

Influence of dispersion medium on thermodynamic parameters of natural graphite exfoliation for manufacturing graphene-based suspensions

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Abstract: In the present study, we report the calculated value of surface energy for liquid-phase exfoliated few-layer graphene platelets based on experimental data for contact angles of graphene-based films. Free mixing energies were calculated via direct technique from data on surface tensions and their temperature coefficients, as well as using Hansen solubility parametersto obtain Flory-Huggins constants. Although the values obtained for different methods vary, qualitatively it was shown that colloidal systems based on few-layered graphene platelets are lyophobic, and freeenergies for ethylene glycol, diethylene glycol and N-methylpyrrolidone are all close and far lower than that for water. For ethylene glycol-based suspension assessment of the structure via transmission electron microscopy and Raman spectroscopy was performed. Polyols were shown to be very promising media for dispersion and exfoliation of natural graphite to manufacture graphene of high structural quality, effective wetting and stabilization of the free surface at low free energy of mixing values. Calculated values of thermodynamic functions can be used in developing new graphene manufacturing technologies based on direct exfoliation and subsequent stabilization of the newly formed free surface.

Keywords: graphene; ultrasound treatment; electrically conductive suspensions; thermodynamics of mixing; surface energy; free energy; graphite; ethylene glycol.

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Влияние природы дисперсионной среды на термодинамические параметры эксфолиации природного графита для получения графеновых препаратов

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Аннотация: На основе экспериментальных данных по краевым углам смачивания пленок малослойных графеновых частиц, полученных методом прямой жидкофазной эксфолиации, рассчитано значение их поверхностной энергии. Расчет свободных энергий смешения проведен прямым методом из данных по поверхностным натяжениям различных дисперсионных сред и их температурным коэффициентам, а также с использованием параметров Хансена для нахождения констант Флори–Хаггинса. Несмотря на количественные отличия в полученных значениях свободных энергий смешения, рассчитанных различными методами, принципиально показано, что дисперсные системы на основе малослойных графеновых частиц являются лиофобными, причем значения свободных энергий смешения для этиленгликоля, диэтиленгликоля и N-метилпирролидона оказались близкими и принципиально более низкими по сравнению с водой. Для суспензий в этиленгликоле проведена оценка структуры получаемых препаратов методами просвечивающей

электронной микроскопии и спектроскопии комбинационного рассеяния. Показана перспективность использования многоатомных спиртов в качестве среды для проведения диспергирования и эксфолиации природного графита с получением графеновых препаратов с точки зрения структуры получаемых частиц, смачивания и высокой способности к стабилизации свободной поверхности графена при низких значениях свободной энергии смешения. Вычисленные значения термодинамических функций могут быть использованы при разработке новых методов получения графена, основанных на непосредственном расслоении и стабилизации получаемой свободной поверхности.

Ключевые слова: графен; эксфолиация; обработка ультразвуком; электропроводящие суспензии; термодинамика смешения; поверхностная энергия; свободная энергия; графит; этиленгликоль.

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1. Introduction

Despite a significant number of described methods of graphite exfoliation with the production of electrically conductive suspensions of few-layer graphene platelets (FLGP), the search for scalable ways to implement the process remains one of the most urgent problems in terms of approaching practical applications. The desired technologies should be characterized by scalability, high technical and economic indicators [1–3] and environmental friendliness [4].

Aqueous suspensions of FLGPs are well studied, but they are of limited application due to their low compatibility with metals and polymers in the subsequent production of films and composite materials (CMs), the need to use expensive surfactants to achieve stabilization of the colloidal system, and the duration of the ultrasonic treatment [5–7]. As shown in a number of studies [5, 8–19], organic media often turn out to be more efficient than water–surfactant systems, but the compounds used are usually expensive and toxic, which limits the scalability of the process; are characterized by poor compatibility with polymers, which is important for the creation of new CMs, inks for the development of flexible and printed electronics technologies. In addition, the existing studies were carried out in the area of low concentrations of the dispersed phase – less than 1 mg·mL⁻¹ [2, 5, 20–22] ml or more) concentrations of electrically conductive suspensions. Thus, the issues of choosing a dispersion medium and increasing the efficiency of the liquid-phase exfoliation process are an important area of research in the development of serial and scalable technologies for the production of graphene preparations.

In order to select a suitable dispersion medium, there are certain well-established theoretical concepts developed by the Coleman group [15] on the basis of previously established regularities for carbon nanotube (CNT) suspensions [23] and fullerene solutions [24]. According to them, it is especially important that the surface tension of the dispersion

medium be sufficient to compensate for the free surface energy of the formed particles, and that the enthalpy of mixing should be as low as possible. According to one of the first similar studies [2] that later were confirmed many times in other sources, the optimal value of the surface tension of the dispersion medium is about 40 mN·m⁻¹, preferably 38–46 mN·m⁻¹ (for comparison, water has 72 mN·m⁻¹ [25]), in connection with which organic substances are widely used during exfoliation, primarily N-methylpyrrolidone (NMP) (40.7 mN·m⁻¹ [2]).

NMP and dimethylformamide (DMF) became widespread for the preparation of CNT suspensions in the 2000s; however, the search for scalable technologies for obtaining FLGP preparations has its own specifics due to the simultaneous occurrence of exfoliation and dispersion processes, as well as the difference in the surface energies of FLGP and CNTs. Thus, the issue of optimizing the dispersion medium for graphite exfoliation to obtain FLGP cannot be considered resolved.

Polyhydric alcohols, primarily ethylene glycol (EG) (48.6 mN·m⁻¹ [26]) and diethylene glycol (DEG) (44.5 mN·m⁻¹ [27]) have similar values of surface tension, and increased hydrophilicity parameters, compared to conventional dispersion media for exfoliation (DMF, NMP), which makes it attractive to study them as promising media to perform the process without using surfactants. An additional argument in favor of using polyhydric alcohols for exfoliation is their increased viscosity, which, on the other hand, is sufficient for efficient propagation of elastic waves of liquid deformation, which, according to the recent study [28], leads to an increase in the graphene yield during exfoliation.

The goal of this study was to refine the value of the free surface energy of FLGP obtained by direct liquid-phase exfoliation, as well as to evaluate the relative efficiency of dispersion media for direct liquid-phase ultrasonic exfoliation based on calculated data on the values of thermodynamic mixing functions.

2. Materials and Methods

2.1. Reagents

Suspensions of the original natural graphite (NG) (GE-1) in EG (99.5 %, Acros) with a concentration of $6.0 \text{ mg}\cdot\text{mL}^{-1}$ were processed using an MEF-391 ultrasonic disperser (acoustic power 200 W, resonant frequency 22, 5 kHz) for 7 hours followed by drying in vacuum at $200 \text{ }^\circ\text{C}$, which, according to the data of [29], makes it possible to obtain stable FLGP suspensions.

2.2. Measuring contact angle

The contact angle of surface of FLGP-based films with various liquids was measured by the sessile drop method (elliptical baseline method). FLGP films were prepared for measurements by the drop-casting method; $20 \text{ }\mu\text{L}$ aliquots of the suspension were successively applied to a substrate (silicon single crystal (cutting direction (111) with a thermal oxide layer of 150 nm) using an F1-ClipTip GLP automatic micropipette (Thermo Scientific, USA), dried at a temperature of $190 \text{ }^\circ\text{C}$ for 60 min. The procedure was repeated until noticeable electrical conductivity appeared (Fluke 175, USA) on the surface of polyethylene terephthalate. The films were placed on the object stage of a UM-401P-1 optical microscope (JSC Opta, Russia) equipped with a UF-705 C01 circular lamp (Ultraflash, China), a micrometer stage, LOMO 751285 lens with a magnification of $3.5\times$ (JSC Lomo, RF) and a high-speed camera. Drops of test liquids (water, EG, DEG) with a volume of $0.4 \text{ }\mu\text{L}$ were applied with an automatic micropipette F1-ClipTip GLP (Thermo Scientific, USA). Wettability was assessed using EG ($> 99 \text{ wt. } \%$, Honeywell, Germany), DEG ($> 99.5 \text{ wt. } \%$, Acros Organics, the Netherlands) and NMP ($> 99.7 \text{ wt. } \%$, Komponent-reaktiv LLC, Russia), as well as vacuum oil grade VM-4. These solvents were used without further purification. According to profilometry (Surftest SJ-210, Mitutoyo, Japan), the surface roughness did not exceed $1.5 \text{ }\mu\text{m}$.

The drop ellipse was built using 6 contour points; image processing and tangent construction were carried out using ImageJ software. Measurements were carried out on 5–10 parallel samples.

2.3. Analytical methods

Raman spectra were obtained on an inVia Reflex confocal spectrometer (Renishaw, UK) with a solid-state Nd-YAG laser (wavelength 532 nm).

Suspensions drops (about $10 \text{ }\mu\text{L}$) were applied to the surface of a silicon single crystal with a thermal oxide layer of 150 nm using an F1-ClipTip GLP automatic micropipette (Thermo Scientific, USA) and dried at a temperature of $120\text{--}130 \text{ }^\circ\text{C}$. The values of the integrated peak intensities were determined using the built-in Wire software. Additional processing of the spectra and their deconvolution were carried out in the OriginPro 2021 software. For an integral qualitative assessment of the distribution of FLGP in the film, the method of mapping over an area up to $200\times 200 \text{ }\mu\text{m}$ was used, the number of spectra per point was 6; the mapping step was $2 \text{ }\mu\text{m}$.

Transmission electron microscopy images were taken with an HT7800 microscope (Hitachi, Japan) at an accelerating voltage of 100 kV .

3. Results and Discussion

The presentation of the grounds for the search for the optimal dispersion medium for exfoliation in the literature was carried out from a thermodynamic point of view [5, 23, 30–32]. Obviously, in order to increase the efficiency of the exfoliation process, it is necessary to strive to minimize the free energy of mixing ΔG_{mix} (1):

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}, \quad (1)$$

where ΔH_{mix} is mixing enthalpy, $\text{kJ}\cdot\text{mol}^{-1}$; T is absolute temperature, K; ΔS_{mix} is mixing entropy, $\text{kJ}\cdot\text{mol}\cdot\text{K}^{-1}$.

The mixing entropy is always positive, and in the general case can be calculated from the Onsager theory similarly to [33] (2):

$$\Delta S_{\text{mix}} = -nk_{\text{B}} \left[x_{\text{p}} \ln x_{\text{p}} + x_{\text{s}} \ln x_{\text{s}} + x_{\text{p}}\sigma_{\text{p}} + x_{\text{s}}\sigma_{\text{s}} + n \left(x_{\text{p}}^2 b_{\text{pp}} P_{\text{pp}} + 2x_{\text{p}}x_{\text{s}} b_{\text{ps}} P_{\text{ss}} + x_{\text{s}}^2 b_{\text{ss}} P_{\text{ss}} \right) \right] \quad (2)$$

where n is the total number of particles; k_{B} is Boltzmann's constant; $x_{\text{p}}, x_{\text{s}}$ are the proportion of plates and molecules of the dispersion medium (numerical concentration), respectively; $\sigma_{\text{p}}, \sigma_{\text{s}}$ are orientational entropy components for plates and solvent, respectively; $b_{\text{pp}}P_{\text{pp}}, b_{\text{ps}}P_{\text{ss}}, b_{\text{ss}}P_{\text{ss}}$ are orientational distribution functions depending on the excluded volumes of two plates, plate and solvent, two solvent molecules.

Thus, the entropy in the general case depends on the terms associated with the actual mixing, orientation and substitution of excluded volumes. The last two sets of functions are extremely difficult to determine [34]; therefore, as a rule, they are limited to calculating only the mixing component.

For anisometric particles, the corresponding expression was obtained for the case of liquid crystal polymers [35]. In a convenient form, it can be written as [25] (3):

$$\overline{\Delta S_{\text{mix}}} = -\frac{k_B}{v_s} \left[(1-\varphi) \ln(1-\varphi) + \frac{\varphi v_s}{v_p} \left(\ln \frac{\varphi}{A} + (A-1) \right) \right], \quad (3)$$

where $\overline{\Delta S_{\text{mix}}}$ is specific entropy of 1 volume unit of a colloidal system, $\text{mJ}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$; v_s, v_p is the solvent molecule volume and the dispersed phase particle, respectively, cm^3 ; φ is volume fraction of the dispersed phase; A is anisometry of dispersed phase particles.

We calculate the mixing entropy values for the case of several solvents, assuming that the dispersed phase particles are cylindrical with a diameter equal to the average diameter of the particles. The number of FLGP layers is assumed to be 3 on average, which corresponds to the previously obtained experimental data [29]. The volumes of the dispersion medium molecules were calculated as the ratio of the molecular weight to the product of the density and the Avogadro number $M_s/\rho N_A$. The volume fraction of the dispersed phase was calculated from a concentration of 6.0 mg mL^{-1} (0.00264). The obtained values are shown in Table 1.

Thus, the mixing entropy as a whole has small values (on the order of $0.1\text{--}1.0 \text{ mJ}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$), with the exception of water as a compound with a noticeably (an order of magnitude) smaller molecular volume, and the effect of the dispersion medium molecule volume, obviously dominates in the entropy component.

The situation is more complicated with the enthalpy component, which mainly determines the value of the free energy of mixing. In general, in [25], it was proposed to measure the mixing enthalpy, reduced to the suspension unit volume $\overline{\Delta H_{\text{mix}}}$ during graphite exfoliation according to (4):

$$\overline{\Delta H_{\text{mix}}} = \frac{\Delta H_{\text{mix}}}{v} \approx \frac{2}{T_{\text{flake}}} \left(\sqrt{E_p} - \sqrt{E_s} \right)^2 \varphi, \quad (4)$$

where T_{flake} is FLGP thickness, m; E_p is free surface energy of FLGP, $\text{mJ}\cdot\text{m}^{-2}$; E_s is surface internal energy of a dispersion medium, $\text{mJ}\cdot\text{m}^{-2}$.

Knowing the surface tension of the dispersion medium γ_s its temperature coefficient, it is easy to calculate E_s by (5):

$$E_s = \gamma_s - T \left(\frac{\partial \gamma_s}{\partial T} \right)_p. \quad (5)$$

Finding the surface energy of FLGP is a much more difficult task. There are data found in various ways (for example, in [25] the value interval was given). In [37], using the method of inverted gas chromatography, the dispersion component value E_p (61 ± 4) $\text{mJ}\cdot\text{m}^{-2}$ was found experimentally and theoretically, which was close to the value found for graphite ($63 \text{ mJ}\cdot\text{m}^{-2}$). Other authors, based on data on contact angles, gave values for graphite ($54.3 \text{ mJ}\cdot\text{m}^{-2}$), graphene ($46.3 \text{ mJ}\cdot\text{m}^{-2}$) [41], and the data given in the literature ranges from 38 up to $70 \text{ mJ}\cdot\text{m}^{-2}$. The situation is complicated by the fact that the FLGP surface properties obtained by different methods can differ markedly.

In this study, we used experimentally obtained data on the contact angles θ of FLGP films obtained by direct liquid-phase exfoliation with various liquids to calculate the surface energy by the Neumann method [39, 40] according to the (6):

$$\cos \theta = -1 + 2 \sqrt{\frac{E_p}{\gamma_s}} e^{-\beta(E_p - \gamma_s)}, \quad (6)$$

where β is an individual parameter for a given hard surface.

Table 1. Calculation of mixing entropy for few-layer graphene platelets (FLGP) and different dispersion media

| Medium | $v_s, 10^{23} \text{ cm}^3$ | $d, \mu\text{m}$ | $v_p, 10^{16} \text{ cm}^3$ | A | $\overline{\Delta S_{\text{mix}}}, \text{mJ}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$ |
|--------|-----------------------------|------------------|-----------------------------|------|--|
| Water | 2.99 | 2.93 | 67.99 | 2934 | 1.217 |
| NMP | 15.99 | 1.20 | 11.33 | 1198 | 0.228 |
| EG | 9.29 | 0.70 | 3.85 | 699 | 0.392 |
| DEG | 15.74 | 1.00 | 7.87 | 998 | 0.231 |

Table 2. Source data for FLGP surface energy calculation

| Medium | θ , degrees | γ_s , $\text{mN}\cdot\text{m}^{-1}$ [41] | $\ln \left[\gamma_s \left(\frac{1 + \cos\theta}{2} \right)^2 \right]$, $\ln[\text{mN}\cdot\text{m}^{-1}]$ |
|-----------------|--------------------|---|--|
| Water | 128.3 ± 0.3 | 72.8 | 2.414 |
| Glycerol | 62.6 ± 0.9 | 59.2 | 4.067 |
| EG | 42.7 ± 2.9 | 47.7 | 3.422 |
| DEG | 32.5 ± 1.8 | 44.8 | 3.493 |
| Vacuum oil VM-4 | 23.7 ± 1.1 | 26.0* | 2.676 |

* The value was determined experimentally by drop counting.

After taking the logarithm, equation (6) can be rewritten as (7):

$$\ln \left[\gamma_s \left(\frac{1 + \cos\theta}{2} \right)^2 \right] = -2\beta\gamma_s^2 + 4\beta E_p \gamma_s + \ln E_p - 2\beta E_p^2, \quad (7)$$

which makes it possible to construct a parabolic dependence in the coordinates $\ln \left[\gamma_s \left(\frac{1 + \cos\theta}{2} \right)^2 \right] - \gamma_s$ and calculate β , E_p , as well as assess the adequacy of the model.

The experimental values obtained for various liquids, as well as the results of their processing, are shown in Table 2 and Fig. 1.

The correlation function in Fig. 1 is described by an equation of the form $y = -0.0021x^2 + 0.2033x - 1.3203$, which makes it possible to estimate the

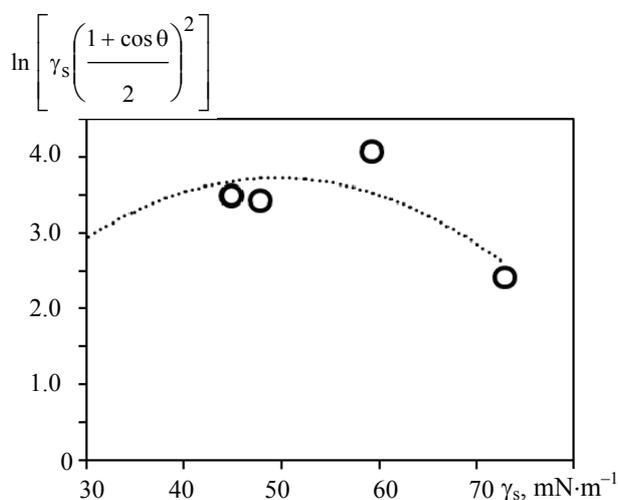


Fig. 1. Calculation of few-layer graphene surface energy based on Neumann's technique

value of the FLGP surface energy E_p with a value of $48.40 \text{ mJ}\cdot\text{m}^{-2}$. The obtained value is within the limits described in the literature. Despite the possible error in measuring the wetting angle of well-flowing liquids, the value can be taken as directly measured for FLGP obtained by direct liquid-phase exfoliation, and the error in checking the adequacy of the free term of the polynomial is within 12 %.

The obtained value of the graphite surface energy allows for direct measurement of the enthalpy and free mixing energy ΔG_{mix} for the case of various organic media using equations (1), (3), (4). The relevant data are shown in Table 3.

In some papers (e.g., [23]) on CNT exfoliation, it was shown that by choosing a suitable dispersion medium, negative values of the free mixing energy can be obtained, which indicates spontaneous dispersion. As can be seen from the data in Table 4, in the case of exfoliation with obtaining FLGP for all studied dispersion media $\Delta G_{\text{mix}} > 0$, i.e. the formation of a colloidal system requires the expenditure of external work, and the resulting system is thermodynamically unstable. Although ΔG_{mix} is a thermodynamic characteristic and does not determine the rate of processes or kinetic potential barriers, it can be seen that for NMP, EG and DEG it is close and 5–8 times less than for water. The minimum value was observed for DEG; however, the increased viscosity of this substance can adversely affect the manufacturability of the exfoliation process. For EG ΔG_{mix} it is also slightly lower than for NMP.

Additional assessment of the solvent quality for exfoliation is the value of the sphere radius in the space of Hansen constants, an approach that is widely

Table 3. Calculation of mixing enthalpy and free energy of FLGP and different dispersion media ($T = 298$ K)

(values for $\left(\frac{\partial\gamma_s}{\partial T}\right)_p$ are taken from [41])

| Medium | $\left(\frac{\partial\gamma_s}{\partial T}\right)_p, \text{mN}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ | $E_s, \text{mJ}\cdot\text{m}^{-2}$ | $\overline{\Delta H_{\text{mix}}}, \text{kJ}\cdot\text{cm}^{-3}$ | $\overline{\Delta S_{\text{mix}}}, \text{kJ}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$ | $\overline{\Delta G_{\text{mix}}}, \text{kJ}\cdot\text{cm}^{-3}$ |
|--------|---|------------------------------------|--|--|--|
| Water | -0.1514 | 117.92 | 68.83 | 1.217 | 68.83 |
| NMP | -0.1156 | 75.24 | 13.33 | 0.228 | 13.33 |
| EG | -0.089 | 74.22 | 12.43 | 0.392 | 12.43 |
| DEG | -0.0841 | 69.86 | 8.88 | 0.231 | 8.88 |

Table 4. Calculation of mixing enthalpy and free energy of FLGP and different dispersion media using Hansen parameters ($T = 298$ K)

| Medium | $\delta_D, \text{MPa}^{0.5}$ | $\delta_P, \text{MPa}^{0.5}$ | $\delta_H, \text{MPa}^{0.5}$ | $R_a, \text{MPa}^{0.5}$ | χ | $\overline{\Delta G_{\text{mix}}}, \text{J}\cdot\text{cm}^{-3}$ |
|-------------|------------------------------|------------------------------|------------------------------|-------------------------|--------|---|
| Water | 15.5 | 16.0 | 42.3 | 35.60 | 9.21 | 2.99 |
| NMP | 18.0 | 17.3 | 7.2 | 8.02 | 2.50 | 0.10 |
| EG | 17.0 | 11.0 | 26.0 | 18.49 | 7.72 | 0.77 |
| DEG | 16.2 | 14.7 | 20.5 | 14.35 | 7.88 | 0.48 |
| FLGP | 18.0 | 9.3 | 7.7 | | n/a | |

developed when choosing “good” solvents for macromolecular compounds [42]. The corresponding constants determine the volumetric density of the dispersion (δ_D), polar (due to the dipole component) (δ_P) cohesion energy, as well as the cohesive energy due to the formation of hydrogen bonds (δ_H). Professor Hansen's group collected data on a significant number of solvents and polymers [43]. Recently, due to the increasing practical importance of dispersive methods for the preparation of FLGP suspensions, significant attention has been paid to the measurement of the corresponding constants for carbon materials (for example, data for FLGP obtained by direct exfoliation in NMP were presented in [15]). The corresponding data are given in Table 4. The calculation of the sphere radius in the space of Hansen constants is carried out from the difference between the components of the phase cohesion energy densities (indices 1, 2) according to equation (8):

$$R_a = \sqrt{4(\delta_{D,1} - \delta_{D,2})^2 + (\delta_{P,1} - \delta_{P,2})^2 + (\delta_{H,1} - \delta_{H,2})^2}. \quad (8)$$

The value R_a in general, can serve as a measure of the affinity of a material for a solvent, however, it

additionally allows estimating the Flory–Huggins constant χ [42] (9):

$$\chi = \frac{v_s}{k_B T} R_a^2, \quad (9)$$

which is directly related to the enthalpy of mixing (10):

$$\overline{\Delta H_{\text{mix}}} = \chi\phi(1-\phi)\frac{k_B T}{v_s}, \quad (10)$$

which, according to equation (1), determines the free mixing energy.

Table 4 shows that the calculation of the free mixing energy using the Hansen constants and the Flory–Huggins equation leads to fundamentally lower values compared to direct calculations based on the data on the surface energy of graphite. In addition, in this case, the difference in values between “good” (NMP, EG, DEG) and “bad” (water) dispersion media is noticeably more pronounced. Additionally, it should be noted that the increased values of R_a and χ for EG and DEG are associated primarily with much higher cohesion energies due to hydrogen bonds (in contrast to the aprotic solvent NMP, cf. data in Table 4), however, this factor can be

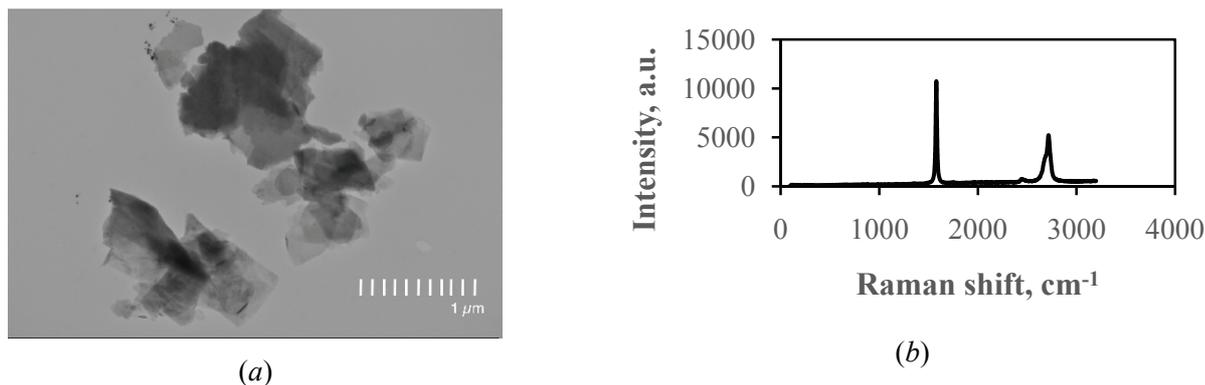


Fig. 2. Structure of FLGP prepared via exfoliation in ethylene glycol:
a – transmission electron microscopy image (scale bar – 1 μm); *b* – typical Raman spectrum

considered as favorable from the point of view of the subsequent application of drugs on hydrophilic substrates and their introduction into polar polymeric materials.

It is worth re-emphasizing that in any case ΔG_{mix} remains positive, i.e. FLGP suspensions are fundamentally stable only kinetically, as evidenced by their noticeable sedimentation in the investigated size range within 2–8 weeks. In addition, thermodynamic data can only be used to a limited extent to assess the suitability of dispersion media in the preparation of colloidal systems.

The results of an experimental verification of the assumptions made were carried out by evaluating the FLGP yield after exfoliation and centrifugation, followed by gravimetry of the resulting suspension, showed that the FLGP yield after centrifugation was 5.7 wt. %, while during exfoliation in NMP and DMF, a yield of 1–2 wt. % is considered normal [1].

Product characterization was done by transmission electron microscopy and Raman scattering. According to transmission electron microscopy (Fig. 2*a*), the particles in the preparation after exfoliation in EG were rather thin (low contrast in the electron beam indicates a thickness of no more than 1–2 nm) plates with a characteristic size of 0.5–1 μm . A representative Raman spectrum is shown in Fig. 2*b*. Attention is drawn to the complete absence of the D-peak in the shear region of 1360 cm^{-1} associated with defects in the carbon structure. The ratio of integral intensities and deconvolution of the 2D-peak (in the region of 2800 cm^{-1}) makes it possible to identify most of the particles as two- and three-layer [8].

Thus, the theoretical approach proposed in this paper to the choice of a dispersion medium suitable for natural graphite exfoliation made it possible to recommend EG as a promising joining technology. Experimental verification confirmed that

exfoliation in EG enables to state that the exfoliation process leads to an increased yield of graphene compared to NMP and DMF traditionally used for these purposes, and leads to the preparation of preparations from two- and three-layer particles with low defectiveness.

4. Conclusion

In the course of the experiments performed, the regularities of the relationship between the contact angle of between the FLGP films and various liquid media were established. It is shown that the maximum of the wetting function falls within the range of surface tensions of about 45 $\text{mN}\cdot\text{m}^{-1}$, which corresponds to such compounds as EG and DEG. The Neumann method calculated the surface energy value for FLGP obtained by direct liquid-phase exfoliation. It turned out to be equal to 48.40 $\text{mJ}\cdot\text{m}^{-2}$, which refines the values of the surface energy of graphite given in the literature. The entropy component of the free mixing energy during the graphite dispersion in liquids turned out to be small compared to the enthalpy one. Both direct thermodynamic calculations and calculations using Huggins parameters and Flory–Huggins constants showed that polyhydric alcohols are a promising non-deficient and low-toxic dispersion medium for direct ultrasonic exfoliation, which has noticeable advantages compared to the aqueous medium and the most widely used NMP. The structure of the resulting particles corresponds to FLGP with an average number of layers of 2–3 and low defectiveness according to Raman spectroscopy data. The obtained values of thermodynamic functions can be used in the development of general theoretical and technological approaches to the description and development of graphite direct exfoliation processes to obtain graphene preparations. Experimental verification by comparing the FLGP yield after exfoliation in EG

showed that this exfoliation method allows obtaining highly perfect FLGP, mainly two- and three-layer, with a high yield (5.7 wt. %).

5. Funding

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6. Conflict of interests

The authors declare no conflict of interest.

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