equilibrium with the pure 1-ROH in the broad temperature range above the melting point. The only peak detected by DSC in these systems was melting of the pure ROH. It was observed for compositions relating to the phase region {(III) + pure 1-ROH}. No incongruent melting of phases (I), (II) or (III) was detected in these systems. For 1-heptanol in the narrow temperature range close to its melting point the formation of the SwSt (IV) was evidenced by XRD (see Fig.5b). The presence of the $d(001)$ reflection of phase (III) at the same temperature shows that equilibrium between 1-heptanol and B-GO was not complete. While vapor-solid phase equilibrium is achieved in the closed system this doesn't guarantee achieving of the equilibrium in the condensed phase between the swollen structures. 1-nonanol with B-GO (see Fig. 8b) forms additional swollen structure, SwSt (V), at low temperatures. This new swollen form melts incongruently at $T=284$ K to give SwSt (IV). This transition was evidenced by DSC and XRD (Fig.7 a,b). SwSt (IV) was detected by XRD in the narrow temperature range. It is worth mentioning that $d(001)$ and c -unit cell parameter of SwSt (IV) considerably varies with temperature (see Fig.7b), which may be explained by interstratification effects in the swollen structure. From the viewpoint of the phase diagram SwSt(IV) may be considered as a non-stoichiometric phase. No DSC peaks were detected in the system B-GO – 1-nonanol above room temperature. Other phase regions of the phase diagram of the system BGO – 1 nonanol are similar to those in Fig.8a. Non-equilibrium XRD confirms formation of phases (I) – (III) in the

system (see Fig.7c). The same diagram is valid for the system B-GO – 1-octanol, where formation and incongruent melting of SwSt (V) was additionally confirmed by high pressure experiment at ambient temperature.

Fig. 8. Schematicall phase diagrams of the systems B-GO – 1-ROH. Shown are swollen structures and heterogeneous regions, experimentally confirmed. Equilibrium solubility of B-GO in 1-ROH is assumed to be zero. No true liquid solutions are formed.

Solid lines are phase boundaries confirmed by experimental data. Circles are compositions determined (see Table 2).

(a) Phase diagram for B-GO – 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol systems. (I) – (III) are swollen structures confirmed by XRD and TG; swollen structures (IV) was detected only for 1-heptanol (see text for discussion). Dash line – change of composition of the sample in the isothermal TG experiment; T_m – melting point of the corresponding normal alcohol, T_{TG} – temperature of the TG experiment. (b) Phase diagram for B-GO- 1-nonanol. Swollen structure (IV) is B-GO $(C_{18}H_{20}O)_{0.14}$, and (V) is B-GO $(C_{18}H_{20}O)_{0.21}$. The compositions were calculated from DSC traces.

Thus equilibrium phase diagrams in Fig. 8a,b adequately represents the whole set of experimental date obtained for the SwSt of B-GO with 1 – ROH, though the description is given at the semi-quantitative level. The systems of B-GO with normal alcohols are similar to the typical binary system where the series of solvates (hydrates) are formed.

Layers of organic liquids within the inter-plane space of B-GO.

The swollen structures (I) – (V) can be regarded as systems with different number of parallel layers of sorbed liquid in between the GO planes. Though it is hardly possible to divide sorbed liquid within one structure into layers the discreet set of inter-plane distances seen in Fig.3,4 and 7c enables to consider SwSt (III), (II) and (I) as the set of structures with the three, two and one parallel layers of sorbed liquid respectively. Also abrupt change of the inter-layer distance during incongruent melting may be considered as removal of a “layer” from a certain SwSt (see Fig.7a,b) and ref.²⁶⁻²⁸). For instance for B-GO-methanol system the incongruent melting is a transition from the SwSt with two layers to SwSt with one layer. In B-GO-1-nonanol the five-layered structure is transformed into four-layered one. It may be assumed that in the B-GO-methanol swollen structure the desorbed layer is partially bonded to the GO surface. In contrast, the desorbed layer of 1-nonanol may be released from the middle of the space between the GO planes. In this case, the desorbed molecules were bonded to the neighboring molecules of 1-nonanol rather than to the GO plane. Enthalpy, entropy (and temperature) of transition in this case is determined by interaction between the alcohol molecules. This may explain the difference between the parameters of incongruent melting in Table 1. One may speculate that transitions in the systems of B-GO-methanol and B-GO-1-nonanol although have similar thermodynamic description are different on molecular level.

The term “layer” or “liquid layer” is widely used in the literature (see ref.¹¹⁻¹⁷ and etc.]. It was assumed that introducing of one additional layer parallel to GO planes increases inter-plane distance in B-GO by $\Delta d = 2.5 - 3.5 \text{ \AA}$ ^{11-13,17}. Packing of different molecules within “layers” may be slightly different. The differences between $d(001)$ of SwSt (I) and (II), (II) and (III), (III) and (IV) are close to these numbers (see Fig.3). Introducing of the fifth “layer” led to $\Delta d(001) \approx 4.5 \text{ \AA}$ (see Fig.7b). Such model obviously excludes formation of layers with the stand up orientation. In the present study we attempted to characterize «one layer» by the averaged value of sorption (see Table 3). Sorption data obtained using isopiestic method at 298 K was considered first. TG and DSC data was additionally used. Data of direct isopiestic measurements correspond to SwSt in equilibrium with the pure liquid at 298K. If SwSt with more than one layer is formed at $T=298\text{K}$ the necessary number for one layer was obtained by dividing of the experimental value of sorption by the number of layers. Table 3 summarized such averaged sorption data for B-GO swollen structures. Most accurately they have to characterize the first sorbed layer which corresponds to the swollen structure (I) with the inter-plane distance $d = 9.5-10 \text{ \AA}$. Initial experimental values are in grams of sorbed liquid per gram of B-GO. In the Table 3 sorption is also expressed in volumetric units and as number of moles of liquid sorbed per unit mass of B-

GO. “Sorption volumes” are surprisingly similar for rather different polar solvents, e.g. numbers for water, $\text{CF}_3\text{CH}_2\text{OH}$ and 1-nonanol may be compared. The average number in Table 3 is $V_1 = 0.36 \pm 0.06 \text{ cm}^3 \text{ g}^{-1}$ B-GO. On the other hand molar sorptions are more scattered. They are visibly higher for liquids with small molecular mass (H_2O , CH_3OH). One may assume that sorption capacity of a layer is restricted by the geometrical factors, namely by the volume, V_0 , available for sorption within the swollen structure. If this volume is constant then sorption expressed in moles per unit mass of B-GO (column 5 in Table 3) should be proportional to (ρ/M) , where ρ , M are density and molar mass of the sorbed liquid, respectively. Such linear dependence is confirmed by the data in Table 3. The volume V_0 , available for sorption within B-GO inter-plane space may be roughly estimated. The square, S , covered by one liquid layer may be estimated from the molar sorptions (Table 3) and the experimental values of molecular cross sections of corresponding molecules on carbon surfaces [33], as $S = 850 \text{ m}^2 \text{ g}^{-1}$ (B-GO). Similar number was calculated for the geometrical square of one side of the B-GO ($\text{C}:\text{O} \approx 2.7$) plane, $S = 870 \text{ m}^2 \text{ g}^{-1}$ B-GO. The width of the space available for sorption was estimated¹⁰ as $\delta \approx 5 \text{ \AA}$ (upper limit). If to assume that such internal space arises *only* from swelling, then the width is equal simply to the width of a layer, $\delta \approx 3 \text{ \AA}$ (lower limit). The volume V_0 available for sorption, then may be estimated as ≈ 0.43 or $0.26 \text{ cm}^3 \text{ g}^{-1}$ B-GO, respectively, in reasonable agreement with the experimental value, $V_1 = 0.36 \text{ cm}^3 \text{ g}^{-1}$ B-GO. Note that sorbed liquid fills more than 84% of the upper limit of geometrical available space. The number of sorbed moles in Table 3 is less than the number of moles of oxygen (0.021 per g of BGO as calculated from XPS data) by a factor 3-10.

Table 3. Sorption in BGO, corresponding to monolayer. $T=298\text{-}380\text{K}$.

Polar liquid	Number of layers	Sorption			
		g g^{-1} BGO	$\text{cm}^3 \text{ g}^{-1}$ BGO	$\text{Mol} \times 10^3 \text{ g}^{-1}$ BGO	Ref.
Acetonitrile	1	0.25	0.32	6.1	¹⁸
$\text{CH}_3\text{CH}_2\text{CN}$	1	0.34	0.43	6.2	a)
$\text{CF}_3\text{CH}_2\text{OH}$	1	0.51	0.38	5.1	a)
THF	1	0.35	0.40	4.9	¹⁸
DMF	1	0.41	0.43	5.6	¹⁸
NMP	1	0.44	0.44	4.2	¹⁸

DMSO	1	0.42	0.38	5.4	¹⁸
H ₂ O	1	0.33(0.43)	0.33	18.3(22,4)	^{18,17}
Methanol	1	0.31(0.31)	0.39 (0.39)	9.7	^{17,18}
1 - propanol	1	0.37	0.46	3.7	¹⁷
1-butanol	3	0.21	0.26	2.8	a)
1-pentanol	3	0.22	0.27	2.8	a)
1-hexanol	3	0.28	0.34	2.7	a)
1-heptanol	3	0.25	0.30	2.2	a)
1-octanol	4	0.22	0.27	1.7	a)
1-nonanol	4	0.38	0.35	2.7	a)
CHCl ₃	1	0.62	0.40	5.2	¹⁷
Mean value		$0.34 \pm 0,13$	0.36 ± 0.06	5.7 ± 3.9	

a) This study

One may assume that geometrical factor, namely the volume available for sorption within the B-GO lattice governs formation of the first liquid layer. Formations of the specific chemical bonds are less important. Sandwich structures with 1 or 3 liquid layers are usually formed in equilibrium with normal alcohols liquids at ambient temperature (see Table 3).

CONCLUSIONS

Graphite oxide is generally regarded as a material rather than a homogeneous chemical substance (phase) with a distinct composition. Thermodynamic parameters of B-GO or of its derivatives were never considered. In the present study it was demonstrated that different swollen structures of B-GO with normal alcohols and other polar liquids may be reasonably treated using conventional tools of chemical thermodynamics. Swollen structures were regarded as binary phases and when exposed to the temperature-composition changes their behavior fitted the predictions of the corresponding binary phase diagrams reasonably well. Swollen structures of BGO experience first order phase transitions, form heterogeneous phase regions, i.e. behave as ordinary solid solvates. Compared to more common and more disordered H-GO, B-GO powders and B-GO swollen structures are materials with more regular and predictable properties which may be a serious advantage in practical use. It is not clear at the moment whether or not these properties of B-GO powders will pass to B-GO membranes. Based on experimental data obtained the internal arrangement of B-GO swollen structures may be described as a system of

regular parallel layers of sorbed liquid in between the B-GO planes. Sorption capacity of one layer expressed as specific volume, $0,36 \text{ cm}^3\text{g}^{-1}$ B-GO was surprisingly similar for different polar liquids. The volume limitations provided both by internal geometry and possible expansion of the inter-plane space of B-GO restrict sorption and led to swelling and to the formation of the next layers. The volume available for sorption may be reasonably estimated from surface area and inter-plane distances in B-GO swollen structures.

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Supporting Information: *XPS spectra, Isothermal Thermogravimetry (TG), Additional XRD data, Determination of sorption and compositions of the swollen structures from the DSC data.* The Supporting Information is available free of charge on the ACS Publications website at DOI:

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Note

The authors declare no competing financial interest.

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TOC Graphic