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Sorption of polar organic solvents and water by graphite oxide: Thermodynamic approach

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Sorption of polar organic solvents CH_3OH, C_4H_8O (THF), CH_3CN, C_3H_7NO (DMF), C_2H_6OS (DMSO), C_5H_9NO (NMP) and water was quantitatively evaluated for Hummers (H-GO) and Brodie (B-GO) graphite oxides at T = 298K and at melting temperature (Tm) of the solvents. H-GO showed stronger sorption compared to B-GO for all studied solvents and the increase of sorption upon lowering temperature was observed for both H-GO and B-GO. Thermodynamic equations allowed to explain earlier reported “maximums” of swelling/sorption in the binary systems H-GO – solvent at Tm. The specific relation between the values of enthalpies of sorption and melting leads to the change of sign in enthalpies of sorption at Tm and causes maximal swelling/sorption. The same thermodynamic explanation was given for the “maximum” on the swelling vs. pressure dependence in B-GO and H-GO – H_2O systems earlier reported at pressure of phase transition “liquid water-ice VI”. Notably higher sorption of H_2O was observed for H-GO compared to H-GO membrane (H-GOm) at high relative humidity (RH), RH > 0.75. Experimental sorption isotherm of H-GOm was used to simulate permeation rates of water through H-GOm and to estimate effective diffusion coefficient of water through the membrane.

1. Introduction

Graphite oxide (GO) is non-stoichiometric derivative of graphite which attracted wide attention recently as a precursor for preparation of various graphene based materials [1,2]. Contrary to graphite, GO is typically hydrophilic, dispersible in polar solvents and easily sorbs polar solvents into inter-layer space inducing the increase of the inter-layer distance (swelling) [3]. Simple sonication in polar solvents leads to exfoliation of GO with formation of graphene oxide [4,5] which can be then reduced to graphene or to chemically modified graphene [4–7].

Very strong interest was recently attracted to multilayered GO materials obtained by deposition of graphene oxide sheets using water and polar solvent solutions: thin films [8,9], papers [10], and membranes [11–18]. In particular, graphene oxide membranes were suggested for nanofiltration [14,15], separation of vapor and liquid mixtures [13,16]. Very thin graphene oxide films (2–3 layer thick) were also demonstrated to be highly selective in separation of gas mixtures, whereas the properties of the membranes can be controlled using variations of humidity [12,17].

Sorption of water and organic solvents by different GO samples was evaluated in a number of studies [19–23]. As revealed by XRD the inter-layer distance in GO at ambient temperature increases with the increase of humidity [19]. H-GO in the excess of CH_3OH, C_2H_5OH and H_2O shows gradual changes of interlayer distance upon both temperature [24] and pressure variations [25] with maximums at the points of solvent freezing/melting. However, such anomalous behavior is poorly understood and lack theoretical explanation. For B-GO the abrupt changes of the inter-layer distance were observed in the systems with CH_3OH, C_2H_5OH, DMF and CH_3CN, suggesting transitions between two solvate phase to occur upon temperature variations [26,27].

In the present study the intercalation of GO with water and typical polar organic solvents was quantitatively characterized and described theoretically using general thermodynamic approach. The values of sorption were measured for several common polar

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solvents at melting temperature of the solvent and at ambient temperature. The water sorption isotherms were obtained at ambient temperature for Hummers H-GO and for H-GOm membrane prepared from H-GO powder. Simple thermodynamic model allows to give interpretation of sorption data along with the XRD values for interlayer distances in swollen GO and to explain the peculiar temperature/pressure dependence of sorption and swelling.

2. Experimental

2.1. Materials

H-GO was purchased from ACS Material. B-GO samples were provided by Dr. T. Szabo and the synthetic procedure was described elsewhere [3]. The comparative description of both these samples was given in Ref. [28]. The samples were dried to a constant mass under vacuum (10^{-4} bar, 12 h) and/or in the desiccators with P_2O_5 for 3–5 days. The C/O ratio as measured by XPS after drying was 2.47 and 2.85, for H-GO and B-GO, respectively [28]. The H-GOm membranes were prepared using vacuum driven filtration, details are available in Ref. [29]. Organic solvents were specially redistilled before use. The resulting purity was >99% according to DSC. Mili-Q water was used for measurements.

2.2. Methods

Sorption measurements at $T = 298 \pm 0.5$ K were performed by isopiestic (ISP) method. Equilibration of GO with H_2O and organic solvents vapors in the thermostated desiccator persisted until the mass of GO saturated with the solvent became constant (5–10 days). Amount of sorbed solvent was also evaluated at the temperature point of solvent melting using DSC heating traces. For this experiments GO powder samples are mixed with certain excess of solvent. The amount of bulk solvent decreases due to the intercalation of some solvent into the GO structure; the sorbed solvent does not contribute to the measured melting enthalpy (see Supplementary Material for details). The amount of solvent sorbed by the GO structure can be calculated using the known enthalpy of solvent melting and measured decrease in melting enthalpy for given amounts of powder and solvent.

DSC-30 TA from Mettler was used for measurements. The quantitative measurements rely on heating traces with the scanning rate 5K/min.

Water sorption isotherms for H-GO and H-GOm were obtained by ISP and for H-GO additionally by dynamic desorption method. To provide necessary level of relative humidity (RH) in ISP the aqueous saturated solutions of the following salts were used: LiCl (RH = 0.11), $MgCl_2$ (RH = 0.33), NaBr (RH = 0.57), NaCl (RH = 0.75), KNO_3 (RH = 0.93), K_2SO_4 (RH = 0.97) [30]. Typical mass of dry H-GO, B-GO and H-GOm in ISP were 10–15 and 2 mg, respectively.

Dynamic desorption measurements (DDM) were performed on the instrument described in Ref. [31]. In the experiment the rate of continuous desorption of water under equilibrium conditions was measured. The relative equilibrium pressures of water were calculated from the rates of desorption using the “film model” [32]. The basics of the method are given in Ref. [33] and in the Supplementary materials. The samples studied were ~130–135 mg of dry H-GO mixed with the excess of water (1 g). To sustain equilibrium conditions typical desorption experiment lasted for 10 days.

3. Results and discussion

3.1. Sorption of organic solvents and water

Summary of sorption experiments is given in Table 1 for several common polar solvents. The amount of sorbed solvents is typically provided in weight, volume (Table 1) and in molar proportion (see Fig. 1) relative to the amount of dry powder. First of all, H-GO and B-GO showed remarkably different sorption properties with H-GO showing higher sorption at ambient temperature for all of studied solvents. It is also general trend that the sorption increases with the decrease of temperature from the ambient down to the melting temperature of the solvent. This was observed for both H-GO and B-GO and for all of the solvents studied. The only exception is sorption of acetonitrile at low temperatures, however for this solvent the deviation is explained by complete delamination of H-GO structure at low temperatures [27]. When melting temperature of solvents was close to ambient (H_2O, DMSO), the values of sorption measured by two different methods (ISP and DSC) were almost equal. At least for H_2O and DMSO no additional sorption was found for the samples in direct contact with liquid solvent (DSC) compared to samples equilibrated with the saturated vapors of the same solvent (ISP).

3.2. Formation of layers

The data presented in Table 1 provide interesting insights into the nature of the inter-layer swelling of graphite oxides. For B-GO the volumetric sorption at ambient temperature (cm^3/g) is almost equal for all of the solvents studied. Fig. 1a shows sorption of studied solvents by B-GO expressed both in molar and volumetric units. Remarkably, the molar fraction of sorbed solvents is almost the same for several solvents except H_2O and CH_3OH. However, the trend becomes almost uniform if the sorption is expressed in volumetric units. The average volume sorption for nine solvents in Fig. 1a is 0.39 ± 0.05 cm^3/g compared to 0.0073 ± 0.0044 and 0.39 ± 0.10 for sorption measured in mol/g and g/g, respectively. These data can be interpreted as following: polar solvents at ambient temperature occupy the same volume in the inter-plane space of B-GO and stoichiometry of sorption sensitive to molar proportion (mol/g) is a less important factor.

Polar solvents form a “volume layer” between two B-GO planes though this layer is not necessarily regularly shaped and its thickness may not be equal to the effective diameter of a solvent molecule. The average volume of the layer is close to 0.45 cm^3/g, the number was earlier suggested as geometric limit of stability of B-GO upon intercalation [22]. However at melting temperatures of the solvents this volume was almost doubled and averaged 0.75 ± 0.08 cm^3/g (solvents 1–5 in Table 1) suggesting formation of “two volume layers” between every two GO planes. For B-GO intercalated with CH_3CN, CH_3OH and DMF the first order phase transition was observed below the ambient temperature with the release of ~0.33 cm^3/g of the solvent and the abrupt decrease of the inter-layer distance on heating [26,27]. This transition detected by XRD and DSC may be considered as incongruent melting of swollen B-GO with two volume layers resulting in formation of B-GO with one volume layer of solvent molecules in the inter-plane space.

The same tendencies are less pronounced for sorption of solvents by H-GO, (see Fig. 1b). Once again, molar sorption of water strongly deviates from other solvents. For H-GO the averaged values for volume/molar sorption are 0.66 ± 0.15 cm^3/g and 0.014 ± 0.012 mol/g (solvents 1–7 in Table 1) and 1.03 ± 0.26 cm^3/g and 0.016 ± 0.012 (solvents 1–5 in Table 1) for ambient temperature and melting temperature of the solvent, respectively. DSC traces didn't show any peaks corresponding to incongruent melting