

Sorption of polar and non-polar liquids by GO powders according to DSC experiments

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PACS 68.43.-h

ABSTRACT The sorption properties of Hummers (HGO) and Brodie (BGO) graphite oxides with respect to various liquids were studied by the DSC method. In the case of HGO, the reduced material (RHGO) was obtained by hydrothermal synthesis. The effective reduction of the material was confirmed by XRD. The difference in the sorption of water and acetonitrile by HGO and RHGO was experimentally observed. The DSC experimental procedure was developed to estimate the selective sorption of the component from the immiscible liquid mixtures. The procedure has been tested on the sorption of the water-octane mixture by HGO. It was shown that water can be sorbed by HGO from the mixture in an amount equal to equilibrium sorption of pure water by HGO at 273 K. The results obtained will serve as the basis for further studies of the sorption properties of GO.

KEYWORDS graphite oxide, sorption, DSC**ACKNOWLEDGEMENTS** The study was supported by the Russian Science Foundation (RSF 22-29-00544).**FOR CITATION** Kaplin A.V., Eremina E.A., Korobov M.V. Sorption of polar and non-polar liquids by GO powders according to DSC experiments. *Nanosystems: Phys. Chem. Math.*, 2024, **15** (1), 130–134.

1. Introduction

Graphite oxide (GO) is a non-stoichiometric graphite derivative, on the basis of which it is possible to obtain materials with various functional properties. Unlike graphite, GO exhibits hydrophilic properties, it can be dispersed in polar solvents and easily sorbs polar solvents in the interlayer space, which leads to the increase of the interplanar distance [1]. Ultrasonication in polar solvents leads to the solubilization of graphite oxide with the formation of the dispersed oxide graphene, which can be further reduced to graphene [2]. In GO, most of the carbon atoms are sp^3 hybridized and are bound to various functional groups ($-COOH$, $-C(O)O-$, $>C=O$, $-OH$). The known methods for the GO synthesis do not provide control over the oxygen content in the resulting substance. As a result, it is impossible to accurately determine the composition of GO and its structure [3, 4].

The preparation of GO was first described by Brodie in 1855 [5]. He used a mixture of potassium chlorate and fuming nitric acid to oxidize graphite. Currently, the Hummers synthesis [6] or its more environmentally friendly version – the improved Hummers method [7] are commonly used. Graphite oxides obtained by the Brodie method (BGO) and the Hummers method (HGO) have different physicochemical properties [8]. These materials differ in the interplanar distance (XRD), the C:O ratio (XPS) and the concentration and composition of the oxygen-containing functional groups (IR-spectra). Also, HGO and BGO differ in their sorption properties with respect to polar liquids [2, 9, 10]. The interaction of GO with polar liquids leads to swelling, that is, sorption with the simultaneous increase in the interplanar space in GO. Sorption and swelling make it possible to actively use GO to remove toxic pollutants and purify water [11–13]. The sorption of water and organic liquids by various GO samples was measured in [2] using isopiestic experiment and the DSC method. The isopiestic experiments makes it possible to measure the sorption into GO at room temperature from the gas phase. The DSC method enables one to evaluate the sorption at the melting point of a liquid upon direct contact of the material with the liquid phase [2]. In this work, we obtained the data on the sorption of some polar and non-polar liquids by the HGO and BGO powders. Also, we obtained the reduced form of HGO (RHGO) using hydrothermal synthesis. Only a few works are known about the sorption of liquids by RHGO materials [17].

We demonstrated that DSC allows one to determine the partial sorptions of the components from the binary mixtures of polar and non-polar liquids into the GO materials. This method is useful to evaluate the properties of the GO materials as sorbents for the purification of water.

2. Materials and methods

2.1. GO powders

HGO powders were prepared by the improved Hummers method with a sulfuric to phosphoric acid ratio of 9:1 [9]. The sample of RHGO was obtained by the hydrothermal synthesis. 30 ml of HGO suspension in water with (3 mg/ml) was autoclaved for 12 hours at 140 °C. The resulting sample was dried from water in a desiccator with P₂O₅ to a constant weight. BGO powders were synthesized by the method described in ref. [14] with double oxidation of the original graphite. The liquids used in the study are: water (deionized, $\approx 0.5 \mu\text{S}/\text{cm}$), octane (Sigma-Aldrich, $\geq 99.8 \%$), trifluoroethanol (Sigma-Aldrich, $\geq 99 \%$), propionitrile (Sigma-Aldrich, $\geq 99 \%$).

2.2. Instruments

XRD measurement were performed using the diffractometer Rigaku D/MAX 2500 (Japan) with Bragg–Brentano geometry with the rotating anode (CuK α radiation, $\lambda = 1.5418 \text{ \AA}$). Registration was carried out in a step-by-step mode in the angle range $2\Theta = (2 - 80)^\circ$ with the step of 0.02° in 2Θ with an exposure of 2 seconds per point. The obtained data were processed using the standard packages of the WinXpow program. Before recording the diffraction patterns of the graphite oxide samples, the samples were dried in a desiccator with P₂O₅.

The DSC method was used to measure the sorption of polar liquids by GO powders at the melting temperature. The mass ratio of the polar liquid to the GO material in the samples studied varied from 1:1 to 5:1. Before the DSC experiments, the GO sample was pre-dried in a desiccator with P₂O₅, then a fixed amount of polar liquid was added to the GO. The DSC experiments were performed with the low-temperature calorimeter “Mettler DSC – 30”. The heating traces were used for the quantitative determination of sorption. The scanning rates were 2, 5 and 10 grad·min⁻¹. The procedure is described in detail in ref. [2].

3. Discussion

3.1. Synthesis and XRD

HGO and BGO were prepared by the common synthetic methods [2, 9, 13, 14]. According to the method of BJH nitrogen desorption, the specific surface area and pore size in the materials were determined (Table 1). The size of nanopores does not correspond to the interplanar distance in the layered structure of both HGO and BGO.

TABLE 1. BJH and XRD data for HGO and BGO powders

HGO	BGO	Method
1519	814	Surface area (BJH), m ² /g
11.0	10.9	Pore radius (BJH), Å
7.8	6.6	Interplane distance (XRD), Å

This confirms that nitrogen does not intercalate into the interplanar space of GO. Hydrothermal synthesis was used to obtain the reduced graphite oxide RHGO from HGO. In hydrothermal synthesis, water acts as the reducing agent. The dried RHGO is a black powder which forms the unstable suspensions in water, even after ultrasonication.

Figure 1 shows the XRD patterns of the studied materials. As compared to the initial HGO, the (001) peak of RHGO is significantly broadened and shifted to higher angles. Decrease in the interplanar distance (to 3.7 from 7.5 Å) almost by the value of the interplanar distance in graphite (3.4 Å) proves the efficient reduction of the material [16]. The broadening of the RGO peak may indicate a decrease in the size of the particles in the reduced material, or/and the formation of the inhomogeneous sample with wide distribution of interplanar distances.

3.2. Sorption properties of HGO and RHGO

A comparative experimental study of the sorption properties of HGO and its reduced analogue RHGO has not been previously presented in the literature. We assumed that the obviously more hydrophobic material RHGO would sorb water and acetonitrile in significantly less amounts than HGO. Table 2 shows the results of sorption measurements by the DSC using the method described in ref. [2]. As seen from the Table 2 RHGO sorbs less water and acetonitrile than HGO, but the difference is not dramatic. It was shown in [17] that the reduced forms of GO sorb water, but in significantly less amounts compared to the initial GO. Only the original graphite does not sorb water at all. It is worth mentioning that acetonitrile was sorbed by all graphite materials studied, regardless of the degree of oxidation, including the pristine graphite. Apparently, the presence of methyl group in a molecule of a liquid plays a significant role in intercalation into materials with a low degree of oxygenation.

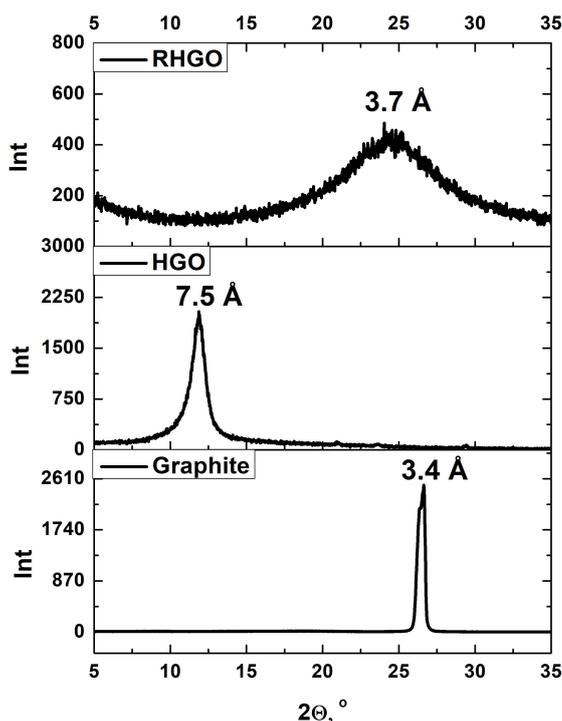


FIG. 1. Parts of the XRD spectra of RHGO, HGO and the original graphite

TABLE 2. Sorption of water and acetonitrile at melting temperatures. *Melting temperature of the sorbed liquid

Material	Sorption of H ₂ O ($T = 273$ K)*, g/g	Sorption of CH ₃ CN ($T = 229$ K)*, g/g
HGO	0.63 ± 0.06 [9]	0.47 ± 0.06 [9]
RHGO	0.50 ± 0.05	0.37 ± 0.03
Graphite	≈ 0	0.24 ± 0.03

3.3. Sorption properties of BGO

Table 2 demonstrates the influence of polarity of a sorbed liquid on the sorption values for the BGO material. The correlation is shown between the values of sorption by the BGO material and the Dimroth–Reichardt “general polarity” parameter [15]. It was previously known that various polar liquids are sorbed by GO materials, but sorption of, e.g. aromatic benzene is close to zero [9]. The authors of [18] demonstrated a slight increase in the interplanar distance in GO after intercalation of liquid benzene due to the π – π interaction of the aromatic system of benzene with the unoxidized regions of GO. We showed that octane is almost not sorbed into BGO, despite the fact that BGO is a less oxidized material than HGO. Octane is also not sorbed in HGO.

In Table 3, the data on sorption of two more polar liquids – propionitrile and trifluoroethanol – are presented. These polar liquids are sorbed into BGO to a significant extent, comparable to the sorption of water and acetonitrile.

3.4. DSC study of system “water + octane” and “HGO + water + octane”

The “water + octane” system was studied by the DSC method. It was shown that the peaks corresponding to the melting peaks of liquids do not overlap and are well spaced along the temperature axis in the DSC trace. This makes it possible to quantify how selectively the highly oxidized HGO material can sorb water from a “water + octane” mixture. The lower part of Fig. 2 shows the DSC curve after adding of HGO to a mixture of water and octane. We conclude from the figure that water was completely removed from the liquid mixture and sorbed by HGO, because the amount of HGO for the experiment was selected based on the data on sorption of pure water in HGO (≈ 0.6 g/g, see Table 1). If both liquids can be individually intercalated into the material, then we would observe a change in the equilibrium sorption values due to the competition at the sorption centers. This was not the case for the water – octane mixture.

TABLE 3. Sorption of polar and non-polar liquids at melting temperatures. *Melting temperature of the sorbed liquid

Sorption (g/g) of	H ₂ O (<i>T</i> = 273 K)*	CH ₃ CN (<i>T</i> = 229 K)*	CH ₃ CH ₂ CN (<i>T</i> = 180 K)*	CF ₃ CH ₂ OH (<i>T</i> = 230 K)*	Octanol-1 (<i>T</i> = 257 K)*	Octan (<i>T</i> = 216 K)*
BGO	0.33 ± 0.04 [2] 0.30 ± 0.02 [8]	0.53 ± 0.04 [2] 0.54 ± 0.09 [8]	0.34 ± 0.04	0.54 ± 0.05	1.13 ± 0.05 [13] 1.05 ± 0.15 [8]	≈ 0
Parameter <i>E_T</i> 30 [14]	63.1	45.6	No data	No data	48.1	31.1
Dielectric constant ϵ	78.5	38.0	No data	No data	9.9	1.9

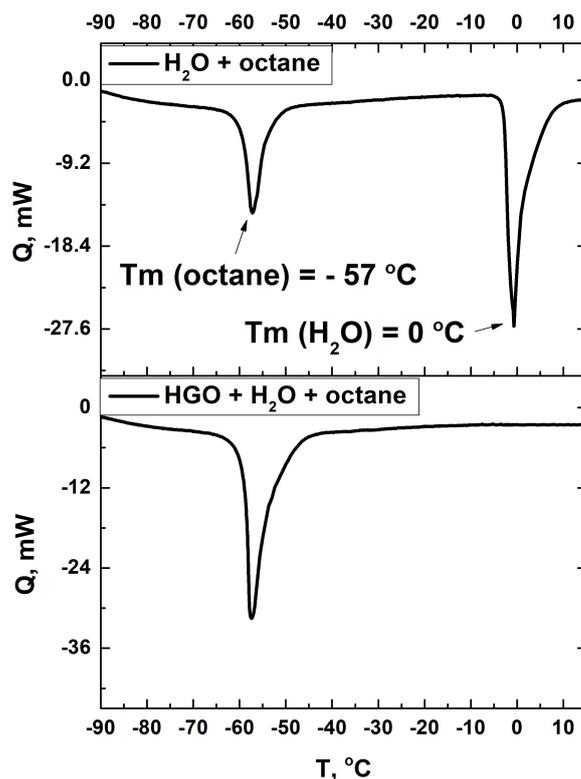


FIG. 2. DSC curves for the systems “water+octane” and “HGO+water+octane”

It is also worth noting that the necessary condition for applying the method described above is the significant difference in the melting temperatures of liquids. For example, sorption from a mixture of benzene ($T_m = 5.5\text{ °C}$) and water ($T_m = 0\text{ °C}$) cannot be measured quantitatively due to the overlap of the melting peaks of these liquids.

4. Conclusion

The reduced RHGO material was synthesized and characterized in comparison with HGO and pristine graphite. It was shown that the RHGO material sorbs water and acetonitrile slightly less than HGO. We plan to compare sorption properties of RHGO reduced by various methods and to follow the trends of sorption properties along the series of liquids with changing polarity.

The sorption of polar and non-polar liquids by BGO was studied with octane, trifluoroethanol and propionitrile. The octane sorption data confirm that non-polar liquids are not sorbed by the HGO and BGO materials. The same result was obtained in [9] for benzene.

The DSC experimental procedure was developed to quantify the selectivity of sorption from the mixtures of the immiscible liquids. We plan to extend the list of water-immiscible liquids in order to test the efficiency of the procedure.

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Submitted 27 November 2023; revised 9 January 2024; accepted 10 January 2024

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Conflict of interest: the authors declare no conflict of interest.